CARBON DEPOSITION ON METAL SURFACES
FROM CARBON MONOXIDE AND METHANE

BY

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DECLARATION

During the prescribed period of study for the degree of Ph. D., I worked as a member of a research team. I declare, however, that I composed this thesis myself and that the content of it is wholly my own, except in the following respects:

1. some routine operations (e.g. sample weighing) in the running of the Inert Environment Autoclave Rig.

2. in the design of the above rig, I worked in co-operation with the technical staff named on the front cover of Appendix I, but I made substantial contribution to the basic design of the system, and also to the construction and commissioning of it.

3. operation of the x-ray diffractometer, and ion microprobe mass spectrometer.

4. chemical analysis of samples.
ACKNOWLEDGEMENTS

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Mr C. Jackson of UKAEA Harwell for operating the ion probe mass analyser, and providing valuable advice on data interpretation;
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and Mrs S.M. Hills for typing the thesis.

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SUMMARY

Some aspects of the kinetics and mechanisms of formation of carbon on metal surfaces are reported. Particular emphasis is placed on the reactions of CO and CH₄ with pure iron, but data are also included for reaction on Cr, Mo, Nb, Ni and a commercially important 20/25 stainless steel. Standard resistance change, and weight gain, techniques are employed to measure kinetics of carbon dissolution and of heavy deposit formation, respectively. In addition, novel techniques involving changes of power dissipation of an electrically heated foil, and simultaneous measurement of resistance and power dissipation are employed to study the early stages of deposition; and a new design is given for an inert environment autoclave for study of reactions at high pressure. X-ray diffractometry and ion microprobe mass spectrometry are employed for analysis of the chemical structure of the carbon deposits.

For the reaction of methane on iron at temperatures of 500-900°C and pressures of 10-100 Torr, carbon dissolution in the metal is shown to occur during an induction period to the formation of surface deposit. A surface adsorption step is shown to be the rate controlling process, for which an apparent activation energy of 190 kJ mol⁻¹ and an isosteric heat of 176 kJ mol⁻¹ are measured in the temperature range 720-900°C. The initial surface deposit is formed by precipitation from a super-saturated solution, and circumstantial evidence strongly indicates that it is a carbide. The apparent activation energy of the Fe/CH₄ reaction is 80 kJ mol⁻¹ during the early stages of formation of surface deposit. As reaction proceeds the metal structure begins to break down, making available additional active area, and an apparent activation energy of 26 kJ mol⁻¹ is measured from rates of CO and CH₄ on iron samples at
2.75 bar and temperatures of 550–850°C. During this stage of reaction, the rate increases, and the kinetics can be represented by plots of weight gain versus log. time. At 515°C the total area made available by disintegration can be related approximately to the metal grain size; however, at temperatures of 550°C and above further breakdown of individual grains occurs.

Surface structure and bulk metal purity are found to effect the rate of dissolution; and gross metal structure, the overall rate of formation of thick deposits. In addition, surface structure influences the morphology of deposition during the early stages of reaction. Thus, for instance, maximum rates of dissolution are measured on well-annealed surfaces and the initial deposit structure is laminar. Lower reaction rates on work hardened surfaces result in nodular structures. On the gross scale, the overall kinetics of formation of heavy deposits are most rapid on samples of smallest grain size.

In general, reaction rates of Fe and Ni in CO are orders of magnitude higher than on the other metals. Adding an inert alloying constituent, e.g. Cr, to iron reduces the reaction rate in proportion to the logarithm of the chromium content, to a minimum at 24% Cr. The variation of reaction rates in methane is less than that in CO, but the products of reaction on Cr, Mo and Nb are mainly the relevant carbide, with little graphitised carbon. The structure of deposit formed on Fe in CO is found to have a complex layered form. In the early stages of growth, the main constituent of the surface deposit is oxide. Carbon depositing reactions occur at the gas/deposit and deposit/metal interfaces, where carbide layers are also detected. A simple mechanism is proposed for reaction on iron, involving non-stoichiometric carbide intermediates.
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11. SCOPE OF THE THESIS
I INTRODUCTION

1. CARBON DEPOSITION IN INDUSTRIAL ENVIRONMENTS

Carbon formation by the disproportionation reaction

$$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$$  \hspace{1cm} (1)

was first studied in connection with the reduction of haematite by producer gas (CO/H$_2$) in blast furnaces (1-3). Deposition, occurring on both the reduced ore and the firebrick linings, caused swelling and disintegration. Reaction within the brick was shown to be due to the presence in the fireclay of iron which catalysed the reaction (4-8). Equilibrium compositions were studied by Boudouard (9) and the reaction subsequently became known as the Boudouard equilibrium. Further studies were made when Fischer-Tropsch type reactions were developed for the large scale production of hydrocarbons, and carbon formation was found to cause swelling and poisoning of the supported metal catalysts (10-12). However, most present day research arises from the operation of nuclear power plant. In order to set the content of this thesis in context, the essential features of the deposition problems encountered will be outlined.

1.1 Carbon Deposition in Nuclear Reactors

In both the Mark 1 and Mark 2 reactors, the heat exchange medium between the nuclear core and the steam generators is compressed carbon dioxide. In the graphite moderator, the following radiolytically induced reaction occurs

$$\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$$  \hspace{1cm} (2)

The CO level is maintained at about 1% by periodic dilution with pure CO$_2$. It has been established empirically that reaction (2) is inhibited by methane, which is added at a concentration of about 500 vppm. Also present in the coolant are low levels of higher hydrocarbon impurities from lubricant oil ingress at bearing
surfaces. Decomposition of carbonaceous material in the gas circuit causes two particular problems - breakaway oxidation and fuel can deposition, which will be discussed separately.

1.1.1 Breakaway Oxidation of Steels

A full and up-to-date description of all aspects of breakaway oxidation can be obtained from the proceedings of the recent conference of the British Nuclear Energy Society (BNES) at Reading University (1974). The main points are

1) The oxidation of steel in high pressure CO₂ or CO₂/CO mixtures initially follows parabolic kinetics ("protective"), but eventually changes to linear kinetics (14-16). Breakaway has not been observed in CO₂ at ambient pressures, although it has been reported to occur in gas mixtures containing high levels of CO (17). However, an alternative interpretation of this data is possible, and will be discussed later.

2) During the latter stages of parabolic growth, and throughout the linear region, it is observed that small mounds of oxide form ("excrescences"). They are located randomly on the surface (18), but tend to concentrate at sites of mechanical damage such as scratches, edges or sites of second phase particles (carbide or sulphide inclusions) (19, 20). Carbide particles have sometimes been observed in sections through excrescences (21, 22).

3) The protective oxide has a duplex structure, which forms by outward diffusion of cations, to form the outer layer and create space for the inner layer, which grows by inward diffusion of oxygen ions (17, 20).

4) Carbon is incorporated into the oxide scale, following similar kinetics to the oxidation process. (20, 23, 24). Breakaway apparently begins when the carbon level reaches a critical value. It is probable that carbon is formed as a product of reaction e.g.


\[ 3\text{Fe} + 2\text{CO}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{C} \] (3)

1.1.2 Fuel Can Deposition

In the Advanced Gas-Cooled Reactor (AGR), the uranium fuel is contained in niobium- and manganese-stabilised stainless steel cans. During operation the temperature gradient, along each can, ranges from \(\sim 400\) to \(\sim 850^\circ\text{C}\). Direct decomposition of carbonaceous species, possibly induced or accelerated by radiation, occurs on the metal surface. The presence of carbon deposits reduces the heat transfer capability of the steel causing hot spots, and localised temperature increases which can be in excess of \(100^\circ\text{C}\). At the highest temperatures, resistance to creep and to oxidation is lowered, thus shortening the useable lifetime of the can, and hence of the fuel.

Carbon, removed from the reactor, has been shown to grow from the metal surface and to be filamentary in nature, with metal particles incorporated in the filaments. Similar deposits have been obtained in the absence of radiation, and in simulation studies where the coolant was dosed with hydrocarbons. It is probable that deposits arise from CO at the lowest temperatures (up to \(\sim 650^\circ\text{C}\)) and from CH\(_4\) and other hydrocarbons elsewhere (25-28).

2. THE LITERATURE OF THE Fe/CO REACTION

2.1 Kinetics of Reaction

CO disproportionation occurs at a significant rate, over iron catalysts, in the temperature range 400-750\(^\circ\text{C}\), with a maximum between 500 and 600\(^\circ\text{C}\) (7, 8, 29). An induction period prior to reaction has sometimes been observed but its cause has not been established (6, 29-31). The average linear rates of deposition for a range of iron catalysts, calculated from the data of Davis and Rigby (6), are given in Table 1.
It can be seen that all six materials catalyse the reaction, but no estimate of relative efficiencies can be made because the quoted rates take no account of surface area. Thus, the rate over iron powder is greater than that over bulk iron, and the very high rate of Fe$_2$O$_3$ is also probably due to a high surface area. Furthermore, with the exception of Fe$_3$C, some proportion of the catalyst underwent irreversible reaction to form carbide, implying that formation of carbon and carbide occurred via an intermediate active species.

Comparison of rates of disproportionation over different catalysts is thus further complicated because the concentration and surface area of both the catalyst and the active intermediate species are continually changing.

The rate of deposition onto rimming steel at 450$^\circ$C from Ar/1.5% CO at 17.25 x $10^3$ kNm$^{-2}$ pressure is 0.09 gm$^{-2}$h$^{-1}$ after 195 h (34). At atmospheric pressure in Ar+ 1% CO + 1% H$_2$ at 500$^\circ$C, Everett et al (31) report a rate which increases linearly, after a 70 hour induction period for deposition onto mild steel, to a maximum of 0.75 gm$^{-2}$h$^{-1}$ after 1600 hours. Over the period 130-200 hours values of 0.03 to 0.07 gm$^{-2}$h$^{-1}$ were measured. The rates over mild steel compare well with that over powdered iron.

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Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate mg/g of catalyst/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron powder</td>
<td>114</td>
</tr>
<tr>
<td>Bulk iron</td>
<td>5</td>
</tr>
<tr>
<td>FeO</td>
<td>110</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>30</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>448</td>
</tr>
<tr>
<td>Fe$_3$C</td>
<td>100</td>
</tr>
</tbody>
</table>

-4-
These results imply that the concentration of active species per unit area of catalyst is approximately the same for both bulk metal and finely divided material.

The maximum in rate at 500-600°C has been shown to apply only to the initial stages of reaction where the overall kinetics can be represented by the equation

\[
\frac{W_c}{W_{Fe}} = a t^n
\]  

(3)

where \(W_c\) = weight of carbon deposited  
\(W_{Fe}\) = weight of iron catalyst  
\(t\) = time

\(a\) & \(n\) are empirical rate parameters

\(W_c/W_{Fe}\) increases slowly with temperature to a maximum of one at 800°C; 'a' exhibits a sharp peak at about 530°C, which causes a peak in the overall rate at this temperature. At \(W_c/W_{Fe}\) values of 0.7 to 2, the overall rate remains constant with time, but has a complex dependence on temperature. It rises steadily from 400-600°C, then remains virtually constant to 730°C, finally rising steeply to a sharp peak at 800°C. The increase in rate above 730°C, the eutectoid temperature, is thought to arise as a result of the phase change in the metal, and the decrease above 800°C is attributed to catalyst sintering (30).

2.2 Characteristics of the Carbonaceous Solid

Carbon formed catalytically is relatively well graphitized. Average crystallite heights \((L_c)\) of 38 to 127 Å have been reported in carbon deposited from CO + 0.5% H₂ on to carbonyl iron powder (29). At 450°C more than 14% of the carbon had three-dimensional ordering, according to the Franklin correlation, increasing to 59% at 576°C. A carbon deposit, produced on mild steel at 450°C from Ar + 1.5% CO,
is reported to contain ~20% graphite in the bulk, increasing to ~35% close to the metal surface (34), thus confirming the report that most of the graphitic material deposited on electrolytic iron at 500°C lay near the metal surface (31). Crystallite heights and ordering of the same degree are found in carbon blacks only after heat treatment to temperatures in excess of 2000°C.

Two-dimensionally ordered carbon, or turbostratic carbon, only gives X-ray lines corresponding to the (hk0) and (00l) lattice planes. Its detection, in the presence of well graphitized carbon, is only possible by careful examination of widths and profiles of lines obtained by powder X-ray analysis, or diffractometry. At present, there is no data available on the contribution of turbostratic carbon. However, it must be assumed to make up most of the balance of carbon in the deposit, because there is no experimental evidence for the presence of "non-graphitizing" ("hard") carbon, which has d-spacings above the turbostratic value of 3.44 Å, nor for "unorganized" carbon, which does not have the layered structure (35).

The same physical structures for the carbon deposit have been found by many workers (29, 36-40). Characteristically, it has a thread of filamentary form, with the filaments, in some cases, twisted together. Their dimensions are in the ranges of 0.01 to 1.0 µm diameter and 1-10 µm in length. They grow from single metal particles as well as on top of thick, compacted deposits. Under the electron microscope they have an electron-transparent core and have a metal-containing particle in their head. On iron exposed to 0.506 N m⁻² of CO, lamellar forms of carbon have been identified (40).
2.3 The Nature of the Catalyst

Experiments on mild steel at 508°C in Ar + 1% CO + 1% H₂ (32) produce the following information about the intermediate active species:

(i) They are formed rapidly during an early stage in sufficient quantity to maintain most of the subsequent reaction, since the concentration of iron in the deposit is 27% w/w initially, falling to a steady state value of 4% after 300 hours.

(ii) They either break-up during the course of reaction to small particles, i.e. greater surface area, or form a secondary more active species, since the fact that the rate increases linearly with time implies that availability of catalyst imposes no limitation on it.

(iii) It can be further concluded that most of the deposition occurs close to the metal surface, since continually sweeping off the deposit reduced the rate by only 25%. That a small amount of deposition can occur in the deposit itself has been demonstrated by Walker and Thomas (1970), who showed that the deposit can sustain further reaction when isolated from the substrate.

There have been many suggestions as to the identity of the active catalyst and these are summarized in Table 2. The choice lies between oxides, carbides and metallic iron. In addition, it has been proposed that transfer of iron and its distribution throughout the deposit occurs by means of a volatile iron carbonyl (41, 42). However, deposition has been reported at temperatures as high as 750°C, which is well above the stability range of known carbonyls.

Experiments on Fe in CO and CO/H₂ mixtures have indicated that the reaction rate is controlled by a slow surface step. It has been
Table 2

MECHANISTIC STUDIES OF THE DISPROPORTIONATION OF CO OVER IRON

<table>
<thead>
<tr>
<th>INVESTIGATOR</th>
<th>YEAR</th>
<th>PROPOSED CATALYST</th>
<th>REF.</th>
<th>MECHANISTIC NOTES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stammer</td>
<td>1851</td>
<td>Iron carbide</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Boudouard</td>
<td>1901</td>
<td>Iron oxides</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Hilpert &amp; Dieckmann</td>
<td>1915</td>
<td>Fe₃C</td>
<td>52a</td>
<td></td>
</tr>
<tr>
<td>Tutiya</td>
<td>1929</td>
<td>Fe₃C</td>
<td>52b</td>
<td></td>
</tr>
<tr>
<td>Hofmann &amp; Grool</td>
<td>1930</td>
<td>Fe</td>
<td>52c</td>
<td></td>
</tr>
<tr>
<td>Olmer</td>
<td>1941</td>
<td>Fe</td>
<td>52d</td>
<td></td>
</tr>
<tr>
<td>Baukloh &amp; Edwin</td>
<td>1942</td>
<td>Fe</td>
<td>52e</td>
<td></td>
</tr>
<tr>
<td>Akamatu &amp; Sato</td>
<td>1949</td>
<td>Fe/Fe₃C</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>Fleureau</td>
<td>1953</td>
<td>Fe + Fe carbonyls</td>
<td>41</td>
<td>3 Fe + 2 CO → Fe₃C + CO₂ Catalysis by Fe₃C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>42</td>
<td>Fe + x CO + Fe(CO)ₙ Catalysis by Fe</td>
</tr>
<tr>
<td>Davis &amp; Rigby</td>
<td>1954</td>
<td>Fe/Fe₃C/Fe₂₀C₉</td>
<td>6</td>
<td>Decomposition of Fe(CO)ₙ accounts +Fe in deposit</td>
</tr>
<tr>
<td>Chatterjee &amp; Das</td>
<td>1954</td>
<td>Fe</td>
<td>52f</td>
<td>6Fe + 4CO → 2Fe₃C + CO₂ → 6Fe + 2C + CO₂</td>
</tr>
<tr>
<td>MacIver &amp; Emmett</td>
<td>1955</td>
<td>Fe₂₀C₉</td>
<td>37</td>
<td>20Fe₃C + 14 CO + 3Fe₂₀C₉ + 7CO₂ →</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20Fe₃C + 7CO₂ + 7C</td>
</tr>
<tr>
<td>INVESTIGATOR</td>
<td>YEAR</td>
<td>PROPOSED CATALYST</td>
<td>REF.</td>
<td>MECHANISTIC NOTES</td>
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<td>------</td>
<td>-----------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Taylor</td>
<td>1956</td>
<td>Fe/Fe$_3$O$_4$ interface</td>
<td>8</td>
<td>Carbon enters the iron lattice at the interface where the spacings are enlarged.</td>
</tr>
<tr>
<td>Berry, Ames &amp; Snow</td>
<td>1956</td>
<td>Fe$_2$O$_9$ from 400-565°C</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe$_3$C with low Curie point at 565-700°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Davis, Slawson &amp; Rigby</td>
<td>1957</td>
<td>Fe$_2$O$_9$ and/or Fe$_3$C</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>Walker et al</td>
<td>1959</td>
<td>Fe</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>MacRae</td>
<td>1966</td>
<td>Iron/Iron oxide interface</td>
<td>52f</td>
<td></td>
</tr>
<tr>
<td>Haas et al</td>
<td>1968</td>
<td>Fe</td>
<td>52g</td>
<td></td>
</tr>
<tr>
<td>Ruston et al</td>
<td>1969</td>
<td>Fe$_7$C$_3$ and Fe</td>
<td>40</td>
<td>Fe$_7$C$_3$ form on Fe and Fe$_3$C surfaces and act as catalysts for filament growth.</td>
</tr>
<tr>
<td>Renshaw et al</td>
<td>1970</td>
<td>y-Fe$_2$O$_3$ or Fe$_3$-zO$_4$ where 0 &lt; z &lt; 1/3</td>
<td>39</td>
<td>Bulk carbon formed on free Fe whose diffusion to the surface is assisted by defects in the oxide. Filaments grow by decomposition of Fe$_2$C.</td>
</tr>
<tr>
<td>Legalland &amp; Bonnetin</td>
<td>1971</td>
<td>Fe</td>
<td>48</td>
<td>Increasing the level of CO$_2$ in the gas to 48% stops deposition at 520°C.</td>
</tr>
<tr>
<td>Fruehan</td>
<td>1973</td>
<td>Fe</td>
<td>43</td>
<td>Rate determining step formation of surface activated transition state complex ${(CO)_2}^\dagger$.</td>
</tr>
<tr>
<td>Turkdogan et al</td>
<td>1974</td>
<td>Fe</td>
<td>30</td>
<td>Rate determining step formation of activated complex ${Fe_3(CO)_2}^\dagger$.</td>
</tr>
</tbody>
</table>
proposed that this involves the formation of the activated transition state complex \((\text{CO})_2\)^\(\dagger\), or \((\text{H}_2\text{CO})^\dagger\) in the presence of \(\text{H}_2\) (43).

Turkdogan and Vinters (30) propose the formation of the activated complex \(\text{Fe}_3(\text{CO})_2\)^\(\dagger\) to be rate determining.

2.3.1 The Role of Oxides

Deposition of carbon onto oxides results in an initial weight loss, associated with the formation of iron or iron carbide (8). Taylor (9) found it necessary to first activate magnetite with \(\text{NH}_3\) at \(400^\circ\text{C}\) to obtain significant deposition. Such a process would be expected to assist reduction or carbide formation by creation of an intermediate nitride.

\(\gamma\)-\(\text{Fe}_2\text{O}_3\), formed on an iron surface, has been proposed as the active catalyst for disproportionation (39). It was considered to be formed in the presence of water vapour, stabilized to \(600^\circ\text{C}\) by an underlying \(\text{Fe}_3\text{O}_4\) lattice, and active because of its p-type semiconductor characteristic, which allows high lattice diffusion rates of \(\text{Fe}^{3+}\) to the solid-gas interface. In the absence of water, \(\alpha\)-\(\text{Fe}_2\text{O}_3\) was formed and the disproportionation rate was considerably slower. No other workers have reported evidence for \(\gamma\)-\(\text{Fe}_2\text{O}_3\), but Ruston et al (4) found \(\alpha\)-\(\text{Fe}_2\text{O}_3\) in deposits formed on pure iron. They considered it to be inactive.

\(\text{Fe}_3\text{O}_4\) has been found in deposits by many workers, for example, in the reaction of \(\text{CO}\) with iron films at \(550^\circ\text{C}\) (44, 45) and on the faces of iron single crystals at temperatures below \(350^\circ\text{C}\). Its presence could be due to direct oxidation of the surface by \(\text{CO}_2\) formed during disproportionation.

An induction period found in mild steel has been attributed to the reduction of a non-catalytic oxide, and the build up of oxidizing reaction products (\(\text{H}_2\text{O}\) and \(\text{CO}_2\)) was found to
retard reaction (30). Further evidence against the catalytic activity of oxides is that similar carbonaceous deposits can be grown in hydrocarbon/metal reactions where no oxides or oxidizing species are present (see for example (47)). No mechanism for carbon filament growth involving oxide species has been proposed.

2.3.2 The Role of Carbides

In the remainder of this section, distinction will be drawn between the catalyst - the material introduced into the gas to provide a surface on which disproportionation can occur, and the active compound - the chemical compound into which the "catalyst" may have to be converted before any enhancement of the rate can commence.

In the case of each catalyst listed in Tables 1 and 2, the final reaction products included some Fe₃C, cementite. When cementite itself was the catalyst no other iron compounds were formed. It can be formed by the reaction

\[ 3\text{Fe} + 2\text{CO} \rightarrow \text{Fe}_3\text{C} + \text{CO}_2 \]  

(4)

and decomposes, for example at 430°C, to give well-graphitized carbon (48). Cementite, however, cannot be the active compound, since if deposition on iron powder at 450-700°C is allowed to run to completion the sole product, apart from carbon, is cementite (29). Its decomposition rate must be slower than the principle carbon formation step and it must be regarded as inactive. An active form of Fe₃C, with a normal X-ray pattern, but low Curie point has been proposed as the active compound (8). It was suggested that it formed from \( \alpha \)-Fe₂O₃ during the induction period where a weight loss occurred. The observations of magnetic properties have not been confirmed.
Fe$_2$C, which can decompose to Fe$_3$C by the reaction
\[ 3\text{Fe}_2\text{C} \rightarrow 2\text{Fe}_3\text{C} + \text{C} \] (5)
has been reported to exist in whisker growths and proposed as a filament-producing catalyst. However, few workers have reported its existence in either the ortho-rhombic (Hgg or x-carbide) or hexagonal (\( \varepsilon \)-carbide) forms. Other carbides with compositions between Fe$_2$C and Fe$_3$C have been invoked (Table 2). However, their unequivocal identification by X-ray diffraction is difficult and there is little agreement about their roles. For instance, the suggestion that the particle observed in the heads of filaments is Fe$_7$C$_3$ is based on very scanty evidence. There is also doubt, in earlier work, that Fe$_{20}$C$_9$ was confused with Hgg carbide (39). In hydrocarbon synthesis from CO and H$_2$ over iron catalysts a sequence of carbides in the order Fe$_3$C + Fe$_5$C$_2$ + Fe$_7$C$_3$ has been found to be involved in the reaction (11).

2.3.3 The Role of Metallic Iron

Iron would appear to be capable of supporting disproportionation otherwise the reaction could not start on a clean surface. In practice, a "clean" surface can only be produced and maintained under ultra high vacuum conditions. The reactants used in all studies listed in Table 2 would have been covered in air-formed oxide film of the order of a few nanometers thick. Initial reaction will be with this oxide and could produce finely divided, highly catalytic iron, by reduction. Elemental iron has not been detected in deposits formed on bulk iron or mild steel and its possible role as an active compound is derived by elimination of other possibilities, rather than direct observation. For instance, on a mineral ore crocidolite, which is a sodium-iron-magnesium silicate, deposition of C from CO occurs after an
induction period. The induction period can be eliminated by pre-reduction with H₂, which is known to produce elemental iron (48) (See also 29).

2.4 The Effect of Gaseous Additives

2.4.1 Hydrogen and Water

The presence of H₂ and/or H₂O in the gas creates the possibility of numerous side reactions, some of which are:

\[
\begin{align*}
\text{CO} + \text{H}_2 & \rightarrow \text{C} + \text{H}_2\text{O} \\
\text{CO} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \\
\text{C} + 2\text{H}_2 & \rightarrow \text{CH}_4 \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{H}_2 \\
\text{Fe} + \text{H}_2\text{O} & \rightarrow \text{FeO} + \text{H}_2 \\
3\text{Fe} + 4\text{H}_2\text{O} & \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2 \\
3\text{Fe} + \text{CO} + \text{H}_2 & \rightarrow \text{Fe}_3\text{C} + \text{H}_2\text{O}
\end{align*}
\]

The equilibria have been discussed in detail, and a diagram presented which allows calculations of H₂/H₂O ratios, and their effect on deposition, in the temperature range 200-900°C (32).

Hydrogen and water have each been reported capable of both accelerating and retarding reaction (7, 13, 29, 39, 50). Fruehan (43, 51) and Turkdogan (30, 52) have recently demonstrated the interdependance of the two in modifying deposition rates. A summary of data is given in Table 3. The following conclusions can be drawn.

1) At all temperatures, both H₂ and H₂O, added at levels <1%, accelerate CO disproportionation on iron.

2) As the H₂ level is increased, its accelerating effect reaches a limiting value at a concentration which increases with
Table 3
EFFECT OF $H_2$ AND $H_2O$ ON RATE OF CARBON DEPOSITION FROM CO

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp $^\circ$C</th>
<th>Rate in $x%H_2O + y%H_2$ mg/g of catalyst/h</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>455</td>
<td>234</td>
<td>512</td>
</tr>
<tr>
<td></td>
<td>540</td>
<td>580</td>
<td>2124</td>
</tr>
<tr>
<td></td>
<td>704</td>
<td>93</td>
<td>200</td>
</tr>
<tr>
<td>Fe</td>
<td>470</td>
<td>300</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>528</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td></td>
<td>576</td>
<td>800</td>
<td>1500</td>
</tr>
<tr>
<td></td>
<td>602</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>Fe</td>
<td>400</td>
<td>110</td>
<td>6000</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>270</td>
<td>3800</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>650</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>x=0</td>
<td>x=2</td>
<td>x=0</td>
</tr>
<tr>
<td></td>
<td>y=0</td>
<td>y=4</td>
<td>x=0</td>
</tr>
</tbody>
</table>
temperature. Thus up to about 530°C, maximum rate occurs at
\(\sim 2\% \text{ H}_2\), and from 530-800°C a broad peak is found between 10 and 60%.

3) As the water level is increased to 1\% in the absence of
\(\text{H}_2\) a sharp increase in rate occurs initially. This is followed by
a further slow rise at water levels >1\% and temperatures <700°C.
Above this temperature, increasing water concentration decreases
deposition rate.

4) The effect of addition of water to a CO/\(\text{H}_2\) mixture varies
with \(\text{H}_2\) level. Thus at low \(\text{H}_2\) concentrations (<2\% at 530°C and
below, <10\% above 530°C), water causes a further slight increase
in rate. At higher concentrations of \(\text{H}_2\), water causes a marked
decrease in rate, as a result of the back reaction of (6), however
except at very high water levels (>5\%) the rate is still greater
than that of pure CO under the same conditions of temperature and
pressure.

Turkdogan demonstrates that, in dry \(\text{H}_2\), the forward
reaction (6) is slow at concentrations <50\%, and proposes that
low levels of \(\text{H}_2\) accelerate the rate by catalysing reaction (1).

Reaction on an Fe sample ceases when it has all been
converted to Fe\(_3\)C. The catalyst can be reactivated by treatment
with hydrogen, presumably by the reaction

\[
\text{Fe}_3\text{C} + 2\text{H}_2 \rightarrow 3\text{Fe} + \text{CH}_4
\]  

(13)

(29, 30, 48).

2.4.2 Carbon Dioxide

The rate of deposition decreases with increasing concen-
tration of CO\(_2\) (10, 52). At high concentrations of CO\(_2\), carbon
oxidation and oxide formation become alternatives to deposition.
The equilibrium diagram relating CO/CO₂ ratio to temperature and CO partial pressure has been presented by Everett et al (32). In an experiment, in which the proportion of CO₂ in a CO/CO₂ mixture was increased, the rate of deposition, at 570°C on iron powder at 1.013 x 10⁵ Nm⁻² total pressure, fell rapidly at 33% CO₂ and ceased at 48% CO₂ (48). Inhibition was attributed to the production of magnetite.

2.4.3 Gas Phase Inhibitors

A number of nitrogen - or sulphur - containing compounds have been shown to inhibit disproportionation over iron oxides, e.g. C₂N₂, NH₃ and H₂S (50). These same gases, plus CS₂ and AsH₃, have been shown to inhibit deposition over powdered iron. If the powder, after having been treated with inhibitor and CO, is dissolved in acid, hydrocarbon gases are evolved showing that carbide formation still occurs. However, there is insufficient data available to show whether the rate of carbide formation is reduced (6). Later experiments on Fe coupons confirm that SO₂ and H₂S have a greater inhibiting effect on the formation of carbon than on formation of carbide (10, 52).

Inhibitors can be divided into two types; those that are effective applied as a single dose e.g. SO₂ and various silanes, and those whose presence is continuously required e.g. H₂O, N₂O, NH₃ and CO₂. The first group are thought to block active surface sites. SO₂ forms a sulphide layer, and is effective even when some carbon is already present. Since its rate of reaction with carbides is likely to be slow, this suggests that elemental iron is the active compound, rather than a carbide. Silanes are thought to form an imperfect silica layer about 10 μm thick, thus reducing the surface activity of iron and extending the induction period. They are less
efficient if some carbon is already present. The inhibiting effect of the second group is due to competitive adsorption with CO. They are most effective during the early stages of reaction, their efficiency decreasing as the deposit thickens, suggesting the possibility of an alternative reaction mechanism in heavy deposits.

The order of efficiency of the various treatments is:

SO₂ > silanes > H₂O > N₂O > CO₂

(14)

2.5 Summary of the Main Features of the CO Reaction

1. Under some conditions, as yet ill-defined, reaction is preceded by an induction period of variable length.

2. Once rapid deposition has begun, the rate of reaction continues to increase over many hundreds of hours over bulk metal specimens. Rates, per unit area, over bulk and powder metal samples, with surface areas differing by a factor of 10⁴, are in good agreement.

3. From 2 above, it appears that the catalytically active compounds form close to the metal surface and that their concentration increases during the early stages of reaction.

4. Deposit removed from the surface can support further deposition, showing that some active compound is transferred from the metal surface. After removal of deposit the rate of deposition on to the metal is reduced by only 25%, again indicating that the main reaction zone is located close to the metal/carbon interface.

5. Both well-graphitized and turbostratically ordered carbon is formed. The former is equivalent to material produced by
graphitization at temperatures above 2000°C.

6. Carbon, formed under different conditions of temperature, pressure, solid catalyst and carbonaceous source, has the same morphology. The most characteristic feature of which is filamentary-type growth.

7. Oxides and/or carbides of iron are always found in the deposit. Cementite-Fe₃C is catalytically inactive, α-Fe₂O₃ is thought to have low activity.

8. Low levels of H₂ or H₂O accelerate the rate at low concentrations. The effect reaches a maximum at H₂ and H₂O levels which depend on both temperature and the H₂/H₂O ratio. High concentrations of oxidants inhibit reaction by oxide formation.

9. Inhibition is possible by two types of process:
   (i) production of an inert surface layer that blocks active sites.
   (ii) competitive adsorption or replacement of adsorbed CO.

The second is more effective during the early stages of deposition.

3. THE LITERATURE OF THE Fe/CH₄ REACTION

   Since little information is available relating directly to pyrolysis of methane over iron, data from other short chain hydrocarbons and other metals are included. It has been reported that the kinetics and morphology of deposition are independent of the reacting species (53, 54).

3.1 Kinetics

   Early studies fall into two categories, which apparently refer to two extremes of an S-shaped weight gain curve:
1) low weight gain measurements show an incubation time, followed by a period where the rate increases to a constant value (55, 57).

2) under conditions of rapid reaction e.g. at high temperatures, no incubation times are found and the rate eventually falls to a low value (58, 59).

Available data are summarised in Table 4.

At high weight gain of C, the rapid reaction rate of CH₄ on Fe is reported to be pressure and temperature dependent with an activation energy of 401-410 kJmol⁻¹. The final slow rate has an activation energy of 220 kJmol⁻¹ and is pressure independent.

Resistivity and microbalance studies of the early stages of reaction of α- & γ- Fe with CH₄/H₂ mixtures show the overall rate to be proportional to p_{H₂}^{3/2} and directly proportional to p_{CH₄}, with activation energies of 213 and 230 kJmol⁻¹ respectively (60, 61). The accuracy of the latter figure is questionable, since it is derived from the relation

\[ \Delta R = k\langle C \rangle \]

where \( \Delta R \) = resistance increase

\( \langle C \rangle_t \) = carbon concentration

\( k \) = constant

k was assumed to be temperature independent, which is demonstrably not the case for the Fe/C system (62).

Complex kinetics have been measured for reaction of Ni with H₂/C₂H₂ mixtures (56) and with CH₄, C₂H₆ and C₂H₄ (54). Apparent negative activation energies are reported in the region of 500-600°C. Two morphologies of deposit (designated laminar and island)
<table>
<thead>
<tr>
<th>Reactant</th>
<th>Temp °C</th>
<th>Hydrocarbon Partial Pressure kNm⁻²</th>
<th>Rate gm⁻²h⁻¹</th>
<th>Substrate</th>
<th>Activation Energy</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄He</td>
<td>900</td>
<td>26.6</td>
<td>21</td>
<td>Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total P</td>
<td>900</td>
<td>80.0</td>
<td>48</td>
<td>Fe</td>
<td></td>
<td>58</td>
</tr>
<tr>
<td>80 kNm⁻²</td>
<td>1000</td>
<td>26.6</td>
<td>210</td>
<td>Fe</td>
<td>401-410</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>80.0</td>
<td>480</td>
<td>Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900-1000</td>
<td>26.6-80.0</td>
<td>20</td>
<td>Ni</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₂/H₂</td>
<td>600</td>
<td>0.6</td>
<td>90</td>
<td>Electro-less Plated Ni</td>
<td>55</td>
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<tr>
<td>Total P</td>
<td>1.3 kNm⁻²</td>
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<td></td>
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<tr>
<td>C₂H₂</td>
<td>400</td>
<td>1.8</td>
<td></td>
<td>Ni</td>
<td>At 400-500 °C</td>
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<td></td>
<td>500</td>
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<td>600</td>
<td>13.3</td>
<td></td>
<td>Ni</td>
<td>At 550-750 °C</td>
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</tr>
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<td>42</td>
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<td>Ni</td>
<td>209</td>
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<td>Hydrocarbon</td>
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<td>Activation Energy</td>
<td>Reference</td>
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<tr>
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<td>-------------</td>
<td>------------------------------------------</td>
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<td>-------------------</td>
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</tr>
<tr>
<td>10%C(_2)H(_2)/H(_2)</td>
<td>525</td>
<td></td>
<td>1800</td>
<td>Nichrome</td>
<td>(40% Cr</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>10</td>
<td>6300</td>
<td></td>
<td>60% Ni)</td>
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<tr>
<td></td>
<td>650</td>
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<td></td>
<td>700</td>
<td>4200</td>
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<tr>
<td>10%C(_2)H(_2)/N(_2)</td>
<td>60</td>
<td></td>
<td>750</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>650</td>
<td>10</td>
<td>2250</td>
<td></td>
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<tr>
<td></td>
<td>700</td>
<td>3750</td>
<td></td>
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<tr>
<td>CH(_4)/H(_2)</td>
<td>800-1040</td>
<td>0.2-1.6</td>
<td></td>
<td>γ-Fe</td>
<td>230</td>
<td>61</td>
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<tr>
<td>CH(_4)/H(_2)</td>
<td>500-700</td>
<td>not specified</td>
<td></td>
<td>α-Fe</td>
<td>213</td>
<td>60</td>
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<tr>
<td>CH(_4)</td>
<td>600</td>
<td>80</td>
<td>0.05</td>
<td>Ni</td>
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<td></td>
</tr>
<tr>
<td>CH(_3)-CH=CH(_2)</td>
<td>600</td>
<td>80</td>
<td>8.7</td>
<td>Ni</td>
<td></td>
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</tr>
<tr>
<td>CH(_3)COCH(_3)</td>
<td>700</td>
<td>80</td>
<td>0.14</td>
<td>Ni</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_2)H(_2)</td>
<td>650</td>
<td>0.3</td>
<td></td>
<td>Fe</td>
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<tr>
<td></td>
<td>970</td>
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<td>Ni</td>
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<td>0.13</td>
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<td>113</td>
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<td>Reactant</td>
<td>Temp °C</td>
<td>Hydrocarbon Partial Pressure kN/m²</td>
<td>Rate</td>
<td>Substrate</td>
<td>Activation Energy</td>
<td>Reference</td>
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<td>-----------</td>
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<td>-----------------------------------</td>
<td>-------------------------------</td>
<td>-----------</td>
<td>-------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>CH₄, C₂H₆</td>
<td>700-1000</td>
<td>0.14-8</td>
<td>Continuous film</td>
<td>Ni</td>
<td>90</td>
<td>54</td>
</tr>
<tr>
<td>C₂H₄</td>
<td></td>
<td></td>
<td>2.8x10⁻³ to 1.7x10⁻² g/g of metal/minute</td>
<td>Island growths</td>
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</table>
are identified after cooling to room temperature. The extent of laminar deposition is controlled by the saturation solubility of C in Ni at reaction temperature. The activation energy of formation is similar to that for diffusion of C in the metal. The deposit thickness increases in inverse proportion to the rate of cooling of the sample, implying that laminar carbon forms by precipitation from the solution phase during cooling. Island growth continues apparently indefinitely with an activation energy of 133 kJmol\(^{-1}\) below 500°C and -180 kJmol\(^{-1}\) above. The number of growth sites decreases with increasing temperature giving rise to the apparent negative activation energy.

3.1.1 The Effects of Hydrogen

Pre-treatment of samples in H\(_2\) reduces induction times, for reaction on Ni, and suppresses island growth formation (53, 54, 56). No quantitative data are available for its effect on reaction rate. For reaction of CH\(_4\) with α- and γ- iron the overall rate varied as \(p_{\text{H}_2}^{3/2}\), from which it was deduced that the rate controlling step is the surface reaction

\[
\text{CH}_3\text{ads} \rightarrow \text{CH}_2\text{ads} + \text{H}_\text{ads}
\]

(15).

3.2 Morphology

Three types of deposit morphology have been reported, they are:

- **laminar**: continuous, plate-like layers of highly graphitic carbon
- **nodular**: islands or clusters of less well oriented carbon growths
filamentary: filaments of up to about 1 \( \mu \)m length and 500 Å diameter

(See Table 5)

Laminar deposits on Ni form preferentially at high temperatures (>750°C) and low gas pressures (<4T) (54, 66, 67). They have also been described as 'polygonal' (66-68) and as 'flake' carbon (47, 57), and consist of plates of well-oriented graphite which grow laterally from preferred sites for precipitation (68).

Nodular growths form at higher gas pressures. They nucleate at isolated sites which tend to be in the region of metal grain boundaries or of surface oxide, and consist of fluffy, ball-like clusters of microfine filaments (47, 53, 54, 59, 68).

The growth of filaments has been extensively studied in-situ in an electron microscope by Baker and co-workers and Baird et al (see for instance 63, 69-72, also 53, 57, 73). They consist of:

1) a relatively oxidation resistant sheath
2) a readily oxidisable electron-transparent core
and 3) a metal particle in the tip ("pear-shaped" according to Baker et al), and occasionally in the core (53).

3.3 Graphitic Nature of the Deposit

Table 5 summarizes the experimental information on the nature of deposit formed from \( \text{CH}_4 \) and \( \text{C}_2\text{H}_2 \) over Fe and Ni surfaces, obtained from X-ray diffraction and selected area diffraction studies. Carbon with polygonal and laminar structure lying close to the metal surface is well-graphitized, but the nodular growths, observed further from the surface, contained less oriented, turbostratic carbon. The graphite is oriented with its 002 plane parallel to the metal surface,
<table>
<thead>
<tr>
<th>Reactant</th>
<th>Experimental Conditions</th>
<th>Description of Deposits</th>
<th>X-Ray Data</th>
<th>Additional Information</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄/Ni</td>
<td>800-1050°C at 0.4-1.3 x 10⁻³ kN m⁻²</td>
<td>Polycrystalline graphite film</td>
<td>Electron diffraction photos. of deposit indistinguishable from those of natural graphite</td>
<td>Preferential growth at scratch lines and grain boundaries</td>
<td>74</td>
</tr>
<tr>
<td>CH₄/FeNi</td>
<td>870-1030°C at sub-atmospheric pressure</td>
<td>Dull, grey and adherent when thin. Crack and blister when thick.</td>
<td></td>
<td></td>
<td>58</td>
</tr>
<tr>
<td>C₂H₄/PtNi</td>
<td>1000°C at &lt;0.13 kN m⁻²</td>
<td>Polycrystalline with some blistering</td>
<td></td>
<td>Preferred growth at scratches, facets and grain boundaries by lateral extension of island sites</td>
<td>68</td>
</tr>
<tr>
<td>Reactant</td>
<td>Experimental Conditions</td>
<td>Description of Deposits</td>
<td>X-Ray Data</td>
<td>Additional Information</td>
<td>Ref.</td>
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<tr>
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</tr>
<tr>
<td>10%C₂H₂/H₂ or 10%C₂H₂/N₂</td>
<td>450-600°C at ambient pressure</td>
<td>Tangled filaments</td>
<td></td>
<td>Filament diameter 350-500 Å</td>
<td>59</td>
</tr>
<tr>
<td>Nichrome</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₂/Ni</td>
<td>1000°C at 0.066 kNm⁻²</td>
<td>Laminar on Ni with some nodular growth. Totally nodular on NiO.</td>
<td>Laminar deposits well oriented.</td>
<td>Degree of orientation increased by annealing</td>
<td>67</td>
</tr>
<tr>
<td>NiO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₂/Ni</td>
<td>800-1200°C at 0.013-0.066 kNm⁻²</td>
<td>Laminar at 50 Nm⁻² (0.4τ). Nodular above 50 Nm⁻².</td>
<td>Laminar Well-ordered graphite with 002 plane parallel to substrate. Nodular Single crystals of graphite embedded in a more turbostratic carbon.</td>
<td>Initiation of nodules at scratches and grain boundaries</td>
<td>66</td>
</tr>
<tr>
<td>CH₄/Fe, Co₃Ni</td>
<td>650-750°C at sub-atmospheric pressure</td>
<td>Flake, polycrystalline and filamentary</td>
<td>Flake Single crystal graphite patterns with 002 d spacings of 3.345-3.354 Å on Fe, 3.358-3.369 Å on Ni. Most of the graphite reflections observed indicating well ordered material.</td>
<td>Filament lengths 0.2-1.4 μ. Filament diameters 600-1350 Å. 002 planes of graphite parallel to filament axis.</td>
<td>47, 75</td>
</tr>
<tr>
<td>Reactant</td>
<td>Experimental Conditions</td>
<td>Description of Deposits</td>
<td>X-Ray Data</td>
<td>Additional Information</td>
<td>Ref.</td>
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<td>--------------------------</td>
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</tr>
<tr>
<td>CH₄/Fe, Co,Ni cont.</td>
<td></td>
<td></td>
<td>Polycrystalline 002 spacings of 3.398-3.420 Å only lines corresponding to 002, 101, 004 and 112 graphite planes found indicating poorly ordered, turbostratic carbon.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₂/H₂ Electroless Plated Ni</td>
<td>600°C at 80 kNm⁻²</td>
<td></td>
<td>Graphitic d-spacing 3.37-3.39</td>
<td></td>
<td>55</td>
</tr>
<tr>
<td>CH₄/Ni</td>
<td>600°C at 0.13-80 kNm⁻²</td>
<td>Flake non-oriented and filamentary. Flake single crystals formed initially, with non-oriented C and filaments in subsequent deposits.</td>
<td>002 planes of graphite parallel to filament axis.</td>
<td>Filaments had metal particles in their tips.</td>
<td>57</td>
</tr>
<tr>
<td>C₂H₂/CH₃COCH₃/Fe,Co,Ni</td>
<td>500-1000°C at 0.01-0.1 kNm⁻²</td>
<td>Filamentary growth</td>
<td>Outer sheath graphitic. Inner core electron transparent.</td>
<td>Metal particle in tips</td>
<td>63, 69-73</td>
</tr>
<tr>
<td>Reactant</td>
<td>Experimental Conditions</td>
<td>Description of Deposits</td>
<td>X-Ray Date</td>
<td>Additional Information</td>
<td>Ref.</td>
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</tr>
<tr>
<td>CH₄/C₂H₂/C₂H₄/Ni</td>
<td>700-1000°C at 0.1-8 kNm⁻²</td>
<td>Continuous laminar films at low P and high T. Island growths at high P and low T.</td>
<td></td>
<td>Laminar films by precipitation during cooling. Pre-treatment in H₂ suppresses nodular deposition.</td>
<td>54</td>
</tr>
</tbody>
</table>
and, on nickel, the amount of oriented graphitic material increases with decreasing pressure or increasing temperature (66). In experiments using Ni single crystals, the (110) plane of Ni was shown to be capable of supporting growth of a better oriented graphite than the (111) face. From crystallographic considerations, it was shown that graphite should be able to epitax better with the (111) face than the (110) (67).

High resolution electron microscopy, which allows resolution of individual graphite crystallites, has shown that the carbon sheath of filaments is graphitic in nature with the 002 planes parallel to the axis (57). The core material is assumed to be less well oriented because of the relative ease with which it can be oxidized.

3.4 The Pyrolysis Reaction Over Carbon and Inert Surfaces

A large quantity of data is available on homogeneous pyrolysis of hydrocarbons, and pyrolysis over carbon and inert surfaces, such as silica and porcelain (76-78). A brief review is clearly relevant since, once the metal surface is covered by carbon, the possibility exists for reaction on pyrolysis products, and also at the vessel wall.

3.4.1 Kinetics of Reaction

The data in Table 6 show that at temperatures of \( \sim 1000^\circ C \) pyrolysis occurs at a rate about three orders of magnitude lower in the absence of a metal surface than in its presence. At temperatures of between 900 and 1400\(^\circ C\), activation energies of 422-443 kJmol\(^{-1}\) have been measured and the reaction has been shown to be first order in methane. These energies are in good agreement
<table>
<thead>
<tr>
<th>Gas</th>
<th>Deposition Conditions</th>
<th>On</th>
<th>Rates</th>
<th>Activation Energy kJ mol⁻¹</th>
<th>Mechanism</th>
<th>Morphology</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>815°C; 101-810 kmN m⁻²</td>
<td>Carbon black</td>
<td>CH₄pP %H₂ Rate gm⁻²h⁻¹</td>
<td></td>
<td>Surface chain reaction</td>
<td></td>
<td>89</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>0 1.1x10⁻²</td>
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<td></td>
<td></td>
<td>5</td>
<td>0 4.8x10⁻³</td>
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<td></td>
<td></td>
<td>1</td>
<td>3.2 9.6x10⁻³</td>
<td></td>
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<td></td>
<td></td>
<td>5</td>
<td>3.2 3.6x10⁻³</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>1</td>
<td>19.2 2.4x10⁻³</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>19.2 9.0x10⁻⁴</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>CH₄</td>
<td>900-1100 0°C in He</td>
<td>Carbon rod</td>
<td>422</td>
<td>Gas phase rupture of C-H bond</td>
<td></td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>1200-1400 0°C</td>
<td>Carbon</td>
<td>Initial 443 Steady state 430</td>
<td>Gas phase rupture of C-H bond</td>
<td></td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>640-700 0°C; 13-101 kmN m⁻²</td>
<td>Quartz</td>
<td>Low P 155 High P 250</td>
<td>2CH₄ + C₂H₆ + H₂ ( \rightarrow ) 2C + 3H₂</td>
<td></td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>30% CH₄ in N₂</td>
<td>101 kmN m⁻²; 975 0°C; 1000; 1050; 1100</td>
<td>Silica</td>
<td>0.15 gm⁻²h⁻¹</td>
<td>Liquid droplet carbonisation</td>
<td>Preferred orientation of basal planes parallel to substrate surface</td>
<td></td>
<td>84</td>
</tr>
<tr>
<td>Gas</td>
<td>Deposition Conditions</td>
<td>On</td>
<td>Rates</td>
<td>Activation Energy $kJ \text{ mol}^{-1}$</td>
<td>Mechanism</td>
<td>Morphology</td>
<td>Ref.</td>
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</tr>
<tr>
<td>$\text{CH}_4, \text{C}_6\text{H}_6$</td>
<td>$1000^\circ \text{C}$ at atmospheric pressure</td>
<td>Carbon black</td>
<td>$\text{CH}_4$ 326</td>
<td>Surface decomposition. Nucleation &amp; growth of isolated particles.</td>
<td></td>
<td>81</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$\text{C}_6\text{H}_6$ 577</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>$\text{C}<em>6\text{H}</em>{12}$ 230</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>$1300-200^\circ \text{C}$ 0.53kN m$^{-2}$</td>
<td>Graphite</td>
<td>196</td>
<td>Gas phase polymerisation</td>
<td>C-axis of deposit parallel to surface. Degree of graphic ordering decreases as P increases.</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_2$</td>
<td>Temperatures $&lt;550^\circ \text{C}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Condensed-ring aromatics formed</td>
<td>95</td>
</tr>
<tr>
<td>$\text{CH}_4, \text{C}_3\text{H}_3$</td>
<td>$800-1300^\circ \text{C}$</td>
<td>Silica</td>
<td></td>
<td></td>
<td></td>
<td>Three types of carbon irrespective of gas : i) shiny vitreous ii) soft pulverulent iii) filamentary</td>
<td>86</td>
</tr>
</tbody>
</table>
Table 6 continued

<table>
<thead>
<tr>
<th>Gas</th>
<th>Deposition Conditions</th>
<th>On</th>
<th>Rates</th>
<th>Activation Energy $\text{kJ mol}^{-1}$</th>
<th>Mechanism</th>
<th>Morphology</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_6\text{H}_6$, $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$</td>
<td>$1200^\circ\text{C}$</td>
<td>Porcelain</td>
<td></td>
<td></td>
<td>$\text{C}_2\text{H}_2$ formation and breakdown via $\text{C}_2\text{H}$ radical. Interlayer spacing 3.61-3.47 Å</td>
<td>Carbon films in hot zone, soot at cool ends. Films shiny and black from $\text{C}_6\text{H}_6$. Whiskery from $\text{C}_2\text{H}_2$</td>
<td>83</td>
</tr>
</tbody>
</table>
| $\text{CH}_4$ and various aromatics | $1200^\circ\text{C}$ | Porcelain |       |                                        | 1) Fragmentation of large molecules  
2) Free radical chain reaction to give $\text{C}_2\text{H}_2$  
3) Breakdown of $\text{C}_2\text{H}_2$  
Interlayer spacing 3.46-3.55 Å | Four types of carbon irrespective of gas  
i) thin film hard & brittle  
ii) soft & smooth  
iii) thick film feathery & soft  
iv) brownish-black, sponge-like | 76   |
with the bond dissociation energy of CH\textsubscript{4} of 435 kJ and indicate that the rate controlling process is the rupture of the C-H bond as suggested by a number of workers (see for instance 76). From thermodynamic considerations, methane should be stable up to about 800°\textsuperscript{C} (for a tabulation of K\textsubscript{p} values see 79). The low temperature work of Odochian and Schneider (80) must follow a different mechanism, which they suggest involves the formation and breakdown of C\textsubscript{2}H\textsubscript{6}.

A comparison of activation energies measured for the homogeneous and heterogeneous pyrolysis of methane has been made and the variation in magnitude explained in terms of differences in surface catalytic efficiency (82). No detailed mechanistic explanation is given, but the implication is that different mechanisms are possible on different types of surface.

### 3.4.2 Morphology

Table 6 gives a summary of the main morphological features of deposits produced by different workers under a variety of conditions. The form of carbon deposited is independent of the gas or surface conditions used and depends on the experimental temperature and pressure conditions. Three basic forms of carbon are commonly found - shiny vitreous thin films, soft filamentary thick films and powdery sooty deposits. In addition, a sponge-like deposit and one which is a mixture of vitreous and sooty carbon has been described (76). Carbon produced in the gas phase forms as spherical particles 100-500 Å in diameter, with graphite crystallites embedded in otherwise amorphous carbon (77). Tesner (81) has described the deposition reaction in terms of a two-stage process of nucleation and growth of particles. He
explains differing degrees of dispersity of carbon under different experimental conditions by considering the degree of supersaturation of the hydrocarbon in the gas phase over carbon. He suggests that a low degree of supersaturation, as attained by high gas velocity or rapid heating rate in the gas, leads to a more dispersed carbon with small particle size.

3.4.3 The Nature of the Deposit

Deposits formed on carbon and inert surfaces consist of turbostratic and amorphous carbon. Carbon with the best degree of ordering is found near the surface. Gas phase formed deposits are largely amorphous (76, 77, 83-85). Because of the non-crystalline nature of the deposit, few X-ray studies have been made; available data are listed in Table 6. Contamination of the deposits by silica has been reported in experiments on the pyrolysis of CH₄ and other hydrocarbons in a silica vessel at 800-1300°C (86).

3.5 Mechanisms

A number of mechanisms have been proposed to explain the pyrolysis of hydrocarbon (76, 77, 87). Two possibilities exist for the pyrolysis of methane, the first is scission of a C-H bond followed by a series of surface reactions resulting in the formation of carbon. Proposers of this mechanism assume that the rate determining step is the gas phase rupture of the C-H bond (76, 82, 88-90). The alternative is polymerization to higher hydrocarbons and breakdown of these; such a mechanism involving dimerization of CH₃ radicles to C₂H₆ has been proposed (80).

Two similar mechanisms are available for pyrolysis of other hydrocarbons and the two main theories of pyrolysis are based on fragmentation or polymerization. The more widely held
view is that the hydrocarbon breaks down to smaller fragments, which then lose hydrogen to form carbon. Acetylene has been suggested as the final fragment before carbon formation (see for instance 76, 77 and 83). The alternative theory is one of formation of liquid droplets of a high molecular weight polymer, which subsequently carbonize (84). The possibility of formation of polymers has been demonstrated (91), but it is concluded that polymer formation and carbon formation occur by means of two competing reactions, and the carbonization of liquid droplets does not occur. The mechanism of carbon formation via acetylene as an intermediate was first proposed by Berthellot (92) and Lewes (93) in the later nineteenth century, to explain results of pyrolysis experiments on ethylene at temperatures up to 1000°C.

3.5 Summary of the Main Features of the Fe/CH₄ Reaction

1. The morphology of deposits is similar to that of carbon formed from CO, and is independent of the reacting species.

2. Laminar, nodular and filamentary deposits are observed. Nodular growths nucleate at active surface sites, such as grain boundaries. The number of sites available on Ni decreases with increasing temperature.

3. Pre-treatment with H₂ suppresses nodular deposition.

4. Kinetics of deposition are complex. There is some disagreement on the value of the reaction activation energy, and apparent negative activation energies are reported under certain conditions.

5. Deposits are highly graphitic in nature, with the 002 plane parallel to the substrate.
6. Filaments have a metal particle in their tips and a
graphitic sheath, with 002 planes parallel to the axis.

7. The homogeneous reaction, and reaction over C and
inert surfaces is orders of magnitude slower than the catalysed
reaction, and can be ignored in short-term experiments.

4. MECHANISTIC ASPECTS OF CARBON DEPOSITION

From the data presented in the previous two sections,
it is clear that the metal is not a true catalyst. It not
only participates in the reaction to form, in some cases, metal-
carbon compounds, but also changes the nature of the deposit.
Carbons formed by the non-catalysed reaction are amorphous soots
or glasses, whereas those formed on metals are highly ordered
graphites. The most active metals for deposition are those
which dissolve carbon and form metastable carbides.

Several different carbon morphologies have been reported.
Direct comparison of the results of different workers is made
difficult by the limited data available in reports, and the use
of different terms to describe apparently similar structures.
Deposits are generally characterised by electron diffraction and
electron optical techniques after cooling to room temperature.
The structures observed are therefore not necessarily representative
of those present at the reaction temperature, and may be affected
by the method (e.g. rate) of cooling. Different morphologies can
be observed on a single sample, although in general similar types
of deposit, and similar reaction rates, have been found in all
reported deposition studies. In Table 7, an attempt has been
made to correlate morphological data and mechanisms. The terms
given in the left hand columns will be those used in the remainder
of this thesis.
<table>
<thead>
<tr>
<th>Description of Deposit</th>
<th>Terminology Used in the Literature</th>
<th>Nature of Deposit</th>
<th>Proposed Reaction Mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitated film</td>
<td>1)Continuous laminar film (54) 2)Thin polycrystalline film (53)</td>
<td>Thin (~50Å), graphitic, uniform film</td>
<td>Precipitation from solution during cooling (53, 54)</td>
</tr>
<tr>
<td>Laminar film</td>
<td>1)Island growths (54) 2)Laminar carbon (66, 67) 3)Flake or single crystal graphite (47, 53) 4)Polygonal (66, 67)</td>
<td>Plates of single crystal graphite growing laterally from isolated sites. Some variation in thickness observed. Eventually plates grow together to give complete coverage.</td>
<td>Nucleation, at plate edges, of gas phase molecules, or by diffusion of surface metal/carbon species (53, 54, 66)</td>
</tr>
<tr>
<td>Nodular carbon</td>
<td>Nodular carbon, cluster growths, non-oriented carbon (47, 53, 66)</td>
<td>Clusters of non-oriented carbon growths, with the appearance of &quot;cotton wool balls&quot;.</td>
<td>Rapid surface nucleation at metal or oxide particles (53)</td>
</tr>
<tr>
<td>Filamentary carbon</td>
<td>Filaments</td>
<td>Tubes with an outer graphitic sheath as inner, readily oxidizable core, usually with a metal particle at the tip and sometimes metal in the sheath.</td>
<td>1)Solution/precipitation in the metal particle (71) 2)Solution/precipitation in a non-stoichiometric carbide particle (96) 3)Extrusion through holes in the laminar film (53)</td>
</tr>
</tbody>
</table>
The general processes expected to be involved in any reaction mechanism are discussed below, with reference to relevant literature data. Detailed reviews of chemisorption, diffusion, phase relationships and carbide structures are then given in the following chapters with particular reference to iron. The topic of cooling/precipitation is discussed from the point of view of steel metallurgy, where it plays an important role. Metallurgical theory is developed sufficiently to describe the principles of the structure of the complex alloys of the type used in nuclear reactors.

4.1 Initial Surface Processes

Reaction must be preceded by chemisorption on to the 'clean' metal surface. In practice, clean surfaces can only be produced and maintained under UHV conditions. Samples used in most studies reported would have been covered by a thin, air-formed oxide layer, which may have to be reduced initially. Nevertheless, reactions of the following type must precede deposition:

\[
\begin{align*}
\text{CO}_g & \rightleftharpoons \text{CO}_{\text{ads}} + \text{C}_{\text{ads}} + \text{O}_{\text{ads}} \\
\text{CH}_4_g & \rightleftharpoons \text{CH}_4_{\text{ads}} \\
\text{CH}_3_{\text{ads}} & \rightleftharpoons \text{CH}_2_{\text{ads}} + \text{H}_{\text{ads}} \\
\text{CH}_2_{\text{ads}} & \rightleftharpoons \text{CH}_{\text{ads}} + \text{H}_{\text{ads}} \\
\text{CH}_{\text{ads}} & \rightleftharpoons \text{C}_{\text{ads}} + \text{H}_{\text{ads}}
\end{align*}
\]

Once the surface is covered by deposit, further adsorption must occur on carbon or carbide. There is evidence that a surface step is rate limiting in the early stages of reaction of iron with both
The adsorbed carbon can react in one of three ways - recombine and desorb, or undergo a surface nucleation and growth process, or dissolve in the metal. Dissolution in nickel (63-65) and iron (60, 61) has been demonstrated, and under some conditions, reaction stops when the metal is saturated (54). Precipitation during cooling is thought to account for the thin layer closest to the metal surface (53, 54).

4.2 Deposit Formation

The laminar carbon, observed to be formed on top of the precipitated film, is believed to grow by a nucleation process (53, 54, 66). The film consists of plates of single crystal graphite, which originate at isolated sites on the surface, close to areas of high activity such as grain boundaries. It has been proposed that lateral growth occurs by either nucleation of gas phase molecules (54), or by surface diffusion across the basal planes of organometallic species, which decompose at the plate edges (53). After an undefined period of reaction, rapid growth at particularly active sites, such as metal or oxide particles, results in the formation of nodular carbon. The detailed structure of this material is not well known because it does not give satisfactory diffraction patterns. It is therefore defined as non-oriented, but may consist of graphite crystals or filaments with diameters smaller than the critical size for diffraction.

4.3 Filament Growth

An essential feature of nodular growths, and of thick deposits in general, is the presence of filamentary carbon. Each filament has a metal particle in its tip, and growth is thought to cease when it becomes completely encapsulated in carbon (53).
The mechanism of growth has received considerable attention, and a number of hypotheses proposed. These are:

1) that long, poorly graphitised filaments grow by a dissolution/precipitation mechanism in the metal particle. Carbon is deposited exothermally on the leading face and dissolves. The heat of reaction tends to create a temperature gradient in the particle. Carbon precipitates at the cooler trailing edge, causing the particle to advance (71).

2) that short, highly graphitic filaments form by a process of extrusion through the laminar deposit. Continued growth occurs by surface diffusion of metal-carbon species to growth points, where decomposition results in the formation of metal and carbon (53).

3) that filaments formed by the reaction of CO with Fe grow from an immobile, non-stoichiometric carbide particle. It is proposed that the carbide stoichiometry is dependant on the lattice perfection of the carbon phase in contact with it, and that it has a greater solubility for disorganised carbon than for graphite. Disorganised carbon, deposited on one crystal space would be expected to precipitate on another as graphite, to form a filament with the same diameter as the particle (96). It has been demonstrated elsewhere that a dissolution/precipitation process can result in the rearrangement of disorganised (amorphous) carbon into graphitic structures (63-65).

5. CHEMISORPTION PROCESSES

Information on the chemisorption of gases on iron is limited, because of the difficulty of obtaining reproducible, atomically clean surfaces. Therefore, in the discussion of the adsorption of CO and CH₄, data from studies on other metals are included, to indicate how
iron might react under rigorous conditions.

5.1 Carbon Monoxide on Clean Metal Surfaces

Carbon monoxide is adsorbed on metals in several discrete states, for example 3 for nickel, 6 for niobium, characterised by different activation energies of desorption in the range 16-400 kJ mol\(^{-1}\). The states with activation energies below about 100 kJ mol\(^{-1}\) are regarded as weakly bound, and designated \(\alpha\)-states. Those with higher energies designated \(\beta\), desorb at temperatures above about 800 K (97). They are found on all crystal planes and therefore cannot be explained simply in terms of surface structure (98). The \(\alpha\)-state fills when the \(\beta\)-layer is \(\sim\)70\% complete and therefore could be occupying sites between \(\beta\)-CO species (99). In addition, 'virgin' adsorption states have been identified at sub-ambient temperatures on tungsten. Virgin states are stable up to 200 K, and field emission microscope studies indicate that they all have the same dipole moment (100).

CO adsorbs on Fe with an initial calorimetric heat of adsorption of about 170 kJ mol\(^{-1}\) (98). On Ni the corresponding figure is 125-135 kJ mol\(^{-1}\), and an additional binding state has been reported with an adsorption heat of 108 kJ mol\(^{-1}\) (101). However, there is evidence that disproportionation occurs on Ni even at ambient temperature (102), and at temperatures above about 460 K the rate of reaction is determined by the rate of incorporation of carbon into the metal lattice (103). Low energy electron diffraction (LEED) and auger electron spectroscopy (AES) studies have established that CO generally adsorbs in the virgin and \(\alpha\)-states without dissociation. In some \(\beta\)-states, however, it may be fully dissociated (104).
5.2 Structure of the Absorbed Species

The structure of gaseous CO is shown in Figure 1.

![Molecular orbital diagram of gaseous carbon monoxide](image)

Fig. 1 The molecular-orbital description of gaseous carbon monoxide. Arrows indicate the possible electronic interactions that may occur during adsorption on a transition metal (100).

Bonding to a transition metal occurs initially by donation of the lone electron pair on the carbon atom to a vacant d-orbital of the metal atom. The donor ability of CO is very small, and stabilisation of the metal-carbon bond is believed to occur by back-donation of electrons from filled d-orbitals into vacant antibonding orbitals (100).

For the adsorption of CO on iron, infrared adsorption peaks are found at 2020 cm$^{-1}$, 1950 cm$^{-1}$ and 580 cm$^{-1}$. The following structures have been considered for the adsorbed species.

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>C</td>
<td>C</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe</td>
<td>Fe</td>
<td>Fe</td>
<td>Fe</td>
</tr>
</tbody>
</table>

(a) (b) (c) (d) (e)
Comparison of force constants with those C-O carbonyl bonds suggests that (a) is the most likely surface structure. A band at 1887 cm\(^{-1}\), which disappears on heating can be attributed to the weakly bound \(\alpha\)-state (105).

In early studies, high frequency stretching modes were attributed, by analogy with known carbonyls, to linearly adsorbed species, and low frequency stretches to bridged species. Thus structures of type (a) to (c) were attributed to absorption bands of >2000 cm\(^{-1}\). However, as more carbonyls were identified, it became clear that the stretching frequency of a bond is determined by its immediate environment, and that a monodentate CO ligand can have a stretching frequency <2000 cm\(^{-1}\) (100). Molecular orbital calculations on the Ni/CO system show that the number of metal atoms involved in the interaction is important in determining the frequency, and that it is not necessary for linear and bridged structures to have widely differing C-O frequencies. The carbon atom loses \(\sigma\) charge to the metal, but gains \(\pi\) charge, such that there is little net transfer. In addition, the electronic properties of the adsorbed species initially change significantly as the number of metal atoms involved is increased, but become constant after 5 nickel atoms have been included in the linear interaction, and 4 in the bridged. It is concluded that the bond is localised on the nearest neighbours in the plane of the interaction, and that the plane below has little influence (106).

5.3 Methane on Clean Metal Surfaces

Early studies showed methane adsorption on relatively impure iron surfaces to be activated. No reaction occurred below
170°C, at which temperature dissociative chemisorption began (107). From deuterium exchange experiments, the rate determining step was found to be breakdown of adsorbed CH₃ radicles (108, 109). On clean Fe surfaces, methane chemisorbs at room temperature, and below, without dissociation. Gas adsorbed at 770K desorbs at 120-1300K with a desorption energy of 28 kJ mol⁻¹ (110, 111). In direct contradiction to early results, a molecular beam scattering experiment on clean Fe failed to detect dissociation at metal temperatures up to 8000K (111).

Chemisorption on metals occurs with decreasing sticking probability as the coverage increases. At the same time the activation energy increases, for instance on Mo from 11.2 kJ mol⁻¹ at low coverage to 25 kJ mol⁻¹ at high (112). Non dissociative chemisorption on W at low temperatures falls to a low level at 300°K. At higher temperatures (>1200°K and 10⁻⁵ Torr), physisorbed species undergo activated decomposition to form surface carbide structures (113-115). Methane adsorbs on clean Ni at ambient temperatures in the form of both ordered and disordered structures. On heating to 350°C, rearrangement of surface species occurs, resulting in a pseudo-clean LEED pattern, where carbon has either formed a structure with the same mesh as the surface nickel atoms, or has dissolved (116). The rate of adsorption on Ni at 300-500°K has a fractional dependence on pressure (117), implying dissociation occurs. A recent review of methane chemisorption and deuterium exchange reactions has been published by Frennet. (118).

5.4 Chemisorption on Carburised and Graphitised Surfaces

Further adsorption of CO on Ni (110) can occur on top of
disproportionation products \((C + CO_2)\) formed at 20\(^\circ\)C (102). Experiments on LEED and AES characterised Ni (110) crystals have shown that:

1) chemisorption occurs on surfaces carburised in ethylene at 600\(^\circ\)K
2) the binding energy is 30-40\% below that on clean Ni (110)
3) the sticking probability and total coverage are similar to those on the clean surface.
4) no adsorption occurs on samples graphitised at 800\(^\circ\)K in \(C_2H_4\)

(101). Chemisorption of CO on Fe\(_3\)C is very much less than on iron (119), which may explain why deposition ceases when an iron catalyst has been completely converted to carbide (29).

No data are available for reaction of \(CH_4\) on carburised surfaces. Hydrocarbon reactions, such as bond scission, have been shown to occur on Pt catalyst, on top of a carbonaceous overlayer, which consists of partially dehydrogenated species directly bonded to the metal. The rate of certain reactions depends critically on the overlayer structure. Thus, for instance, conversions of cyclohexane to benzene or of n-heptane to toluene, only occur if it is ordered (120).

6. **DIFFUSION OF CARBON IN IRON**

Carbon dissolves interstitially in both the face-centred-cubic (fcc) and body-centred-cubic (bcc) forms of iron, occupying in each case octahedral sites in the metal lattice. To describe the diffusion process, a crystal plane can be regarded as a periodic potential energy surface, with interstitial atoms occupying equilibrium positions of minimum energy. Each atom is surrounded
by potential energy barriers which must be surmounted for diffusion to occur. Fick's Laws of diffusion, derived by analogy with heat conduction, can be represented as follows:

\[
\text{Diffusion flux } J = -D \frac{\partial c}{\partial x} \quad (22)
\]

where \( \frac{\partial c}{\partial x} \) = concentration gradient

\( D \) = constant

\( = \text{Diffusivity} \)

\( c \) = concentration

and

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (23)
\]

The diffusivity, equivalent to thermal conductivity, is temperature dependant according to the relation

\[
D = D_0 \exp \left( -\frac{\Delta H}{RT} \right) \quad (24)
\]

where \( D_0 \) = frequency factor

\( \Delta H \) = activation enthalpy

(121, 122).

In a perfect crystal, \( D \) is independent of concentration. However, for the diffusion of \( C \) in \( \gamma \)-Fe (fcc structure) both \( \Delta H \) and \( D_0 \) decrease with increasing carbon concentration (123, 124). At any fixed carbon level, \( D \) obeys equation 24, but \( \Delta H \) decreases from 150 kJg atom\(^{-1}\) at 1 atom percent \( C \) to 120 kJg atom\(^{-1}\) at 6 atom percent. No such concentration dependence has been found for diffusion of \( C \) in \( \alpha \)-Fe, possibly because of the low solubility (maximum of 0.1 atom % at 720\(^{o}\)C). The diffusivity in \( \alpha \)-Fe over the temperature range -40 to 350\(^{o}\)C, can be represented by the equation

\[
D = 0.394 \exp \left( -80, 150/RT \right) \text{mm}^2\text{s}^{-1} \quad (25)
\]

(125). Above these temperatures, deviations occur towards higher
values of $\Delta H$, which increases to 105 kJ mol$^{-1}$ at 850°C (126, 127, 122, p. 142).

In a polycrystalline material, grain boundaries act as sinks for imperfection, dislocations and interstitial atoms. The region between adjacent grains is more disordered than the bulk grain. Between two crystallites of the same orientation, this disturbed region may only be 2 or 3 atoms wide. Its width increases between, for instance, grains of high and low index, where orientation differences are largest. The activation energy for grain boundary diffusion is lower than that for bulk diffusion. However, boundary widths are small in comparison to grain diameters (typically fractions of a nanometer, compared to tens of microns), and diffusion down boundaries is only significant if:

$$D(b) \times \text{average grain boundary width} > D(\ell) \times \text{average grain diameter}$$

where $D(b)$ and $D(\ell)$ are the grain boundary and lattice diffusivities respectively. If typical values are substituted in equation 26 for grain diameter and boundary widths of 50 µm and 0.5 nm respectively, it is obvious that this condition can arise only if $D(b)$ is $10^5$ times larger than $D(\ell)$. No direct comparison is available of $D(b)$ and $D(\ell)$ for diffusion of carbon in iron, and the contribution of grain boundaries in the values quoted above is not known.

However, enhanced diffusion down dislocations has been invoked to explain the more rapid growth of carbide precipitates at grain boundaries, from a saturated solution of C in α-Fe (129). Evidence from internal friction measurements shows that C is more stable at dislocation sites (122, p. 158). Carbon diffusion
through the metal is inhibited by high concentrations of dislocations, and it would be expected to be located preferentially at grain boundaries. A pure Fe sample exposed to a carburising atmosphere will take up carbon initially at grain boundaries. Rapid saturation and precipitation might occur at points where a number of boundaries meet, or where surface imperfections (caused for instance by work hardening during rolling) exist.

7. PHASE RELATIONSHIPS

7.1 Phase Diagrams

The iron-carbon phase diagram is given in Figure 2a. At temperatures up to 910°C, iron exists as the bcc α-phase. The transformation temperature to fcc γ-phase decreases, with increasing carbon content, to 723°C at 0.095 atom percent. Complete conversion to γ-Fe iron at 723°C occurs at 3.61 atom percent carbon. The phase α-Fe+dissolved C is often referred to as ferrite, and γ-Fe+dissolved C as austenite. The stable carbon phase is graphite (dashed lines), but under conditions of rapid cooling the metastable carbide Fe₃C precipitates (solid lines).

The Cr/C and Ni/C diagrams are given in Figure 2b and 2c. The chromium structure is bcc at all temperatures. It has a very low solubility for C (130) but forms the series of stable carbides Cr₂₃C₆, Cr₇C₃, Cr₃C₂ (Table 8). Nickel (fcc structure) has a relatively high solubility for C (1.5 atom % at 1000°C, dropping to 0.4% at 700°C (130)). It forms the unstable carbide Ni₃C at 250–300°C by reaction with CO; decomposition occurs above 400°C (130 and Table 8).

Fe/Cr and Fe/Cr/C diagrams are given in Figures 3a, b and c. The following substitutional binary alloy phases are stable in the
FIG. 2 METAL-CARBON PHASE DIAGRAMS
(a) IFON  (b) CHROMIUM  (c) NICKEL
FIG. 3 ALLOY PHASE DIAGRAMS
(a) Fe/Cr/C AT 20°C (b) Fe/Cr/C AT 850°C (c) Fe/Cr
temperature range 0-1000°C

1) $\alpha^-$, bcc structure

2) $\gamma^-$, fcc, stable in the absence of C over the limited Cr contents of 0-13% and at temperatures above 830-910°C (the "$\gamma$-loop"). In the presence of carbon it is stabilised to higher Cr concentrations.

3) $\sigma^-$, tetragonal, stable over the limited range 44-50 wt% Cr at temperatures <815°C, the sigma phase is likely to be present at 600°C and below in alloys containing 24-70 wt% Cr (130). Carbon solubility in it is very low, but it is reported to be able to dissolve "metastably significant amounts" (132).

The stable phases in the ternary diagram are $\alpha^-$ and $\gamma^-$ plus the mixed carbides $M_3C$ at low Cr levels, $M_7C_3$ and $M_{23}C_6$ at high Cr, where $M = Fe$ or Cr. The $\sigma$-phase enters the ternary diagram below 815°C by direct co-existence with $(CrFe)_{23}C_6$.

7.2 Carbides of Fe, Cr, Ni

Table 8 lists the properties of known carbides. All the iron carbides are metastable; cementite, Fe$_3$C, is the most stable and the only one which can be isolated at room temperature. $\varepsilon$-carbide and Hagg carbide are formed in steels at intermediate tempering temperatures (see next section) and decompose above about 400°C to cementite. The carbides tend to be non-stoichiometric, thus for instance cementite with the defect structure $Fe_{(C_{1-x} II_x)}$, where II represents a missing carbon atom, has been reported to form at tempering temperatures of 150-400°C (140). The composition of the $\varepsilon$-(hexagonal) carbide $Fe_xC$ varies from $x = 1.5$ to $x = 2.8$ depending on temperature, particle size and degree of cold plastic deform-
Table 8

METAL CARBIDE DATA

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Structure</th>
<th>Unit cell dimensions ( \text{Å} )</th>
<th>Formation Temperature (^\circ\text{C})</th>
<th>Decomposition Temperature (^\circ\text{C})</th>
<th>Heat of Formation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cementite ( \text{Fe}_3\text{C} )</td>
<td>Orthorhombic</td>
<td>( a = 4.526 ) ( b = 5.087 ) ( c = 6.744 )</td>
<td>( &gt;450 )</td>
<td>( 700-800 )</td>
<td>10</td>
<td>131, 132, 136</td>
</tr>
<tr>
<td>( \varepsilon )-carbide ( \text{Fe}_x\text{C} ) ( x &lt; \frac{3}{2} )</td>
<td>Hexagonal</td>
<td>( a = 2.73 ) ( b = 4.33 )</td>
<td>( 100-250 )</td>
<td>( 300-400 )</td>
<td>-</td>
<td>119, 132, 135, 136</td>
</tr>
<tr>
<td>Hagg carbide ( \text{Fe}_5\text{C}_2 )</td>
<td>Monoclinic</td>
<td>( a = 11.562 ) ( b = 4.573 ) ( c = 5.060 )</td>
<td>( 200-300 )</td>
<td>( 400-500 )</td>
<td>-</td>
<td>119, 132, 136</td>
</tr>
<tr>
<td>( \text{Fe}_7\text{C}_3 )</td>
<td>Complex hexagonal</td>
<td>N/A</td>
<td>( 1400 )</td>
<td>( 80 \text{ k bar} )</td>
<td>N/A</td>
<td>136-138</td>
</tr>
<tr>
<td>( \text{Fe}_6\text{C} )</td>
<td>Complex cubic</td>
<td>N/A</td>
<td>( 400-480 ) in thin iron films in CO</td>
<td>N/A</td>
<td>-</td>
<td>139</td>
</tr>
<tr>
<td>Carbide</td>
<td>Structure</td>
<td>Unit cell dimensions</td>
<td>Formation Temperature °C</td>
<td>Decomposition Temperature °C</td>
<td>Heat of Formation</td>
<td>Reference</td>
</tr>
<tr>
<td>----------</td>
<td>------------------</td>
<td>----------------------</td>
<td>---------------------------</td>
<td>-------------------------------</td>
<td>------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Cr₂C₆</td>
<td>Complex cubic</td>
<td>10.60</td>
<td>N/A</td>
<td>&gt;1500</td>
<td>-69</td>
<td>132</td>
</tr>
<tr>
<td>Cr₇C₃</td>
<td>Complex hexagonal</td>
<td>a = 4.53, b = 14.01</td>
<td>N/A</td>
<td>&gt;1500</td>
<td>-178</td>
<td>132</td>
</tr>
<tr>
<td>Cr₃C₂</td>
<td>Orthorhombic</td>
<td>a = 2.82, b = 5.53, c = 11.47</td>
<td>N/A</td>
<td>&gt;1500</td>
<td>-88</td>
<td>132</td>
</tr>
<tr>
<td>Ni₃C</td>
<td>Orthorhombic</td>
<td>N/A</td>
<td>100-200</td>
<td>300-400</td>
<td>-</td>
<td>130, 132</td>
</tr>
</tbody>
</table>

N/A = not available
Hagg carbide, sometimes referred to as iron per-carbide was initially given the formula Fe$_2$C by Hagg (133), this was later redesignated Fe$_{20}$C$_6$ by Jack (134), but is now accepted to be Fe$_5$C$_2$ (136). The carbide Fe$_7$C$_3$ is normally only detected at high temperatures and pressures during diamond synthesis, when iron is used as a solvent for carbon (137, 138). However, it has been reported to be involved in filament growth during carbon deposition on iron (40), but the observation has not been confirmed. The existence of a carbide FeC has been reported in connection with Fischer-Tropsch synthesis reaction (141), but it has not been detected in steel.

Nickel carbide Ni$_3$C is unstable and readily decomposes above 400°C. The chromium carbides, however, are stable up to their melting points of around 1600–1800°C. They have a high substitutional solubility for iron, similarly Cr can substitute for Fe in cementite. Thus carbides in alloy steels tend to be the mixed carbides of Figure 3b.

CARBON PRECIPITATION PROCESSES IN IRON AND STEEL

1 Plain Carbon Steels

Steel metallurgy is based on the two simple facts that:

1) γ-Fe can dissolve ~ forty times more C than can α-Fe
2) carbon-containing precipitates in the metal can cause hardening.

The form of precipitates and degree of hardness is largely controlled by the rate of cooling from the austenite phase, where all the carbon is present in the dissolved state. Hardness results from rapid cooling (quenching), the precipitate size and structure are then determined by the temperature of the quenching medium.
<table>
<thead>
<tr>
<th>Cooling Rate</th>
<th>Quench Temp. °C</th>
<th>Precipitate</th>
<th>Characteristics of Steel</th>
<th>Structure of Precipitate</th>
<th>Metallographic Features</th>
<th>Cooling Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very slow</td>
<td>-</td>
<td>Graphite</td>
<td>Very soft, ductile</td>
<td>Nodular</td>
<td></td>
<td>In furnace</td>
</tr>
<tr>
<td>Slow</td>
<td>-</td>
<td>1) C content &lt; 0.8% Ferrite + pearlite 2) C content &lt; 0.8% Pearlite + cementite</td>
<td>soft, ductile</td>
<td>Ferrite - α-Fe + dissolved C</td>
<td>Indistinguishable from Iron</td>
<td>In air</td>
</tr>
<tr>
<td>Rapid</td>
<td>600-700</td>
<td>Pearlite</td>
<td>Ductile</td>
<td></td>
<td></td>
<td>Quench into molten salt</td>
</tr>
<tr>
<td>Rapid</td>
<td>Ambient</td>
<td>Pearlite</td>
<td>Hard and brittle</td>
<td>Particle size small</td>
<td>Particle size can be removed by reheating to ~ 350°C (tempering)</td>
<td>Cooling in an air blast</td>
</tr>
</tbody>
</table>
Table 9 continued

<table>
<thead>
<tr>
<th>Cooling Rate</th>
<th>Quench Temp, °C</th>
<th>Precipitate</th>
<th>Characteristics of Steel</th>
<th>Structure of Precipitate</th>
<th>Metallographic Features</th>
<th>Cooling Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very rapid</td>
<td>400-500</td>
<td>Upper Bainite</td>
<td>Hard</td>
<td>Mixture of ferrite and cementite</td>
<td>Feathery structures, no individual cementite grains</td>
<td>Quench into molten salt or heated oil</td>
</tr>
<tr>
<td>Very rapid</td>
<td>300-400</td>
<td>Lower Bainite</td>
<td>Hard</td>
<td>Ditto</td>
<td>Acicular structures</td>
<td>Ditto</td>
</tr>
<tr>
<td>Very rapid</td>
<td>200-300</td>
<td>Martensite + some retained austenite</td>
<td>Very hard, brittle</td>
<td>Tetragonal</td>
<td>Needle-like structures</td>
<td>Ditto</td>
</tr>
<tr>
<td>Very rapid</td>
<td>Ambient</td>
<td>Retained austenite + martensite</td>
<td>Hardness depends on relative proportion of austenite and martensite. Austenite being soft and ductile.</td>
<td>Austenite visible in form of sharp, angular white patterns, in dark martensite areas.</td>
<td>Quench into water (iced)</td>
<td></td>
</tr>
</tbody>
</table>
Table 9 summarises the effects of cooling rate. The quench temperatures are approximate and will vary according to the steel composition.

For many applications the most important metallurgical processes are the formation and decomposition of martensite, because of the extreme hardness which can be obtained. Steels have characteristic quench temperatures, $M_S$ and $M_F$ ($M_S > M_F$). Above $M_S$, carbon diffusion rates are too rapid for martensite to form, below $M_F$, formation can go to completion. A steel quenched to a temperature between $M_S$ and $M_F$ will, virtually instantaneously, form a fixed proportion of martensite plus retained austenite, no more is formed unless the temperature is lowered. Martensite forms by diffusionless transformation of austenite. Its structure can be regarded as bcc distorted by the presence of carbon, because the quenching rate is so rapid that carbon does not have time to diffuse out of the sites it occupied in the fcc lattice. As such it is highly stressed.

Martensite structures can be retained by a further quench in iced water, however the stresses in the metal are so great that it can disintegrate on standing. The stresses can be relieved by heat treatment (tempering). Maximum hardness is attained by treatment at $\sim 100^\circ$C. Above $100^\circ$C, ductility increases but hardness decreases. The chemical processes occurring during tempering are:

1) at 80-200°C, nucleation and precipitation of $\varepsilon$-carbide
2) 200-300°C, decomposition of austenite
3) 300-400°C, precipitation of Hagg carbide
4) >400°C, precipitation of Fe₃C

Prolonged tempering results in carbide particle growth and loss of hardness.

8.2 Alloy Steels

Carbon steels rapidly lose hardness above about 300°C, they also lose strength because of carbide coagulation and growth. The presence of carbide at dislocations and grain boundaries increases the activation energy for dislocation diffusion. Coagulation releases vacancies and dislocations; if sufficient energy is injected into the lattice, e.g. by straining it, they diffuse through the metal. By aligning themselves parallel to the strain direction, they allow adjacent metal crystallites to slip over each other and the metal is said to creep. A large increase in strength at high temperatures can be achieved by the addition of up to 10% Cr. This reduces carbon mobility, by forming stable carbides, and has the added benefit of increased resistance to oxidation, by the formation of Cr₂O₃ at the surface.

A detailed discussion of alloying effects would be lengthy and complex and is not appropriate in the context of this thesis. However, references will be made in the experimental section to a 20(%Cr) 25(%Ni) Nb stabilised stainless steel. A brief discussion of the characteristics of this particular alloy is therefore relevant.

The addition of Cr at levels >12%, and up to 18-20%, greatly increases the oxidation resistance of steels. Little further improvement can be gained above 20% Cr, except by the addition of Ni (25% or more) or of Si (2-3%). Above about 700°C, the
creep resistance of ferritic (high Cr) steels decreases markedly as a result of metal crystal growth, during transformation to the γ-phase, as well as by dislocation movement. Grain growth in austenite steels occurs at higher temperatures. Nickel stabilises the austenite phase by depressing the γ to a transition temperature. Its presence in the steel thus provides creep, as well as oxidation resistance. Further resistance to creep is attained by the presence of low levels (1-2%) of Mn, which also stabilises the austenite phase, and of Nb, Mo and W. Being large atoms, they precipitate, generally as carbides, at sites of lowest energy such as grain boundaries and dislocations, which are effectively 'locked' in position. To summarise, therefore, a 20/25/Nb steel is oxidation resistant by virtue of the presence of high levels of Cr and Ni, and low levels of Si. Creep resistance is provided firstly by stabilisation of the austenite phase by Ni and Mn, and secondly by the presence of Nb, Mo and W carbides at grain boundaries and dislocations. (For further discussion of carbon and alloy steel structures see 142, 143).

9. ELECTRICAL MEASUREMENTS IN THE STUDY OF CHEMICAL REACTIONS

The work in this thesis is a study of reactions occurring in the bulk metal and on the metal surface. Bulk reactions such as dissolution and precipitation affect metal resistivity; surface deposition affects sample emissivity, and hence power dissipation. Electrical measurements thus provide a simple means of following the kinetics of the early stages of carbon formation.

9.1 Resistivity

When an electric field is applied to a metal, free electrons, i.e. those close to the Fermi surface, are accelerated. They lose energy by collision with atoms in the lattice. The resulting current is proportional to the average electron velocity, which is
determined by the strength of the applied field and the collision frequency. At absolute zero, electrons can move through a perfect crystal without resistance. In practice metals have a residual resistivity $\rho_R$, due to scattering at grain boundaries, crystal imperfections and interstitial atoms. $\rho_R$ is independent of temperature. The total resistivity $\rho$ includes a temperature component $\rho_T$, due to scattering by lattice vibrations (phonons), and is given by

$$\rho = \rho_T + \rho_R$$

Equation 27 is known as Matthiessen's Rule (144). The effect of increasing the concentrations of scattering centres by addition of interstitial atoms, vacancies or dislocations is to increase $\rho_R$. For low levels of impurity $\rho_R$ is given by

$$\rho_R(x) = Ax (1-x)$$

where $x$ = impurity concentration and $A$ is a constant (Nordheim's Rule) (145). For $x \ll 1$ equation 28 can be reduced to

$$\rho_R(x) \approx Ax$$

Equation 27 and 28 hold for many systems at low temperatures and low levels of impurity and have been extensively used in the study of the behaviour of interstitial atoms, and of vacancies and dislocations. Deviations have however been observed, and have been reviewed by Bass (146). In particular, the constant $A$ in equation 28 has been shown to be temperature dependent for the dissolution of C in iron at high temperatures. The specific resistivity increment ($\Delta\rho/\Delta x$) of $\alpha$-Fe has approximate values of 4.5 $\mu\Omega$cm/at\% at 0\(^{\circ}\)K, 6.0 at 400-700\(^{\circ}\)K, then falls to about 2 $\mu\Omega$cm/at\% at 1100\(^{\circ}\)K. That of $\gamma$-Fe at temperatures above 1200\(^{\circ}\)K is constant at about 1.0 $\mu\Omega$cm/at\%. 
9.2 Power Dissipation

The power (W) dissipated from an electrically heated sample is given, in vacuo, by

\[ W = \sigma \varepsilon A_g (T - T_o) \quad (30) \]

where

\( \sigma = \) Stefan's constant
\( = 5.72 \times 10^{-8} \text{ J m}^{-2} \text{s}^{-1} \text{K}^{-4} \)

\( \varepsilon = \) emissivity

\( A_g = \) geometric area

\( T = \) sample temperature in °K

\( T_o = \) temperature of surroundings (Stefan's Law). In the presence of a gas, convection and conduction add to the heat loss expression complex terms which depend on the geometry of the system, as well as temperature and pressure (see for instance 150). However at constant temperature and pressure, \( W \) is determined by the emissivity only, which for metals is \( \sim 0.2-0.4 \), but is close to one for carbon (151). The power dissipation of a carbon coated metal sample is therefore \( \sim 3 \) times that of the clean metal.

9.3 Previous Work

No reference has been found to the use of power dissipation changes to study chemical reactions. Resistivity, however, has been used extensively in the following fields:

1) Study of metal defect structures, dislocations, and damage caused by irradiation.

2) Phase diagrams and phase transformations.

3) Diffusion/precipitation phenomena of interstitial solutes in metals, and analytical determination of alloy concentrations.
A brief survey of topics 1-3 will be given. Detailed information can be obtained from references 152-153.

9.3.1 Defects and Dislocations in Metals

High concentrations of defects can be induced by deformation, rapid quenching from high temperatures, or irradiation. At liquid nitrogen temperatures they are immobile, but isochronal plots of resistivity vs temperature show discontinuities, due to annealing, which are characteristic of the diffusion process occurring. In addition to identifying particular defect types, resistivity measurements allow kinetics of diffusion to be measured. The processes occurring are

1) 0-500K - recombination of interstitial/vacancy pairs.
2) 500K to ambient - long distance migration of interstitial atoms to vacancies or other interstitials.
3) > room temperature - void formation by diffusion and coalescence of vacancies, release of interstitial atoms from low energy traps ('recovery') at \( \sim 0.3 T_m \) (where \( T_m \) is the melting point) and recrystallisation at \( \sim 0.4 T_m \).

8.3.2 Phase Diagrams and Phase Transformations

Within a single alloy phase, resistivity changes uniformly with composition, and can be used as an analytical tool. Discontinuous resistivity changes, due to changes in crystal structure and of concentrations of interstitial atoms, can be used to identify transformation temperatures and phase boundaries, and to measure rates of transformation.
9.3.3 Diffusion/Precipitation Phenomena

Since the resistivity of a metal is proportional to the concentration of dissolved interstitial atoms, resistivity changes can be used to measure rates of dissolution and precipitation. Thus, for instance, the precipitation of pearlite from a supersaturated carbon steel causes a measurable decrease in resistivity, by reducing the total number of scattering sites.

10. ION MICROPROBE MASS SPECTROMETRY (IMMS)

Analytical work in previous studies of carbon deposits has been concentrated on characterising the carbon product. Metal-containing compounds are generally only reported in thick deposits, where carbides and oxides have been identified. There are no reports of the chemical changes occurring at the reaction interface, where intermediate active species, if involved, might be expected to be formed. Labile compounds may decompose during slow cooling to ambient temperature. However, their existence can be inferred if chemical composition differences at the metal interface can be demonstrated. Ion microprobe mass spectrometry (IMMS) is capable of detecting such effects with high sensitivity. Although the technique is not yet sufficiently advanced to allow compound identification, the secondary ion emission is characteristic of the surface species, and structural changes can be observed.

10.1 The Technique

IMMS is a surface analysis technique related to secondary ion mass spectrometry (SIMS). The sample is bombarded by energetic primary ions, with energies in the keV range, sputtered secondary ions are analysed by mass spectrometry. The SIMS technique is normally used for the study of adsorbed monolayers. Primary ion bombardment is restricted to an intensity just sufficient to eject adsorbed
species, without damaging the metal surface. In microprobe studies, high intensity bombardment erodes away a pit in the sample surface, providing a depth profile of surface layers.

A schematic diagram of the Cameca ion probe mass analyser used in this work is given in Figure 4. The instrument has both mass analysis and mass imaging facilities. A duoplasmatron gun provides primary ions (usually Ar⁺ or O⁺) in the form of a focused beam, which can be made to scan the sample for imaging purposes. The secondary ions are focused by an electrostatic immersion lens into a double focusing mass spectrometer, which incorporates a low-pass energy filter in the form of an electrostatic mirror. The mirror located between the two electromagnetic prisms is used to cut out the high energy tail of the ion peaks and reduce overlap, thus improving isotope separation. The mass analysed current can be measured or imaged via an ion/electron convertor and a photomultiplier or a scintillator and fluorescent screen respectively. The beam size can be varied between 20 and 400 µm diameter, and ultimate detection levels of <1 ppm can be obtained (155, 156).

10.2 Interpretation of Data

10.2.1 The Ion-Surface Interaction

The following description of the IMMS process is taken largely from references 157 and 158. Impact of primary ions with the surface causes emission of atomic or molecular particles, as well as electrons and photons. The particles can be positive, negative or neutral, and may or may not be in an excited state. The bombardment process also causes lattice damage, e.g. amorphization or creation of imperfections, below the surface. Figure 5
FIG. 4 THE ION PROBE MASS ANALYSER

[PROVIDED BY J.P. LENOIR AND P. JANICHEWSKI OF C.A.M.E.C.A.]
FIG. 5 INTERACTION PROCESSES OF AN ION WITH A SURFACE RESULTING IN THE EMISSION OF HEAVY PARTICLES
illustrates the processes occurring. These are:

1) ion reflection
2) sputtering
3) recoil sputtering
4) ion implantation

Primary ions hitting the surface are either reflected, or adsorbed into the lattice (implanted). Reflection causes surface atoms of the sample to be 'knocked on' into the bulk. Implanted primary ions dissipate their kinetic energy to the surroundings either in a single, or a multiple collision process. A proportion of the energy will be directed towards the surface and cause ejection of surface atoms (sputtering). Those ejected as a result of a single collision are emitted with higher energy (recoil sputtering). Emitted ions have energies of a few eV, for primary ion energies of a few keV.

In order to obtain quantitative structural information, it is necessary to relate the composition and intensity of sputtered ions to the lattice structure of the target. At the present time, however, the calculation of absolute secondary ion yields is not possible, although some empirical data are available. It is generally assumed that the components of an emitted cluster ion originally occupied adjacent sites in the sample lattice. In a multi-component crystal, composed of atoms A, B and C, secondary ions of the general for \( A_a B_b C_c \) would be expected, where \( a, b \) and \( c = 0, 1, 2, \) etc. Statistical considerations predict a decreasing formation probability for multiple atom clusters, and are generally confirmed experimentally. It is found that emitted ions usually retain the
electrical neutrality of the sample lattice, thus for instance for an oxidised sample, metal ions are predominantly positive, oxygen ions negative. Ions of the type Me$_x$O$_y$ show an increased tendency to be emitted negative as $x$ increases ($y = 1$) or positive as $y$ increases ($x = 1$) (157). Parent ions of surface compounds would not normally be expected, because of their low formation probability and the possibility of breakup, after emission, by collision with primary, or other secondary, ions.

The secondary ion current for an ion X$_n$ ($n = 1, 2, 3 ...$) can be calculated from the empirical equation.

$$I(X_n) = AJp\theta S(X_n)f$$  (31)

where $A =$ bombarded area

$Jp =$ primary ion current density

$\theta =$ fractional coverage of surface by ion X$_n$

$S(X_n) =$ absolute secondary ion yield of X$_n$

$$S(X_n) = \frac{\text{number of emitted particles of } X_n}{\text{number of impinging primary ions}}$$  (32)

and $f =$ transmission factor of the mass spectrometer

$$f = \frac{\text{number of detected particles of } X_n}{\text{number of particles of } X_n \text{ ejected from } A}$$  (33)

Table 10 gives experimental values of secondary ion yields for a few relevant ions (157). The figures illustrate the general principle that the ion yield is greater from atoms in the bound state than from those in the metallic state. For this reason, oxygen ion bombardment is frequently used to amplify ion currents by forming surface oxides. Similar amplification occurs in the presence of high background pressures of oxygen (i.e. $10^{-6}$ to $10^{-5}$ Torr) (158). However, this technique has the following disadvantages:
Table 10

IMMS SECONDARY ION YIELDS

<table>
<thead>
<tr>
<th>Surface Composition</th>
<th>Secondary Ion Yields</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean metal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.0015</td>
<td>157</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0006</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.0012</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.0006</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>0.0006</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.0084</td>
<td></td>
</tr>
<tr>
<td>O₂ covered metal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.045</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.58</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Me⁺</th>
<th>MeO⁺</th>
<th>MeO₂⁺</th>
<th>MeO⁻</th>
<th>MeO₂⁻</th>
<th>MeO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.35</td>
<td>0.014</td>
<td>-</td>
<td>0.0007</td>
<td>0.0085</td>
<td>0.0035</td>
</tr>
<tr>
<td>Ni</td>
<td>0.045</td>
<td>-</td>
<td>-</td>
<td>0.007</td>
<td>0.06</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>1.2</td>
<td>0.2</td>
<td>0.0025</td>
<td>0.00025</td>
<td>0.018</td>
<td>0.07</td>
</tr>
<tr>
<td>Mn</td>
<td>0.3</td>
<td>0.007</td>
<td>-</td>
<td>0.004</td>
<td>0.03</td>
<td>0.004</td>
</tr>
<tr>
<td>Nb</td>
<td>0.05</td>
<td>0.3</td>
<td>0.06</td>
<td>-</td>
<td>0.0008</td>
<td>0.02</td>
</tr>
<tr>
<td>Si</td>
<td>0.58</td>
<td>0.011</td>
<td>-</td>
<td>0.00038</td>
<td>0.058</td>
<td>0.058</td>
</tr>
</tbody>
</table>
1) no oxide data can be obtained from the sample
2) the ion spectrum is swamped by oxide and metal isotope ions which may interfere with other peaks, e.g. carbides.

10.2.2 Depth Profiling

Bombardment of the sample by energetic primary ions gradually erodes the surface by sputtering, a crater develops, which in principle allows depth profiling of the sub-surface layers. No useful data can be obtained, however, if secondary ions, emitted from the whole area of the pit, are analysed. Contributions from the walls can be eliminated by a process of selective area aperturing (SAA), where ions emitted from the centre of the pit are focused on to an aperture, before being admitted to the spectrometer. The sputtering rate is different for different materials and crystallographic orientations. The bottom of the craters would not, therefore, be expected to have uniform topology. Therefore, within the volume fraction sampled, averaging effects may interfere with the sharp delineation of deposit layer boundaries. The erosion rate is given by

$$\frac{\Delta Z}{\Delta t} = \frac{J_p S}{N}$$

where \( N \) = sample atom density

For constant values of \( J_p \), \( S \) and \( N \), the crater depth (\( \Delta Z \)) is proportional to the erosion time.

11. SCOPE OF THE THESIS

Our interest in carbon depositing reactions arose initially from experiments on the effect of carbon on excrescence formation during the breakaway oxidation of mild steel. The study demonstrated the involvement of both surface and bulk carbon in the oxi-
dation reaction. It also highlighted the problem of solvent cleaning of samples, and led directly to the procedure adopted in the work reported in this thesis. Some aspects have already been reported and reprints of two papers are included inside the back cover. For completeness, further data will be presented in a chapter of oxidation results.

Further incentive for the work was provided by UKAEA papers reporting examinations of carbon deposits on fuel cans removed from the Windscale, prototype, advanced, gas-cooled reactor (WAGR). These showed localised reaction, with evidence for attack of the underlying metal; a situation slightly analogous to excrescence formation. A literature survey indicated that bulk processes, e.g. carbide formation, occurred simultaneously with surface reaction. It was clear that several reaction mechanisms could be operative, and there were suggestions of catalytic intermediates, but no firm evidence. At that time, there was no discussion of solution/precipitation processes, and little information on gross effects of deposition on metal structure, such as sample disintegration.

The object of the work reported in this thesis was therefore:

1) To study the mechanism of carbon formation with particular reference to processes occurring within the bulk metal, and at the metal deposit interface.

2) To study the formation of thick deposits, on metals, and under reaction conditions, relevant to the operation of nuclear power stations.

The gaseous reactants used were CO, because significant reaction occurs at temperatures below about 700°C, where metastable carbides
are formed and may participate in the reaction; and CH₄, because reaction occurs at higher temperatures where stable carbides are unlikely to exist, and because oxide interference in the reaction does not occur. This is particularly important in power dissipation measurements, since oxide, as well as carbon, has a higher emissivity than the metal. Deposition studies reported refer mainly to pure iron; comparative data are given for reaction on the metals Cr, Ni, Mo and Nb, the important constituents of stainless steel. Deposition on Fe/Cr and Fe/C binary alloys and on a 20/25 Nb steel is also discussed.

The techniques employed are:

1) resistivity measurements on furnace heated foils, to obtain kinetics of the dissolution stage of reaction on Fe. Limited results on Ni are also included.

2) simultaneous resistivity/power dissipation measurements, to study the early stages of deposition from CH₄ on electrically heated iron foils.

3) weight gain experiments on a range of metal coupons to obtain comparative kinetic data for growth of heavy deposits at approximate AGR partial pressures, and to study metal break-up by using thin samples of different thickness.

4) IMMS analyses of reaction products. The results reported were mainly obtained on Fe, but some data are included from Cr and 20/25 steel samples.

In addition, the work has involved the development of new high pressure equipment for the study of metal-gas reactions under simulated reactor operating conditions. A novel design for a totally demountable, inert environment autoclave system is given, with some
preliminary performance data.

In order to present the data clearly, the results section has been split into five chapters, with a discussion of experimental detail at the end of each. The final chapter of the thesis is then restricted to a general discussion of mechanistic aspects of the results.
II EXPERIMENTAL

1. MATERIALS

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1.1.2 Binary Alloys
1.1.3 Other Metals

1.2 Gases

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2.2 Resistance Measurement
2.3 The Reaction Cells
2.3.1 Resistivity Experiments
2.3.2 Resistivity/Power Dissipation Experiments
2.4 An Inert Environment Autoclave System

3. EXPERIMENTAL PROCEDURES

3.1 Resistivity Measurements
3.2 Resistivity/Power Dissipation Measurements
3.3 Operation of the Autoclave Rig
3.4 IMMS Analysis
3.5 Other Analytical Techniques
1. MATERIALS

1.1 Metals

1.1.1 Pure Iron and Nickel Foils

Foils were supplied in 400 mm lengths of 1 mm or 10 mm width and 25, 50, 100 and 200 μm thickness by Johnson Matthey Ltd. A typical manufacturer's analysis in ppm is Ca 20, Al 10, Cr 10, Ag 10, Cu 7, Mg 5, Mn 5, other <5 except C and N which were not analysed for. In addition, iron foils contained about 10 ppm Ni and nickel foils about 10 ppm Fe. They were manufactured from high purity sponge, which was sintered at 1100°C for several days in an atmosphere of cracked ammonia, acid pickled to remove nitrides (of iron) and pressed at 1100°C into a compact. After acid treatment to remove the surface layers, degreasing and vacuum annealing at 1100°C, the compact was cold rolled, using a light hydrocarbon oil as a lubricant. After degreasing and cutting the metal was coated with a water-repellant oil (soluble in chloro-hydrocarbons) before being despatched, without further annealing. On receipt, the foils were stored, undisturbed, in an evacuated desiccator. After cutting to size, samples were degreased by wiping between pads soaked in trichloroethylene, followed by ultrasonic washing in trichloroethylene and ether, and immediately installed in the apparatus.

1.1.2 Binary Alloys

Samples 20 mm × 10 mm were cut from strips 200 mm long × 80 mm wide × 0.6 to 0.7 mm thick supplied by CEGB South East Region laboratories (Cockfosters). A range of Fe/Cr and Fe/C alloys, from 1 to 34% Cr and 0.005 to 0.91% C respectively, were manufactured from high purity iron chromium and carbon, melted in
an electric arc furnace. The samples were hot forged to 50 mm thickness, and hot rolled to about 1.5 mm thickness. Final rolling was carried out after a further anneal for 30 minutes in vacuo and an acid pickle to remove oxide. A similar heat treatment was given before despatching, with the metal sandwiched between niobium strips to getter oxygen. On receipt, the alloys were stored in an evacuated desiccator. Samples were cut from the central 60 mm of each strip and their thickness reduced by about 25% by grinding both faces on carborundum paper, to remove oxide, and any compositional inhomogeneities at the edge or surface. They were then polished to a 6 μm diamond finish, degreased as described above, and stored in an evacuated desiccator. Analysis of the alloys are given in Table 11.

Table 11

<table>
<thead>
<tr>
<th>Specimen code</th>
<th>Nominal Cr Content (%)</th>
<th>Actual Cr Content (%)</th>
<th>C analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B686</td>
<td>1</td>
<td>1.10</td>
<td>0.005</td>
</tr>
<tr>
<td>B687</td>
<td>3</td>
<td>3.00</td>
<td>0.003</td>
</tr>
<tr>
<td>B688</td>
<td>8</td>
<td>8.55</td>
<td>0.004</td>
</tr>
<tr>
<td>B689</td>
<td>14</td>
<td>14.60</td>
<td>0.004</td>
</tr>
<tr>
<td>B690</td>
<td>24</td>
<td>24.60</td>
<td>0.008</td>
</tr>
<tr>
<td>B691</td>
<td>34</td>
<td>34.20</td>
<td>0.005</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Specimen code</th>
<th>Actual C Content (%)</th>
<th>Nominal C Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B680</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>B681</td>
<td>0.005</td>
<td>0.004</td>
</tr>
<tr>
<td>B682</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>B683</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>B684</td>
<td>0.75</td>
<td>0.74</td>
</tr>
<tr>
<td>B685</td>
<td>0.90</td>
<td>0.95</td>
</tr>
</tbody>
</table>
1.1.3 Other Metals

Other metals suppliers and analyses were:

Cr - Metals Research Corp. arc melted bars of Iochrome, 99.996% quoted purity. Main impurities in ppm: O, 20; N, 5; Cl, 10; Fe, 10; S, 2; other elements <1.

Nb - Koch Light Ltd. quoted purity 99.5%. 20/25 Nb steel was supplied by UKAEA Springfields.

1.2 Gases

Experiments were carried out in CH₄ and CO (BOC Grade X and CP grades). Manufacturers quoted purities are:

- CP grade 99.2% for CH₄
- 99.8% for CO
- Grade X 99.99% for CH₄

Typical impurities in vppm: N₂, 30; O₂, 1; CO₂, 1; H₂, 1; hydrocarbons, 30.

- 99.95% for CO

Typical impurities: N₂, 400; CO₂, 2; H₂, 2; O₂, 2; hydrocarbons, 30; moisture, 1.

In addition HP argon (BOC quoted purity 99.998%) was used as an inert flushing medium in autoclave experiments.

CP grade gases were used in autoclave experiments because of the large quantities involved. Typical cylinder analyses, obtained by gas chromatograph/mass spectrometric analysis are:

- CO, impurities in vppm: O₂, 20-40; N₂, 50-100; moisture, 20-30; hydrocarbons, 50-100; CO₂, 20-30.

- CH₄, impurities in vppm: CO₂, O₂ and moisture <5; N₂, 50-100; hydrocarbons, 25-50.

Electrical measurements were made in CP grade CH₄ and Grade X CO.
2. APPARATUS

2.1 Gas Handling Arrangements

The same gas and vacuum lines were used for resistivity and resistivity/power dissipation measurements. A similar gas handling system was also used in an autoclave rig, described later. The arrangement is shown in Figure 6 for resistivity experiments. Methane is purified of O₂ by conversion to H₂O in a catalytic bed (Engelhard Type D) at 450°C. Water and higher hydrocarbons are removed by beds of 5A and 13X molecular sieves (Linde) respectively. The final analysis of the gas obtained by gas chromatography is:

- oxygen < 1 vppm
- water < 20 vppm
- hydrocarbon <20 vppm
- nitrogen ~ 75 vppm
- hydrogen < 20 vppm

Carbon monoxide for resistivity experiments is taken direct from the Grade X cylinder using a stainless steel precision regulator (BOC model 3502). For autoclave experiments the catalyst bed was maintained at 350°C. This arrangement proved to be unsatisfactory and was replaced by Engelhard Type M catalyst at 50°C.

Hydrogen (BOC White Spot), used in pretreatments of foils, was purified by molecular sieve beds as above, followed by a palladium/silver diffusion unit (Johnson-Matthey Ltd. Type H28) at 200°C and 75 psi pressure. Under the conditions used, the reaction vessel can be filled to ambient pressure in about ten minutes. A spring-loaded, relief valve was incorporated into the gas line adjacent to the vessel, to prevent over-pressurisation. Flow rates were measured
FIG. 6 DIAGRAM OF EXPERIMENTAL SYSTEM FOR RESISTIVITY MEASUREMENT
using a calibrated float-type flowmeter (Rotameters Ltd.).

The gas and vacuum lines, apart from those connecting to the reaction vessel, were stainless steel. Standard twin olive couplings and \( \frac{1}{4} \) OD pipe were used on the gas side, and 50 mm pipe and copper gasket/knife edge sealed flanges on the vacuum side. All valves were bellows sealed and stainless steel (Nupro for gas and Vacuum Generators for vacuum). Vacuum was achieved using standard Edwards rotary, and oil diffusion pumps, with appropriate vapour traps. Gas was admitted to the system, and flows controlled, by a vacuum leak valve (V.G. MD6).

2.2 Resistance Measurements

The resistance of a 50 \( \mu \text{m} \) thick iron foil of 12 cms length varies from 1.5 to 2.5 ohms according to reaction temperature. From the data of Swartz and Cuddy (149), it can be calculated that the maximum resistance change which can be expected to be observed is \( \leq 0.1 \, \Omega \) at 735\( ^\circ \)C. To obtain initial rate data it is necessary to measure at least a 1\% change, i.e. \( 10^{-3} \, \Omega \). This is the absolute limit of detection of DC bridging systems, such as those based on the Wheatstone bridge, which are limited by the galvanometer sensitivity. Sufficient accuracy can be obtained by a potentiometric measurement technique, however, it requires stable resistance conditions and best accuracy is only obtained when a number of determinations can be averaged (152). Preliminary experiments indicated that, at the highest temperature and pressure conditions, 10\% of reaction would occur within the first few minutes of reaction.

To obtain sufficient accuracy and rapid response times, a pre-calibrated 10 \( \mu \text{V} \) resistance D.V.M. (Fluke 8375A) was used. A
10 mA constant current is applied to the sample, and potential changes monitored by a standard 4-terminal method, to reduce contact resistance errors. A logic circuit converts potential to resistance for a direct display to a quoted accuracy of $\pm 1 \times 10^{-4}$ ohms.

For simultaneous resistance/power dissipation measurements on electrically heated foils, a four terminal method was again adopted. The positive leads of the Pt/Pt 13% Rh thermocouples, spot-welded to the foil in the central, constant temperature region, were used as potential probes. Probed voltage and current (as pd-across a standard 0.01 $\Omega$ manganin resistor) were measured using potential dividers and 10 $\mu$V D.V.M. The circuit is shown in Figure 7 with some typical resistance values. Switch 1 reversed the heating current from a constant current d.c. supply (Hewlett-Packard Model 6285A), Switch 2 in conjunction with a second one at the D.V.M. allowed current, total foil voltage and probed voltage to be monitored at one meter. Similarly switches 3 and 4 directed both thermocouple potentials to a second 100 $\mu$V D.V.M. (Fluke 8120A).

2.3 The Reaction Cells

2.3.1 Resistivity Experiments

Measurements were carried out on the apparatus shown in Figure 6, which consisted of a silica glass vessel 500 mm in diameter by 700 mm long, evacuable to better than $10^{-7}$ Torr. Entry for specimens was via a metal vacuum flange using a copper gasket/knife edge sealing system. The top plate was modified by the manufacturers (Vacuum Generators Ltd.) to incorporate four 100 mm long by 6 mm diameter, copper, electrical feedthroughs (Type EFT 13). Platinum electrodes, 2 mm diameter by 500 mm long, supported the sample, which consisted of a 130 mm loop of metal foil spot-welded to the end so as
FIG. 7  DIAGRAM OF ELECTRICAL CIRCUIT
to give a 120 mm sample length. Electrical connections to the feedthroughs were made with brass barrel connectors, the temperature of which did not exceed 80-100°C. In early experiments, tungsten electrodes, sheathed at each end in Pt foil to reduce contact resistance errors, were used. It was found that they had to be replaced at intervals of 6-8 weeks, because they became brittle due to recrystallisation. Measurements taken with newly installed tungsten electrodes gave abnormally low rates in the first experiment after installation, due, it is thought, to contamination of the sample by impurities from the tungsten.

The reaction vessel was heated by a vertical tube furnace, with three windings of lengths 300 mm, in the centre zone, and 150 mm each end zone. The temperature was maintained to an accuracy of ± 5°C by a 3-zone, proportional drive thyristor controller, which allowed the total power input to be disproportionately distributed between the windings, as required to obtain a level temperature gradient. In practice a constant temperature region 100 mms long was achieved. It was monitored continuously by six stainless steel sheathed, chromel-alumel thermocouples, spaced at 20 mm intervals in a pocket in the side of the vessel, and displayed on a multi-point recorder. Details of the heater control circuits and over-temperature cut-outs are the same as those given later in Appendix 1, in the description of an inert environment autoclave system.

Gas entry and exit ports were located at the top of the vessel, a side tube took ingoing gas to the bottom, to ensure pre-heating, and adequate flushing of reaction products. Methane flows were established by balancing the gas flows through the inlet
and outlet valves, at the required pressure in the reaction vessel, and a fixed outlet pressure of $6 \times 10^{-1}$ Torr in the pumping line. This gave a flowrate of approximately 50 stn$^2$. min$^{-1}$ calculated from pressure rise measurements after closing the exit valve. Gas pressures were measured using two standard, calibrated dial gauges covering the ranges 1-100 Torr, and -15 to 30 psi.

2.3.2 Resistivity and Power Dissipation Experiments

Measurements were made using the experimental cell shown in Figure 8. This consisted of a pyrex tube 250 mm long by 80 mm diameter, narrowing to 50 mm at one end to accommodate a vacuum electrical feedthrough (V.G. Type EFT 5) on which the sample was mounted. The cell incorporated an optically flat window for pyrometry, which was protected from evaporating metal, during pretreatments, by a shutter, operated externally by means of a rotatable magnet, acting on a soft iron rod encapsulated in the winding spindle.

The sample consisted of a foil 150 mm long by 1 mm wide by 0.025 mm thick, to which were spot welded two 0.075 mm diameter, Pt, Pt 13% Rh thermocouples (Thermopure grade ex Johnson Matthey) centrally positioned about 50 mm apart. The foil was spot welded to two 3 mm diameter tungsten electrodes and the thermocouples to 1 mm tungsten rods. External connections were made through the feedthrough.

2.4 An Inert Environment Autoclave System

In order to study carbon deposition reactions under simulated reactor running condition, high pressure equipment is required which is made of a material which will not itself react. Existing autoclaves were manufactured from steel, with an externally wound
FIG. 8  DIAGRAM OF EXPERIMENTAL SYSTEM FOR RESISTIVITY/POWER DISSIPATION MEASUREMENTS
heater. To prevent interference from products formed at the hot walls, an autoclave has been designed based on a silica reaction vessel. The construction is such that it is totally demountable for easy access in the event of a fault, e.g. furnace failure. The problem of the mechanical weakness of glass has been overcome by balancing the internal reactant pressure, with an equal external pressure of argon.

Operation of high pressure equipment can introduce considerable delays into an experiment, for instance, large metal vessels can take 24 hours to cool to ambient temperature. This problem has been partially overcome by making provision to handle a large number (typically ~50) samples in each autoclave.

The rig has been partially automated, e.g. gas balancing, to simplify operation, and all switching operations, including gas handling are carried out from a mimic diagram.

Full design details are presented in Appendix 1, which is a reproduction of CERL internal report, and in the CEGB Technical Disclosure Bulletin no.244 in the back cover of the thesis.

3. EXPERIMENTAL PROCEDURES

3.1 Resistivity Measurements

The degreased foil was spot welded to the electrodes and bolted into the reaction vessel. After evacuation to 10^{-7} Torr, the furnace was heated to 990°C over a period of about four hours, and hydrogen admitted to pressure of 1 bar. Flowrate adjustment (to ~50 std. m³.s⁻¹) was made using the inlet valve, to prevent overpressurisation of the glass sections of the apparatus. Samples were cleaned in H₂ and outgassed in vacuo prior to reaction. The pretreatment conditions were the object of a separate study which is
reported in the following chapter. Vacuum conditions were such that a pressure of $10^{-7}$ Torr was achieved after about 10 minutes pumping and the ultimate pressure of $\approx 5 \times 10^{-8}$ Torr after 30 minutes. After overnight pretreatment, the furnace temperature was reset for the experiment.

When the temperature had stabilised (after about 6 hours), methane was admitted to a pre-determined pressure. Resistance readings were taken periodically using a $\frac{1}{10}$ second stop-watch as a timer. The gas flow (approximately $50 \text{ st ml min}^{-1}$) was set up by opening the exit valve sufficiently to give a pressure of $6 \times 10^{-1}$ Torr in the pumping line, and balancing the inlet flow to maintain a constant pressure. The total volume of CH$_4$ consumed by reaction, at the saturation limit of C in Fe at $900^\circ$C, is approximately 10 st ml, which at 50 Torr pressure is <1% of the cell volume. Reaction could be stopped at any time, to obtain samples of a particular carbon content, by evacuating the vessel. Cooling to ambient temperatures, after an experiment, took 10-12 hours.

Experiments were carried out at 10-100 Torr on 50 μm foils, which gave measurable rates of dissolution over the temperature range 500-900°C. Results are plotted in terms of the dimensionless parameter $\Delta R / R_0$ where $\Delta R$ is the increase in resistance, and $R_0$ the initial resistance obtained by extrapolation of the initial readings to zero time. Introduction of gas caused a slight increase in temperature, and hence of contact errors, at the electrical feedthrough connections. The change was complete within 5 sec., but its magnitude was not totally reproducible, and $R_0$ could not therefore be obtained from the pre-reaction value in vacuo.
3.2 Resistivity/Power Dissipation Measurements

The use of electrical heating demanded the following modifications to the procedures described in the previous section.

1) after evacuation, the system was filled with gas (H₂ or CH₄), and the pressure and flow stabilised, before setting the foil to the required temperature.
2) resistivity and power dissipation were calculated from measurements of current and probed voltage.
3) temperature was measured using either a micropyrometer, or the thermocouples, and was controlled manually by adjusting the heating current.

In preliminary experiments, the total spectral emissivity of a sample was measured after the pretreatment, by measuring the power dissipation of the central region for a range of temperatures between 650°C and 850°C, in a vacuum of ~5 × 10⁻⁸ Torr. Because the thermocouple junction had a finite area, it picked up some of the potential drop applied to the ribbon. To obtain the true potential, it was necessary to reverse the current polarity and take the average of the two readings. The temperatures thus measured were, in vacuo, ~50°C below the corrected pyrometer values, as a result of cooling of the junction by conduction down the wires. During deposition experiments, the presence of a gas increased heat losses from the wires and raised the difference to about 150°C. All quoted temperatures were therefore obtained by pyrometry and are accurate to better than ±10°C.
Kinetic measurements on the growth of carbon were made at temperatures of 700-900°C in methane at a pressure of 1 bar and a flow rate of 25 st.mls min⁻¹, which gave residence times of ~30 minutes. Higher flow rates caused uneven cooling of the ribbon. An estimated figure for the methane consumption rate of ~0.5 mls/min was calculated from the weight of carbon deposited. Mass spectrometric analysis of the effluent gas failed to detect any increase in H₂ concentration. Pretreatment conditions were used of 4h in H₂ and 16h in vacuo at 650°C (later referred to as low temperature pretreatment conditions), to remove surface oxide and dissolved gases. It was calculated from data presented by Fast (122) that the dissolved N₂ concentrations should be reduced to a low level in ¼h, in H₂ at 650°C and eliminated completely in 2h. For a deposition experiment, the reaction cell was filled with methane, a flow established and the sample temperature set with the pyrometer. Current and voltage were then measured, and the true thermocouple emfs calculated by reversing the current polarity. This figure was maintained constant by increasing the voltage applied to the foil, and current and probed voltage measured periodically. Reaction had to be completed in a single treatment, because precipitation processes during temperature cycling affected the physical state of the sample, and hot spots developed on reheating. The reaction temperature was measured at the end of the experiment, by optical pyrometry, when the metal was fully covered by carbon. An emissivity of one was assumed.

In presenting the results, power dissipation increase is expressed in terms of ΔW/W₀ where ΔW is the measured increase and W₀
the initial value. The carbon formation rate is calculated as follows:

From equation 30

\[ W = \sigma c Ag(T^4 - T_0^4) \]

The power dissipation \( W(t) \) at any time, \( t \), is

\[ W(t) = \sigma(T^4 - T_0^4)(\varepsilon_F e (Ag - Ac(t)) + \varepsilon_C Ac(t)) \quad (35) \]

where \( \varepsilon_F e \) = emissivity of iron
\( \varepsilon_C \) = emissivity of carbon \( \% \)
\( Ac(t) \) = area of carbon at time \( t \)
\( Ag \) = constant

The rate of formation of carbon is given by

\[ \frac{dAc(t)}{dt} \]

and

\[ Ac(t) = \frac{W}{\sigma(T^4 - T_0^4)(\varepsilon_C - \varepsilon_F e)} - Ag \frac{\varepsilon_F e}{(\varepsilon_C - \varepsilon_F e)} \quad (36) \]

Thus

\[ \frac{dAc(t)}{dt} = \frac{dAW}{dt} \frac{1}{\sigma(T^4 - T_0^4)(\varepsilon_C - \varepsilon_F e)} \quad (37) \]

This equation is applicable to the formation of a "two-dimensional" carbon layer, i.e. when the surface is fully covered with carbon
\( Ac(t) = Ag \), and \( \frac{dAc(t)}{dt} = 0 \). In practice, such growth is approximated to during the initial stages of reaction.

3.3 Operation of the Autoclave Rig

Full operating and sample handling arrangements are given in Appendix 1. In the experiments reported, the following procedure was adopted. Cleaned samples, weighed on a five figure automatic balance (Sartorius), were stood vertically (to allow equal gas
access to both sides) in platinum wire frames and contained in thin-walled silica buckets 25 mm diameter by 10 mm high. After reweighing, they were installed in the autoclave and the system evacuated to \(5 \times 10^{-2}\) Torr. To flush out residual air, the autoclave was filled with H.P. argon and evacuated, and the procedure repeated twice. The furnace temperature was raised and stabilised, over a period of about six hours, with the samples in an atmosphere of H.P. argon, flowing at 25 st. ml/min at a pressure of 40 psia (2.75 bar). Temperatures of 500-850°C were used.

A run was initiated by evacuating the reaction vessel and refilling with test gas (CO or CH₄), to the same pressure, and was terminated by evacuation and filling with argon. After cooling to room temperature (12-16 hours), samples were removed and weighed. Kinetic data was obtained from single samples weighed periodically, or from a number of different samples reacted for increasing lengths of time. Air exposure between runs was kept to a minimum by storing the samples in a vacuum desiccator. To compensate for scatter in results due, for instance, to small temperature fluctuations, at least three samples were used for each datum point.

3.4 IMMS Analyses

Analyses were carried out on the CAMECA ion probe mass analyser system at UKAEA Harwell. It was operated with an Ar⁺ primary ion beam at accelerating voltages of 14.5 kV for negative, and 5.5 kV for positive ion erosion. A beam current of 200 nA was used for all samples except a 20/25 Nb steel, for which it was raised to 300 nA to increase the secondary ion yields of the minor constituents. An area of surface 250 \(\mu\)m square was irradiated and secondary ions sampled, by selective area aperturing, from a central circle of diameter 100 \(\mu\)m.
The irradiated area is determined by the aspect ratio, the ratio of the magnitude of the sides of the square. It is also effected by the primary ion accelerating voltage, the potential difference between the ion source and sample determines the angle of incidence of the ion beam. To attain similar areas of bombardment, aspect ratios of \(1 \times 2\) and \(1 \times 1\) were used for positive and negative ion erosions respectively. Better depth resolution can be attained, at the cost of lower secondary ion intensities, at higher aspect ratios, because the primary beam is spread over a larger area and the current density of equation 34 is reduced. In practice increasing the aspect ratio from \(1 \times 1\) to \(1 \times 2\) made little difference, and results are plotted on the same graph. Results obtained at \(3 \times 3\), however, showed much improved resolution and are plotted separately.

It is normal practice in SINS papers to express the bombardment intensities in terms of a current exposure density. Approximate figures, in A.S.cm\(^{-2}\), for the samples examined are:

- Fe/\(CH_4\) and Fe/CO Resistivity samples: \(3 \times 10^{-4}\) to \(3 \times 10^{-2}\)
- Fe/CO Autoclave samples: \(3 \times 10^{-4}\) to \(1 \times 10^{-2}\)
- Fe/CO and 20/25 steel/CO Autoclave samples: \(5 \times 10^{-4}\) to \(8 \times 10^{-2}\)

In obtaining reproducible data, the following experimental parameters were found to be important:

1) Primary gas purity - if, for instance, the gun had previously been used for oxygen ion bombardment, it was necessary to thoroughly purge the gun and the specimen chamber before starting any analyses.

2) Primary ion energy, beam current and focus - all tended to drift slowly, and required to be checked periodically.
3) **Ultimate vacuum** - \( <5 \times 10^{-7} \) Torr required to prevent oxygen interference.

4) **Area analysed** - aspect ratio and selected area aperturing. Specimens in the form of 1 mm ribbons or 10 mm square coupons were analysed. It was found that slight curvature of samples had no detectable effect on the results, but that sharp changes of inclination of the sample to the primary beam (e.g. a twisted ribbon) could not be tolerated. All analyses reported were made on flat samples apart from the steel results, where the material had approximately a 10 mm radius.

3.5 **Other Analytical Techniques**

Wet analyses for C in iron, and Fe and Cr in carbon deposits were carried out by CERL analytical department. The techniques used were:

1) To analyse for C in iron foils a procedure was adopted based on a method described by Jones et al. (161, 162). The sample was burnt in a tin envelope, which acted as a flux, in a stream of pure oxygen in a tube furnace at 1200\(^{\circ}\)C. The evolved CO\(_2\) was adsorbed in a solution of ethanolamine and dimethyl formamide, and titrated against 0.02 N tetrabutylammonium hydroxide in toluene/methanol, using alkaline blue as indicator.

2) To analyse for Fe and Cr in carbon, 25 mg of deposit were ashed in air at 900\(^{\circ}\)C. The residue was fused with 0.5 g of Na\(_2\)O\(_2\) in a nickel crucible. The melt was taken up in water, plus 5 mls of HCl, the solution was reduced with 0.03 g Al wire (to Fe(II) and Cr(II)) and made up to 50 ml with water. Fe and Cr were determined by atomic adsorption spectroscopy.

In both cases, background levels were measured in blank experiments.
X-ray analysis was carried out by CERL Materials Division, and X-ray fluorescence analysis by the Electrical Research Association (Leatherhead), under contract. Scanning electron micrographs were obtained on a Cambridge Instruments S4-10 stereoscan. The machine was operated at low accelerating voltages (5-10 kV) to reduce charging effects and obtain maximum detail. The fine structure of the deposit was transparent to more energetic electrons.
III RESULTS 1 SOLVENT CLEANING OF SAMPLES

1. EVAPORATION OF THIN SOLVENT FILMS

2. THE EFFECT OF SURFACE CARBONACEOUS IMPURITIES ON THE INITIATION OF EXCRESCENCE GROWTH DURING THE OXIDATION OF MILD STEEL
III RESULTS 1 SOLVENT CLEANING OF SAMPLES

Experiments, carried out in this laboratory as part of an investigation of the breakaway oxidation of mild steel in high pressure CO₂/CO/CH₄ mixtures, highlighted the problem of solvent cleaning of samples. Soxlet and ultrasonic cleaning were found to be inefficient and a separate study of cleaning techniques was undertaken. The effects of solvent evaporation were studied, and the initiation of excrescences, during oxidation, due to the presence of surface contamination was used as a test of cleaning efficiency. The results have been discussed in references 159 and 160, reprints of which are included in the back cover of the thesis. It is not proposed, therefore, to give a detailed presentation in this chapter, but to merely summarise the salient points.

1. EVAPORATION OF THIN SOLVENT FILMS (159)

The evaporation characteristics of low molecular weight organic liquids from a glass plate were examined, using a Schlieren optical technique and shadow photography. Solvent films, containing either dissolved hydrocarbons or finely divided material in suspension, initially broke up into droplets. Contraction of a drop occurred discontinuously such that the boundary receded stepwise. After all the solvent had evaporated, concentric rings of material, generally around a central deposit, were observed on the glass. Ring formation can be explained by analogy with the spreading of liquids on solid surfaces. A thin, primary film, with a surface tension greater than that of the bulk liquid, moves ahead of the droplet boundary, pulling it out in a secondary spreading process. During evaporation, a drop contracts to maintain a stable contact angle, a hysteresis lag in the angle causes the boundary to move discontinuously. As a result of
evaporation, the thin primary film reaches saturation during the static periods. A ring of material is precipitated and remains when the boundary recedes.

2. THE EFFECT OF SURFACE CARBONACEOUS IMPURITIES ON THE INITIATION OF EXCRESCENCE GROWTH DURING THE OXIDATION OF MILD STEEL (160)

Rimming steel specimens, 10 mm square by 2 mm thick, were oxidised at 450°C in CO₂ containing 1.5% CO + 100 vppm CH₄ (BOC special gas mixture), to which was added 1000 vppm H₂O, at 250 psia (17.25 × 10⁶ Nm⁻²) and a flowrate of 20 ml.min⁻¹, in standard high pressure autoclaves. Samples were deliberately contaminated by smearing a thin film of Apiezon M grease on to the surface, and ultrasonically washed in 60/40 petroleum ether and Analar methanol. After 20 hours oxidation solvent drying structures, in the form of rings and apparent flow patterns, were visible on the surface. Close examination in an SEM revealed the presence of C and a large number of small excrescences in these areas. After about 100 h reaction, the patterns disappeared, but the excrescences continued to develop. Excrescence growths on the 'clean' areas of the surface did not appear until after approximately two hundred hours oxidation.

It was found that efficient cleaning of samples could be achieved by 'scrubbing' between tissue pads soaked in trichloroethylene, followed by ultrasonic washings in trichloroethylene and ether. The method was adopted in all experiments reported in this thesis.
IV RESULTS 2 ELECTRICAL MEASUREMENTS ON THE Fe/CH₄ INTERACTION

1. KINETICS OF THE SOLUTION STAGE OF REACTION
   1.1 Sample Preparation
   1.2 Temperature Variation of Reaction
   1.3 Pressure Variation of Reaction
   1.4 Isosteric Heat of Adsorption
   1.5 Deposition from CO on Iron and from CH₄ on Nickel

2. KINETICS OF FORMATION OF SURFACE CARBON
   2.1 Measurements at 1 bar Pressure
   2.2 Measurements at 50 Torr Pressure

3. PRODUCT MORPHOLOGY AND ANALYSIS
   3.1 Morphology of Carbon Deposits
   3.2 X-ray Analysis of Reaction Products

4. DISCUSSION
   4.1 The Effect of Pretreatment
   4.2 Temperature Variation of Nordheim's Constant
   4.3 The Resistance Decrease
   4.4 Mechanistic Implications
IV  RESULTS 2 ELECTRICAL MEASUREMENTS ON THE Fe/CH₄ INTERACTION

1. KINETICS OF THE SOLUTION STAGE OF REACTION

Preliminary results for reaction, at 830°C and 50 Torr pressure, on foils of thickness 25, 50 and 100 μm are plotted in Figure 9. During reaction, the resistance rose from its initial value \( R₀ \) to a maximum \((ΔR/R₀ \text{ max})\), then decreased by 10-20% to a constant level, which was maintained for up to 100 h on 25 μm samples. It eventually increased again to an open circuit value (not plotted in Figure 9), when the metal structure began to break up. The resistance rise was linear with time for the first 30-40% of the total reaction (0.6-0.8 weight % C at 830°C), then deviated towards lower rates. The initial rates and times to peak resistance \((t \text{ max})\) are tabulated for each thickness \((y)\) in Table 11. The initial rates are approximately proportional to \(1/y\); \(t \text{ max}\) is given by the equation

\[
  t \text{ max} = 0.013 y^{1/2} - 0.06
\]

(38)

where \(t \text{ max}\) is in minutes for \(y\) in microns.

Times to 30% \((t_{30})\) and 95% \((t_{95})\) saturation for \(α\) and \(γ\)-Fe were calculated from standard solutions of the diffusion equation, for a material which is sufficiently thin that diffusion through the edges can be ignored (166), and are included in Table 11. Values for the diffusion constants were taken as \(5 \times 10^{-4} \text{ mm}^2\text{sec}^{-1}\) for \(α\)-Fe, and an average value of \(8 \times 10^{-6} \text{ mm}^2\text{sec}^{-1}\) for \(γ\)-Fe (122). The observed initial rates are very much slower than those calculated on the basis of diffusion control in either \(α\)- or \(γ\)-Fe. The metal structure is initially bcc \((α\)-Fe\), but \(γ\)-Fe is stable at 830°C at carbon levels of about 0.05 atom per cent and above. Deviation of
### Table 11
EFFECT OF THICKNESS ON THE RESISTANCE INCREASE AT 830°C AND 50 TORR PRESSURE

<table>
<thead>
<tr>
<th>Thickness y(μm)</th>
<th>Initial Rates (Ω/Ω/min)</th>
<th>Time to 30% reaction (secs)</th>
<th>Time to peak resistance (secs)</th>
<th>Thickness Ratios</th>
<th>Ratio of Reaction Rates</th>
<th>calculated values of t₃₀(secs)</th>
<th>t max(secs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>7.4 x 10⁻²</td>
<td>10</td>
<td>100</td>
<td>1</td>
<td>4.11</td>
<td>0.02</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>50</td>
<td>3.9 x 10⁻²</td>
<td>20</td>
<td>300</td>
<td>2</td>
<td>2.17</td>
<td>0.08</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>100</td>
<td>1.8 x 10⁻²</td>
<td>60</td>
<td>840</td>
<td>4</td>
<td>1</td>
<td>0.32</td>
<td>22.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.0</td>
</tr>
</tbody>
</table>
FIG. 9  RESISTANCE INCREASE VS TIME FOR DISSOLUTION OF C IN IRON FOILS
AT 830°C AND 50 TORR METHANE-HIGH TEMPERATURE PRE-TREATMENT
reaction rate from linearity does not coincide with any specific feature of the phase diagram. It occurs within the $\gamma$-Fe phase field at 0.5 - 0.6 wt % C. The time to reach the resistivity peak is largely determined by the slow rise which follows the deviation from linearity. The reduction in the reaction rate could occur for a number of reasons viz:

(i) that the rate of the back-reaction of adsorbed products is becoming appreciable
(ii) that surface sites for chemisorption are blocked by strongly adsorbed products
(iii) that the rate of chemisorption on $\gamma$-Fe is lower than that on $\alpha$-Fe
(iv) that the rate of diffusion of C in $\gamma$-Fe, which is two orders of magnitude lower than that in $\alpha$-Fe, becomes rate limiting, as the concentration of dissolved C increases and the diffusion gradients decrease.

Item (iv) would be expected to lead to a $y^{1/2}$ dependence for $t_{\text{max}}$ in the form of equation 38.

1.1 Sample Preparation

It was found that the sample pretreatment conditions affected both the rate of dissolution of C in Fe and the morphology of the deposit, but not the total uptake of carbon. The initial reaction rate increased with pretreatment temperature, ultimate vacuum, and $H_2$ and vacuum treatment times. The effect of pretreatment on morphology is discussed later.

Above 1000°C evaporation of iron became significant and set an upper temperature limit for pretreatments. The effects of hydrogen and vacuum were investigated at an ultimate vacuum of
5 \times 10^{-8} \text{ Torr} \text{ and a temperature of } 990^\circ\text{C by:}

(a) varying the hydrogen time at a constant pretreatment time of 19 h

(b) varying the vacuum anneal time for a fixed hydrogen time of 3 h.

The relative efficiencies of the treatments were monitored by measuring rates of resistance increase in CH$_4$ under constant reaction conditions. The results are summarised in Figure 10 and Table 12. Reproducible rates were obtained on samples up to 100 \mu m thick after 3 h in hydrogen and 16 h in vacuo. An increase of 3 orders of magnitude in the system pressure caused a decrease of a factor of two in the initial rate (Figure 11).

The outgassing rate of samples was found to be indistinguishable from background even after short pretreatment times. It is not likely, therefore, that reaction was inhibited by residual dissolved gas. The surface of as-received material, examined in an SEM, showed heavy cold work, which completely masked the metal structure. The damage was almost completely removed by the pretreatment at 990^\circ\text{C}. Thermal grooving caused delineation of grain boundaries, but there was no evidence for facetting of the type reported for Ni after 15 minutes heating in vacuo at 1000^\circ\text{C} and 5 \times 10^{-5} \text{ Torr} (68). Treatments at lower temperatures (e.g. 650^\circ\text{C}) failed to remove the cold work.

1.2 Temperature Variation of Reaction

Experimental curves are presented in Figure 12 for the early stages of reaction of 50 \mu m Fe foils in methane at 50 Torr pressure and temperatures of 493-890^\circ\text{C}. Each curve was obtained on a new sample, since initial rates from consecutive experiments
<table>
<thead>
<tr>
<th>$H_2$ Treatment Time (h)</th>
<th>Vacuum Anneal Time (h)</th>
<th>Initial Reaction Rate $\bar{\omega}/\bar{\Omega}$ min $\times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19</td>
<td>1.19</td>
</tr>
<tr>
<td>0.67</td>
<td>18.33</td>
<td>1.73</td>
</tr>
<tr>
<td>1.67</td>
<td>17.33</td>
<td>2.15</td>
</tr>
<tr>
<td>3</td>
<td>16</td>
<td>2.20</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>2.20</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>1.60</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>1.90</td>
</tr>
<tr>
<td>3</td>
<td>16</td>
<td>2.20</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>2.20</td>
</tr>
</tbody>
</table>
Fig. 10. Effect of H₂ and vacuum pre-treatment times on the initial rates of dissolution of C in 50 μm Fe foils.
FIG. II  EFFECT OF PRE-TREATMENT VACUUM CONDITIONS ON THE RATE OF DISSOLUTION OF C IN A 50 μm Fe FOIL AT 735°C AND 70 Torr CH₄.
FIG. 12  RESISTANCE INCREASE VS TIME FOR 50um Fe FOILS IN METHANE AT 50 TORR PRESSURE
on a single foil were higher than those measured on fresh foils. Despite extensive H₂ and vacuum treatments between consecutive runs (up to 6 h in H₂ and 40 h in vacuo), the initial resistance Ro increased progressively. It is thought that small amounts of carbon or carbide were retained and influenced the rate of subsequent reactions.

In the temperature range 640-750°C, two stages of reaction could be identified. An initially rapid resistance increase ceased after less than a minute. After 1-2 minutes, the resistance rose to a constant rate, which then decreased as the maximum was approached. Below 640°C, only the primary reaction was observed, possibly because of a long induction period to the secondary reaction, and above 750°C only the secondary. The temperature variation of the initial rates is represented in Arrhenius form in Figure 13. The apparent activation energy of the secondary reaction changes discontinuously in the region of the Curie point, from 260 to 60 kJmol⁻¹. That of the primary reaction has an apparently negative value of -55 kJmol⁻¹.

The anomalies of the activation energy plot are explained by the temperature variation of Nordheim's constant, which was measured, in the temperature range 735-890°C, by stopping reaction, by evacuation, at points along the resistance curve and analysing for carbon (Table 13). The results are plotted in Figures 14 and 15. Additional points (solid circles in Figure 15) were obtained from single determinations at other temperatures. Nordheim's rule is obeyed at each temperature to 80-90% of the total resistance change. The proportionality constant, however, decreases with increasing temperature above 735°C, as reported by Swartz and Cuddy for α-Fe (149). It also decreases between 500 and 690°C and rises to a
Table 13
CARBON ANALYSIS DATA FOR MEASUREMENT OF TEMPERATURE VARIATIONS OF NORDHEIM’S CONSTANT

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$\frac{\Delta R}{R_0} \times 10^2$</th>
<th>$\frac{\Delta \sigma}{\sigma} \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>735</td>
<td>1.709</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>2.035</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>4.866</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>5.204</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>5.569</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>8.355</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>15.037</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>15.470</td>
<td>1.14</td>
</tr>
<tr>
<td>773</td>
<td>2.983</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>5.560</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>6.390</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>7.293</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>8.562</td>
<td>1.02</td>
</tr>
<tr>
<td>812</td>
<td>1.757</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>1.921</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>4.198</td>
<td>0.65</td>
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<tr>
<td></td>
<td>4.327</td>
<td>0.74</td>
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<tr>
<td></td>
<td>5.547</td>
<td>1.05</td>
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<tr>
<td>874</td>
<td>2.625</td>
<td>0.54</td>
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<tr>
<td></td>
<td>2.650</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>2.858</td>
<td>1.13</td>
</tr>
<tr>
<td>565</td>
<td>0.524</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>0.305</td>
<td>&lt;0.015</td>
</tr>
<tr>
<td>614</td>
<td>0.937</td>
<td>0.08</td>
</tr>
<tr>
<td>640</td>
<td>0.492</td>
<td>0.08</td>
</tr>
<tr>
<td>663</td>
<td>0.706</td>
<td>0.14</td>
</tr>
<tr>
<td>692</td>
<td>1.563</td>
<td>0.22</td>
</tr>
<tr>
<td>721</td>
<td>1.950</td>
<td>0.26</td>
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<tr>
<td></td>
<td></td>
<td>1.80</td>
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<td></td>
<td></td>
<td>0.98</td>
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<td></td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.47</td>
</tr>
</tbody>
</table>
FIG. 13 ARRHENIUS PLOT OF LOG (INITIAL RATE) vs \(1/T\) FOR 50\(\mu\)m Fe FOILS IN 50 TORR CH\(_4\)
FROM RESISTANCE MEASUREMENTS
**FIG. 14**  SPECIFIC RESISTANCE INCREASE vs CARBON CONTENT FOR 50μm Fe FOILS
POINTS OBTAINED AS AVERAGE OF 4 OR MORE DETERMINATIONS

• POINTS FROM SINGLE DETERMINATION ONLY

EUTECTOID TEMPERATURE

CURIE POINT

\[ \frac{AR}{R_0} \] PER %C FOR DISSOLUTION OF C IN IRON

FIG. 15  EFFECT OF TEMPERATURE ON THE SPECIFIC RESISTANCE INCREMENT
sharp peak at the eutectoid temperature.

The initial rate data is replotted in Figure 16 in terms of dissolved carbon concentrations. Lines were fitted to the graph by the method of least squares, and show

(a) zero activation energy for the primary reaction
and (b) apparent activation energies of 190 ± 5 kJmol⁻¹ and 176 ± 20 kJmol⁻¹ for the secondary reaction above and below the eutectoid respectively.

The error in the secondary activation energy is such that the same figure may apply throughout the temperature range. The line corresponding to 190 kJmol⁻¹ is shown dashed below 720°C. The break at the eutectoid temperature probably arises as a result of a change in the pre-exponential factor of the Arrhenius expression, caused, for instance, by the change of volume, and hence of the geometric area, during phase transformation. Different pre-exponential factors and activation energies have been reported previously for reaction of CH₄ on α- and γ-Fe (61, 62).

The carbon contents of samples at maximum resistance were measured at different temperatures (Table 14) and are plotted as open circles in Figure 17, superimposed on to the Fe/C phase diagram. The points for the secondary reaction peaks above the eutectoid lie close to the γ-Fe/γ-Fe + cementite phase boundary. Below the eutectoid, the points lie to higher carbon concentrations than indicated by the α-Fe/α-Fe + cementite phase line. The peak heights corresponding to the end of the primary reaction (calculated from resistance change and values of Nordheim's constant estimated from Figure 15) are approximately constant at 0.02ZC (solid circles in Figure 17). Corresponding resistance maxima are plotted for comparison in Figure 18,
<table>
<thead>
<tr>
<th>Temperature ( ^\circ C )</th>
<th>Secondary Reaction Peak</th>
<th>Primary Reaction Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \frac{\Delta R_{\text{MAX}}}{R_0} \times 10^2 )</td>
<td>Measured C Concentration (weight %)</td>
</tr>
<tr>
<td>614</td>
<td>0.937</td>
<td>0.08</td>
</tr>
<tr>
<td>640</td>
<td>0.492</td>
<td>0.08</td>
</tr>
<tr>
<td>663</td>
<td>0.706</td>
<td>0.14</td>
</tr>
<tr>
<td>692</td>
<td>1.563</td>
<td>0.22</td>
</tr>
<tr>
<td>713</td>
<td>1.152</td>
<td>N/A</td>
</tr>
<tr>
<td>721</td>
<td>1.950</td>
<td>0.26</td>
</tr>
<tr>
<td>735</td>
<td>15.037</td>
<td>0.94</td>
</tr>
<tr>
<td>750</td>
<td>11.172</td>
<td>0.94</td>
</tr>
<tr>
<td>773</td>
<td>8.206</td>
<td>1.00</td>
</tr>
<tr>
<td>830</td>
<td>6.000</td>
<td>1.10</td>
</tr>
<tr>
<td>899</td>
<td>5.809</td>
<td>1.29</td>
</tr>
</tbody>
</table>

N/A = not available
FIG. 16  ARRHENIUS PLOT OF INITIAL RATES OF DISSOLUTION OF C IN 50 \( \mu m \) Fe in 50 TOrR METHANE

- \( \Delta E = 190 \text{ kJ mol}^{-1} \)
- \( \Delta E = 176 \text{ kJ mol}^{-1} \)

- **SECONDARY REACTION DATA FROM LANGMUIR PLOTS**
- **SECONDARY REACTION DATA FROM SINGLE DETERMINATIONS**
- **PRIMARY REACTION DATA FROM SINGLE DETERMINATIONS**

**EUTECTOID TEMPERATURE**
FIG. 17  CARBON CONTENTS OF SATURATED 50μm Fe FOILS VS TEMPERATURE
FIG. 18  RESISTIVITY MAXIMA OF SATURATED FOILS vs TEMPERATURE
and show a discontinuity in the region of the Fe/Fe carbide eutectoid temperature.

1.3 Pressure Variation of Reaction

Initial reaction rates increased with pressure over the range 10-100 Torr according to an expression derived from the Langmuir adsorption isotherm, which states that

\[ \theta = \frac{bp}{1+bp} \]  

(39)

where \( \theta \) = fractional surface coverage of adsorbed species  
\( p \) = pressure  
\( b \) = constant

If the initial rates are assumed to be directly proportional to \( \theta \), this can be rearranged into the form

\[ \frac{p}{r} = \frac{K}{b} + Kp \]  

(40)

where \( r \) = initial rate  
\( K \) = constant

and \( \theta = Kr \)  

(41)

Plots of \( p/r \) vs \( p \) for the primary and secondary reactions are given in Figures 19 and 20 respectively.

The datum points in Figure 20, representing reaction at 805°C, were obtained from consecutive experiments on a single foil. The foil was treated for up to 6h in H\(_2\) and 40h in vacuo between each run. The resistance decreased to a constant value after 1-2h in H\(_2\), however, the magnitude of \( R_0 \) increased after each experiment. By comparison with the results at 812°C it can be seen that initial rates measured by this method of experimentation are approximately a factor of two too large.
FIG. 19  LANGMUIR RATE PLOTS FOR PRIMARY REACTION ON 50µm Fe FOILS
RESULTS AT 805°C (*) OBTAINED FROM CONSECUTIVE REACTIONS ON A SINGLE FOIL

FIG. 20  LANGMUIR RATE PLOTS FOR SECONDARY REACTION ON 50 µm Fe FOILS
FIG. 21  ISOSTERIC HEAT OF ADSORPTION OF CH₄ ON Fe

$\Delta E_{ST} = 170 \text{kJ mol}^{-1}$

- ○ SECONDARY REACTION
- ○ PRIMARY REACTION
1.4 The Isosteric Heat of Adsorption

An initial value of the heat of adsorption can be calculated from the Clapeyron-Clausius equation

\[
\frac{d\ln p}{d(1/T)} = \frac{\Delta H}{R_g}
\]

(42)

where

- \( p \) = pressure
- \( \Delta H \) = enthalpy
- \( R_g \) = gas constant
- \( T \) = absolute temperature

For adsorption processes at low coverage

\[
\Delta H = Q = \text{isosteric heat of adsorption}
\]

and

\[
Q = R_g \frac{d\ln p}{d(1/T)}
\]

(43)

Values of \( \log p \) and \( \frac{1}{T} \) at constant surface coverage are plotted in Figure 21. The isosteric heat is calculated to be \( 170 \pm 20 \text{ kJmol}^{-1} \) for the secondary reaction.

1.5 Deposition from CO on Fe and from CH\(_4\) on Nickel

At this time, only limited data are available on the Fe/CO and Ni/CH\(_4\) reactions. They demonstrate, however, that similar processes occur in these systems. Resistance curves for Fe in CO at \( 500^\circ C \) were similar to those for the primary reaction in CH\(_4\) (Figure 22). Initial rates were approximately a factor of 5 \times\ greater than methane rates measured at \( 565^\circ C \). They were a reasonable fit to the Langmuir expression at pressures of 10 to 65 Torr. Above 70 Torr, deviation towards higher rates were observed (Figure 23).

The Ni/CH\(_4\) interaction was studied at a temperature of \( 805^\circ C \) (Figure 24), and the following differences from the reaction on
FIG. 22 RESISTANCE INCREASE VS TIME FOR REACTION OF 50 μm Fe FOILS WITH CO AT 550°C

- △ 53 TORR
- ○ 21 TORR
FIG. 23  LANGMUIR RATE PLOT FOR REACTION OF CO WITH Fe AT 550°C
FIG. 24  RESISTANCE INCREASE VS TIME FOR REACTION OF 50 µm Ni FOILS IN CH₄ AT 803°C
iron were observed:

1. having risen to a maximum value, the resistance then remained constant. No decrease was observed over a period of several hours.

2. reaction was independent of pressure over the range 10-100 Torr.

3. similar results were obtained from consecutive experiments on a single sample and from single experiments on different samples. The rate of reaction cannot be compared with that on iron because carbon concentration measurements were not made. Similarly the effect of variation of temperature was not measured. A separate study of reaction on Ni is planned.

2. KINETICS OF FORMATION OF SURFACE DEPOSITS ON Fe FROM CH₄

The emissivity of a clean Fe foil, electrically heated in vacuo, was calculated using equation 30 and the power dissipation/temperature measurements plotted in Figure 25. A value of 0.32 ±0.02 was obtained for \( \sigma_{Fe} \).

2.1 Measurements at Atmospheric Pressure

The increase in power dissipation with time is shown in Figure 26 for carbon formation on 25 μm foils in the temperature range 740-860°C. Reaction is preceded by an induction period, the approximate duration of which decreases from 30 minutes at 740°C to 5 minutes at 860°C. The data obeys the logarithmic law

\[
\Delta W = k \log(t + to) - k \log(ti + to) \tag{44}
\]

where ti is the induction time, k and to are constants (Figure 27).

During this stage of reaction, the resistance fell to a constant level, which was maintained until excessive local reaction caused the formation of hotspots after \( \approx 10 \) h at 860°C and \( \approx 36 \) h at 740°C. The resistance then rose steadily until the ribbon burnt out.
FIG. 25 GRAPH OF $T^4 - T_0^4$ vs POWER DISSIPATION IN THE TEMPERATURE REGION WHERE STEFAN'S LAW IS OBEYED
FIG. 26 GRAPH OF CHANGE OF POWER DISSIPATION vs TIME FOR RIBBONS AT FIVE TEMPERATURES IN CH₄ AT 1 BAR PRESSURE
FIG. 27 GRAPH OF ∆W vs LOG (t + t₀)
The constants of equation 44 are obtained as follows:

The logarithmic growth law can be written as

\[ \Delta W + c = k \log (t + t_o) \]  (45)

where \( c, k \) and \( t_o \) are constants

\( \Delta W = \) change in power dissipation

\( t = \) time

\( t_i = \) induction period

since \( \Delta W = 0 \) when \( t = t_i \):

\[ c = k \log (t_o + t_i) \]  (46)

\[ \Delta W = k \log (t + t_o) - k \log (t_o + t_i) \]  (47)

when \( t >> t_o \)

\[ \Delta W = k \log t - k \log (t_o + t_i) \]  (48)

Extrapolation of a plot of \( \Delta W vs \log t \) from high values of \( t \) to the intercept \( (I_1) \) at \( \Delta W = 0 \) gives

\[ I_1 = t_o + t_i \]  (49)

If a new equation is written

\[ \Delta W + c' = k' \log (t + I_1) \]  (50)

Then

\[ c' = k' \log (t_o + 2t_i) \]  (51)

Thus the intercept \( (I_2) \) at \( \Delta W = 0 \) is

\[ I_2 = t_o + 2t_i \]  (52)

\( t_o \) and \( t_i \) can be calculated from equations (49) and (52).

The values of \( t_o \) and \( t_i \) thus derived are listed in Table 15.

The discontinuities in the curves at 740 and 760°C can be removed by further processing of the data. However, the necessary values of \( t_i \) are then different from those observed experimentally.
Table 15

<table>
<thead>
<tr>
<th>T°C</th>
<th>t₀(calc)</th>
<th>t₁(calc)</th>
<th>t₁(obs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>740</td>
<td>0.33</td>
<td>0.56</td>
<td>0.4-0.5</td>
</tr>
<tr>
<td>760</td>
<td>0.26</td>
<td>0.53</td>
<td>0.4-0.5</td>
</tr>
<tr>
<td>788</td>
<td>0.38</td>
<td>0.20</td>
<td>0.3-0.4</td>
</tr>
<tr>
<td>805</td>
<td>0.23</td>
<td>0.20</td>
<td>0.2-0.3</td>
</tr>
<tr>
<td>866</td>
<td>0.24</td>
<td>0.06</td>
<td>0-0.08</td>
</tr>
</tbody>
</table>

The apparent activation energy for carbon deposition during the early stages of growth may be obtained from initial values of \( \frac{d(\Delta W)}{dt} \), where by differentiation of equation 44,

\[
\frac{d(\Delta W)}{dt} = \frac{k}{T+t_0}
\]  

Figure 28 shows a plot of log (initial rate) vs \( \frac{1}{T} \), from which an apparent activation energy of 80 ± 8 kJ mol\(^{-1}\) can be calculated. The error bars indicate the variation in calculated initial rates which can arise by successive iterations to obtain linear plots of the experimental data.

2.2 Measurements at Reduced Pressure

To establish the processes occurring during the induction period noted in the previous section, simultaneous resistance/power dissipation measurements were made on 25 μm iron foils at 885°C and 50 Torr methane. Temperature was measured by means of a micropyrometer, focused initially on an area of clean metal. As surface carbon formed, the pyrometer was refocused on a heavily deposited area, and reset to compensate for the apparent temperature increase (35°C), arising as a result of the different emissivities.
FIG. 28  Arrhenius plot of \( \log(\frac{da}{dt}) \) v \( \frac{1}{T} \)
The results from a sample subjected to a low temperature pre-treatment are plotted in Figure 29. A resistance peak was again observed. During the period of rising resistance, the power dissipation remained at a constant low value (the induction period). A small sharp increase in power dissipation occurred at the resistance peak, followed by a linear increase over the next 3-4 hours, during which the resistance dropped to a constant level. Further reaction resulted in deviation from linearity of the \( \Delta W/W_0 \) plot towards lower values of power dissipation. Eventually, the resistance increased again, and hot spots in the foil, due to excessive local reaction, were observed through the pyrometer.

In similar experiments on foils pretreated at high temperatures, the kinetic changes were too rapid to follow at temperatures in the effective range of operation of the pyrometer (750°C and above). Thus, for instance, at the reaction temperature of 885°C, the resistance rise was complete within the first minute of reaction (consistent with resistivity experiments).

3. MORPHOLOGY AND ANALYSIS OF DEPOSITS FORMED FROM METHANE ON IRON

3.1 Morphology of Carbon Deposits

The pre-treatment of the foils was found to be a major influence on the morphology of deposits. Pyrometer observation of reaction on low temperature pretreated samples showed that deposition occurred at isolated points. Further reaction then occurred at these sites, which spread laterally over the surface. After high temperature pretreatment, however, deposition occurred uniformly over the whole metal surface. In both cases, the initial deposit formed at the resistance peak and was shown to have been precipitated from solution by raising the foil temperature by 10-15°C. The deposit dissolved
FIG. 29 RESISTIVITY \( \frac{\Delta R}{R_0} \) AND POWER DISSIPATION \( \frac{\Delta W}{W_0} \) vs TIME FOR A 25 \( \mu \)m Fe FOIL AT 885°C AND 50 TORR METHANE LOW TEMPERATURE PRE-TREATMENT
Isolated groups of nodules

The continuous laminar film formed on cooling

As (b), but new area with nodules located mainly between large metal structures

Widespread development of nodules after longer reaction time

PLATE 1A NODULAR DEPOSITS FORMED AT 850°C IN 50 TORR CH₄ ON 25µm IRON FOIL, AFTER LOW TEMPERATURE PRETREATMENT

S.E.M. ACCELERATING VOLTS, IN (a) AND (d) 30 kV, IN (b) AND (c) 10 kV.
REACTION TIMES (a), (b) AND (c) 2 hrs., (d) 5 hrs.
PLATE 1B  THE CONTINUOUS FILM FORMED AFTER HIGH TEMPERATURE PRETREATMENT. REACTION FOR 2 hrs., at 850°C IN 50 TORR CH₄.

S.E.M. ACCELERATING VOLTAGE = 20 kV
and re-appeared on cooling to the original temperature. After reaction had proceeded further, raising the temperature 10°C did not fully re-dissolve the deposit.

Samples were examined in an SEM after rapid cooling to room temperature (sample temperature dropped to <100°C in ~30 secs) and the results are presented in Plate 1. On high temperature pretreated samples, laminar-type carbon, uniformly distributed over the surface, is observed. Some areas are apparently thicker than others (Plate 1b). Similar laminar deposits were observed on samples cooled slowly in the furnace after resistivity experiments. The deposit on low temperature pretreated samples is nodular in nature (Plate 1a), with a laminar film, formed during cooling, visible in unreacted areas. The reason for the formation of hot spots after extended reaction times was evident from a polished section through a 25 μm foil reacted in CH₄ at 1 bar for 15h at 805°C. It was observed that areas of metal, which may have corresponded to single grains, had been removed or destroyed by reaction.

3.2 X-Ray Analysis of Reaction Products

X-ray data for two rapidly cooled 25 μm foils are given in Table 16. Powder was removed from the sample with a fine camel-hair brush and analysed separately in the Debye-Scherrer camera. Foils for diffractometry were mounted in strips on a flat glass plate using an X-ray transparent glue (Devcon). Analysis of the pattern shows that the powder consisted of highly graphitized carbon, containing α- and γ-iron, and that graphite and γ-Fe were also present in the metal. The γ-Fe d-spacings are calculated from known lattice dimensions. These vary with dissolved carbon concentration and therefore a range of values is quoted. The degree of graphitization of the carbon can be calculated using the Franklin correlation (163)
Table 16
X-RAY ANALYSES OF CARBON DEPOSITS

<table>
<thead>
<tr>
<th>Powder X-ray</th>
<th>Diffractometry</th>
<th>After 14h in CH₄ at 760°C and 1 bar pressure</th>
<th>After 10h at 860°C and 1 bar</th>
<th>ASTM 6-0696 α-Fe</th>
<th>ASTM 13-148 Graphite</th>
<th>Calc d γ-Fe lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>I/I₀</td>
<td>d</td>
<td>I/I₀</td>
<td>d</td>
<td>I/I₀</td>
<td>d</td>
</tr>
<tr>
<td>3.35-7</td>
<td>100</td>
<td>3.36</td>
<td>33</td>
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<td>2.13</td>
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<td>2.08-9</td>
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<td></td>
<td></td>
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<td>1.680</td>
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<td>10</td>
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<td>1.76-7</td>
<td>10</td>
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<td>10</td>
<td>1.79</td>
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<td></td>
<td>1.68-9</td>
<td>40</td>
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<td>40</td>
<td>1.79-1.82</td>
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<td></td>
<td>1.58</td>
<td>20</td>
<td>1.58</td>
<td>20</td>
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</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>1.541</td>
<td>60</td>
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</table>

\[ d = \text{lattice spacing in } \AA \]

\[ I/I₀ = \text{relative line intensity} \]
Table 16 (cont)

<table>
<thead>
<tr>
<th>Powder X-ray Diffractometry</th>
<th>After 14 h in CH₄ at 760°C and 1 bar pressure</th>
<th>After 10h at 860°C and 1 bar</th>
<th>ASTM 6-0696 α-Fe</th>
<th>ASTM 13-148 Graphite</th>
<th>Calc d γ-Fe lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>d I/I₀</td>
<td>d I/I₀</td>
<td>d I/I₀</td>
<td>d I/I₀</td>
<td>d I/I₀</td>
<td>d I/I₀</td>
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<tr>
<td>1.44 10</td>
<td>1.430 1.2</td>
<td>1.43 5</td>
<td>1.433 19</td>
<td>1.433 5</td>
<td>1.43-7 10</td>
</tr>
<tr>
<td>1.23 40</td>
<td></td>
<td>1.26-7 10</td>
<td>1.23 20</td>
<td>1.230 90</td>
<td>1.23-7 10</td>
</tr>
<tr>
<td>1.17 40</td>
<td>1.170 1.7</td>
<td>1.16-7 20</td>
<td>1.170 30</td>
<td>1.170 30</td>
<td>1.17-20 10</td>
</tr>
<tr>
<td>1.16 20</td>
<td></td>
<td>1.15-6 10</td>
<td>1.154 90</td>
<td>1.154 90</td>
<td>1.15-6 10</td>
</tr>
<tr>
<td>1.12 &lt;5</td>
<td></td>
<td>1.07-8 &lt;5</td>
<td>1.073 &lt;5</td>
<td>1.073 &lt;5</td>
<td>1.07-8 &lt;5</td>
</tr>
<tr>
<td>1.02 &lt;5</td>
<td></td>
<td>1.04 5</td>
<td>1.013 9</td>
<td>1.013 9</td>
<td>1.04-1.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.993 &lt;5</td>
<td>0.991 80</td>
<td>0.991 80</td>
<td>0.993 &lt;5</td>
</tr>
<tr>
<td>0.907 10</td>
<td>0.906 0.6</td>
<td>0.906 12</td>
<td>0.8275 6</td>
<td>0.8275 6</td>
<td>0.907 10</td>
</tr>
</tbody>
</table>

d = lattice spacing in Å

I/I₀ = relative line intensity
\[ d = 3.440 - 0.086 (1 - P^2) \]  
(54)

where \( d \) = interlayer spacing

\( P \) = proportion of disorientated carbon.

From the data the deposit can be shown to be 85-90% graphitized. A few weak lines, namely 2.025, 2.017, 1.76, 1.58 and 1.12, cannot be fully identified. They appear in all the iron carbide patterns but insufficient data are available to characterise any one compound.

The x-ray patterns of foils reacted for 2-4h at 50 Torr pressure are similar except that the possible carbide lines listed above are absent. Those of foils from resistivity experiments, stopped at or before the peak, show \( \alpha \)-Fe only (because of the slow rate of cooling) with a weak graphite line at 3.35-3.37 Å, due to carbon precipitated during cooling.

4. DISCUSSION

4.1 Effect of Pretreatment

The possible changes in the foil occurring during pretreatment are:

(1) In hydrogen

(a) reduction of surface oxide

(b) removal of dissolved impurities

At 990°C it is assumed that a thin, air-formed oxide layer will be reduced in a time far shorter than the 3 hours required to obtain consistent results. Similarly, \( N_2 \), probably the main impurity of the material, should be removed in the first few minutes of reaction (see ref. 122). Long reaction times must therefore be required to remove trace impurities such as C, Si or S which might otherwise reduce the rate of chemisorption by blocking surface sites. Further details of the chemical aspects of pretreatment will be discussed in Chapter VII.
(2) In vacuo

(a) outgassing (e.g. of H₂)
(b) annealing of cold work induced during rolling
(c) exposing of grain boundaries
(d) grain growth
(e) faceting
(f) reorganising the metal structure by conversion to the γ-phase.

Outgassing was completed within 2 hours even at 650°C, whereas 16 hours at 990°C were required for consistent results. Annealing of cold work went virtually to completion at 990°C, but not at 650°C, and the grain boundaries were exposed and thermally grooved. Little or no faceting occurred. Thus maximum rates of dissolution were observed on chemically clean surfaces on which the grain boundaries had been exposed by annealing. The effect of any reorganisation occurring in the metal cannot be assessed.

4.2 Temperature Variation of Nordheim's Constant

The effect of temperature on Nordheim's constant (i.e. the specific resistivity increment) for solutions of C in α-Fe, at concentrations up to 0.08% C, has been studied by Swartz and Cuddy (149). Their data is reproduced in Figure 30 as circular datum points, the results from the work reported in this thesis, for C concentrations up to 1.1%, are added as triangular datum points. The presence of γ-Fe causes the resistivity increment to decrease more rapidly with increasing temperature than that of α-Fe. The experimental points fall to a value of 1.25 μΩ cm per at% C at 899°C, in excellent agreement with the data of Swartz and Cuddy, for γ-Fe at 910°C and above. No data are available for comparison with the results
FIG. 30 COMPARISON OF EXPERIMENTAL VALUES OF NORDHEIMS CONSTANT FOR Fe WITH LITERATURE DATA

- DATA OF SWARTZ AND CUDDY (149) FOR α-Fe
- EXPERIMENTAL DATA FROM 4 OR MORE DETERMINATIONS
- EXPERIMENTAL DATA FROM SINGLE DETERMINATIONS

EUTECTOID TEMPERATURE

TEMPERATURE, K

SPECIFIC RESISTIVITY INCREMENT μΩcm/AT %C

100 200 300 800 900 1000 1100 1200

DATA OF SWARTZ AND CUDDY (149) FOR α-Fe
EXPERIMENTAL DATA FROM 4 OR MORE DETERMINATIONS
EXPERIMENTAL DATA FROM SINGLE DETERMINATIONS
below 735°C, probably because of the difficulty of obtaining accurate analysis of the low dissolved carbon concentration. The experimental data was obtained from single determinations at the highest carbon levels, close to the resistivity peak. They may therefore be in error due to deviations from Nordheim's rule in this region. However, the good straight line obtained, at temperatures <735°C, on the Arrhenius plot of Figure 16 confirms the general trend of the results. Deviations from the mean squares line in Figure 16 indicate maximum errors of ±20% in the specific resistivity increments.

4.3 The Resistance Decrease

The decrease in resistance of high temperature pretreated iron samples from the maximum value can be explained by a decrease in the number of scattering centres by coagulation and precipitation of interstitial atoms. This implies supersaturation of the metal at the peak, which is confirmed by analyses of the foils (Fig. 17). The nature of the precipitate is of some interest, since it may provide active centres for further growth. The data of Figures 17 and 18 are a better fit to the Fe/Fe carbide phase diagram than to that of Fe/graphite, indicating a carbide structure for the initially formed precipitate. Further evidence for this supposition is obtained from the final steady value of the resistance after precipitation. This was measured at three temperatures above the eutectoid, where the Fe/Fe carbide and Fe/graphite lines are well separated. The results are given in Table 12. The dissolved carbon levels are calculated from the data of Figure 15. Deviations from Nordheim's rule in the region of the resistivity peak could introduce small errors, but the results show dissolved carbon concentrations falling to a value close to that in equilibrium with the carbide phase.
Table 17

DISSOLVED CARBON LEVELS AFTER PRECIPITATION

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Final value of ΔR/Ro</th>
<th>% Resistance Decrease</th>
<th>Final C concentration</th>
<th>C level at phase boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe/Carbide</td>
</tr>
<tr>
<td>750</td>
<td>10.772</td>
<td>2.9</td>
<td>0.92</td>
<td>0.87</td>
</tr>
<tr>
<td>773</td>
<td>9.711</td>
<td>4.7</td>
<td>0.99</td>
<td>0.92</td>
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<tr>
<td>830</td>
<td>5.232</td>
<td>12.78</td>
<td>1.00</td>
<td>1.07</td>
</tr>
</tbody>
</table>

The resistance rise of the low temperature pretreated sample of Figure 29 (reacted at 885°C) is linear through to the peak. The slope, however, is a factor of 50 lower than the initial slope of a high temperature pretreated sample reacted at 890°C (Figure 12b), and the surface reaction may be rate controlling throughout. The resistance decrease is greater than that of a well annealed sample and apparently drops below the saturation value. It is thought that this discrepancy arises as a result of annealing during reaction.

4.4 Mechanistic Implications

The following conclusions can be drawn from the results.

1. The formation of surface deposit is preceded by an induction period during which carbon dissolution in the metal occurs.

2. On well annealed samples the initial experimental rate of dissolution is << the rate of diffusion of C in Fe. The effects of pressure variation imply that the initial rate of reaction is controlled by a surface step, but diffusion in γ-Fe may become rate controlling as the concentration of dissolved carbon increases.
(3) The rate of dissolution in a well-annealed sample at $890^\circ$C is $50 \times$ greater than in a work hardened sample at $885^\circ$C, where the surface reaction is probably rate controlling throughout.

(4) Reaction on well-annealed samples at temperatures $>720^\circ$C occurs in two stages. The first is non-activated. The second has an apparent activation energy of $190 \pm 5 \text{ kJmol}^{-1}$ and an isosteric heat of adsorption of $170 \pm 20 \text{ kJmol}^{-1}$.

(5) Two stages of reaction are also observed at temperatures of $600-720^\circ$C. The first is non-activation; the second has an apparent activation energy of $176 \pm 20 \text{ kJmol}^{-1}$.

(6) At all temperatures the end of the primary reaction corresponds approximately to the saturation level of carbon in $\alpha$-Fe.

(7) A supersaturated solution forms prior to precipitation. Above the eutectoid the degree of supersaturation decreases from $\approx 12\%$ at $730^\circ$C to $\approx 5\%$ at $830^\circ$C. Below the eutectoid it may be as high as $50-100\%$.

(8) Precipitation occurs at reaction temperature, the final dissolved carbon level is close to that expected in equilibrium with a carbide phase.

(9) The morphology of the initial deposit is determined by the pre-treatment of the sample. The deposit on well-annealed samples pretreated at $990^\circ$C is laminar, that on samples with retained cold work, pre-treated at $650^\circ$C, is nodular.

(10) The activation energy for growth of a nodular deposit is $80 \pm 8 \text{ kJmol}^{-1}$.

The measured activation energies for dissolution can be compared to figures quoted by Grabke, for reaction of Fe in $\text{CH}_4/\text{H}_2$ mixtures, of $211 \text{ kJmol}^{-1}$ for $\alpha$-Fe and $230 \text{ kJmol}^{-1}$ for $\gamma$-Fe (60, 61).
The discrepancy could arise for one of the following reasons:

(a) The experiments reported by Grabke were carried out consecutively on single samples, which yield anomalously high reaction rates on the second and subsequent runs;

(b) The samples were apparently not pre-annealed and (c) in resistivity experiments on γ-Fe, no account was taken of the temperature variation of Nordheim's constant at temperatures below 910°C.

The secondary reaction below the eutectoid temperature probably corresponds to the formation of either a supersaturated solution of C in α-Fe, or of finely dispersed particles of carbide. On the basis of this and of points 3-5 above it is proposed that the dissociative chemisorption on Fe occurs preferentially at sites suitable for C diffusion into the metal. The primary reaction on α-Fe therefore ceases at the equilibrium saturation concentration of carbon in the metal. Further reaction occurs after reorganisation of the metal lattice to a form capable of taking up more carbon, i.e. γ-Fe formation above 720°C or carbide formation below 720°C.
RESULTS 3 FORMATION OF THICK CARBON DEPOSITS

1. KINETICS
   1.1 Comparative Data for the Metals Fe, Ni, Cr, Mo, Nb and 20/25 Nb Stainless Steel
   1.2 Effect of Metal Thickness

2. DEPOSIT MORPHOLOGY AND ANALYSIS
   2.1 Morphological Changes during Deposition on Fe and Ni
   2.2 Morphology of Deposits on Other Metals
   2.3 X-Ray Analysis
      2.3.1 Deposits formed in CO at 515°C
      2.3.2 Deposits formed in CH₄ at 865°C

3. DISCUSSION
   3.1 The Effect of Metal Thickness
   3.2 Mechanistic Conclusions
As a result of the long time scales required to obtain kinetics of formation of thick deposits, which can be appreciated by inspection of the time axes of the following figures, the data presented in this chapter is only a preliminary survey of the topic. Results are reported which demonstrate the following features of the deposition reaction:

1. the wide variation of reaction rates observed on different metals
2. the effect of metal thickness/grain structure on the kinetics
3. the variation of type of reaction product and deposit morphology on different metals
4. the destruction of the metal lattice, which occurs after prolonged reaction.

1. KINETICS

1.1 Comparative Data for Cr, Fe, Nb, Ni, Mo and 20/25 Nb Stainless Steel

Reaction rates in CO were obtained at 515°C and 2.75 bar pressure. Those of Cr, Mo and stainless steel were too low to measure. Kinetic curves for Ni and Nb are presented in Figure 31, and can be compared with those of iron in Figure 33 for reaction under the same conditions. Kinetic curves for reaction of all six metals in methane at 865°C and 2.75 bar are presented in Figure 32. Sample thicknesses were 1 mm unless otherwise stated, and data are normalised to original sample weight (wo), since the available area changed during reaction, due to disintegration of the metal structure. The relative orders of reactivity were:
FIG. 31(a)  WEIGHT GAIN KINETICS FOR Ni IN CO AT 515°C AND 2.75 bar

FIG. 31(b)  WEIGHT GAIN KINETICS FOR Nb IN CO AT 515°C AND 2.75 bar
FIG. 32. WEIGHT GAIN KINETICS FOR Cr, Mo, Nb AND STAINLESS STEEL IN CH₄ AT 865°C AND 2.75 bar

INCREASE IN WEIGHT
ORIGINAL WEIGHT

TIME, h

0 10 20 30 40

0 10 20 30 40

200 μm IRON
NON AIR-EXPOSED

200 μm NICKEL
NON AIR-EXPOSED

20/25 Nb STEEL
AIR-EXPOSED

20/25 Nb STEEL
NON AIR-EXPOSED

MOLYBDENUM

NIQUEM

CHROMIUM

NIQUEM

SILICA BUCKET

NIQUEM
(1) in CO at 515°C
   Fe > Ni >> Cr, Mo and 20/25 Nb Steel

(2) in CH₄ at 865°C
   Fe and Ni > 20/25 Nb steel > Mo and Cr > Nb and silica

The kinetic data are summarised in Table 18.

The curves plotted through open datum points were obtained from single samples periodically removed from the vessel for weighing. The solid points for Fe and 20/25 Nb steel in Figure 32 represent the weight gains of non-air exposed samples, and demonstrate that exposure to the air retarded further reaction in methane. It is thought that oxide or adsorbed oxygen blocked reaction sites. A similar effect was measured for the Ni/CH₄ reaction, but air exposure caused a slight acceleration in the rate of reaction of Fe and Ni in CO, possibly as a result of oxide formation aiding disintegration of the metal. Air exposure had little effect on the other metals.

1.2 Effect of Metal Thickness

Figures 33 and 34 show weight gain data for reaction of iron samples of thickness 25, 50, 100 and 200 μm in CO at 2.75 bar and 515°C and 550°C respectively. Figures 35 and 36 show corresponding data for reaction of Fe and Ni in methane at 700°C and 2.75 bar. In all cases, except Fe/CO at 550°C, reaction rates were initially low. They then increased to a maximum value, as the samples disintegrated, finally falling to a constant low rate after disintegration was complete. In CO at 550°C, the initial slow rise was completed within 25 hours and was not observed. The total carbon uptake per unit weight of metal increased with temperature, and was thickness dependant for reaction in CO but not in CH₄. Approximate values of the induction time to the onset of disintegration, maximum rates and carbon uptake are given in
<table>
<thead>
<tr>
<th>Metal</th>
<th>Thickness µm</th>
<th>Gas</th>
<th>Temperature °C</th>
<th>Induction time h</th>
<th>Maximum rate (g·g⁻¹·h⁻¹)</th>
<th>Total C pickup</th>
<th>Log. Rate</th>
</tr>
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<tbody>
<tr>
<td>Fe</td>
<td>25</td>
<td>CO</td>
<td>515</td>
<td>&lt;25</td>
<td>7.2x10⁻²</td>
<td>11.8</td>
<td>23.0</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td>&lt;25</td>
<td>4.0x10⁻²</td>
<td>7.4</td>
<td>11.0</td>
</tr>
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<td></td>
<td>100</td>
<td></td>
<td></td>
<td>100</td>
<td>7.0x10⁻³</td>
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<td>14.0</td>
<td>5.0</td>
</tr>
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<td></td>
<td>&lt;25</td>
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<td>5.0</td>
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<tr>
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<td>100</td>
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<td>500</td>
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<td>150</td>
<td>5x10⁻³</td>
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<td>-</td>
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<tr>
<td>Nb</td>
<td>10³</td>
<td>CO</td>
<td>515</td>
<td>0</td>
<td>1.0x10⁻⁵</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>25</td>
<td>CH₄</td>
<td>700</td>
<td>&lt;50</td>
<td>2.2x10⁻¹</td>
<td>22</td>
<td>-</td>
</tr>
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<td></td>
<td>50</td>
<td></td>
<td></td>
<td>70</td>
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<td>90</td>
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<tr>
<td>Ni</td>
<td>25</td>
<td>CH₄</td>
<td>700</td>
<td>0</td>
<td>1.1x10⁻¹</td>
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<td>50</td>
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<td>N/A</td>
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<td>N/A</td>
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<td>Fe</td>
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<td>3.0x10⁻¹</td>
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<td></td>
<td></td>
<td>0</td>
<td>3.0x10⁻¹</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>10³</td>
<td></td>
<td></td>
<td>0</td>
<td>1.1x10⁻¹</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Nb</td>
<td>10³</td>
<td></td>
<td></td>
<td>0</td>
<td>3x10⁻²</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Mo</td>
<td>10³</td>
<td></td>
<td></td>
<td>0</td>
<td>3x10⁻²</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>20/25 Nb Steel</td>
<td>500</td>
<td></td>
<td></td>
<td>0</td>
<td>5x10⁻³</td>
<td>N/A</td>
<td>-</td>
</tr>
</tbody>
</table>

N/A = not available
FIG. 33  EFFECT OF THICKNESS ON WEIGHT GAIN KINETICS OF IRON IN CO AT 515°C AND 2.75 bar
FIG. 34 EFFECT OF THICKNESS ON THE WEIGHT GAIN KINETICS OF IRON IN CO AT 550°C AND 2.75 bar
FIG. 35 EFFECT OF THICKNESS ON THE WEIGHT GAIN KINETICS OF IRON IN CH$_4$ AT 700°C AND 2.75 bar
FIG. 36 EFFECT OF THICKNESS ON WEIGHT GAIN KINETICS OF Ni IN CH₄ AT 700°C AND 2.75 bar
FIG. 37 ARRHENIUS PLOT OF MAXIMUM RATES OF 25 μm IRON SAMPLES
FIG. 38  LOG TIME PLOT OF KINETIC DATA FOR IRON IN CO AT 515°C AND 2.75 bar
**FIG. 39** LOG-TIME PLOT OF KINETIC DATA FOR REACTION OF IRON IN CO AT 550°C AND 2.75 bar.
Table 18. The approximate maximum rates of reaction of 25 μm Fe samples, calculated by drawing tangents to the curves, are plotted against temperature in Arrhenius form in Figure 37. The data from 550 to 865°C fit a good straight line corresponding to an apparent activation energy of 27 kJmol⁻¹.

The overall kinetics of the Fe/CO reaction during the period of increasing rate can be represented by plots of weight gain vs log time as shown in Figures 38 and 39. Insufficient data are available to obtain similar plots for reaction in methane.

2. DEPOSIT MORPHOLOGY AND ANALYSIS

2.1 Morphological Changes Occurring During Deposition on Fe and Ni

The following observations were made of thin samples reacted in CO at 515°C, similar effects have also been found in CH₄:

(1) When first removed from the reactor after 10-20 h reaction, the surface of the samples was covered by a thin powdery layer of nodular carbon. The detailed structure was similar to that shown in Plate la for the early stages of deposition onto iron foils.

(2) After further reaction, increases in the sample dimensions of up to 10% were measured, and the samples began to bend and cockle (Plate 2). This expansion of the metal coincided approximately with the start of the period of increasing reaction rate.

(3) As the rate continued to increase, further expansion, cockling and curling occurred (Plate 2) until the metal structure was almost totally destroyed and the samples took up a lace-like appearance (Plate 3).

(4) The last stage of reaction was total disintegration to a coarse, granular powder (Plate 4), and the decrease of the rate to its final low value.
PLATE 2  EXAMPLES OF EXPANSION AND CURLING OF 25 μm IRON SAMPLES AFTER 20 hrs., REACTION IN CO AT 515°C
PLATE 3A   EXTREME EXPANSION OF 25 μm IRON SAMPLES AFTER 50 hrs., REACTION IN CO AT 515°C. ORIGINAL SAMPLE SIZE 20x10 mm.
PLATE 3B  LACE-LIKE STRUCTURE OF 25 \( \mu \text{m} \) IRON SAMPLE AFTER 50 hrs. REACTION IN CO AT 515\( ^{\circ} \text{C} \)

PLATE 4  DISINTEGRATED 25 \( \mu \text{m} \) IRON SAMPLE AFTER 120 hrs., REACTION IN CO AT 515\( ^{\circ} \text{C} \)
PLATE 5  OXIDE STRUCTURES ON 20/25Nb STEEL AFTER 22 hrs.,
REACTION IN CO AT 550°C

PLATE 6  HEAVY CARBON DEPOSITS ON 20/25Nb STEEL AFTER 285 hrs.
REACTION IN CO AT 550°C
PLATE 7  FILAMENTARY STRUCTURES ON 20/25Nb STEEL
AFTER 285 hrs. REACTION IN CO AT 550°C

PLATE 8  TYPICAL DEPOSITS FORMED ON CHROMIUM AND 20/25Nb STEEL
AFTER 395 hrs. REACTION IN CH₄ AT 865°C
(5) The total volume of carbon formed was such that at $\Delta w/w_0$ values of $\sim 10$ the reaction products from a sample 10 mm square by 25 $\mu$m thick completely filled the containment bucket, the dimension of which were 25 mm diameter x 10 mm deep.

2.2 Morphology of Deposition on Other Metals

In CO at 515°C, no substantial deposition was observed on the other metals studied. Only Cr and 20/25 Nb steel showed any indications of changes of surface structure. Both formed blue/green films, which were probably interference colours arising as a result of changes in the oxide structure. Examined in the SEM, both showed typical oxide features (Plate 5). After prolonged reaction, fluffy, filamentary deposits formed on the steel (Plate 6 and 7).

In CH$_4$ at 865°C, the structures of deposits on Cr, Mo, Nb and stainless steel was more granular than those on Fe and Ni and showed no evidence of the characteristic ball-like structures of Plate 1a. Typical photo-micrographs of deposit on Cr and 20/25 Nb steel are given in Plate 8.

2.3 X-Ray Analysis

In the measurement of x-ray patterns of thick carbon deposits, some difficulty was experienced in accurately mounting the sample surface in the centre of the diffractometer circle, due to the roughness of the surface and non-uniformity of deposit thickness. This is reflected in small variations in line positions in the following tables.

2.3.1 Deposits Formed in CO at 515°C

X-ray diffractometry patterns of deposits on non air-exposed Fe samples at increasing times of reaction are given in Table 19 and relevent data from the ASTM tables in Table 20. Carbide is detected
Table 19

X-RAY DATA FOR Fe IN CO AT 515°C AND 2.75 BAR

<table>
<thead>
<tr>
<th>Identification of Line</th>
<th>After 7.5h</th>
<th>After 21h</th>
<th>After 52h</th>
<th>After 127h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>G</td>
<td>3.365</td>
<td>5</td>
<td>3.375</td>
<td>12</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>2.923</td>
<td>3</td>
<td>2.560</td>
<td>6</td>
</tr>
<tr>
<td>Fe₃C</td>
<td>2.372</td>
<td>1</td>
<td>2.377</td>
<td>6</td>
</tr>
<tr>
<td>Fe₃C</td>
<td>2.263</td>
<td>1</td>
<td>2.258</td>
<td>6</td>
</tr>
<tr>
<td>Fe₃C</td>
<td>2.217</td>
<td>1</td>
<td>2.226</td>
<td>11</td>
</tr>
<tr>
<td>Fe₃C</td>
<td>2.102</td>
<td>2</td>
<td>2.104</td>
<td>16</td>
</tr>
<tr>
<td>Fe₃C</td>
<td>2.027</td>
<td>2</td>
<td>2.024</td>
<td>580</td>
</tr>
<tr>
<td>α-Fe</td>
<td>1.977</td>
<td>10</td>
<td>1.980</td>
<td>70</td>
</tr>
<tr>
<td>Fe₃C</td>
<td>1.871</td>
<td>0.7</td>
<td>1.874</td>
<td>9</td>
</tr>
<tr>
<td>Fe₃C</td>
<td>1.588</td>
<td>0.5</td>
<td>1.589</td>
<td>7</td>
</tr>
<tr>
<td>Fe₃C</td>
<td>1.432</td>
<td>120</td>
<td>1.432</td>
<td>130</td>
</tr>
<tr>
<td>Fe₃C</td>
<td>1.170</td>
<td>55</td>
<td>1.019</td>
<td>25</td>
</tr>
</tbody>
</table>

I = peak height in arbitrary units
### Table 20
ASTM X-RAY DATA FOR RELEVANT IRON COMPOUNDS

<table>
<thead>
<tr>
<th>Fe 6-0696</th>
<th>Fe₃C 6-0688</th>
<th>Graphite 13-148</th>
<th>Fe₃O₄ 19-629</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.38(65)</td>
<td>2.38(65)</td>
<td>3.35(100)</td>
<td>2.079(20)</td>
</tr>
<tr>
<td>2.26(25)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.20(25)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.10(70)</td>
<td>2.10(70)</td>
<td>2.13(50)</td>
<td>2.099(20)</td>
</tr>
<tr>
<td>2.02(60)</td>
<td></td>
<td>2.04(50)</td>
<td></td>
</tr>
<tr>
<td>2.01(100)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.97(55)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.87(30)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.85(40)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.76(15)</td>
<td></td>
<td>1.80(30)</td>
<td></td>
</tr>
<tr>
<td>1.68(15)</td>
<td>1.68(15)</td>
<td>1.675(80)</td>
<td>1.71(10)</td>
</tr>
<tr>
<td>1.61(7)</td>
<td>1.61(7)</td>
<td></td>
<td>1.616(30)</td>
</tr>
<tr>
<td>1.58(20)</td>
<td>1.58(20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.539(7)</td>
<td>1.539(7)</td>
<td>1.541(60)</td>
<td></td>
</tr>
<tr>
<td>1.506(24)</td>
<td>1.506(24)</td>
<td></td>
<td>1.485(40)</td>
</tr>
<tr>
<td>1.433(19)</td>
<td>1.433(19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.409(7)</td>
<td>1.409(7)</td>
<td></td>
<td>1.281(10)</td>
</tr>
<tr>
<td>1.326(50)</td>
<td>1.326(50)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.255(15)</td>
<td>1.255(15)</td>
<td>1.230(90)</td>
<td></td>
</tr>
<tr>
<td>1.221(50)</td>
<td>1.221(50)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.212(60)</td>
<td>1.212(60)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.189(30)</td>
<td>1.189(30)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.170(30)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.159(70)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.149(45)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Additional data for Fe₃C (below 1.58) from ref. 165.
Relative intensities in brackets.
after 7.5 h, carbon (55-65% graphitised) after 52 h and oxide after 127 h. The carbide line intensities increase steadily, and the \(\alpha\)-Fe line becomes weaker, as reaction proceeds. Further diffractometry was not possible after 127 h because of sample disintegration. Debye-Scherrer powder patterns show the final products to be carbon, cementite and magnetite.

Only limited data are available for other metals because of the slow rates of reaction. X-ray patterns for Ni, Cr, Nb, Mo and 20/25 Nb steel after 1000 h reaction are given in Table 21. Individual lines are identified from the ASTM cards listed below the table. Although all but Mo support carbon formation, it is only substantially graphitised (50-60%) on Ni. Mo and Nb form carbides, and there is evidence for \(\text{Cr}_2\text{O}_3\) formation on Cr and 20/25 Nb steel. A number of unidentified lines are present in the nickel pattern at 2.25, 2.11 and 1.95 Å. The same lines appear strongly in the \(\text{Fe}_3\text{C}\) pattern, but they do not correspond to the reported data for \(\text{Ni}_3\text{C}\). It is unlikely that they can be attributed to contamination from iron samples, since (i) they appeared in x-ray patterns of all Ni samples in two separate experiments and (ii) they do not appear in the patterns of any other samples.

### 2.3.2 Deposits Formed in \(\text{CH}_4\) at 865°C and 2.75 Bar

X-ray diffractometer data for samples reacted for 112 h without air-exposure are given in Table 22. Strongly graphitised carbon is formed on Fe, Ni and 20/25 Nb steel. \(\text{Fe}_3\text{C}\) is also present on iron samples, and \((\text{FeCr})_7\text{C}_3\) on the steel, as expected from the Fe/Cr/C phase diagram. On nickel, similar unidentifiable lines appear to those recorded for deposit formed in CO. The only reaction products on Cr, Nb and Mo were the carbides \(\text{Cr}_3\text{C}_2\), \(\text{Nb}_2\text{C}\) and \(\text{Mo}_2\text{C}\) respectively. \(\text{Cr}_3\text{C}_2\) is not normally formed in steels, but might be expected in strongly
<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cr</th>
<th>Nb</th>
<th>Mo</th>
<th>20/25 Nb Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d</td>
<td>I</td>
<td>d</td>
<td>I</td>
<td>d</td>
</tr>
<tr>
<td>3.367</td>
<td>0.4</td>
<td>G</td>
<td>3.650</td>
<td>0.1</td>
<td>G</td>
</tr>
<tr>
<td>2.249</td>
<td>0.2</td>
<td>?</td>
<td>2.041</td>
<td>2.8</td>
<td>Cr</td>
</tr>
<tr>
<td>2.112</td>
<td>0.2</td>
<td>?</td>
<td>1.675</td>
<td>0.2</td>
<td>Cr</td>
</tr>
<tr>
<td>2.037</td>
<td>25</td>
<td>Ni</td>
<td>1.443</td>
<td>0.3</td>
<td>Cr</td>
</tr>
<tr>
<td>1.950</td>
<td>0.2</td>
<td>?</td>
<td>1.827</td>
<td>0.2</td>
<td>Nb_2C</td>
</tr>
<tr>
<td>1.763</td>
<td>2.5</td>
<td>Ni</td>
<td>1.656</td>
<td>9</td>
<td>Nb</td>
</tr>
<tr>
<td>1.247</td>
<td>6.6</td>
<td>Ni</td>
<td>1.352</td>
<td>7.4</td>
<td>Nb</td>
</tr>
<tr>
<td>1.063</td>
<td>0.4</td>
<td>Ni</td>
<td>1.170</td>
<td>0.4</td>
<td>Nb</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.046</td>
<td>0.8</td>
<td>Nb</td>
</tr>
<tr>
<td>I = intensity in arbitrary units</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni 4-0850</td>
<td>Nb 16-1</td>
<td>Mo 4-0809</td>
<td>Fe_3O_4</td>
<td>6-0504</td>
<td></td>
</tr>
<tr>
<td>Cr 6-0694</td>
<td>Nb_2C 15-127</td>
<td>Mo_2C 11-680</td>
<td>Cr_2O_3</td>
<td>19-629</td>
<td></td>
</tr>
</tbody>
</table>
Table 22
X-RAY DATA FOR Fe, Ni, Cr, Nb, Mo AND 20/25 Nb STEEL IN Cr1 AT 865°C

<table>
<thead>
<tr>
<th>IRON</th>
<th>NICKEL</th>
<th>CHROMIUM</th>
<th>NIOBIUM</th>
<th>MOLYBDENUM</th>
<th>20/25 Nb STEEL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>I</td>
<td>d</td>
<td>I</td>
<td>d</td>
<td>I</td>
</tr>
<tr>
<td>3.363</td>
<td>70 G</td>
<td>3.357</td>
<td>17 G</td>
<td>2.774</td>
<td>4 Cr₂C₂</td>
</tr>
<tr>
<td>3.387</td>
<td>6 Fe₃C</td>
<td>2.247</td>
<td>0.4</td>
<td>2.763</td>
<td>2</td>
</tr>
<tr>
<td>2.256</td>
<td>4 Fe₃C</td>
<td>2.128</td>
<td>3.9 G</td>
<td>2.556</td>
<td>9</td>
</tr>
<tr>
<td>2.138</td>
<td>30 G</td>
<td>2.036</td>
<td>40 Ni</td>
<td>2.198</td>
<td>23</td>
</tr>
<tr>
<td>2.110</td>
<td>7 Fe₃C</td>
<td>1.945</td>
<td>0.9</td>
<td>2.346</td>
<td>60</td>
</tr>
<tr>
<td>2.075</td>
<td>8(Br) γ-Fe</td>
<td>1.762</td>
<td>73 Ni</td>
<td>2.125</td>
<td>22</td>
</tr>
<tr>
<td>2.063</td>
<td>2 Fe₃C</td>
<td>1.678</td>
<td>0.8 G</td>
<td>2.054</td>
<td>11 Or</td>
</tr>
<tr>
<td>2.030</td>
<td>590 α-Fe</td>
<td>1.375</td>
<td>0.2</td>
<td>1.230</td>
<td>0.5 G</td>
</tr>
<tr>
<td>1.980</td>
<td>6 Fe₃C</td>
<td>1.245</td>
<td>25 Ni</td>
<td>1.916</td>
<td>8</td>
</tr>
<tr>
<td>1.879</td>
<td>4 Cr</td>
<td>1.155</td>
<td>1.5 G</td>
<td>1.899</td>
<td>3</td>
</tr>
<tr>
<td>1.859</td>
<td>4 Cr</td>
<td>1.155</td>
<td>1.5 G</td>
<td>1.856</td>
<td>2</td>
</tr>
<tr>
<td>1.680</td>
<td>3 Cr₃C₂</td>
<td>1.062</td>
<td>20 Ni</td>
<td>1.826</td>
<td>35</td>
</tr>
<tr>
<td>1.434</td>
<td>260 α-Fe</td>
<td>1.786</td>
<td>2</td>
<td>1.756</td>
<td>5</td>
</tr>
<tr>
<td>1.231</td>
<td>36 G</td>
<td>1.701</td>
<td>2</td>
<td>1.370</td>
<td>38</td>
</tr>
<tr>
<td>1.171</td>
<td>120 α-Fe</td>
<td>1.325</td>
<td>4</td>
<td>1.298</td>
<td>2</td>
</tr>
<tr>
<td>1.013</td>
<td>100 α-Fe</td>
<td>1.208</td>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
carburising atmospheres, since it is the most carbon rich carbide.

The main features of carbon-containing deposits formed in CH₄ are:

(i) that the carbon is more strongly graphitised than that formed in CO. For instance, on nickel the Franklin correlation gives a figure of 82% graphitised and the presence of the reflections at 2.13 and 1.155 Å indicates a high degree of ordering within the basal planes.

and (ii) that Debye-Scherrer photographs of fully disintegrated Fe and Ni samples, where the reaction rate has fallen to its final low value, show the presence of strong metal lines as well as graphite and weak carbide lines.

3. DISCUSSION

3.1 The Effect of Metal Thickness

The weight gain curves for the reaction of iron in methane at 700°C and CO at 515°C show effects that could be predicted from results in Chapter IV, i.e.

(1) rapid reaction is preceded by an induction period

(2) the duration of the induction period (t₁) increases with metal thickness

(3) the magnitude of t₁ increases approximately in proportion to the square root of the thickness

(4) the time to metal saturation is longer than observed in resistivity experiments because surface, air-formed oxides, and any residual cold work not removed by polishing, have inhibited reaction.

After the apparent induction period, the rates of carbon uptake increased to a maximum and the samples disintegrated. The overall kinetics of the Fe/CO system can be represented by plots of Δw/w₀
vs log $t$ during this stage of reaction. This relationship can be derived by assuming that the disintegration process makes available additional active metal area as follows:

Let the active metal area ($A_t$) increase with carbon uptake $q (\equiv \Delta w/w_0)$ according to the equation

$$A_t = A_g \exp \alpha q$$  \hspace{1cm} (55)

where $A_g =$ original geometric area

$\alpha =$ constant

then

$$\frac{dA_t}{dq} = \alpha A_g \exp \alpha q$$ \hspace{1cm} (56)

The rate of carbon uptake is given by

$$\frac{dq}{dt} \cdot \frac{dA_t}{dt} = \frac{1}{\alpha A_g} \exp (-\alpha q) \frac{dA_t}{dt}$$  \hspace{1cm} (58)

If $\frac{dA_t}{dt} =$ constant ($\beta$)

the logarithmic relationship follows from integration of

$$\frac{dq}{\alpha A_g} = \beta \exp -\alpha q$$ \hspace{1cm} (59)

which, between the limits $t_i$ (since $A_g$ remains constant during the induction period) and $t$, gives

$$q = \frac{\beta}{\alpha A_g} \ln (t + t_o) - \frac{\beta}{\alpha A_g} \ln (t_i + t_o)$$ \hspace{1cm} (60)

where $t_o =$ constant of integration

Using the procedure described in section 2.1 of Chapter IV to calculate $t_o$ and $t_i$, it can be shown that $t_o \geq 0$ in all cases, and the expression therefore reduces to

$$q = \frac{\beta}{\alpha A_g} \int_{t_i}^t \ln t - \ln t_i$$ \hspace{1cm} (61)
The above analysis thus derives the experimentally observed kinetics from the two assumptions that

(i) the net available surface area, i.e. that created by disintegration less that destroyed by carbide or oxide formation, increases exponentially with the amount of carbon deposited.

and (ii) the rate of increase of available area reaches a steady state value such that \( \frac{dA_t}{dt} = \text{constant} \).

The latter requirement would lead to the result that the rate of reaction of massive samples (such that the time to total disintegration was long compared to the duration of the experiment) increases at a constant rate with time. Such an observation has been reported for the reaction of mild steel with CO (32). It also provides an alternative explanation for the apparent breakaway oxidation kinetics reported to occur at atmospheric pressure in CO\(_2\)/CO mixtures of high CO content (17). The observed increase in rate after a period of apparently parabolic oxidation can possibly be related to an increase in surface area, due to breakup of the metal structure as a result of carbon formation. It also follows that the rate of reaction will decrease when the available area decreases, because the sample is fully disintegrated, no further increase in area is possible and termination processes are annihilating active area. These processes could be carbide or oxide formation in, for instance, the Fe/CO system, or encapsulation of metal particles, as proposed by other workers (e.g. 53), in the Fe/CH\(_4\) system.

Estimation of the total active area demands a knowledge of the final particle size in the disintegrated sample. In the Fe/CH\(_4\) interaction, this is clearly determined by the sample weight \( w_0 \), since
total carbon pickup ($\Delta w_m$) is directly proportional to $w_o$ (Fig. 35, Table 18). In CO, however, $\Delta w_m/w_o$ decreased with increasing metal thickness (Fig. 34, 35 and Table 18). Metallurgical examination of the metal revealed that the grain size increased with thickness (Plate 9), which could yield lower total areas in the specimens if the final particle size is that of the grains.

Total grain surface areas were measured, using an image analysing computer, as follows:

1. Samples were initially mounted flat and marked areas examined in depth, by repeatedly removing small amounts of metal ($\sim 5\mu m$ in thickness) by grinding on a coarse diamond wheel, to estimate grain shape. The results showed little variation of grain dimensions with depth, but a wide variation in grain size. It was therefore assumed that any arbitrary section would be representative of the whole, but that a simple sizing procedure (e.g. the standard ASTM method (167)) would not be accurate.

2. Sections were prepared of three mutually perpendicular planes. Overlapping photographs were taken, and composites made up which contained at least 50 grains. The grain boundaries were highlighted in ink to avoid counting errors (Plate 10).

3. Grains were arbitrarily divided into four size ranges in each section, so as to maintain approximately the same proportional number of grains in each range. Details of size ranges are given in Table 23. Grain areas were then measured in each section (referred to as sectional areas in Table 23) and average areas and total number of grains in each size range computed.

4. Grain surface areas were then calculated by assuming an orthorhombic grain shape, and that any one grain was detected in the
PLATE 9  METALLURGICAL SECTIONS THROUGH AS-RECEIVED Fe SAMPLES SHOWING GRAIN SIZE VARIATIONS
(a) 25 μm  (b) 50 μm  (c) 100 μm  (d) 200 μm
PLATE 10  METALLURGICAL SECTIONS OF IRON
SAMPLES OF GRAIN SIZE ANALYSIS

A1  500 µm

A2  190 µm

A3  190 µm

B1  380 µm

B2  380 µm

B3  380 µm

A1, 2, AND 3  50 µm  THICKNESS
B1, 2, AND 3  200 µm  THICKNESS
Table 23

ANALYSIS OF VARIATION OF METAL GRAIN SIZE WITH SAMPLE THICKNESS

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Number of Grains in Size Range (1-4)</th>
<th>Average sectional area in size range (mm$^2$) (1-4)</th>
<th>Area analysed (mm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface Section</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>201</td>
<td>97</td>
<td>30</td>
</tr>
<tr>
<td>50</td>
<td>161</td>
<td>85</td>
<td>31</td>
</tr>
<tr>
<td>100</td>
<td>318</td>
<td>176</td>
<td>39</td>
</tr>
<tr>
<td>200</td>
<td>35</td>
<td>45</td>
<td>36</td>
</tr>
<tr>
<td><strong>Cross Section 1</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>73</td>
<td>38</td>
<td>14</td>
</tr>
<tr>
<td>50</td>
<td>32</td>
<td>18</td>
<td>22</td>
</tr>
<tr>
<td>100</td>
<td>80</td>
<td>35</td>
<td>4</td>
</tr>
<tr>
<td>200</td>
<td>41</td>
<td>27</td>
<td>12</td>
</tr>
<tr>
<td><strong>Cross Section 2</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>25</td>
<td>70</td>
<td>28</td>
<td>15</td>
</tr>
<tr>
<td>50</td>
<td>73</td>
<td>42</td>
<td>11</td>
</tr>
<tr>
<td>100</td>
<td>33</td>
<td>26</td>
<td>10</td>
</tr>
<tr>
<td>200</td>
<td>36</td>
<td>11</td>
<td>10</td>
</tr>
</tbody>
</table>

Grain Surface Areas

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Average No. of Grains in Area Size Range (1-4)</th>
<th>Average grain surface area (mm$^2$) (1-4)</th>
<th>Volume analysed (mm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>$0.10 \times 10^{-2}$</td>
<td>$3.21 \times 10^{-2}$</td>
<td>$7.93 \times 10^{-2}$</td>
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<td>50</td>
<td>$6.13 \times 10^{-3}$</td>
<td>$2.54 \times 10^{-3}$</td>
<td>$8.66 \times 10^{-3}$</td>
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<tr>
<td>100</td>
<td>$9.16 \times 10^{-3}$</td>
<td>$4.00 \times 10^{-3}$</td>
<td>$3.94 \times 10^{-3}$</td>
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<td>200</td>
<td>$2.27 \times 10^{-3}$</td>
<td>$1.15 \times 10^{-3}$</td>
<td>$6.57 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Key to size ranges (all areas in mm$^2$)

Surface Section 1 = $<9.75 \times 10^{-4}$; 2 = $9.75 \times 10^{-4}$ to $4.87 \times 10^{-3}$; 3 = $4.87 \times 10^{-3}$ to $1.95 \times 10^{-2}$; 4 = $>1.95 \times 10^{-2}$

Cross Sections 1 and 2

- 25μm 1 = $<7.38 \times 10^{-5}$; 2 = $7.38 \times 10^{-5}$ to $3.69 \times 10^{-4}$; 3 = $3.69 \times 10^{-4}$ to $1.11 \times 10^{-3}$; 4 = $>1.11 \times 10^{-3}$
- 50μm 1 = $<3.40 \times 10^{-4}$; 2 = $3.40 \times 10^{-4}$ to $1.38 \times 10^{-3}$; 3 = $1.38 \times 10^{-3}$ to $3.40 \times 10^{-3}$; 4 = $>3.40 \times 10^{-3}$
- 100μm 1 = $<1.12 \times 10^{-3}$; 2 = $1.12 \times 10^{-3}$ to $2.80 \times 10^{-3}$; 3 = $2.80 \times 10^{-3}$ to $4.22 \times 10^{-3}$; 4 = $>4.22 \times 10^{-3}$
- 200μm 1 = $<1.85 \times 10^{-3}$; 2 = $1.85 \times 10^{-3}$ to $9.23 \times 10^{-3}$; 3 = $9.23 \times 10^{-3}$ to $2.77 \times 10^{-2}$; 4 = $>2.77 \times 10^{-2}$
same size range in each section. Calculations showed that any 
arbitrary simple grain shape yielded approximately the same figure 
for the total surface area. It is not possible to allow for the fact 
that, in practice, the shapes are not simple, due to distortion during 
rolling.

A detailed analysis of grain sizes is given in Table 23, 
and total grain areas are correlated with reaction parameters in Table 
24. Total grain surface area/unit volume of metal (Gv) is plotted 
against thickness on logarithmic axes in Figure 40. Gv increases 
with sample thickness according to a complex power function (slope 
of graph = 1.39). Similarly, complex functions relate Gv to the total 
weight increase per unit mass of iron (Δw_m/w_o), and to the maximum rate 
of reaction per unit mass (r_m/w_o) of samples reacted in CO at 515°C 
and 550°C (Fig. 41 and 42a respectively). The r_m/w_o values of iron 
samples reacted in CH_4 at 700°C and 865°C increase slightly with Gv 
(Fig. 42b), but Δw_m/w_o figures are independent of Gv (Fig. 41 and Table 
24). It is interesting to note that r_m/w_o for reaction of 25 μm samples 
at 550°C in CO is greater than for those at 700°C in CH_4.

Table 24 shows also that total carbon pick up per unit grain 
area (Δw_m/Gv), and maximum rates per unit grain area (r_m/σ), are constant at 515°C, but increase with increasing sample thickness (i.e. 
increasing grain size) at higher temperatures. This implies further 
disintegration of individual grains at 550°C and above, which is also 
consistent with the changes in slope, and increases in magnitude of 
Δw_m/w_o and r_m/w_o, which occur with increasing temperature in Figures 
41 and 42.
Table 24
CORRELATION OF REACTION PARAMETERS TO TOTAL METAL GRAIN AREA FOR THE Fe/CO INTERACTION

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Metal Thickness μm</th>
<th>Sample Volume (mm³)</th>
<th>Total Weight Increase Δω_m (g)</th>
<th>Maximum Reaction Rate r_m (g.g⁻¹.h⁻¹)</th>
<th>Total grain area G (mm²)</th>
<th>Total grain area per unit volume G_v (mm⁻¹)</th>
<th>Δω_m</th>
<th>r_m</th>
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</thead>
<tbody>
<tr>
<td>515</td>
<td>25</td>
<td>1.35</td>
<td>×10⁻¹</td>
<td>×10⁻⁴</td>
<td>×10⁻²</td>
<td>×10²</td>
<td>×10⁻⁴</td>
<td>×10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.74</td>
<td>1.452</td>
<td>7.45</td>
<td>5.07</td>
<td>1.49</td>
<td>5.32</td>
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</tr>
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<td>2.62</td>
<td>3.55</td>
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<td>0.76</td>
<td>2.65</td>
</tr>
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<td>11.32</td>
<td>1.052</td>
<td>1.19</td>
<td>2.65</td>
<td>0.3</td>
<td>0.21</td>
<td>4.35</td>
</tr>
<tr>
<td>550</td>
<td>25</td>
<td>1.17</td>
<td>×10⁻¹</td>
<td>×10⁻³</td>
<td>×10⁻¹</td>
<td>as</td>
<td>×10²</td>
<td>×10⁻⁵</td>
</tr>
<tr>
<td></td>
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<td>2.31</td>
<td>1.951</td>
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<td>3.08</td>
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<td>4.200</td>
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<td>3.22</td>
<td>0.40</td>
<td>4.66</td>
<td>1.44</td>
</tr>
<tr>
<td>700</td>
<td>25</td>
<td>0.96</td>
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<td>×10⁻¹</td>
<td>as</td>
<td>×10²</td>
<td>×10⁻⁵</td>
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<tr>
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<td>2.19</td>
<td>3.693</td>
<td>23.76</td>
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<td>1.63</td>
<td>3.27</td>
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<td>1.78</td>
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<td>20.12</td>
<td>7.34</td>
<td>1.18</td>
<td>1.67</td>
<td>4.37</td>
</tr>
<tr>
<td>865</td>
<td>25</td>
<td>1.08</td>
<td>×10⁻¹</td>
<td>×10⁻³</td>
<td>×10⁻¹</td>
<td>as</td>
<td>×10²</td>
<td>×10⁻⁵</td>
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<tr>
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<td>1.76</td>
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<td>8.96</td>
<td>13.950</td>
<td>26.25</td>
<td>15.50</td>
<td>2.14</td>
<td>1.92</td>
<td>8.09</td>
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FIG. 40  CORRELATION OF AVAILABLE GRAIN SURFACE AREA OF Fe SAMPLES WITH METAL THICKNESS
FIG. 41 CORRELATION OF TOTAL CARBON PICKUP TO AVAILABLE GRAIN SURFACE AREA
**FIG. 42(a) CORRELATION OF MAXIMUM REACTION RATES TO AVAILABLE GRAIN AREA FOR THE Fe/CO REACTION**
FIG. 42(b) CORRELATION OF MAXIMUM REACTION RATES TO AVAILABLE GRAIN AREA FOR THE Fe/CH₄ REACTION
3.2 Mechanistic Conclusions

The following proposals are made to explain the results reported in this chapter for the formation of heavy carbon deposits on iron:

1. The formation of carbon occurs, after an apparent induction period, on an available area of metal which increases, as reaction proceeds, to a maximum value, when the sample is fully disintegrated.

2. Each atom of metal undergoes more than one interaction with the gas, since the weights of carbon deposit per unit mass of metal are greater than those predicted from a single interaction (for which \( \Delta w_m/w_o = 0.21 \)).

3. After the metal area has reached its limiting value the reaction rate falls to a final low level as a result of termination steps such as carbide and oxide formation, or encapsulation of metal particles.

4. Since the total weight of carbon deposited increases with increasing reaction temperature, it follows that the number of metal/gas interactions must increase. This could occur as a result of a greater number of interactions at individual active sites, or an increase in the number of active sites, by the formation of smaller particles, with a consequent increase in available area.

5. In order that the numbers of gas/metal interactions can increase by either of the mechanisms suggested in (4) above, the rate of carbon forming reactions must increase more rapidly with temperature than that of termination reactions. The relative rate of termination at 515°C is apparently so high that the particle size does not fall below the metal grain size. At higher temperatures, however, termination is sufficiently slow to allow individual grains to breakdown further.
(6) The effect of periodic exposure to the air on the rates of reaction can now be explained if it is assumed that iron oxide is stable in the presence of CO but not of CH₄. (Stability in CO is proved by the presence of magnetite in the deposits.) Then the formation of oxide during air exposure provides an additional termination step and reduces the number of active sites and hence the reaction rate in CO. If, however, air-formed oxides are reduced under methane reaction conditions to small, highly reactive particles, the observed increase in reaction rate would be predicted.
VI RESULTS & DEPOSITION ON BINARY ALLOYS

1. REACTION OF Fe/Cr ALLOYS WITH CO
   1.1 Kinetics
   1.2 Analysis of Reaction Products
      1.2.1 Wet Analyses
      1.2.2 X-Ray Analyses
   1.3 Morphology

2. REACTION OF Fe/Cr ALLOYS WITH CH₄

3. REACTION OF Fe/CARBON ALLOYS WITH CO

4. DISCUSSION
   4.1 Kinetics
   4.2 Mechanistic Aspects
RESULTS 4 DEPOSITION ON BINARY ALLOYS

1. REACTION OF Fe/Cr ALLOYS WITH CO

1.1 Kinetics

Data are plotted in Figure 43 for the reaction at 550°C and 2.75 bar of binary alloys of Cr content from 1-34%. A logarithmic weight gain axis is used to accommodate the large variations in weight gain. The results fit the standard log. time plot represented by equation 44, as shown in Figure 44. Values of $t_i$ and $t_o$ are given in Table 25. The slopes of the graphs in Figure 44 decrease as the logarithm of the chromium content of the alloy (Figure 45), to a minimum at 24% Cr. The zero Cr point was obtained from an approximate extrapolation of data for Fe presented in the previous chapter. Metallurgical examination of samples revealed differences in grain size, with markedly smaller grains in the 34 Cr alloy. The solid datum points and dashed line in Figure 45 represented the slopes of the logarithmic graphs after correction for grain size.

<table>
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<tr>
<th>%Cr</th>
<th>$t_o$</th>
<th>$t_i$</th>
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</thead>
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</tr>
<tr>
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<td>15.27</td>
</tr>
<tr>
<td>8</td>
<td>4.47</td>
<td>77.00</td>
</tr>
<tr>
<td>14</td>
<td>11.86</td>
<td>41.60</td>
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<td>24</td>
<td>9.98</td>
<td>72.81</td>
</tr>
<tr>
<td>34</td>
<td>6.15</td>
<td>12.13</td>
</tr>
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</table>
FIG. 43  RATE CURVES FOR BINARY ALLOYS  
OF DIFFERENT CHROMIUM CONCENTRATIONS
FIG. 44  LOGARITHMIC RATE PLOTS FOR Fe/Cr BINARY ALLOYS
FIG. 45  EFFECT OF Cr CONTENT OF BINARY ALLOYS ON THE SLOPE OF THE LOGARITHMIC DEPOSITION PLOTS
1.2 Analysis of Reaction Products

1.2.1 Wet Analysis

Loose deposit from samples stopped at different stages of reaction was quantitatively analysed for Fe and Cr by the method described in Chapter II. The results are presented in Figure 46 and Table 26 for alloys of 1 and 8% Cr. The carbon content of the metal was measured for all six alloys after 285 h reaction after first removing surface deposit by means of a soft brush, and ultrasonic washing in ether. The results are included in Table 26. It can be seen that in the most reacted samples (1-8 Cr) the carbon content in the bulk metal is high, and that the amount of metal in the deposit increases at a constant rate. The Fe/Cr ratios in the deposit are generally higher than in the bulk, indicating a preferential transfer of Fe. It is thought that Cr is only incorporated as a result of break-up of the metal structure. The total weight of metal in the deposits after 285 h reaction decreases from 72.66 mg in 1 Cr alloy to 1.40 in 14 Cr alloy.

1.2.2 X-Ray Analysis

X-ray diffractometry was used to establish

(1) the effect of chromium alloying on the iron lattice in the "as-received" alloys

(2) the reaction products on the various alloys

(3) the depth of penetration of carbide into the bulk metal on the most heavily reacted samples (1-8% Cr).

The results are presented in Figures 47-51 and Tables 27-29. Cubic lattice parameters were calculated graphically by extrapolation of a plot of the approximate parameter for each x-ray line versus $\sin^2\theta$, to $\sin^2\theta = 1$ (177, p.330). The orthorhombic parameters of Fe3C were calculated
<table>
<thead>
<tr>
<th>% Cr in Alloy</th>
<th>Total Wt.Gain of C (g)</th>
<th>Initial Sample Wt. (g)</th>
<th>%Fe</th>
<th>%Cr in the deposit, balance C</th>
<th>Wt.of Fe (mg)</th>
<th>Wt.of Cr (mg)</th>
<th>%C</th>
<th>Wt.of C (mg)</th>
<th>Wt.of sample after removal of deposit (g)</th>
<th>Fe/Cr in deposit</th>
<th>Fe/Cr in alloy</th>
</tr>
</thead>
<tbody>
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<td>72.28</td>
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<td>-</td>
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<td>-</td>
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Table 26
WET ANALYSES OF Fe/Cr BINARY ALLOY SAMPLES
FIG. 46 INCORPORATION OF METALLIC SPECIES INTO THE THICKENING DEPOSIT
### Table 27

**VARIATION OF LATTICE DIMENSIONS IN AS-RECEIVED Fe/Cr ALLOY**

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<tr>
<th>Lattice Plane</th>
<th>X-Ray Line Position and Intensity</th>
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<td>α-Fe</td>
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<td>Parameter</td>
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</table>
Table 28

<table>
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<tr>
<th>d(Å)</th>
<th>I (arbitrary units)</th>
<th>1Cr</th>
<th>3Cr</th>
<th>8Cr</th>
<th>14Cr</th>
<th>24Cr</th>
<th>32Cr</th>
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<td>1.856</td>
<td>19</td>
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<td>1.856</td>
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<td>1.715</td>
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<td>1.684</td>
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<td>1.641</td>
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</table>

Legend:
- Graphite
- M₃O₄
- M₂O₃
- MnO₄
- Fe₃C
- Fe₃C/Cr₇C₃
- Fe₃C/Cr₇C₃
- Cr₇C₃
- Fe₃C/Cr₇C₃
- Metal
- Fe₃C/Cr₇C₃
- Fe₃C
- Cr₇C₃
- Graphite/Fe₃C
- Cr₇C₃
Table 28 (continued)

<table>
<thead>
<tr>
<th>( d(\AA) )</th>
<th>1Cr</th>
<th>3Cr</th>
<th>8Cr</th>
<th>14Cr</th>
<th>24Cr</th>
<th>34Cr</th>
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<tr>
<td>(arbitrary units)</td>
<td>1.617</td>
<td>10</td>
<td>1.589</td>
<td>9</td>
<td>1.588</td>
<td>3</td>
</tr>
<tr>
<td>1.590</td>
<td>7</td>
<td>1.545</td>
<td>2</td>
<td>1.546</td>
<td>1.524</td>
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</tr>
<tr>
<td>1.512</td>
<td>3</td>
<td>1.517</td>
<td>2</td>
<td>1.485</td>
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<td>( \text{Graphite/Fe}_3\text{C} )</td>
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<tr>
<td>1.435</td>
<td>130</td>
<td>1.435</td>
<td>20</td>
<td>1.435</td>
<td>5</td>
<td>1.436</td>
</tr>
<tr>
<td>1.331</td>
<td>5</td>
<td>1.329</td>
<td>3</td>
<td>1.308</td>
<td>3</td>
<td>1.308</td>
</tr>
<tr>
<td>1.226</td>
<td>6</td>
<td>1.229</td>
<td>4</td>
<td>1.217</td>
<td>6</td>
<td>( \text{M}_2\text{O}_4 )</td>
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<tr>
<td>1.170</td>
<td>32</td>
<td>1.172</td>
<td>20</td>
<td>1.172</td>
<td>10</td>
<td>1.173</td>
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<tr>
<td>1.163</td>
<td>4</td>
<td>1.014</td>
<td>25</td>
<td>1.015</td>
<td>4</td>
<td>( \text{Fe}_3\text{C} )</td>
</tr>
<tr>
<td>1.014</td>
<td>4</td>
<td>1.015</td>
<td>4</td>
<td>( \text{Metal} )</td>
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Table 29
CARBIDE PARAMETER DATA FOR 1, 3 AND 8% Cr ALLOYS

<table>
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<tr>
<th>Depth of Grinding (μm)</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Unit Cell Volume</th>
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<td>1%</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>0</td>
<td>4.5417</td>
<td>5.1017</td>
<td>6.6860</td>
<td>154.92</td>
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<td>10</td>
<td>4.5337</td>
<td>5.1011</td>
<td>6.6386</td>
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<td>20</td>
<td>4.5203</td>
<td>5.0977</td>
<td>6.6067</td>
<td>152.24</td>
</tr>
<tr>
<td>50</td>
<td>4.5212</td>
<td>5.0925</td>
<td>6.6051</td>
<td>152.07</td>
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<tr>
<td>80</td>
<td>4.5207</td>
<td>5.0884</td>
<td>6.6067</td>
<td>151.97</td>
</tr>
<tr>
<td>3%</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>4.5226</td>
<td>5.0820</td>
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<td>10</td>
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<td>5.0885</td>
<td>6.7466</td>
<td>155.51</td>
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<td>4.5198</td>
<td>5.0800</td>
<td>6.7283</td>
<td>154.48</td>
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<td>5.0735</td>
<td>6.7191</td>
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<tr>
<td>80</td>
<td>4.5134</td>
<td>4.0709</td>
<td>6.7176</td>
<td>153.75</td>
</tr>
<tr>
<td>8%</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>4.5175</td>
<td>5.0741</td>
<td>6.7222</td>
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</tr>
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<td>4.5045</td>
<td>6.0765</td>
<td>6.7185</td>
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<td>5.0767</td>
<td>6.7300</td>
<td>154.42</td>
</tr>
<tr>
<td>80</td>
<td>4.5083</td>
<td>5.0714</td>
<td>6.7222</td>
<td>153.09</td>
</tr>
<tr>
<td>Literature Value</td>
<td>4.5234</td>
<td>5.0883</td>
<td>6.7426</td>
<td>155.19</td>
</tr>
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</table>
FIG. 47 VARIATION OF CUBIC LATTICE PARAMETER WITH CHROMIUM CONTENT OF AS-RECEIVED Fe/Cr BINARY ALLOYS

100% Fe VALUE FROM ASTM 6-0696
100% Cr VALUE FROM ASTM 6-0694
Fig. 48 Variation of carbide line intensity with depth in the alloy. Average curves for 1.97, 2.06, 2.10, 2.20 and 2.26 A lines after 285h reaction.
FIG. 49  DEPTH VARIATION OF LATTICE PARAMETERS OF ORTHORHOMBIC Fe₃C IN 1 Cr ALLOYS
FIG. 50  DEPTH VARIATION OF LATTICE PARAMETERS
OF Fe₃C IN 3Cr ALLOYS
FIG. 51 DEPTH VARIATION OF LATTICE PARAMETERS OF Fe₃C IN 8Cr ALLOYS
on a computer by linear regression analysis to obtain the best fit to the Bragg equation for 10, or more, lines.

The iron lattice parameter increases progressively as the chromium content of the as-received alloy increases, but the rate of increase changes discontinuously between 8.5% and 9.0% chromium (Figure 47 and Table 27). There were indications that the lattice parameter at the surface of the low chromium alloys decreased during reaction, towards that of iron, which might arise as a result of preferential transfer of iron to the reaction interface.

X-ray patterns after 285 h reaction are given in Table 28. The main products of reaction on samples of 1-8 Cr are graphite, cementite and an M3O4 type oxide, where M could be either Fe or Cr. There is also evidence for the presence of Cr7C3 (or (CrFe)7C3). Most of its x-ray lines overlap the Fe3C pattern, however the lines 2.14, 2.04 (100% line) and 1.62 can be uniquely attributed to Cr7C3. At 14Cr and above, the graphite and cementite lines are very weak or missing altogether, but weak Cr7C3 lines are still detected. Also, the character of the oxide changes from M3O4 to M2O3, consistent with the formation of the more stable oxide Cr2O3.

To investigate the depth of penetration of carbide into the metal, deposit was ultrasonically removed from 1 Cr, 3 Cr and 8 Cr alloy, after 285 h reaction. They were then thinned by grinding on a 6 µm diamond wheel and x-ray patterns taken at known depths (measured by means of a 3-figure micrometer). The carbide line intensities were normalised relevant to the 1 Cr surface and variation in intensity with depth averaged over a number of lines. The line intensities decreased with increasing chromium content, but the total depth of penetration remained
PLATE 11  OPEN BOOK EFFECT ON THICK DEPOSITS ON 1Cr BINARY ALLOY SAMPLES AFTER 285 hrs. REACTION IN CO AT 550°C

PLATE 12  COLUMNAR GROWTHS ON 14Cr BINARY ALLOYS AFTER 285 hrs. REACTION IN CO AT 550°C
constant at about 140 μm (Figure 48). Depth variation of the orthorhombic lattice parameters is given in Table 29 and Figures 49 to 51. The average values of the a and b parameters decrease with increasing chromium content, while that of the c parameter increases markedly between 1 and 3% Cr. The lattice parameters of the 1 Cr alloy decrease with increasing penetration into the lattice, the major change occurring in the first 20 μm (Figure 49). Those of the 3 Cr alloy also decrease after a small initial rise (Figure 50). The parameters of the 8 Cr alloy show no significant variation with depth and have approximately constant values 0.2-0.3% below the literature figures (Figure 51).

1.3 Morphology

The basic morphology of deposits on 1-8 Cr alloys was similar to that described for Fe in the previous two chapters. In the early stages of reaction, a blue/green oxide film was visible beneath the carbon layer. On 14 Cr alloy and above, little carbon was formed, and a coloured oxide layer developed at an early stage. As the deposit thickened, layers of carbon became detached from the surface of the lower chrome samples producing an "open-book" effect (Plate 11). Thick deposit on 14 Cr samples, and eventually on 24 and 34 Cr, had a columnar appearance, as if growing from localised sites (Plate 12).

2. REACTION OF Fe/Cr BINARY ALLOYS WITH CH₄

Only limited data are available for reaction in methane. Weight gain curves at 2.75 bar pressure and 700 and 865°C are presented in Figures 52 and 53 respectively (sample thickness 550 ±50 μm). At both temperatures, 3 Cr and 8 Cr samples reacted at a lower rate than the remainder, and the rate of reaction of 14 Cr samples at 865°C also tended to be slightly low. The 3 Cr and 8 Cr alloys would be expected to be within the γ-loop of the phase diagram at 865°C, and 1 Cr and 14 Cr
FIG. 52 RATE CURVES FOR Fe/Cr BINARY ALLOYS IN CH$_4$ AT 700ºC AND 2.75 bar
FIG. 53 RATE CURVES FOR Fe/Cr BINARY ALLOYS IN CH₄ AT 865°C AND 2.75 bar
very close to the boundary. The reaction rate may thus be adversely affected by the presence of γ-structure, e.g. carbon diffusion becomes rate limiting as proposed in Chapter IV. The γ-phase is not expected to be stable at 700°C, and the lower rates of the 3 and 8% samples may suggest the presence of retained γ-phase in the "as-received" alloy.

X-ray patterns from samples reacted for 250 h at 865°C were similar for all six alloys. A typical analysis is given in Table 30. The main products of reaction were poorly oriented graphite, Cr$_7$C$_3$ (or (CrFe)$_7$C$_3$) and Fe$_3$C. A weak oxide line at 2.54 Å probably arises as a result of oxidation during exposure to the air, and may explain an observation that the colour of the deposit turned from very dark to a light grey, when first removed from the reaction vessel. Neither colour change, nor oxide lines, were observed at 700°C.

3. REACTION OF Fe/CARBON BINARY ALLOYS IN CO

The results of Chapter IV showed that the initial deposition process is controlled by the rate of reaction on the surface, and those of Chapter V confirm this observation; although the rate of production of fresh area by break-up of the metal structure is rate determining overall. To further test the supposition of surface rate control, samples pre-loaded with carbon, in the form of Fe/C binary alloys of carbon content 0.004% to 0.917%, were reacted in CO. Results are presented in Figures 54 and 55 in the form of weight gain vs log. t + t$_0$ for reaction at 2.75 bar and 515°C and 550°C respectively. At 550°C, the reaction rate decreased with increasing carbon content, implying a diluent effect, similar to that found for Fe/Cr alloy. At 515°C, increased scatter in the data partially masked the dilution effect, and 0.08C and 0.91C are apparently out of sequence. Reaction rates at 515°C are an order of magnitude lower than at 550°C, and the influence on the
Table 30
X-RAY ANALYSIS OF 1Cr ALLOY AFTER 250h IN CH₄ AT 865°C

<table>
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<th></th>
<th>1 Cr Alloy</th>
<th>Cr₇C₃ 11-550</th>
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<tr>
<td></td>
<td>d (Å)</td>
<td>Intensity (Arb. units)</td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>3.371</td>
<td>145</td>
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<tr>
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<tr>
<td>1.174</td>
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<td>1.195</td>
</tr>
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Graphite
Fe₃O₄
Fe₃C
Metal
Fe₃C
Fe₃C
Fe₃C
Graphite
Fe₃C
Fe₃C
Fe₃C
Metal
Fe₃C
Fe₃C
Metal
FIG. 54 LOGARITHMIC RATE CURVES FOR Fe/C BINARY ALLOYS IN CO AT 515°C AND 2.75 bar
FIG. 55 LOGARITHMIC RATE CURVES FOR Fe/C BINARY ALLOYS IN CO AT 550°C AND 2.75 bar
rate of grain size variations in the as-received alloys may have been of similar magnitude to the dilution effects.

4. DISCUSSION

4.1 The Kinetics of the Fe/Cr/CO Reaction

In addition to providing data relevant to carbon deposition on chromium steels, the reaction of CO with Fe/Cr binary alloys also provides a test of the kinetic theory developed in the previous chapter for disintegrating samples, since the chromium dependance of the slope of log. time plots can be simply derived. The rate of reaction of Cr is so low compared to that of iron, that it can be regarded as an inert diluent. The area created by disintegration is therefore reduced by a fixed proportion determined by the chromium concentration \( CCr \). Assuming that reaction occurs at a specific number of active sites \( Z \), which is directly proportional to the available area, equation 55 can be rewritten

\[
Z_t = Z_0 \exp \alpha'qC_{Cr} \\
\text{where } Z_0 = \text{initial number of active sites} \\
\text{and } \alpha' = \text{constant}
\]

Equation 59 then reduces to

\[
\frac{dq}{dt} = \frac{\beta}{\alpha'Z_0} \exp -\alpha'qC_{Cr} \\
\text{where } \frac{dq}{dt} \text{ is the slope of the log. time plot}
\]

Thus by taking logs the observed chromium dependance is obtained:

\[
ln \frac{dq}{dt} = ln \frac{\beta}{\alpha'Z_0} - \alpha'qC_{Cr} \\
(64)
\]

The results of the reaction with CO also provide confirmation of the effects of grain size on reaction rate. The correction applied in Figure 45 reduces the apparently increased rate of the 34Cr alloy to that of 24 Cr. At the reaction temperature, both samples are expected
to contain significant amounts of sigma phase alloy, and it is thought that the rate remains constant with Cr content to the far side of the phase field (65-70% Cr), then falls to the pure Cr figure.

4.2 Mechanistic Aspects

The results of the reaction of Fe/Cr binary alloys with CO represent earlier stages of reaction than those of iron reported in the previous chapter, since the samples are so thick that only partial disintegration occurs, and the reaction rates are reduced by the presence of Cr. The presence of carbide below the metal/deposit interface suggests that disintegration may occur as a result of precipitation of carbide at grain boundaries, thus reducing the cohesive forces between grains and eventually 'jacking' them apart. The observed logarithmic kinetics are thus those of a physical process which makes available fresh metal area.

The observed variation in carbide parameters implies changes in stoichiometry with immediate environment. Deviation from the literatures values are most marked on the more heavily reacted 1Cr and 3Cr alloys, and particularly close to the metal deposit interface. The 1Cr data indicates a change in unit cell structure at the reaction interface, where the carbide lattice is expanded in the a and b direction and contracted along the c axis. The parameters decrease rapidly with depth into the metal and indicate a contracted unit cell in the bulk.

The results of reaction of Fe/C alloys with CO show that the rate of deposition is independant of the concentration of carbon in the bulk metal. Not only do high concentrations of precipitated carbon not accelerate reaction, it is probable that they cause retardation by reducing the amount of active area made available by disintegration.
VII RESULTS 5 IMM5 ANALYSES OF DEPOSITS

1. THE CHEMICAL EFFECTS OF PRETREATMENT

2. METHANE RESISTIVITY SAMPLES

3. Fe/CO SAMPLES
   3.1 CO Resistivity samples
   3.2 Autoclave samples

4. DISCUSSION OF RESULTS ON IRON
   4.1 The Structure of Deposits from CH₄ and CO
   4.2 Silicon Contamination of Samples

5. DEPOSITS FROM CO ON A 20/25 Nb STEEL
   5.1 Surface Composition of "As-received" Alloy
      5.1.1 Emission Depth of Secondary Ions
      5.1.2 Metal Ions
      5.1.3 Oxide Ions
      5.1.4 Carbide Ions
   5.2 Surface Composition after Reaction in CO
      5.2.1 Comparison of Deposits on the Ribbed and Smooth Surfaces
      5.2.2 Metal Ion Depth Profiles
      5.2.3 Oxide Layers
      5.2.4 Carbon-containing Ions
      5.2.5 Impurity Ions

6. DISCUSSION
   6.1 The Effect of CO on the Air-formed Oxide Film
   6.2 Carbon and Carbonitride Ions
In the study of reaction products on pure iron, most ions can be uniquely identified and attributed to oxide or carbide structures. The identification of free carbon and of nitrogen however is difficult, since carbides contribute to M/e 12 and 24, and M/e 14 and 28 include the ions \( \text{CH}_2^+ \) and \( \text{C}_2\text{H}_4^+ \) or M/e 56\(^{2+} \) respectively. It has been found that the \( \text{C}^- \) and \( \text{C}_2^- \) ions follow carbide ions, as might be expected if they retain the charge they carried in the lattice (155), and that \( \text{C}^+ \) and \( \text{C}_2^+ \) frequently have a different depth profile. The positive ions are therefore generally taken as indicative of free carbon. Ions of M/e 26 can be assigned as \( \text{CN}^- \) or \( \text{C}_2\text{H}_2^- \). In the presence of carbides, the 26 peak is generally strong and follows the carbide ions. It also appears strongly in iron nitride spectra (178) and is thought to represent a carbonitride structure. In the absence of carbides, M/e 26 is assigned by inspection of other ions (e.g. M/e 26, \( \text{C}_2\text{H}^- \) or M/e 42, \( \text{CNO}^- \)). Where M/e 25 is weak, M/e 26 is assumed to indicate nitrogen.

In the study of the stainless alloy, positive identification of peaks is frequently difficult because of the number of elemental and isotopic combinations which can arise, some ions have therefore been assigned more than one structure.

1. **The Chemical Effects of Pretreatment**

Analyses were made of iron foils in their "as-received" and "as-prepared" condition, i.e. before and after pretreatment respectively. The only foreign elements present were C, O, N and Si. All were detected only at maximum sensitivity indicating concentrations of a few ppm or less. Depth profile curves from the "as-received" material are given for the strongest ions in Figures 56 and 57, and selected ions are compared to those from "as-prepared" material in Figure 58.
FIG. 56  NEGATIVE ION EROSION CURVES FOR "AS RECEIVED" PURE IRON FOILS
FIG. 57  POSITIVE ION EROSION CURVES FOR 'AS RECEIVED' PURE IRON FOILS
ARGON PRIMARY IONS. BEAM CURRENT = 200 A. ASPECT RATIO (1X2) UNLESS STATED

FIG. 58 EFFECT OF THE CLEANING PROCEDURE ON CARBON DEPOSITION SPECIMEN PURITY
THE INFLUENCE OF CARBONACEOUS SURFACE IMPURITIES ON EXCRESCEENCE INITIATION IN THE RIMMING STEEL/CO₂/CO SYSTEM

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Central Electricity Research Laboratories, Kelvin Avenue, Leatherhead, Surrey KT22 7SE, U.K.

Abstract—The influence of surface carbon contamination in determining the sites of excrescence growth has been studied, for the reaction of rimming steel in carbon dioxide containing 1.5%CO + 1000 ppm H₂O + 10 ppm CH₄ at 1725 x 10⁶ N m⁻² and 450°C. Patterns visible in the oxide layer in the early stages of oxidation can be attributed to hydrocarbon impurities remaining on surfaces not rigorously cleaned. The impurity can accumulate at specific areas on the surface and can then accelerate oxidation such that excrescences start growing early in the normally protective stage. Surface cleaning procedures and their limitations for corrosion studies are discussed.

INTRODUCTION

The corrosion of rimming steel in high pressure CO₂/CO mixtures follows parabolic growth kinetics in the early stages, eventually changing to a linear type of growth.¹ During the latter stages of parabolic growth and throughout the linear region it is observed that small mounds of oxide are formed, commonly called excrescences, and most of the specimen weight change in the linear region can be associated with their growth. Concurrently with oxide growth there is a carbon build-up in the scale that follows a roughly similar rate curve.²

The growth sites of excrescences cannot be attributed to any particular type of surface feature. Part of the difficulty in understanding this system is that industrial corrosion tests are usually carried out on specimens with relatively ill-defined surfaces. However, there are some experimental observations that must be considered in any study of excrescence formation.

1. Shot blasted surfaces, which go into "breakaway" before smooth surfaces, tend to corrode by formation of many small excrescences,¹,³ whereas large isolated excrescences are formed on polished and pickled surfaces.⁴ Preferred growth of excrescences along scratches occurs in some cases, although other apparently identical scratches remain free of them.

2. They are reported to be located at positions previously occupied by carbide particles or pearlite regions.⁴ However, the number of individual carbide inclusions in the surface plane of either the "rim" or "core" of rimming steel far exceeds the number of excrescences formed.⁵ There is conflicting evidence as to whether the carbide particles below excrescences are preferentially attacked.¹,⁴

3. The protective oxide develops regions of a more porous character detectable within the first 20 h of reaction, and some of these areas grow into excrescences that have a porous central region and a surrounding non-porous oxide that tends to peel away. Carbon is believed to contribute by depositing in the oxide thereby causing mechanical failure, and as a consequence, a more open pore structure.⁴ Additives

*Manuscript received 9 January 1975; in revised form 20 July 1975.
that increase the rate of carbon deposition from carbon monoxide over iron surfaces, e.g. \( \text{H}_2 \) and \( \text{H}_2\text{O} \), also increase the rate of oxidation and reduce the time to breakaway.\(^6\,^7\)

In this paper we report on the influence of localized concentrations of carbonaceous impurities on the initiation stage. In some of our early oxidation experiments, ring patterns in the oxide layer were observed, caused by surface carbon contamination, which were highly active areas for excrescence growth. Because trace impurities had apparently influenced the oxidation behaviour, the effects were investigated using deliberately contaminated surfaces.

**EXPERIMENTAL**

Rimming steel specimens were oxidized at 450°C in \( \text{CO}_2 \) containing 1.5% \( \text{CO} \) + 1000 ppm \( \text{H}_2\text{O} \) + 10 ppm \( \text{CH}_4 \) at a total pressure of 250 psi absolute (17.25 x 10^6 N m\(^{-2}\)) and a flow rate of 20 ml min\(^{-1}\) in standard high pressure autoclaves.

The material, in the form of 10 mm square coupons 2 mm thick, was cut from the centre of a 30 mm wide strip of steel to avoid any compositional or mechanical work variations that might have existed near the edges.

The specimens were abraded under 60/80 petroleum ether to (00) grade emergy and then cleaned by ultrasonic treatment in trichlorethylene followed by washing in Analar grade methanol. Hydrocarbon contamination was introduced by coating the surface with a film of Apiezon M grease, and the specimens were given a final rinse for ca. 15 s in 60/80 petroleum ether followed by an equally brief wash in methanol. The inadequacy of this final solvent cleaning led directly to the effects reported.

**RESULTS**

Specimens oxidizing at 450°C to form approx. 7.5 g m\(^{-2}\) in 3000 h with a time to breakaway in the range 100–1000 h were examined after the first 20 h of oxidation (wt gain = 0.15 mg cm\(^{-2}\)). Structures consisting of concentric rings and apparent flow patterns had developed, as shown in Figs. 1 and 2, and also the first indications of excrescence formation were visible. No patterns were detectable on the surface before oxidation.

The centres of the patterns had areas composed of large numbers of very small excrescences, with the usual appearance of the magnetite corrosion product (Fig. 3). These regions were very reactive throughout the remainder of the oxidation experiment and eventually, when the individual excrescences had intergrown, a large nodular structure was produced with ill-defined boundaries.

Some of the rings were observed as brighter bands due to isolated whisker-type growths on top of the main magnetite layer. Both iron carbides, e.g. \( \text{Fe}_3\text{C} \), and \( \alpha\text{-Fe}_2\text{O}_3 \) are known to form whiskers, the latter under conditions of higher oxygen potential than exists in this carbon dioxide gas mixture. Neither carbides nor haematite were detectable by X-ray diffraction, possibly because they are not present in sufficient concentration. On well-cleaned surfaces reacted under identical conditions, both the rings and the whiskers were undetectable, suggesting that the surface contamination had influenced the oxide morphology and/or permitted the transient existence of a whisker-type carbide, as well as initiating excrescence growth. Within the next 20–100 h of reaction, the oxide growth on the contaminated specimens reverted to the normal type without rings, and the only evidence of an abnormal process was the continuing growth of the clustered small excrescences.

The patterns have the appearance of solvent drying marks, believed to be caused
Fig. 3. Fine structure of the oxide in the centre of the rings.
Fig. 4. The ring system examined by X-ray fluorescence giving the data of Table 1.
Fig. 1. Rimming steel surface after 20 h oxidation at 450°C in the high pressure CO₂ mixture, showing isolated ring patterns.

Fig. 2. Oxidized rimming steel showing solvent marks and central excrescences.
Fig. 5. Type of excrecence growth obtained on a surface free of residual hydrocarbon impurities.

Fig. 6. Intergrown excrescences (with lighter shading) detectable early in the oxidation reaction on a contaminated surface.
excrescences is not detectable. A comparison of the two types is given in Figs. 5 and 6.

Earlier work indicated that excrescences may have a short induction time, if the porous regions observed in the protective film after 20 h oxidation are correctly identified as precursor states. The porous regions did not grow into excrescences in every case. These observations are exactly paralleled by the effects of localized carbon impurities. Premature carbon deposition could assist excrescence initiation and growth in several ways. For example, increased carburization of metal grains at the surface could cause break up of the ferrite grain structure thus increasing the active area of metal exposed. The carbon could also create a more open pore structure in the protective film, possibly leading to cracking, and exposure of fresh metal. Another alternative is that break-up of the protective film could occur if the carbon forms large carbide particles. Some of the ring patterns did not have excess carbon at the centres and did not show premature excrescence growth, which may explain the variability in the initiation over porous regions in the oxide scale.

Although the effects reported were deliberately enhanced by the addition of hydrocarbon contamination, the results are sufficiently similar to those of conventional studies to suggest that the influence of trace impurities is an important factor in the breakaway oxidation of rimming steel in high pressure CO$_2$/CO mixtures. In particular, the apparently random location of excrescences and the variability of the time to breakaway will depend on the location and concentration of surface impurities.

*Surface cleaning procedures*

Various cleaning techniques for iron surfaces have been reported in the literature. High-temperature annealing in vacuum or in a hydrogen atmosphere will not necessarily remove carbonaceous impurities. Pyrolysis will occur before rather than during oxidation and therefore the same flow patterns would be expected. Furthermore, solution of carbon in the bulk metal may be enhanced, and other inhomogeneous transformations may occur with prolonged heat treatment.

It has been reported that carbon can be lowered to a concentration below 5 ppm by reduction at 890°C in hydrogen saturated with water vapour at room temperature. Reduction to levels as low as $5 \times 10^{-8}$ ppm can be achieved by treatment in a hydrogen atmosphere continuously purified with zirconium hydride.

Ultra-clean iron surfaces are required for low energy electron diffraction work. Elaborate cleaning procedures are adopted which start with mechanical and electropolishing, use high-temperature oxidation and reduction cycles to remove carbon and sulphur, followed by argon ion bombardment, and thermal annealing to remove the surface damage caused by ion bombardment. Long-term annealing can cause segregation of alloying components from the bulk to the surface, particularly of interstitials such as sulphur. The oxidation/reduction treatment alone is likely to produce a surface composed of finely divided metal with properties not necessarily characteristic of the bulk material.

In general, where surface carbon contamination is expected to be troublesome, the most satisfactory treatment will be in wet hydrogen. However, if the risk of changes in composition at the surface due to segregation of an alloying component or diffusion of interstitial impurities from the bulk metal is unacceptable, then efficient solvent cleaning will be necessary.
The influence of carbonaceous surface impurities

by the deposition of impurities during solvent evaporation. A liquid film or a solid surface usually breaks up into droplets, the size depending on such factors as surface roughness, adsorbed films, wetting, surface tension, etc. It is suggested that both symmetrical and asymmetrical patterns arise in this way. The specimens were arranged in the autoclaves to lie in a plane perpendicular to the gas flow and were contained in silica buckets to catch any spalled oxide. It is improbable that unusual gas flow effects, or iron transport phenomena resulting from gas phase or surface diffusion, could satisfactorily explain the results. Independent experiments in this laboratory have confirmed that impurities can be concentrated during solvent evaporation.

Carbon, oxygen and iron concentrations have been measured using a Cambridge Stereoscan wavelength dispersive X-fluorescence analyser for the ring system shown in Fig. 4, by counting in a fixed area of each ring for 200 s. The data is given in Table 1.

<table>
<thead>
<tr>
<th>location (see Fig. 4)</th>
<th>Carbon $K_{\alpha}$ (c.p.s.)</th>
<th>Oxygen $K_{\alpha}$ (c.p.s.)</th>
<th>Iron $K_{\alpha}$ (c.p.s.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area 1</td>
<td>27·5</td>
<td>194·0</td>
<td>2242</td>
</tr>
<tr>
<td>Area 2</td>
<td>56·2</td>
<td>243·0</td>
<td>2193</td>
</tr>
<tr>
<td>Area 3</td>
<td>37·0</td>
<td>209·5</td>
<td>2237</td>
</tr>
<tr>
<td>Area 4</td>
<td>69·0</td>
<td>249·0</td>
<td>2183</td>
</tr>
<tr>
<td>Area 5</td>
<td>60·0</td>
<td>248·5</td>
<td>2173</td>
</tr>
</tbody>
</table>

The operating conditions were accelerating volts = 10 kV, specimen current = $1 \times 10^{-6}$ A, count time = 200 s, take-off angle = $45^\circ$. Average background count levels were $C_{K_{\alpha}} = 12$·8 c.p.s., $O_{K_{\alpha}} = 6$·6 c.p.s. and $Fe_{K_{\alpha}} = 17$ c.p.s.

Two sources of carbon contribute to the measured values, viz. that remaining on the surface after cleaning and that deposited during the oxidation reaction. There are significant carbon variations with correspondingly smaller oxygen variations. The lower values in areas 1 and 3 cannot be due to topographical effects because they correspond with the higher iron $K_{\alpha}$ values, indicating that the oxide layer is thinner or less dense in these regions and therefore the underlying metal can make a greater contribution to the observed iron count. There are wide variations in the carbon concentration at the centres of the ring systems. In some cases no excess carbon is detected, in others the central region is almost entirely composed of carbon.

**DISCUSSION**

*Excrescence formation*

The results show that localized concentrations of carbonaceous impurities can provide sites for excrescence growth. In these areas, many small excrescences are found growing in the early stages of oxidation, when much of the surface is reacting with parabolic kinetics, to give the uniform protective oxide layer.

At later stages, for example, in the linear kinetics period, the impurity sites can be identified as areas where many excrescences have intergrown randomly to give a large irregular nodular growth, in which the circular symmetry of the individual
Degreasing in a hot solvent, e.g. trichloroethylene or benzene, using a Soxhlet apparatus has been used.\textsuperscript{4} In this laboratory it has been found that a mechanical scrubbing followed by ultrasonic agitation under trichloroethylene, and then a final thorough wash in a high vapour pressure solvent such as AnalaR grade diethyl ether, gave specimens that showed none of the spurious oxidation effects discussed above.

Acknowledgements—This work forms part of a Ph.D. research programme with the University of Edinburgh (A.M.E.), and is published by permission of the Central Electricity Generating Board.

REFERENCES

5. A. M. Emsley and M. P. Hill, unpublished results.
mens that have deliberately received inadequate cleaning, e.g. a brief rinse in 60/80 petroleum ether and/or methanol, we have found nodule growth starting within the first 20 h of oxidation compared to times of several hundred hours for well-cleaned surfaces. Groups of small nodules are located at the centres of concentric ring patterns that are visible in the oxide layer only during the early stages of reaction (Figure 1). The rings and also the patterns around the edges of the specimens have the appearance of drying marks, suggesting that they are due to hydrocarbon impurities left after solvent evaporation.

![Figure 1](image_url)  
**Figure 1.** Solvent evaporation marks on a rimming steel surface after 20 h oxidation in a high pressure CO$_2$+CO mixture at 450°C.

It is proposed that impurities are concentrated as the solvent layer breaks up into droplets, and in the final stage of evaporation a relatively high level of impurity is deposited at specific points. To check whether concentric rings are formed by discontinuous evaporation, a droplet of a low molecular weight organic solvent containing a small quantity of a hydrocarbon oil or magnesium oxide in suspension was placed on a glass plate, and the contraction of the droplet boundary observed. In both cases the boundary contracted in steps and after complete evaporation a series of concentric rings of the contaminant were visible (Figure 2). Similar effects were observed with

![Figure 2](image_url)  
**Figure 2.** Ring patterns remaining on glass surfaces after evaporation of organic solvents. (a) 60/80 petroleum ether containing traces of a hydrocarbon oil; (b) industrial methylated spirits with magnesium oxide powder in suspension.
Impurity Deposition from an Evaporated Solvent and its Effect on Steel Oxidation

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(Paper received 10 September 1975, amended paper accepted 10 November 1975)

It is shown that the evaporation of an organic solvent from a solid surface can result in the concentration of dissolved or suspended impurities at specific sites. Concentric ring patterns of the contaminant, which remain on the surface when evaporation is complete, can be explained by analogy with the spreading of liquid films. Trace hydrocarbon impurities can be concentrated on mild steel surfaces in this way, giving similar ring patterns in the early stages of the oxidation reaction in high pressure carbon dioxide atmospheres. Excessive localised oxidation occurs leading to the early development of oxide nodules.

1. Introduction

The oxidation of mild and some low alloy steels in CO₂/CO atmospheres at high pressure and temperatures (e.g. 250 lb/in² and 450°C) is characterised by the initial formation of a protective oxide film, which is later disrupted by the development of oxide nodules also known as excrescences. The nodules grow at randomly isolated points which cannot be associated with any specific surface feature. The number formed and the time in the oxidation reaction at which they are first observed are unpredictable, but are important in determining the time to complete corrosion of the specimen.

The life of steel components in these atmospheres might be extended if the reasons for nodule growth were understood. We have considered the possibility that the variability in the number formed, and the randomness of their location, might be due to trace impurities remaining on the surface after the normal cleaning procedure. However, to provide isolated growth centres the impurities would require concentrating at some stage. In this paper it is shown that such a process is a normal consequence of the evaporation from a solid surface of a solvent containing either dissolved or suspended matter.

2. Experimental

High pressure oxidation in carbon dioxide containing 1.5% CO + 1000 v.p.p.m. H₂O + 10 v.p.p.m. CH₄ at 250 lb/in² pressure was carried out at 450°C with a flow rate of 20 ml min⁻¹. The rimming steel specimens were prepared for reaction by abrasion with (00) grade emery paper followed by a brief solvent rinse. The average oxidation test would normally run for several thousand hours, but the effects reported here were noted within a few hours of reaction.

The experiments on solvent evaporation were carried out using 60/80 petroleum ether containing a few grams of a hydrocarbon grease (Apiezon M) in solution, and also industrial methylated spirits (IMS) containing finely divided magnesium oxide in suspension. Single drops of the liquids were placed on glass plates, and allowed to evaporate in the atmosphere at room temperature. The residues were photographed by the Schlieren and shadow techniques respectively.

3. Results

It is normal practice to remove cutting oil and grease from specimens by immersion in organic solvents. In much corrosion testing this is the only cleaning they receive. With coupon type speci-
satisfying the relation \( \tan \theta = h/r \) where \( \theta \) = contact angle, \( h \) = height of droplet, \( r \) = radius. The primary film follows the movement of the bulk liquid and so impurities are deposited during periods when the rate of contraction is lower. This mechanism is shown schematically in Figure 4. The net increase in impurity concentration as the drop contracts depends on the relative rates of evaporation and of solute depletion by deposition.

The accelerated oxidation can be attributed to carbon arising from pyrolysis of hydrocarbon impurity, although the mechanism by which carbon promotes the reaction is not yet understood. The nodules form predominantly in the central area rather than within the rings, indicating that some critical carbon concentration is necessary for initiation. It is suggested that impurity allows this critical level to be reached earlier than would normally occur in a carbon containing oxidant on a clean surface. Oxidation studies on steels with varying concentrations of initial surface carbon deposit would help to clarify this point.

The normal corrosive attack proceeds in two stages, i.e. initially a protective oxidation with typical parabolic kinetics which gives way to a rapid growth with a linear weight gain versus time curve known as “breakaway” oxidation. The nodules start growing while the major part of the surface is still oxidising protectively, and they become the principal areas of surface attack during the linear kinetics stage. The time to reach the inflection region depends on the initiation time, the number, and the rate of growth of nodules. The impurities reduce the initiation time, and increase the number of nodules formed in the early stages by creation of additional sites for attack.
Impurity deposition from evaporated solvent

polished metal surfaces but we were unable to obtain satisfactory photographs. The relationship of the ring radius ($R$) to ring number ($n$) for oxidation specimens and for the IMS/MgO system follows the equation:

$$\frac{R}{R_{\text{max}}} = Kn$$

where $R_{\text{max}}$ is the radius of the outer ring, i.e. the first deposited, and $K$ is a constant (Figure 3). The rings of the hydrocarbon residues were not sufficiently symmetrical to measure radii for inclusion in the figure. Possible ring boundaries are marked for the MgO deposits. The fractional radii for several systems have been used for the linear plot. There is some doubt as to whether all the positions marked are true concentration discontinuities. The slopes in Figure 3 are influenced by the choice of ring boundaries and the number included. For this reason, and also because of the dependence of evaporation and deposition rates on the solvent vapour pressure, type of impurity, and the wetting characteristics of the surfaces, agreement of the $K$ values is not expected. However, the results confirm that rings in both systems can be formed by the same process. The relationship above is not in agreement with the mathematical dependence reported for the periodic precipitation phenomenon known as Liesegang rings.$^2,^3$

![Figure 3. Relationship between ring positions for (a) oxidation specimens, and (b) evaporated IMS containing MgO powder, on glass surfaces.](image)

4. Discussion

A mechanism of ring formation can be deduced by analogy with the spreading characteristics of organic liquids on solid surfaces. When a drop of liquid spreads, a thin film (~1 μm) moves ahead of the bulk liquid boundary. This primary film has a surface tension higher than that of the bulk liquid and it pulls the droplet out in a secondary spreading process.$^4,^5$ With an evaporating liquid the above process is reversed. The evaporation of a low molecular weight organic solvent is fairly rapid at room temperature. The droplet contracts in order to maintain a stable contact angle as solvent evaporates from the secondary liquid layer. In the thin primary film evaporation is also rapid causing solute saturation in this region, and therefore the contaminant is deposited on the surface when the boundary recedes. A hysteresis lag in the contact angle occurs for the advancing or receding boundary of a moving liquid.$^6$ Therefore, contraction is slow while the contact angle is decreasing, but eventually a critical value is reached. At this point a rapid contraction of the boundary occurs as the droplet dimensions transform to give a higher, more stable, contact angle.
bulk metal attack is severe in the linear kinetics region, we have found that the rates are similar regardless of the initial state of surface cleanliness. Therefore continued growth, as well as the initiation on clean surfaces, must depend on other parameters such as gas composition, the type and distribution of inclusions in the alloy, and the carbon uptake activity of the alloy and/or oxide.

5. Conclusions

a. The evaporation of an organic solvent on a metal or glass surface proceeds discontinuously, and trace impurities can be concentrated as the liquid film boundary recedes. Both dissolved and suspended material can be transported across the surface. Deposits of the impurity can remain at specific surface sites.

b. Residual hydrocarbon impurities on rimming steel surfaces, concentrated after solvent cleaning, can give rise to localised sources of carbon that provide centres for nodule growth during subsequent oxidation. The random location of nodules initiated by impurities is explained by the way in which the solvent film breaks up into droplets during evaporation, and is independent of the detailed surface topography.

Acknowledgements

The authors thank Mr B. B. Ackland for photographing the solvent residue patterns. This work is part of a Ph.D. research programme with the University of Edinburgh (A.M.E.), and is published by permission of the Central Electricity Generating Board.

References

3. Fe/CO SAMPLES

3.1 CO Resistivity Samples

Three samples were studied at different times of reaction at 550°C, as indicated in Figure 62. Erosion curves for CDM5 (pre-peak) are given in Figure 63, for CDM6 (peak) in Figures 64 and 65 and for CDM7 (post peak) in Figures 66-69. Comparisons of the data with as-received and as-prepared material are made for carbon ions in Figure 70, oxygen ions in Figure 71 and silicon ions in Figure 72. All ions show a strong narrow peak at the surface falling to a low level or zero in the bulk. The heights of surface peaks of a few important ions are plotted against reaction time in Figure 73, and the corresponding integrated secondary ion intensities in Figure 74.

From an examination of general shape of the erosion curves, the ions can be grouped into 3 categories:

1) those with a sharp surface peak rapidly falling to a low level in the bulk, e.g. FeC-type ions, C$_2^+$, C$_4^+$, O$_2^+$ and M/e 26 (C$_2$H$_2^-$).

2) those with a sharp surface peak plus either a second peak below the surface, or a long tail into the bulk, e.g. FeO$^-$, FeO$_2^-$, SiC$^-$, SiO$_2^-$, SiO$_3^-$, O$^-$ and O$_2^-$.  

3) those with only the broad inner peak, e.g. SiO$^+$, FeO$^+$, O$^+$, FeO$_2^+$ and Fe$_3^+$.  

Both Si$^+$ and Fe$^+$ rise initially sharply to form single broad peaks.  

The following conclusions can be drawn:

1) With the exception of SiO$_3^-$, the total secondary ion emission current, i.e. the integrated intensities, increase to a peak at the resistivity peak and decrease slightly with further reaction.  

2) SiO$_3^-$ has a minimum value at ΔR/Ro max. then increases steadily.
both cases, the highest concentration of impurities was at the surface. After pretreatment the bulk concentration of all elements was reduced to a low level or zero. The effects of pretreatment can be summarised as follows:

1) Reduction of the oxide level (O\(^-\)) by a factor of 10\(^3\).
2) Reduction of the silicon level by a factor of 10.
3) Reduction of free carbon level as indicated by C\(_2^+\) to zero (C\(_2^+\) not detectable on as-prepared).
4) Reduction of carbide level (FeC\(_2^-\) and C\(_2^-\)) by a factor of 10 (N.B. C\(_2^-\) as prepared on lower aspect ratio).
5) Reduction of nitrogen (CN\(^-\), M/e 25 absent) by a factor of 10\(^2\).
6) Reduction of silicate complexes (indicated by SiO\(_3^-\) ions) by a factor of 10.

2. METHANE RESISTIVITY SAMPLES

Two samples were examined, CDK2 and CDK5, both at the peak of the secondary resistivity rise. CDK2 was reacted at 750\(^\circ\)C (carbon uptake 0.94\%) and CDK5 at 614\(^\circ\)C (carbon uptake 0.08\%). Erosion curves are presented in Figures 59 - 61 and the results are summarised in Table 31. A thin deposit of carbon is detected at the surface and is probably the laminar layer formed during cooling. The region immediately below the surface of sample CDK5 is carbon depleted, but the C\(_2^-\) ion current rapidly rises to a constant level in the bulk. M/e 26 is taken as C\(_2\)H\(_2^-\) at the surface where M/e 25 is strong, but is indicative of carbide in the bulk (CN\(^-\)). Carbides are not detected on CDK2, but M/e 26 rises slightly into the bulk metal. Both samples have a thin oxide layer at the surface, which could arise from air-exposure after removal from the reaction vessel, and/or oxidation by impurities during reaction or during cooling.
FIG. 59  ION EROSION CURVES FROM SAMPLE FeCDK2 AT RESISTIVITY PEAK IN CH₄ AT 750°C
FIG. 60 NEGATIVE ION EROSION CURVES FROM SAMPLE FeCDK5 AT RESISTIVITY PEAK IN CH₄ AT 614°C
FIG. 61  POSITIVE ION EROSION CURVES FROM SAMPLE FeCDK5 AT RESISTIVITY PEAK IN CH₄ AT 614°C
# Table 31

**IMMS EROSION DATA FOR IRON/METHANE RESISTIVITY SAMPLES AT 750°C AND 614°C**

<table>
<thead>
<tr>
<th>Ion Species</th>
<th>Main Features of Erosion Curves</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Carbon</strong>&lt;br&gt;C, C₂, C₂H</td>
<td>Narrow peak at surface, C⁺ and C₂H⁻ fall to low uniform level in the bulk. C₂⁺ rises in the bulk.</td>
<td>Carbides not expected to be stable at 750°C.</td>
</tr>
<tr>
<td><strong>2. Carbide</strong>&lt;br&gt;FeC, Fe₂C, FeC₂</td>
<td>Very low or zero</td>
<td>FeO⁺ surface peak broader at 750°C.</td>
</tr>
<tr>
<td><strong>3. Oxygen/oxide</strong>&lt;br&gt;O, FeO, FeO₂</td>
<td>Strong surface peak rapidly falling to zero in bulk.</td>
<td>Surface peak probably C₂H₂⁻. Bulk ions probably CN⁻ and associated with C₂⁻.</td>
</tr>
<tr>
<td><strong>4. M/e 26</strong></td>
<td>Narrow surface peak, rises in the bulk where C₂H⁻ remains constant. Shape in the bulk similar to C₂⁻.</td>
<td></td>
</tr>
<tr>
<td><strong>5. Silicon</strong></td>
<td>Broad surface peak similar to FeO. Si⁺ intensity stronger than as-prepared.</td>
<td>Possibility of silicates on CDK₂. SiO₃⁻ not analysed for.</td>
</tr>
</tbody>
</table>
FIG. 62. RELATION OF CO RESISTIVITY SAMPLES FOR 1MMS ANALYSIS TO RESISTANCE CURVE
ARGON PRIMARY IONS
POSITIVE SECONDARIES (1X2) ASPECT RATE
NEGATIVE SECONDARIES (1X1) ASPECT RATE

FIG. 63 IMMS EROSION CURVES FOR CARBON DEPOSITION
SPECIMEN PRE-PEAK ΔR Fe–C0 CDM5
FIG. 64 IMMS EROSION CURVES FOR ΔR PEAK CARBON DEPOSITION SPECIMEN CDM6 OXYGEN AND SILICON IONS
FIG. 65 IMMS EROSION CURVES FOR ΔR PEAK CARBON DEPOSITION SPECIMEN CDM 6 CARBON CONTAINING SECONDARY IONS
FIG. 66 IMMS EROSION CURVES FOR CARBON DEPOSITION
POST ΔR PEAK SPECIMEN CDM7.
CARBON CONTAINING SECONDARY IONS
FIG. 67 IMMS EROSION CURVES FOR CARBON DEPOSITION POST ARGON PEAK SPECIMEN CDM 7
FIG. 68 IMMS EROSION CURVES FOR SILICON CONTAINING IONS IN CARBON DEPOSITION POST ΔR PEAK SPECIMEN CDM7
Fig. 69 IMMS erosion curves for oxygen containing ions from carbon deposition post Δr peak. Specimen CDM7.
Curve (a) As-received foil, solvent cleaned
Curve (b) As-prepared for reaction: 3 hrs. in H₂ and 16 hrs. in vacuum (10⁻⁸ Torr) at 950°C
Curves (c), (d) and (e): Prepared as in (b) then reacted in CO at 550°C for (c) 50 secs, (d) 8.0 mins, (e) 35.0 mins.

Repeat the process for different carbon uptakes.

FIG. 70 EROSION CURVES FOR CARBON SECONDARY IONS, PURE IRON - AS RECEIVED, AS-PREPARED AND FOR DIFFERENT CARBON UPTAKES.
Curve (a) As-received foil, solvent cleaned.
Curve (b) As-prepared for reaction: 3 hrs. in H₂ + 16 hrs. in vacuum (10⁻⁸ Torr) at 950°C.
Curves (c), (d) and (e) Prepared as in (b) then reacted in CO at 550°C for (c), 55 secs. (d) 8.0 mins, (e) 35.0 mins.

FIG. 71 COMPARISON OF O⁺, O⁻, and Fe⁺ EROSION CURVES AT DIFFERENT LEVELS OF DISSOLVED CARBON FOR Fe–CO DEPOSITION
Curve (a) As-received foil, solvent cleaned.
Curve (b) As-prepared for reaction: 3 hrs. in H₂ and 16 hrs. in vacuum (10⁻⁸ Torr) at 950°C
Curves (c), (d) and (e): Prepared as in (b), then reacted in CO at 550°C for (c) 55 secs. (d) 8.0 mins. and (e) 35.0 mins.

FIG. 72 EROSION CURVES FOR SILICON CONTAINING IONS. PURE IRON - AS-RECEIVED, AS-PREPARED, AND AT DIFFERENT POINTS ON THE R/R₀ CURVE FOR CO DEPOSITION.
FIG. 73 SECONDARY ION SURFACE PEAK HEIGHTS AS A FUNCTION OF REACTION TIME IN CO AT 550°C
FIG. 74  TOTAL EMISSION OF VARIOUS SECONDARY IONS AS A FUNCTION OF REACTION TIME IN CO
3) The peak widths at half height remain approximately constant with reaction time, at 5-10 secs. of erosion for the outer peak, and 80-100 secs. for the inner.

4) The deposit has a layered structure. The outer layer is mainly carbon/carbide and the inner layer oxide. Figure 67, at higher aspect ratio, shows evidence of twin carbide peaks in the outer layer after 35 minutes reaction.

5) The samples are contaminated with silicon. It is present mainly in the inner layer and associated with iron and oxygen, and not with carbon or carbide.

3.2 Autoclave Samples

Two pure iron samples reacted in the silica autoclave system at 515°C and 2.75 bar CO were examined. The sample weight gains were:

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Weight Gain (mg/cm²)</th>
<th>Weight Gain Ratio (Δw/w₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D(2)18(2)</td>
<td>0.04</td>
<td>2.56 x 10⁻⁴</td>
</tr>
<tr>
<td>D(2)22(2)</td>
<td>1.11</td>
<td>2.13 x 10⁻³</td>
</tr>
</tbody>
</table>

Erosion curves are given in Figures 75-78 for D(2)18(2) and Figures 79-82 for D(2)22(2).

Comparison of the assembled curves shows that the layered structure of the deposit has developed further. The composition of the layers, working from the gas/deposit to the deposit/metal interfaces, can be identified as:

1) Carbon
2) Carbide
3) A duplex oxide

in approximate relative proportions of 1:1:30. The average times required to erode through each layer give an indication of thickness. The principle ion currents and erosion times are given in Table 32. The erosion times for positive and negative ions are different because
FIG. 75 POSITIVE ION EROSION CURVES FOR IRON, OXYGEN AND CARBON FROM SAMPLE D(2)18(2)
FIG. 76 POSITIVE ION EROSION CURVES FOR CARBIDE SPECIES FROM SAMPLE D(2)18(2)
FIG. 77 NEGATIVE ION EROSION CURVES FOR CARBON AND CARBIDE FROM SAMPLE D(2)18(2)
FIG. 78  EROSION CURVES FOR NEGATIVE Si AND O ION SPECIES FOR SAMPLE D(2)18(2)
FIG. 79  POSITIVE ION EROSION CURVES FOR CARBON, CARBIDE AND SILICON FROM SAMPLE D(2)22(2) RANGE.
FIG. 80  POSITIVE OXIDE ION EROSION CURVES FROM SAMPLE D(2)22(2)
FIG. 81. NEGATIVE ION EROSION CURVES FOR CARBIDE AND CARBON FROM SAMPLE D(2)22(2)
FIG. 82  NEGATIVE OXIDE ION EROSION CURVES FROM SAMPLE D(2)22(2)
Table 32

PRINCIPAL ION CURRENT INTENSITIES FOR Fe/CO AUTOCLAVE SAMPLES

<table>
<thead>
<tr>
<th>Ion</th>
<th>Carbon Layer Ion Current ×10⁻¹⁵A</th>
<th>Carbide Layer</th>
<th>Outer Oxide</th>
<th>Inner Oxide</th>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+ve</td>
<td>-ve</td>
<td>+ve</td>
<td>-ve</td>
<td>+ve</td>
</tr>
<tr>
<td><strong>D(2)22(2)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Layer Thickness (secs)</td>
<td>0-10</td>
<td>10-25</td>
<td>25-200</td>
<td>200-350</td>
<td>350+</td>
</tr>
<tr>
<td>C</td>
<td>30R</td>
<td>R</td>
<td>80P</td>
<td>&gt;10³P</td>
<td>2C</td>
</tr>
<tr>
<td>C₂</td>
<td>10R</td>
<td>10³P</td>
<td>20P</td>
<td>500P</td>
<td>2C</td>
</tr>
<tr>
<td>O</td>
<td>R</td>
<td>10³P</td>
<td>R</td>
<td>100C</td>
<td>70C</td>
</tr>
<tr>
<td>O₂</td>
<td>&lt;10</td>
<td>10³P</td>
<td>R</td>
<td>R</td>
<td>30C</td>
</tr>
<tr>
<td>FeC</td>
<td>&lt;1</td>
<td>N/A</td>
<td>50P</td>
<td>2C</td>
<td>2R</td>
</tr>
<tr>
<td>FeC₂</td>
<td>1P</td>
<td>1P</td>
<td>&lt;1</td>
<td>15P</td>
<td>&lt;1</td>
</tr>
<tr>
<td>FeO</td>
<td>20P</td>
<td>2×10³P</td>
<td>&lt;1</td>
<td>10³R</td>
<td>300C</td>
</tr>
<tr>
<td>FeO₂</td>
<td>2P</td>
<td>100P</td>
<td>R</td>
<td>&lt;1</td>
<td>20P</td>
</tr>
<tr>
<td>Si</td>
<td>9P</td>
<td>N/A</td>
<td>16P</td>
<td>1C</td>
<td>10P</td>
</tr>
<tr>
<td>CN/C₂H₂</td>
<td>-</td>
<td>800P</td>
<td>-</td>
<td>&gt;10³P</td>
<td>200C</td>
</tr>
<tr>
<td>C₂H</td>
<td>-</td>
<td>10³P</td>
<td>-</td>
<td>300P</td>
<td>-</td>
</tr>
<tr>
<td>CNO</td>
<td>-</td>
<td>1P</td>
<td>-</td>
<td>&lt;1</td>
<td>-</td>
</tr>
</tbody>
</table>

Key to symbols:  R = Rising  P = Peaking  F = Falling  
N/A = not available  C = Constant
Table 32 (continued)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Carbon Layer Ion Current x10^{-15}A</th>
<th>Carbide Layer</th>
<th>Outer Oxide</th>
<th>Inner Oxide</th>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+ve</td>
<td>-ve</td>
<td>+ve</td>
<td>-ve</td>
<td>+ve</td>
</tr>
<tr>
<td>D(2)18(2) Layer</td>
<td>Thickness (secs)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0-5</td>
<td>5-10</td>
<td>10-70</td>
<td>70-140</td>
<td>140+</td>
</tr>
<tr>
<td>C</td>
<td>100P</td>
<td>F</td>
<td>400P</td>
<td>1C</td>
<td>2P</td>
</tr>
<tr>
<td>C2</td>
<td>40P</td>
<td>700P</td>
<td>10P</td>
<td>200P</td>
<td>3C</td>
</tr>
<tr>
<td>O</td>
<td>R</td>
<td>100P</td>
<td>60R</td>
<td>5R</td>
<td>70R</td>
</tr>
<tr>
<td>O2</td>
<td>&lt;1</td>
<td>N/A</td>
<td>20R</td>
<td>30R</td>
<td>40C</td>
</tr>
<tr>
<td>FeC</td>
<td>90P</td>
<td>1P</td>
<td>F</td>
<td>3P</td>
<td>2C</td>
</tr>
<tr>
<td>FeO</td>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeO2</td>
<td>N/A</td>
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<td></td>
</tr>
<tr>
<td>Si</td>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN/C2H2</td>
<td>-</td>
<td>10P</td>
<td>-</td>
<td>90P</td>
<td>-</td>
</tr>
<tr>
<td>C2H</td>
<td>-</td>
<td>4x10^3P</td>
<td>-</td>
<td>20P</td>
<td>-</td>
</tr>
<tr>
<td>CNO</td>
<td>-</td>
<td>1P</td>
<td>-</td>
<td>&lt;1</td>
<td>-</td>
</tr>
</tbody>
</table>

Key to symbols:  
R = Rising  
P = Peaking  
F = Falling  
N/A = not available  
C = Constant
of the different aspect ratios and primary ion currents. Those quoted are for positive ion erosions. The thickness of each layer in sample D(2)22(2) are a factor of 2 to 3 times greater than those of sample D(2)18(2).

The chemical structure of the carbide layer cannot be determined, but the existence of Fe-C bonds is confirmed by the presence of the complex secondary ions Fe$_2$C$_2^+$, Fe$_3$C$^+$, Fe$_3$C$_2^+$ and FeC$_3^+$ (Figure 76). The oxide can be divided into two layers of approximately equal thickness and slightly different composition. The outer layer is depleted of carbon, carbide and silicon (Figures 75, 76, 78 and 79), but CNO$^-$ ions peak strongly (Figure 78). FeO$_2^-$ ions are not detected in the inner layer and the O$^-$ ion intensity is lower (Figure 82). The carbon and carbide ions rise steadily to a constant level in the metal (Figure 81). CN$^-$ and CNO$^-$ peak again close to the metal oxide interface (Figure 81). All ions fall to zero in the metal apart from C, C$_2^-$, FeC, FeC$_2^-$, M/e 26 and C$_2$H$_2^-$, indicating both carbon and carbide in the bulk. The main deposition reactions, however, occur at the metal/gas and oxide/metal interfaces. The structures of the deposits on the two samples are summarised in schematic form in Figure 83. The layer thicknesses are not to scale.

The samples are again contaminated with silicon (Figures 78 and 79), which is present at the sample surface and in the inner oxide layer. Extended erosion of sample D(2)18(2) showed that silicon was also present below the metal surface (Figure 84). Observation of the sample in the imaging facility showed the element to be concentrated at grain boundaries.
FIG. 8.4 EVIDENCE FOR THE PRESENCE OF SILICON AT THE OUTER SURFACE, THE METAL INTERFACE AND ISOLATED GRAIN BOUNDARIES WITHIN THE METAL OF SAMPLE D(2)18(2).
4. DISCUSSION OF RESULTS ON IRON

4.1 The Structures of Deposits Formed From CH₄ and CO

The results presented in Chapter IV appeared to indicate the precipitation of a carbide at the resistivity peak of iron samples reacted in CH₄. Carbides will not necessarily be detected after slow cooling to room temperature because of their inherent instability. However, carbide ions were detected on CDK2, reacted at 614°C, and, although no FeC type ions were detected on CDK5, reacted at 750°C, M/e26 did tend to rise below the metal surface, where M/e 25 was absent. The deposit from CO, however, yielded strong secondary ion carbide lines after only 55 seconds reaction at 550°C and 50 Torr pressure. There was evidence for the development of a multilayered reaction zone at the surface of samples soon after the end of the solution stage of reaction, which thickened as reaction proceeded.

A major component of the reaction zone at this early stage of reaction is iron oxide. The results suggest that it has a two-layer structure, possibly with differences in stoichiometry between the two layers. The outer layer, furthest from the metal, contains low levels of carbon/carbide and overlaps a carbide layer at its outermost extent. The inner layer emits carbon/carbide ions in increasing intensity as the metal surface is approached during erosion. A thin carbon layer is detected overlying the outer carbide layer, and it is clear that deposition occurs predominantly at the gas/deposit and deposit/metal interfaces. For deposition to occur at the metal surface, the oxide must be sufficiently porous to allow CO to diffuse through it. Deposition at the gas interface probably occurs after reduction of the oxide. Carbon ion intensities from both CO and CH₄ deposited samples rise to a constant level in the bulk metal.
4.2 Silicon Contamination of Samples

Silicon is detected on samples as Si and SiO\textsubscript{x} ions, generally associated with FeO ions, indicating the presence of silicates. In resistivity experiments, the silicon level is reduced by pre-treatment and remains virtually unchanged after reaction in CH\textsubscript{4}. However, it increases strongly after 55 seconds reaction in CO at 550°C and 50 Torr pressure, and continues to rise to the resistance maximum. After the maximum Si and SiO ion intensities decrease slightly, but SiO\textsubscript{3} increases again. Contamination of autoclave samples reacted for two hours in CO at 515°C at 2.75 bar also occurs, but the silicon ion intensities are two orders of magnitude lower. In all cases, the silicon species are located at the gas/deposit interface and close to the deposit interface. No silicon was detected in the bulk of resistivity samples, but low concentrations of the element were detected at grain boundaries below the deposit of autoclave samples. Since the latter had not been pre-reduced in H\textsubscript{2}, it is possible that the bulk silicon was introduced prior to reaction, during manufacture.

There is some evidence of silicon transport in the literature. Thus, for instance, reduction of SiO\textsubscript{2} and volatilisation of SiO occurs in blast furnaces at temperatures in excess of 1200°C (167). Other instances are reported at temperatures in excess of 1000°C in steam (168) and in various organic compounds (169), and at low temperatures (700–900°C) in low vapour pressures of water (170). In the experiments reported in this Chapter, transport is clearly associated with the presence of CO, although, in resistivity experiments, it may have been assisted by pre-conditioning of glass surfaces by H\textsubscript{2}. The transporting species may be a form of silicon carbonyl, although no reference to such a compound has been found. Decomposition on the metal surface is foll-
owed by diffusion into the deposit of either an Fe-Si-O compound, or
an Fe-Si compound which oxidises on exposure to the air.

5. **DEPOSITS FROM CO ON A 20/25 Nb STEEL**

Samples of steel were supplied by UKAEA Springfields in the
form of tubes machined on the outer face into a ribbed structure.
Specimens were manufactured by cutting the tube into quadrants 20 mm
long by about 10 mm width. The specimens were solvent-cleaned and
reacted in CO at 515°C and 2.75 bar in the silica autoclave system.
Two samples were examined, with total weight gains of 0.03 mg cm⁻² and
0.3 mg cm⁻² after 96 h and 214 h reaction respectively. Visual obser-
vation indicated that both samples had picked up appreciably more carbon
on the smooth inner face, than on the outer ribbed face. The deposit
was patchy on both samples and surface oxide, blue on the 0.03 mg cm⁻²
sample and straw-coloured on the 0.3 mg cm⁻² sample, was visible between
deposited areas. IMMS was used to investigate compositional differ-
ences between smooth and ribbed faces of the alloy, and to study the
surface structures after reaction.

5.1 **Surface Composition of "As-Received" Alloy**

The complexity of spectra obtained from the metal is illus-
trated by the positive secondary ion spectra from the outer ribbed and
the smooth inner surfaces of the alloy, shown in Fig. 85. Ions from
all the principle alloy constituents were detected. Surface contami-
nation was evident as Na⁺, K⁺, Cl⁺, Al⁺ and Ca⁺. A comparison of
several groups of ions is made in Tables 33–37; intensity ratios
are given to avoid corrections for absolute sensitivity. At higher
mass numbers, the possible alternative interpretations for an individual
ion increased, and in some cases an unequivocal identification of an ion
could not be achieved because of overlap of parent ions with isotopic
peaks from other ions.
FIG. 85  POSITIVE SECONDARY ION SPECTRA OF UNREACTED A.G.R. FUEL CAN ALLOY. THE SPECTRUM OF THE RIBBED SURFACE IS TAKEN FROM AN AREA BETWEEN THE RIBS
Table 33

Comparison of Secondary Ion Intensities for the Ribbed and the Inner Smooth Face of "As-received" Can Alloy
Monatomic and Polyatomic Metal Ions

<table>
<thead>
<tr>
<th>Ion</th>
<th>M/e</th>
<th>Intensity Ratio</th>
<th>Other Contributing Ions</th>
<th>Possible Alternative Ions</th>
<th>Spark Source Mass Spectral Data Ratio Rib/Smooth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr+</td>
<td>52</td>
<td>1.09</td>
<td></td>
<td></td>
<td>0.60</td>
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<tr>
<td>Mn+</td>
<td>55</td>
<td>1.96</td>
<td></td>
<td></td>
<td>1.10</td>
</tr>
<tr>
<td>Fe+</td>
<td>56</td>
<td>1.36</td>
<td>Si₂</td>
<td></td>
<td>2.40</td>
</tr>
<tr>
<td>Ni+</td>
<td>58</td>
<td>1.27</td>
<td>Fe⁵⁺</td>
<td></td>
<td>1.82</td>
</tr>
<tr>
<td>Nb+</td>
<td>93</td>
<td>1.47</td>
<td></td>
<td></td>
<td>0.74</td>
</tr>
<tr>
<td>Cr₂+</td>
<td>104</td>
<td>1.86</td>
<td>Fe⁵⁺, Cr⁵⁺Ni⁶⁺Ni⁶⁺O₃</td>
<td>Cr⁵⁺Ni⁶⁺</td>
<td></td>
</tr>
<tr>
<td>Mn₂+</td>
<td>110</td>
<td>1.72</td>
<td>Fe⁵⁺, Cr⁵⁺Ni⁶⁺Ni⁶⁺O₃</td>
<td>Cr⁵⁺Ni⁶⁺</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>112</td>
<td>2.16</td>
<td>Cr⁵⁺Ni⁶⁺</td>
<td>Cr⁵⁺Ni⁶⁺</td>
<td></td>
</tr>
<tr>
<td>Ni₂+</td>
<td>116</td>
<td>3.07</td>
<td>Fe⁵⁺Ni⁶⁺</td>
<td>Cr⁵⁺Ni⁶⁺</td>
<td></td>
</tr>
<tr>
<td>Nb₂+</td>
<td>186</td>
<td>1.13</td>
<td>Cr⁵⁺Ni⁶⁺</td>
<td>Cr⁵⁺Ni⁶⁺</td>
<td></td>
</tr>
<tr>
<td>Cr₃+</td>
<td>156</td>
<td>2.95</td>
<td>CrFeO₃CrFeC₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₃+</td>
<td>168</td>
<td>2.80</td>
<td>Cr⁵⁺Ni⁺Cr₅⁺Cr₂O₄⁺</td>
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<td></td>
</tr>
<tr>
<td>Ni₃+</td>
<td>174</td>
<td>1.80</td>
<td>Fe₃⁺</td>
<td>Cr₂⁵⁺Cr₅⁺O⁺Cr₂Ni⁺Cr₂Ni⁺</td>
<td></td>
</tr>
</tbody>
</table>

*Most abundant isotope is assumed unless indicated.*
## Table 34

**Intensity Ratios of Oxide Ions for "As-received" Can Alloy**

<table>
<thead>
<tr>
<th>Ion</th>
<th>M/e</th>
<th>Intensity Ratio</th>
<th>Other Contributing Ions</th>
<th>Possible Alternative Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO⁺</td>
<td>72</td>
<td>3.45 x 10⁻¹</td>
<td>Ni₂⁺</td>
<td>Cr₂C₂⁺</td>
</tr>
<tr>
<td>Fe₂O⁺</td>
<td>128</td>
<td>1.92</td>
<td>Ni₆₄⁺</td>
<td>Cr₂C₂⁺</td>
</tr>
<tr>
<td>Fe₂O₂⁺</td>
<td>144</td>
<td>1.06</td>
<td>Ti³⁺, CrFeC₃⁺</td>
<td></td>
</tr>
<tr>
<td>CrO⁺</td>
<td>68</td>
<td>1.74 x 10⁻¹</td>
<td>FeC⁺</td>
<td></td>
</tr>
<tr>
<td>Cr₂O⁺</td>
<td>84</td>
<td>6.67 x 10⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr₃O⁺</td>
<td>100</td>
<td>3.33 x 10⁻¹</td>
<td>Cr₂⁵₀⁺</td>
<td>CrFeC⁺</td>
</tr>
<tr>
<td>Cr₂O₂⁺</td>
<td>120</td>
<td>1.29</td>
<td>Ni₆₀⁺</td>
<td>Fe₂C₂⁺</td>
</tr>
<tr>
<td>Cr₃O₂⁺</td>
<td>136</td>
<td>1.96</td>
<td>Ni₆₀⁺, Cr₂⁵₀⁺</td>
<td>FeNi₂⁺, Cr₂Fe⁺, CrFeO₄⁺</td>
</tr>
<tr>
<td>Cr₃O₂⁺</td>
<td>172</td>
<td>2.23</td>
<td>FeNi₂⁺, Cr₂Fe⁺, CrFeO₄⁺</td>
<td></td>
</tr>
<tr>
<td>Cr₃O₂⁺</td>
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<td>1.22</td>
<td></td>
<td>FeNi₂⁺</td>
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<tr>
<td>MnO₃⁺</td>
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<td>9.7 x 10⁻¹</td>
<td>Cr⁵₀⁺, Cr₅₃⁺</td>
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</tr>
<tr>
<td>NiO₃⁺</td>
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<td>1.35</td>
<td>Cr₅₃⁺</td>
<td>CrFeC₂⁺</td>
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<td>NbO⁺</td>
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<td>6.38 x 10⁻¹</td>
<td>Ni₆₁O₃⁺, Cr₅₂Fe₅₇⁺</td>
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<td>NbO₂⁺</td>
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<td>3.2 x 10⁻¹</td>
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<td></td>
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<tr>
<td>Ion</td>
<td>M/e</td>
<td>Intensity Ratio</td>
<td>Other Ions Contributing to Peak</td>
<td>Possible Alternative Ions</td>
</tr>
<tr>
<td>--------------</td>
<td>-----</td>
<td>-----------------</td>
<td>--------------------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>CrFeO⁺</td>
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<td>2.55</td>
<td>Ni⁺⁺⁺, Cr₂O⁺, Fe₂O⁺</td>
<td>Fe₂C⁺</td>
</tr>
<tr>
<td>CrFeO₃⁺</td>
<td>156</td>
<td>2.95</td>
<td>Cr⁺</td>
<td>CrFe₂C⁺, Fe₂O₄⁺</td>
</tr>
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<td>Cr₂FeO⁺</td>
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<td>2.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrFe₂O⁺</td>
<td>180</td>
<td>9.0 x 10⁻¹</td>
<td>Ni₆⁺</td>
<td>Fe₃C⁺, Cr₃C₂⁺, CrNi₂C⁺</td>
</tr>
<tr>
<td>FeNiO₃⁺</td>
<td>162</td>
<td>2.23</td>
<td>Cr⁺⁺⁺, Fe⁺⁺⁺</td>
<td>Cr₂Ni⁺, CrMn₂⁺</td>
</tr>
<tr>
<td>Fe₂NiO⁺</td>
<td>186</td>
<td>1.13</td>
<td>Ni⁺</td>
<td>Cr⁵⁺⁰Cr₂⁵²O₂⁺, Ni₃C⁺, Cr₂NiC₂⁺</td>
</tr>
<tr>
<td>FeNi₂O⁺</td>
<td>188</td>
<td>1.22</td>
<td></td>
<td>Cr₃O₂⁺</td>
</tr>
<tr>
<td>Cr₂NiO</td>
<td>178</td>
<td>1.22</td>
<td></td>
<td>Fe⁵⁺⁴Fe₂⁵⁶C⁺</td>
</tr>
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</table>
### Table 36

Intensity Ratios of Mixed Bimetallic Ions for "As-received" Can Alloy

<table>
<thead>
<tr>
<th>Ion</th>
<th>M/e</th>
<th>Intensity Ratio</th>
<th>Other Contributing Ions</th>
<th>Possible Alternative Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ribbed Face</td>
<td>Smooth Face</td>
<td></td>
</tr>
<tr>
<td>CrMn⁺</td>
<td>107</td>
<td>1.39</td>
<td>Cr⁺ Cr⁵⁴⁺</td>
<td>CrSi₂⁺</td>
</tr>
<tr>
<td>CrFe⁺</td>
<td>108</td>
<td>1.89</td>
<td>Fe⁵⁴⁺, Ni⁶⁰⁺, Cr⁵⁴⁺</td>
<td></td>
</tr>
<tr>
<td>CrNi⁺</td>
<td>110</td>
<td>1.72</td>
<td>Fe⁺, Fe⁵⁴⁺, Fe⁵⁶⁺, Cr₂⁺</td>
<td></td>
</tr>
<tr>
<td>FeMn⁺</td>
<td>111</td>
<td>2.15</td>
<td>Mn₂⁺, Fe⁵⁴⁺, Fe⁵⁶⁺</td>
<td></td>
</tr>
<tr>
<td>MnNi⁺</td>
<td>113</td>
<td>1.80</td>
<td>Fe⁵⁶⁺, Fe⁵⁷⁺</td>
<td></td>
</tr>
<tr>
<td>FeNi⁺</td>
<td>114</td>
<td>2.23</td>
<td>Fe⁺ Fe₂⁺, Cr⁵⁰⁺ Cr⁵²⁺</td>
<td></td>
</tr>
<tr>
<td>FeNb⁺</td>
<td>149</td>
<td>2.22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 37

Cr/Fe and Fe/Ni Ratios for a Metal Region Below the Carbon Deposit. Comparison with Values for the Bulk Alloy

<table>
<thead>
<tr>
<th>Ion</th>
<th>Smooth Face</th>
<th>Ribbed Face</th>
<th>Smooth Face</th>
<th>Ribbed Face</th>
<th>Cr/Fe</th>
<th>Fe/Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M^+ )</td>
<td>1.79</td>
<td>1.24</td>
<td>0.38</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( M_{2}^+ )</td>
<td>0.12</td>
<td>0.13</td>
<td>0.13</td>
<td>0.16</td>
<td>0.36</td>
<td>2.20</td>
</tr>
</tbody>
</table>

(A.D.R. Can Alloy | Bulk Alloy)

(Deposit = 0.03 mg cm\(^{-2}\))
5.1.1 Emission Depth of Secondary Ions

As the spectrum was being recorded the ion beam was eroding the surface layer away and so peaks at high mass number were taken from a region closer to the metal interface than those at low mass number. The intensities of Cr\(^+\) and CrO\(^-\) ions recorded continuously during erosion are shown in Fig. 86. The interface was reached by the ion beam after approximately 60 seconds. The spectra of Fig. 85 were recorded over a period of 38 seconds (M/e = 10 to M/e = 200) and therefore secondary ions throughout the scan came from the oxide layer.

Spark source mass spectrometry was used to compare the ribbed and smooth surfaces (Table 33). It gave an elemental analysis of material in the bulk metal close to the oxide/metal interface, and therefore results were not directly comparable to IMMS data from the oxide surface. It was used to identify possible segregation effects.

5.1.2 Metal Ions

Ions of the type M\(_x^+\) (x = 1 to 3) given in Table 33 showed a higher intensity for the ribbed face than the smooth face. The ratios for M\(^+\) ions suggest that Mn, Fe, Ni and Nb were present in greater quantities on the ribbed than on the smooth surface. Spark source mass spectrometry data indicates that at a greater depth there was a corresponding enhancement of Ni, Fe and Mn, and a depletion of Cr and Nb on the ribbed face relative to the smooth face (Table 33).

Many of the possible bimetallic ions were observed (Table 36); they could have arisen as fragmentation products of mixed oxides. Every combination of the M\(_2M'\) type ion is possible but they are not tabulated because of the difficulty of uniquely identifying a high mass number ion from among the many possible intermetallic and polyatomic oxide ions. An iron niobide phase is a constituent of this alloy,
FIG. 86 VARIATION OF THE SECONDARY ION CURRENT DURING EROSION THROUGH THE PROTECTIVE OXIDE FILM ON THE UNREACTED CAN ALLOY
the Fe$_2$Nb particles being located at intragranular sites (172). FeNb$^+$ was detected but not Fe$_2$Nb$^+$ (M/e = 205). A chromium niobide ion Cr$_2$Nb$^+$ was observed.

5.1.3 Oxide Ions

The protective film on stainless steels is known to be a chromium-based oxide (143), so a substantial contribution from these ions was expected. The data of Table 34 shows that, in addition to the chrome oxide ions, there were oxide ion contributions from the other principal constituents. The air-formed film, therefore, appeared to be a mixture of oxides. The presence of manganese oxides could not be confirmed. The MnO$_3^+$ ion was likely but MnO$^+$ and MnO$_2^+$ were absent, and the Mn$_2$O$_x^+$ series of ions coincided with a possible mixed oxide series CrNiO$_x^+$. Only a limited number of nickel and niobium oxide ions were detected. Several iron oxide ions could have been present but only FeO$^+$ was at all certain, although Fe$_2^+$ and Fe$_2$O$_2^+$ were probable. The chromium and iron oxide ion intensity ratios each fell into two groups, indicating that more than one type of oxide compound was contributing to each of the secondary ion patterns and that they were present in different proportions on each face of the alloy. The mixed oxides of iron and chromium also had some variation in the intensity ratios between ribbed and smooth faces (Table 35). Many possible mixed oxide ions are missing from Table 35 because of the difficulty of confirming their presence due to the overlap with other alternatives, e.g. the CrNiO$_x^+$ series.

5.1.4 Carbide Ions

Secondary ions were expected from the M$_{23}$C$_6$ and M$_6$C constituents of the steel. The parent ions, if formed, would not have been observed because they lay outside the mass range of the instrument.
Ions such as $\text{MC}^+$, $\text{M}_2\text{C}^+$, $\text{M}_3\text{C}^+$ and $\text{M}_2\text{C}_2^+$ could have been present ($\text{M} = \text{Cr, Fe}$). The ions $\text{MC}_2^+$, $\text{MC}_3^+$ and $\text{M}_2\text{C}_3^+$ were absent. Some carbide ions are listed as alternatives in Tables 33-36. Mixed carbide ions could have been sputtered from the surface or formed in the ion beam, but it was not possible to confirm their presence because of low intensity and overlap with other peaks. The carbide and carbonitride of niobium are significant constituents of the alloy. $\text{NbC}^+$ and $\text{NbCN}^+$ ions were detected; the higher polyatomic ions were not obtained. Nickel carbide ions were not detected.

5.2 Surface Composition after Reaction in CO

5.2.1 Comparison of Deposits on the Ribbed and Smooth Surfaces

Sections of secondary ion spectra obtained from reacted samples are reproduced in Figures 87 and 88. Major differences between the two surfaces of the sample with the light deposit were seen in the $\text{M}^+$ group of ions (Fig. 87). They could be formed from all metal compounds present, e.g. oxides, carbides, etc. The ribbed side compared with the smooth side had

- $\sim 1.9 \times$ the intensity of chromium,
- $\sim 0.17 \times$ the intensity of iron,
- $\sim 2.8 \times$ the intensity of manganese.

Chromium metal is less active to deposition than iron, therefore the results suggest that the ribbed surface is protected by chromium oxide and the smooth face had increased reactivity owing to an enhanced level of iron. At the beginning of the reaction the air-formed film had approximately equal levels of $\text{Cr}^+$, $\text{Fe}^+$ and $\text{Ni}^+$ on the two surfaces (Fig. 87). The relative intensities based on the $\text{M}_2^+$ group of ions, which presumably arose from a more limited range of fragmentations in the primary ion beam, were not in good agreement with the differences shown by the $\text{M}^+$ ions. For example, the excess of $\text{Cr}^+$ on the ribbed
FIG. 67 DISTRIBUTION OF METAL IONS (M⁺, M₂⁺ AND M₃⁺) FROM THE CARBON DEPOSITED SURFACES AND THE UNREACTED ALLOY. WEIGHT OF DEPOSIT = 0.03 mg cm⁻²

--- INSIDE SURFACE

--- RIBBED SURFACE
FIG. 88 DISTRIBUTION OF CHROMIUM OXIDE IONS FROM THE CARBON DEPOSITED SURFACE AND THE UNREACTED ALLOY. WEIGHT OF DEPOSIT = 0.03 mg cm$^2$
face was not paralleled by an equivalent excess in the \( \text{Cr}_2^+ \) intensity. Similarly, the \( M^+/M_{2}^+ \) ratios for several metals were quite different for "deposited" and "as-received" surfaces. The discrepancies suggested that both the proportions and composition of the metal compounds had changed under the action of carbon monoxide.

Chromium oxide ion intensities are compared in Fig. 88. The \( \text{CrO}_n^- \) group with \( O^+ \) and \( O_2^+ \) were in excess on the ribbed face, whilst the positive groups of ions with \( O^- \) and \( O_2^- \) were in excess on the smooth face. Without a knowledge of the fragmentation reactions of different oxides and the relative sensitivities, it was not possible to decide which surface had the higher oxide concentration. Differences in composition could also have explained these observations and, taken with the results for the \( M^+ \) ions, it is feasible that the smooth surface contained more of a mixed Fe-Cr oxide. The distribution of oxide ions in the deposit had changed compared with the air-formed oxide. The principal contributors had become \( \text{CrO}^+ \) and \( \text{Cr}_2\text{O}^+ \), whereas initially the predominant ions had been \( \text{Cr}_2\text{O}^+ \) and \( \text{Cr}_3\text{O}^+ \).

From spectra obtained from bulk metal immediately below the deposit, \( \text{Cr}/\text{Fe} \) and \( \text{Fe}/\text{Ni} \) concentration ratios were calculated for \( M^+ \) and \( M_{2}^+ \) ions for comparison with known values for the alloy. Sensitivity adjustment factors, determined on the Harwell Cameca instrument, were used of 70 : 14 : 1 for the ratios \( \text{Cr} : \text{Fe} : \text{Ni} \) (173). The results are given in Table 37. They are not in good agreement and may indicate segregation effects, e.g. Cr depletion, Fe and Ni enrichment, in the metal. Agreement between \( M^+ \) and \( M_{2}^+ \) ions is not expected, since the latter arise from a more limited number of surface interactions.

### 5.2.2 Metal Ion Depth Profiles

These curves permitted an estimate of the deposit/metal inter-
face position to be made in terms of the erosion time (Fig. 89). The nickel and iron intensities rose sharply after about 25 seconds erosion and reached a maximum after about 40 seconds. It was assumed that the interface region lay between these limits. The Cr\(^+\) ion showed an enhancement in the outermost region (0 to 2 seconds), followed by a steady rise through the deposit and oxide to the interfacial region. The variations were similar but less marked with the Cr\(_2\)^+ ion.

5.2.3 Oxide Layers

The chromium oxide ion erosion curves can be interpreted in terms of two or possibly three compositions at different depths (Fig. 90 and 91). The ions CrO\(^+\), Cr\(_2\)O\(^+\) and CrO\(_3\)^− (Fig. 90) showed the enhanced intensity in the first 2 seconds of erosion similar to that observed with Cr\(^+\). During this early stage, the ions O\(^−\), CrO\(^−\) and CrO\(_2\)^− had a reduced intensity (Fig 91). The inner chromium oxide layer was characterised by a small intensity rise for both sets of ions, with a maximum in the region previously proposed as the deposit/metal interface. The FeO\(^−\) ion showed an enhancement in the outer layer, suggesting a possible mixed Fe-Cr oxide parent compound, although its intensity was down by a factor of √10 (concentration down by √2 using the sensitivity factors of ref. 173) compared with most of the chromium ions. It had another maximum in the interface region which could have indicated an enrichment as iron particles were transferred to the deposit, and then air-oxidised during handling for the IMMS work.

The same relationship between the oxide ions with respect to erosion existed with the thickly deposited specimen (Fig. 92), with the exception of the CrO\(_2\)^− curve. The discrepancy may have been due to non-equivalent areas being sampled.
**FIG. 89 ION INTENSITY - DEPTH PROFILE THROUGH THE DEPOSIT ON THE SMOOTH SURFACE, FOR METAL IONS. WEIGHT OF DEPOSIT = 0.03 mg cm$^{-2}$**
FIG. 90  ION INTENSITY - DEPTH PROFILE THROUGH THE DEPOSIT ON
THE SMOOTH SURFACE FOR VARIOUS OXIDE IONS.
WEIGHT OF DEPOSITS = 0.03 mg cm$^{-2}$

AME/ GH( CON) (4. 12. 75) RL. 4. 1. 2972
FIG. 91  ION INTENSITY - DEPTH PROFILE THROUGH THE DEPOSIT ON THE SMOOTH SURFACE FOR VARIOUS OXIDE IONS.
WEIGHT OF DEPOSIT = 0.03 mg cm$^{-2}$
FIG. 92  ION INTENSITY - DEPTH PROFILE THROUGH A HEAVIER DEPOSIT
FOR OXIDE IONS AND M/e = 26 (CN^−/C_2H_2^−). WEIGHT OF
DEPOSIT = 0.3 mg cm^−2
The air-formed film appeared to have the same oxide thickness (Fig. 86) as the light deposit specimen (Fig. 90, 91). The presence of a thin outer oxide layer different from the bulk oxide was indicated by the enhanced Cr⁺ and reduced CrO⁻ intensities.

5.2.4 Carbon-containing ions

Variations of the carbon ion intensities (Fig. 93), indicated an enhancement of C₂⁻ and CN⁻ in the thin outer oxide layer. The ion C⁺ showed no significant change throughout this and the main underlying oxide. Both C₂⁻ and CN⁻ had a falling intensity through the main oxide layer, and then, along with the C⁺ ion, the intensity rose in the metal interface region at erosion times of ~25 seconds. The rise in CN⁻ was particularly marked in this region and it became the dominant carbon-containing ion. The lowered intensity of CN⁻ in the main oxide layer was confirmed in the erosion curves of the thicker deposit and the "as-received" alloy (Fig. 86). The CN⁻ intensity increased after the primary beam penetrated into the bulk metal of the "as-received" alloy, whilst both deposited specimens indicated an enhancement in the interface region. The specimen removed immediately after the induction period (0.03 mg cm⁻²) had a CN⁻ intensity ~10× higher than either the "as-received" material or the heavily deposited specimens.

5.2.5 Impurity Ions

The erosion technique was used to establish the location of Na⁺ and SiO₂⁻ ions, to investigate whether they arise together as impurities. The majority of the Na⁺ ions came from the oxide-carbon region (Fig. 94). Silica reached a maximum in the deposit/metal interface region and may have arisen from silicon in the steel that had segregated to the alloy surface.
FIG. 93  ION INTENSITY - DEPTH PROFILE THROUGH THE DEPOSIT ON THE SMOOTH SURFACE, FOR CARBON CONTAINING IONS.
WEIGHT OF DEPOSIT = 0.03 mg cm$^{-2}$
FIG. 94 ION INTENSITY - DEPTH PROFILE THROUGH THE DEPOSIT ON THE SMOOTH SURFACE, FOR Na⁺ AND SiO₂ IONS. WEIGHT OF DEPOSIT = 0.03 mg cm⁻²
6. DISCUSSION

6.1 The Effect of Carbon Monoxide on the Air-formed Film

The air-formed film was a complex mixture of oxides with the chromium oxide ions predominating in the secondary ion pattern. During the initial reaction period, CO caused a colour change (transparent to blue) but no significant change of thickness was detectable. A further 120 hours of reaction, required to produce the 0.3 mg cm\(^{-2}\) deposit, caused a change to a straw-coloured film and a corresponding thickness increase (Fig. 92). The initial effect of CO was to cause a compositional change (Section 5.2.1), observed as a marked intensity change of the predominant oxide ions. In particular, the CrO\(^+\) intensity increased by \(\approx 100\times\) compared with the unreacted alloy, the Cr\(_2\)O\(^+\) by \(\approx 5\times\) and the Cr\(_3\)O\(^+\) ion decreased by \(\approx 10\times\). We have observed a similar effect on pure chromium which had received the same treatment.

There are many possible dissociation reactions that could account for the secondary ions observed, and therefore without calibrations on well-characterized oxides any proposed mechanism must remain speculative.

A simple scheme is given briefly, that can explain the formation of the most intense ions and account for the deposition activity. Ions from catalytic material such as Fe and Ni were readily detected in the "as-received" oxide film, which must therefore have been a mixture of oxides or a mixed oxide. A mixed spinel such as FeCr\(_2\)O\(_4\) has been reported among the oxides present on chromium steels (174). The stable, protective chromium oxide film is known to be Cr\(_2\)O\(_3\) (143). The IMMS results suggest that the air-formed film was a mixture of these oxides.
The simple fragmentation reactions below assume a single stage dissociation process in the ion beam and the maintenance of electrical neutrality. Only the most abundant secondary ions were considered as possible products. For the iron-chromium spinel

\[ \text{FeCr}_2\text{O}_4 \rightarrow 2\text{Cr}^+ + \text{Fe}^+ + \text{O}_2^- + 20^- \] (65)

\[ \text{Cr}_2\text{O}_4^+ + \text{Fe}^+ + \text{O}_2^- + 0^- \] (66)

\[ 2\text{FeCr}_2\text{O}_4 \rightarrow \text{Cr}_3\text{O}^+ + 2\text{Fe}^+ + \text{Cr}^+ + 30_2^- + 0^- \] (67)

For the protective oxide

\[ \text{CrO}^+ + \text{CrO}_2^- \] (68)

\[ \text{Cr}_2\text{O}_3 \rightarrow \text{Cr}_2\text{O}^+ + \text{O}_2^- \] (69)

\[ \text{Cr}^+ + \text{CrO}_3^- \] (70)

Any of the polyatomic fragments may have undergone further dissociation leading to \( \text{Cr}^+ \) and \( 0^- \), which were the largest contributors to the secondary ion pattern.

It is proposed therefore that the effect of carbon monoxide is to remove iron from the air-formed mixed oxide and use it to support deposition. This compositional change in the "as-received" oxide may account for the enhanced deposition in the thin outer oxide layer. Continued deposition, resulting ultimately in break-up of the bulk alloy structure, would have occurred either by iron and nickel diffusion into and through the protective oxide or by direct attack at the oxide/metal interface.

An equally complex secondary ion pattern and a multilayer oxide structure is obtained with a chemisorbed monolayer of oxygen on an ultra-clean chromium surface (175, 176). Erosion studies of these thin films showed a two-layer structure with \( \text{CrO}^+ \) and \( \text{CrO}_3^- \) ions enhanced, and \( \text{CrO}_2^- \) ion intensity diminished in the outermost layer.
These results are in excellent agreement with observations on the "thick" oxides above, Section 5.2.3.

6.2 Carbon and Carbonitride Ions

The depth variations observed with the $C_2^-$ and $CN^-$ ions show C at the gas and metal interfaces, and the absence of $C_2H^-$ ions that a carbide/carbonitride was the source of $CN^-$. The enhanced $CN^-$ intensity in the interface region could have been due to carburization, the effect being greater immediately after the induction period before much surface carbon had been formed. When deposition became rapid, this carbide would have been dispersed in the deposit and so a lower level would have been detected at the interface, Fig 93. The "as-received" alloy showed an increasing intensity of $CN^-$ in the bulk alloy where carbides (or carbonitrides) occurred as normal constituents, Fig. 86. During the long-term deposition, which eventually broke up the can, the $CN^-$ would have reached a steady-state level determined by the rate of transfer of iron and nickel out of the alloy. The enhanced $CN^-$ in the thin outer oxide could have arisen if iron extracted from a mixed oxide were transiently converted to a carbide or carbonitride.

The nitrogen in the alloy may have been introduced during processing stages in a supposedly "inert" atmosphere. It is known to exist as a carbonitride of niobium and the ratio Nb/C+N determined which carbides were stabilized in the steel (172). To be effective in carbon deposition a carbonitride would have been associated with iron and/or nickel.
VIII CONCLUSIONS

1. SUMMARY OF MECHANISTIC IMPLICATIONS OF THE RESULTS

2. A MECHANISM FOR THE REACTION ON IRON
   2.1 The Induction Period
   2.2 The Formation of Surface Deposit
VIII CONCLUSIONS

It is the object of this chapter to summarise the mechanistic implications of the work presented in the previous chapters for carbon depositing reactions on iron and nickel, and to suggest a simple chemical mechanism for the deposition process on iron.

1. SUMMARY OF MECHANISTIC IMPLICATIONS OF THE RESULTS

(1) The appearance of surface deposit is preceded by an induction period during which carbon dissolution in the metal occurs. Deposit precipitates when the metal reaches a level of supersaturation which, for iron, varies from 10-20% at temperatures above the eutectoid temperature, and from 50-100% below. The duration of the induction period is thus partially determined by the volume of the metal sample. It is also affected by the state of the metal surface, i.e. the number of exposed grain boundaries and bulk purity.

(2) The rate determining step during the solution stage of reaction of CH₄ on iron is a surface process, which has a Langmuir-type pressure dependance in the range 10-100 Torr. In the temperature range 600-750°C, the reaction occurs in two stages, the first (primary reaction) is non-activated, the second (secondary reaction) has an apparent activation energy of 190 ±5 kJ mol⁻¹ and an isosteric heat of adsorption of 170 ±20 kJ mol⁻¹, above 720°C; and an apparent activation energy of 176 ±20 kJ mol⁻¹, below 720°C. The scatter of results below 720°C is too large to allow positive identification of a change in the apparent activation energy, because of the difficulty of obtaining accurate analysis of the low concentrations of dissolved C. Above 750°C only the secondary reaction is observed, and below 600°C only the primary reaction.
(3) The primary reaction ceases at carbon concentrations which correspond closely to the end of the ferrite phase field. Above 720°C the secondary reaction occurs under conditions where γ-Fe forms, and below 720°C where the metal is supersaturated. It appears therefore that chemisorption occurs only when the metal is able to absorb the carbon product of dissociation.

(4) Above 720°C precipitation occurs at carbon concentrations which agree more closely with the γFe/γFe + Fe₃C phase boundary than with the corresponding graphite boundary. After precipitation the dissolved C level drops to the carbide phase boundary value, strongly indicating a carbide structure for the initial deposit. Below 720°C the graphite and carbide phase boundaries are too close to be able to distinguish between them.

(5) A possible carbide structure for the initial deposit from methane at 614°C is confirmed by IMMS analysis of samples at the point of precipitation. FeC ions are not detected from a sample reacted at 750°C, but the ion M/e 26, often associated with carbide structures, is detected in the bulk metal. Carbides would be expected to have a limited lifetime at methane reaction temperatures, and to decompose during cooling.

(6) The surface state of the sample also determines the morphology of the initial deposit. Thus on a work hardened surface, where dissolution is slow, the deposit is nodular in nature. Rapid dissolution occurs on fully annealed surfaces and laminar deposits are precipitated. The apparent activation energy of formation of nodular deposit is 80 ±8 kJ mol⁻¹.

(7) The composition of the initial deposit from CO on iron is a complex layered structure of carbon, carbide and oxide. During the early stages of growth, oxide is the main contributor to the surface deposit. Separate, thin carbon and carbide layers grow at the oxide/gas
interface. Carbon and carbide are present in the oxide close to the metal/oxide interface, and in the metal beneath the deposit. The oxide has a two-layer (duplex) structure, with possible stoichiometric variations between the layers, as indicated by changes in secondary oxide ion intensities in IMMS depth profile analyses. As reaction proceeds, the thickness of all the layers increases and it is clear that carbon depositing reactions occur mainly at the gas/deposit and the deposit/metal interfaces.

(8) Further reaction beyond the end of the induction period results in progressive break-up of the metal structure, leading eventually to total disintegration of the sample. The kinetics can be represented by a plot of weight gain per unit weight of metal versus log. time. The reaction rate is controlled by the rate of exposure of fresh metal area during the disintegration process. At low temperatures, the total area available is approximately equal to the sum of the individual grain surface areas. At temperatures of 700°C and above, the final particle size is independent of the grain size and the total weight of carbon deposited is determined by the weight of metal available and the reaction temperature. The particle size decreases as reaction temperature increases, and, at 865°C, is so small that the deposit spontaneously oxidises on exposure to the air.

(9) A carbide layer is formed in the metal beneath the growing deposit, and probably provides the means of breaking down the metal structure. Preferential precipitation at grain boundaries is expected to cause stresses which could eventually prise individual grains from the metal surface. At a fixed temperature, the depth of penetration of carbide appears to remain approximately constant as the deposit thickens, but the average intensity of carbide x-ray lines increases.
The concentration of carbide is highest at the deposit/metal interface. Changes of stoichiometry with distance into the metal and with extent of reaction are indicated by systematic variations of the orthorhombic lattice parameters.

(10) Graphite is produced on metals which have a high solubility for C and form metastable carbides, e.g. Fe and Ni. Metals such as Cr, Mo and Nb which form stable carbides react at a lower rate and carbon, if formed, is poorly graphitised. The effect of adding an 'inert' metal, such as chromium, to a reactive metal, such as iron, is to dilute the area made available by disintegration. The resulting reaction rate in CO at 550°C decreases inversely as the logarithm of the chromium content.

2. A MECHANISM FOR THE REACTION ON IRON

A tentative mechanism is proposed for carbon depositing reactions on iron, which explains the observation summarised in the previous section. The proposition of Boehm (96), that the carbide stoichiometry is determined by the composition of the phase in equilibrium with it, is incorporated into a general mechanism for carbon formation via carbide intermediates. A number of possible catalyst regeneration steps are included, to explain the observation that the total amounts of carbon formed are far greater than would be predicted from a single interaction at each metal atom, which would yield $\Delta w/w_0$ values of 0.21.

2.1 The Induction Period

The processes occurring during the induction period to the formation of surface deposit are chemisorption and dissolution reactions of the type:
For methane

\[
\begin{align*}
\text{CH}_4^g & \rightarrow \text{C}_{\text{ads}} + 4 \text{H}_{\text{ads}} \\
2\text{H}_{\text{ads}} & \rightarrow \text{H}_2^g \\
2\text{H}_{\text{ads}} & \rightarrow \text{H}_2^{\text{diss}} \\
\text{C}_{\text{ads}} & \rightarrow \text{C}_{\text{diss}}
\end{align*}
\]

where \(\text{ads} = \text{adsorbed}\), \(g = \text{gas phase}\), \(\text{diss} = \text{dissolved phase}\)

For carbon monoxide

\[
\begin{align*}
\text{CO}^g & \rightarrow \text{CO}_{\text{ads}} \\
2\text{CO}_{\text{ads}} & \rightarrow \text{C}_{\text{ads}} + \text{CO}_{2\text{ads}} \\
\text{CO}_{\text{ads}} & \rightarrow \text{C}_{\text{ads}} + \text{O}_{\text{ads}} \\
\text{C}_{\text{ads}} & \rightarrow \text{C}_{\text{diss}} \\
2\text{CO}_{2\text{ads}} + 3\text{Fe} & \rightarrow \text{Fe}_3\text{O}_4 + 2\text{C}_{\text{ads}} \\
4\text{O}_{\text{ads}} + 3\text{Fe} & \rightarrow \text{Fe}_3\text{O}_4
\end{align*}
\]

Then

\[
\begin{align*}
\text{C}_{\text{diss}} & \rightarrow \text{C}_{\text{surface}} \\
\text{C}_{\text{diss}} + 2\text{Fe} & \rightarrow (\text{Fe}_2\text{C})_{\text{surface}}
\end{align*}
\]

The rate determining step in the chemisorption of methane on Fe is reported to be the dissociation of adsorbed CH\(_3\) radicals (60,61, 107). The true activation energy for the surface process can be calculated from the data reported in Chapter IV as follows:

The Langmuir isotherm for competitive adsorption can be written as (179):

\[
S_i = S \cdot \frac{b_i^P_i}{1 + \Sigma b_j^P_j} \quad \text{(83)}
\]
where $S_i = \text{surface coverage of species } i$, $S = \text{total surface area}$

$P_i = \text{partial pressure of species } i$

$j = \text{all species}$

$b_i = \frac{Q_i}{RT}$

$b_j = \frac{Q_j}{RT}$

$Q = \text{heat of adsorption}$

For a unimolecular reaction of the type

$A \rightarrow B + C$ (85)

The rate of dissociation $= \frac{-dn_A}{dt} = kS$ (86)

$$= kS \cdot \frac{b_{PA}}{1 + b_{PA} + b_{PB} + b_{PC}}$$

(87)

The observed simple dependence on methane pressure arises only if the surface concentration of reaction products is low, such that $b_{PB}$ and $b_{PC}$ can be ignored. This generally implies weak chemisorption, but in this particular case the surface concentration can be reduced by dissolution in the metal after further reaction (C or $H_2$ formation).

The activation energy of the surface process ($E_s$) is related to the apparent activation energy measured experimentally ($E_a$) by the equation

$$\frac{d \ln k^1}{dT} = \frac{E_a}{RT^2} = \frac{E_s - Q}{RT^2}$$

(88)

In equations 87 and 88, $k$ is the rate constant expressed in terms of concentration of surface species and $k^1$ that expressed in terms of non-surface species, in this case dissolved carbon concentrations.

Thus $E_s = E_a + Q$ (89)

$$= 360 \pm 20 \text{ kJ mol}^{-1}$$

$E_s$ can be compared to the bond dissociation energies of CHx species.
given in Table 38 after Cottrell (180). It can be seen to be in excellent agreement with the CH₂-H energy and thus also with the literature findings that the dissociation of CH₃ radicles is the rate determining step in the chemisorption process.

Table 38

BOND DISSOCIATION ENERGIES OF CHₓ SPECIES

<table>
<thead>
<tr>
<th>Species</th>
<th>Bond Dissociation Energy kJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>334</td>
</tr>
<tr>
<td>CH-H</td>
<td>518</td>
</tr>
<tr>
<td>CH₂-H</td>
<td>368</td>
</tr>
<tr>
<td>CH₃-H</td>
<td>422</td>
</tr>
</tbody>
</table>

2.2 The Formation of Surface Deposit

The following tentative reaction scheme is proposed for the formation of thick carbon deposits. A non-stoichiometric carbide Fe₂C, where Z > 3, is assumed to be a labile intermediate. Carbon is formed by the following reactions

\[ nFe₂C + CO \rightarrow Fe₃C + (nZ - 3)Fe + nC + O_{ads} \quad (90) \]

or

\[ nFe₂C + CH₄ \rightarrow Fe₃C + (nZ - 3)Fe + nC + 2H₂ \quad (91) \]

where \( n = 1 \) for \( Z > 3 \)

\[ n = \frac{4}{Z} \] for \( Z < 3 \)

Also for a carbon rich carbide \( (Z < 3) \)

\[ m(Fe₂C) = (m-1)Fe₃C + C \quad (92) \]

where \( m = \frac{3}{3-Z} \quad (93) \)

for an iron rich carbide \( (Z > 3) \)

\[ Fe₂C \rightarrow ZFe + C \quad (94) \]

or

\[ Fe₂C \rightarrow Fe₃C + (3-Z)Fe \quad (95) \]
Fe\textsubscript{3}C is regarded as an inert product, but at high temperatures (e.g. \textgreater 600\textdegree C) the following dissociation reactions will be expected to occur

\begin{align*}
\text{Fe}_3\text{C} & \rightarrow 3\text{Fe} + \text{C} \quad (96) \\
\text{Fe}_2\text{C} & \rightarrow 2\text{Fe} + \text{C} \quad (97)
\end{align*}

Equations 94, 95, 96, and 97 regenerate Fe catalyst for further reaction.

In the case of the Fe/CO reaction the following additional steps can occur to terminate reaction

\begin{align*}
\text{O}_{\text{ads}} + \text{CO}_g & \rightarrow \text{CO}_2g \quad (98) \\
4\text{O}_{\text{ads}} + 3\text{Fe} & \rightarrow \text{Fe}_3\text{O}_4 \quad (99) \\
(4Z+6)\text{O}_{\text{ads}} + 3\text{Fe}_2\text{C} & \rightarrow Z\text{Fe}_3\text{O}_4 + 3\text{CO}_2g \quad (100)
\end{align*}

Termination could also occur by encapsulation of catalyst by inert products such that diffusion of gas through the deposit becomes rate limiting.

Carbon deposition reactions at the deposit/gas interface can occur as a result of reduction of the oxide

\begin{align*}
\text{Fe}_3\text{O}_4 + 4\text{CO} & \rightarrow 3\text{Fe} + 4\text{CO}_2 \quad (101)
\end{align*}

The above mechanism also explains break up of the metal structure since iron is continually being removed from the surface. Also reaction would be expected to occur preferentially down grain boundaries, where crystal structure is disordered, and whole grains could therefore become isolated from the bulk and incorporated into the deposit. It is appreciated, however, that such a mechanism is difficult to prove, but results presented in Chapter VI do indicate changes in carbide stoichiometry in a reaction zone below the metal surface. Calculations of the stoichiometry of the unit cell show that Z varies from \textasciitilde 3 at the surface of the most heavily reacted
sample (1Cr alloy) to 4.3 in the bulk, most of the change occurring in the first 20-30 μm below the surface. Positive proof of the existence of non-stoichiometric carbide intermediates can only be obtained by in-situ studies at reaction temperature. We are planning to carry out such an experiment in a high temperature diffractometer, where it is intended to measure kinetics from changes of x-ray line intensity as well as identifying the composition and stoichiometry of the deposit.
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A DEMOUNTABLE GAS-BALANCED AUTOCLAVE WITH A CHEMICALLY INERT REACTION VESSEL

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A DEMOUNTABLE GAS-BALANCED AUTOCLAVE  
WITH A CHEMICALLY INERT REACTION VESSEL  

- by -  

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M.T. Theobald and B.W. Vine
A high pressure autoclave with several novel design features is described. Test specimens are held in an inner vessel made of a chemically inert material e.g. silica, thus eliminating the possibility of spurious side reactions that could alter the test gas composition. This vessel is surrounded by the furnace and an outer steel pressure vessel. A semi-automatic gas-balancing system is used to prevent excessive differential pressures which could rupture the inner vessel. The autoclave has been designed to operate at 650 p.s.i. (44 bars) pressure and 1000°C with a uniform temperature zone of ~30 cm in a reaction vessel diameter of 10 cm. At maximum design rating the outer autoclave walls reach a temperature of ~175°C.

The autoclave is completely demountable. The specimen holder is of a modular form and can accommodate several hundred small test coupons or alternatively a few large ones. Details of heater design, thermal insulation, control systems, data acquisition and recording and rig layout are given, together with the operator arrangements designed to minimise sample handling problems. The performance and long-term temperature stability are discussed.
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APPENDIX 1: PRESSURE VESSEL DESIGN

APPENDIX 2: STANDARD HEAT LOSS CALCULATIONS FOR FURNACE DIMENSIONS
1. **INTRODUCTION**

The conventional high pressure autoclave for gas-solid reaction studies usually consists of a cylindrical steel pressure vessel and a single-winding external heater. Such a simplified system has a number of disadvantages. (1) Single zone heaters give wide variations in temperature gradient throughout the autoclave which can cause difficulties in defining precisely the specimen temperature at any point. (2) With large volume vessels and low gas flow rates, the gases may have a residence time of several hours. The autoclave walls, which have the higher temperature of the heater winding, may react with the test gas and significantly alter its composition. (3) There is also a danger of material spalling from the walls and contaminating specimens, thus giving spurious weight gain data and analytical results.

These disadvantages can be overcome by constructing the autoclave of a chemically inert material. The most satisfactory chemically will be a ceramic or glass, but these have inadequate mechanical strength for pressure containment and therefore can only be used if a pressure balanced reaction vessel is adopted. This approach requires a sophisticated control and protection system to simplify operation.

This Note describes a pressure balanced autoclave and the necessary control system, with several novel features. All operator actions including valve movements and sequencing, specimen handling and data acquisition, normally associated with high pressure autoclave work have been considered for improvement or automation. It has been designed to achieve pressure and temperature conditions of 650 p.s.i. and 1000°C, which allows gas-solid reaction studies to be carried out under conditions relevant to gas-cooled reactors. A rig consisting of five autoclaves has been built, and is being used initially to study carbon deposition on A.G.R. metals.

Several of the new techniques used on this 'carbon deposition autoclave rig' have been adopted for other C.E.R.L. rigs such as the high pressure microbalance system, the 'octaclave' bench, the pre-oxidation rig and the fast reactor nitriding rig, and are also being used in other C.E.G.B. laboratories.

2. **GENERAL LAYOUT OF THE RIG**

Five autoclaves are mounted in a single frame facing an electrical console containing the monitoring, control, and alarm systems. The floor level between has been raised to facilitate access to the autoclave closure (loading) flange and to simplify operation of the specimen rack lifting and transfer frame. The underfloor space houses electrical trunking, the 110 V transformer, and the refrigeration bath used for water concentration control. The overall arrangement is shown in Plate 1. Located at one end of the platform are five evacuable specimen storage vessels, an analytical balance and microscope bench and teletype. Behind each autoclave is a panel carrying the pressure gauges and manually operated valves (Plate 2), which has the main pipework mounted on the reverse side. Overhead beams carry a small block and tackle set for lifting the top section of the autoclave during dismantling.
3. DETAILED DESCRIPTION OF THE AUTOCLAVE AND GAS CIRCUIT

3.1 The Pressure Vessel

The autoclave is constructed in two sections. The lower part containing the heater, power input and furnace control thermocouple feedthroughs, balance gas connections, and the spring-type pressure relief valve, is bolted onto the aluminium box section frame via three support lugs. The top section fitted with the test gas and vacuum connectors and the specimen thermocouple feedthroughs, is removable to allow access to the heater and the reaction vessel supporting clamp. It is sealed to the lower section with a teflon-coated stainless steel O-ring. A cutaway diagram of the complete autoclave is given in Fig. 1.

Access to the specimen test region is through the top blanking plate which is sealed with a viton or p.t.f.e. O-ring. Under normal operating conditions, no external autoclave connections are disturbed when specimens are inserted or removed. Test gas enters through the p.t.f.e. sealed Banjo joint, Fig. 2, which is demountable to allow removal of the specimen racks.

The autoclave shell, flanges, bosses etc. were designed in accordance with the Taylor-Forge principle (see references), of which details are given in Appendix 1. Dimensions, materials and 'O'-ring specifications are given in Tables 1, 2 and 3.

3.2 The Reaction Vessel

The reaction vessel is a clear silica glass tube 1.0 ± 0.01 m long, 102.5 mm internal diameter, with a wall thickness of 2.5 to 3 mm except at the buttress end where it is thickened to a maximum of 15 mm. It is fixed to the underside of the large autoclave flange of the top section by means of a clamping ring, the seal being made with a silver or p.t.f.e. coated 'O'-ring (Table 3). A bolt torque of approximately 1.2 m kg (6 ft lb) was required to achieve a vacuum and pressure-tight seal. The thickened end of the glass tube is ground to create a 5 mm flat flange for the clamp to bear on, Fig. 3. The mild steel ring has a 1 mm clearance on the glass. The gap is packed with a heat resistant material (Walkerite) to prevent metal/glass contact. Expansion effects of the mild steel bolts are minimised by placing stainless steel spacers, 13 mm long, (coefficient of thermal expansion 1.5 x that of mild steel) under each bolt head.

The sealing surface of the silica needs careful preparation. After grinding, it is polished on a flat glass plate using coarse and fine carborundum paste, and finally buffed with jewellers' rouge to an optical quality finish. At this stage it is fused to the main silica tube, ensuring that the plane of the sealing surface is at right angles to the axis of the tube in order to prevent breakage when making the main seal between the two halves of the autoclave. Tests on these joints showed that they were capable of withstanding a tightening torque on the bolts in excess of three times that required for sealing.

The buttress joints and tubes are supplied, and assembled after grinding and polishing, by Heraeus Quartz Fused Products of Cobham, Surrey. A design using a steel clamping ring acting on a 5° taper on the buttress end proved to be unsatisfactory because thermal expansion of the ring and clamping bolts allowed the vessel to drop sufficiently to open the seal.
3.3 The Heater

The general arrangement is shown in the cutaway drawing Fig. 4 and Plate 3. It is a single unit consisting of a former with three sets of windings surrounded by thermal insulation, the whole being contained in a heat reflecting metal can that fits into the lower section of the main pressure vessel. Three different types of heater were constructed with silica, ceramic and stainless steel formers respectively. The first two were successful. The first type uses a silica tube closed at one end 120 mm diameter by 750 mm long, which is wound with 16 s.w.g. nichrome wire for the three zones. The windings are preformed on a steel mandril. Individual wires are held at the correct pitch by grooved silica spacer rods and silica tape (Refrasil T5 Y19 11T). The spacers for the two upper windings are made by grinding 1.5 mm square grooves at 1.5 mm spacing, into a 2 mm wide flat surface that has previously been ground onto a 6 mm diameter silica rod. The wire for the lower winding is insulated with silica sleeving (Refrasil T5, Y12, 11T) and bound in place with Refrasil tape with the turns packed as close as possible. One turn of 18 s.w.g. nichrome wire is twisted into the end winding of each coil to make a "cold tail" for electrical connections. The 18 s.w.g. leads are brought to the top of the heater through 6 mm bore alumina tubes spaced symmetrically and bound in place with silica tape. Four 2 mm bore 60 cm long, closed alumina thermocouple pockets are likewise bound onto the windings.

The winding details are as follows:

<table>
<thead>
<tr>
<th>Zone</th>
<th>Length</th>
<th>Turns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top zone</td>
<td>240 mm</td>
<td>74</td>
</tr>
<tr>
<td>Middle zone</td>
<td>250 mm</td>
<td>80</td>
</tr>
<tr>
<td>Bottom zone</td>
<td>150 mm</td>
<td>51</td>
</tr>
</tbody>
</table>

The live ends of the top and middle windings are adjacent, and the neutral ends of the middle and bottom zones are placed together, to reduce the risks of short circuits. The live ends are separated by an 8 mm wide, D-section, circular silica spacer, Fig. 3.

The heater is contained in a 220 mm diameter can, made from 26 gauge stainless steel, to be a good fit into the bottom section of the autoclave. The silica tube is located by its base in a 145 mm diameter well in the can, the gap being filled with insulation material. At the top the can is 'closed' by an 20 cm pyrex dinner plate cut and ground to make a good fit around the heater former, cold-tails and thermocouple tubes.

Thermal lagging consists of 6 cm of insulant (Kaowool) tightly packed into the can. The as-received material was unsuitable due to formation of cavities during packing and drying out. Excellent insulation is achieved by firing the wool to 1200°C for two days in air, and crushing to a powder, which is then packed tightly into the furnace can. A polished aluminium heat reflector, 25 μm thick, is fixed to the inside of the can with heat resistant glue.

A heater with identical characteristics has been constructed with a ceramic former (manufactured by Severn Sciences Ltd). The wires are held in place with a heat resistant cement. The electrical and mounting arrangements are unchanged. A heater with a stainless steel former sprayed
with a 0.5 mm thick ceramic layer as insulant proved unsatisfactory. Prolonged heating at temperatures in excess of 750°C made the ceramic electrically conducting.

Four control thermocouples are fitted, one in the centre of each winding, with an extra 'alarm' thermocouple in the middle winding. For accuracy and stability thermocouples of Pt/13% Rh.Pt sheathed in Pt/10% Rh.Pt were selected. The thermocouples and electrical leads are brought out of the autoclave via high pressure feedthroughs in bosses welded onto the lower section. Details of feedthroughs are given in Table 4. Furnace dimension, lagging thicknesses etc. were calculated using standard heat loss equations as outlined in Appendix 2.

### 3.4 The Sample Holder

The demountable sample holder (Fig. 5) has a central metal rod supporting a set of 100 mm diameter silica plates, each 3 mm thick, held at a separation of 50 mm by cylindrical silica spacers that have 5 mm diameter flanges at each end. The central rod is made of any metal which is unreactive in the chosen experimental conditions, e.g. for CO deposition up to 650°C stainless steel is used, whereas for CH₄ deposition reactions requiring temperatures up to 950°C molybdenum is preferred. It is fully enclosed by the spacers to minimise any surface reaction and to prevent any solid reaction products contaminating specimens. Its main purpose is to give strength to the assembly. The complete specimen rack is suspended via a stirrup from the upper flange of the autoclave top section.

Seven of the silica plates are cut by ultrasonic drilling to each accommodate six thin-walled silica sample buckets 25 mm diameter by 15 mm deep. The buckets have six 1 mm diameter holes in the walls located 5 mm from the base to aid gas circulation, and also a 1 mm lip around the top edge to allow them to be suspended from the silica plates.

The seven sample holding plates are positioned to coincide with the uniform temperature zone. One blank plate below the sample plates and seven above act as gas baffles to reduce convective heat losses.

Additional cut-outs accommodate the specimen temperature thermocouples and the gas inlet tube, the latter being taken to the bottom of the reaction vessel to preheat the gas. The sample plates and bucket holes are numbered, using a fired-on organic gold solution, so that specimen positions can be uniquely identified.

The sample assembly is raised or lowered by means of a lifting system, Fig. 6, which bolts directly onto the top flange. A conventional locking fishing reel with nylon line is used for lifting and lowering the rack. Alteration of the plate arrangements, for example to accommodate fewer larger specimens or many small ones, is achieved by removing the stirrup and hook unit (Fig. 5) and then sliding off the plates and spacers.

### 3.5 Gas Handling and Purification

The system is constructed with independent gas lines to two of the five autoclaves (A and D). Two different gas mixtures and/or two gas pressures can be used, with the autoclaves crosslinked in four combinations viz:
A and (B+C+D+E)
2. (A+B) and (C+D+E)
3. (A+B+C) and (D+E)
4. A+B+C+D+E

A flow diagram of the gas lines and valve arrangements to autoclaves A and B, as represented on the mimic control diagram, are shown in Fig. 7, and a photograph of the complete diagram is given in Plate 4. A description of the function and type of each valve is listed in Table 5.

All stop valves are of the electrically actuated solenoid type, operated from the mimic diagram. Manually operated needle valves used for flow control, gas dumping, sampling, and for admitting gas through the rotameter and hygrometers, are mounted on the gauge panel behind each autoclave. The system can handle a minimum flow rate of 10 Std m³ min⁻¹ at a pressure drop of 600 p.s.i. (40 bar). The Budenberg gauges used to monitor pressures at the gas reservoir, inlet, test or balance gas sections of the main vessel, the dome load pressure regulator region (see later), and the differential pressure, are specified in Table 6.

Gases are exhausted into a common manifold which is vented externally via a fan. To aid flushing and purging operations when filling the autoclaves with gas, evacuation is carried out via a large bore ball valve connected to the common vacuum manifold and rotary pump. Slow pumping may be necessary to avoid disturbing loose deposits and so the main vacuum valve (item 21, Fig. 7) is paralleled by a needle valve.

All piping is ¼", 0.065" wall 321 stainless steel, with the exception of the exhaust and vacuum manifolds which are ½" and 1" N.B. copper pipes respectively. High pressure unions are either welded or utilize standard twin-olive compression fittings.

The test gases (CO and CH₄ initially in the carbon deposition programme) are freed from impurities by

1. a deoxygenating catalyst (Engelhard type M) at 350°C for CO and 450°C for CH₄.
2. 5A molecular sieve to remove water.
3. 13X molecular sieve to remove unwanted hydrocarbons.
4. filters to remove solids.

3.6 The Pressure Balancing System

Precise balance is achieved with pairs of gas controlled, dome-loaded pressure control valves (items 11, Fig. 7), and back pressure regulators (items 18, Fig. 7). Duplication of the regulators eliminates inherent pressure differential characteristics of the valves. Imbalances of less than 20 p.s.i. (140 N m⁻²) are within the safe working limit for the silica vessels. Preset needle valves are used on the entry and exit lines (item 13, Fig. 7) to balance gas flows and control the rate of pressure rise. The silica vessel is protected from damage by the following safety devices.
1. A differential pressure gauge with alarm contacts set at ±20 p.s.i.g. (140 N m⁻²).

2. A nickel disc assembly bursting at ±30 p.s.i.g. (210 N m⁻²).

3. Soft seat needle valves in the exit lines to allow manual dumping of excess gas.

4. Electrical interlocking of the inlet stop valves to prevent gas being admitted to one side of the autoclave only.

5. Alarm contacts on the test gas and balance gas inlet gauges, (gauges at 21 and 22 Fig. 7).

To reduce fatigue effects on the bursting disc caused by positive and negative pressure fluctuations a dual system was designed incorporating two conventional dome-shaped discs with heavy duty vacuum supports and large sealing flanges. The test gas is fed to the central chamber and the balance gas to each end of the unit.

3.7 The Vacuum Storage Vessels

The five cylindrical vacuum vessels are designed to accommodate the complete sample holding rack. The internal diameter and flange dimensions correspond exactly to those at the top of the autoclave, and the same system of suspension from the flange is used. The lifting frame engages with the vacuum vessel flange thus permitting direct transfer to storage of the specimens and silica holding rack. The vessels are connected via individual diaphragm valves (Edwards-Saunders) to the vacuum manifold. The pressure in each vessel is monitored with a thermocouple gauge.

4. ELECTRICAL SYSTEMS

4.1 General Arrangements

All electrically operated valves are controlled from a single mimic display diagram (Synoptica Ltd), which therefore shows the state of the system at any time. The same console contains mass flowmeters, hygrometers, temperature controllers, pressure transducer controls, vacuum gauges, data processing equipment, and a recorder.

Power is supplied to the heaters and the instruments by a 50 A 110 V centre-tapped transformer, giving a maximum potential to earth of 55 V. This is reduced to 12 V d.c. for the solenoid valves which are actuated via relays. Details of thermocouples and instrumentation are given in Tables 7 and 8 respectively.

4.2 Heater Control and Temperature Measurement

Heater temperature is set and stabilised by a three-term controller, a thyristor power unit on each winding and a thyristor driver, which allows the total power to be disproportionately distributed between the windings as required to attain a level temperature gradient. The control thermocouple is Pt/13% Rh Pt situated on the hottest winding. An independent thermocouple is used to activate alarm circuits in the event of temperature excursions from the set point. The alarm limits are adjustable between 1% and 10% of the set point. The power to the
furnace is cut when the alarm is actuated to avoid exceeding the design limits of the pressure vessel and to minimise errors in the experimental rate data. A flow diagram of the control circuit is given in Fig. 8, a logic diagram of the alarms in Fig. 9, and details of the control units in Table 9. A complete diagram of the circuit with additional noise immunity is available (see reference).

The heater temperatures are initially set up using a temperature test section, Fig. 10, that has identical dimensions to the specimen holder, and is built onto a standard autoclave closure plate. It is seen in position in Plate 2, with the box of thermocouple connecting sockets on top. The section consists of 16 axial thermocouples spaced at 50 mm intervals. Additional thermocouples, situated midway between the centre and wall of the test vessel, supply extra information about the radial temperature distribution. Four chromel/alumel thermocouples are located down the side of the reaction vessel as permanent monitors of the temperature gradient. Two of them are positioned together at the central point of the middle winding to provide an internal calibration, the other two being 150 mm above and below this position.

During commissioning, additional thermocouples were strapped to the autoclave body to monitor wall temperatures. Also, eight thermocouples were introduced into the sample region through a specially modified lid, Plate 5, to provide additional information when checking that the test section temperature profile accurately represented the specimen zone gradient. Details of all thermocouples are given in Table 7.

4.3 Electrical Interlocks and Alarm Circuits

To prevent overpressurisation on one side of the silica vessel occurring by incorrect valve switching, certain operations have been interlocked using standard relay circuitry (drawing available - see references). For example, to ensure that balance gas is not admitted without test gas, valve ASV7 can be opened only in conjunction with either ASV6 or the two valves ASV4 + ASV8. The logic of the various interlocks is given in Table 10(a). The individual valves are indicated in Fig. 7 and the overall layout is shown in Plate 4. Incorrect operation is indicated by illumination of the switch, the logic circuit preventing the valve operation actually occurring.

In addition to controlling gas switching, the following alarm conditions are monitored and displayed on the mimic diagram.

2. Differential pressure gauges showing excessive pressure imbalance.
3. Gas cylinder pressure gauges showing minimum working pressure level (i.e. autoclave pressure).

The system utilises a standard accept/reset unit, Table 8. An alarm condition on one of the above components is indicated by a flashing light on the mimic diagram and a simultaneous sounding of a klaxon. The fault may be "accepted" pending investigation, which leaves a continuous light on the diagram but switches the klaxon off. For the duration of the fault, the data acquisition system is programmed to display operating parameters at an increased frequency. When the fault is cleared, the "reset" button returns the system to the normal condition.
4.4 Other Instrumentation

Gas flow is measured on thermal conductivity type mass flowmeters that provide an electrical read-out. They are backed-up by conventional float-type flowmeters. Pressure is recorded from transducers (Bell and Howell Ltd), and water levels from electrolytic hygrometers (S.E.I. Ltd). Oxygen levels in the test or balance gases are measured with an electrolytic meter (Hersch type) which may be fitted to any of the gas sampling points. The pressure in the vacuum manifold is measured with an Edwards' Pirani gauge, and in the vacuum vessels with individual Edwards' thermocouple gauges connected back to a common control unit fitted with a five-way switch.

4.5 Data Acquisition

The output from the various monitoring instruments is fed to the C.E.R.L. central data processing and acquisition system which displays via a teletype on the rig platform. At a later stage it is intended to link the Sartorious five-figure digital print balance into this system. Continuous recording on a Speedomax potentiometric recorder fitted with a 20-position input switch is available as a back-up facility.

5. SYSTEM OPERATION AND PERFORMANCE

5.1 Start-up Procedure and Depressurisation

Before an experimental run, the silica vessel and test gas lines are purged of air (to an oxygen concentration below 1 p.p.m) by argon filling and evacuation, at least three cycles being necessary. The system is pressurised by setting the required balance gas level in the dome reference line using the pressure regulating valve PRV1 (item 12, Fig. 7). Referring to autoclave A, valves ASV6, ASV10 and ASV7 are opened to admit test and balance zones simultaneously up to the reference pressure, via the dome-loaded pressure-regulating valves (item 11, Fig. 7). The state of balance is observed on the differential pressure gauge. Any out-of-balance condition in either direction can be brought immediately under control by venting excess gas through the manually operated soft-seat needle valves in the exit lines (item 17, Fig. 7).

Valves ASV4 and ASV8 provide access to a facility for dosing the test gas with any additive, for example water from a temperature-controlled water-saturated molecular sieve bed.

An autoclave can be pressurised to 600 p.s.i. (40 bar) in approximately 30 minutes with differential pressure fluctuations of <10 p.s.i. (0.67 bar) provided that the needle valves in the inlet lines (item 13, Fig. 7) have been set previously for the required balanced flow rates.

Because of the volume differences between the test and balance gas sides of the system, rapid temperature rises cause substantial pressure differentials at high pressures, and therefore it is preferable to stabilise the heater temperature before pressurising. The warm up period is carried out with oxygen-free argon flowing in the test gas lines via valve ASV9, and the change to test gas is made when the system is at operating temperature. This procedure has the additional benefit of allowing the start and finish of experimental runs to be timed. Because of the large gas volumes involved it is necessary to evacuate before gas switching. During normal running, pressure fluctuations are automatically
controlled by admission or release of gas by the dome-loaded pressure regulators or the back pressure regulators, components 11 and 18, Fig. 7 respectively.

At the end of the run, the test gas is replaced by high purity argon with the specimens maintained at the reaction temperature. The autoclave is depressurised through the back pressure regulators by closing the main pressure regulating valve (PRV1) which is self-venting thus releasing the reference gas pressure.

5.2 Temperature Characteristics

A uniform temperature zone of \(\sim300\) mm is readily achieved at atmospheric pressure. If the heater control settings are left in this state, then increasing the pressure causes a deleterious change in the temperature gradient due to the improved heat transfer, Fig. 11. As a consequence, wall temperatures rise in a region near the top of the heater, as indicated in Fig. 11. Adjustment of the power distribution between the three windings allows a uniform temperature zone to be achieved at high pressures, as shown in Fig. 12 for 650°C and 600 p.s.i. (40 bars). The temperature profiles of the heated reaction vessel and the outer wall, when the autoclave is operating close to its maximum design rating, are given in Fig. 13. The highest wall temperature is well below the specified maximum of 300°C.

The long term temperature stability is influenced by the position of the control thermocouple, when arbitrarily placed at the centre of the middle heater winding, long term variations (over several hundred hours) of \(\pm20^\circ\)C may occur. This can be reduced to \(\pm5^\circ\)C by placing the thermocouple at the hottest point of the heater winding. The short term fluctuations are better than \(\pm2^\circ\)C.

5.3 Vacuum Capability

Vacuum leak testing was used in addition to conventional pressure testing for checking the gas tightness of the system during commissioning. Pirani gauges were fitted to the autoclave lid and to appropriate positions in the gas circuit, and hydrogen was used as the probe gas. The system was considered to be satisfactorily sealed for high pressure work when an ultimate vacuum of \(10^{-2}\) Torr (1.3 N m\(^{-2}\)) and the maximum working pressure of 650 p.s.i. (44 bars) could be maintained in all sections for at least 24 hours.

The storage vessels reached an ultimate vacuum of \(10^{-2}\) Torr (0.13 N m\(^{-2}\)), with no significant pressure rise when isolated from the pumps over a period of one week.

5.4 Specimen Information Record

Because of the high autoclave specimen capacity it has been necessary to devise a simplified system for recording specimen details. Information such as material, dimensions, surface treatments, experimental conditions, weight gain data taken during the run, and subsequent specimen examination details, are recorded on a punched card (Fig. 14). The system allows specimens and results to be sorted on the basis of any of the features represented by the edge holes. The twin hole gas composition section is for use with gas mixtures, the major or more important constituent being double punched.
12.

Each sample in an experimental run is uniquely numbered in such a way as to identify its composition and autoclave position according to the scheme:

Material code/Autoclave code/Level number/Position number/
Sequential experiment number/Run number

6. POSSIBLE MODIFICATIONS

Early experience with the system has suggested some modifications that would simplify operation.

6.1 Independent Gas Lines to Each Autoclave

Operating the autoclaves in groups is satisfactory, but gas balancing in two or more simultaneously during pressurisation or depressurisation is fairly complicated and slow. Independent operation would be an improvement and would also make the system more versatile, permitting more gas mixtures or pressures to be used at any one time and allowing outages to be staggered thus easing specimen handling and minimising air exposure. Modified valve interlock arrangements are suggested in Table 10(b).

6.2 Independent Control of Heater Windings

With the control circuits described in Section 4.2, the power input to the three heater zones is interdependent. Thus changing the temperature profile induced by one winding alters the contribution by the other two, slowing the setting-up procedure. Completely independent control on each zone would ease this problem but at increased cost.

6.3 Minor Modifications

The following minor changes are recommended.

1. The replacement of valves ASV7, ASV10 and corresponding ones on autoclaves B to E, each by two valves positioned back to back and wired in parallel. This would prevent back flow of gas which occurs if the test gas and balance gas pressures are not equal, because the solenoid valves do not seal satisfactorily against back pressures.

2. The insertion of an additional solenoid valve in the test gas line between the autoclave and the dome-loaded pressure regulator, to prevent leakage across the seating of the regulator during evacuation of the autoclave.

3. The faces of the main flange on the balance gas side only to be coated with a high temperature grease to prevent oxidation by moisture released from the thermal insulation during initial heat-up.

4. The use of an additional pressure gauge at the inlet point of the balance gas to the autoclave, and to change gauges to the 0-1000 p.s.i. standard test type throughout.
7. **ACKNOWLEDGEMENTS**

The authors thank Messrs P. Madden, P. Church, W. Chaffin, and Messrs D. Higginbotham, J.H. Harrison, R.W. Mills and their staffs for much help throughout the project.

8. **REFERENCES**

British Standard 1515 (1968) Part 1, "Specification for fusion welded pressure vessels".


Circuit diagram of the "OFF TEMPERATURE ALARM", see: C.E.R.L. drawing RL 4.1.1778.


Appendices 1,2, Tables 1-10, Plates 1-5 and Drg No. RL 4.1.2533,35,43,44 4.1.2842,2534,2535,2843-2848 and Fig. 14 attached
APPENDIX 1

PRESSURE VESSEL DESIGN

The vessel shell, bosses, end cap etc., were designed generally in accordance with BS 1500, Pt.1. Reference was made to ASME, Section VIII, Division I, particularly for the flange designs. Specific details are given in Table 2 regarding dimensions, allowable stresses and gasket specifications.

To obtain a combination of large vessel diameter and small flange size, thereby reducing the weight of the Top Hat Section, a relatively small bolt pitch circle diameter was used. Materials are specified in Table 1.

Main vessel tubes were calculated as follows:

**TOP TUBE:**

\[
t = \frac{pD_i}{2fJ} + c \quad \text{where } t = \text{thickness}
\]

\[
t = 2.74 \text{ mm (0.108 in)} + c \quad p = \text{pressure}
\]

Actual thickness: 4.47 mm (0.176 in)

**MAIN SHELL:**

\[
t = \frac{6.02 \text{ mm (0.237 in)} + c}{2fJ} \quad f = \text{design stress}
\]

Actual thickness: 7.14 mm (0.281 in)

**The End Plate:** Semi-ellipsoidal to BS 1965, Part I or BS 1640, Part I.

\[
t = \frac{pD_0 K_1 K_2}{2fJ K_3} + c \quad \text{using } K_1 = 1.15 \frac{R_i}{D_0} \quad K_2 = 0.94 \quad K_3 = 1.
\]

**The Top Blind Cover:**

\[
t = G \sqrt{\frac{c + 1.78 Wh}{f + \frac{G}{fG^3}}} \quad \text{where } c = \text{factor 0.3}
\]

For carbon steel:

\[
t = 19.3 \text{ mm (0.76 in)} \quad G = \text{gasket load reaction dia.}
\]

For stainless steel:

\[
t = 17.7 \text{ mm (0.697 in)} \quad n_g = \frac{c - G}{2}
\]

\[
W = \text{flange design bolt load.}
\]
The following calculations refer only to the autoclave tube adjacent to the heater. However, if the resulting outside wall temperature is used for the remaining surface area of the autoclave to determine the total heat loss, a conservative power rating should result.

\[ \Delta t_A = t_1 - t_4 \]
\[ \Delta t_B = t_4 - t_5 \]

Radii \( R_1 - R_4 \) measure from axis of furnace.

The thin stainless steel can and aluminium reflector have been ignored for the purpose of these calculations, since they should only reduce the wall temperature.

\[ Q = 2\pi L \Delta t_A \left( \frac{\log_e R_2/R_1}{K_1} + \frac{\log_e R_3/R_2}{K_2} + \frac{\log_e R_4/R_3}{K_3} \right) = 2\pi L \Delta t_B hCR \]
where $h_{CR}$ is the overall heat transfer coefficient for natural convection and radiation (see McAdams, 1954).

Simplified equation for air:

$$X = L^3 \frac{C_p \mu}{k} \times \text{Const.}$$

$C_p$ specific heat

$\mu$ viscosity

$k$ conductivity.

Values of the constant were taken from McAdams' Fig. 7-8 for various temperatures.

Coefficient of Natural Convection ($h_c$)

For values of $X$ from $10^9$ to $10^{12}$:

$$h_c = 0.19 \Delta t^{1/3}.$$

For values of $X$ from $10^9$ to $10^4$:

$$h_c = 0.29 (\Delta t/L)^{0.25}.$$

Radiation Coefficient ($h_r$)

$$q_r = 0.171 \times 10^{-8} \alpha (T_2^4 - T_1^4)$$

where $\alpha = \text{emissivity}$

$T_1$ and $T_2$ are absolute temperatures.

$$q = h_r \Delta t$$

therefore $h_r = \frac{0.171 \alpha (T_2^4 - T_1^4)}{10^8 (T_2 - T_1)}$

The overall heat transfer coefficient is given by:

$$h_{CR} = h_c + h_r.$$

Typical values:

- $L = 610 \text{ mm (2 ft)}$
- $K_1 = 0.505 \times 10^{-2} \text{ W/M.}^\circ C$
- $K_2 = 0.114 \times 10^{-2} \text{ W/M.}^\circ C$
- $K_3 = 31.49 \times 10^{-2} \text{ W/M.}^\circ C$
- $R_1 = 53.3 \text{ mm (0.175 ft)}$
- $R_2 = 61 \text{ mm (0.20 ft)}$
- $\alpha = 0.9$

(0.42 Btu/h ft$^2$ °F/ft)

(0.095 Btu/h ft$^2$ °F/ft)

(26.2 Btu/h ft$^2$ °F/ft)
<table>
<thead>
<tr>
<th>Item</th>
<th>Material</th>
<th>Specification</th>
<th>Design Temperature °C</th>
<th>Allowable Design Stress Ambient</th>
<th>Allowable Design Stress Design Temp.</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blind top cover</td>
<td>Carbon steel</td>
<td>BS 1501-161 28</td>
<td>145</td>
<td>108 MN/m² (15700 psi)</td>
<td>108 MN/m² (15700 psi)</td>
<td>R.G. Brown Warley, Worcs.</td>
</tr>
<tr>
<td></td>
<td>Stainless steel</td>
<td>BS 1449 Pt.4 321512</td>
<td></td>
<td>129 MN/m² (18700 psi)</td>
<td>119 MN/m² (17300 psi)</td>
<td>Stainless Steel Profile</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cullers Ltd. Maidenhead</td>
</tr>
<tr>
<td>Top slip-on flange</td>
<td>Carbon steel</td>
<td>BS 1501-161 28</td>
<td>145</td>
<td>108 MN/m² (15700 psi)</td>
<td>108 MN/m² (15700 psi)</td>
<td>R.G. Brown Warley Worcs.</td>
</tr>
<tr>
<td>Bottom slip-on flange</td>
<td>Carbon steel</td>
<td>BS 1501-161 28</td>
<td>145</td>
<td>108 MN/m² (15700 psi)</td>
<td>108 MN/m² (15700 psi)</td>
<td>R.G. Brown Warley Worcs.</td>
</tr>
<tr>
<td>Weld neck flange</td>
<td>Carbon steel</td>
<td>BS 1503-161 Gr.B</td>
<td>145</td>
<td>108 MN/m² (15700 psi)</td>
<td>108 MN/m² (15700 psi)</td>
<td>Brown-Bayley Sheffield</td>
</tr>
<tr>
<td>Top tube</td>
<td>Carbon steel</td>
<td>BS 3602-CDS 27</td>
<td>145</td>
<td>104 MN/m² (15100 psi)</td>
<td>104 MN/m² (15100 psi)</td>
<td>Markland-Scowcroft Bolton</td>
</tr>
<tr>
<td>Main shell</td>
<td>Carbon steel</td>
<td>BS 3602-HFS 27</td>
<td>145</td>
<td>104 MN/m² (15100 psi)</td>
<td>104 MN/m² (15100 psi)</td>
<td>Markland-Scowcroft Bolton</td>
</tr>
<tr>
<td>End plate</td>
<td>Carbon steel</td>
<td>ASTM 515 Grade B</td>
<td>145</td>
<td>120 MN/m² (17500 psi)</td>
<td>120 MN/m² (17500 psi)</td>
<td>Barr Thompson Kilmarnock</td>
</tr>
<tr>
<td>Bosses</td>
<td>Carbon steel</td>
<td>BS 971: 1958 EN3B</td>
<td>145</td>
<td>112 MN/m² (16240 psi)</td>
<td>112 MN/m² (16240 psi)</td>
<td>R.G. Brown Warley Worcs.</td>
</tr>
</tbody>
</table>
### Table 1(b): Autoclave Components

<table>
<thead>
<tr>
<th>Bolt Size</th>
<th>Specification</th>
<th>Design Temperature °C</th>
<th>Allowable Design Stress</th>
<th>Bolt Torque</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>1⁄2&quot; UNC x 57 mm</td>
<td>BS 1750 Grade B7A (BS 1506-621 B)</td>
<td>200 max.</td>
<td>193 MN/m² (28000 psi)</td>
<td>15 ft lb</td>
<td>Entwhistle</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>167 MN/m² (24300 psi)</td>
<td></td>
<td>Oldham Lancs.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bolt Size</th>
<th>Specification</th>
<th>Design Temperature °C</th>
<th>Allowable Design Stress</th>
<th>Bolt Torque</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>1⁄2&quot; UNC x 127 mm</td>
<td>BS 1750 Grade B7A (BS 1506-621 B)</td>
<td>200 max.</td>
<td>193 MN/m² (28000 psi)</td>
<td>120 ft lb</td>
<td>Entwhistle</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>167 MN/m² (24300 psi)</td>
<td></td>
<td>Oldham Lancs.</td>
</tr>
</tbody>
</table>

Nuts 1⁄2" UNC and 3⁄8" UNC  
Carbon steel  
BS 1750 Grade 2H  
Entwhistle
<table>
<thead>
<tr>
<th>Flange</th>
<th>Large Weld Neck</th>
<th>Large Slip-on</th>
<th>Small Slip-on</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design pressure °C</td>
<td>770</td>
<td>770</td>
<td>770</td>
</tr>
<tr>
<td>Bolt stress at design temperature kN m⁻²</td>
<td>17084</td>
<td>17084</td>
<td>17084</td>
</tr>
<tr>
<td>Bolt stress at ambient temperature kN m⁻²</td>
<td>19685</td>
<td>19685</td>
<td>19685</td>
</tr>
<tr>
<td>Flange stress at design temperature kN m⁻²</td>
<td>11038</td>
<td>11038</td>
<td>11038</td>
</tr>
<tr>
<td>Flange stress at ambient temperature kN m⁻²</td>
<td>11038</td>
<td>11038</td>
<td>11038</td>
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<tr>
<td>Effective gasket width mm</td>
<td>1.19</td>
<td>1.19</td>
<td>1.57</td>
</tr>
<tr>
<td>Gasket seating load kN m⁻²</td>
<td>7272</td>
<td>7272</td>
<td>70</td>
</tr>
<tr>
<td>Gasket factor</td>
<td>6</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Thickness of hub-small end mm</td>
<td>7.14</td>
<td>114</td>
<td>105</td>
</tr>
<tr>
<td>Thickness of hub-back of flange mm</td>
<td>13.49</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Inside diameter of flange mm</td>
<td>230</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gasket load reaction diameter mm</td>
<td>251</td>
<td>251</td>
<td>124</td>
</tr>
<tr>
<td>Bolt circle diameter mm</td>
<td>298</td>
<td>298</td>
<td>152</td>
</tr>
<tr>
<td>Outside flange diameter mm</td>
<td>343</td>
<td>343</td>
<td>177</td>
</tr>
<tr>
<td>Bolt size - core diameter mm</td>
<td>15.9</td>
<td>15.9</td>
<td>7.57</td>
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<tr>
<td>Bolt load kN</td>
<td>67.2</td>
<td>67.2</td>
<td>0.422</td>
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<tr>
<td>Joint surface compression load kN</td>
<td>60.0</td>
<td>60.0</td>
<td>18.99</td>
</tr>
<tr>
<td>Hydrostatic end force</td>
<td>263</td>
<td>263</td>
<td>62.2</td>
</tr>
<tr>
<td>Number of bolts</td>
<td>16</td>
<td>16</td>
<td>12</td>
</tr>
<tr>
<td>Min. bolt area mm²</td>
<td>19.29</td>
<td>19.29</td>
<td>4.85</td>
</tr>
<tr>
<td>Bending moment kN m</td>
<td>8.687</td>
<td>18.50</td>
<td>1.655</td>
</tr>
<tr>
<td>Bolt pitch correction factor m</td>
<td>0.8947</td>
<td>-</td>
<td>1.011</td>
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<tr>
<td>Flange thickness mm</td>
<td>41.36</td>
<td>52.8</td>
<td>23.88</td>
</tr>
<tr>
<td>Gasket width mm</td>
<td>2.730</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Flange stresses kN m⁻²</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Longitudinal hub stress</td>
<td>12942</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2. Radial flange stress</td>
<td>2455</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3. Tangential flange stress</td>
<td>8713</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4. Max. combined stress</td>
<td>10827</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### Table 3: 'O' Ring Seals Specification

<table>
<thead>
<tr>
<th>Application</th>
<th>Type</th>
<th>Size</th>
<th>Material</th>
<th>Plating Material</th>
<th>Supplier</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top flange</td>
<td>TEC ring seal with coil spring 0-248-CS-1F</td>
<td>3.17 mm (127 mm)</td>
<td>Jacket PTFE spring elgaloy or inconel 750</td>
<td>Neetertech Bognor Regis Sussex</td>
<td>Alternative for lower temperature work</td>
<td></td>
</tr>
<tr>
<td>Centre flange</td>
<td>Advanced products 10000-5-3TC metal seal</td>
<td>2.388 mm (254 mm)</td>
<td>Stainless steel</td>
<td>Neetertech Bognor Regis Sussex</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass/metal seal</td>
<td>ditto 5000-7-3-SPSF 5000-7-3-TC</td>
<td>3.17 mm (127 mm)</td>
<td>Stainless steel</td>
<td>ditto Alternative: Fothergill and Harvey Ltd. Bridgewater, Somerset</td>
<td></td>
<td></td>
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</tbody>
</table>

### Table 4: Details of High Pressure Feedthroughs

<table>
<thead>
<tr>
<th>Application</th>
<th>Type No.</th>
<th>Material</th>
<th>Specification</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heater control and test section thermo-couples</td>
<td>MHGO62-A-4-T</td>
<td>303 Teflon</td>
<td>4 x 0.062&quot; probe diameters ¼&quot; NPT thread</td>
<td>West Instrument Div. Gulton Europe Ltd. Brighton BN2 4JU</td>
</tr>
<tr>
<td>Description</td>
<td>Specification</td>
<td>Remarks</td>
<td>Supplier</td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>----------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------</td>
<td>---------------------------</td>
<td></td>
</tr>
<tr>
<td>Needle valve</td>
<td>20 MN/m² 232°C soft sealing</td>
<td>No.3252G4Y. Stainless steel. Used as stop valve</td>
<td>Clockhouse Eng. and</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3-way ball valve</td>
<td></td>
<td>Instrument Co., New</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14 MN/m² 177°C P.T.F.E. seats</td>
<td>No.7663G4Y. Stainless steel. Switch over valve</td>
<td>George Mellor Ltd.,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas compressor</td>
<td>Burton-Corblin. CP.700. 1 m³/h⁻¹ @ 90 bar inlet P</td>
<td>Ealing, London W13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Relief valve</td>
<td>1¼ BSP. Part No.1507/2</td>
<td>Pressure Control Ltd.,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filter</td>
<td>Miniaturised micro porous filter. Circle seal.</td>
<td>Chessington, Surrey</td>
<td></td>
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<tr>
<td></td>
<td>Pressure reducing valve</td>
<td>4205T.2PP</td>
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</tr>
<tr>
<td></td>
<td>5 µm filter</td>
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<tr>
<td></td>
<td>Solenoid stop valve</td>
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<tr>
<td></td>
<td>Relief valve</td>
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<tr>
<td></td>
<td>Relief valve</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dome loaded regulator</td>
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<tr>
<td></td>
<td>Pressure reducing valve</td>
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<td></td>
<td>Needle valve</td>
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<tr>
<td></td>
<td>Relief valve</td>
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<td></td>
<td>Relief valve</td>
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<tr>
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<td>Bursting disc assembly</td>
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<td></td>
<td>Needle valve</td>
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<td></td>
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<td></td>
<td>Needle valve</td>
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<td></td>
<td>Flowmeter</td>
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<td></td>
<td>25 mm Ball valve</td>
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<td>Fine evacuation valve</td>
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<td></td>
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<td>Mass flowmeter</td>
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<td></td>
<td>Hygrometer</td>
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<tr>
<td>G1 Type A</td>
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<td>Gas cylinder pressure</td>
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<tr>
<td>G2 Type B</td>
<td></td>
<td></td>
<td>Test gas cylinder pressure</td>
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<tr>
<td>G3 Type B</td>
<td></td>
<td></td>
<td>Argon gas cylinder pressure</td>
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<tr>
<td>G4 Type B</td>
<td></td>
<td></td>
<td>Test gas after regulator</td>
<td></td>
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<tr>
<td>G5 Type B</td>
<td></td>
<td></td>
<td>Argon gas after regulator</td>
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</tr>
<tr>
<td>G6 Type C</td>
<td></td>
<td></td>
<td>Dome reference pressure</td>
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</tr>
<tr>
<td>G7 Type C</td>
<td></td>
<td></td>
<td>Autoclave pressure</td>
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<tr>
<td>G8 Type D</td>
<td></td>
<td></td>
<td>Differential pressure</td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td>Pressure Range</td>
<td>Description</td>
<td>Supplier</td>
<td></td>
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<tr>
<td>------</td>
<td>-------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>-------------------------------</td>
<td></td>
</tr>
<tr>
<td>1+1</td>
<td>A 0-20 MN/m² (0-3000 psi)</td>
<td>Sec. IC/13CF.132C Electrical contact required for falling pressure. 150 mm dial blow-out back</td>
<td>Budenburg Gauge Co. Ltd</td>
<td></td>
</tr>
<tr>
<td>3+1</td>
<td>B 0-20 MN/m² (0-3000 psi)</td>
<td>Sec. IC/13CF. Aluminium case, blow-out back. Triplex glass window</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>C 0-7 MN/m² (0-1000 psi)</td>
<td>Sec. IC/11/215. 150 mm dial, Flush mounting. Knife edge pointer. Steel tube 'standard test gauge'.</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>D 137-0-137 kN/m² (20-0-20 psi)</td>
<td>Sec. IC/180 Am 150 mm dial Flush mounting 'Microvar' differential pressure gauge. Double melinex diaphragms. Stainless steel body. Fitted with minimum and maximum electrical contacts adjustable throughout the scale by a removable key</td>
<td>&quot;</td>
<td></td>
</tr>
</tbody>
</table>
Table 7: Details of Thermocouples

<table>
<thead>
<tr>
<th>Use</th>
<th>Number</th>
<th>Type</th>
<th>Specification</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement of gas temperature</td>
<td>8 off</td>
<td>Pt/13% Rh.Pt.</td>
<td>Insulated junction. 1.6 mm dia. inconel sheath. Length 915 mm and 1219 mm. Type A end caps with 6 metres of compensating table to BS 1826</td>
<td>Johnson Matthey Metals Ltd.</td>
</tr>
<tr>
<td>profile</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Furnace control and alarm</td>
<td>4 off</td>
<td>Pt/13% Rh.Pt.</td>
<td>Insulated junction, 1.6 mm diam. 10% Rh.Pt. sheath. Length 610 mm. Type end caps with 6 m of compensating cable to BS 1826</td>
<td>Johnson Matthey</td>
</tr>
<tr>
<td>Permanent temperature monitors</td>
<td>4 off</td>
<td>Chromel/alumel</td>
<td>Insulated junction. 1.5 mm diam. stainless steel sheath. Overall length 3.4 m, route length 3.0 m, tail length 400 mm stranded 7/0076 with ½&quot; BSF externally threaded, crimped seal</td>
<td>Pyrotenax Ltd.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Hebburn-on-Tyne, Co. Durham</td>
</tr>
</tbody>
</table>

N.B. Additional thermocouples in Test Section, and temporary thermocouples used during commissioning are chromel/alumel with above specification, but suitable overall lengths.
<table>
<thead>
<tr>
<th>Item No. on Fig. 7</th>
<th>Unit</th>
<th>Type</th>
<th>Specification</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>12</strong></td>
<td>Flow indicator</td>
<td>Hastings/ Raydist</td>
<td>Mass flow indicator, calibration 0-150 sccm 0/P 5 V d.c. into 2000 Ω Accuracy 1% of range 20% variation of pressure and temperature. Worst case accuracy better than ±2% over whole temperature and pressure range. Linearity ±1/2% of range. Repeatability 1/2% of range</td>
<td>Mechanisms Ltd</td>
</tr>
<tr>
<td><strong>11</strong></td>
<td>Pressure transducer</td>
<td>Bell and Howell 4-366-0102</td>
<td>0-1000 psig Sensitivity 35 mV ±1% o/c of rated excitation at 25°C. Residual unbalance 0 mV ±1% F.R.O. with zero applied pressure at rated excitation and 25°C</td>
<td>Bell and Howell</td>
</tr>
<tr>
<td><strong>11</strong></td>
<td>Transducer controller</td>
<td>Transducers CEL Ltd. MIF 100</td>
<td>Signal 0-50 mV, bridge resistance 40-1000 Ω. Excitation 6-12 Volts d.c. Temperature coefficient 0.002%/°C stability ratio 2000 : 1</td>
<td>Transducers Coutelectronics Ltd.</td>
</tr>
<tr>
<td><strong>11</strong></td>
<td>Alarm Annunciator</td>
<td>Synalarm</td>
<td>Alarm on opening or closing maintained on fleeting contact sequence - alarm, audible and flashing - accept steady light - reset cancels indicator.</td>
<td>Synoptica Ltd.</td>
</tr>
<tr>
<td><strong>13</strong></td>
<td>Hygrometer</td>
<td>Electrolytic</td>
<td>0 - 1000 ppm</td>
<td>S.E.I. Ltd.</td>
</tr>
<tr>
<td><strong>13</strong></td>
<td>Vacuum gauge on manifold</td>
<td>Pirani</td>
<td>1 bar to 10 N m^{-2}</td>
<td>Edwards High Vacuum Ltd.</td>
</tr>
<tr>
<td><strong>13</strong></td>
<td>Vacuum gauge on storage vessels</td>
<td>Thermocouple</td>
<td>1 bar to 10 N m^{-2}</td>
<td>Edward High Vacuum Ltd.</td>
</tr>
<tr>
<td><strong>13</strong></td>
<td>Oxygen Meter</td>
<td>Engelhard Type Mark II</td>
<td>1 vppm - 100 vppm type</td>
<td>Engelhard</td>
</tr>
</tbody>
</table>

* not indicated on fig 7, used at any of gas sampling points or exit lines.
<table>
<thead>
<tr>
<th>Unit</th>
<th>Type</th>
<th>Specification</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>DHS</td>
<td>Three term controller with 1/P for 1 mV. Internal C.J. compensation for Pt/13% Rh.Pt.</td>
<td>Eurotherm Ltd.</td>
</tr>
<tr>
<td>controller</td>
<td></td>
<td>0-5 V d.c. 0/P</td>
<td></td>
</tr>
<tr>
<td>(with alarm</td>
<td></td>
<td>2-12 mV 1/P</td>
<td></td>
</tr>
<tr>
<td>contacts)</td>
<td></td>
<td>Temperature coefficient 0.01% /°C of span. Long term drift &lt;10 μV.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Set point resolution of 1 μV</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Off limits alarm.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Contact closure adjustable over range of 1-10% of span above and below the set point</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1/P B.S. Pt 13% Rh.Pt.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0-1200°C</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>017</td>
<td>1/P 5 V d.c.</td>
<td></td>
</tr>
<tr>
<td>alarm</td>
<td>(less</td>
<td>Three O/P's fast cycling pulses proportional to input and front panel controls</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O/P</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>board</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Driver (3-</td>
<td>028</td>
<td></td>
<td></td>
</tr>
<tr>
<td>zone)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Input fast cycling pulses</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0/P 15 A.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Option with ammeters.</td>
<td></td>
</tr>
<tr>
<td>Thyristor</td>
<td>031</td>
<td></td>
<td></td>
</tr>
<tr>
<td>stacks</td>
<td></td>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>
Table 10: Details of Electrical Valve Interlocks

(a) Interlocks as Originally Wired

<table>
<thead>
<tr>
<th>Valve</th>
<th>Interlocked With</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASV7</td>
<td>PRV1 (Item 12 on Fig 7) (ASV6 (ASV4 (ASV8 (SV1 (SV3 (SV5 (SV7</td>
<td>PRV1 must be closed before gas is applied to the system. Gas must be admitted to both sides of vessel, therefore ASV7 must be opened in conjunction with ASV6 or ASV4 and ASV8. To admit gas to B all valves must be opened at the same time as ASV7.</td>
</tr>
<tr>
<td>ASV4</td>
<td>ASV8</td>
<td>These valves must operate together to make a complete circuit.</td>
</tr>
<tr>
<td>SV1</td>
<td>(SV2 (SV3 (SV4</td>
<td>All 4 valves operate together.</td>
</tr>
</tbody>
</table>

(b) Proposed Modification to Interlocks for Independent Operation

<table>
<thead>
<tr>
<th>Valve</th>
<th>Interlocked With</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASV7</td>
<td>PRV1</td>
<td>As above.</td>
</tr>
<tr>
<td></td>
<td>ASV4, 6 and 8</td>
<td>As above.</td>
</tr>
<tr>
<td></td>
<td>ASV9 and ASV10</td>
<td>To admit gas to the inner vessel, one of the two valves must be opened with ASV7.</td>
</tr>
<tr>
<td></td>
<td>ASV1, 2 and 3</td>
<td>These valves should be shut with ASV7, i.e. when the rig is depressurised. If, then, the autoclave is evacuated, ingress of air cannot occur.</td>
</tr>
<tr>
<td></td>
<td>ASV additional</td>
<td>The additional valve in the test gas line, used to prevent leakage across the seat of the DLPR during evacuation, must be opened with ASV7 to admit gas to the vessel.</td>
</tr>
</tbody>
</table>
PLATE 1 GENERAL ARRANGEMENT OF THE AUTOCLAVE RIG

PLATE 2 DETAIL OF THE AUTOCLAVE TOPS AND BACK PANELS. THE TEMPERATURE TEST SECTION IS FITTED IN THE LEFT-HAND AUTOCLAVE; THE SPECIMEN HOLDER LIFTING FRAME IS IN POSITION ON THE RIGHT-HAND AUTOCLAVE. THE CIRCULAR PLATE, ATTACHED TO THE AUTOCLAVE FOR LIFTING OPERATIONS, IS SHOWN SUSPENDED FROM THE OVERHEAD BEAM.
PLATE 3  THE HEATER WOUND ON THE SILICA TUBE FORMER.  
(N.B. ELASTIC BANDS HOLD THE WINDINGS IN PLACE IN THIS PHOTOGRAPH)
PLATE 4  THE COMPLETE MIMIC CONTROL DIAGRAM FOR THE FIVE AUTOCLAVES
THE PART SHOWN IN FIG. 7 HAS SOME LATER MODIFICATIONS
FIG. 5 AN AUTOCLAVE LID MODIFIED TO TAKE THERMOCOUPLE FEEDTHROUGHS FOR ADDITIONAL MONITORING OF THE REACTION ZONE TEMPERATURE
FIG. 2 THE SYSTEM FOR ADMITTING TEST GAS TO THE VERTICAL GLASS INLET TUBE
(SEE SECTION 3.1)
FIG. 1 CUTAWAY DRAWING OF THE AUTOCLAVE, WITH GAS INLET AND EXIT AND VACUUM MANIFOLD PIPES OMITTED.
Fig. 4 The heater wound on the silica former; see also Plate 3. The heater wound on the ceramic former has a similar basic construction and containment.
FIG. 3 THE 'O'-RING AND CLAMPING ARRANGEMENTS FOR SEALING THE GLASS REACTION VESSEL TO THE LOWER FLANGE OF THE AUTOCLAVE TOP-SECTION, (SEE SECTION 3.2)
FIG. 6 THE SAMPLE HOLDER ASSEMBLY LIFTING FRAME.
SECTION THROUGH SAMPLE HOLDING ASSEMBLY

SUSPENSION STIRRUP

HOOK ASSEMBLY

LOCKING NUT

STAINLESS STEEL SUPPORT ROD

GAS BAFFLE PLATES

SILICA SPACERS (FLANGED TO SUPPORT PLATES)

SAMPLE HOLDING PLATES

PLAN OF SAMPLE HOLDING PLATE (ACTUAL SIZE)

CUT-OUTS FOR THERMOCOUPLES AND GAS INLET TUBE

FIG. 5 THE SAMPLE HOLDER ASSEMBLY AND THE CUT-OUTS OF A TYPICAL SAMPLE BUCKET HOLDING PLATE
FIG. 8 THE HEATER CONTROL CIRCUIT
FIG. 10 THE TEST SECTION USED FOR SETTING-UP AND CHECKING THE TEMPERATURE PROFILE IN THE REACTION VESSEL.
FIG. 9 LOGIC DIAGRAM OF THE ALARM SYSTEM
FIG. 12 A TYPICAL LINEAR TEMPERATURE PROFILE OBTAINED AT 650°C AND 600 p.s.i. (40 BARS)
FIG. 11  TEMPERATURE PROFILE CURVES AT DIFFERENT PRESSURES, FOR A LINEAR SETTING AT ATMOSPHERIC PRESSURE. THE TEMPERATURES IN BRACKETS INDICATE THE MAXIMUM WALL TEMPERATURES OBSERVED.
FIG. 13 REACTION VESSEL AND OUTER WALL TEMPERATURE PROFILES FOR OPERATING CONDITIONS CLOSE TO THE MAXIMUM RATING,

\[ T = 935^\circ C, \quad p = 600 \text{ p.s.i. (40 BARS)} \]
<table>
<thead>
<tr>
<th>Outage No.</th>
<th>CDAPS TIME</th>
<th>DATE</th>
<th>TIME</th>
<th>CUMULATIVE TIME</th>
<th>WEIGHT</th>
<th>WEIGHT GAIN</th>
<th>ΔW/A</th>
<th>COMMENT</th>
</tr>
</thead>
</table>

INITIAL SAMPLE WEIGHT: [IAL SAMPLE WEIGHT]

INITIAL WT of SPECIMEN (incl. bucket): [INITIAL WT]
### Fig. 14: Specimen Record Card (reduced from A4)

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Time of Run</th>
<th>Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Start Date</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flow Rate</th>
<th>Total Pressure</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gas Composition</th>
<th>Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Specimen Details (Form, Dimensions, Etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Specimen Details (Form, Dimensions, Etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Details of Subsequent Examination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run Objective</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>General Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>General Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

---

**Surface Preparation**

**Details of Subsequent Examination**

**Run Objective**

**General Notes**
Conventional high pressure autoclaves for gas/solid interaction work usually consist of a cylindrical steel pressure vessel and a single winding external heater. Such a simplified system has a number of disadvantages. With large volume vessels and low gas flow rates, the residence time of the test gas in the autoclaves can be several hours. Consequently the autoclave walls, which will be at an elevated temperature because they are in contact with the heater windings, can react with the test gas and may significantly alter its composition. Solid reaction products spalling from the walls may contaminate the specimens. Furthermore, single-zone heaters tend to introduce severe temperature gradients throughout the autoclave making it difficult to define precisely the temperature at any point, or to obtain an adequate reaction volume at a uniform temperature.

A new autoclave is described, that has many novel features, and in which all these problems have been overcome (Fig. 1). It consists of an outer steel pressure vessel sealed at the bottom and terminating at the top with a flange. A "top-hat" assembly fits to this flange, sealed with teflon coated O-ring, and is itself closed with a blanking plate. Access to the test region is through this plate.

The cylindrical silica reaction vessel is bolted to the underside of the top section. The buttress end of the silica is ground to a flange configuration, which in our prototype is 5 mm deep to take a mild steel clamping ring located 18 mm from the flange face (Fig. 2). Heat resistant packing (Walkerite) is used to prevent metal/glass contact. Expansion of the mild steel clamping bolts at operating temperature is minimised by means of stainless steel spacers placed under the bolt heads. To obtain a high pressure and high vacuum seal at the silica/metal interface it is necessary to grind and polish the glass to an optical quality finish, which is normally don on the buttress end before it is faced to the rest of the silica vessel. This flange-type clamping arrangement can withstand a pressure in excess of three times that required for sealing. A silver or PTFE coated stainless steel O-ring is used for the actual seal.

Access to the heater and outer autoclave vessel is achieved by removing the 'top-hat' section and silica vessel in one piece. A three-zone heater is used to ensure a 30 cm long uniform temperature zone in the centre of the autoclave. It is wound onto a silica or ceramic former which is held in a 26 gauge stainless steel can made a close fit to the autoclave walls. The inside of the can walls are covered with a 25 µm aluminium foil heat reflector. All available empty space in the can is fitted with insulation material.

An important feature of the design is that the control thermocouple, heater electrical feedthroughs, and the pressure relief valve are located in the main autoclave wall. Also the gas inlet, gas outlet and vacuum manifold connections are in the 'top-hat' section. Thus, under normal operating conditions, no external connections to the autoclaves are disturbed when specimens are removed.
A MODULAR GAS-BALANCED HIGH PRESSURE AUTOCLAVE

Inventors:

Dr. M.P. Hill  
A.M. Emsley  
B.W. Vine  
Central Electricity Research Laboratories  
Kelvin Avenue  
Leatherhead  
Surrey

Summary:

A high pressure autoclave, that has several novel design features, is described. Test specimens are held in an inner vessel made of a chemically inert material, e.g. silica, thus eliminating spurious side reactions that could alter the test gas composition. An automatic gas balancing system is used to prevent the inner reaction vessel rupturing under excessive differential pressures. The autoclave is of modular construction simplifying replacement of any component or modification of the specimen holding arrangements. It has been designed to work at 650 lb/in² pressure and 1000°C and to have a uniform temperature zone for the test specimens of 30 cm in a reaction vessel of 10 cm diameter.

March 1975
The gas is taken to the bottom of the reaction vessel through a silica tube for preheating. The tube is held at the top in a PTFE collar which itself is part of a PTFE sealed demountable "Banjo" joint, the complete arrangement being shown in Fig. 3. The tube must be removed from the PTFE collar when the specimen rack is manipulated.

A 'cakestand' type assembly is used to hold specimens (Fig. 4). It consists of a stack of silica plates separated by removable silica flanged spacers, the whole assembly being mounted on a central stainless steel rod. The rod terminates in a steel frame that rests on the edges of the uppermost flange of the top section such that the entire specimen assembly hangs within the reaction volume. Sample holding plates have holes to accommodate ultra-thin wall silica buckets containing test specimens, and in addition there are cut-outs to accommodate the gas inlet and thermocouple tubes. The assembly also carries blank plates at both top and bottom to act as gas baffles, as shown in Fig. 4. Holes and cut-outs in the silica plates are prepared by ultrasonic machining. The rack is moved in and out of the autoclave with the aid of the lifting winch shown in Fig. 4. The lower flange of the lifting frame engages with the uppermost autoclave 'top-hat' flange and ensures that the specimen rack is aligned vertically during lifting and lowering operations. It also operates in conjunction with a set of vacuum vessels and so permits the direct transfer of the specimens and rack to storage.

An important feature of the specimen rack is that it is completely demountable. Any arrangement or spacing of specimen holding or gas baffle plates is possible. Hence the specimens can be positioned easily in the uniform temperature zone. Plates can be omitted from the stack to enable extra large specimens to be accommodated, which can be hung in the reaction vessel if required. The central metal support rod is completely sheathed in silica in the high temperature region of the autoclave.

To extend heater life, a chemically inert gas is used to balance the pressure across the silica reaction vessel. Precise pressure balance is achieved with pairs of gas-controlled, dome-loaded pressure control valves and back pressure regulators. The complete system for pressure balancing, control, and alarm condition indications is discussed in a separate report.

The approximate dimensions of the prototype are as follows. Heater length = 66 cm; uniform temperature zone = 30 cm; reaction vessel and specimen entry flange diameter = 10 cm; overall height of the autoclave = 150 cm; overall inside diameter excluding flanges, inlet bosses and feedthroughs, etc. = 23 cm; length of 'top-hat' section = 50 cm; main flange diameter = 34 cm.

A description of the complete system including control arrangements and circuitry, component specification, and performance characteristics is available from the authors.
CENTRAL ELECTRICITY GENERATING BOARD

STAINLESS STEEL SPACER

CLAMPING BOLT

FIGURE 2
PLAN OF SAMPLE HOLDING PLATE

SECTION THROUGH SAMPLE HOLDING 'CAKESTAND' ASSEMBLY

FIGURE 4