

OXIDATION OF FE CR AL ALLOYS IN SIMULATED COAL

GASIFIER ATMOSPHERES AT ~~H₂-H₂O~~

550-1050°C.

THESIS PRESENTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

by

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ABSTRACT

A number of yttrium oxide dispersion strengthened, mechanically alloyed FeCrAl alloys in the range Fe 16-25Cr 4-6.5Al have been studied in simulated coal gasifier atmospheres with pO_2 1.5×10^{-18} to 1.4×10^{-14} atm, pS_2 3.4×10^{-8} to 1.5×10^{-4} atm. from 1123 to 1323K. A carbon and nitrogen potential was also established in the atmosphere. The effect of a preformed oxide scale on the sulphidation kinetics was examined in some cases.

Two distinct types of corrosion have been identified.

In atmospheres with pS_2 up to 3.4×10^{-8} atm. at 1123K, 3.9×10^{-5} atm. at 1223K and 1.5×10^{-4} atm. at 1323K, thin adherent alpha alumina scales were formed. The scales grew slowly and the growth kinetics showed a slight negative deviation from parabolic behaviour.

Atmospheres with pS_2 7.3×10^{-7} atm. at 1123K and 3.9×10^{-5} atm. at 1223K caused severe sulphidation. A duplex scale consisting of a pyrrhotite $Fe(1-x)S$ outer layer covering a multiphase sulphospinel inner layer was formed. Diffusion through the inner layer is rate determining. After a period of parabolic kinetics a negative deviation occurs; this is due to the formation of alumina 'laths' in the inner layer which reduce the cross section for outward cation diffusion. Some porosity was also observed in the scales.

Oxide layers formed at 1100°C in air were shown to retard the onset of sulphidation by up to 500h. The preformed oxide layers broke down in all specimens exposed to pS_2 8.1×10^{-6} atm. at 1123K within 1500h.

PREFACE

I would like to express my gratitude to all those who have helped and advised during the course of this work. Particular thanks is due to my supervisor, Dr M G Hocking, for his advice and suggestions throughout the project. Also to Dr V Vasantasree and Dr P S Sidky for helpful discussion and amicable assistance.

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Considerable appreciation is due to Mrs D Cook for typing the manuscript.

During the course of this work one paper was presented and published: "An Evaluation of FeCrAl Alloys in Simulated Coal Gasifier Environments from 850-1050°C" at "High Temperature Alloys - Their Exploitable Potential", Petten, The Netherlands, October 1985.

One poster, "The Effects of Preoxidation on the Behaviour of MA956 and Related Alloys in a Simulated Coal Gasifier Atmosphere at 850°C" was displayed at "High Temperature Corrosion of Superalloys", The Royal Society, London, February 1986.

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CHAPTER I

INTRODUCTION

1 Introduction

(a) General

World demand for energy and chemical feedstock is continually increasing. Traditional resources are becoming depleted and increasingly expensive to recover.

The major fuels are coal, oil and natural gas; coal has the largest estimated reserves of about 8×10^{10} tonnes (Bishop and Maitlis (1983), Wilson (1977)). Much of this coal is of low rank or high ($> 2\%$) sulphur content, and it is unsuitable for conventional combustion systems. A method of utilising this coal is to gasify it; the gaseous products are suitable for a variety of applications.

(b) Gasification - a Brief Outline

Commercial gasification of coal started with water gas production in the mid 19th century (Skinner (1980)); this was developed sporadically until the 1950s when it was a major source of synthesis gas ($\text{CO} + \text{H}_2$). Today coal gasification is again being considered.

Conversion of coal to substitute natural gas (mainly CH_4) has the advantage that existing distribution and utilisation equipment is suitable (Stringer (1984), Cooke et al (1978)). Combined cycle electricity generation from coal via a gasification step offers a potentially large increase in overall efficiency (Lloyd (1983)).

The major remaining technical problem is availability of economically viable material for construction of commercial scale gasifiers.

(c) The Chemical Nature of Coal

Coal has formed by the action of heat and pressure on vegetable matter over a period of about 300 million years - coalification. During this time the original carbohydrates have been converted to hydrocarbons and finally to carbon. Table 1 (Sharman et al (1982)) shows the ultimate analysis of a number of coals which are suitable for gasification.

Coal Type	^w / _o	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur	Chlorine
Frances Scottish		83.0	5.5	9.2	1.4	0.5	0.4
Rossington English		83.5	4.9	7.7	1.7	1.7	0.5
Ohio 9 USA		79.6	6.1	7.4	1.2	5.6	0.1
Pittsburgh USA		83.7	5.7	6.9	1.6	2.0	0.1
Manton English		85.1	5.1	5.5	1.6	2.3	0.4
Markham English		83.5	4.6	8.0	1.8	1.6	0.5

Table 1

Ultimate Analysis of Various British and American Coals
Which are Suitable for Gasification (Sharman et al, 1982)

For gasification the most important components of the coal are carbon and to a lesser extent heavy hydrocarbons which are thermally cracked to give gaseous fractions.

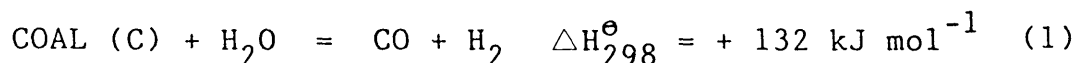
Most coal contains sulphur, mainly as sulphides formed by the reduction of sulphates during coalification. European coals are generally below 2%, some American varieties are over 5% sulphur which is undesirable and considerably reduces their market value.

Chlorine, if present, is usually as organic compounds and is released at low temperature as hydrogen chloride (Gibb (1983)).

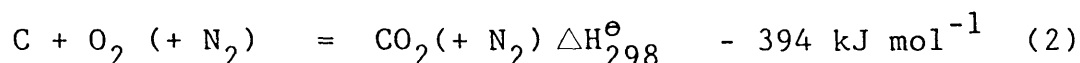
Coal contains 5-10 wt% ash. This is inorganic material, such as silicates, which are laid down with the coal. It does not participate in the gasification reactions and is rejected as a waste product from the reactor.

(d) Conditions in a Gasifier

The most significant gasification reactions is:



because this reaction is endothermic a source of heat is needed. Most reactors under development are of the autothermal type; heat is generated by the oxidation of carbon and hydrocarbons by air or oxygen.



Reactions 1 and 2 are generally run simultaneously.

Nitrogen, present in air, acts as a diluent, this is acceptable in combined cycle power generation systems where the sensible heat can be recovered. If fuel gas production is envisaged it is preferable to use oxygen to fire the reaction.

A large number of minor reactions may occur in a reactor, these produce compounds such as H_2S , CS_2 , COS and NH_3 . Most of the sulphur content of the coal ends up as H_2S in the reducing atmosphere present in gasifiers, this is the sulphidising agent considered in this work.

It is convenient to describe the chemical conditions in

System	Operating Pressure/atm	Operating Temperature/K	Oxygen Pressure/atm	Sulphur Pressure/atm	Carbon Activity	Source
FB	1	1123	10^{-18}	3×10^{-9}		Lloyd (1983)
Texaco	1	1144	10^{-17}	10^{-5}		Perkins (1980)
Texaco	80	1144	10^{-16}	10^{-6}		
MPC	65	1144	10^{-15}	2×10^{-6}	3×10^{-3}	Douglass(1981)
	1	1023	$10^{-23} - 10^{-30}$	4×10^{-8}		Stott (1983)
	1	1123	10^{-14}	6×10^{-7}		Lloyd (1983)
	1	1123	2×10^{-18}	4×10^{-5}		Sidky (1984)

Table 2
Some Representative Atmospheres Found in Coal Gasifier
Systems or Used in Laboratory Tests

a gasifier in terms of temperature and activity or partial pressure of particular species (Kane (1980)). A very wide range of values of pO_2 , pS_2 & T is quoted by workers in this area, some of these are given in Table 2. Variation in coal composition and process account for this range.

Physical conditions in a gasifier are severe. Hot, abrasive particles of coal and ash will contact the reactor vessel. Some systems operate at elevated pressure and/or at temperatures above the fusion point of the ash ($>1800^{\circ}\text{C}$). Thermal cycling of the system will occur during start up and shut down periods. Suitable materials must be able to operate for long periods in these conditions without requiring major maintenance or replacement.

The concept of using iron-based alumina forming alloys in sulphidising environments was put forward by Setterlund and Prescott (1961).

(2) High Temperature Alloys

- (a) The alloys considered in this work are designed to maintain good mechanical properties at high temperature whilst resisting oxidation in industrial environments.

The commercially available alloy, MA956, was developed as a material for jet engine combustion chambers (Lovett, (1983) but has subsequently been shown to possess good oxidation resistance in other high temperature applications. Kane (1983) detected almost no weight change after 504h exposure to air/5% H_2O at 1100°C . The alloy also shown good cyclic oxidation resistance when exposed to an H_2 /45% CO_2 /1% H_2S mixture at 980°C .

These alloys form alumina protective scales on exposure to oxidising atmospheres. The use of an iron rather than a nickel base prevents the problem of low melting point nickel/nickel sulphide eutectic formation during exposure to sulphidising atmosphere.

(b) Alloy Composition

Manufacturer's Code	Laboratory Code	Cr	Al	Y ₂ O ₃	Ti	Ni	Other
ABB00 49	A	23.50	4.41	0.50	0.34	0.16	Balance
ABB00 50	B	20.23	3.16	0.50	0.25	0.17	iron in
ABB00 51	C	16.04	4.36	0.50	0.27	0.20	all alloys
ABB00 52	D	24.73	6.58	0.50	0.42	0.16	
ABB00 57	E	19.40	4.61	0.49	0.06	0.07	0.82 Ta
ABB00 67	F	20.07	4.36	0.49	0.36	0.12	
ZG00 57	G	19.30	4.30	0.52	0.36	0.13	
ABB00 58	H	19.42	4.68	0.49	0.01	0.07	1.40 Ta
ABB00 59	I	19.52	4.65	0.49	0.01	0.06	1.88 Ta
ABB00 60	J	19.85	4.37	0.91	0.30	0.13	
ABB00 61	K	19.88	4.42	0.49	0.35	4.17	
	MA956	20.00	4.50	0.5	0.5	—	

Table 3
Composition (weight %) of Alloys Supplied by Incomap UK Ltd

The composition of alloys used are given in Table 3.

- (i) Yttrium oxide: this is added to improve the mechanical properties of the alloy particularly its creep resistance. A second major beneficial effect is an improvement in scale properties, see section (d).
- (ii) Chromium imparts strength and aids the rapid formation of an alumina layer during oxidation.
- (iii) Aluminium is selectively oxidised to form an alumina protective scale.
- (iv) Titanium is added to improve processing characteristics, it acts as a getter for nitrogen present during milling, it is not intended to participate in the corrosion behaviour of the alloy (White (1985)).
- (v) An iron base alloy has specific advantages over nickel in sulphidising applications. It is also a more economic alternative to nickel or cobalt.

Three of the pilot alloys contain tantalum, this has been shown to be beneficial by maintaining the oxide dispersion during welding operations (Hack, (1985)).

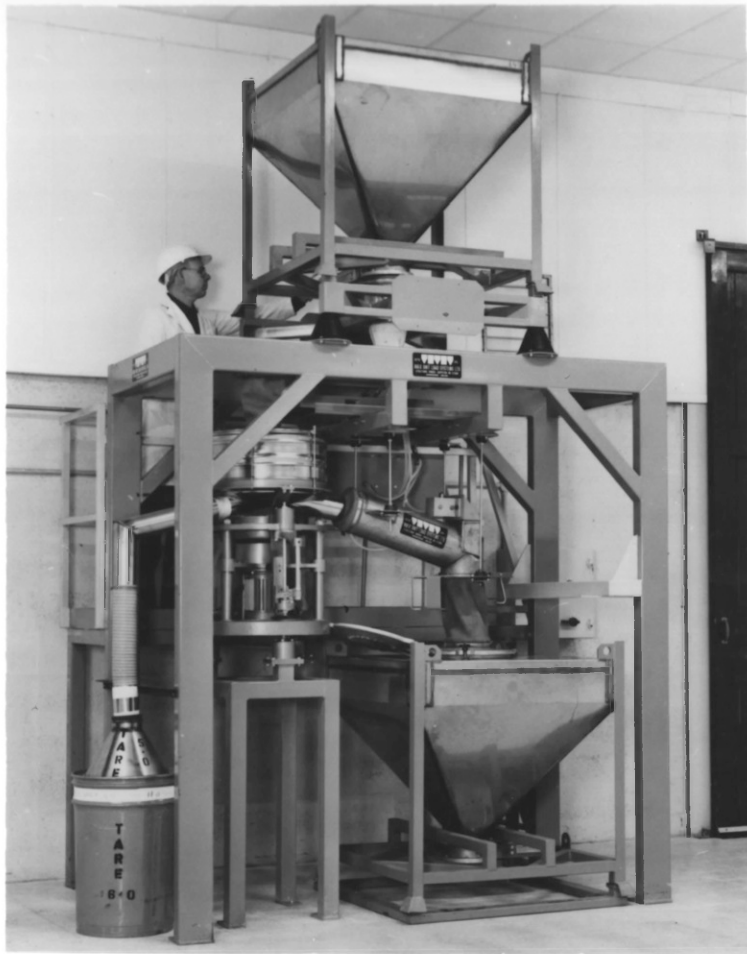
One of the alloys has some nickel present to determine whether this adversely affects the sulphidation behaviour at these levels.

(c) Alloy Manufacture

Alloying of these elements is achieved by a mechanical alloying method, this was first proposed by Benjamin (1970)..

The alloy components are mixed as sized powder in a mill containing approximately a 10:1 weight ratio of steel balls to powder Plate 1. No surface active agent is added to the mill. it is sealed with the air remaining in it and run at 40-50 rpm for about 24h.

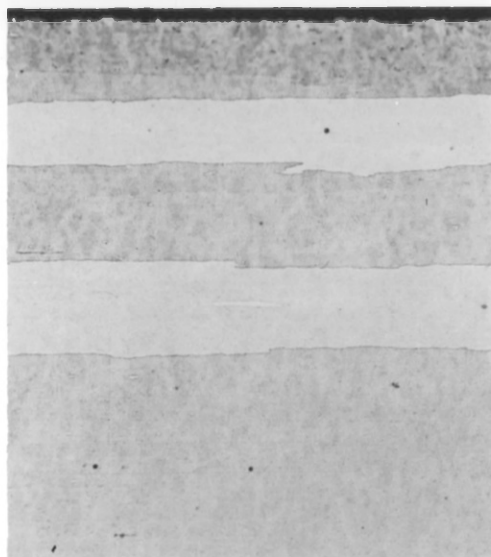
During milling the balls become coated with a layer of compacted alloy components, this layer undergoes continuous deformation and impaction which causes new material to pressure weld into it; the outer surface work hardens and flakes off. After a suitable time a homogeneous



Powder sizing sieve at Incomap plant,
Wednesbury, West Midlands



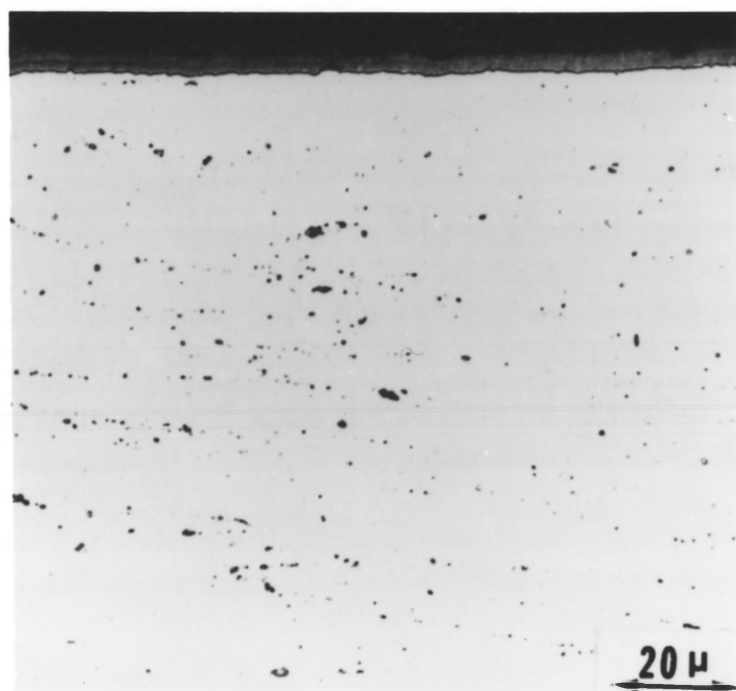
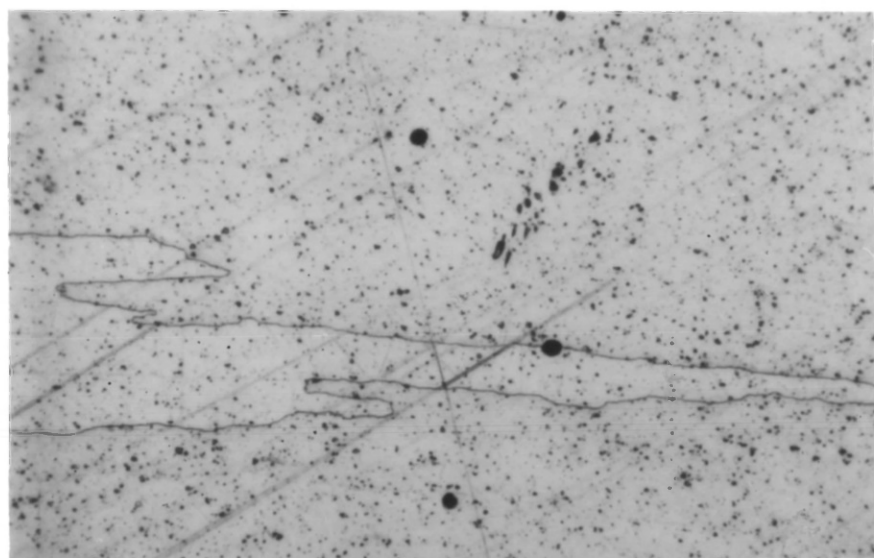
High energy ball mill used to produce
mechanical alloys at the Wednesbury plant



a) Microstructure of MA956,
etched glyceric

X70

X125



b) Al_2O_3 substrate interface morphology of FeCrAl
containing a dispersion of alumina (Tien & Pettit [1972]).

powder of alloy is produced. The powder is canned in mild steel cylinders and hot extruded to produce rolling or forging billets.

The material used in this work is in the form of rolled and annealed sheet 0.7 to 1.55mm thick. The grain structure is large pancake-shaped grains lying in the plane of the sheet, Plate 2 shows the microstructure of MA956.

(d) The Effects of Active Element Additions

- (i) This phenomenon is frequently referred to as the 'rare earth effect', though it is not exclusively confined to these elements. The most important properties of a high temperature service alloy are that it forms an adherant, slow forming scale which maintains good contact with the underlying metal. Chromia or alumina scales are most commonly employed; the latter is of relevance to the present work.

Improved scale adherence was first noted by Pfeil (1937), it was subsequently found that small (0.01 - 0.5 wt%) additions of various rare earth elements, notably Y and Sc, to Ni 20Cr alloys produced a marked increase in service life especially when subjected to thermal cycling.

Whittle and Stringer (1980) have reviewed the earlier work on alumina forming alloys. The general effects of additions are an improved degree of contact between the scale and substrate, a shorter time to produce a complete covering of protective oxide (ie a reduction in the transient oxidation time), a reduction in the level of alloying element required to produce a protective oxide, and in some cases the formation of inward-growing protrusions or pegs. Similar effects are reported regardless of the method of doping - whether with a metallic or finely dispersed metallic oxide addition. This is not surprising since the additions used usually form very stable oxides (eg $2Y + \frac{3}{2} O_2 = Y_2O_3$ pO_2 1273K $\sim 10^{-45}$ atm), and would internally oxidise before any of the major alloy components.

Additions have been made by various means such as melt

additives, dispersions of oxides via a powder metallurgy route or by coatings which decompose to produce surface oxides.

- (ii) The first mechanism proposed by Pfeiffer (1957) suggests that a layer of compound oxide, with a thermal expansion coefficient intermediate between the oxide scale and substrate, forms and compensates for the thermal stresses. No evidence is offered in support of this.

It has been suggested that doping increases scale plasticity (Antill and Peakall (1967), Francis and Jutson (1968)). Scale deformation at the temperatures of interest would occur by grain boundary sliding, this would be aided by the presence of more smaller grains rather than fewer larger ones. Stott et al (1983) and Ramanarayanan et al (1984 b) showed that the presence of yttrium in FeCrAl alloys promoted formation of larger columnar oxide grains rather than the finer equiaxed ones found in undoped material. Also grain boundary sliding would be favoured in pure rather than two phase scales; Ramanarayanan et al (1984 a) found that in MA956 additions were present in the scale as garnets and mixed oxides, often crossing grain boundaries, this would be a further barrier to slip.

A modification of scale growth processes has been proposed. Marker experiments have shown that alumina grows largely by inward diffusion of oxygen, mainly by short circuit paths (Kingery and Oishi 1960). Golightly et al (1976 & 1980) suggest that scale growth is not exclusively by this route but that some Al^{3+} diffuses out and reacts at grain boundaries to form alumina; this intrascale alumina formation produces high compressive stresses which cause the scale convolution observed on undoped alloys. It is suggested that the dopant suppresses the migration of Al^{3+} and hence intrascale oxidation. Anderson et al (1985) have calculated the energies for diffusion of Al^{3+} and Y^{3+} cations through the oxide lattice and conclude that yttrium is likely to build up at the scale metal interface and block diffusion

paths for aluminium - this would result in a slight reduction in scale growth rate and lower growth stresses in the scale; this is consistent with the observations.

Giggins and Pettit (1975) bent oxidised samples of CoCrAl and CoCrAlY, far less scale detachment occurred from the doped sample; suggesting that there is a real improvement in scale adhesion as well as any reduction in growth stresses. This is further reinforced by the generally reported improvement in spalling resistance where the stresses produced by differences in thermal expansion would be very high:

$$\bar{\sigma}_{ox} = \frac{E_{sub} \times E_{ox}}{E_{sub} + 2 E_{ox} \frac{t_{ox}}{t_{sub}}} T(\alpha_{sub} - \alpha_{ox}) \quad (3)$$

Oxx (1958)

ox = oxide, sub = substrate

$\bar{\sigma}$ = stress

E = Young's modulus

α = thermal expansion coefficient

T = temperature change

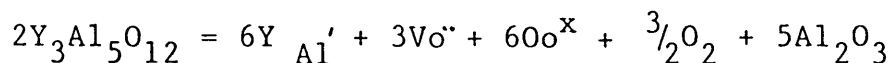
t = thickness

For a 1mm thick sheet specimen with 5 μ m of aluminium oxide on it the stress created in the oxide by cooling through 1000°C would be 2.8 GPa compressive.

Anderson et al (1985) also suggest that the presence of an yttrium rich region at the oxide/metal interface will increase the bond strength in this region, Tien and Pettit (1972) however noted that a dispersion of alumina in an alumina former also produced a high degree of oxide adherence, see Plate 2b.

Other workers Allam et al (1978), Ramanarayanan et al (1981b) as well as Tien and Pettit note that the absence of voids between the scale and metal, it is suggested that these voids form due to vacancy condensation at asperities such as polishing marks, the presence of a dopant provides preferential sites for this to occur. The problem is to find a source of vacancies, some would be present during the transient stage when elements such as Fe and Ni

were oxidising , but alumina formation would not be expected to produce vacancies, unless some p-type behavior were to occur, this is not commented on in the literature. Ramanarayanan et al (1984 a) suggest a mechanism for vacancy formation in an Y doped alloy - an $Y_3Al_5O_{12}$ garnet forms and is in equilibrium with Al_2O_3 in the scale:



oxygen vacancies formed are balanced by aluminium vacancies which condense out as grain boundary microvoids.

Allam et al (1978) examined the effects of Hf additions to Co 10Cr 11Al and concluded that the improvements in properties were due to a reduction in void formation and the presence of alumina protrusions into the matrix of the alloy. Lustman (1950) first proposed a pegging theory to explain improved adherence. Pegs have been reported by a number of workers, generally they consist of the scale material with a quantity of the dopant present, it has been suggested that optimising the distribution of dopant could further improve scale properties. Pendse and Stringer (1985) using cast Co 10Cr 11Al 1Y or Hf find that Y, because it is in excess of its solid solubility limit segregates to grain boundaries, this may be undesirable because a network of internal oxides build up causing rapid loss of section. Hf remains in solid solution and does not cause this to happen. They conclude that pegs are responsible for the improvements in adherence.

Although the peg theory has extensive support a number of investigators comment on the absence of pegs despite considerable improvement in scale adherence:- Tien and Pettit (1972) report no pegs in FeCrAl.01Y and pegs which are overgrown by oxide in FeCrAlSc. Ramanarayanan et al do not report pegs on MA956 (1984 a) or FeCrAlY (1984 b). The present author has not found any evidence of pegs on mechanically alloyed Y_2O_3 dispersion strengthened FeCrAls.

Funkenbusch et al (1985) propose that traces of sulphur, present in the alloy as an impurity, segregate to the

oxide/metal interface and weaken the bond between them. They have profiled a scale in an Auger electron spectrometer and shown a large reduction in the oxide/metal interface sulphur concentration in the presence of an addition. The effect is explained as either .

(i) gettering of sulphur ($2Y + \frac{3}{2}S = Y_2S_3$ is very thermodynamically favoured) in the case of elemental additions.

or (ii) an increased oxide/metal surface area to which sulphur can segregate in the case of an oxide disperation, hence the concentration is reduced.

No single theory is conclusively proved by the evidence available. The common elements of the effect ie improved scale metal contact, small reduction in scaling rate constant, change in morphology of scale metal interface, suggest that an improved bond exists between the scale and metal.

The sulphur gettering theory may fit this, also the improvement in scale properties reported by Tien and Pettit using Al_2O_3 to dope an alumina former is broadly in agreement with Funkenbusch et al (1985), an added benefit of a rare earth addition may be the reduction in scale growth rate as well as an improvement in scale adherence, Tien and Pettit do not state whether or not sub-micron alumina additions reduce the alumina growth rate - it would be unlikely that it would change. A reduction in Al^{3+} diffusion due to a rare earth being present as suggested by Anderson et al (1985) would be consistant with this.

The two theories together could explain the experimental findings put forward.

(e) The Effects of Preformed Oxide Films

(i) Introduction

Protection in the alloys considered in this work is afforded by the presence of a thin (1-5 μ m) layer of alpha-alumina. Although alumina is thermodynamically stable (dissociation $pO_2 - 10^{-40}$ atm. at 850°C) in almost all atmospheres, protective scaling may not occur spontaneously

in multicomponent gas mixtures.

If a layer of alumina is preformed by treatment in a high pO_2 (eg air) atmosphere the film formed has an effect similar to a coating, it provides a barrier to reactants which can significantly increase the time to onset of sulphidation. The delay period is often referred to as an incubation period.

(ii) Related Work

The diffusion barrier produced by preoxidation is, unfortunately, not permanent. The exact mechanism by which sulphur and the alloy components come into contact is still open to question.

Hunt and Strafford (1980) examined the behaviour of a Co.30Cr alloy in a pS_2 10^{-4} atm. pO_2 2×10^{-9} atm. gas mixture at 900°C . Samples with and without preformed Cr_2O_3 scales were used.

Specimens preoxidised at 850 and 900°C showed an incubation period of about 40h; those preoxidised at 1000°C started to sulphidise from the start of exposure. It is suggested that the greater thermal stress in cooling from 1000°C causes increased scale disruption. Sulphidation occurs at preferred sites which, it is suggested, relate to short-circuit diffusion paths in the Cr_2O_3 . Stott and Chong (1983) found little difference between the sulphidation properties of preoxidised Fe 28Cr and Fe 27Cr 0.8Y suggesting that improved scale adhesion alone does not reduce the number of short circuit paths.

Stott et al (1983 a+b) investigated the effect of preformed Al_2O_3 films on Fe 27Cr 4Al + 0.023 or 0.8Y cast alloys. Yttrium was found to be present as YFe_9 .

A 20h preoxidation treatment at 900°C in a pO_2 2.6×10^{-23} atm. atmosphere was followed by exposure to one of a range of low pO_2 gas mixtures with sulphur pressures from 9×10^{-9} to 4×10^{-8} atm. at 750°C .

Specimens examined during the incubation period show sulphide nodules on the surface of the alumina, Auger spectroscopy did not reveal sulphur in the scales after 2h expo-

sure. The yttrium-free alloy performed less well.

It is suggested that localised defects, such as grain boundaries, which are responsible for oxygen transport in alumina (Golightly et al 1976) also allow the ingress of sulphur. An exact mechanism is not conclusively demonstrated but the initial formation of Al_2S_3 which becomes incorporated in the scale and allows easier outward diffusion of alloy elements is also suggested. Subsequent growth of iron sulphide leads to the formation of rapid diffusion ducts for sulphur and the sulphidation rate increases. When sulphidised samples were treated with hydrochloric acid, which dissolved out any sulphides, an increase in the number of pores was observed demonstrating that a network of sulphides exists in the scale.

Singh and Birks (1983) considered CoCr alloys. A solution diffusion model for sulphur transport is discussed and analysed in terms of free energy of formation of various sulphides. It is demonstrated that this mechanism cannot account for sulphur transport in relatively oxidising environments; such an environment was produced and subscale sulphide formation was observed. It is concluded that molecular transport of oxidant through the scales must have occurred.

A number of other workers offer evidence of scale permeation by sulphurous species: Mrowec et al (1966) considered sulphidation of cobalt; Gilwicz-Wolter (1977) examined iron in SO_2 atmospheres at 800°C and Jallouli et al (1977) examined various FeCrAls in sulphur and $\text{H}_2\text{S}/\text{H}_2$ atmospheres.

Mari, Chaix and Larpin (1982) investigated sulphidation of preoxidised Fe 22Cr 5.5Al and Fe 10Cr 5Al alloys. Both alloys showed an immunity period which was linearly related to the preoxidation time.

The preoxidised samples were exposed to one of two gas mixtures: $10\%\text{H}_2\text{S}/\text{H}_2$ $p_{\text{S}_2} 1.5 \times 10^{-5}$ atm. and sulphur vapour $p_{\text{S}_2} 8 \times 10^{-5}$ atm. It was observed that faster weight gain occurred in the hydrogen sulphide gas mixture; subscale sulphide formation and surface nodules were found on

specimens exposed to this. No sulphidation was detected in the specimens exposed to sulphur vapour. It is suggested that diatomic sulphur resulting from dissociation of H_2S is not the only species responsible for sulphur entering the scale, H_2S may dissociate at the surface of the preformed oxide and provide a higher sulphur concentration sufficient to enable inward transport of sulphur at a sufficient concentration to cause sulphidation.

The limited work available and results of this investigation suggest that preformed alumina scales do break down by a mechanism involving inward transport of sulphur.

3 Thermodynamic Aspects

(a) Introduction

Where sufficient data is available, thermodynamic calculations may be used to determine the relative stability of compounds which may form in an oxidation reaction. It is often useful to calculate the pressure of a particular compound eg CrO_3 in equilibrium with a scale in order to determine the degree of thickness loss due to volatilisation.

Thermodynamics is not wholly predictive because it does not take into account various kinetic considerations such as protective scaling. It is, however, a useful tool for deducing a reaction path when used in conjunction with analysis data from a corroded specimen; from a knowledge of the phases present in a scale it is possible to estimate the pressure of oxidant at specific areas in the scale.

(b) Equilibrium Thermodynamics

The majority of practical gas-solid reactions considered occur at constant temperature and pressure. In this case a convenient measure of thermodynamic reactivity is the Gibbs' free energy change for the reaction. A system which reduces its free energy by reacting will tend to react spontaneously.

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

where ΔG = Gibbs' free energy, ΔH = enthalpy change and

ΔS = entropy change for a given reaction at temperature T.
Consider a reaction of the form



$$\Delta G^\ominus = -RT \ln K \quad \begin{array}{l} R = \text{gas constant} \\ K = \text{equilibrium constant} \end{array} \quad (6)$$

$$K = \frac{a_{AB_x}}{a_A a_B^x} \quad \text{where } a = \text{equilibrium activity} \quad (7)$$

The equilibrium constant for a particular reaction at temperature T enables calculation of the activity of one component from those of the others.

A detailed account of the application of thermodynamics and use of thermodynamic data is given by Kubaschewski and Alcock, Metallurgical Thermochemistry (1979).

(c) Equilibrium Dissociation Pressure

A practical measure of thermodynamic stability is the equilibrium dissociation pressure (p_{dis}) of a compound at a given temperature. In the simple case of a pure metal which forms a single oxide which is insoluble in the metal $p_{dis} = \frac{1}{K}$. In cases where the metal activity is reduced, or reactions with the oxide and metal occur, the appropriate activities must be inserted in equation 7. The lower the dissociation pressure of an oxide the more stable it will be. Some values of p_{dis} are only of academic interest and reflect the relative stability of an oxide eg $p_{dis} \text{ Al}_2\text{O}_3$ at 1123K - 10^{-40} atm, the practical limit of gas purity is - 10^{-11} atm. Redox mixtures such as CO/CO₂ may be used to produce slightly lower p_{O_2} values than this.

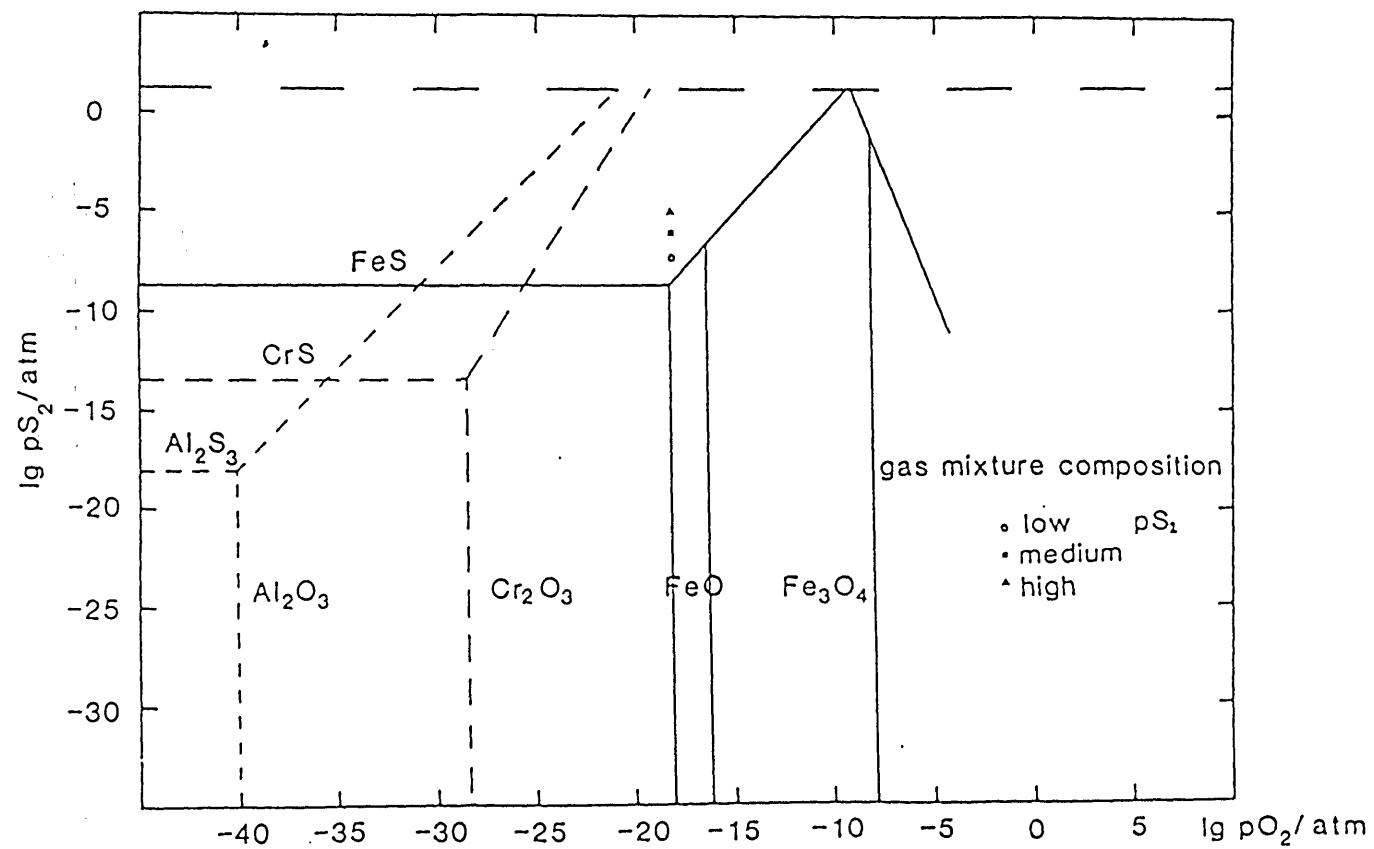
(d) Graphical Representation of Thermodynamic Data

A number of methods have been used to represent data graphically. The primary advantage of this method is that relative stabilities of compounds can be seen as a function of selected variables.

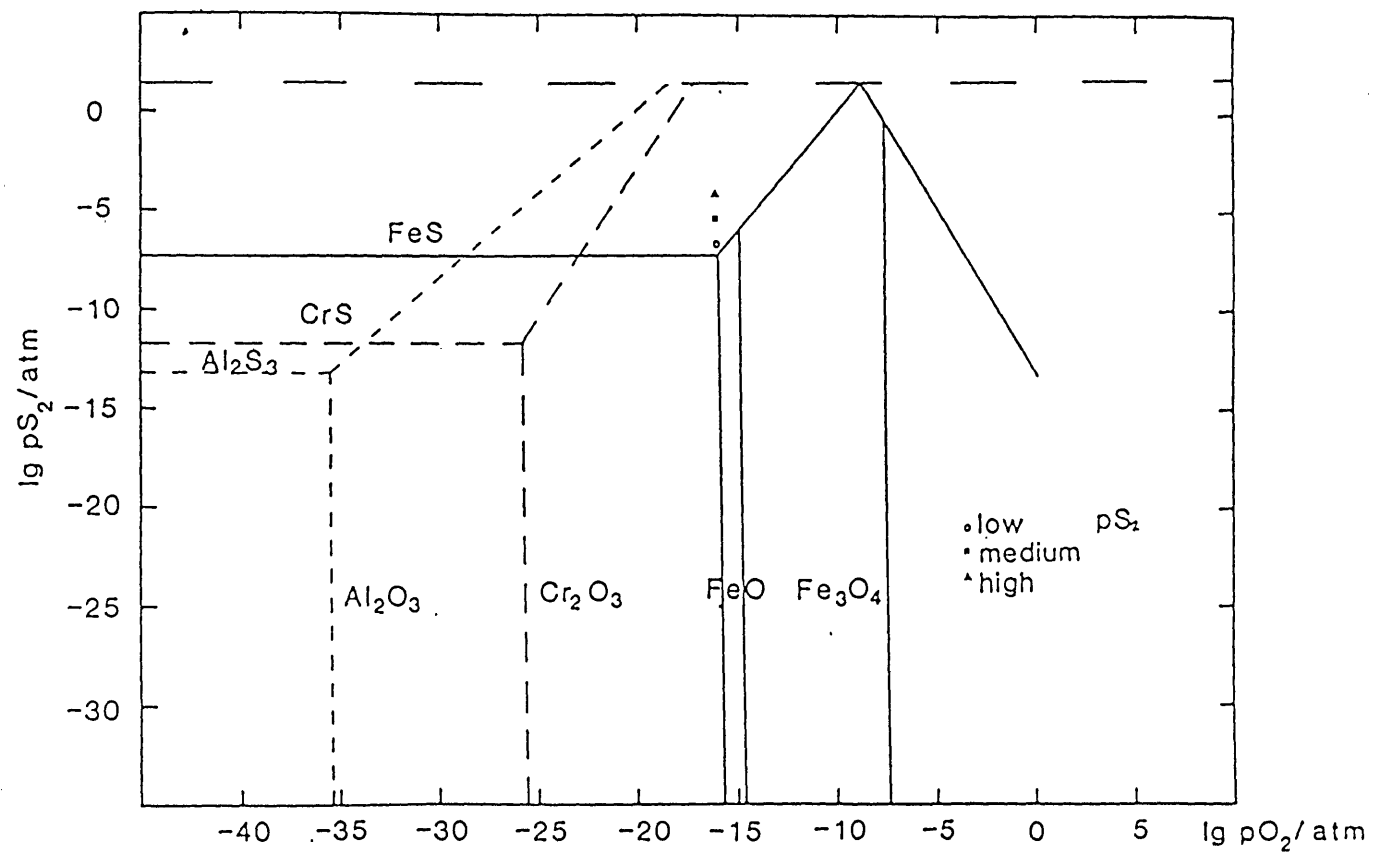
(i) Ellingham Diagrams

The diagram for the formation of oxides is given in Appendix I. The standard free energy change for the formation of a number of compounds is plotted as a function of temperature. Because the lines are plotted for reaction of elements with one mole of gas, where solid reaction

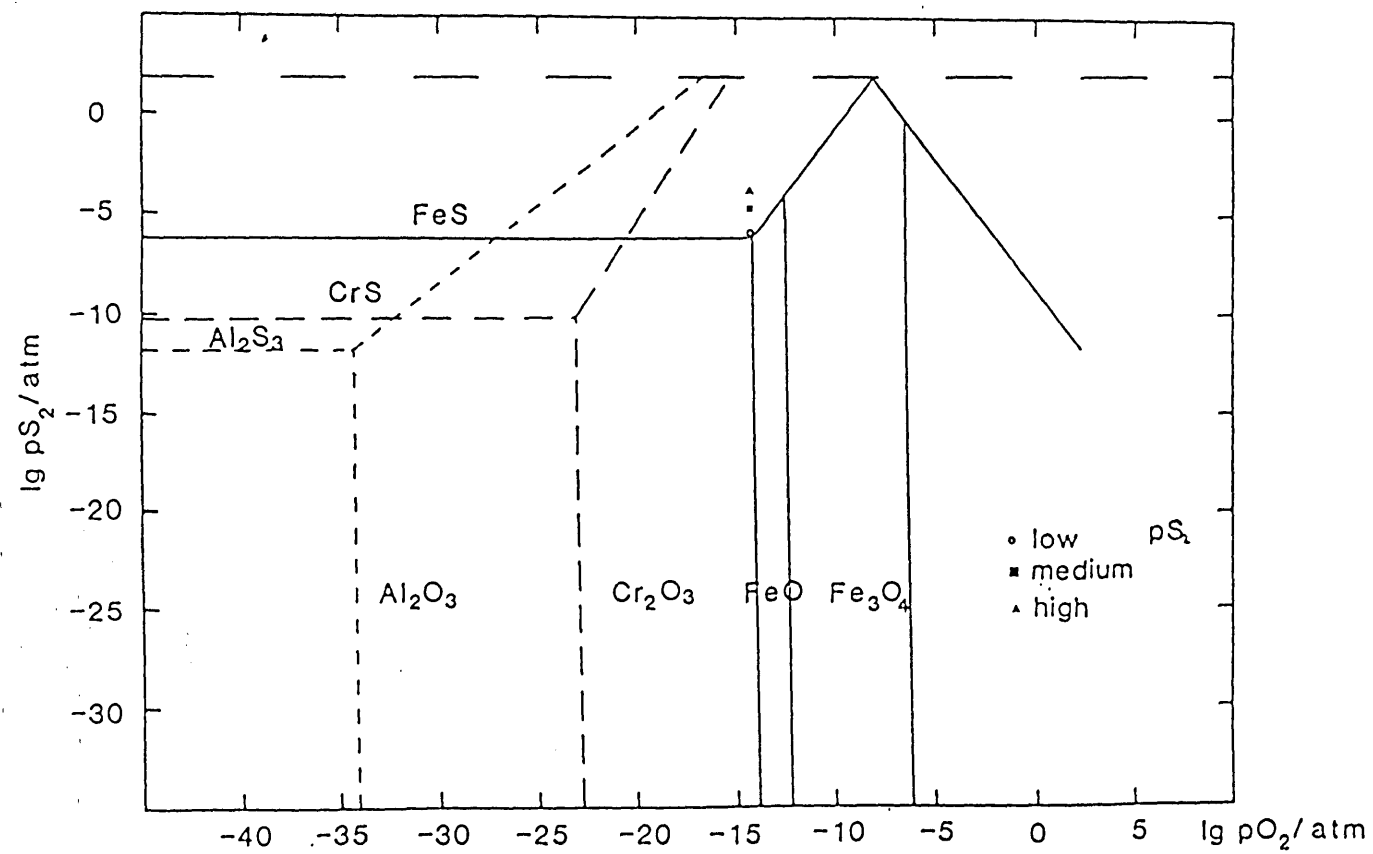
Combined Al, Cr & Fe Stability Diagram 1123K figure 1 (a)



Combined Al, Cr & Fe Stability Diagram 1223K (b)



Combined Al, Cr & Fe Stability Diagram 1323K (c)



products are produced the entropy change is very similar, so the hierarchy of stability remains constant with respect to temperature.

(ii) Isothermal Stability Diagrams

These diagrams (fig 1 a-c) represent the stability of a metal with respect to two oxidants at a given temperature. It is possible to calculate changes in stability field size for metals or oxides at less than unit activity.

The oxidising potential of an atmosphere may be plotted on a diagram; it is then possible to see which compounds will be stable in equilibrium with the gas mixture.

Gas composition is normally presented in terms of thermodynamic potentials of oxidants, this does not take account of the chemical nature of the oxidising gas, Perkins et al (1979) indicate that a considerable number of minor species may be present in high temperature industrial environment such as a coal gasifier. Kane (1980) indicates that in the case of coal gasifier type atmospheres it is sufficient to calculate an equivalent pO_2 , pS_2 etc. for the system; these values can then be set in the laboratory by the most convenient means available to test a material.

Reaction paths may be used to elucidate the mechanism of scale formation once the scale composition and morphology is known. Figure 2 is adapted from Perkins et al (1977). Both metals A and B can form stable sulphides and oxides at oxidant pressures indicated by the dashed lines; four possible situations are represented.

(i) Sulphur penetrates the scale and pS_2 at the scale/metal interface is sufficient to form AS at the boundary. Oxygen mobility is insufficient to form oxide ahead of the interface.

In case ii neither oxidant reaches the scale/metal interface in sufficient concentration to react; oxide growth continues, governed by outward cation diffusion through the scale.

When voids are present in the scale (iii), it is possible

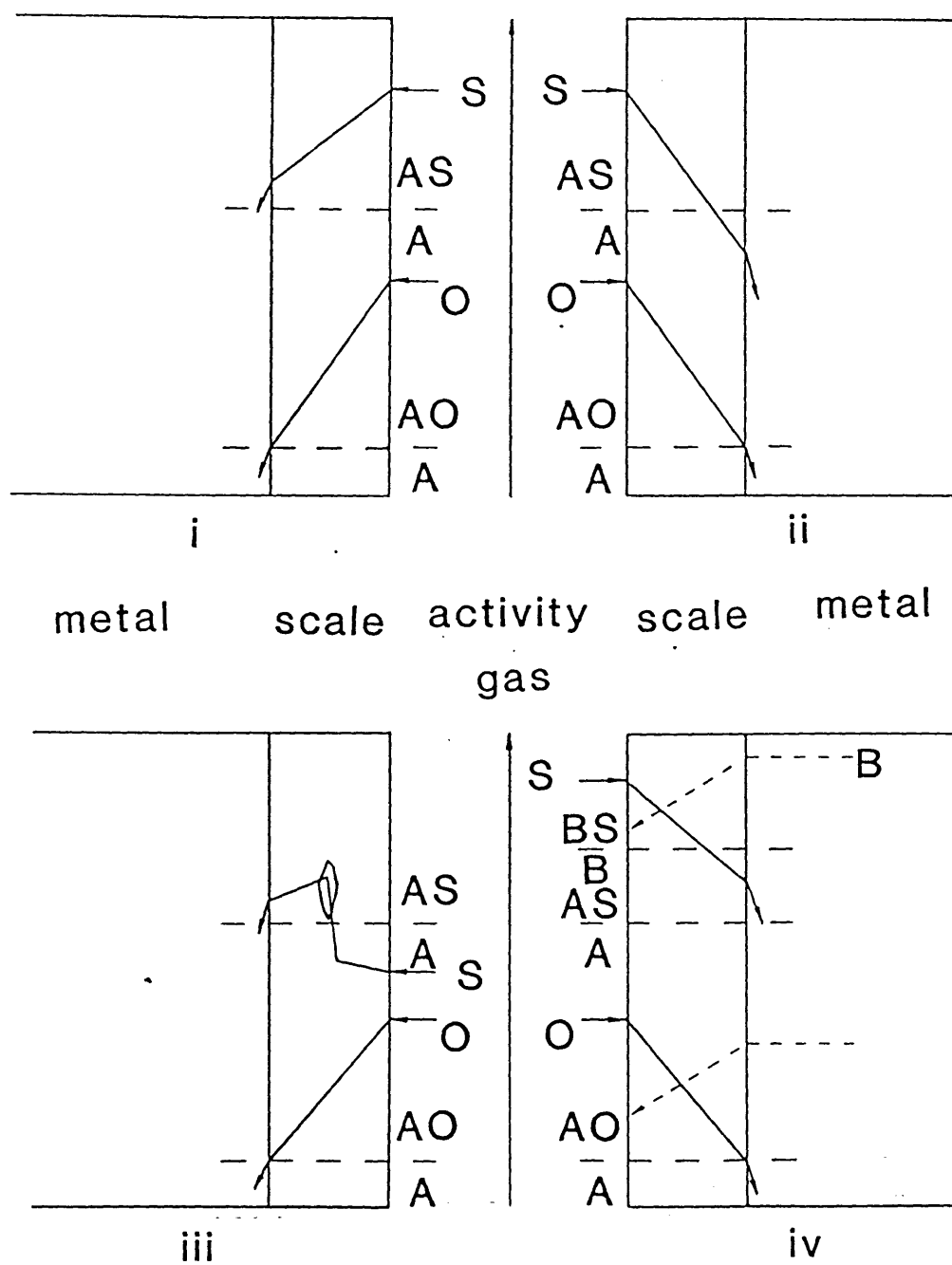


Fig. 2 Possible Reaction Routes in a Binary Gas Mixture

that sulphurous species may accumulate in a pore, raising pS_2 above the dissociation pressure of AS, subsequent inward diffusion of sulphur from the pore produces AS at the scale/metal interface. This effect has been noted by Birks (1976) with SO_2 .

Case (iv) indicates a situation in which another cation, B, also diffuses outwards through AO, if a sufficient activity of B is reached it may oxidise or sulphidise forming new phases in the scale.

It can be seen that the function of stability diagrams is largely retrospective; they cannot predict the outcome of exposing an alloy to a multioxidant environment because no mechanism is provided to take account of scale transport properties.

The thermodynamic scope of the diagrams is limited by the availability of data; a three dimensional diagram (Giggins and Pettit, 1980) may be needed to represent a system of two metals.

(iii) Oxide Maps

These are isothermal sections of a ternary metal system in equilibrium with a gaseous oxidant at fixed pressure, commonly oxygen at 1 atm.

Wallwork and Hed (1971) and Tomaszewicz and Wallwork (1983) have produced maps for NiCrAl at 1000°C , CoCrAl at 1100°C and FeCrAl at 800°C based on oxidation data for a number of alloys in the parent metal-rich area of the diagram. The areas where preferential formation of either chromia or alumina scales are marked. Appendix II shows the map for FeCrAl.

The primary use of these maps is in alloy design because they give a guide to compositions which will produce protective scales. The use of the diagrams in corrosion research is limited by the conditions used to produce the map; multi-component atmospheres may produce other compounds not covered by the map.

(a) Introduction

As well as the thermodynamic considerations discussed in section 3 it is important to consider factors which affect the rate of oxidation of a metal. Initially in this section the general principles of oxidation of pure metals will be discussed; later these concepts will be extended to particular types of alloy.

(b) Pilling - Bedworth Ratio

Pilling and Bedworth (1923) proposed a criterion for deciding whether an oxide of a given metal would be protective. Provided the ratio:

$$\frac{\text{molar volume of oxide}}{\text{molar volume of metal}}$$

the oxide scale would be in compression and cover the surface of the metal. This principle tacitly assumes that the oxide grows at the metal/oxide interface which is not always the case, it cannot therefore be applied as a general rule.

(c) Oxidation Rate Laws

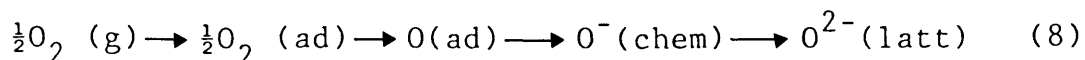
Two rate laws are of relevant interest to this work. The dissociative scale growth model will also be discussed.

(i) Linear Rate Law

$$x = kt \quad \text{where } x = \text{scale thickness, } k = \text{linear rate constant, } t = \text{time.}$$

this condition applies in the early stages of all oxidation processes initially involving clean surfaces. In systems which produce protective scales the duration of linear kinetics is generally short. Bé nard (1948) reports 20s for oxidation of iron in air at 950°C, after this the reactants are separated by a layer of products. In order for linear kinetics to continue the flux of reactants through the scale must equal the rate of the slowest step in the oxidation reaction; otherwise a reduction in rate will occur.

During the linear stage the rate of reaction is determined by a series of processes :



oxidant gas is physically adsorbed onto the metal surface, chemisorption occurs when the atom becomes partially ionised, then complete ionisation occurs and the ion joins the anion lattice. Chemisorption requires an activation energy and is frequently the rate determining step in this sequence of events.

(ii) Parabolic Rate Law.

$$x^2 = k_p t \quad k_p = \text{parabolic rate constant.}$$

The end of the linear stage of oxidation is marked by a transition to steady state kinetics.

Parabolic scale growth is diagnostic of a diffusion controlled reaction the progressive increase in scale thickness leads to a reduction in its rate of growth. Parabolic kinetics will be observed until the scale attains a constant thickness or is disrupted in some way, such as cracking or spalling.

(iii) Dissociative Scale Growth.

In some cases, particularly where scale growth is rapid, as with a highly defective oxide such as Wustite, a duplex scale may be formed even on a pure metal. This effect is sometimes accompanied by a temporary change in kinetics.

Bruckman (1967) and Mrowec (1967) proposed a mechanism to explain the formation of an inner, porous scale layer on pure metals.

If no inward migration of oxidant occurs through the scale and the scale detaches from the metal due to an influx of vacancies, then the source of oxidant becomes dissociation of the scale at its underside, $p_{\text{oxidant}} = p_{\text{diss. oxide}}$; the cation formed by the dissociation diffuses out through the scale. There is a tendency for the oxidant to equalise its chemical potential across the scale.

The oxidant released by dissociation oxidises the surface of the alloy beneath the scale and new oxide is nucleated, eventually this recontacts the outer layer and outward

diffusion of metal from the bulk resumes. Generally, insufficient oxidant is released to produce enough new oxide to fill the void between the detached scale and metal; where this is the case the inner layer will be porous.

Mrowec (1967) notes that in a polycrystalline scale, dissociation tends to occur preferentially along grain boundaries; this may produce fissures which allow the ingress of gaseous oxidant if scale perforation occurs.

Diffusion

(i) Ficks Law (1855)

$$J = -D \times \text{concentration gradient} \quad (9)$$

This states that the flux of matter, J , is proportional to the concentration gradient. The constant of proportionality is the diffusion coefficient, D , in dimensions of L^2T^{-1} . It has subsequently been demonstrated that the driving force for diffusion is a chemical potential rather than a concentration gradient. †

(ii) Temperature Dependence of Diffusion

Diffusion is an activated process and it is related to absolute temperature by an Arrhenius type equation:

$$D = D_0 e^{-\frac{Q}{RT}} \quad (10) \quad \text{where } D_0 \text{ is a frequency of jumping term and } e^{-\frac{Q}{RT}} \text{ is a measure of the number of particles with a given energy.}$$

Two main types of diffusion occur in a polycrystalline material. Bulk and grain boundary or short circuit diffusion. The activation energy for bulk diffusion is generally about twice that for short circuit diffusion (Kofstad (1966) p108)), consequently bulk diffusion tends to predominate at higher temperatures ($\sim 0.6T_m$).

† Darken (1953, p462) gives an example of the preferential migration of carbon from an Fe-Si-C to an Fe-C alloy after heating; initially no carbon concentration gradient existed in the couple.

It is important to remember that the diffusion coefficient is a function of composition and will change with time as the distribution of components changes.

Observation of parabolic kinetics alone does not confirm that mass transport is by bulk diffusion only. The effective diffusion rate is a composite term made up of bulk and short circuit components. The contribution of grain boundary transport will clearly be a function of the grain size of the oxide. The activation energy for diffusion in a given system may be estimated from an Arrhenius plot of $\lg k$ against $1/T$, where $\lg k_p$ is the logarithm of the parabolic rate constant and T is the absolute temperature; this may be used to confirm or disprove a proposed mechanism in specific experimental conditions.

(e) Wagner's Theory of Oxidation (1933)

This theory was advanced to account for parabolic scale growth. The mathematical treatment is well presented in High Temperature Oxidation of Metals by Kofstad (1966).

It is assumed that a compact scale is formed in chemical equilibrium with the gas at the gas/scale interface and with the metal at the scale/metal interface. Reactants can migrate only as ions with a corresponding number of electrons. The rate determining step is the movement of one of these species across the scale.

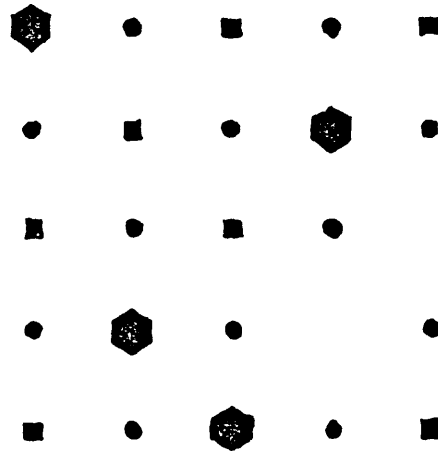
Because the mobility of cations, anions and electrons is different a local electric field is produced, this maintains a steady state separation between the ion and electron such that no net electric current flows through the scale. The effective diffusion rate of ions and electrons is therefore mutually dependent.

Scale growth may occur as a result of cation or anion transport through it. One process usually predominates and this a function of the scale defect structure.

(f) Defect Structure

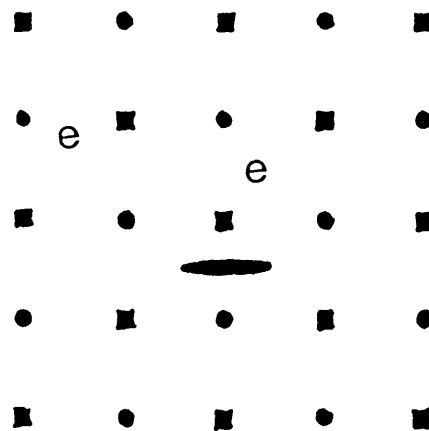
Several defect models have been proposed in order to explain bulk matter transport in electrically neutral crystals. In the case of highly stoichiometric compounds, Schottky and Frenkel type defects may be used to explain ionic mobility.

Fig.3 Representation of
p and n-type semiconduction



(a) p-type semiconductor

- cation
- anion
- hexagon electron hole
- interstitial cation



(b) n-type semiconductor

To explain movement of electrons and ions simultaneously it is necessary to assume that the scales formed during oxidation are non-stoichiometric compounds: semiconductors.

Two main classes of semiconductor are described.

(i) p - type semiconduction

Charge is transferred by electron holes (cations in a higher valency state than those in the main lattice), this may be due to a deficit of metal $M(1-x)O$ or to an excess of oxygen in the compound. Only the former type will be described.

Figure 3a represents a lattice containing divalent cations (eg NiO); the hexagons represent trivalent cations which allow transfer of charges. Chemisorption and subsequent ionisation of oxygen on the lattice will remove further electrons from other divalent cations and create more holes and vacancies. It may be shown that the concentration of holes is a function of $pO_2^{1/6}$ in ideal cases.

Addition of cations of higher valency to cation sites will cause an increase in metal ion vacancy concentration, increasing the conductivity of the oxide.

(ii) n - type semiconduction

Charge is transferred by electrons in the conduction band. These may arise due to an excess of metal $M(1+x)O$, represented in Figure 3b, or due to a deficit of non-metal. Either ionisation of an interstitial metal atom or "oxidation" of an oxygen ion will release electrons. An increase in oxygen pressure will reduce the defect concentration.

Addition of higher valency cations to the oxide will either cause a reduction in interstitial metal ion concentration or a decrease in oxygen vacancy concentration, reducing the conductivity of the oxide.

g Use of Markers

If sufficient diffusion and defect structure data were available it would, in principle, be possible to deduce particular scale growth mechanism from Wagner's oxidation

theory. Such information is often unavailable and marker experiments may be of use.

If an inert marker such as some fine platinum wires or a thin deposit of gold (Hocking 1962) is placed at an interface, its position relative to the metal lattice is unaffected by diffusion past it; it is altered by bulk movement of atoms past it, the Kirkendall effect.

In a system where the scale grows by outward migration of cations, as in a p-type semiconducting oxide, a corresponding inward migration of vacancies will occur into the metal. Provided the growth rate of the scale is not excessive, plastic deformation will compensate for this and the marker will be found at the scale/metal interface. If the scale growth rate is too high to allow plastic deformation of the scale, vacancy injection may form voids at the interface.

Mrowec (1961) comments on the possibility of finding a marker part way through a scale which has grown almost exclusively by outward cation and inward vacancy migration. If scale detachment occurs, and the marker stays on the underside of the scale, then new oxide could grow up by a dissociative mechanism from the metal surface and embed the marker.

Where scale growth occurs exclusively by anion transport markers will be found at the scale/gas interface.

In cases involving further oxidation of oxides marker experiments need careful interpretation on chemical grounds. Davies et al (1953) and Hocking (1962, 1966) comment on oxide forming on both sides of a marker even though only cation transport is occurring. This is due to a change in cation valency.

(h) Effect of Specimen Size on Rate Data

When kinetic data is determined by continuous weight change monitoring it is convenient to relate weight change per unit area to time.

In situations where the rate of scale growth is slow and total scale thickness formed in the duration of the

experiment is small ($\sim 10\mu\text{m}$) relative to the specimen dimensions, it is reasonable to assume that the area of metal oxidising is constant with time.

When high scale growth rates occur then, in practical laboratory situations, the area of metal oxidising will be a function of time. This effect was considered by Romanski (1968) to explain the dependence of scaling rate data on specimen geometry.

It is suggested that a practical value of specimen area for use in calculations is the mean area of metal during oxidation:

$$\bar{A} = \frac{A_{\text{initial}} + A_{\text{final}}}{2} \quad (11)$$

the value $\bar{A}$, mean area, is then used in calculations. In the case of continuous weight change monitoring instantaneous data about the change in metallic core size are not available it is however possible to calculate the change in core area for a given weight change provided sufficient data about the metal and oxide is available. Examination of published data and experimental methods indicate that an area correction is rarely made, this may account for the wide range of values often quoted for a sulphidation rate.

(i) Oxidation of Alloys

The ideal of this area of study would be to provide a single theory which could predict the effect of an alloy's composition on its behaviour in a complex environment. This is not yet the case.

When, as is the case in the systems considered here, an alloy is exposed to an environment in which all its components form stable compounds (see Figure 1), distinct stages occur in the oxidation. Initially nuclei of all stable compounds form (transient stage), then a protective scale grows by selective oxidation of components and steady state kinetics are obeyed until the scale properties are changed in some way (often cracking or loss of contact with the alloy). Figure 4 represents this.

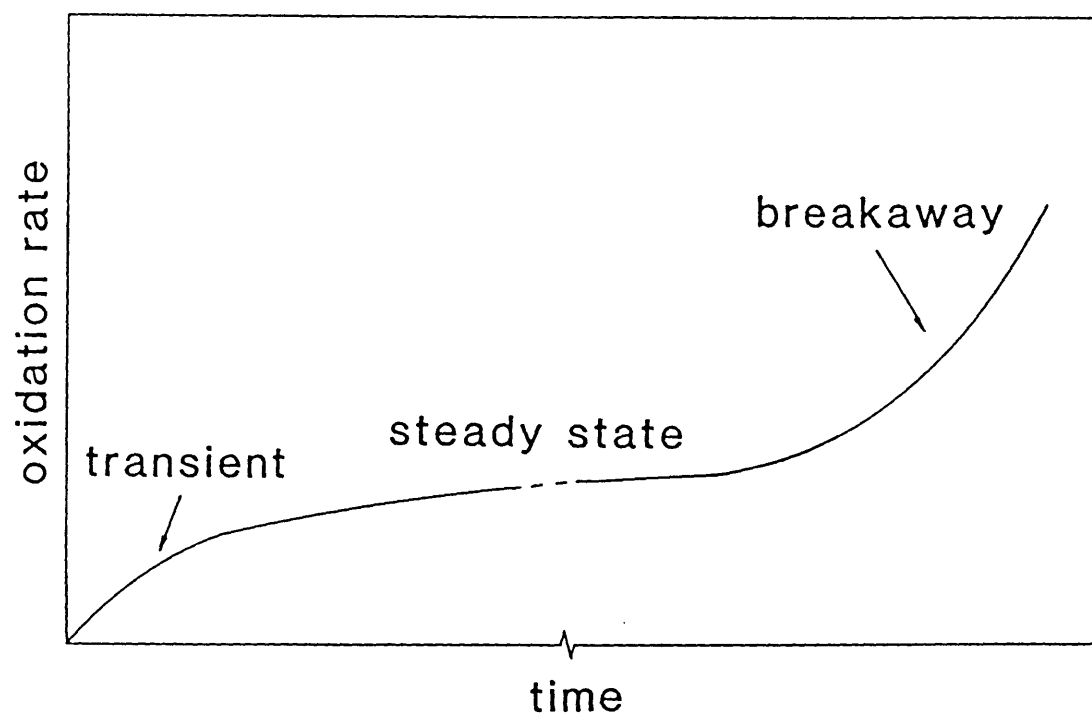


Fig.4 Representation of the Change in Oxidation rate Rate with Time for Oxidation of an Alloy

In the case of semiconducting scales the Wagner-Schottky-Hauffe semiconductor valence approach suggests ways of reducing the growth rate of a scale. Considering a predominantly p-type semiconductor, as already described, the substitution of a lower valency ion eg Li^+ into Ni^{2+} sites would reduce the concentration of cation vacancies in the lattice, hence the rate of cation diffusion would fall. Doping of this type is rarely, if ever, a practical solution to reducing scaling rate to a realistic value.

Selective oxidation of specific alloy components, notably aluminium and chromium, which have very low growth rates is generally the approach adopted in industrial situations. Selective oxidation may be promoted by a controlled atmosphere pretreatment or by using a sufficiently high concentration of scale former to ensure formation of a complete protective layer; working of the surface has also been shown to promote selective oxidation (Hindam & Whittle (1982)). It is important to bear in mind that where an alloy component is selectively oxidised its concentration in the alloy may fall below that required to heal damage to the scale in service.

Selective oxidation may also be promoted by the presence of discontinuities in an alloy, Rapp (1961) describes preferential In_2O_3 nucleation at scribe marks on an Ag 6.8In alloy; the beneficial effects of an "inert" oxide dispersion in alumina and chromia forming alloys is well documented (Hindam & Whittle (1982)).

Practical examples of alloy behaviour are discussed in section 5 of this chapter.

5 Related Work

(a) Introduction

The majority of theoretical work has been carried out in purely oxidising or purely sulphidising atmospheres, the processes involved in these cases are relatively well understood.

Evaluation of alloys in complex environments is less well documented and the work tends to be qualitative; primarily attempting to rank materials for suitability in particular applications. The work will be reviewed under headings of oxidation, sulphidation and multi-component atmospheres; the latter will also include carburisation to a limited extent.

(b) Oxidation

Discussion will be confined to the effects of chromium and aluminium additions to iron-based alloys. Work has been concentrated on determining the compositional limits at which alloys form protective scales. Wallwork and Hed (1971) and Tomaszewicz and Wallwork (1983) examined alloys ranging from 0.25%Cr 1-10%Al exposed to oxygen at 800°C.

Specimens with up to 2.4%Al and 13%Cr formed primarily Fe_2O_3 scales with an intermediate FeCr_2O_4 spinel covering a thin aluminium-rich inner film. Iron oxide is the fastest growing stable oxide and grows by outward cation diffusion. However as the inner spinel layer becomes thicker, and alumina and FeAl_2O_4 spinel forms by inward oxygen ingress through the iron oxide, these phases limit the growth rate of iron oxide. Spinel formation frequently occurs in alloys where the outer scale forms from one of the nobler alloy components eg Ni, Fe. The thermodynamics of spinel formation in the FeCrAl system have been discussed by Gordon et al (1979).

Low aluminium content (<2.4%) alloys with more than 13% Cr favour Cr_2O_3 formation at the expense of iron oxides, some Fe_2O_3 is formed as nodules at preferred sites. An internal alumina layer was detected, this forms due to a reduction in $p\text{O}_2$, by reaction with chromium, to a value at which only alumina is stable. At 9-1100°C Ike and Okabe (1979) found that Fe 14Cr 0.8Al forms a continuous chromia layer which is penetrated by iron at preferred sites.

Increasing the aluminium content favours alumina rather than chromia formation. Nodules of iron-rich oxides still form, these continue to grow until a protective

alumina layer encapsulates them, preventing further expansion. Stott et al (1971) note that in experiments at 1000 and 1200°C FeCrAl alloys form a continuous alumina layer more readily than the corresponding cobalt or nickel-base alloys, it is suggested that a combination of relatively high alloy interdiffusion coefficient and low oxygen solubility in the alloy promote this. The adhesion of the alumina on iron-base alloys is, however, inferior to its adhesion on the cobalt and nickel base specimens.

Alloys with 3-7%Al form a continuous, protective alumina scale at 800°C. Some small outcrops of iron oxide are present on the surface of the alumina, but not penetrating it. Discrete superscale iron oxides have also been reported by Golightly et al (1980) on yttrium-free FeCrAl alloys oxidised at 1000 and 1200°C; it is suggested that these form preferentially at asperities, such as polishing marks, where the greater surface area: volume ratio allows easier access for oxygen. Alumina then forms as an internal oxide. This effect is confined to the early stages of oxidation, after which time the surface oxide dissolve into the alumina. It is possible that at 800°C the dissolution process has not occurred in the duration of the experiment.

The superior protective properties of alumina scales make them desirable in high temperature applications.

(c) Sulphidation

Sulphides are generally less stable than the corresponding oxides. They tend to show larger deviations from stoichiometry, suggesting that they would be less protective than oxide scales. Certain refractory metals, notably molybdenum and niobium, show very low rates of sulphidation $k = 10^{-11} - 10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ at 850°C, $p_{\text{S}_2} 10^{-6} \text{ atm}$ (Strafford et al 1985) cf iron $k_p = 10^{-6} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ in similar conditions (Young and Smeltzer (1976)).

Strafford and Manifold (1969) examined the sulphidation behaviour of Fe 5%Al alloys at 5-700°C in a $p_{\text{S}_2} 1.3 \times 10^{-2} \text{ atm}$

For about the first hour parabolic kinetics were obeyed forming single phase FeS scales, as with sulphidation of pure iron. The parabolic stage was followed by a transition to linear kinetics, during this stage a subscale containing iron and aluminium sulphides was formed. In the duration of the tests (24h) the weight gains for pure iron specimens was about an order of magnitude greater than for the alloy.

The reduction in cation diffusion rate during the parabolic stage, contrary to the Wagner-Hauffe semiconductor valence model, is accounted for by the formation of strain fields around Al^{3+} ions in the $\text{Fe}(1-x)\text{S}$, these strained areas provide sinks for cation vacancies and actually reduce the concentration of vacancies available for diffusion. Subsequent scale detachment leads to further inner scale growth by a dissociative mechanism and a heterogeneous $\text{FeS} + \text{Al}_2\text{S}_3$ mixture is formed. The rate controlling step is then the supply of iron to the outer scale, this in turn limits the vacancy supply to the inner scale leading to linear kinetics.

Narita and Smeltzer (1984) a & b examined the sulphidation of Fe 2.6Cr over the temperature range 973-1123 K at $p\text{S}_2$ ranging from 10^{-1} - 10^{-11} atm. The type of scale formed was a function of sulphur pressure.

At sulphur pressures greater than 10^{-5} atm. a triplex scale was formed. An outer layer of $(\text{FeCr})\text{S}_x$ and an inner layer of $(\text{CrFe})\text{S}_x$ was separated by an intermediate $(\text{CrFe})_3\text{S}_4$ layer. Electron probe microanalysis showed that the chromium content of the outer scale was almost nil, it is essentially lightly doped $\text{Fe}(1-x)\text{S}$, this is similar to the findings of Mrowec et al (1969) on FeCr alloys with 3-40%Cr exposed to pure sulphur at 1atm.; the inner layer was, however, found to be a heterophase mixture of sulphides and iron-chromium sulphospinel (FeCr_2S_4).

Duplex scales were found at lower $p\text{S}_2$ (10^{-5} - 10^{-9} atm) and it was found that the outer $(\text{FeCr})\text{S}_x$ layer could transform to $(\text{CrFe})_3\text{S}_4$ and sulphospinel on cooling. A distinct Cr concentration gradient from inner to outer surface was reported.

At lower sulphur pressure, where pS_2 is almost equal to $p_{\text{diss FeS}}$, preferential $(\text{CrFe})S_x$ formation occurred. Internal sulphidation of chromium was also noted in agreement with the findings of Strafford et al (1983) at low sulphur pressures.

Markers were located at the scale/metal interface indicating that outward cation diffusion is the growth process. Evidence that some dissociative growth occurs at lower temperatures was provided; reduced scale plasticity causes separation, this causes an experimentally reproducible reduction in growth rate, after some time, when scale contact resumes, parabolic kinetics are again observed.

Mrowec et al (1969) reports parabolic kinetics for sulphidation of Fe .3 - 74%Cr alloys in sulphur vapour at 1atm. Alloys with up to 3%Cr form an $\text{Fe}(1-x)\text{S}$ scale with a trace of spinel at the scale/metal interface.

Alloys with 3-40%Cr show a decreasing scaling rate with increasing Cr content. All alloys in this range form an $\text{Fe}(1-x)\text{S}$ outer scale, an inner scale bounded by porous zones at each side was found to be composed of a mixture of $\text{Fe}(1-x)\text{S}$ and FeCr_2S_4 . Markers were found embedded in the inner side of this scale layer. In order to explain the marker location it is necessary to assume that plastic flow of the scale occurs to compensate for the inward flux of vacancies during scale growth. For plastic deformation to occur sufficiently quickly it is necessary that the scale is monophasic or for the inner region to be monophasic; two possible mechanisms are proposed:

(a) A solid solution of chromium and iron sulphides forms at the interface, this is effectively monophasic until one component of the solution is rejected on cooling.

(b) The inner layer is homogeneous at high temperatures consisting of a complex $\text{Fe}(\text{Fe}_{2-x}\text{Cr}_x)\text{S}_4$ sulpho-spinel which decomposes on cooling to form the mixture identified in corroded specimens.

The second model is also invoked by Mrowec (1978) to explain the position of markers beneath a heterophase scale on Fe 20Cr 0-20Al alloys; in this case it is suggested that an $\text{Fe}(\text{Fe}_x \text{Al}_y \text{Cr}_{2-x-y})\text{S}_4$ type spinel is formed from the parent FeCr_2S_4 structure.

It is suggested that the rate controlling step is outward diffusion of iron through the spinel phase, the presence of substitutional iron or aluminium ions in the lattice would alter the diffusion rate through it but not the mechanism; this is consistent with the activation energy for diffusion as determined by Mrowec.

In studies of FeCr and FeCrAl alloys at 540°C Zelanko and Simkovich (1974) find a large reduction in scaling rate in the presence of aluminium, it is suggested that traces of oxygen in the corroding gas (nominally $\text{H}_2/\text{H}_2\text{S}$) form a thin, undetected barrier layer of alumina.

Alumina growth would not be expected to be very rapid in these conditions, indications in work by the present author (Weber and Hocking, 1985) suggest that this is improbable.

Rao and Nelson (1978) report the formation of a sulpho-spinel inner scale covered with an $(\text{FeNi})_x\text{S}$ outer layer on a 25Cr 20Ni stainless steel; the inner layer is essentially similar to that found on iron chromium alloys of similar composition, this is in agreement with the quoted parabolic rate constant at 923K which is almost equal for iron and nickel sulphidation. Mrowec also quotes activation energies for nickel diffusion 92 kJ/mol and iron diffusion of 92.1 kJ/mol at 923K in sulphur vapour at 1 atm.

(d) Multicomponent Atmospheres

Work in multicomponent atmospheres, which are representative of coal gasification environments, has been carried out on a number of alloys; these may be classified as nickel-base, iron-base and cobalt-base chromia forming and oxide dispersion strengthened (ODS) alumina forming materials.

The gas mixtures are characterised by being simultane-

ously oxidising and/or sulphidising, carburising or nitriding. Low oxygen ($<10^{-15}$ atm) and high sulphur ($>10^{-10}$) pressures generally characterise coal gasifier atmospheres. Some possible atmospheres may be too weakly oxidising to stabilise chromium oxide ($p_{\text{diss}} 10^{-22}$ atm at 1273K), making sulphidation almost inevitable in a chromia forming alloy.

Tiearnay and Natesan (1982) conducted a wide ranging series of tests at 923 and 1144K exposing nickel, iron and cobalt-base chromia forming alloys and ODS MA956 to atmospheres with $p_{\text{O}_2} 10^{-25} - 10^{-18}$ atm., $p_{\text{S}_2} 10^{-11} - 10^{-6}$ atm with a range of carbon activity.

At 923K the nickel-base alloys formed duplex scales with an outer Ni (and Co if present) sulphide layer over an inner $(\text{CrFe})_x \text{S}$ layer at higher p_{S_2} ($>10^{-6}$ atm), at lower p_{S_2} nickel sulphides formed only in isolated areas over a predominantly chromium sulphide scale, some chromium oxide was found beneath the sulphide layer. Scale thicknesses up to 220 μm were examined after 120h corrosion. A similar morphology scale was found on cobalt base alloys, with cobalt sulphide replacing nickel; the thickest scales found were 80 μm .

MA956 produced an external $(\text{FeCr})_x \text{S}$ layer over chromium sulphide covering a semi-continuous aluminium-oxide rich subscale at higher p_{S_2} . Lowering p_{S_2} reduced the development of the outer layer of the scale. The thickest scales formed were 50 μm .

Tests at 1144K produced generally similar results; where nickel sulphidation occurred the presence of liquid phases accelerated sample degradation. Oxide formation was favoured in the chromia forming alloys at lower p_{S_2} and these were protected in some atmospheres tested.

MA956 formed a duplex scale in a $p_{\text{O}_2} 10^{-18}$, $p_{\text{S}_2} 2 \times 10^{-7}$, atmosphere with $a_{\text{C}} = 0.06$, an outer void containing iron-rich sulphide layer (probably pyrrhotite) covered a thinner chromium-rich sulphide zone. The two layers were separated by a thin Al-rich layer. The matrix was depleted in chromium near to the scale/metal interface

and Cr-rich carbides were formed about 100 μ m into the bulk alloy. It is interesting to note that Douglass et al (1981) specifically comment on NOT finding carbides on this alloy when corroded in contact with a char aC 0.7. Preoxidation of MA956 was found to prevent growth of sulphide-containing scales.

It is concluded that the outcome of competitive growth of protective oxide (Al or Cr) and nobler metal sulphide (Fe, Ni) during the transient stage of oxidation plays a decisive role in determining whether protective kinetics are observed. The presence of an oxide dispersion promotes nucleation of oxides, the presence of even some oxide will reduce the area for outward diffusion of metals and hence reduce the scaling rate.

McColvin and Smith (1985) tested MA956 and Incoloy 800* (Fe 30Ni 20Cr) in a variety of atmospheres.

Acoustic emission tests indicated that the alumina scale formed on MA956 at 1100°C in air/5% water withstands cooling to 700°C without cracking, below this temperature some, slight cracking was detected. Lowell et al (1982) performed high velocity burner rig tests on MA956. An 1100°C aviation fuel/air flame was impinged on test pins for 1h followed by high velocity air quenching. After 3790 cycles the scale formed showed no signs of spallation.

Preoxidised MA956 was shown to resist two 100h exposures to a N₂/0.025CO atmosphere at 1200°C without significant nitridation (wt gain < 0.5mgcm⁻²). Kane (1983) reports the absence of nitridation of preoxidised MA956 in similar exposure conditions. Some local nitridation of a grit blasted sample was detected however.

10h exposures to an oxidising atmosphere with aC = 1 produced no detectable carburisation at 1000 or 1100°C; Floreen et al (1981) also failed to detect carburisation after exposure to a slightly (aC not given) carburising helium atmosphere at 1000°C for up to 5000h. The presence of an alumina layer is reported to prevent carburisation even in atmospheres where pO₂ is too low to

* Trademark Inco family of companies.

form chromium oxide. Norton et al (1983) investigated the carburisation of some stainless steels and model alloys in the range Fe 25Cr 20-35Ni in H_2/CH_4 atmospheres at 850 and 1000°C, $a_C = 0.8$. It was found that a preformed oxide layer reduces carbon pick up. The presence of a small concentration ($p_{S_2} 10^{-10}$ atm) of sulphur in the atmosphere was also shown to reduce the amount of carbon dissolved in the alloy.

McColvin and Smith report relatively good sulphidation behaviour of MA956 at 816°C in $p_{O_2} 10^{-18}$, $p_{S_2} 10^{-6}$ atm and at 980°C $p_{O_2} 10^{-14}$, $p_{S_2} 10^{-5}$ atm. atmospheres. Weight gains of $< 0.5 \text{ mg cm}^{-2}$ were recorded in 240h compared to about 10 mg cm^{-2} for Incoloy 800. Sidky (1984) corroded MA956 at 450 and 850°C in $p_{O_2} 2 \times 10^{-18}$, $p_{S_2} 4 \times 10^{-5}$ atm. At the lower temperature a very small weight gain ($< 0.5 \text{ mg cm}^{-2}$ in 23h) was recorded, this was associated with the formation of some iron and chromium oxides on the specimen surface. Very little alumina was formed. At 850°C a more general alumina scale grew, no sulphidation was reported.

Lloyd (1983) performed pilot studies in an atmospheric fluidised bed gasifier. Tests were conducted with FeCrAlY, MA956 and MA754 (Ni 20Cr 1Fe 0.3Al 0.5Ti 0.6Y₂O₃) at 950°C $p_{O_2} 10^{-18}$, $p_{S_2} 3 \times 10^{-9}$ atm. The bed contained a mixture of coal and limestone.

Some MA956 samples were preoxidised for 18h in air at 1200°C prior to exposure; this treatment produced an adherent $\sim 2 \mu\text{m}$ thick alumina scale; some iron-rich inclusions were detected in this layer. It is suggested that the inclusions in the alumina could lead to scale failure in the long term, though no evidence is offered to support this and the concept is not developed.

240h exposures in the bed indicate that preoxidised MA956 resisted attack and retained good scale adhesion. Non-preoxidised specimens generally behaved well with some slight internal oxidation of aluminium at specimen corners. No sulphidation was detected. The nickel base alloy performed badly, extensive sulphidation of chromium

lead to its depletion in the alloy bulk and subsequent nickel oxide formation.

Douglass et al (1981) conducted a series of tests on high temperature alloys in coal char at 1144 and 1255K. The chars contained 0.9 and 2.7 %S with almost 70% carbon. The atmosphere had pO_2 10^{-15} and pS_2 2×10^{-6} atm.

The degree of sulphidation was found to depend on the frequency of char replacement, after about 12h sulphur depletion in the char lead to a reduction in sulphidation rate.

In an unpreoxidised condition MA956 and GE1541 (Fe 14Cr 3.8Al 1Y) performed badly compared to nickel-base alloys and 310 stainless steel (Fe 20Ni 25Cr). Extensive sulphidation produced chromium- and iron-rich sulphides on the iron-base alloys or chromium sulphides with some nickel present on the nickel-base alloys. The effect of preoxidation was not discussed.

Work by Perkins and Vonk (1979) comments on the beneficial effect of chromium oxide scales in reducing scaling rates on Fe, Ni and Co-base alloys. The beneficial effects of alumina scales in low pO_2 , high pS_2 environments is not commented on, this seems to be the direction of current interest and probably of most industrial relevance. It is interesting to note that the sulphidation rate of some metals is very low k_p Mo 2.6×10^{-12} , k_p Nb 8.2×10^{-13} cf k_p Cr 1.9×10^{-8} $g^2 cm^{-4} s^{-1}$ pS_2 10^{-6} atm. 750°C as reported by Strafford (1985); this may be another avenue to explore in the search for viable sulphidation resistant alloys.

(6) Objective of the Present Study

The aim of this project is to design and carry out experiments to test the environmental resistance of selected iron-base mechanical alloys in similar chemical conditions to those likely to be encountered in a coal gasification system.

Kinetic data will be obtained where possible and correlated with the type of scale formed. The effect of a

preformed surface oxide layer will be examined in selected cases.

The results obtained will be presented and subsequently discussed in the context of related work.

CHAPTER II

EXPERIMENTAL METHODS

1 Equipment and Materials

(a) Gas

(i) Source and Purity

Where possible, gases were drawn directly from cylinders via a two stage regulator with needle valves for fine adjustment of flow rate.

The test atmospheres were produced by mixing carbon dioxide, carbon monoxide, hydrogen and forming gas in an appropriate ratio.

Hydrogen, forming gas and carbon monoxide were purchased from British Oxygen Company Ltd,. the quoted analyses were:

Hydrogen: O₂ 3ppm, N₂ 20ppm, CO 1ppm, CO₂ 1ppm, H₂O 4ppm, hydrocarbons 1ppm.

Forming gas: 90% nitrogen, 10% hydrogen.

Carbon monoxide: CO₂ 200ppm, H₂ 1000ppm, CH₄ 750ppm, H₂O 25ppm, O₂ 25ppm.

Carbon dioxide from Distillers Co Ltd: CO 1ppm, H₂O 10ppm, hydrocarbons 10ppm.

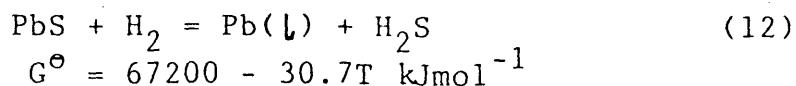
Hydrogen sulphide from Matheson Gases Ltd: O₂ 500ppm, H₂O 500ppm, N₂ 300ppm, hydrocarbons 3500ppm.

With the exception of carbon dioxide, cylinder contents was monitored by the pressure gauge. The relatively low critical pressure of carbon dioxide made it necessary to weigh the cylinder periodically to estimate the amount of gas remaining.

(ii) Use of Hydrogen Sulphide

Two methods were used to produce the required concentration of hydrogen sulphide.

Where a low level of H₂S was required, the exchange reaction between lead sulphide and hydrogen was used, as described by Sidky (1984).

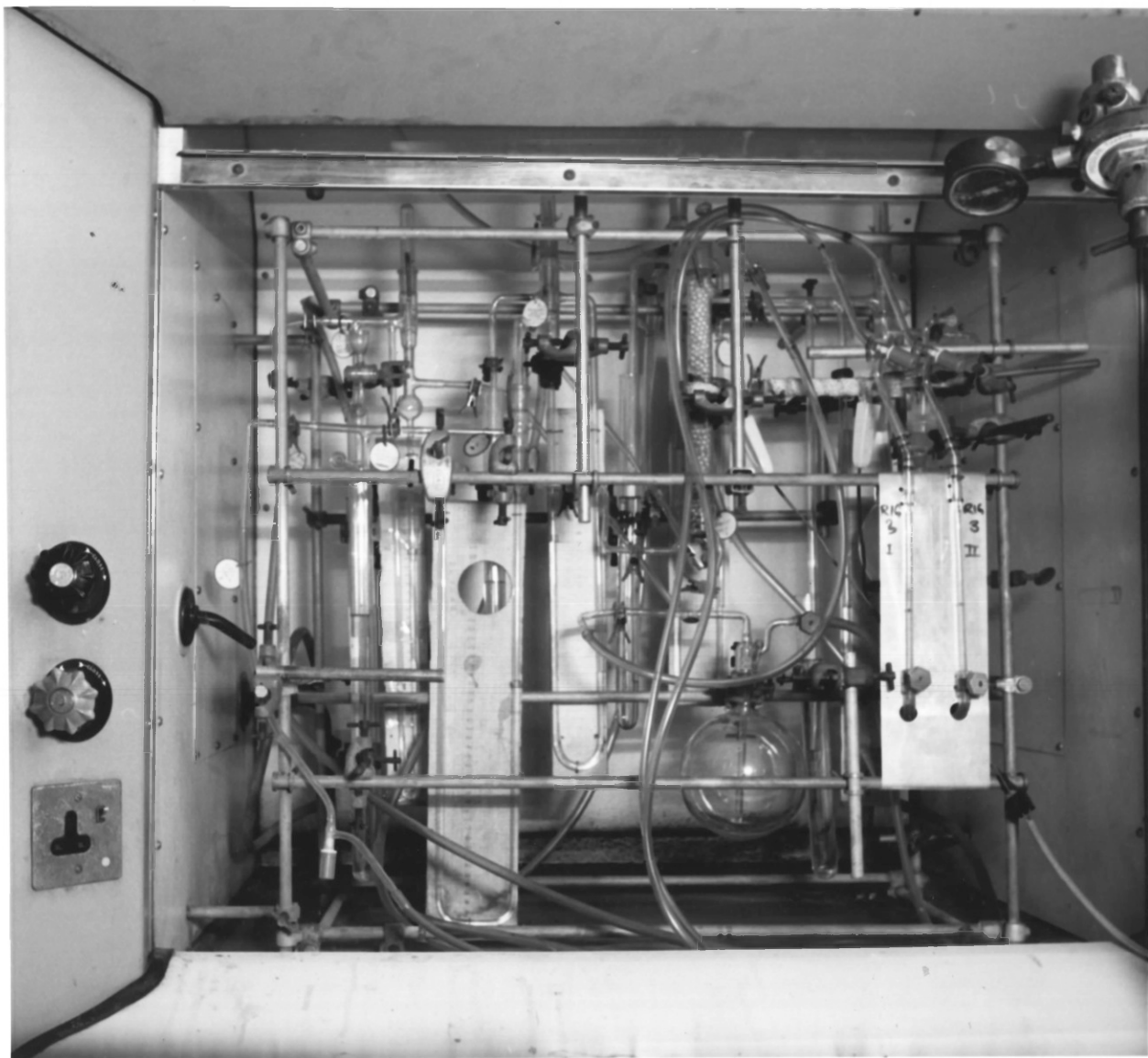


A proportion of the forming gas was passed over a boat containing granular lead sulphide (British Drug House, general purpose reagent grade) heated to a suitable temperature.

This method was found to be very satisfactory where a low H_2S concentration was required. Where a higher concentration was used, the increased forming gas flow rate and the higher temperature of the lead sulphide tended to cause particle transport. A gas mixture containing H_2S was used.

Economic considerations necessitated production of a mixture in the laboratory. An empty size J (approximately 3m^3 of gas at STP) cylinder was pumped out. A mixing system comprising a cylinder of hydrogen sulphide, a high pressure valve (Hale-Hamilton, type SV47), a pressure gauge (Barnet Instruments), the empty cylinder and a length of copper high pressure tubing with collars and stems to fit the cylinders was set up in a large fume cupboard. Hydrogen sulphide was let into the empty cylinder to a pressure of 10atm. The H_2S cylinder was replaced by an oxygen-free nitrogen one and the total pressure in the mixture cylinder was made up to 100atm. Sufficient time was allowed for the cylinder to cool to room temperature before checking the pressure. The toxic nature of hydrogen sulphide meant that considerable care was necessary during these procedures.

The brass components of the regulator to be used with the gas mixture were 'run in' by tarnishing in hydrogen sulphide prior to use. The H_2S concentration in the gas mixture was determined by absorbing a known volume of it in concentrated zinc acetate solution. A known amount of iodine in solution was added and the zinc sulphide formed during absorption of H_2S was reacted with concentrated hydrochloric acid to re-release the H_2S . Iodine displaced sulphur from the H_2S , excess iodine was then determined by back titration with 0.01M sodium thiosulphate solution, the H_2S concentration was calculated by difference. A number of determinations were



Photograph of the gas mixing train.

Key to Figure 5

- a Gas inlet from cylinder via 2-stage regulator
- b Gas flow rate controller, charged with dibutylphthalate
- c Gas mixing tower
- d Gas mixture outlet
- e Outlet flow meter - rotameter type
- f Ballast flask
- g S13 ball and socket joint closed with clip
- h Long path gasifier filled with hydrochloric acid

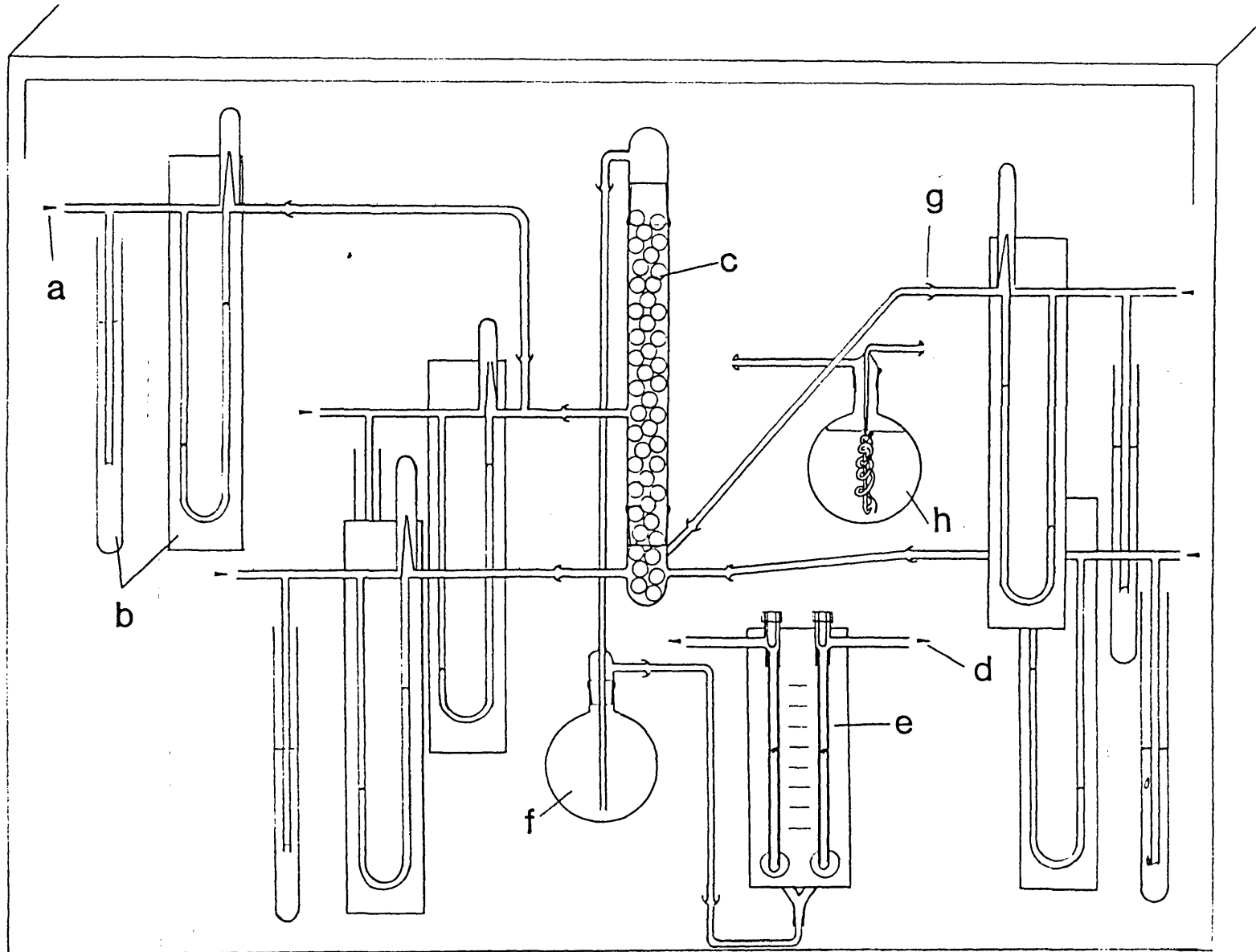


Fig. 5 Schematic Diagram of Gas Mixing Train

made with the H_2S /nitrogen mixture cylinder in either a vertical or horizontal position; the results were similar in both cases.

The mean H_2S concentration was found to be 9.4% in the first cylinder made up and 8.6% in the second one.

(iii) Corrosion Test Atmospheres Used

After discussions with the sponsoring company (Wiggin Alloys Ltd.) and a review of previous work, including some carried out in this research group by Dr Sidky (1981), two test atmospheres were selected, a low pS_2 composition at 1123 and 1323K as shown in Table 4.

Early results indicated that the alloys tested showed good resistance to these environments and the higher pS_2 atmospheres were introduced; these were supplemented by studies at 1223K.

Some of the early tests were carried out in an atmosphere containing 2×10^{-4} atm. of hydrogen chloride. HCl was introduced by bubbling hydrogen through a long path saturator containing hydrochloric acid of the appropriate concentration held at constant temperature (Dunn and Rideal (1924), Bates and Kirschman (1919)). In order to prevent water droplets from forming in the delivery tube to the gas train, heating tape was used to maintain the tube at about 80°C .

The concentration of HCl in the gas from the gasifier was determined by Mohr titration (Vogel (1964)) using 0.01M silver nitrate solution made up from British Drug House concentrated volumetric solution.

(iv) Gas Mixing Train

Two similar gas mixing trains were used in order to produce mixtures equilibrated for different temperatures. Figure 5 & Plate 3 show the gas train layout; these are fairly self descriptive. The corrosive and toxic nature of the gas mixture used necessitated constructing the gas trains in fume cupboards. The glassware was built into a framework made from $\frac{1}{2}$ inch (13mm) diameter light alloy rod secured with pinch clamps.

Temperature/K	Flow rate		10%H ₂ S								a C
	cm ³ min ⁻¹	/100cm ³	CO ₂	CO	H ₂	Forming	H ₂ mix.	pO ₂ /atm	pS ₂ /atm	pN ₂ /atm	
1123	Low	pS ₂	10.2	8.4	4.7	76.8	*		3.4x10 ⁻⁸		
	Med	pS ₂	10.2	8.4	4.9	73.5	3.0	1.5x10 ⁻¹⁸	7.3x10 ⁻⁷	0.70	1.8x10 ⁻²
	High	pS ₂	10.2	8.4	5.6	66.8	10.0	(8x10 ⁻¹⁷)	8.1x10 ⁻⁶		
1223			11.6	6.7	6.1	75.6	*		1.6x10 ⁻⁷		
			11.6	6.7	6.4	73.3	3.0	2.1x10 ⁻¹⁶	3.6x10 ⁻⁶	0.70	3.9x10 ⁻³
			11.6	6.7	7.1	65.6	10.0	(9x10 ⁻¹⁵)	3.9x10 ⁻⁵		
1323			13.0	5.0	7.7	74.3	*		6.4x10 ⁻⁷		
			13.0	5.0	8.0	71.0	3.0	1.4x10 ⁻¹⁴	3.6x10 ⁻⁵	0.70	1.0x10 ⁻³
			13.0	5.0	8.7	64.3	10.0	(6x10 ⁻¹³)	1.5x10 ⁻⁴		

*from reduction of lead sulphide

Table 4
Flow Rates Used to Produce 100cm³ of Gas Mixture per Minute

Borosilicate glass with S-13 connectors was used wherever possible for construction, gases were lead to and from the mixing train by reinforced PVC tubing secured by Unex isostatic hose clamps. All ground glass joints in the mixing train were smeared with Dow Corning high vacuum silicone grease; ball joints were secured with suitable clips.

Gas flow to the mixing tower was regulated by capillary effusion flow meters. The flow rate is a function of the capillary dimensions, the feed pressure and the gas molecular weight, at constant temperature. The flow-meters were charged with dibutyl phthalate; this is fairly unreactive and has a very low vapour pressure at ambient temperature. The flow rates were set using gas of similar composition to that which was to be metered. A soap bubble gas burette was used to determine the flow rate, adjustments to feed pressure and capillary dimensions were made as required.

To balance the flow rate to two furnaces from one gas train, the gas was led from the mixing tower, via a plenum chamber, to a pair of floating ball-type flow-meters.

Before use all joints in the system were leak tested by applying a few drops of Teepol solution. Prevention of leaks is important both from a safety point of view and to prevent unpredictable changes in gas chemistry due to ingress of air.

(v) Waste Gas Disposal

Gas exiting from the furnaces was led via a narrow tube loosely coupled into a long closed-one-ended tube. Air was drawn into the closed-one-end tube by a high volume flow rate filter pump running into a fume cupboard drain.

(b) Furnaces

(i) General Considerations

One platinum wound furnace was used, all other furnaces were Kanthal wound. The windings were made on alumina or silica formers; these were then shrouded in a

refractory board casing lined with firebrick. Thermal cycling of the furnaces was avoided in order to reduce thermal stresses on the winding. One burn-out occurred during the project, apparently due to part of the winding reacting with a zinc plated wire end locating clip.

When using a gas mixture it is important to select a flow rate high enough to prevent thermal segregation of the gases in the mixture. The flow rate required is a function of the furnace tube diameter and the temperature gradient (Richardson and Alcock (1959)). A flow rate of $100\text{cm}^3\text{min}^{-1}$ was used in the 25mm inside diameter furnaces and $200\text{cm}^3\text{min}^{-1}$ in the 70mm inside diameter furnace.

Both gravimetric and non-gravimetric tests were started by holding the specimens in the cooler part of the furnace (at around 100°C) with the gas mixture passing through the furnace for 30 minutes. After this period the specimens were rapidly moved into the hot zone of the furnace; this took approximately 30 seconds.

The reaction tubes were made of silica. Initially clear thin-walled quartz tube was used but at 1050°C this devitrified over about twelve weeks; replacement tubes were made from thicker walled sand surface silica which was more durable and less expensive. Thermodynamic calculations based on the atmospheres used indicated that silicon transport as SiS (Alcock et al (1971)) would not be a significant effect (pSiS at 1050°C , high pS_2 atmosphere $\sim 10^{-11}\text{atm.}$).

(ii) Temperature Control and Monitoring

Power was supplied to the furnaces by Eurotherm proportional controllers; a Pt/Pt 13%Rh thermocouple placed between the reaction tube and the furnace tube was used to feed the controller monitoring circuit.

A temperature survey was conducted on each furnace with oxygen-free nitrogen flowing through it at the required rate. The controller was adjusted to give a hot zone temperature within $\pm 1^\circ\text{C}$ of the desired value. Occasional checks indicated that the furnaces had good

Key to Figure 6

- a Gas tight neoprene seal
- b Furnace tube, 70mm inside diameter sand surface silica
- c Furnace
- d Specimen holder
- e Specimen on silica support rod
- f Ground glass flange secured with silastic silicone rubber sealant
- g Greased rubber sheet gasket
- h Sheet rubber baffle to reduce turbulence
- i Gas inlet
- j Specimen holder support rod (2mm diameter silica)
- k Specimen holder, detail, made from 8 100mm lengths of 15mm diameter silica tube
- l Specimen holder hanger rod
- m Platinum ties to hold tubes together

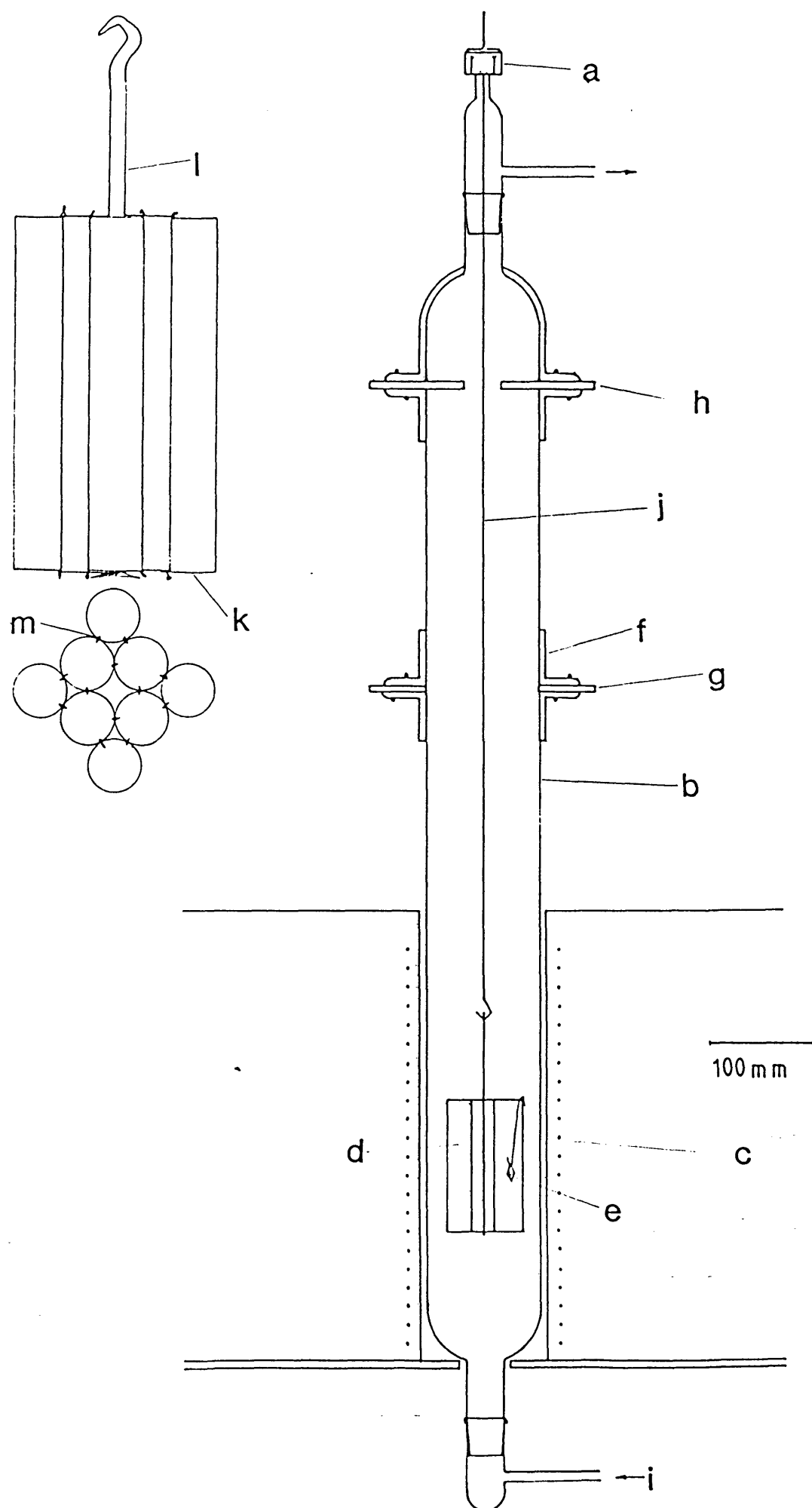


Fig6 Schematic Diagram of Non Gravimetric Rig

temperature stability, fluctuations did not exceed $\pm 2^{\circ}\text{C}$.

(iii) Furnace Atmosphere Monitoring

In order to determine whether chemical equilibrium of the gas mixture was being attained in the hot zone, the furnace was probed with an oxygen meter while the gas was flowing.

The probe used comprised a 150mm length of 6mm outside diameter stabilised zirconia tube (closed one end) joined to a 450mm length of chromia tube with 'Cerastil' refractory cement (supplied by Industrial Science Ltd., Dover). A platinum wire was connected to a blob of platinum paste on the tip of the zirconia tube, a Pt/Pt 13% thermocouple was put into the bore of the tube and tightly butted against the inside of the closed end with a spring. Air was used as the reference gas in the probe.

A value of thermocouple emf and the oxygen meter emf were taken using a high impedance digital voltmeter. The oxygen pressure was calculated using the Nernst relationship between emf and equilibrium constant (Maskell (1985)).

Table 4 shows the measured value of $p\text{O}_2$ in brackets underneath the calculated value. The agreement between the two values is good and suggests that equilibrium is being reached in the mixture.

(iv) Non-Gravimetric Rigs

The non-gravimetric rigs were used to expose several specimens to a similar environment simultaneously; this procedure economised on furnace space.

The first non-gravimetric rig (Figure 6) was made from a 700mm length of 70mm inside diameter sand surface silica. A specimen holder was made from 15mm diameter quartz tubing; originally the lengths of tube were fused together but this design proved to be too fragile to be practical; a modification was made by drilling 1mm holes at the tube ends and lacing them into a cluster with platinum wire. The first exposure was made at 1050°C and included a specimen of 5N co balt (Metals Research Ltd.) along with a selection of alloys; subsequent energy

Key to Figure 7

- a Furnace, Kanthal winding
- b Silica furnace tube, 25mm inside diameter
- c Specimens mounted on silica hooks
- d Silica support rod (2mm diameter)
- e Gas tight neoprene seal
- f Gas inlet
- g B29 cone with Teflon sleeve
- h Gas outlet
- i Spring x4

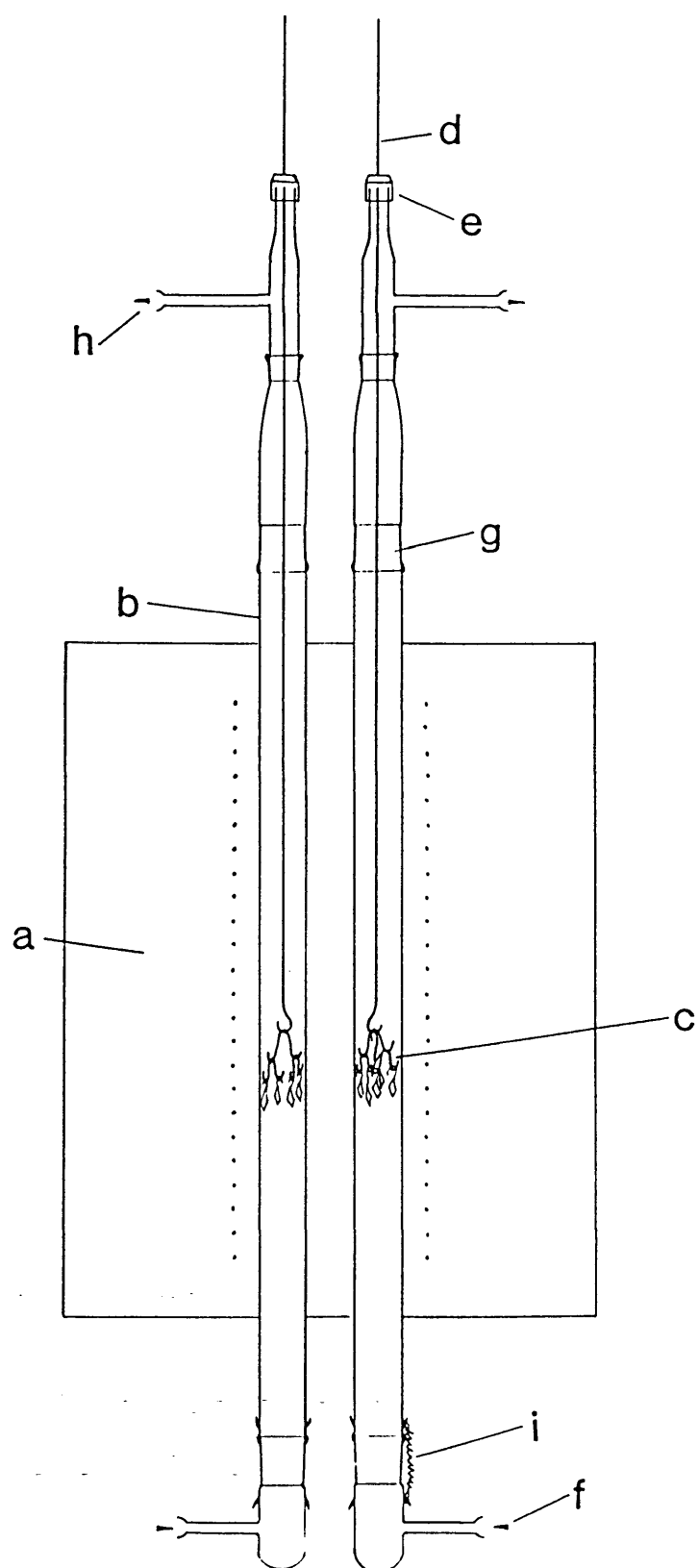


Fig.7 Improved Design
Non-gravimetric Rig

Key to Figure 8

- a Microbalance
- b Heavy top plate on welded steel rig
- c Baffle assembly
- d Specimen support rod (1mm diameter silica)
- e Furnace tube, silica
- f Specimen held on S-hook
- g Movable furnace on bushed sliders with Counterbalance weights (not shown)
- h Thermocouple tube
- i Optical window
- j Gas inlet

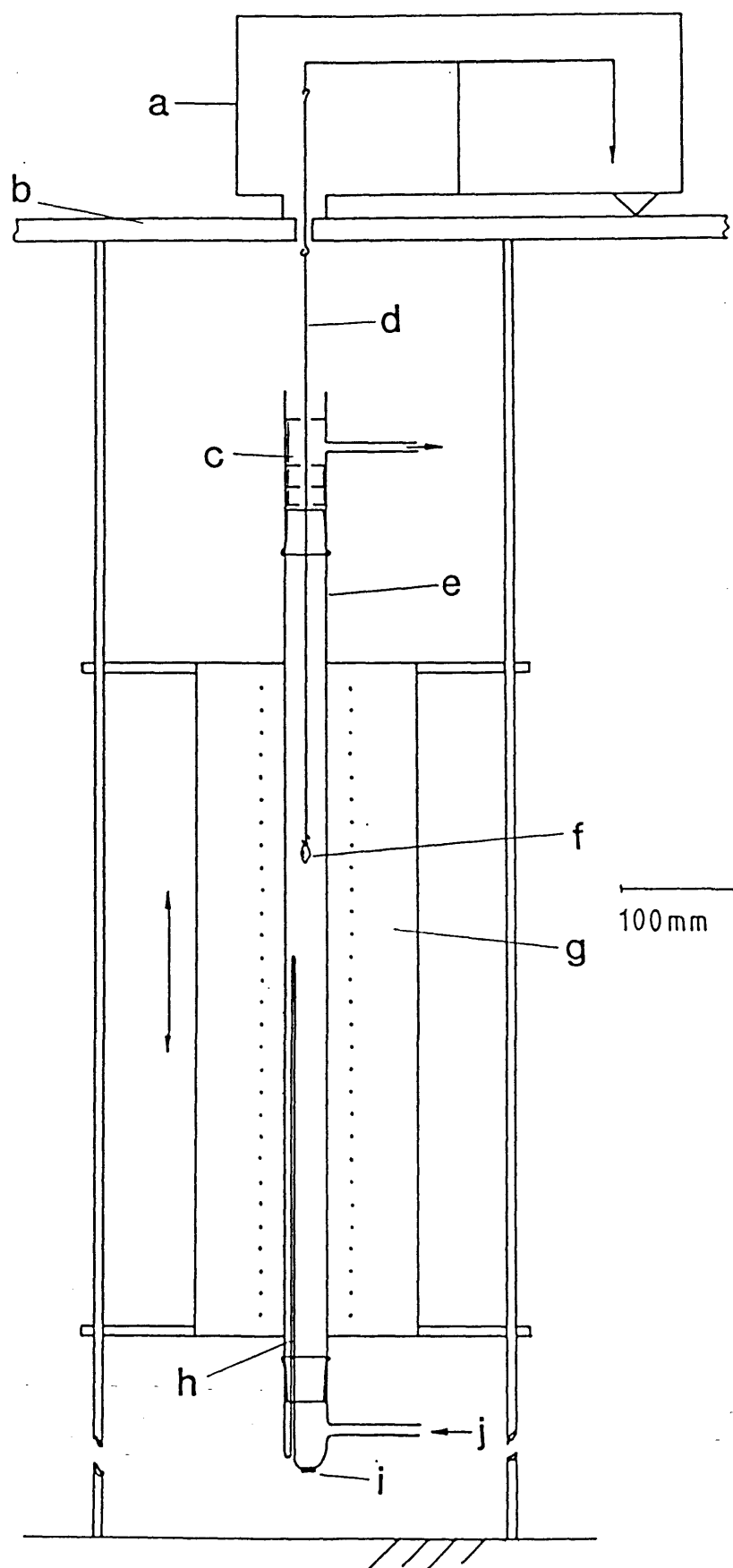
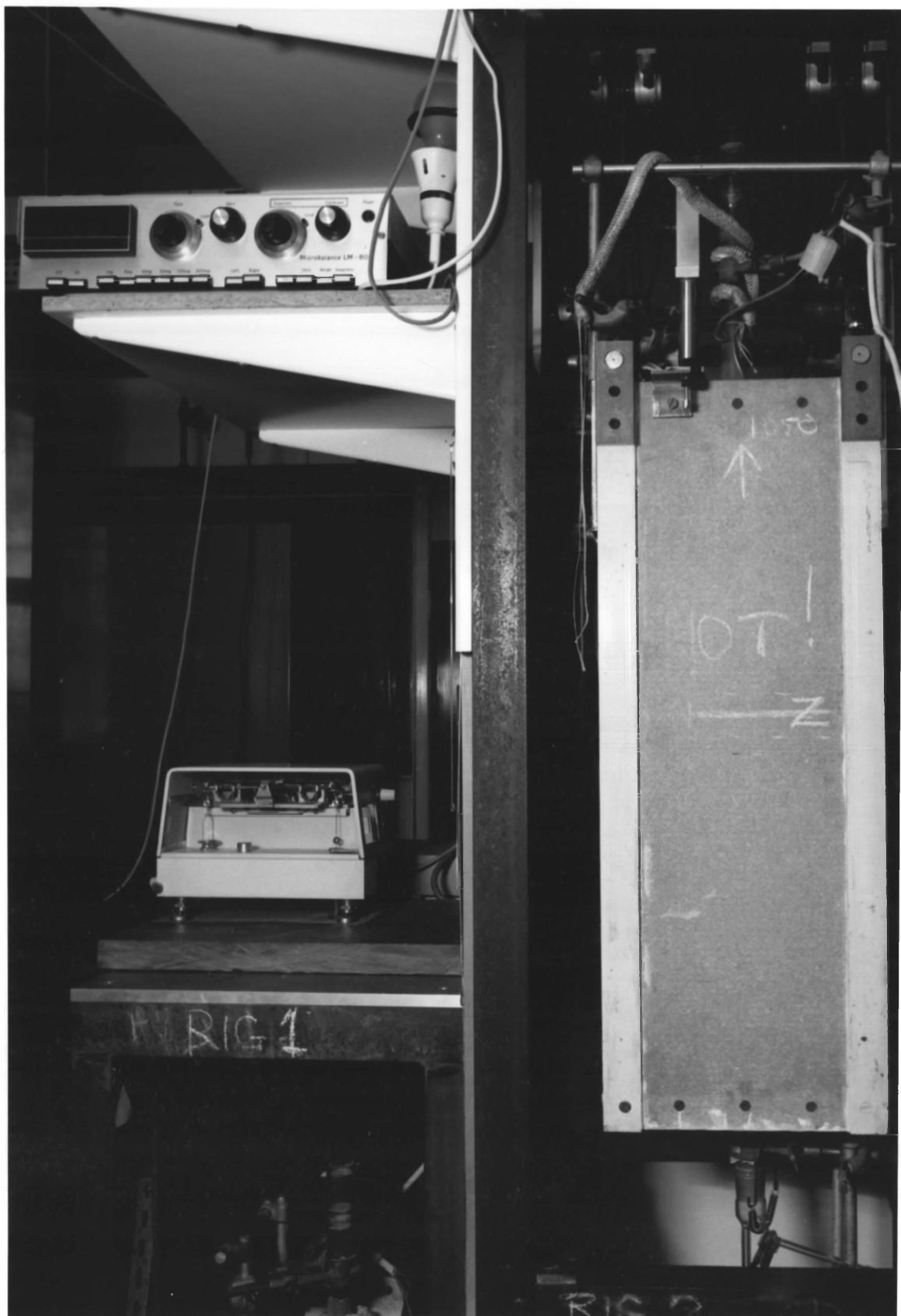


Fig8 Schematic Diagram of Gravimetric Rig



Photograph of the gravimetric rigs.

dispersive X-ray analysis of the cobalt specimen showed no other elements present; this suggests that no vapour phase transport of elements had occurred between specimens.

The furnace proved unsuitable for the study because connective effects caused a high volume 'refluxing' through the gas exit tube; this had the effect of drawing air into the furnace and changing the gas chemistry; corrosion results were not reproducible in the rig. Initially the exit tube was extended from a few centimetres to about 1m and an empty Winchester bottle was put in series with the waste tube to act as a ballast of gas to damp the refluxing but the effect persisted and the modification did not improve the situation. A redesigned furnace tube was used.

The second design non-gravimetric rig comprised two 25 cm diameter quartz reaction tubes; the specimens were suspended from a series of 1mm diameter quartz hooks mounted on a quartz rod (Figure 7). This rig was found to give consistent results and to be trouble free.

(v) Gravimetric Rigs

Two rigs were used (Figure 8 & Plate 4); each comprised a rigid welded steel frame with a heavy top plate for balance mounting. The specimen was connected to the balance arm by a length of 1mm diameter quartz rod and a small quartz S-hook.

The specimen remained static relative to the framework and the furnace and reaction tube could be moved so as to bring the hot zone adjacent to the specimen. One rig used a manual winch, one an electric winch for moving the furnace.

Specimen weight changes were detected by microbalances. A Sartorius model 4135 and a Beckman model LM800 balance were used, the balance was set up by counterbalancing the specimen and support weight with small washers and copper clippings. In ideal circumstances the balances are capable of detecting weight changes of less

than $10\mu\text{g}$; in practice Archimedian buoyancy effects caused by the flow of gas around the specimen limit this to about $100\mu\text{g}$ usable sensitivity.

In order to prevent burning back or 'popping' of the flammable gas mixture due to ingress of air into the open top of the furnace tube, with the associated problems of possible specimen dislodgement or changes in gas chemistry, a baffle system was used.

The baffle comprised four Teflon disks, three spaced about 5mm apart below the gas exit tube, one above the gas exit tube; the disks were separated with sections of glass tube concentric with and touching the furnace top tube. When set up correctly, 6mm central holes in the disks allowed unimpeded movement of the silica rod.

Both microbalances provide an analogue voltage output; the output was recorded on a Smiths Servoscribe 2s voltage-time 2 channel pen recorder. A suitable chart speed was found to be 120mm per hour; a standard chart would provide about 200 hours of recording at this speed. It was necessary to optimise the recorder sensitivity for the corrosion kinetics; where small weight changes occurred over long periods an oversensitive range could produce excessive 'flutter' in the trace due to buoyancy effects making it difficult to determine the weight change.

The recorder charts were read manually, the balance system was calibrated to give a value of pen displacement per unit weight change on the ranges used; this was then used to calculate weight changes. Two computer programmes were used to process the data. 'Areacal' converts weight change to weight change per unit area.

'Plot' enables linear or parabolic plots of weight gain against time to be made.

(c) Specimen Preparation

(i) Cutting and Polishing

The alloys examined were supplied as rolled sheet approximately 1mm thick. Specimens of roughly 1cm side length

were guillotined from the sheet. The higher aluminium content alloys tended to crack or exfoliate if cut at room temperature, heating in hot water raised the metal to above its brittle/ductile transition temperature and enabled clean cutting. A 1.2mm diameter suspension hole was drilled in one corner of each specimen.

Specimens were deburred with a fine file and then polished on each face through 320 and 600 grade down to 800 grade silicon carbide paper in flowing water. Between grades the specimens were ultrasonically cleaned in distilled water for 2 mins. After 800 grade a 5 min ultrasonic cleaning was followed by acetone rinsing and warm air drying.

The thickness of the polished specimens was measured with a micrometer; the surface area of the specimen was calculated from side length measurements. Where awkward shaped (kite shaped) specimens occurred area was estimated by weighing a cut out photocopy of the specimen and comparing the weight to the weight of 1cm^2 of photocopy paper.

Specimens were weighed on a Stanton MC3 semi microbalance. They were stored in a desiccator prior to exposure.

(ii) Preoxidation Treatment

Some specimens were preoxidised in air prior to exposure to the sulphidising atmosphere. The preoxidation treatment was carried out at 1100°C in a muffle furnace.

Specimens were mounted on a 1mm silica rod by their suspension holes. The rod was located in two grooves in a short length of 3 inch diameter alumina tube. After oxidation the assembly was placed in still air to cool; the small specimens cooled rapidly. Various preoxidation times ranging from 2 mins to 3h were used.

2 Specimen Examination

(a) General

Corroded specimens were cooled in the flowing gas mixture and removed from the furnace. The specimens were weighed

on a semi-microbalance, the S-hooks used to suspend the specimens were weighed before use; in cases where severe corrosion had occurred it was sometimes necessary to weigh the specimen and hook together and calculate the specimen weight change by difference.

In some cases loose scales were scraped from one of the large surfaces of a specimen with a steel scalpel blade; the scrapings were subsequently studied by X-ray diffraction.

The main method of study used was scanning electron microscopy supplemented by optical metallography of selected samples. As required specimens were mounted in a free flowing cold setting epoxy resin (B & K Resins Ltd) and polished down to 1µm surface finish on a diamond lap. Specimens were stored in a desiccator.

(b) Scanning Electron Microscopy

Three microscopes were used; a Jeol T-200, mainly used for topographic study, a Joel JSM 35CF with Link System 860, 500 series software (this microscope had "digimap" and ZAF corrected analysis available). A Cambridge model 180 with Link System 860, 200 series was used at Wiggin Alloys in Hereford; this analyser used a windowless X-ray detector and could provide qualitative analysis for oxygen.

In many cases the larger surfaces of the specimen were examined with the specimen stub-mounted, subsequently it was resin mounted and a polished section was examined.

(c) X-ray Diffraction

Either powdered scrapings or corroded specimens were examined on a Philips 1700 series X-ray diffractometer operating at 40kV, 40mA, with a copper target. The lattice parameter data produced was compared with standards tabulated in Hanawalt powder diffraction data file (1983).

(d) Transmission Electron Microscopy

A selection of oxide scales were examined in a high voltage electron microscope (AEI model EM7). The scales

were produced by air oxidation of the alloys at 1100°C.

The oxide film was isolated by polishing one of the large surfaces on 600 grit silicon carbide paper to remove the oxide; the oxide layer was then coated with carbon in a Nanotech coater. The specimen was laid oxide film uppermost on a platinum wire cradle and gently lowered onto the surface of the 10% bromine in methanol solution warmed to about 80°C (as used by Pendse et al (1985)). With care the oxide film could be placed on a grid and examined, electron diffraction patterns were produced for some samples.

CHAPTER III

RESULTS

1 General Introduction

Six alloys were selected from the range available: MA956 and alloys A, C, D, I and K; these represent Fe 16-25Cr 4-6.5Al (w^t/o) and a small tantalum addition to alloy I; nickel is present in alloy K. Alloys will be referred to by their laboratory code (see Table 3) and the w^t/o of the major alloying elements shown in brackets eg alloy C (Fe 16Cr 4Al). Nine exposure conditions were used as shown in Table 4. It was not possible to acquire kinetic data for all alloys in all exposure conditions: only non-gravimetric tests were made in some cases.

Two distinctly different types of corrosion behaviour have been observed: a protective type in which thin scales are formed which is associated with small weight increases ($\sim 1-2 \text{ mgcm}^{-2}$ in 200h) and a sulphidation-type attack which produces relatively large weight increases ($\sim 50 \text{ mgcm}^{-2}$ in 200h). The presence of oxide scales preformed in air greatly reduced the rate of corrosion in sulphidation-promoting atmospheres.

The results will be presented under the headings 'Low Weight Gain', 'High Weight Gain' and 'Preoxidised'.

High weight gains only occurred in three of the atmospheres tested: med pS_2 (7.3×10^{-7} atm) and high pS_2 (8.1×10^{-6} atm) at 850°C and high pS_2 (3.9×10^{-5} atm) at 950°C . All the other atmospheres tested produced low weight gains.

2 Low Weight Gain

(a) Introduction

These specimens were usually characterised by the formation of thin, ($\sim 5 \mu\text{m}$) uniform, slow growing scales. Examination of the specimens, by eye, generally showed an even pale grey coloured surface with no obvious discontinuities. Some scales tend to a brown (alloy I) or blue colour after $\sim 500\text{h}$ at higher temperatures.

Graphs 1-6 represent 'normal' behaviour for a selection of alloys. Kinetic data is presented in Table 5.

(b) Description of Plates

Plate 5 shows general views of the surface of scales formed in conditions which promoted protective kinetics.

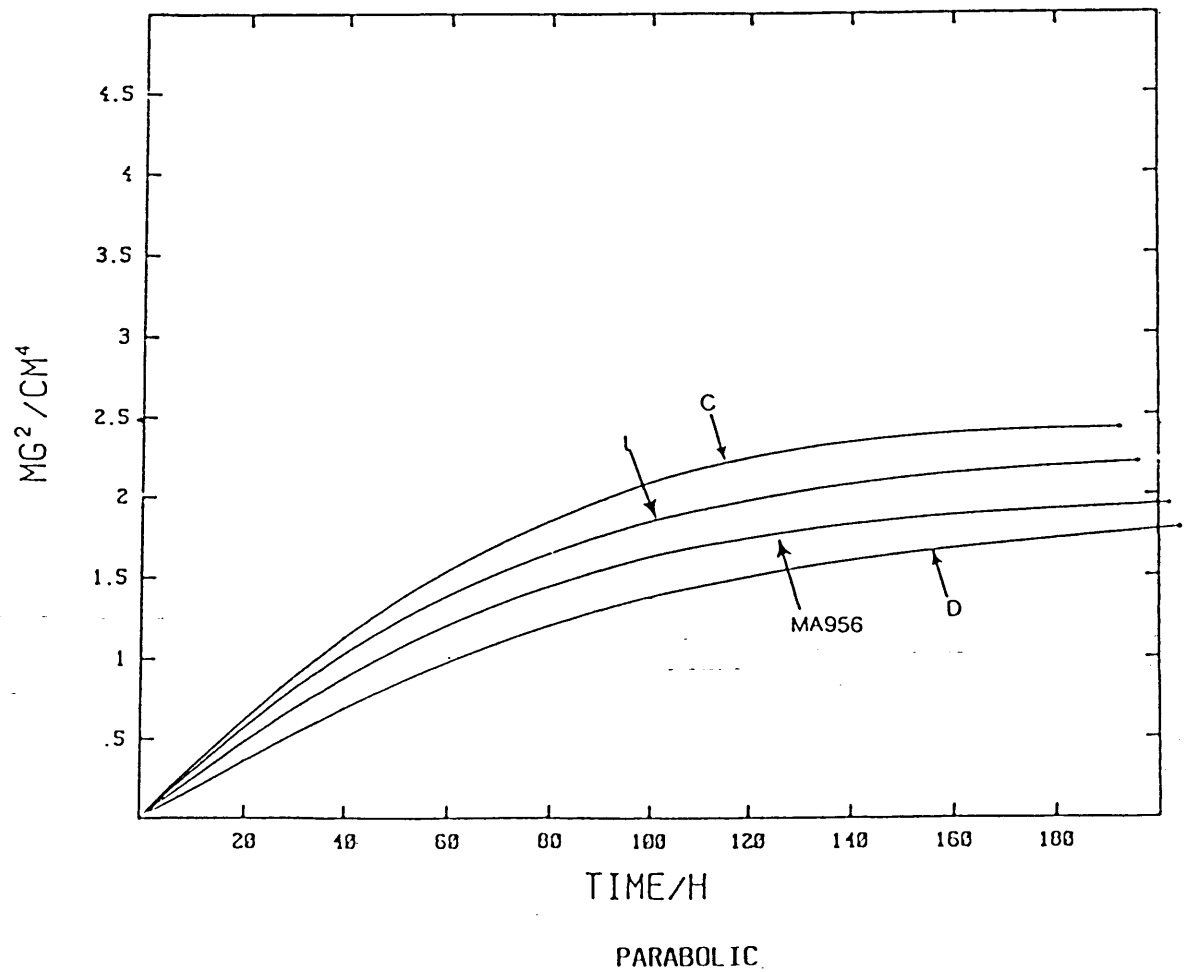
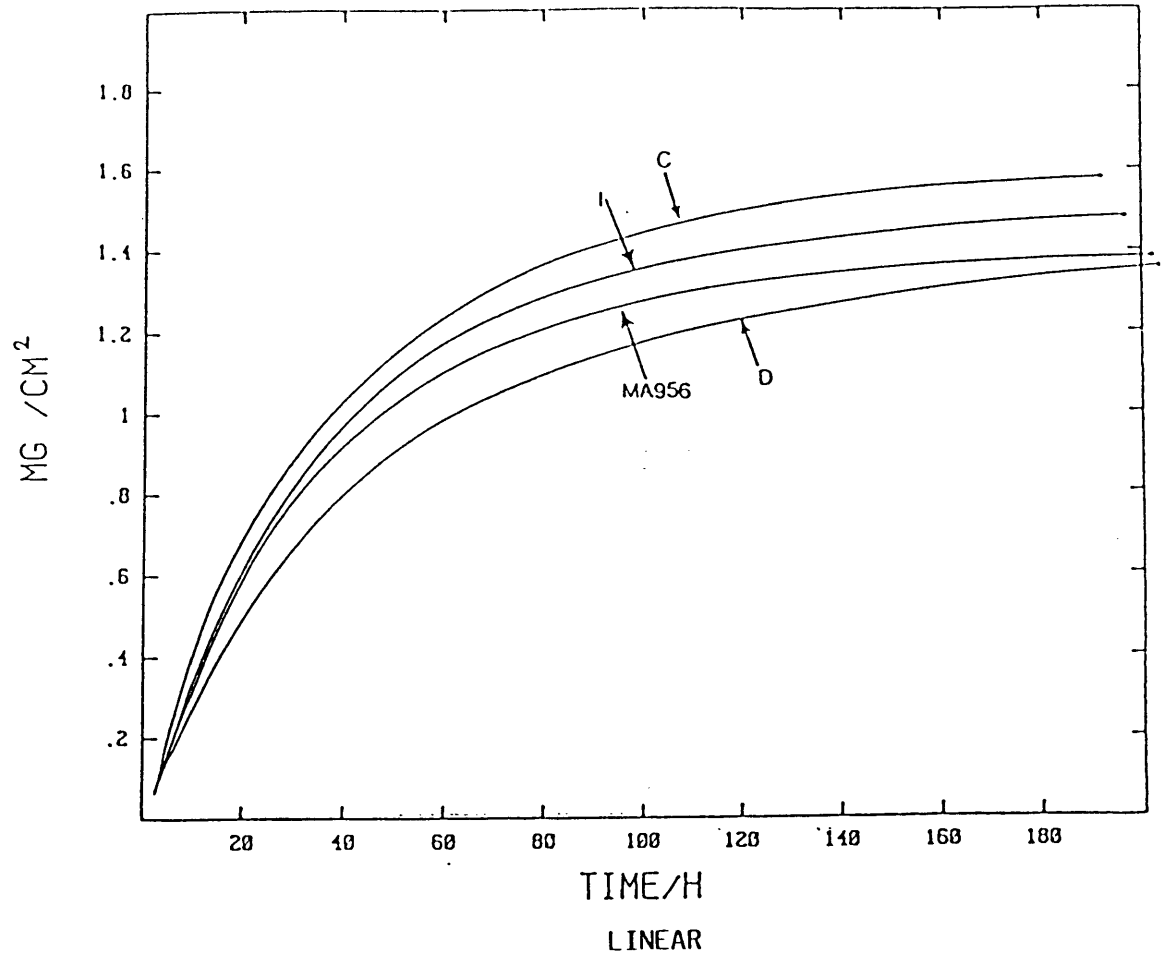
The surfaces are not uniform and small globules are present in some areas or (alloy K) some paler coloured areas are present arrowed on the electron image.

Plate 6 shows analysis for the surfaces of two specimens. The results suggest that the scale is mainly aluminium oxide (Al_2O_3 is 52 $\text{w}\%$ Al). The paler areas are associated with Y enrichment and a slight increase in iron and chromium concentration. Sulphur was not detected.

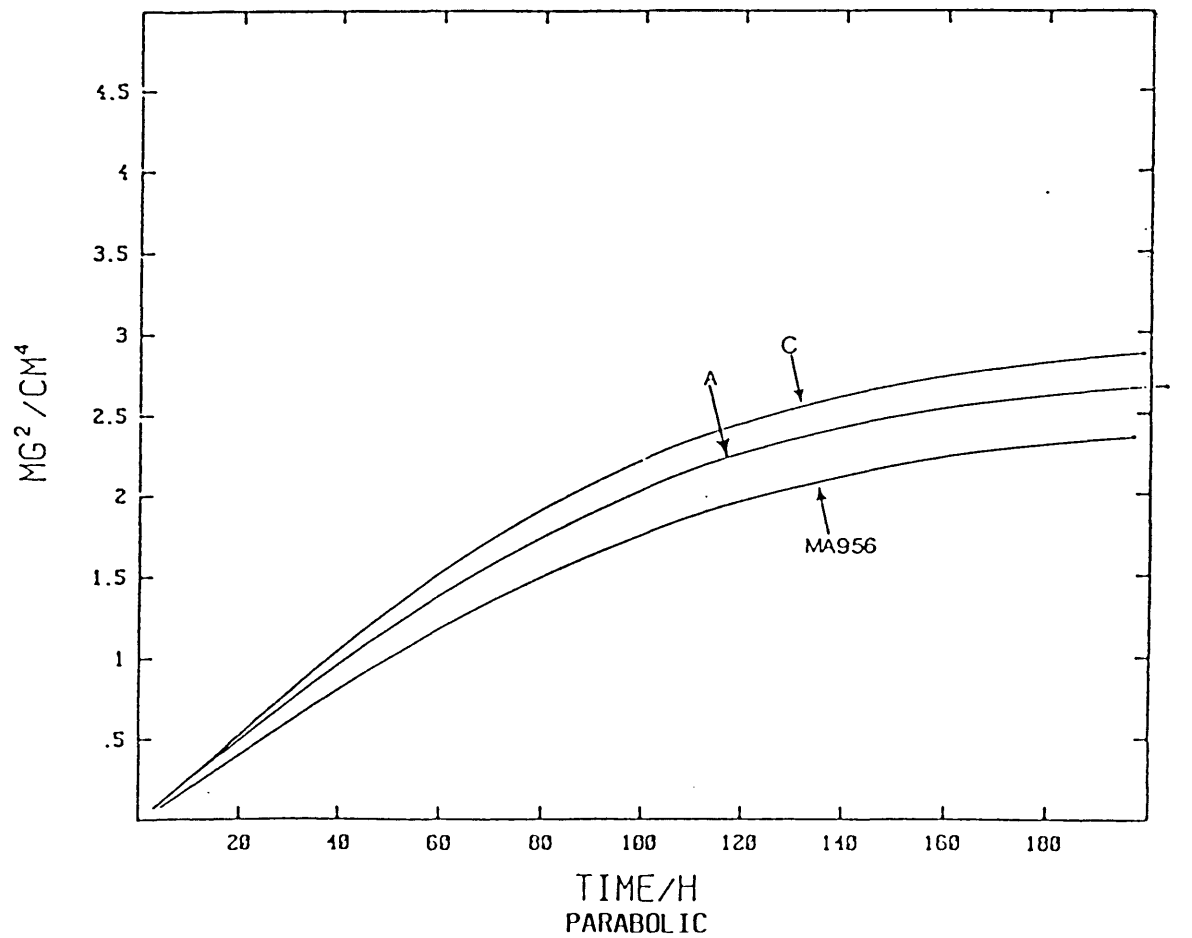
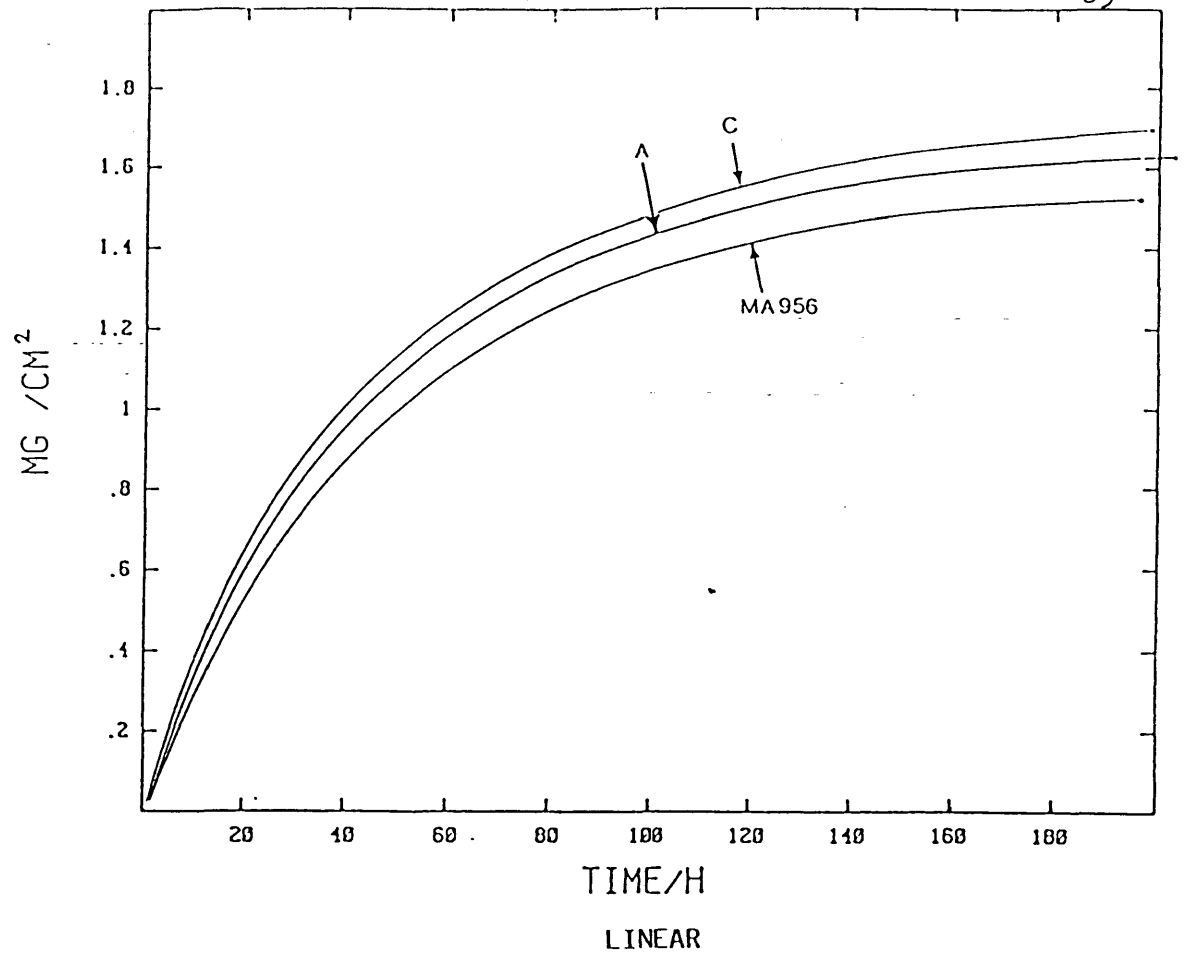
X-ray diffraction studies were made of the surfaces of corroded specimens of MA956 and alloys C and D; the results were inconclusive and no form of Al_2O_3 was positively identified, some small peaks associated with alpha Al_2O_3 were recorded however.

Some examples of scale detachment are shown in plate 7. This was not normally seen. When detached areas were seen in specimens which had been corroded in a gravimetric rig no sudden weight loss was seen on the kinetic plot; this suggests that the spalling occurs during cooling to room temperature rather than while at the exposure temperature.

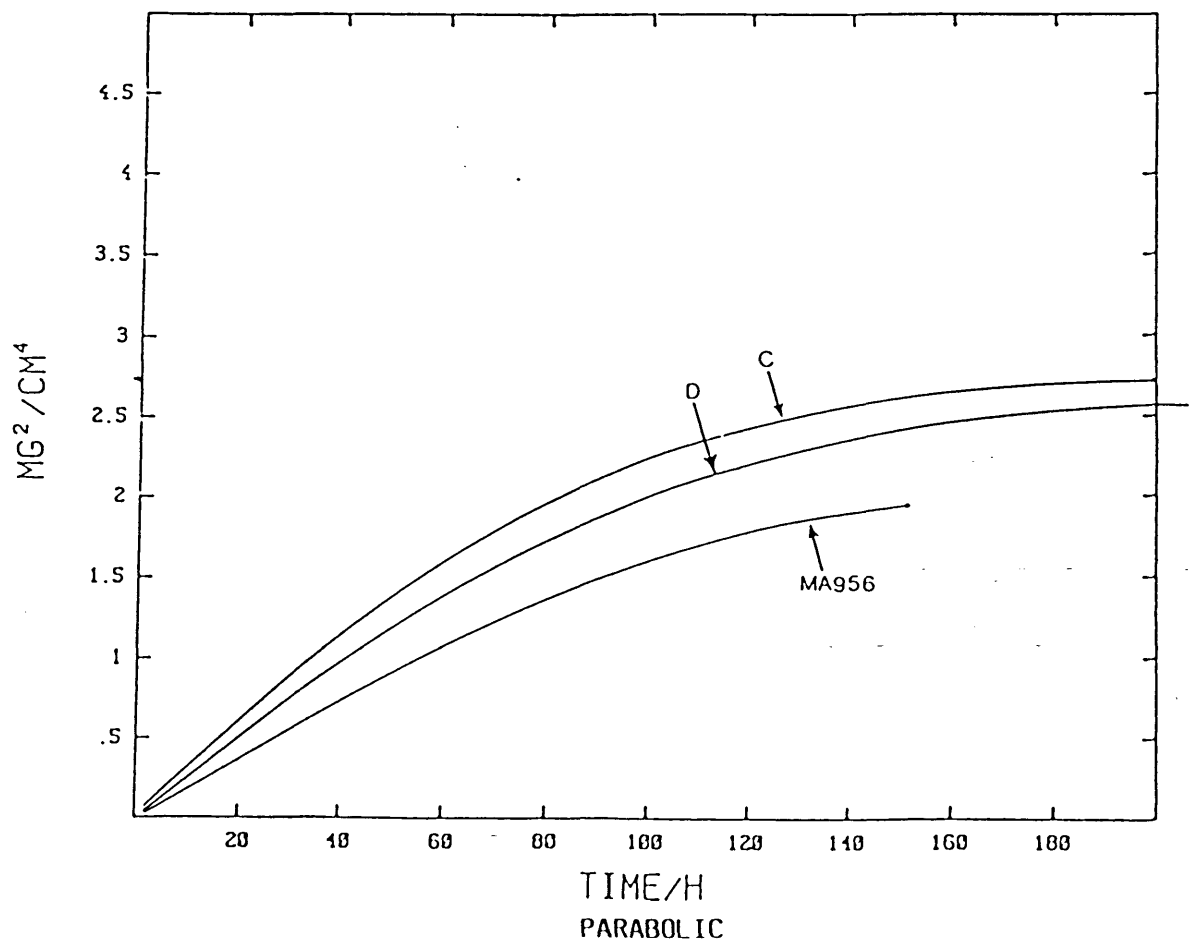
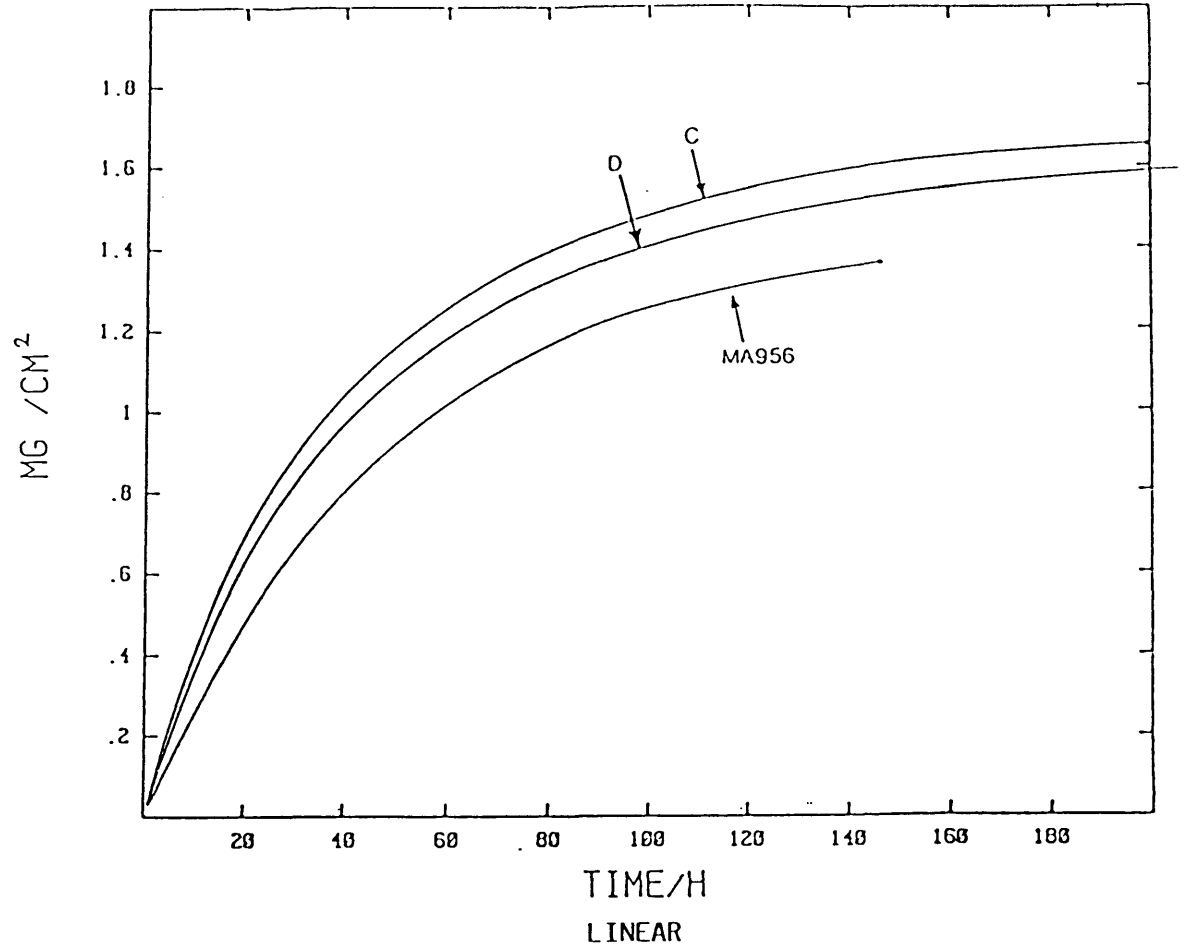
Analysis indicates an Al-rich scale with the unattacked



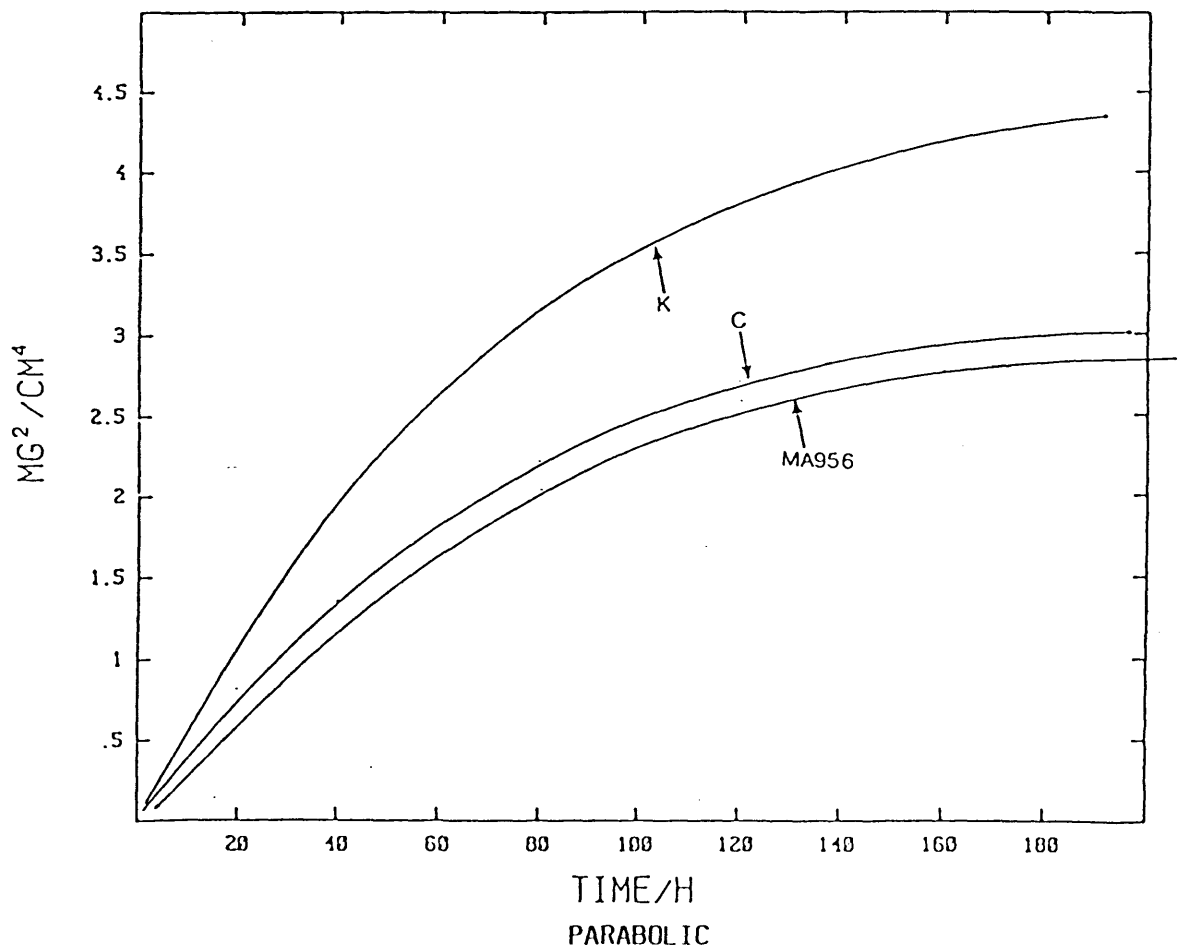
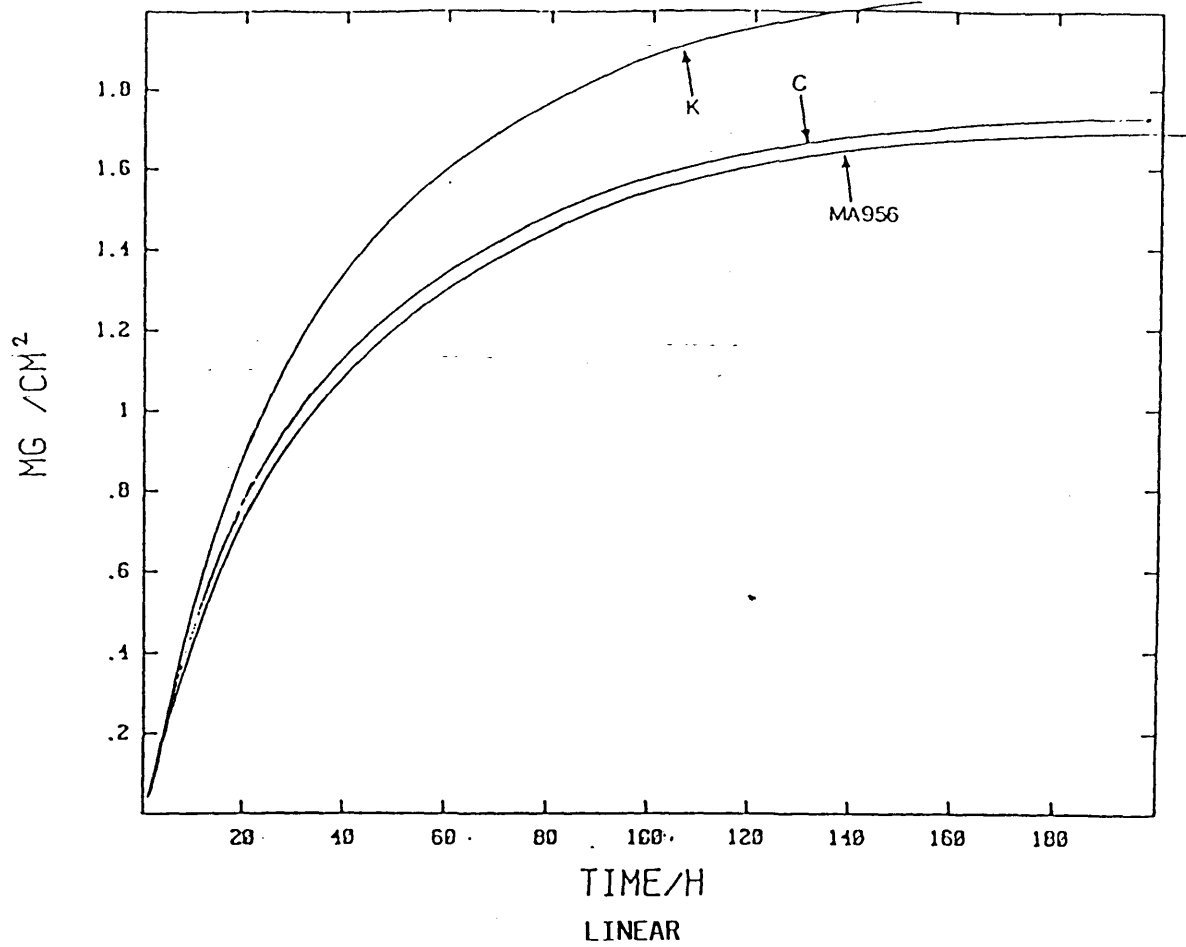
Kinetic plots for alloys MA956 C, D, I, in low pS_2 atmosphere at 1123 K



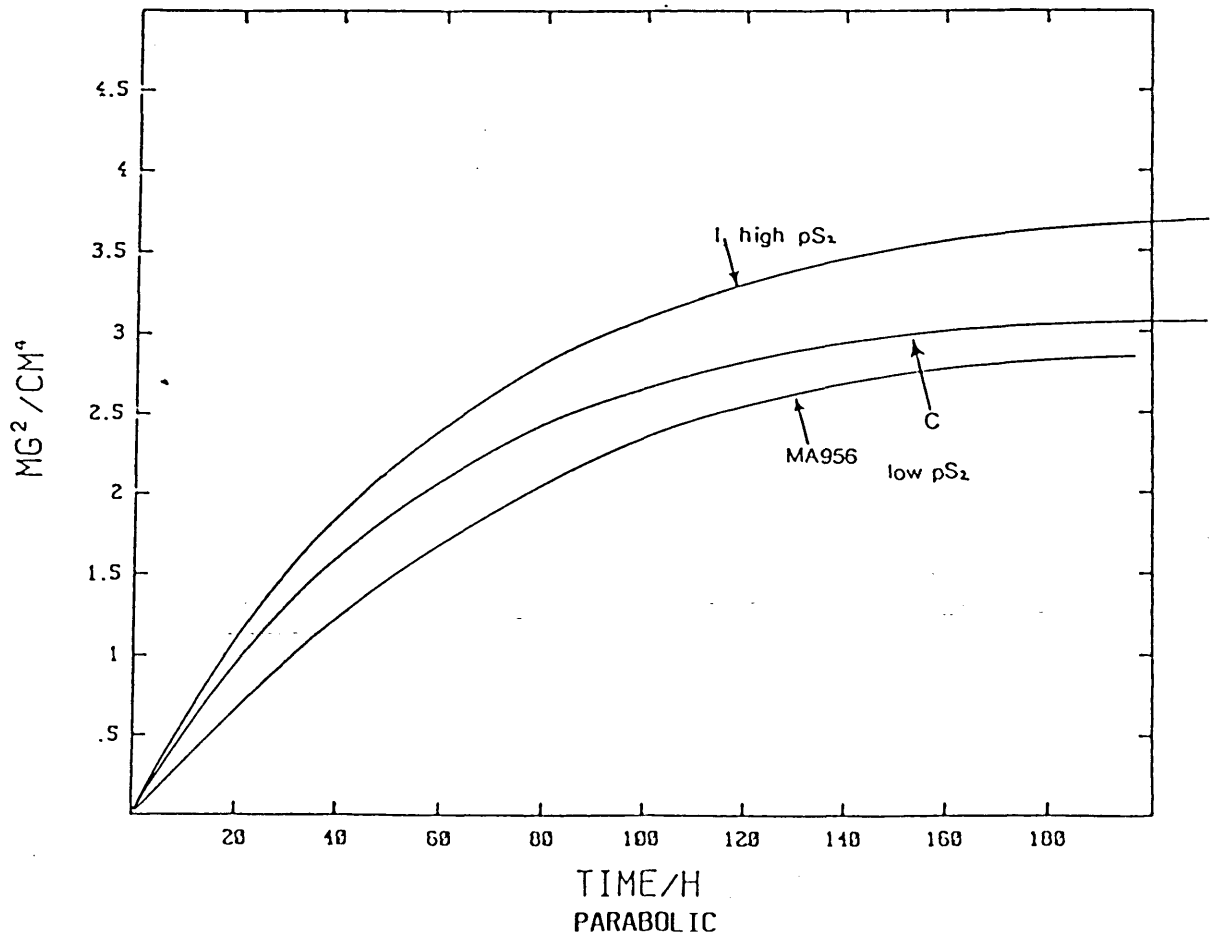
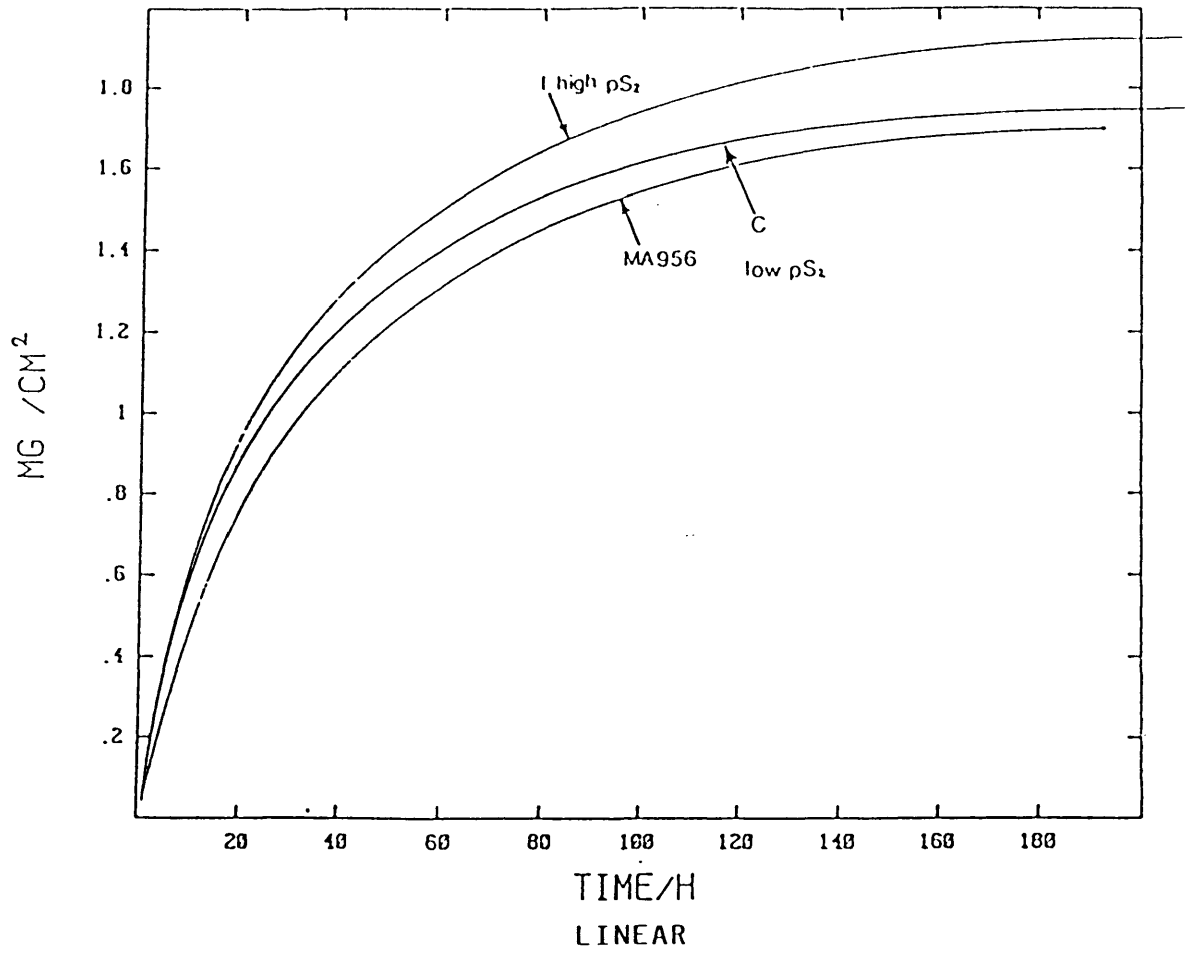
Kinetic plots for alloys MA956 A, C, in low pS₂ at 1223 K



Kinetic plots for alloys MA956 in med. pS₂ atmosphere at 1223 K

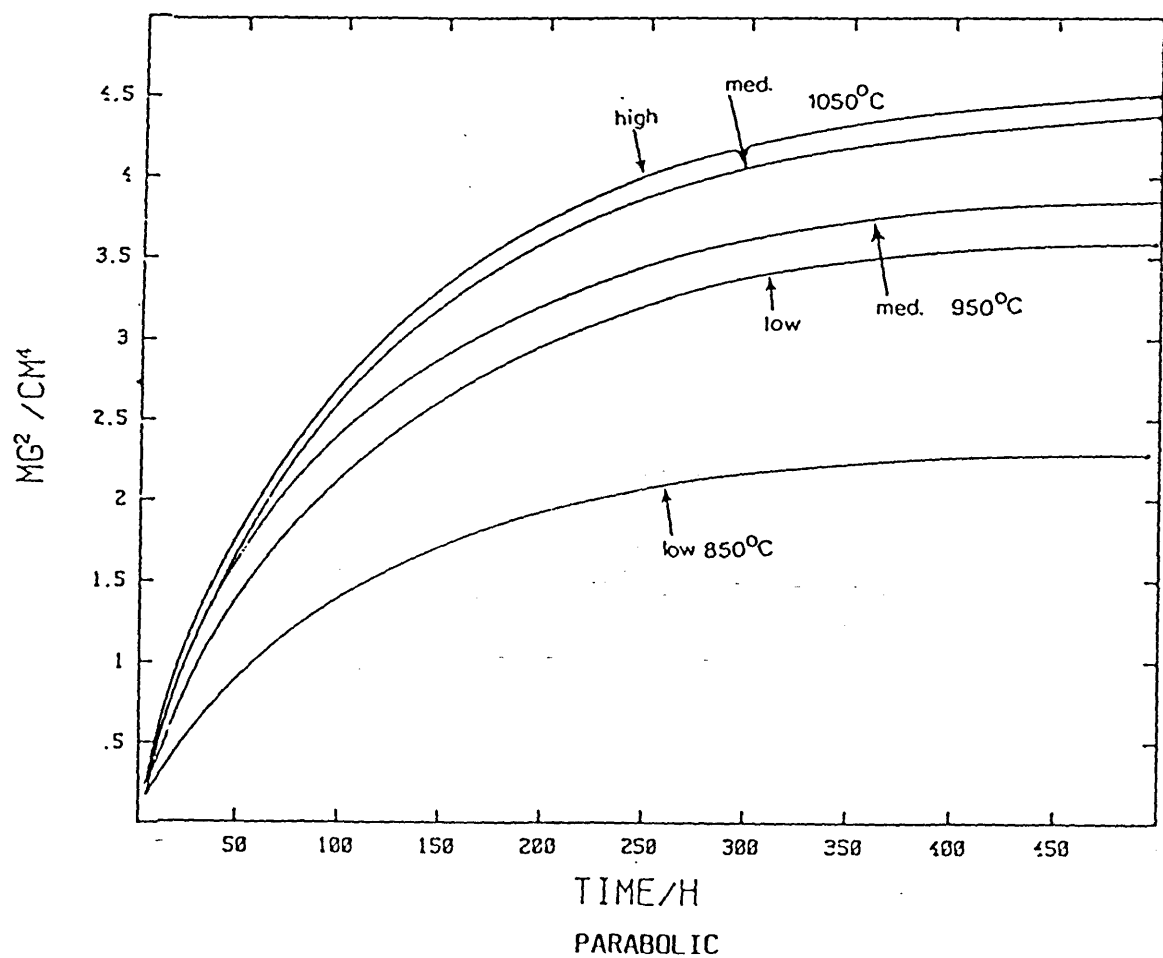
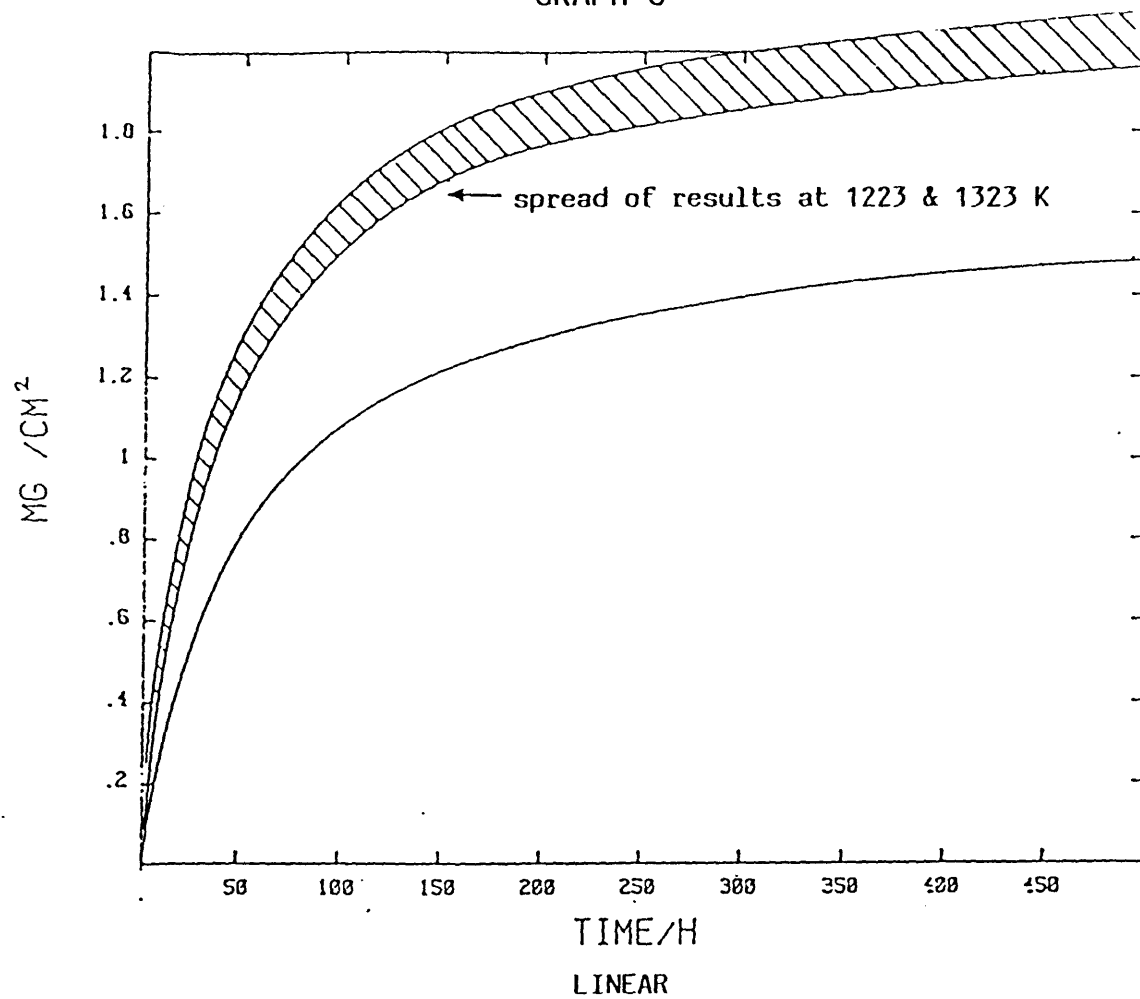


Kinetic plots for alloys MA956 C, K in med. pS₂ atmosphere at 1323 K



Kinetic plots for alloys in MA956 C in low pS_2 atmosphere at 1323 K and alloy I in high pS_2 atmosphere at 1323 K.

GRAPH 6



MA956 corroded in various atmospheres as indicated

ALLOY	ENVIRONMENT	LINEAR RATE CONSTANT/ $\text{g cm}^{-2} \text{S}^{-1} \times 10^{10}$	PARABOLIC RATE CONSTANT/ $\text{g}^2 \text{cm}^{-4} \text{S}^{-1} \times 10^{13}$
A		2.0	5.6
C		1.9	4.8
D	1123K,	2.1	5.6
I	low pS_2	2.1	5.7
MA956		1.4	3.0
A		2.4	6.3
C	1223K	2.7	6.5
K	low pS_2	2.3	6.2
MA956		1.9	5.8
			all 100-200h values
C		2.8	6.7
D	1223K,	2.0	5.7
MA956	med pS_2	1.8	5.6
C		2.1	5.7
I	1323K,	1.8	5.4
MA956	low pS_2	1.9	6.0
I	1323K,	2.1	6.1
MA956	med pS_2	2.0	5.8
C		2.2	6.3
K	1323K,		8.2
MA956	high pS_2	2.1	6.1
			1.3
	1123K, low pS_2		1.5
	1223K, low pS_2		1.6
	1223K, med pS_2		2.5
	1323K, low pS_2		2.3
	1323K, med pS_2		2.8
	1323K, high pS_2		
MA956			200-500h values

Table 5

Linear and Parabolic Rate Constants for Selected Low Weight Gain Specimens.

alloy exposed where detachment has occurred. The pattern of lighter areas on the upper surface of the scale appears to follow the pattern of craters in the underlying alloy. The lighter areas on the scale are slightly enriched in Y. The craters and smooth exposed alloy show little difference in composition.

The element distributions in plate 9 refer to a section of alloy D from plate 8. The scale is aluminium-rich; the matrix is homogeneous except for some small areas of Cr-depletion associated with dark dots on the electron image. Scans for Y and Ti showed a homogeneous distribution.

Plate 9 shows an example of scale disruption near to the apex of a corner of the specimen. This area was most frequently associated with scale damage, when this occurred.

The disruption of the scale has allowed some Fe and Cr to 'leak' out from the alloy beneath, sulphur was absent from this specimen.

Scale disruption at edges and corners was not uncommon but did not lead to sulphidation; the damage was always contained despite the stability of iron sulphide in the environment.

Plate 10 shows a scale formed at high pS_2 and 1323K on alloy I. The scale is slightly enriched in Ta relative to the subadjacent matrix; the presence of Ta in the scale may be responsible for the brown colour of scales seen on this alloy.

Sulphur is absent from the scale and subadjacent matrix; it is however present in the bulk alloy and associated with dark areas in the matrix where the Ta concentration is also increased.

These effects were not displayed by other alloys in this atmosphere, the presence of Ta in the alloy is associated with the sulphur.

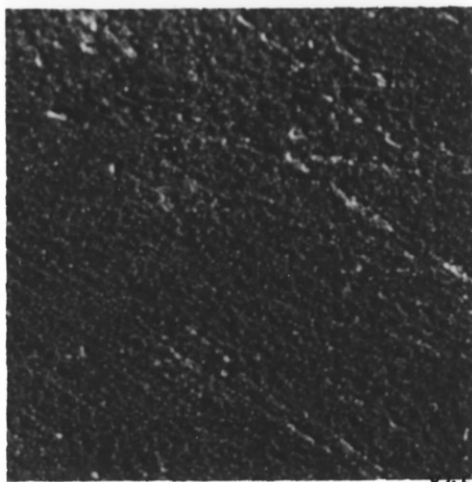
Plate 11 shows the distribution of Fe Cr and Al near to a specimen corner.

The scale is Al-rich and is not penetrated by iron or chromium. The dark areas in the matrix are slightly enriched in Al; these areas, analysed in other specimens, generally have aluminium contents of 40-50 % associated with small concentrations of the other alloying elements. It is possible that these are internally formed oxides, analysis with equipment capable of detecting oxygen (Philips 180 at Wiggin Alloys) gave inconclusive results, probably due to the small size of the areas.

Plate 12 shows X-ray spectra for the matrix and the scale formed on MA956. The scale is mainly aluminium oxide and traces of iron and chromium may be present in the scale or may result from spurious excitation of the matrix; this analysis was made with 10kV accelerating voltage.

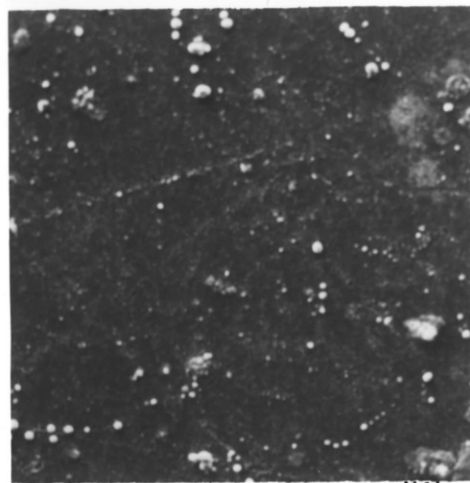
A Ti peak is clearly evident in the scale spectrum, it is not obvious whether titanium enrichment has occurred or whether the lighter elements in the scale have allowed a higher apparent Ti concentration to be recorded.

Analysis on a Jeol JSM35 at Imperial College has consistently failed to detect a Ti concentration gradient in specimens examined either by localised ZAF analysis or digimap element distribution maps.



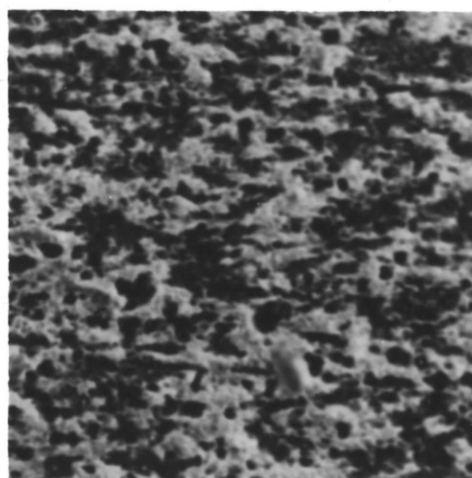
X450

Alloy A ($\text{Fe}_{24}\text{Cr}_{4.5}\text{Al}$), 506h,
low $p\text{S}_2$, 1323K surface



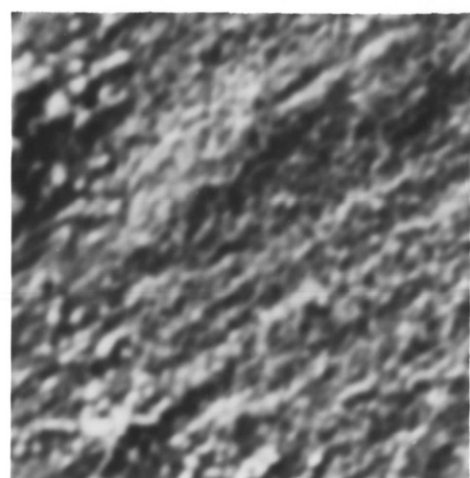
X1k

MA956 ($\text{Fe}_{20}\text{Cr}_{5}\text{Al}$), 197h,
low $p\text{S}_2$, 1223K surface



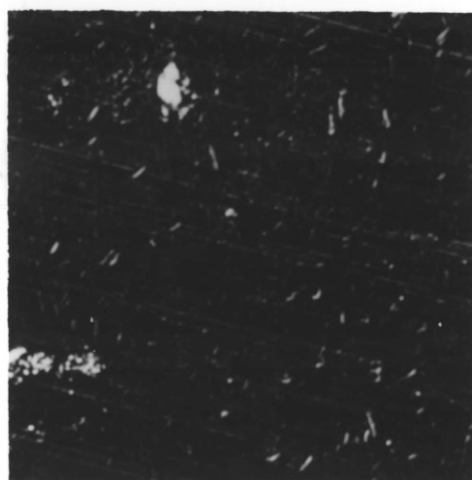
X600

Alloy K ($\text{Fe}_{20}\text{Cr}_{4.5}\text{Al}_{14}\text{Ni}$),
191h, med. $p\text{S}_2$, 1323K surface



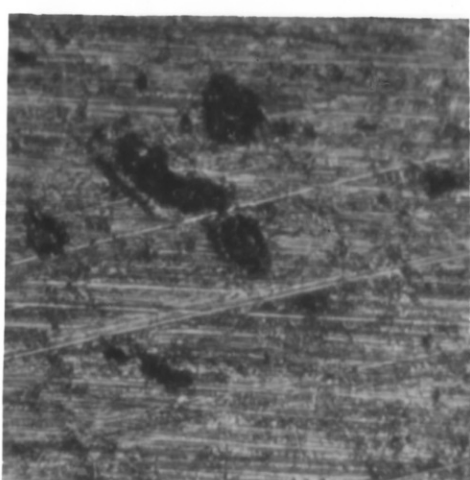
X1.5k

Alloy D ($\text{Fe}_{25}\text{Cr}_{6.5}\text{Al}$), 213h,
med. $p\text{S}_2$, 1223K surface



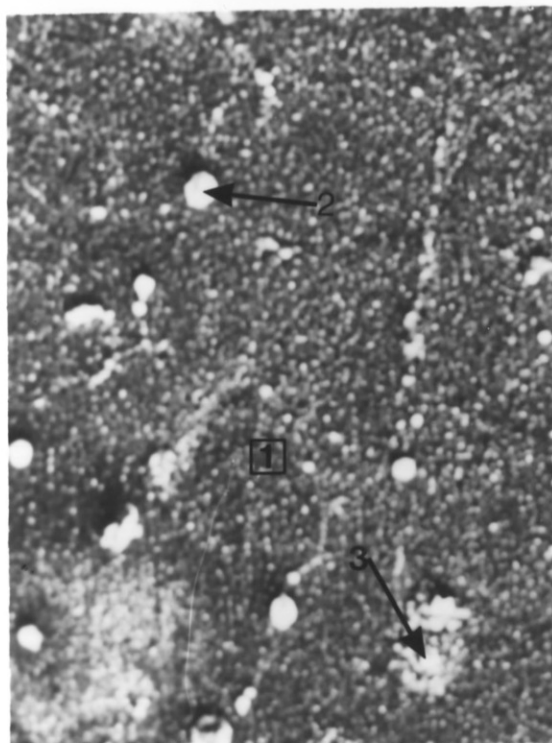
X150

MA956 ($\text{Fe}_{20}\text{Cr}_{5}\text{Al}$), 202h surface



X90

optical micrograph
low $p\text{S}_2$, 1123K



X3.5k

Alloy D (Fe25Cr6.5Al), 506h, low pS₂
1323K surface

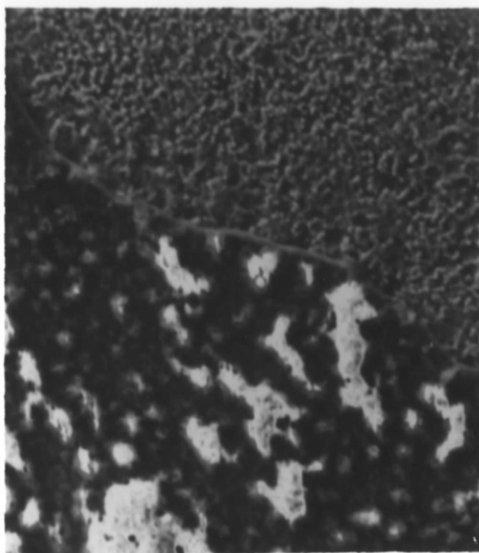


X1.2k

MA956 (Fe20Cr5Al) 192h, med. pS₂
1223K surface

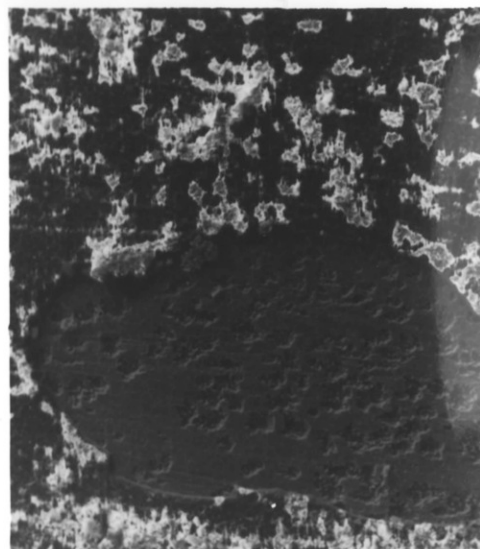
Element	Wt.% Area of Print					
	1	2	3	1	2	3
Fe	2.4	1.9	4.8	2.2	3.6	4.1
Cr	1.2	0.9	4.3	0.7	1.5	3.6
Al	44.9	40.5	41.9	47.3	44.6	43.7
Ti	0.1	0.2	0.1	0.1	0.1	0.2
Y	0.2	1.4	1.3	0.1	1.2	0.9
S	-	-	-	-	-	-
Total	48.8	44.9	52.4	50.4	51.0	52.2

ZAF Analysis of Selected Areas of Specimens



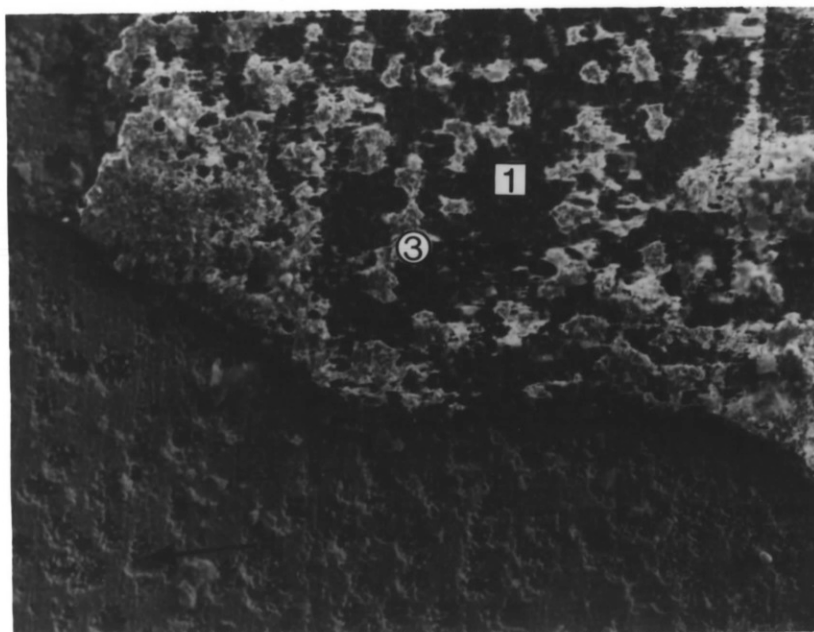
X600

Alloy 1 (Fe20Cr4.6Al1.9Ti), 559h
med. pS₂, 1323K surface showing
detached scale



X300

MA956 (Fe20Cr5Al), 559h, med.
pS₂, 1323K surface showing
detached scale



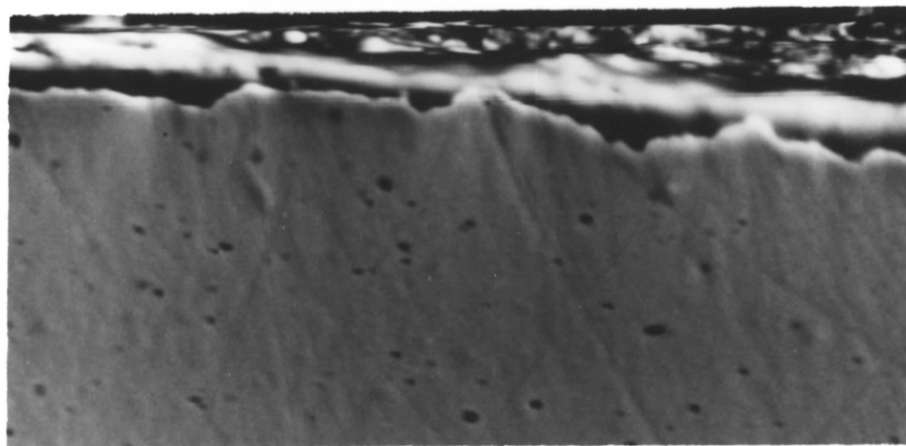
X400

Alloy D (Fe25Cr6.5Al), 213h, med. pS₂, 1223K surface
showing detached scale

Element	wt.% Area of Print			
	1	2	3	4
Fe	1.8	65.7	2.1	68.1
Cr	0.9	23.1	1.1	23.2
Al	47.2	6.3	45.3	5.9
Ti	0.1	0.3	0.2	0.2
Y	0.1	0.2	0.6	0.2
S	-	-	-	-
Total	50.1	95.6	49.3	97.6

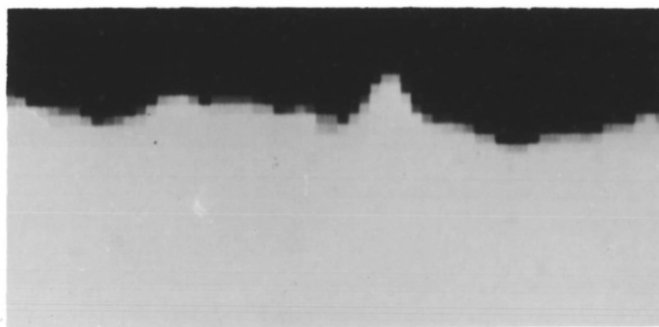
ZAF Analysis of selected areas of above

PLATE 7

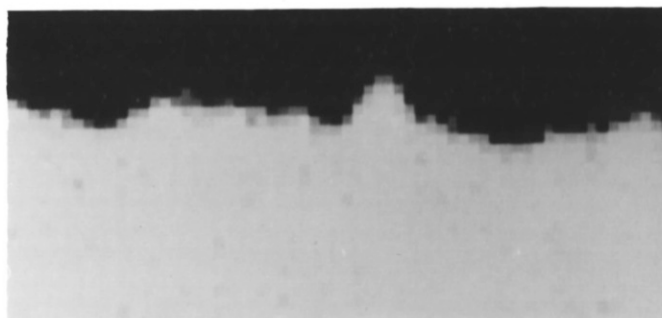


X2k

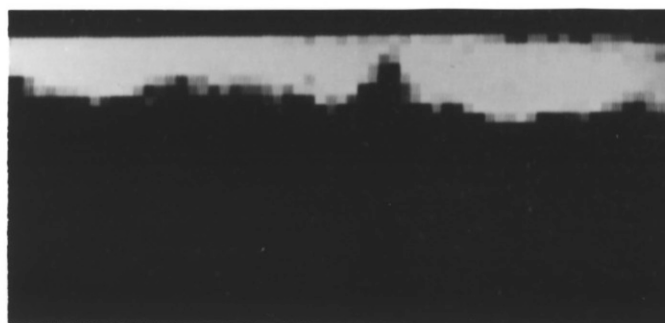
Alloy D (Fe25Cr6.5Al), 213h, med. pS_2 , 1223K



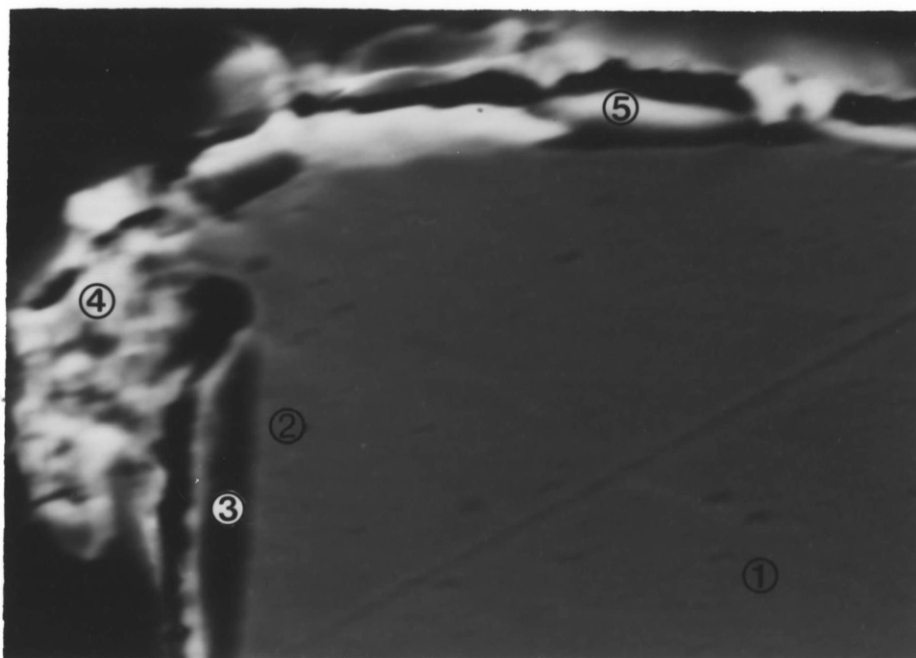
Iron distribution near to scale



Chromium distribution near to scale



Aluminium distribution near to scale

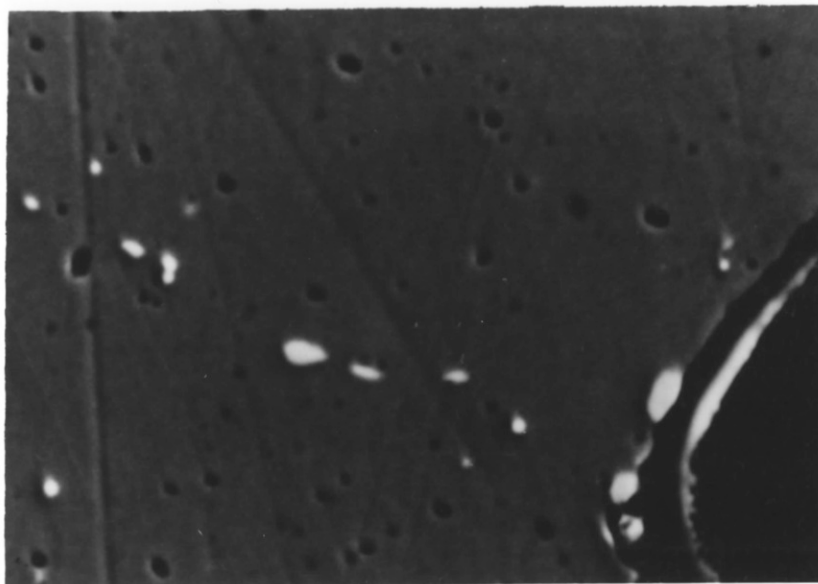


X2.5k

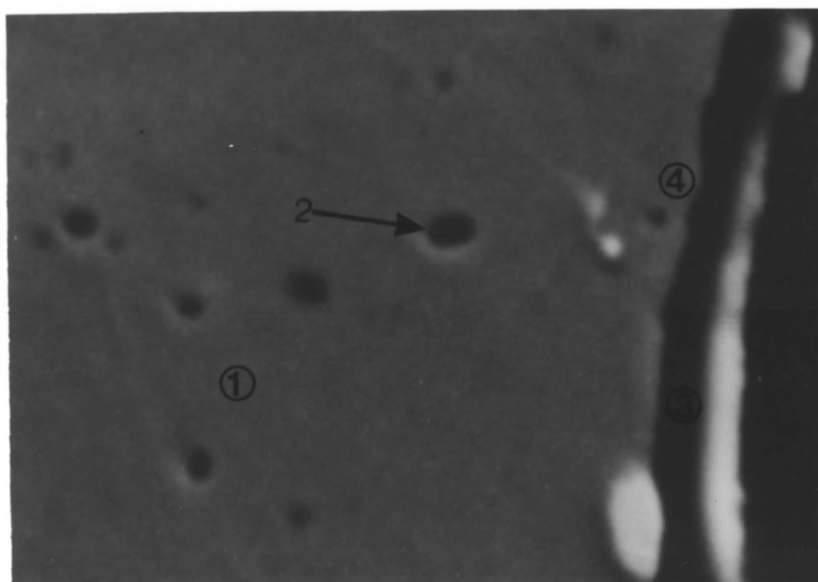
Alloy C (Fe16Cr4Al), 197h, med. pS₂, 1223K.
Section near to corner

<i>Element</i>	<i>Wt.% Area of Print</i>				
	1	2	3	4	5
Fe	77.2	77.9	76.2	12.5	1.8
Cr	16.2	16.4	16.2	3.8	0.4
Al	3.6	3.9	3.7	56.5	58.7
Ti	0.3	0.4	0.4	0.3	0.2
Y	0.1	0.1	0.1	0.1	0.1
S	-	-	-	-	-
<i>Total</i>	97.4	98.7	96.6	73.3	61.2

ZAF Analysis of Selected Areas of Specimen



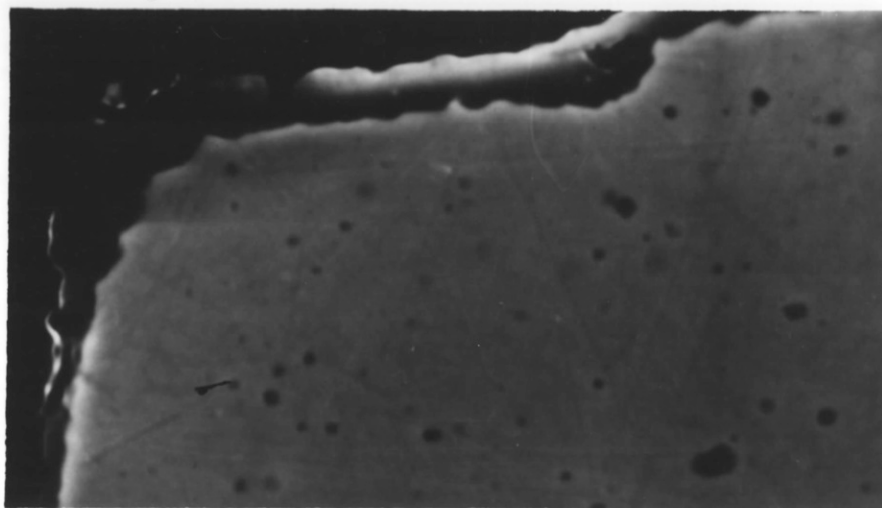
X2k



Alloy 1 (Fe20Cr4.6Al1.9Ta), 92h, high pS₂, 1323K X5k

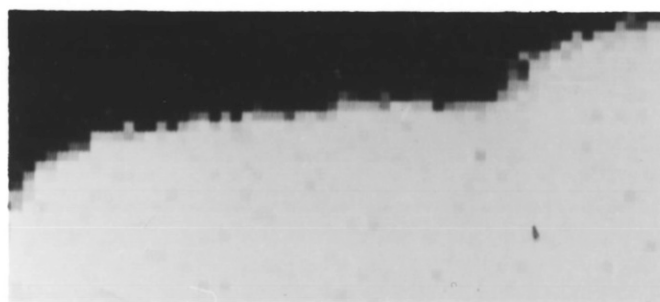
<i>Element</i>	<i>Wt.% Area of Print</i>			
	1	2	3	4
Fe	70.5	68.7	2.8	70.4
Cr	19.6	19.4	0.9	19.5
Al	4.1	3.5	60.3	4.1
Ta	0.6	4.8	1.1	0.6
Y	0.2	0.4	0.1	0.2
S	0.2	0.2	-	-
<i>Total</i>	95.2	97.0	65.1	94.8

ZAF Analysis of Selected Areas of Specimen

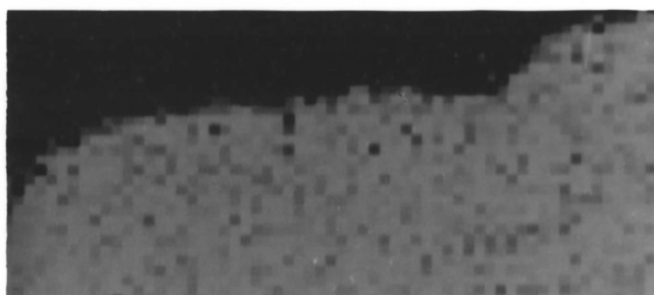


X2.4k

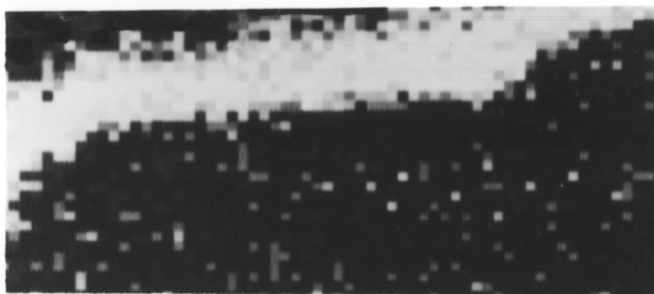
Alloy C (Fe16Cr4Al), 223h, low pS_2 , 1323K corner section



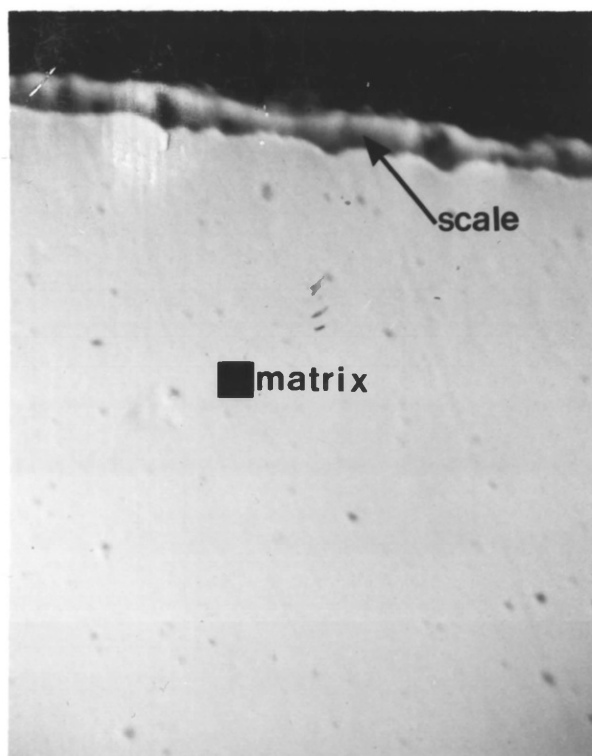
Iron distribution near to scale



Chromium distribution near to scale

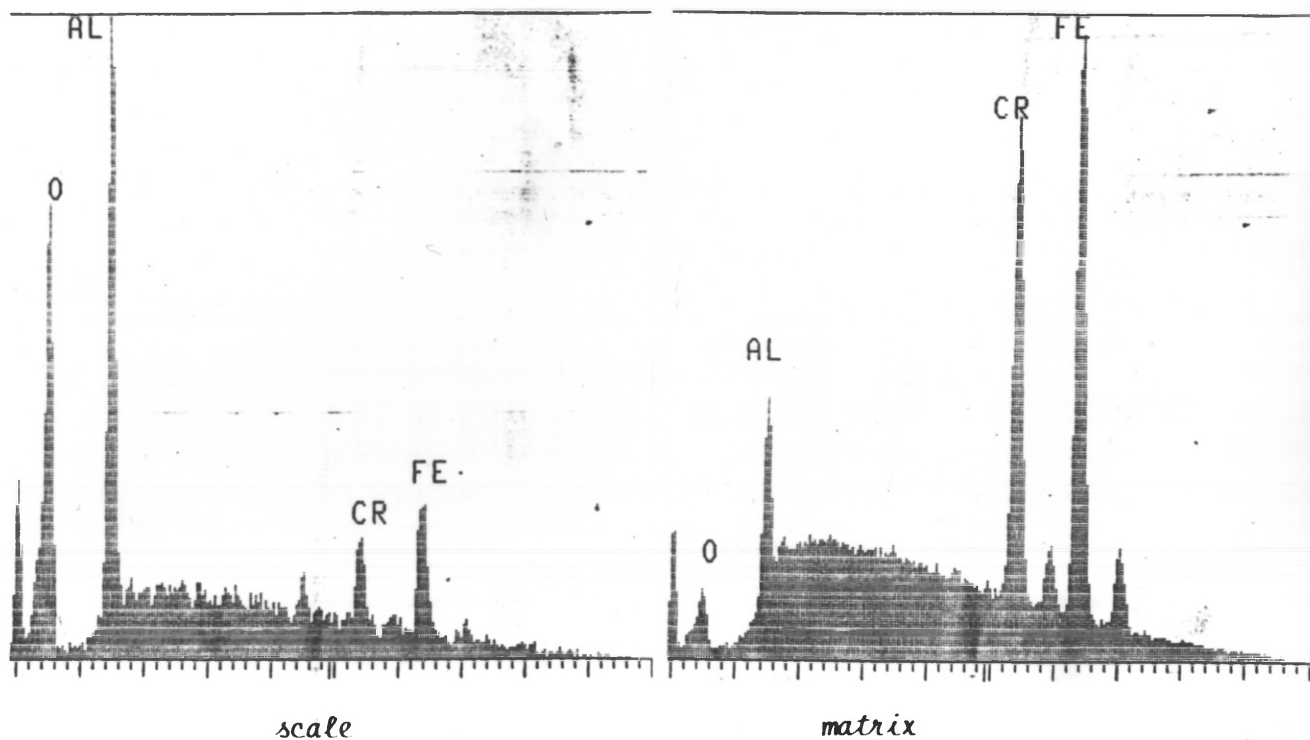


Aluminium distribution near to scale



X2k

Section of the scale formed on MA956
(Fe20Cr5Al) 500h, med. pS_2 , 1323K



X-ray spectrum

PLATE 12

3 High Weight Gain

(a) Introduction

The specimens were usually characterised by the formation of thick ($\sim 100\text{ }\mu\text{m}$) scales. The scale growth rate was high and considerable loss of section occurred.

The outer scale was a dark grey-brown friable layer. The scale surface was frequently crystalline in appearance with a deep purple lustre; occasionally a more 'glassy' surface was seen, usually with a yellow lustre. The superficial appearance of the scale did not correlate with any experimental variable. In section, the outer scale was normally porous at its innermost edge often with large voids ($\sim 50\text{ }\mu\text{m}$) and a number of through-cracks.

The outer scale was easily detached with a scalpel blade; it could then be powdered for X-ray diffraction study. A number of outer scale samples were examined in an X-ray diffractometer. Samples were invariably found to be pyrrhotite $\text{Fe}(1-x)\text{S}$, $x=0.086$. The presence of iron and sulphur was confirmed by X-ray analysis. Some chromium was usually present in this area.

The boundary between the outer and inner scale was usually marked by a thin band of scale at the original specimen surface.

The inner scale was frequently composed of a thick middle zone with lath-shaped structures forming a chequered pattern; this 'lath zone' was bounded by thin porous areas at its inner and outermost extremity.

The inner scale was not readily detached and scraping with a steel scalpel blade did not remove it. Some specimens were ground on one of the larger flat surfaces to expose the inner scale. X-ray diffraction studies were made of this area; the results were inconclusive, pyrrhotite was identified; sometimes Daubreelite FeCr_2S_4 was detected, but it has not been possible to present a positive identification on the basis of the X-ray diffraction

study. It is likely that a number of sulphides and possible oxides coexist in this region; this is described in section (b) plate 19.

The ratio of outer to inner scale thickness correlated well with the alloy composition.

<u>Alloy</u>		<u>Outer : Inner Scale Thickness Ratio</u>
MA956	Fe 20Cr 5Al	2.0 : 1
A	Fe 25Cr 5Al	1.5 : 1
C	Fe 16Cr 4Al	5.2 : 1
D	Fe 25Cr 6.5Al	1.6 : 1
I	Fe 20Cr 5Al 1.9Ta	1.9 : 1
K	Fe 20Cr 5Al 5Ni	2.0 : 1

Table 6

Ratios of Outer to Inner Scale Thickness in High Weight Gain Specimens

The higher the Cr content of the alloy the thicker the inner scale was, relative to the outer scale. The total scale thickness in a given time was also reduced in more highly alloyed specimens.

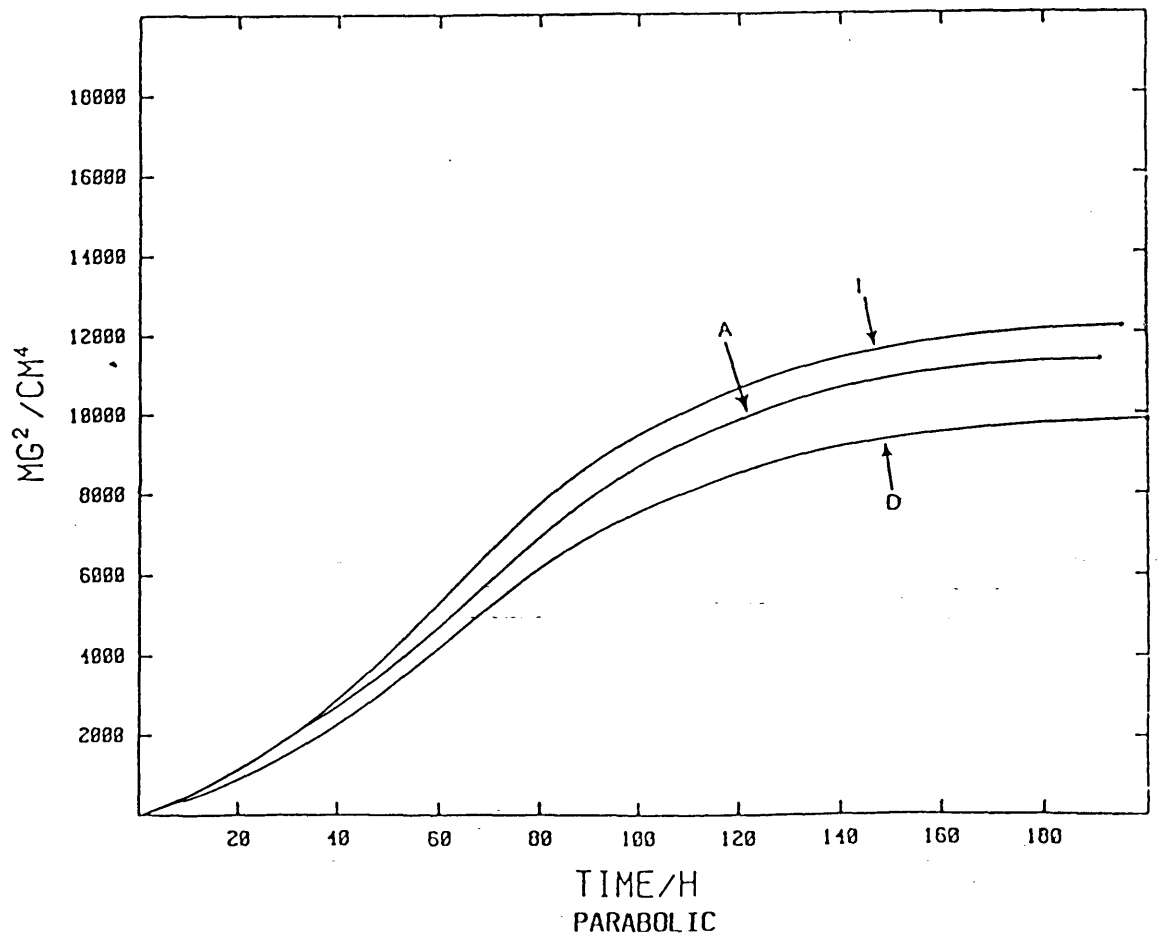
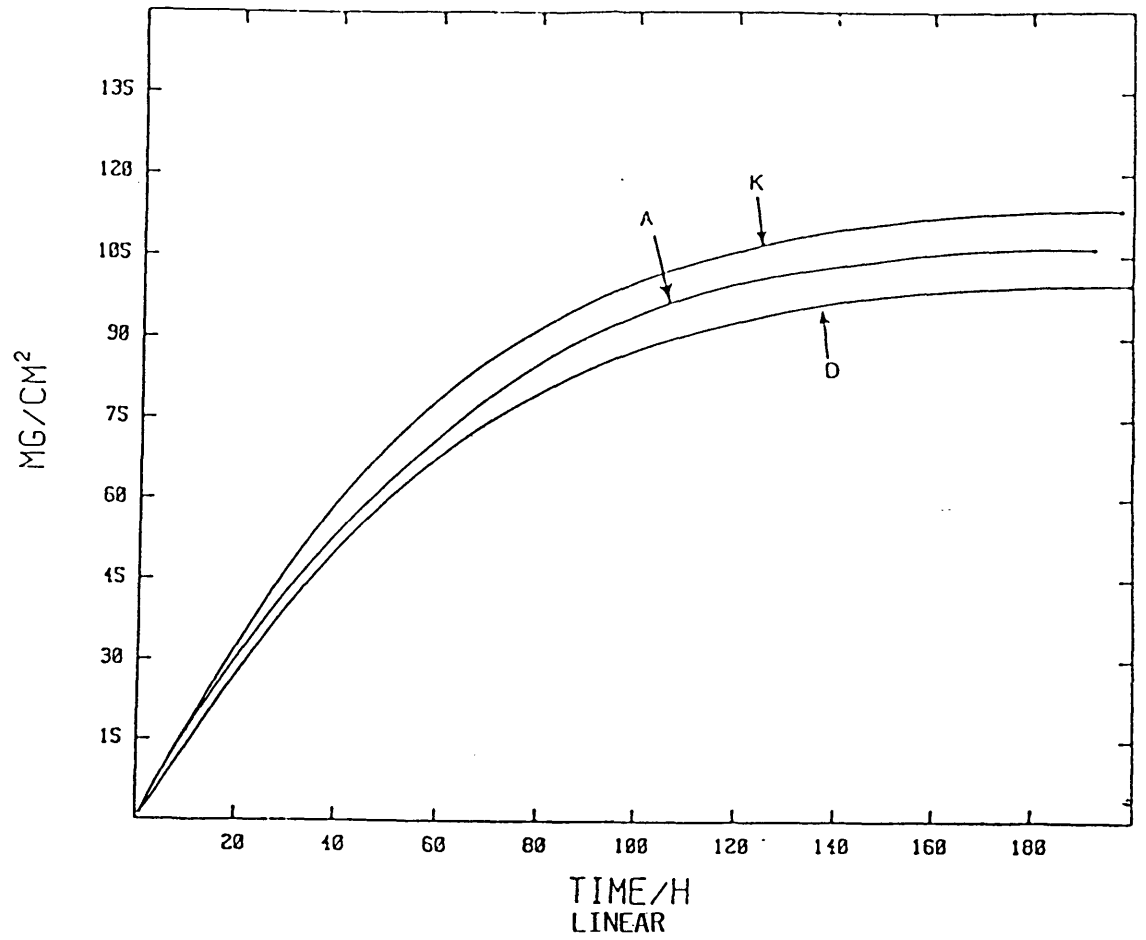
There were frequently strings of internal attack extending ahead of the inner scale. Some evidence that this may be exacerbated by grain boundaries has been seen, occasionally the attack penetrates deeper into the alloy in one direction than another. When this occurs, the greater penetration depth is at the ends of the specimen where the pancake-shaped grains have been cut transversely.

In isolated cases a 'semi-protective' type of scaling occurred in atmospheres which usually produced a high weight gain. The specimen suffered little general attack but sulphidation occurred at localised areas.

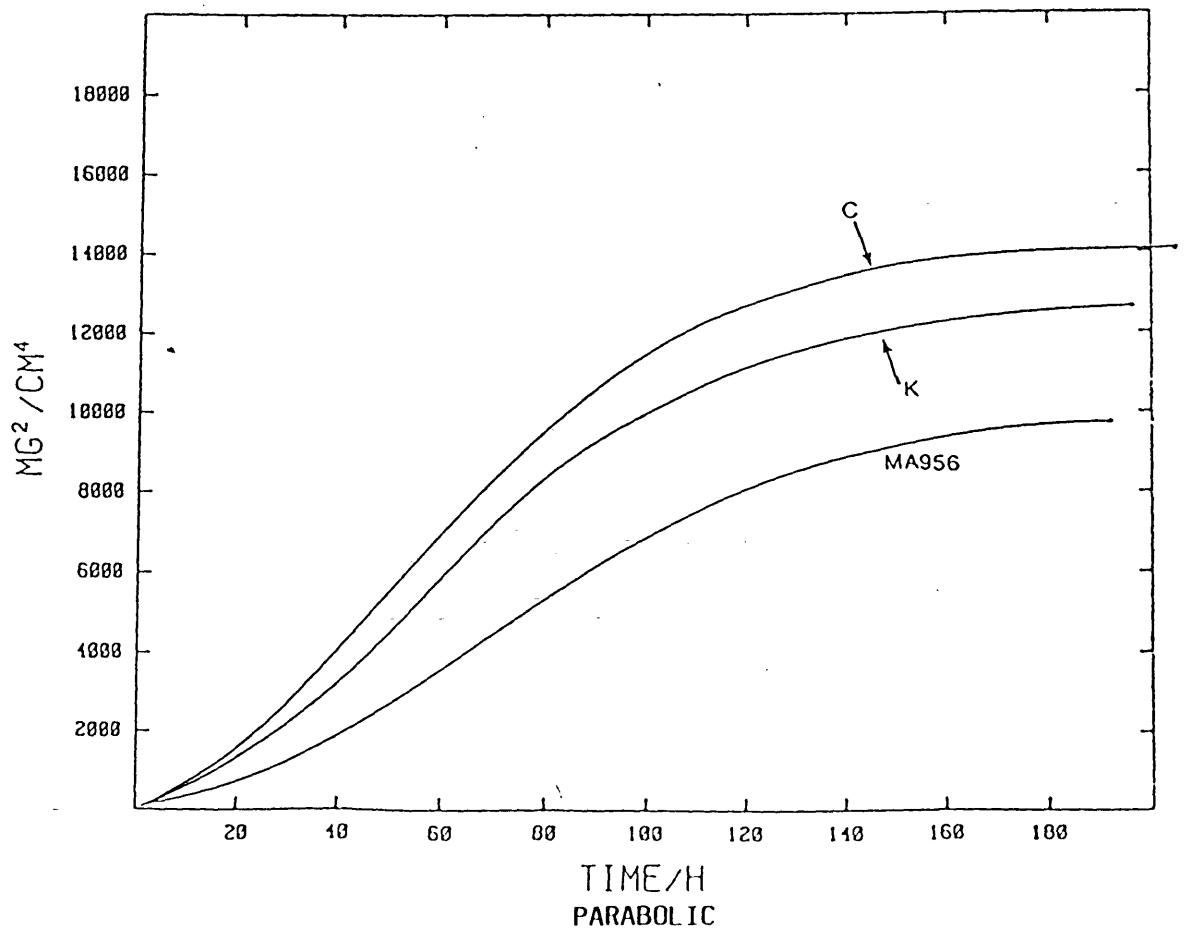
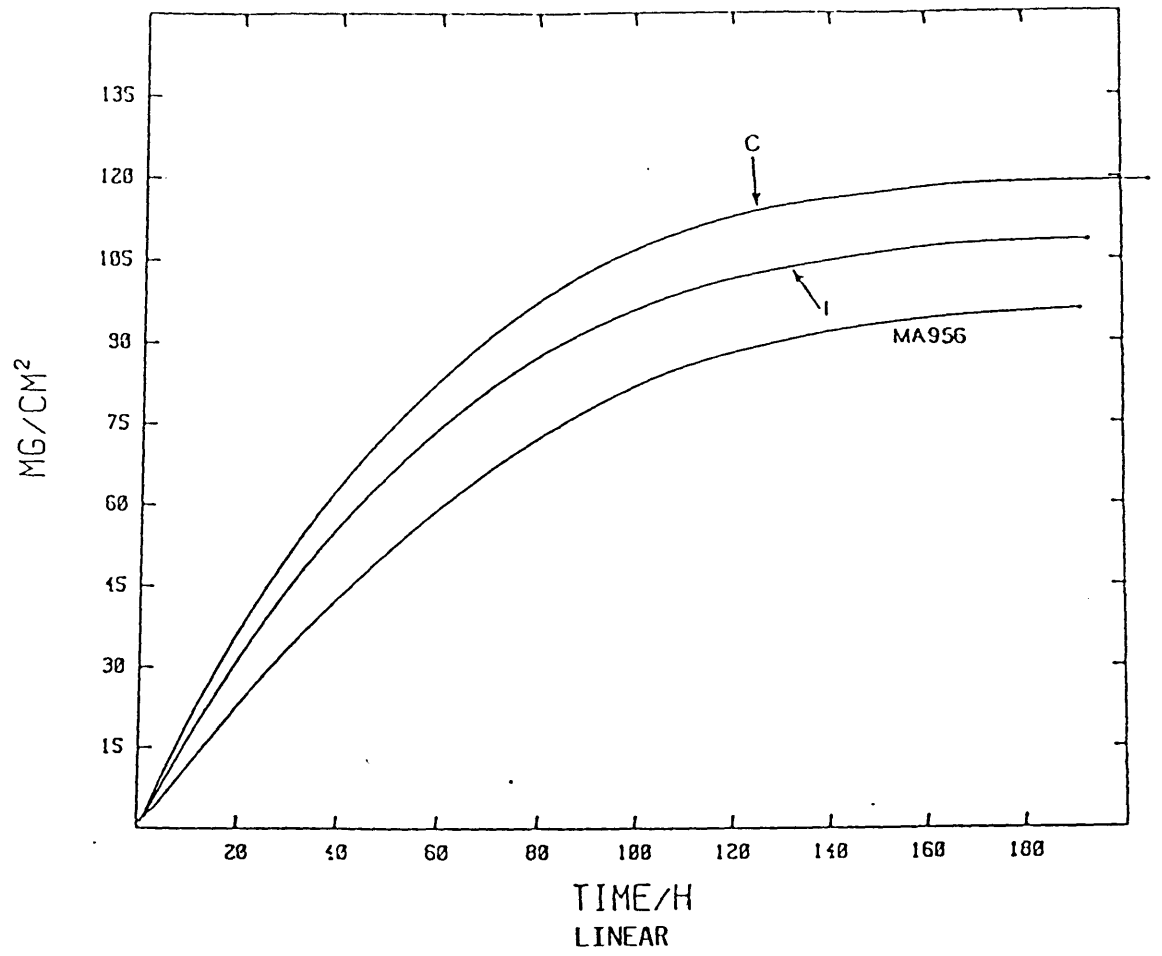
Graphs 7-12 show the kinetic trends in these alloys; the graphs are summarised in Tables 7-9. The apparent reduction in scale growth rate may be misleading in some cases. Where very severe sulphidation has occurred (eg alloy C, high pS_2 1123K) there is so little metal left to supply the sulphidation reactions that a reduction in growth

GRAPH 7

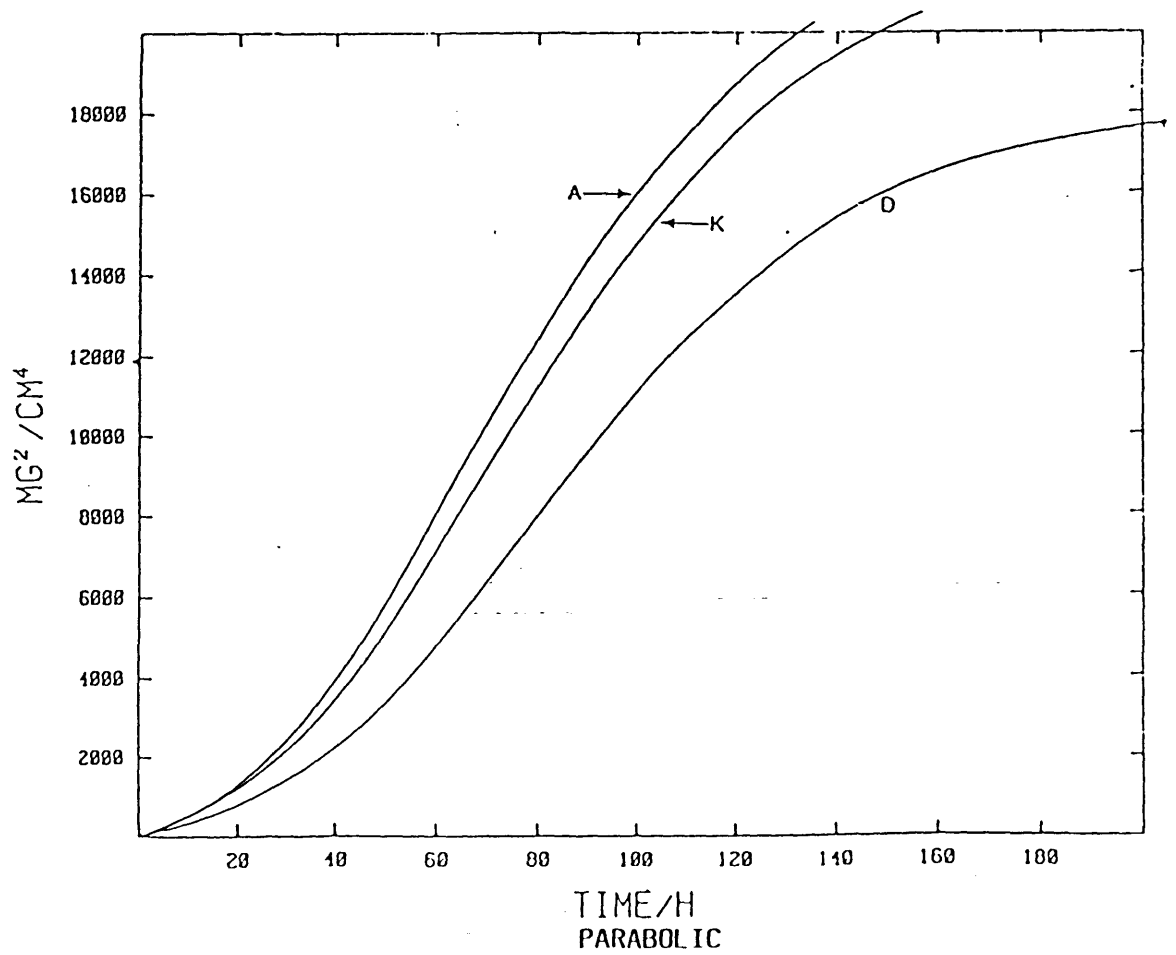
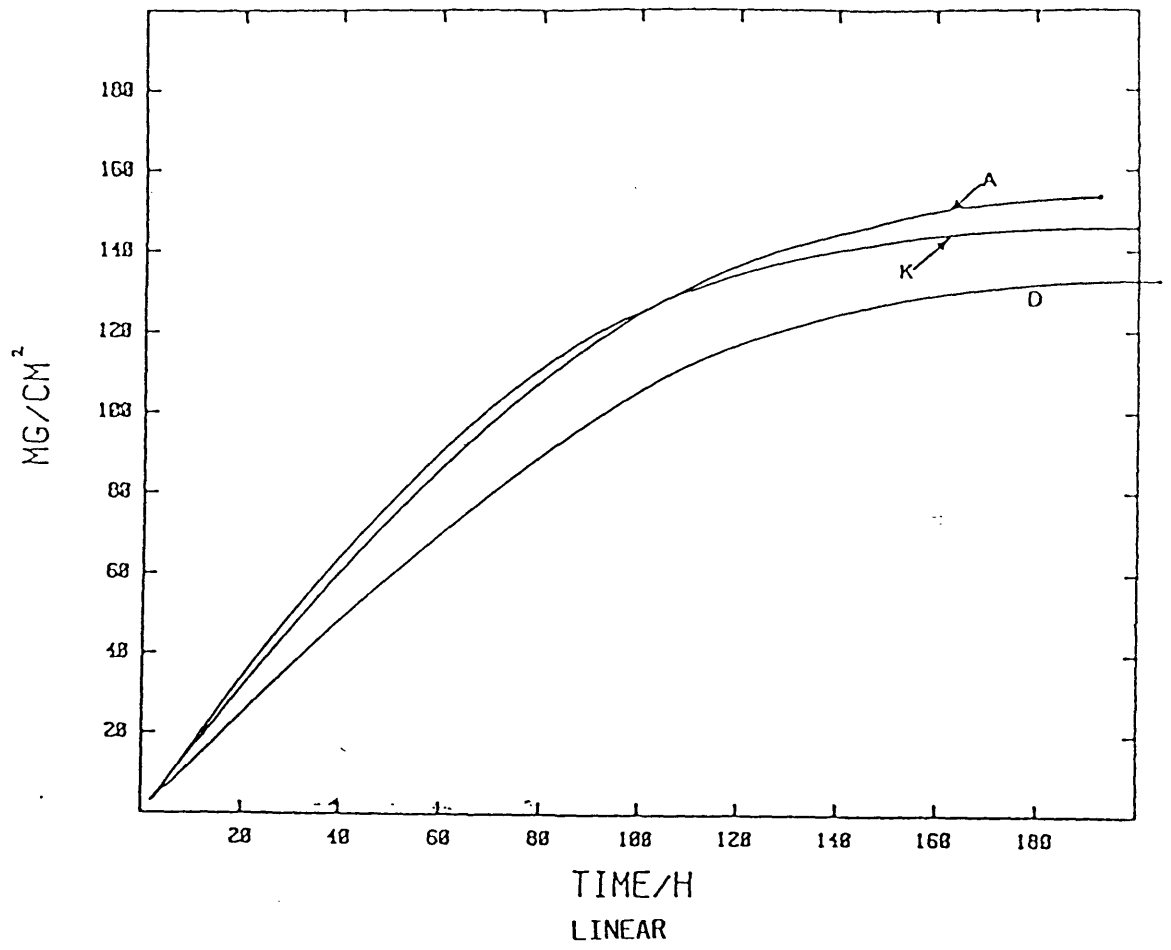
101

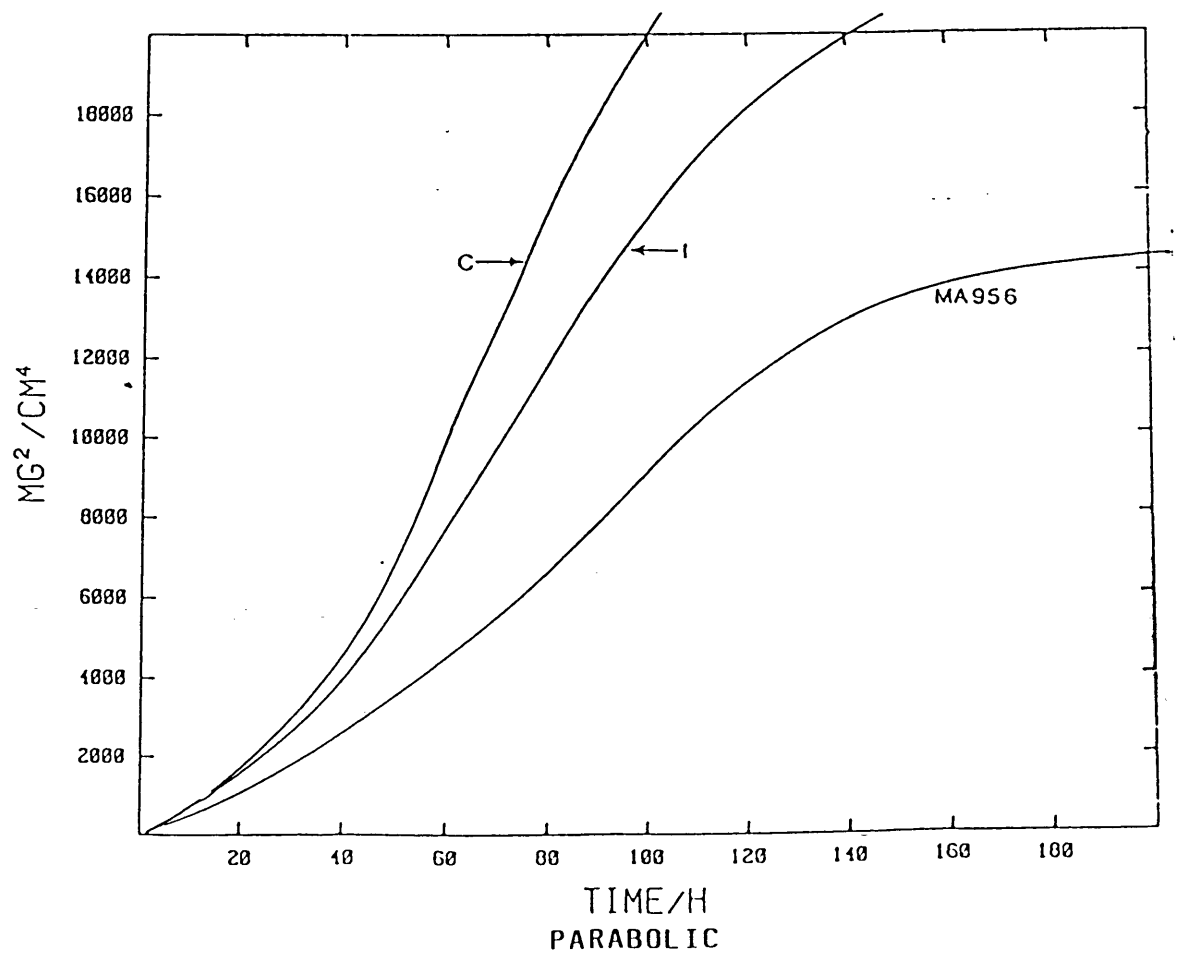
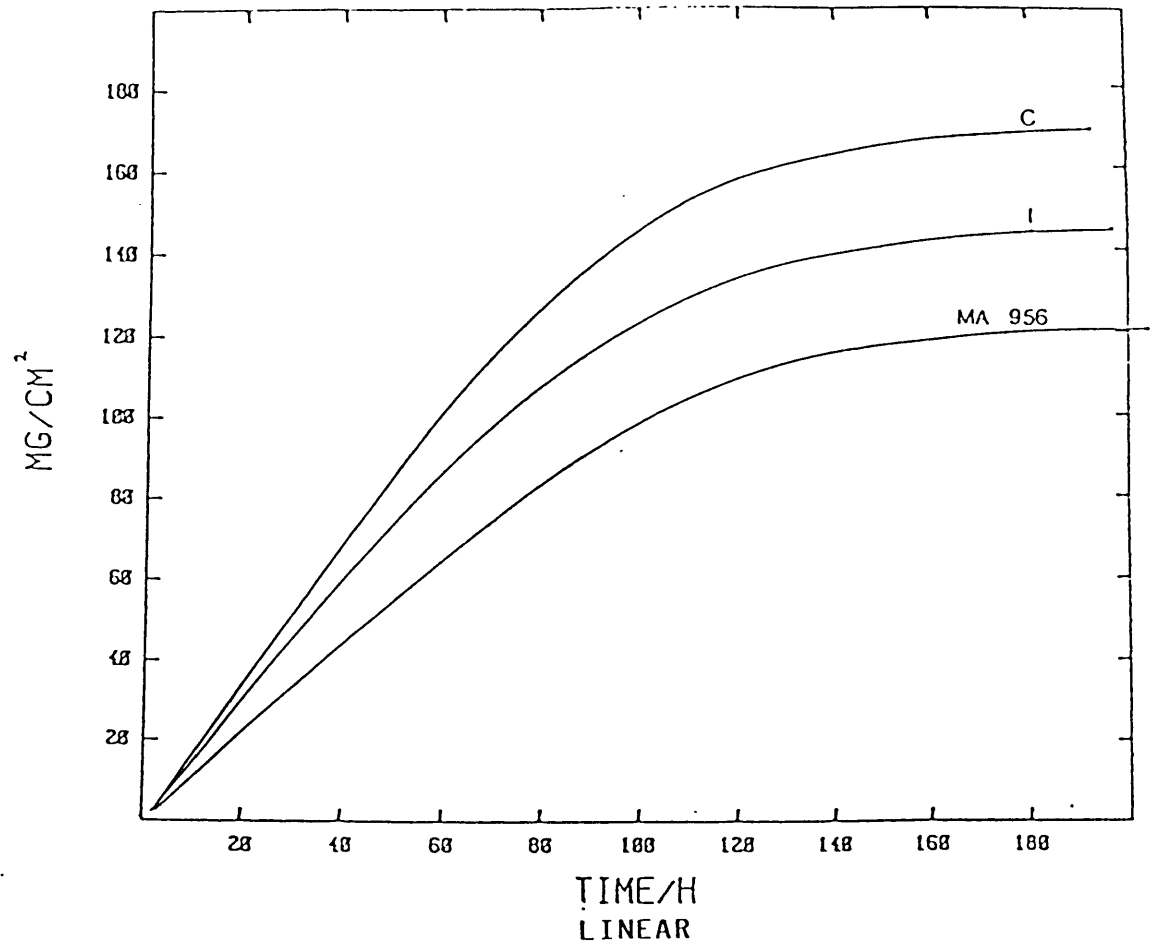


Kinetic plots for alloys A, K, D, in med. pS₂ atmosphere at 1123 K

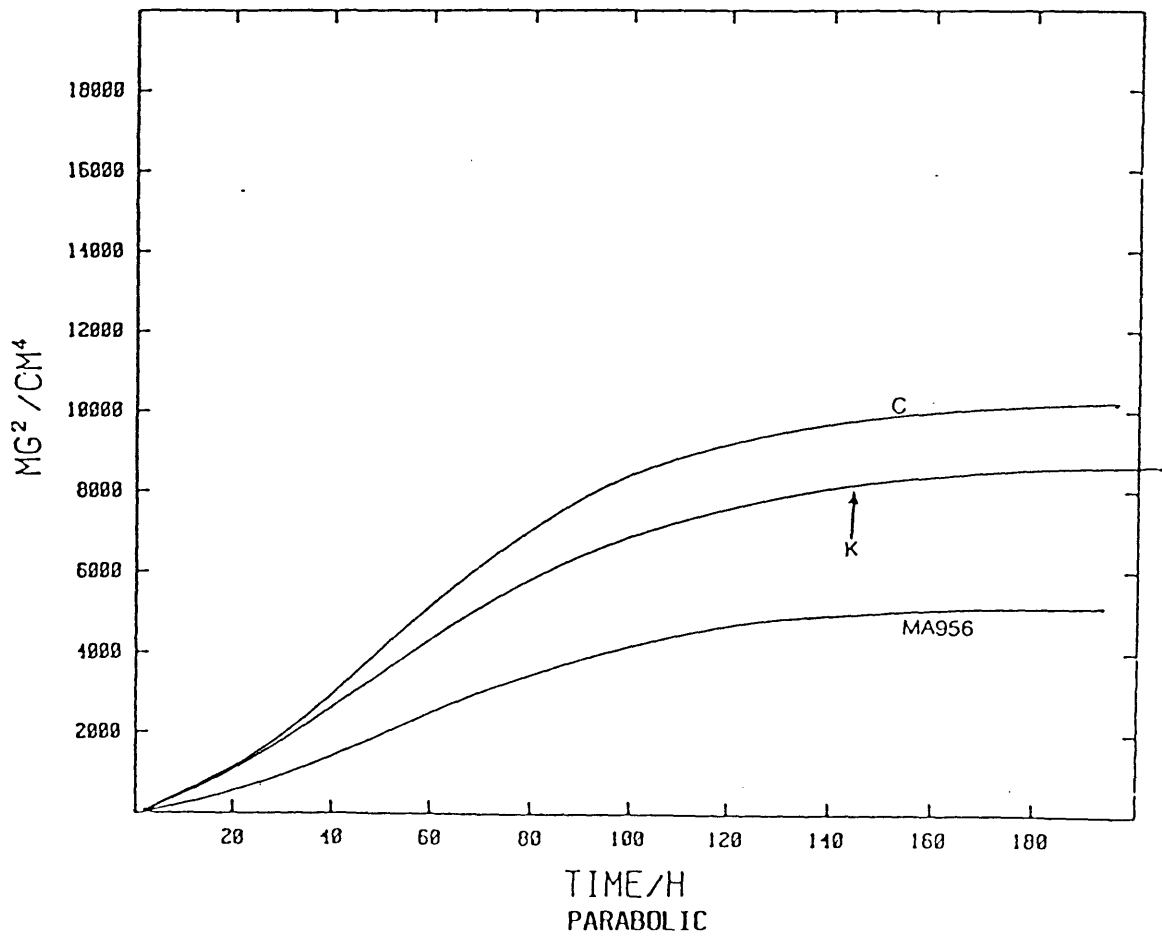
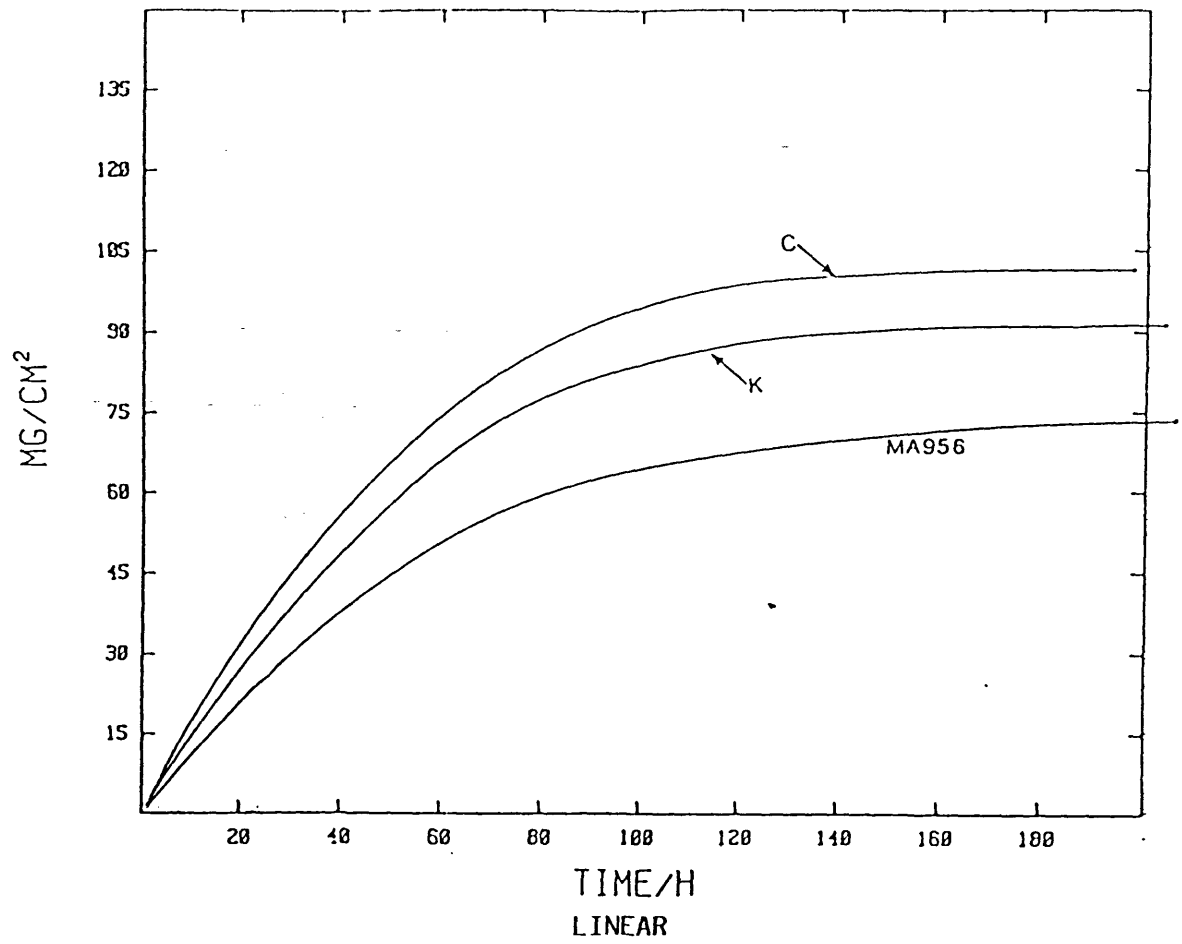


Kinetic plots for alloys MA956, C, I in med. pS₂ atmosphere at 1123 K

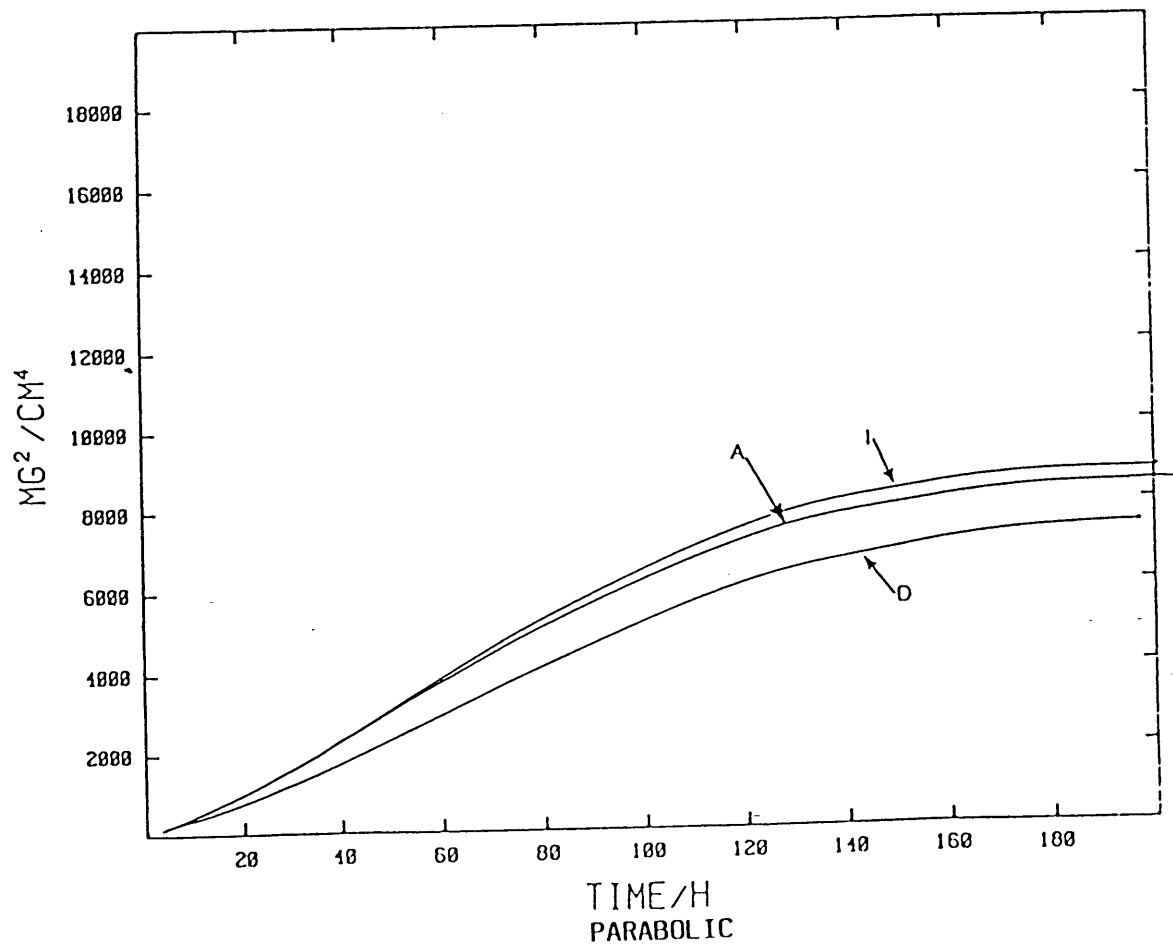
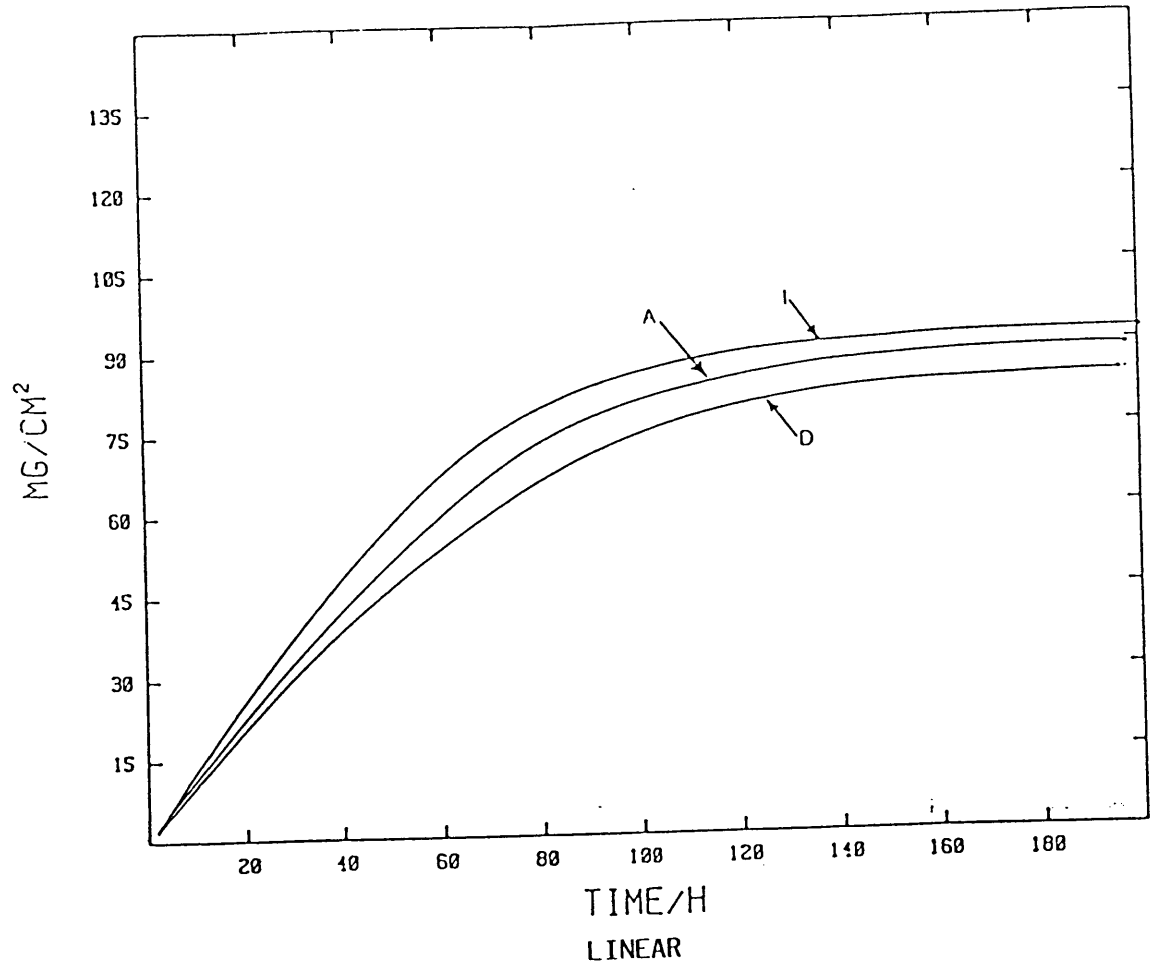
Kinetic plots for alloys A, K, D in high pS₂ atmosphere at 1123 K



Kinetic plots for alloys MA956, C, I in high pS_2 atmosphere at 1123 K



Kinetic plots for alloys MA956, C, K in high pS₂ atmosphere at 1223 K



Kinetic plots for alloys A, I, D in high pS_2 atmosphere at 1223 K

ALLOY	LINEAR RATE CONSTANT/ $\text{gcm}^{-2}\text{S}^{-1}\times 10^7$	PARABOLIC RATE CONSTANT/ $\text{g}^2\text{cm}^{-4}\text{S}^{-1}$	
	0-100h	0-100h $\times 10^8$	100-200h $\times 10^9$
MA956	2.2	1.9	3.5
A	3.0	2.5	2.8
C	3.3	3.5	2.1
D	2.9	2.3	2.7
I	2.8	2.8	3.4
K	3.3	3.0	2.3

Table 7

Rate Constants for Corrosion of Various Alloys at 1123K in Medium Sulphur Pressure Atmosphere.
 ($p\text{S}_2 = 7.3 \times 10^{-7}$ atm.)

ALLOY	LINEAR RATE CONSTANT/ $\text{gcm}^{-2}\text{S}^{-1}\times 10^7$	PARABOLIC RATE CONSTANT/ $\text{g}^2\text{cm}^{-4}\text{S}^{-1}$	
	0-100h	0-100h $\times 10^8$	100-200h $\times 10^9$
MA956	2.9	2.6	4.1
A	3.9	4.7	-
C	4.7	5.6	-
D	3.1	3.2	5.8
I	4.0	4.4	-
K	3.9	4.2	-

Table 8

Rate Constants for Corrosion of Various Alloys at 1123K in High Sulphur Pressure Atmosphere.
 ($p\text{S}_2 = 8.1 \times 10^{-6}$ atm.)

ALLOY	LINEAR RATE CONSTANT/ $\text{gcm}^{-2}\text{S}^{-1}\times 10^7$	PARABOLIC RATE CONSTANT/ $\text{g}^2\text{cm}^{-4}\text{S}^{-1}$	
	0-100h	0-100h $\times 10^8$	100-200h $\times 10^9$
MA956	2.2	1.3	1.7
A	2.7	1.8	1.8
C	3.1	2/4	3/5
D	2.3	1.4	4.2
I	3.0	1.9	3.8
K	2.9	2.8	3.8

Table 9

Rate Constants for Corrosion of Various Alloys at 1223K in High Sulphur Pressure Atmosphere.
 ($p\text{S}_2 = 3.9 \times 10^{-5}$ atm.)

rate is inevitable. The 0-100h data is probably more representative of the bulk alloy behaviour.

(b) Description of Plates

Plates 13 and 14 show the type of damage often seen in high weight gain specimens. The scaling is uniform, although sometimes thicker at the specimen corners. MA956 is characterised by a non-uniform internal corrosion front with localised intrusions into the matrix. All the other alloys which suffered high weight gains formed a more even internal corrosion front; they also produced an inner layer with a 'lath zone' structure.

Plate 15 shows analyses of alloy D. Chromium depletion has occurred in the matrix adjacent to the inner scale.

The inner scale contains all the alloying elements in approximately the same concentration ratio as the alloy, sulphur is also present. The analysis totals less than 100%, this may be due to the presence of oxygen in the scale.

There was a concentration gradient of Cr and Al with a higher concentration at the outer surface of the scale.

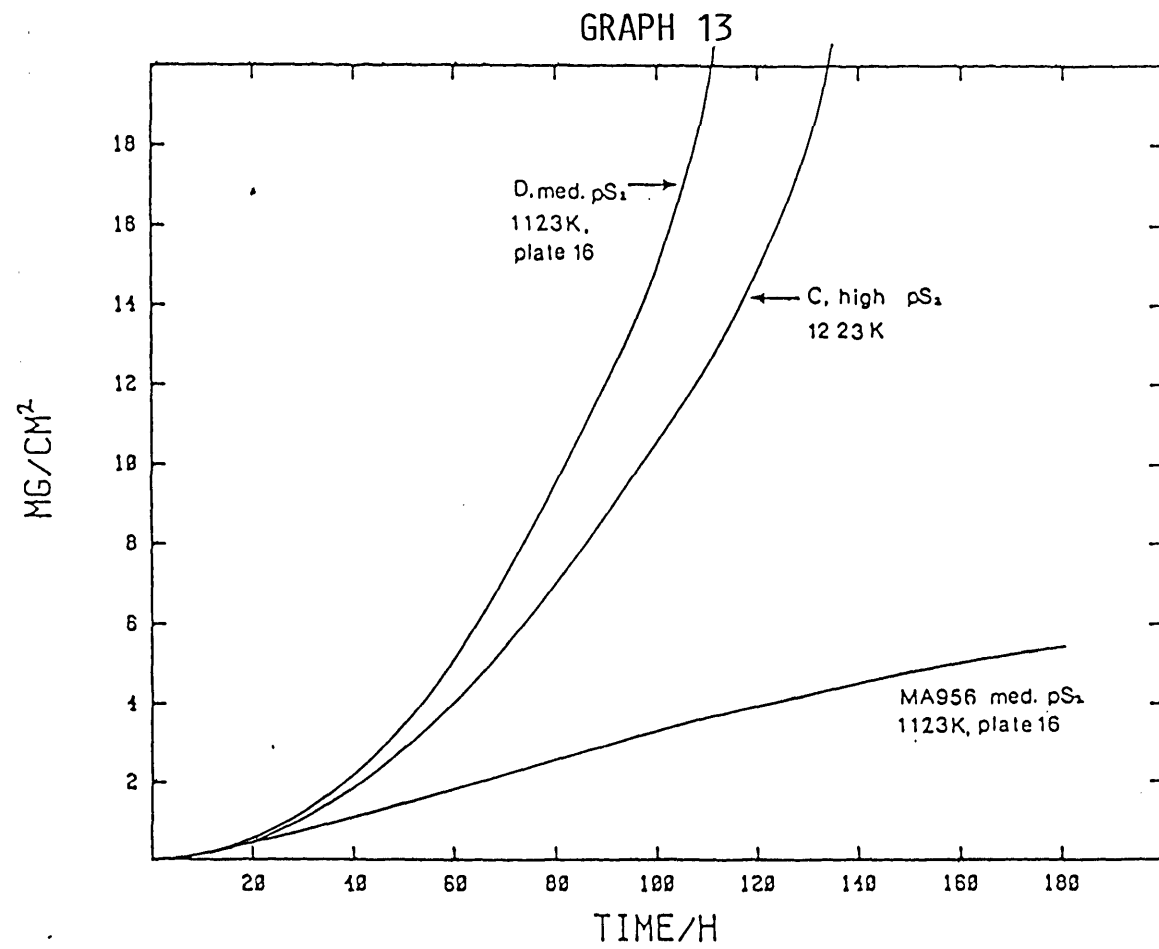
The outer scale is composed of iron and sulphur with a small amount of chromium present. X-ray diffraction has shown this layer to be pyrrhotite.

Plate 16 shows examples of semiprotective scaling.

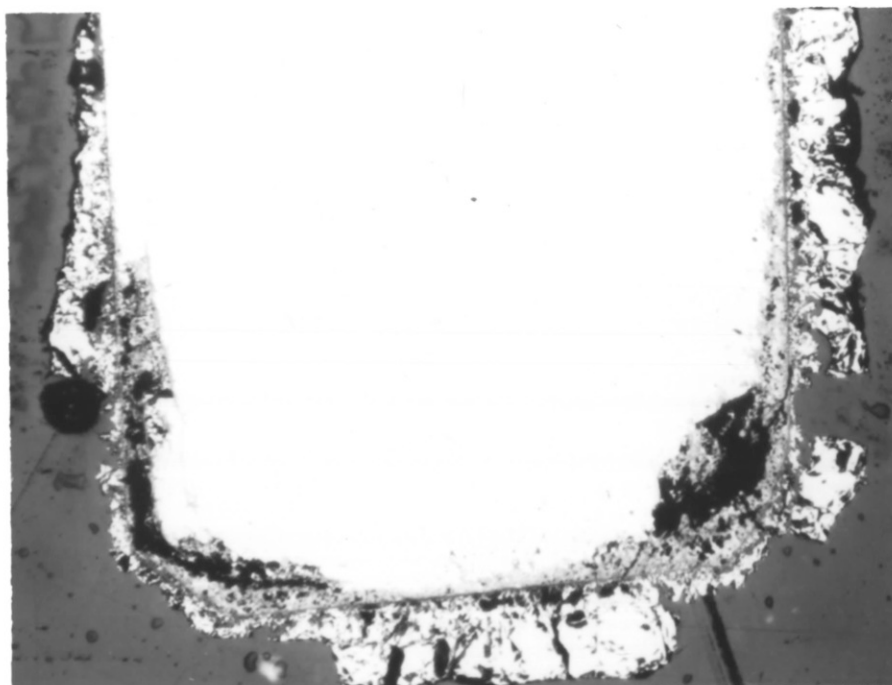
'Mottled' type attack occurred several times and areas of crystallites of iron sulphides grew around areas of aluminium rich scale. The kinetic plot in Graph 13 shows a steady weight increase throughout the exposure time.

Alloy D suffered very localised blistering-type attack. Several blisters had formed at various locations on the specimen surface. The structure of the blister was similar to the scale formed on this alloy during the general sulphidation normally seen in this atmosphere. Graph 13 shows that the weight gain increased rapidly, presumably as the blister grew. Silicon was not detected in the blister.

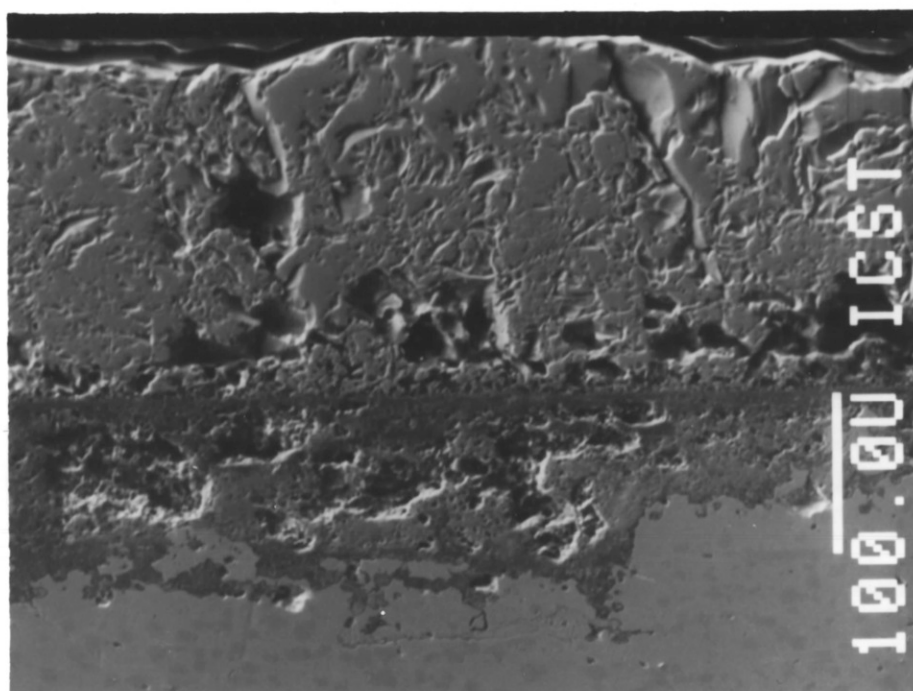
The localised nature of the attack means that kinetic



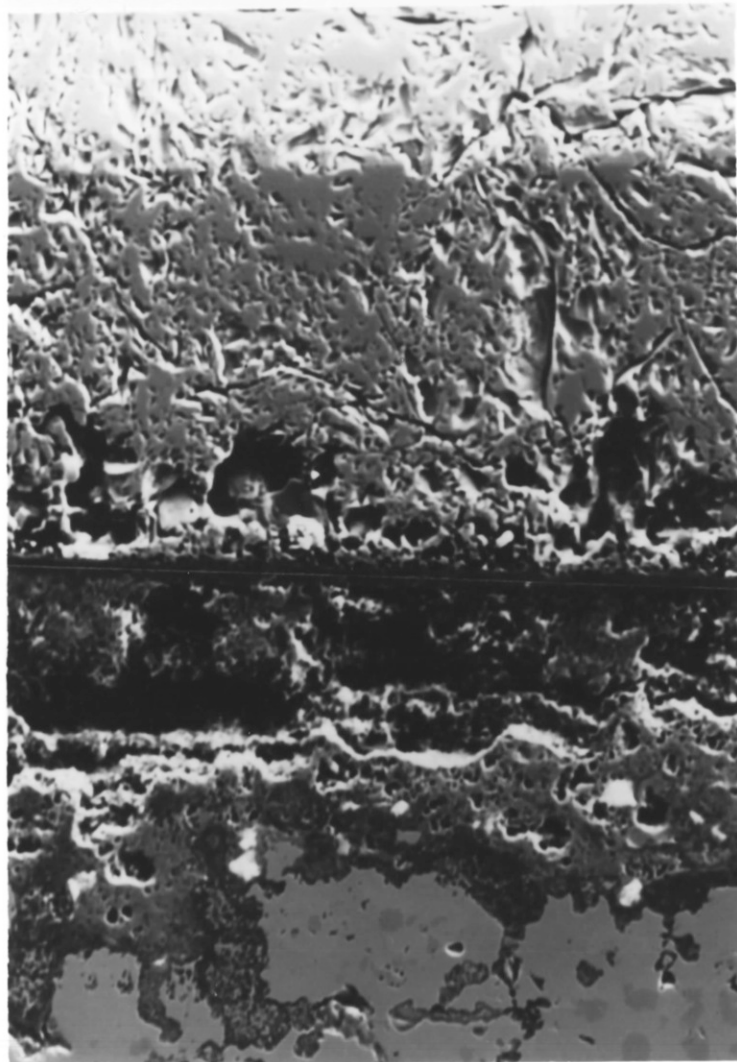
Kinetic plots for alloys which suffered localised attack



Alloy C (Fe16Cr4Al), 206h, med. pS_2 , 1123K
(optical micrograph) X90

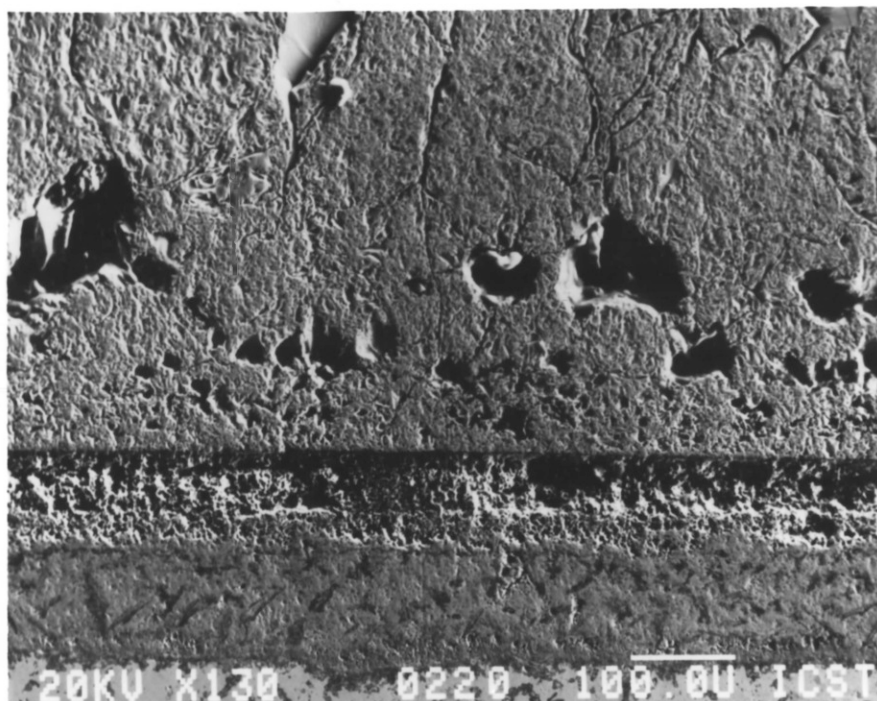


MA956 (Fe20Cr5Al), 192h, high pS_2 , 1223K
(electron image) X200



X400

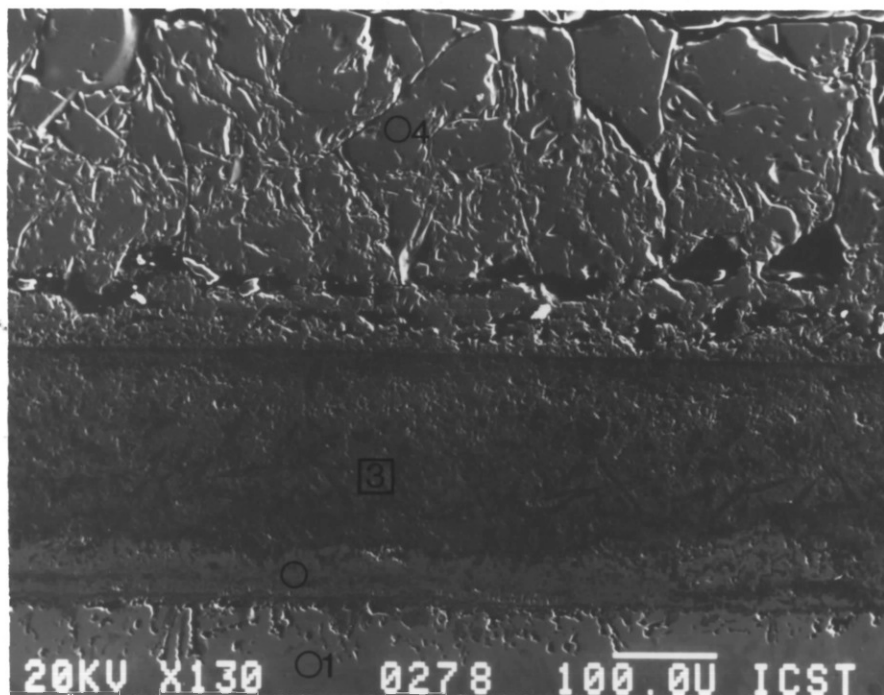
MA956 (Fe20Cr5Al), 205h, high pS_2 , 1223K



X130

Alloy K (Fe20Cr4.5Al4Ni), 196h, high pS_2 , 1223K

PLATE 14

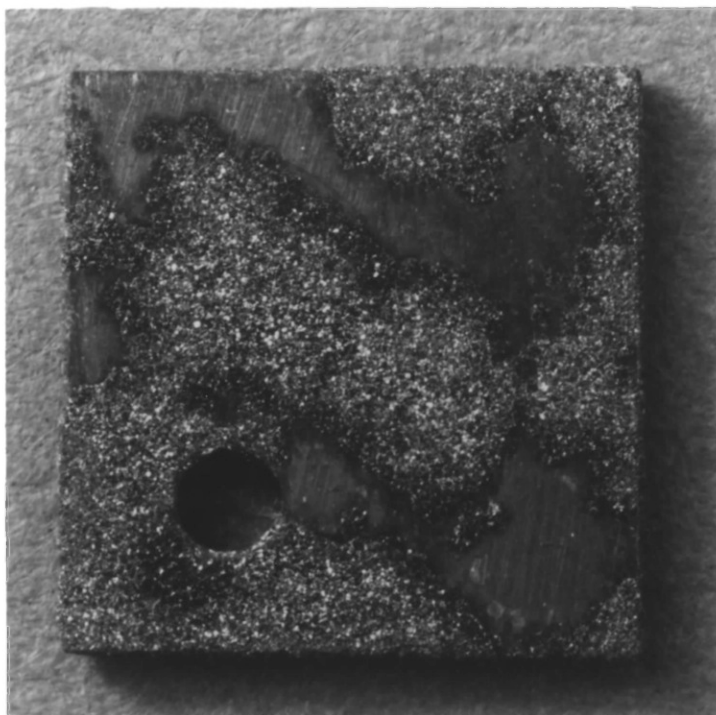


X130

Alloy D (Fe25Cr6.5Al), 203h, high pS_2 , 1123K

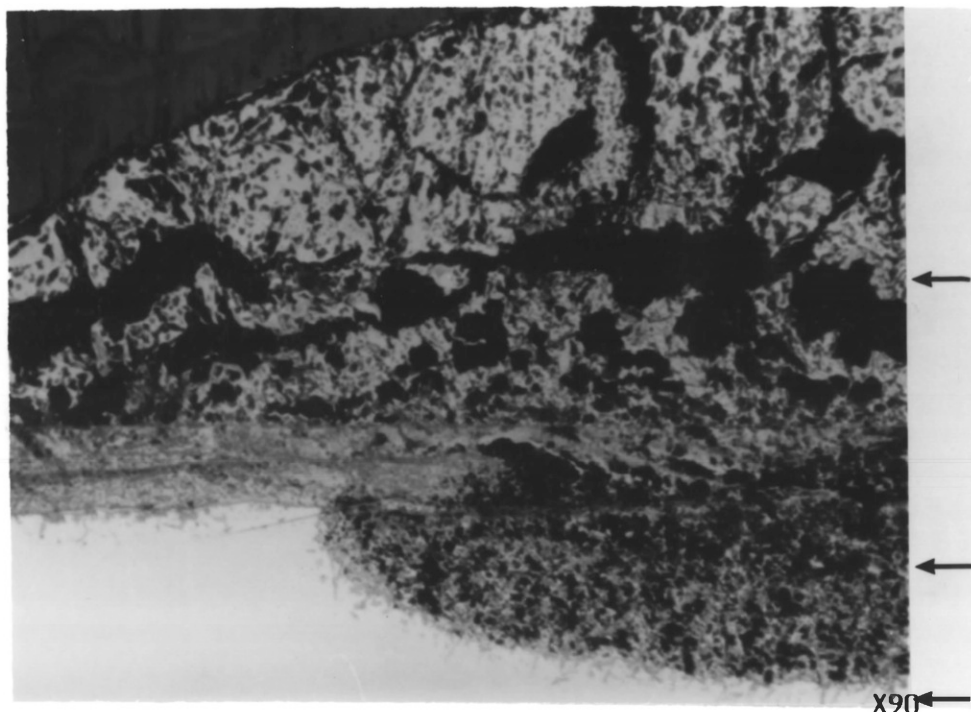
<i>Elements</i>	<i>Wt.% Area of Print</i>			
	1	2	3	4
Fe	69.3	41.1	39.6	48.6
Cr	20.5	17.4	19.2	4.1
Al	6.1	2.8	7.8	0.1
Ti	0.3	0.2	0.3	0.2
Y	0.2	0.2	0.2	0.2
S	-	33.9	29.8	32.6
<i>Total</i>	96.4	95.6	96.9	85.8

ZAF Analysis of Selected Areas of the Specimen



X10

MA956 (Fe20Cr5Al), 201h, med. pS₂, 1123K, macro picture
showing 'mottled' type of attack



outer scale

internal
attack

matrix

X90

Alloy D (Fe25Cr6.5Al), 200h, med. pS₂, 1123K optical
micrograph of blister

data based on weight change per unit area is of little use in characterising the scale growth.

Plate 17 shows alloy C with an element distribution. This specimen suffered severe sulphidation. The two corrosion fronts from the large surfaces of the specimen almost met at the specimen centre (approximately the position of the micron marker on the plate).

The outer scale layer contained a high proportion of iron and sulphur with a small amount of chromium and aluminium. X-ray diffraction showed this layer to be pyrrhotite. A number of large voids was present in this layer.

The original metal surface is marked by a thin Al-rich layer (indicated by the black arrowhead to the left of the print), little iron or sulphur is present in this band.

A porous layer immediately beneath the original surface contains mainly chromium. Oxygen was also detected in this area by microprobe analysis.

Just ahead of the porous layer Cr, Fe and S coexist. The aluminium concentration rises towards the specimen centre in this region; this leads to an Al-rich band at the upper edge of the 'lath-zone'.

The 'lath-zone' consists of a matrix rich in chromium and sulphur with dark laths, rich in Al, corresponding to areas of depletion of the other elements.

Ahead of the 'lath zone' the alloy is depleted in chromium and enriched in iron. Small dark areas correspond to Al enrichment. Sulphur has penetrated right through the specimen.

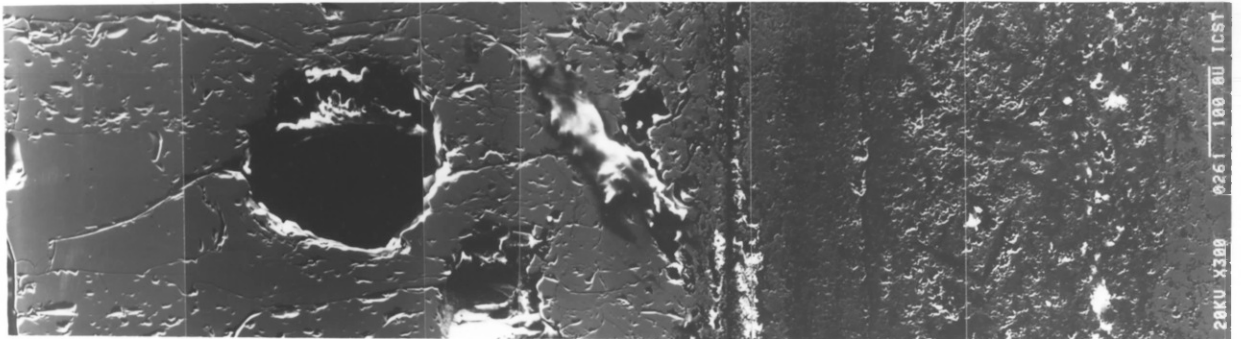
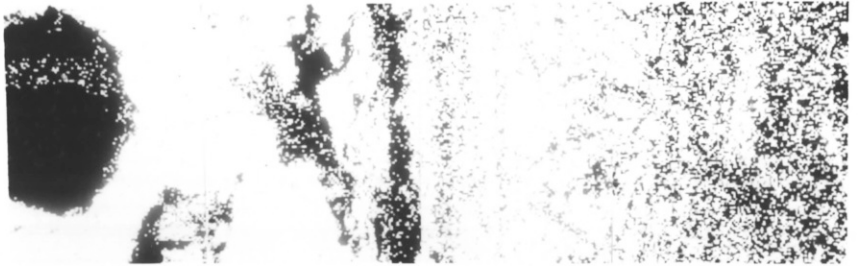
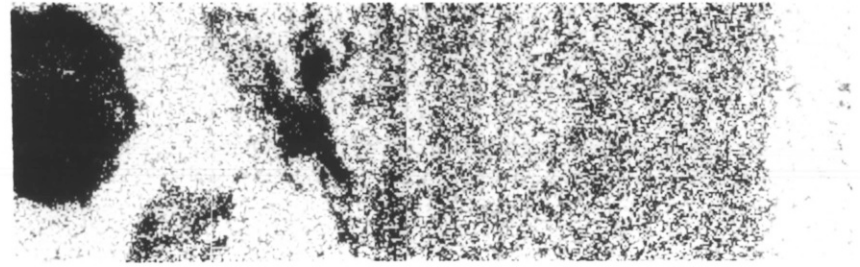
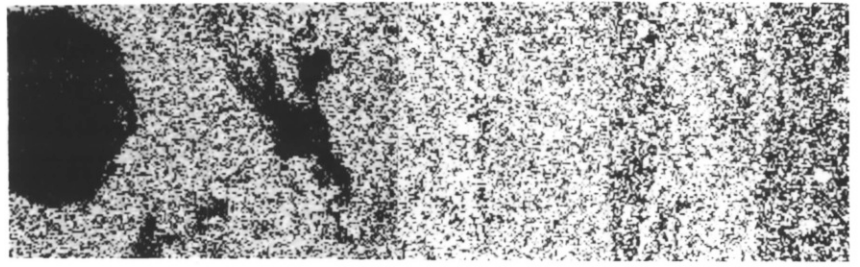
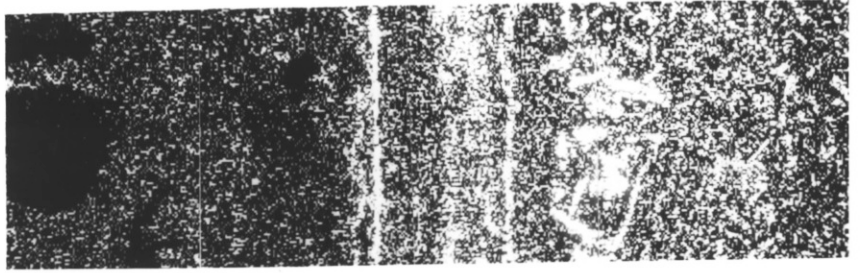
Plate 18 shows X-ray spectra for the laths and matrix in the lath zone of Plate 17. The matrix consists of iron and chromium sulphides with little oxygen. X-ray diffraction detected some FeCr_2S_4 in this layer.

The laths consist mainly of aluminium and oxygen, probably as alumina. A similar spectrum was obtained from other Al-rich areas of the specimen.

Plate 17

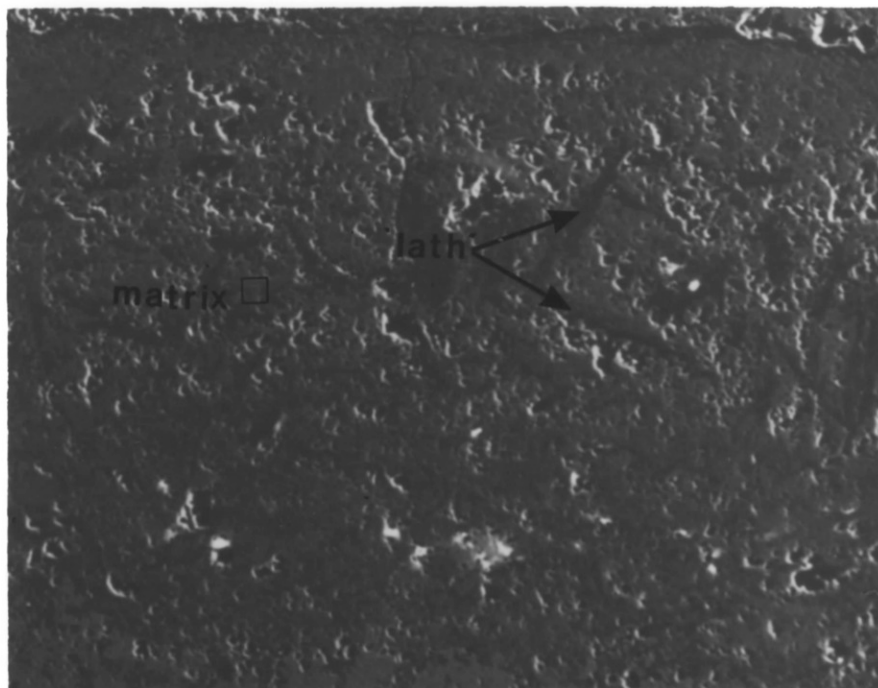
Alloy C (Fe16Cr4Al) 206h high pS_2 1123K

Electron Image Sulphur Iron Chromium Aluminium distribution



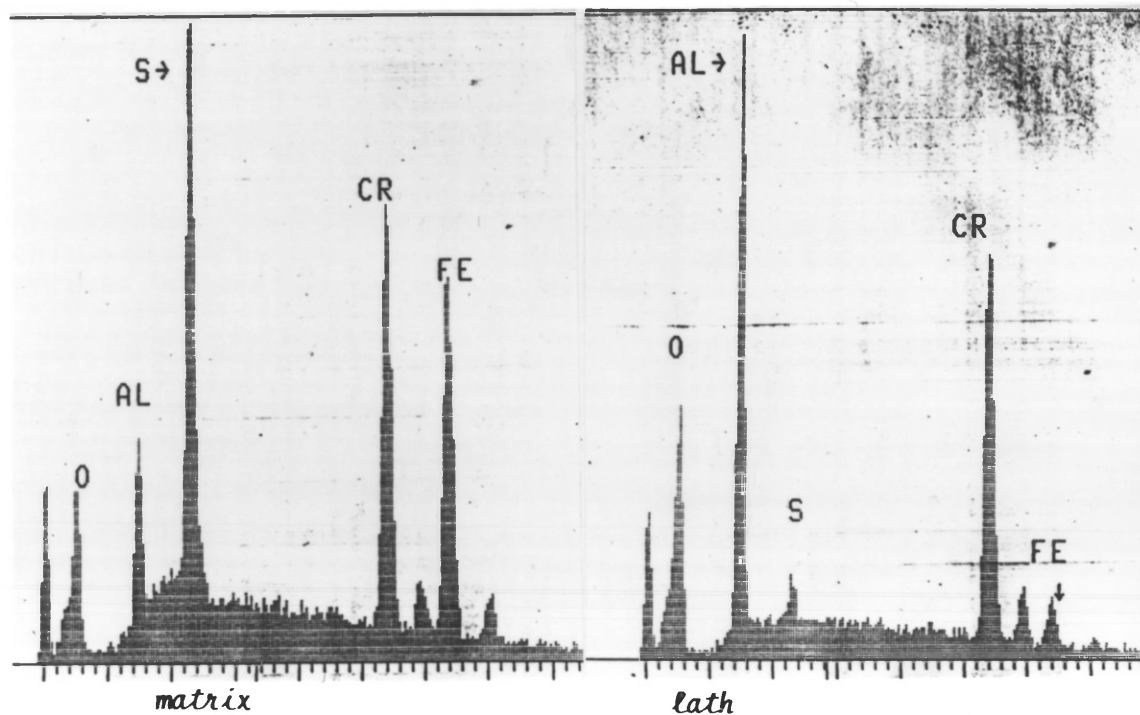
20KV X300 0261 100 BU TCSY





X300

Alloy C (Fe16Cr4Al), 194h, high pS_2 , 112K
Detail of the 'lath' zone area from Plate 17



X-ray Spectra

PLATE 18

Plate 19 shows a section of scale formed on alloy D with an element distribution. The element distribution maps are not in perfect registration with the print and this has been allowed for in the description.

The outer scale was rich in iron and sulphur and was shown to be pyrrhotite by X-ray diffraction. The inner edge of the pyrrhotite layer was porous and contained a number of voids.

The interface between the inner and outer scales is marked by a dark Al-rich band (indicated by the arrow-head) at the original metal surface.

The inner scale consists of chromium and sulphur with some aluminium present in isolated areas. The chromium and aluminium concentration is high at the inner edge of the 'lath zone' of this inner scale.

The alloy ahead of the inner scale is chromium-depleted with dark areas rich in aluminium present.

Plate 20 shows X-ray spectra of the matrix and laths in the lath zone. The matrix contains chromium, iron and sulphur. The laths are aluminium and oxygen rich. Other dark Al-rich areas in the matrix were also found to be mainly aluminium and oxygen.

Plate 21 shows a corroded section of alloy K with analysis. The matrix about 50 microns ahead of the inner scale has a composition similar to that of the bulk alloy. The immediate subadjacent matrix is depleted in chromium and aluminium and enriched in nickel. The dark internal areas (3) were found to be rich in aluminium.

Chromium and aluminium concentration rises towards the outer surface of the inner scale as iron concentration falls.

The outer scale consists of iron and sulphur with some chromium and nickel present. This layer was identified as pyrrhotite by X-ray diffraction.

Plate 19

Alloy D (Fe25Cr6.5Al)

193h

high 1123K

Electron Image

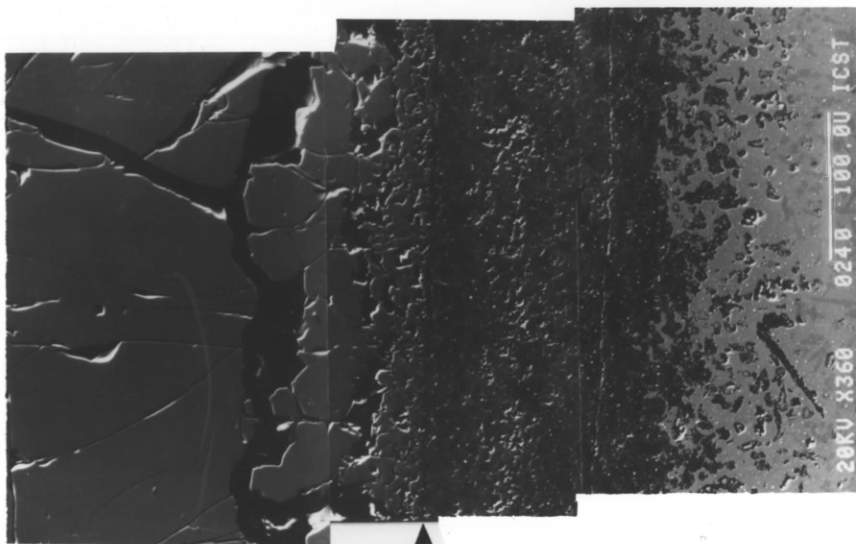
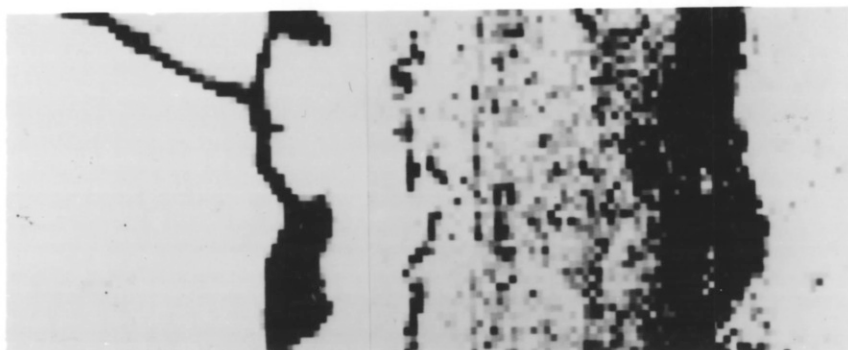
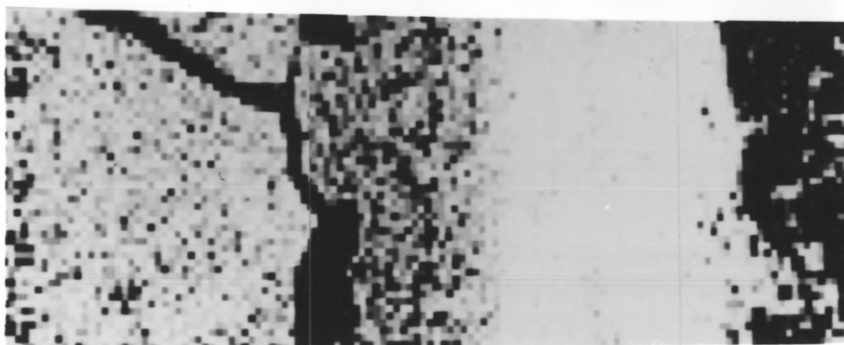
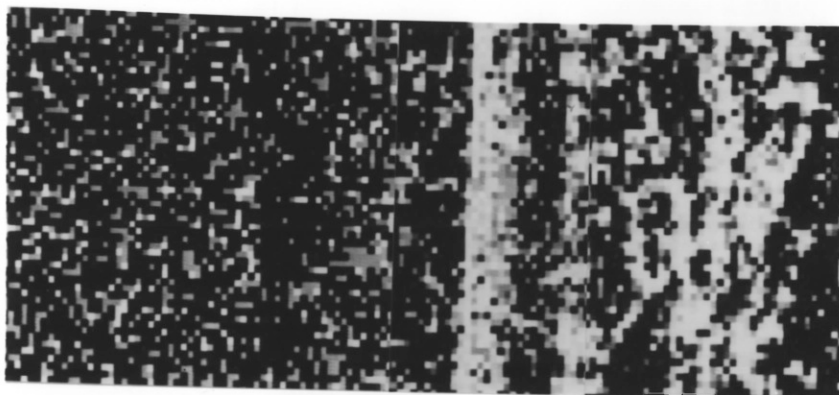
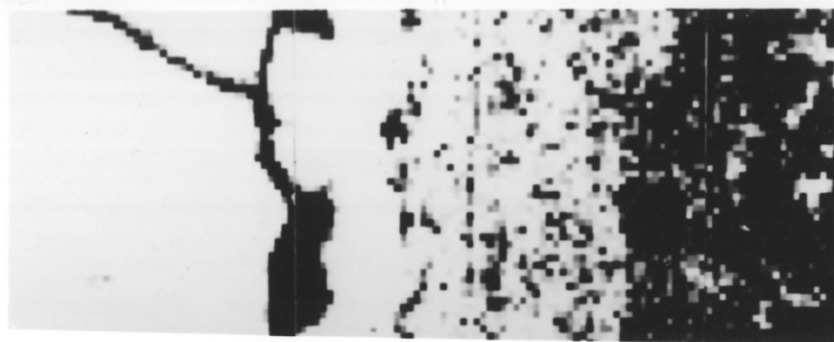
Iron

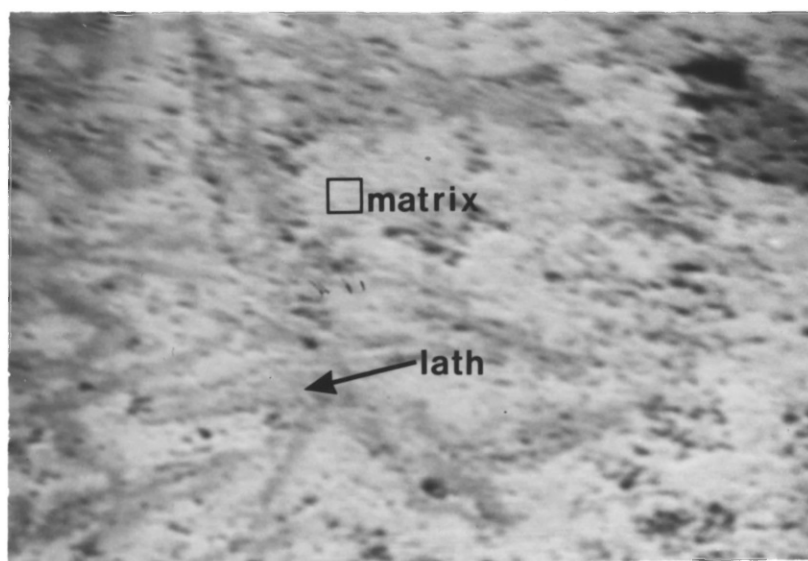
Chromium

Aluminium

Sulphur

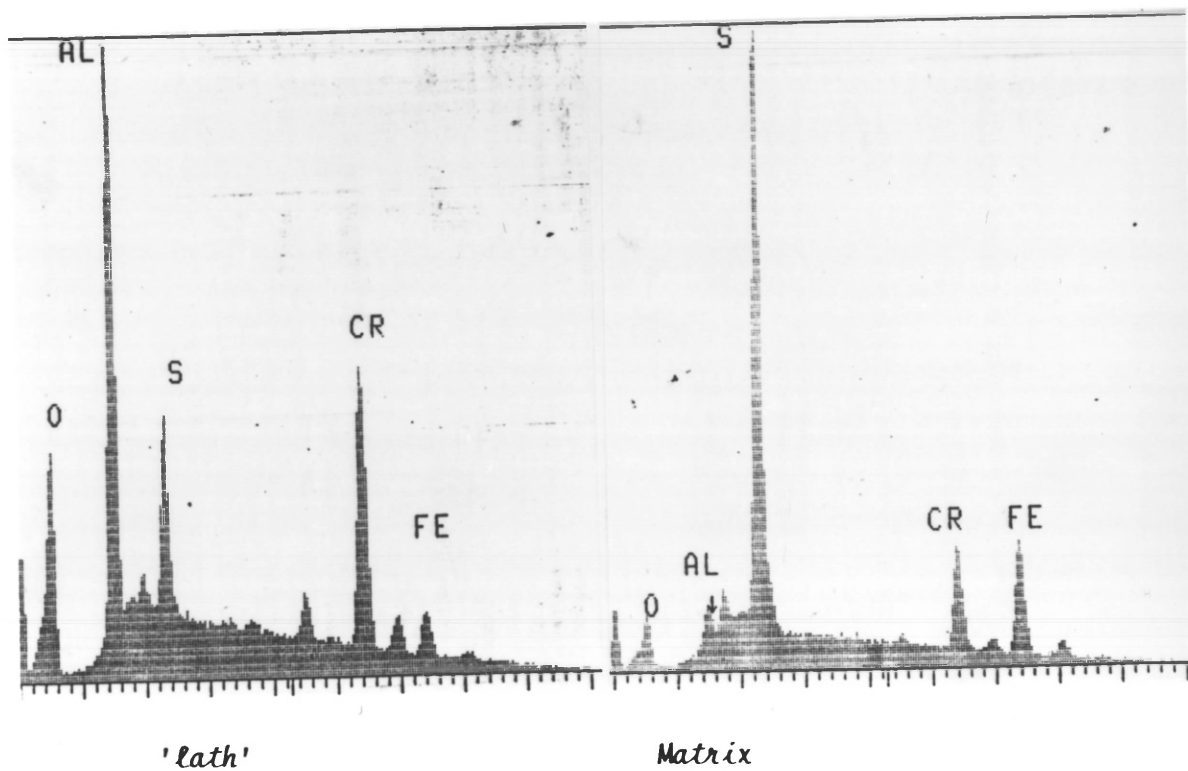
distribution



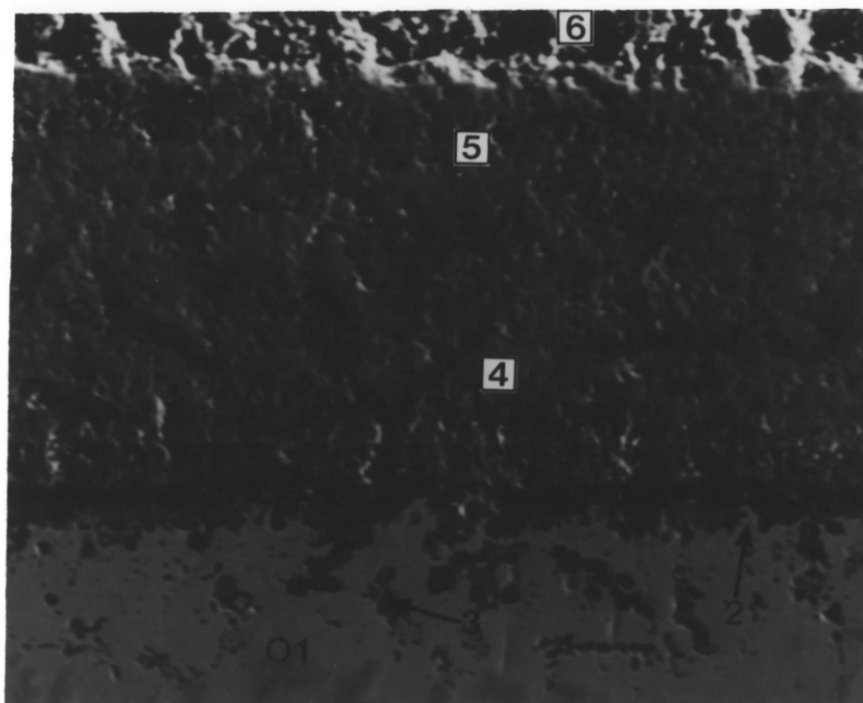


X1k

Alloy D (Fe₂₅Cr_{6.5}Al), detail of 'lath zone' from Plate 19



X-ray Spectra



Alloy K (Fe20Cr4.5Al4Ni), 207h, high pS₂, 1223K X700

Element	Wt.% Area of Print					
	1	2	3	4	5	6
Fe	76.1	83.1	21.5	40.8	13.3	48.2
Cr	9.8	4.9	10.6	12.8	26.9	8.7
Al	5.0	1.9	38.7	5.1	7.3	0.3
Ti	0.3	0.1	0.5	0.4	0.5	0.2
Y	0.2	0.2	0.3	0.2	0.1	0.2
Ni	4.6	7.4	0.5	2.2	0.7	2.6
S	-	0.5	2.4	32.0	9.1	37.3
Total	96.0	98.1	74.5	93.5	57.9	97.5

ZAF Analysis of Selected Areas of the Specimen

4 Preoxidised Specimens

(a) Introduction

The presence of an oxide layer preformed in air or another suitable atmosphere (preoxidation) is generally considered to be beneficial in promoting protective scaling in sulphidising atmospheres (Chapter 1 Section 2e). The effect of preoxidation on corrosion behaviour was examined in the atmosphere found to be most aggressive in the earlier work - high pS_2 , 1123K.

The scale formed during preoxidation, at 1100°C in air, was almost always very adherent and only once did scale detachment occur. The scale has been found to be alpha-alumina.

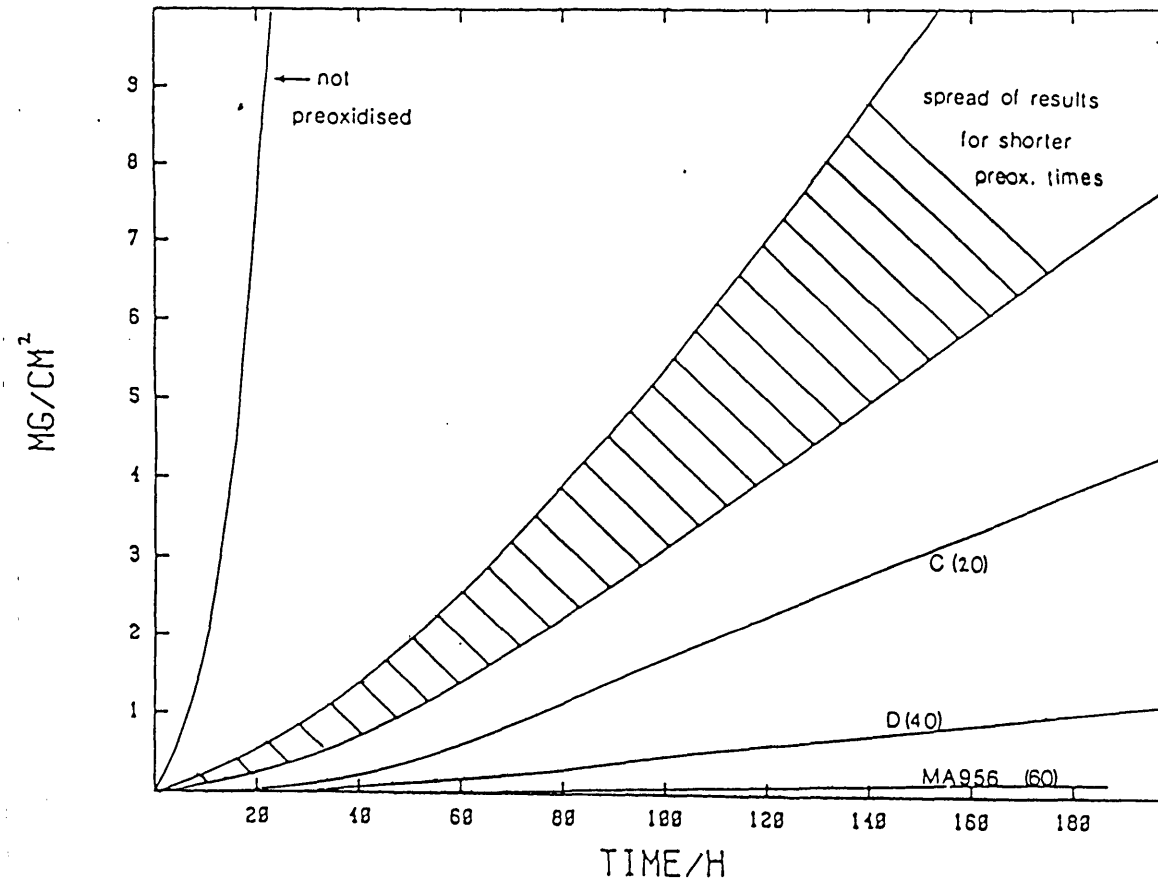
The effect of varying the preoxidation time on the subsequent corrosion behaviour was examined. Graph 14 indicates the trends found.

With short preoxidation times; 2, 5 and 10 minutes, the results were inconsistent. Rapid sulphidation frequently occurred. The rate of weight gain was always considerably lower than the similar alloy exposed without pre-oxidation.

Longer preoxidation times steadily reduced the rate of weight increase. This was accompanied by an initial period of no apparent weight increase - an incubation period.

Corrosion took the form of localised blistering, often at discontinuities such as edges or the suspension hole. Frequently large areas of the specimen remained unattacked. The localised attack usually developed a morphology similar to non-preoxidised specimens. Where longer preoxidation times were used (1h or more) damage took far longer to manifest itself. In these cases the scale formed usually contained a higher level of chromium than iron in the outer scale. Internal attack was usually less pronounced in these specimens.

GRAPH 14



Kinetic trends for alloys preoxidised at 1100°C in air.
Sulphidised in high pS_2 1123 K.

The uneven nature of the damage make kinetic rate constant data rather unreliable because the values obtained would not reflect the degree of local section loss.

A 0-200h parabolic rate constant of $5 \times 10^{-14} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ has been estimated for a specimen of MA956 preoxidised for 60min. which showed no apparent attack after exposure; this value is about six orders of magnitude lower than for the non-preoxidised alloy.

(b) Description of Plates

Plate 22 shows an example of the scale formed on alloy D during preoxidation. The scale is about 1.8 μm thick and is aluminium-rich. Slight Cr-enrichment has occurred just adjacent to the inner surface of the scale. Yttrium is evenly distributed throughout the scale and alloy. Microprobe analysis detected Al and O_2 as the main components of the scale.

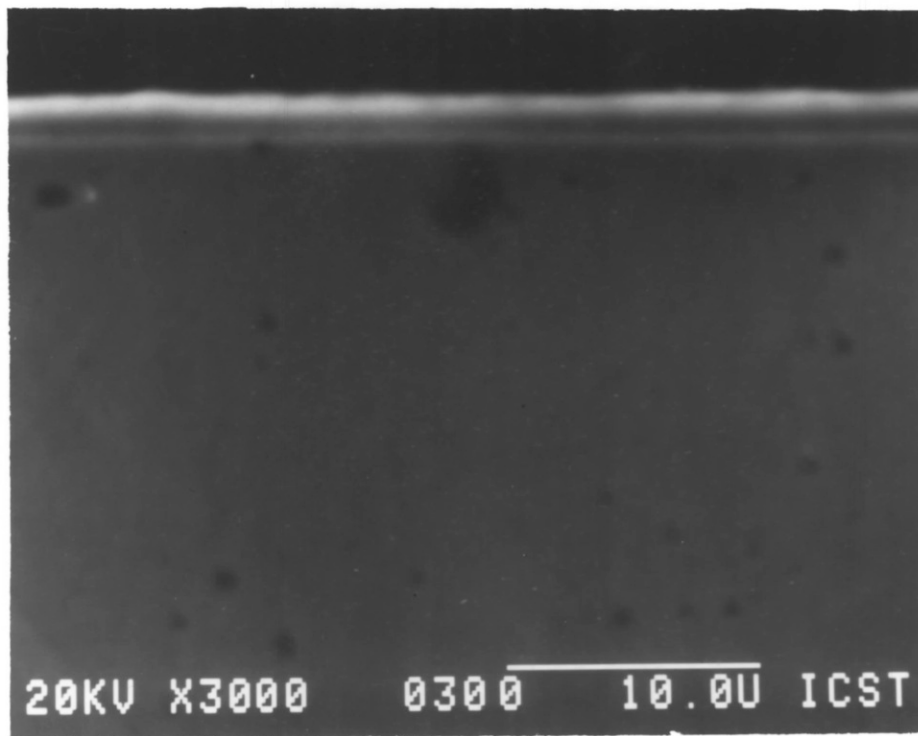
Plate 23 shows a selection of transmission electron microscope pictures of scales isolated from the metal by dissolving it away. It was only possible to isolate the scales from MA956 and alloy C. The scale formed on alloy A, D, I and K broke up into fine flocs during metal dissolution.

The scale consists of small equiaxed grains of random orientation. Electron diffraction studies suggest that alpha-alumina is the main component. The protusion (arrowed in plate) was found to be of similar composition to the bulk scale.

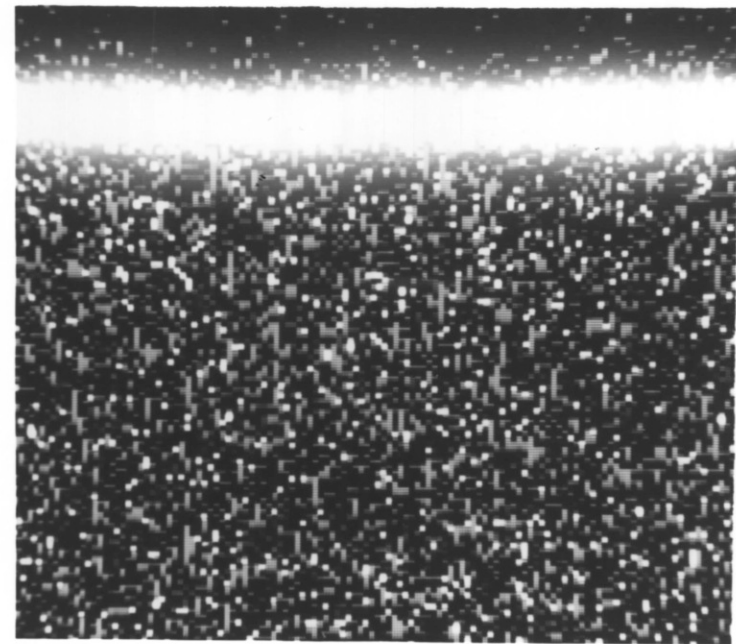
Plate 24 shows a scale which detached from the alloy during the preoxidation cycle. This effect was only observed once and it is not typical.

The scale appears to have detached from the apex of the specimen corner and to have rolled back on itself forming two low radius curves. There is no sign of cracking along the rolled edge of the scale.

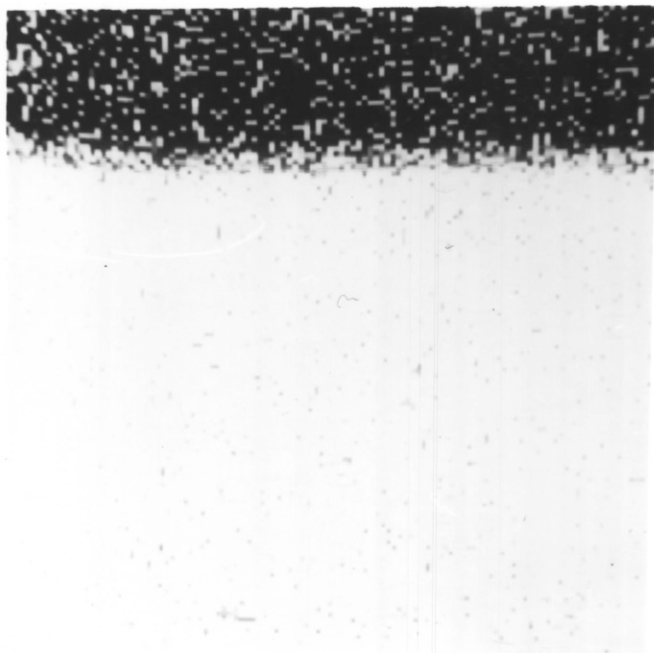
The underside of the scale is generally smooth. Analysis indicates that the scale is Al-rich and the lighter areas have a slightly lower iron content than the rest of the



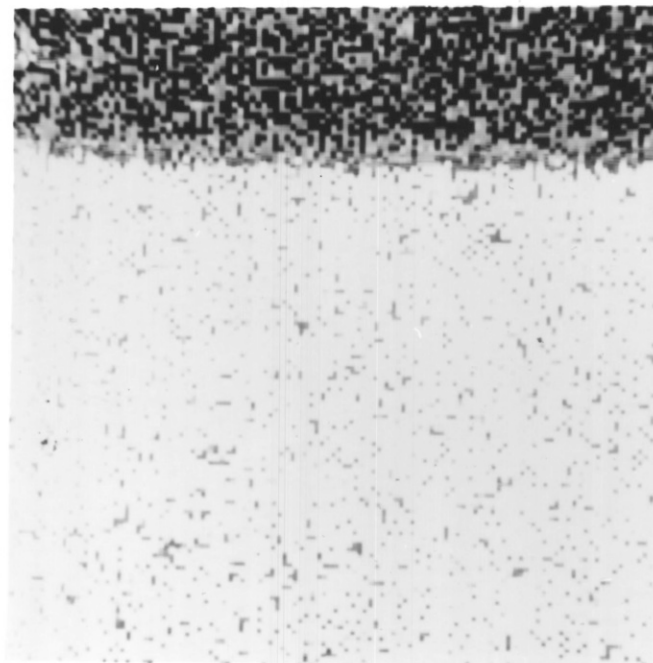
Alloy C(Fe16Cr4Al), oxidised 3h in air at 1100°C.
Weight gain 0.7 mgcm^{-2}



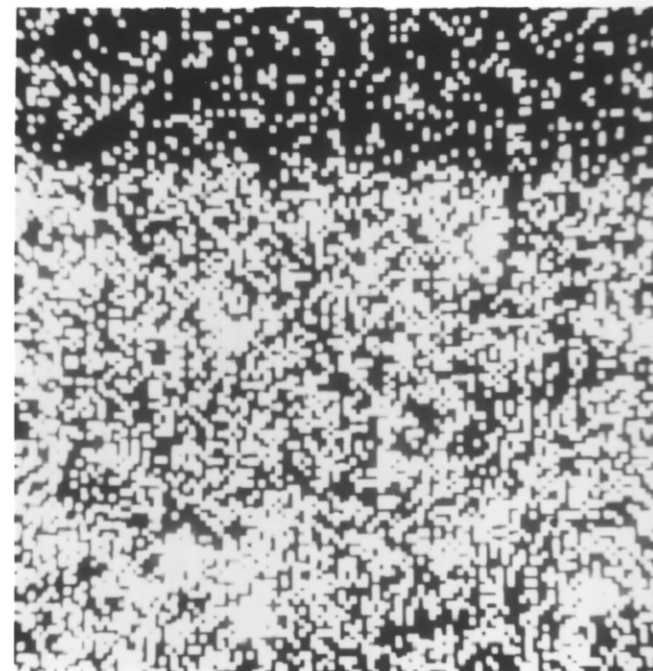
Aluminium distribution



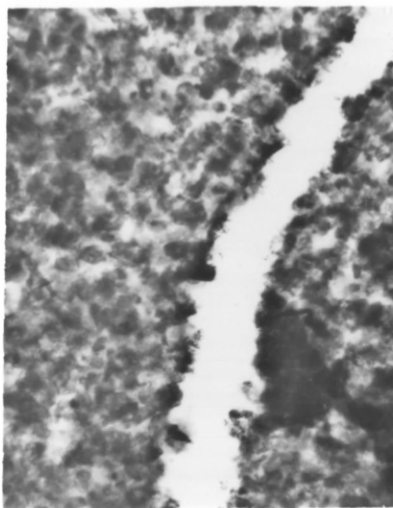
Iron distribution



Chromium distribution

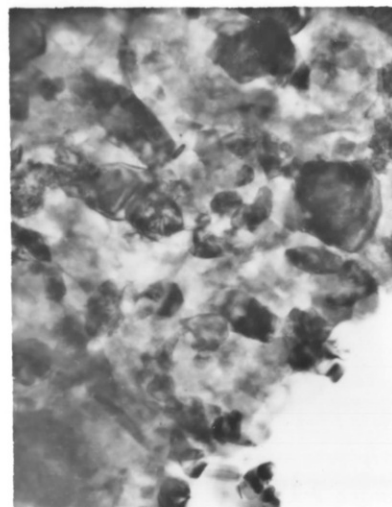


Yttrium distribution



X6.3k

Scale formed on MA956 2h in
air at 1100°C



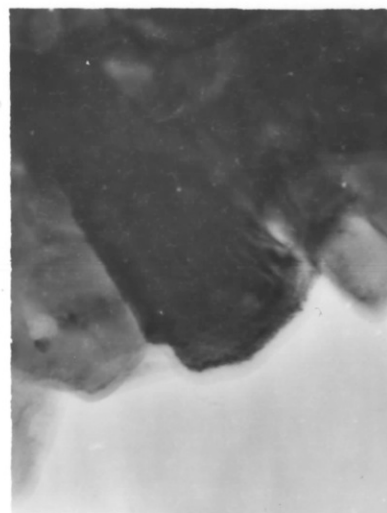
X25k

Scale formed on Alloy C 2h
in air at 1100°C



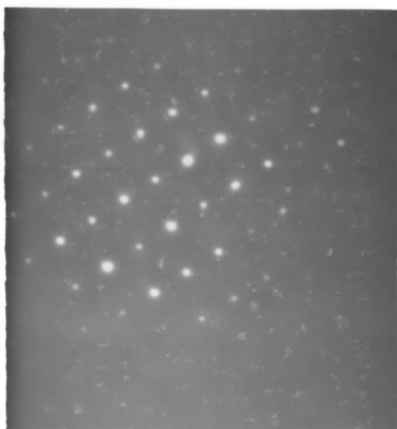
X10k

Scale formed on MA956, 2h in
air at 1100°C



X63k

Scale formed on Alloy C, 2h
in air at 1100°C



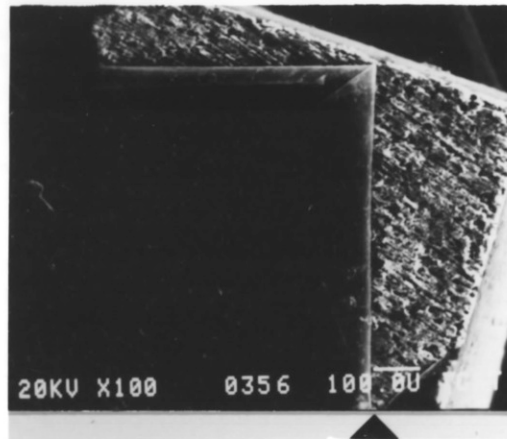
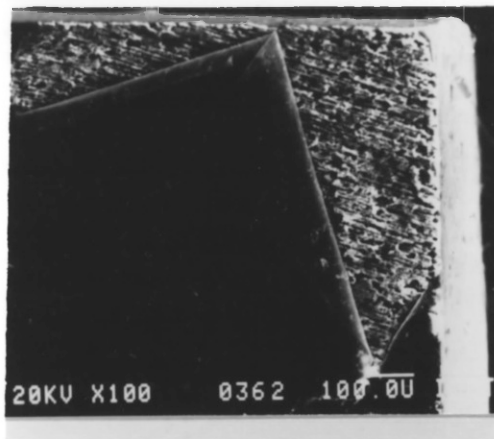
Diffraction pattern of
arrowed area above



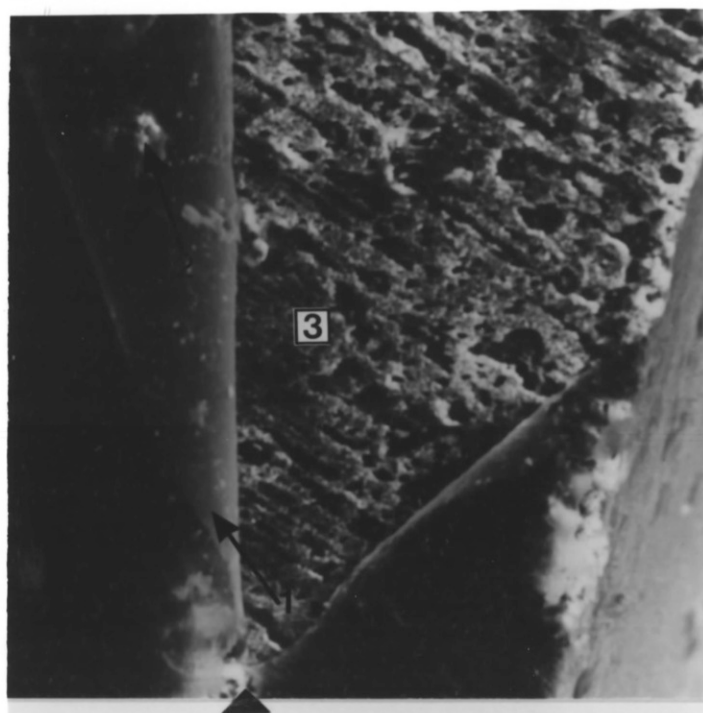
Diffraction pattern of
grains above

TEM PICTURES

PLATE 23



Alloy D (Fe25Cr6.5Al), oxidised in air at 1100°C for 3h, note the curl in the detached scale



Detail of the arrowed area with ZAF analysis

X500

Element	Wt.% Area of Print		
	1	2	3
Fe	2.6	1.1	66.3
Cr	0.8	0.7	21.7
Al	59.7	42.3	7.2
Ti	0.1	-	0.3
Y	0.1	-	0.2
S	-	-	-
Total	63.3	44.1	95.7

scale. The surface of the underlying exposed alloy is slightly richer in aluminium than the bulk material.

Plate 25 shows examples of localised sulphidation. Occasionally, a plate-like morphology was observed in the outer scale. This was found to be of similar chemical composition to the more nodular sulphides usually seen.

Damage was frequently initiated at an edge or near to the suspension hole in the specimen. Scale cracking occurred around some nodules, there is no evidence of attack on the exposed alloy however. It is possible that cracks have formed during cooling of the specimen.

Plate 26 shows specimens exposed for 1660h. In a 200h exposure none of these specimens would be expected to have shown any significant damage.

Of the 1h preoxidised specimens, alloy C and D suffered the most severe sulphidation with general attack all over the surface. MA956 performed slightly better with sulphidation confined to the upper edges of the specimen.

Increasing the preoxidation time has reduced the level of attack in all cases; 'mottled' attack is shown in alloys C and D.

MA956 with a 3h preoxidation treatment has performed relatively well with only isolated blistering.

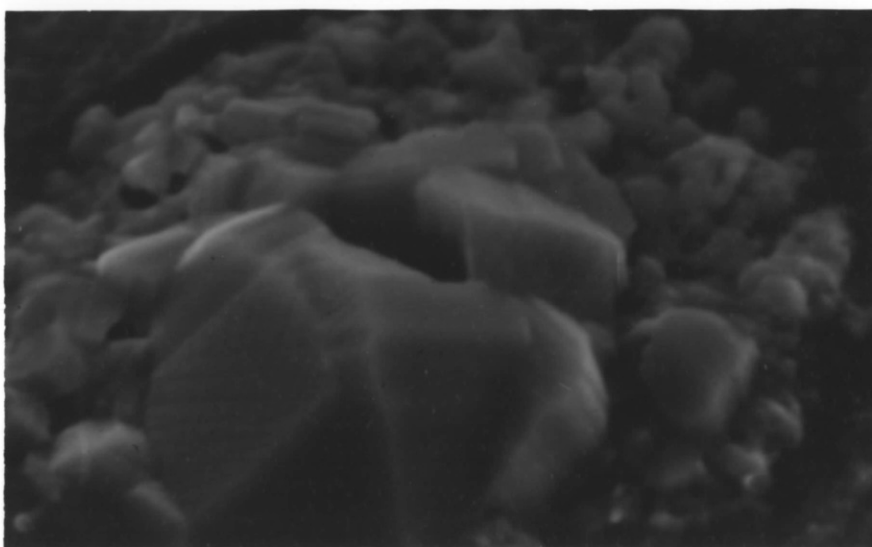
Plate 27 shows a section of a damaged corner and an unattacked surface of alloy C, 3h preoxidation, from the previous plate. The sulphide scale shows a similar morphology to that formed on non-preoxidised specimens. In the protected area, slight scale thickening and some uneven growth has occurred, but there is no evidence of scale penetration by sulphide channels.

Plate 28 shows the distribution of the major elements in alloy C which suffered heavy sulphidation.

An Al-rich band is present at the original specimen surface this is the remains of the preoxidation layer. Gaps are evident in this layer. Aluminium is homogeneously distributed in the inner scale and hardly present in the outer layer.



MA956 ($\text{Fe}_{20}\text{Cr}_{5}\text{Al}$), preoxidised 20 min. at 1100°C in air, 90h, high $p\text{S}_2$, 1123K. Damage near to suspension hole X100



Detail of a crystallite formed on preoxidised MA956 X3.5k



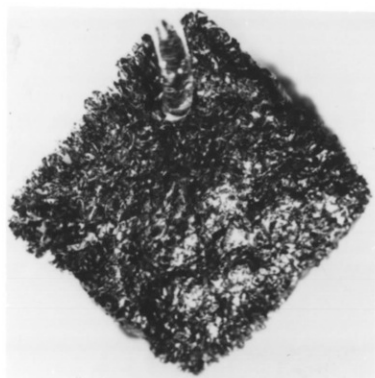
Alloy D ($\text{Fe}_{25}\text{Cr}_{6.5}\text{Al}$) preoxidised 1h at 1100°C in air, 204h, high $p\text{S}_2$, 1123K X2k

ALLOY

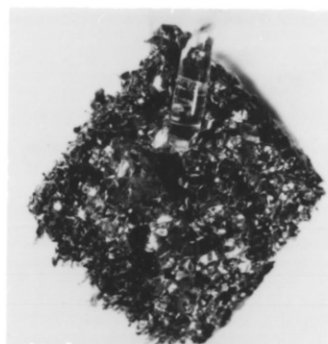
C

D

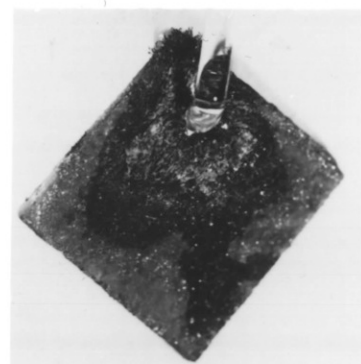
MA956



126.7 mg

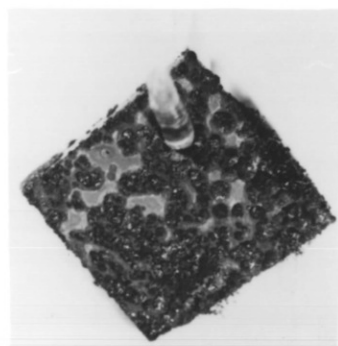


94.3 mg

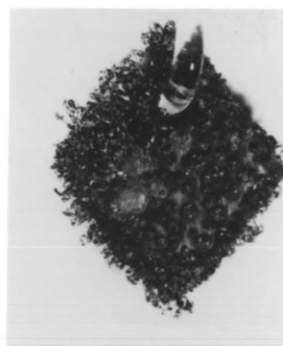


24.6 mg

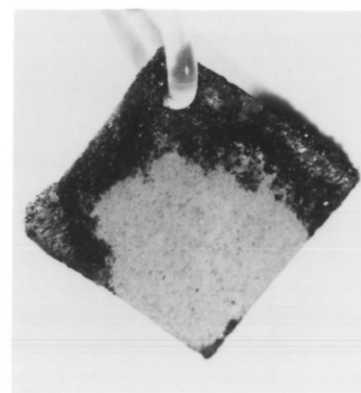
weight gain



13.2 mg

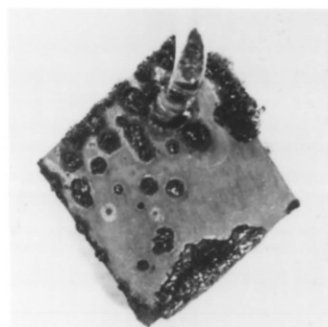


16.4 mg

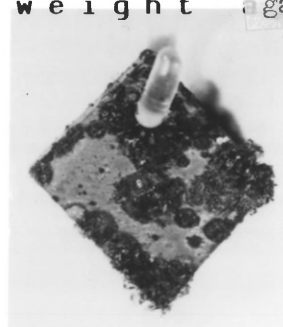


11.3 mg

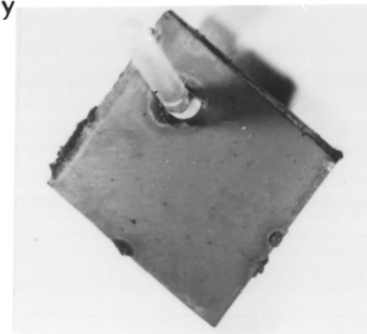
weight gain



7.7 mg



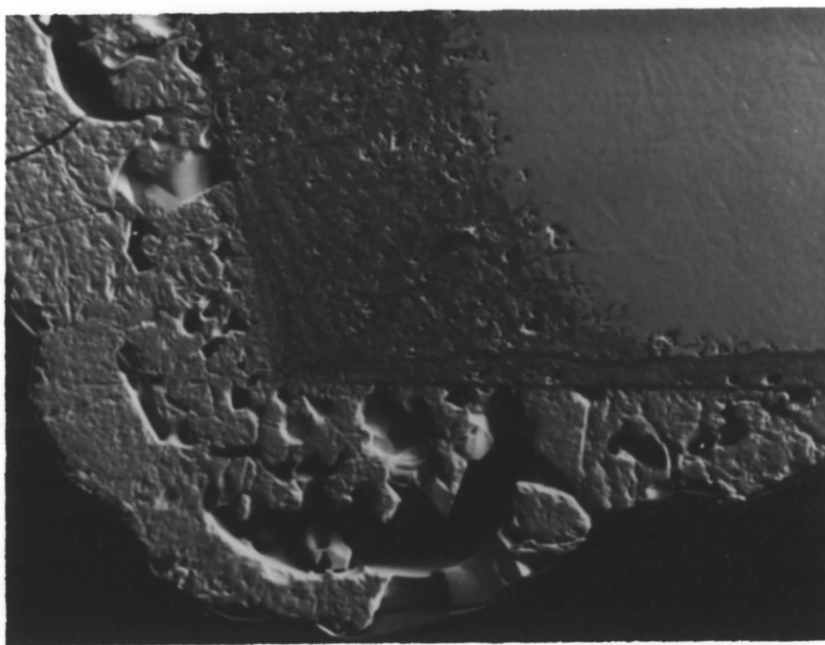
8.1 mg



2.9 mg

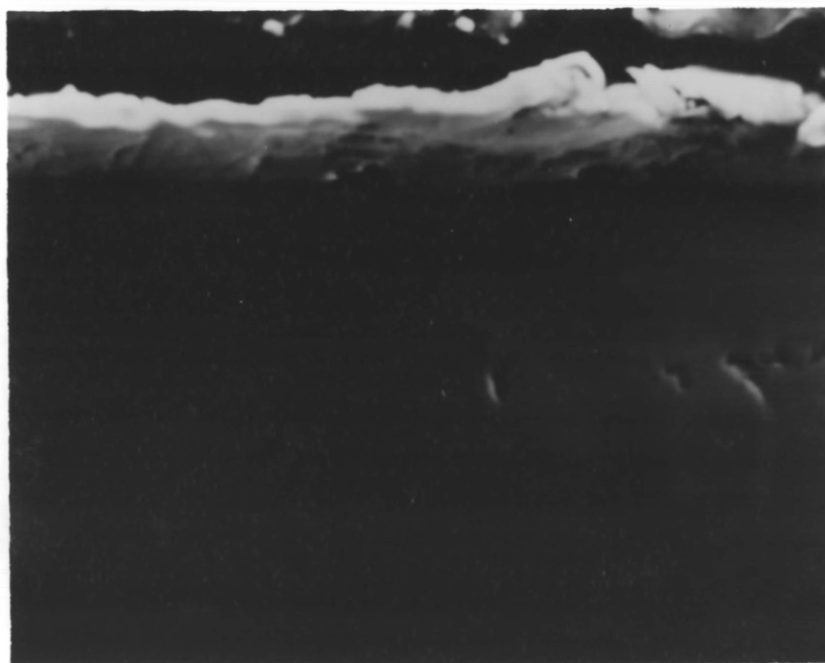
weight gain

Specimens preoxidised in air at 1100°C, 1h top row, 2h centre row
3h bottom row. Exposed 1660h, high pS_2 , 1123K.



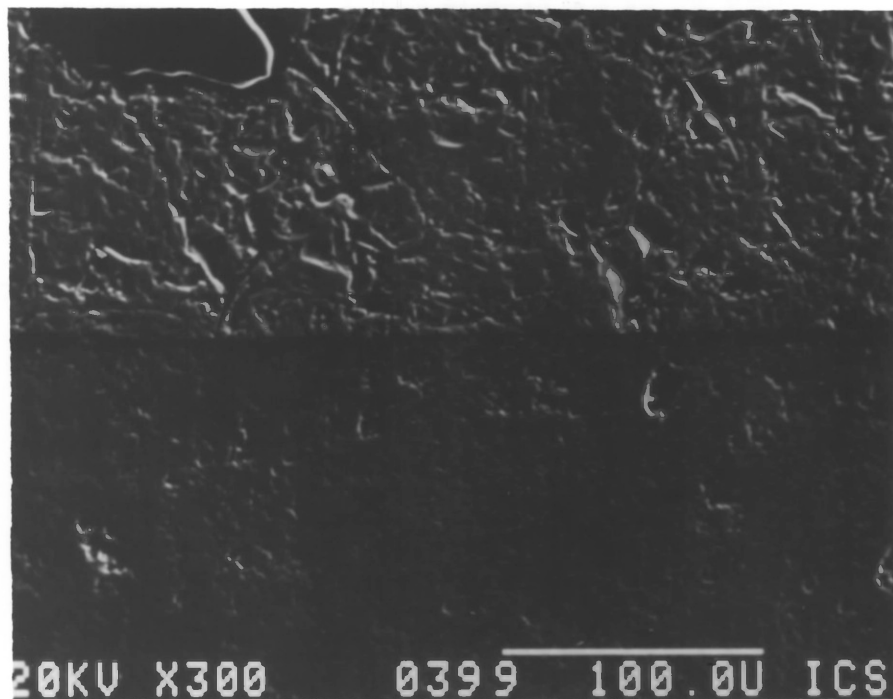
X100

Alloy C (Fe16Cr4Al), preoxidised 3h at 1100°C in air, 1660h, high pS_2 , 1123K. Section showing attack at the specimen corner.



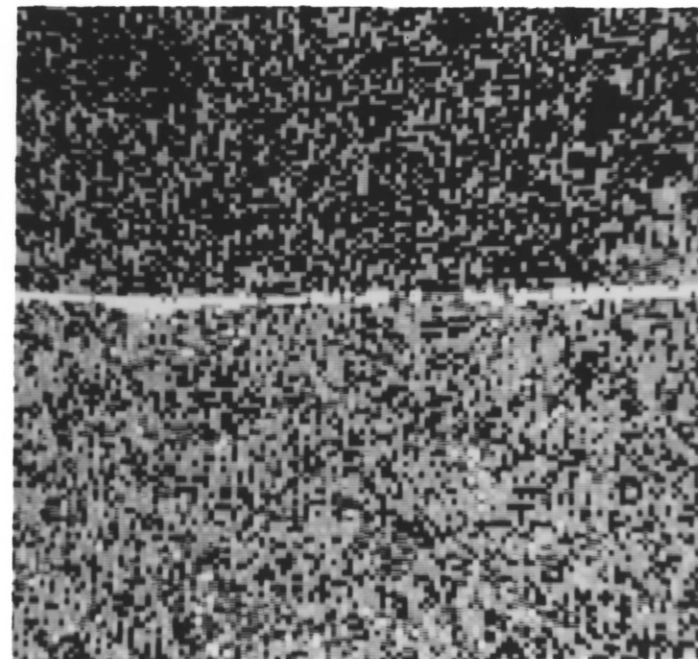
X2k

Unattacked area of above

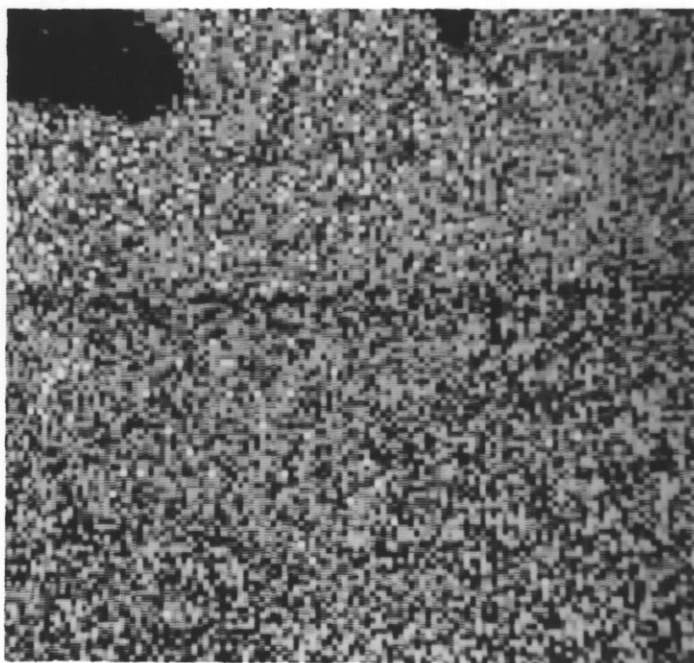


X300

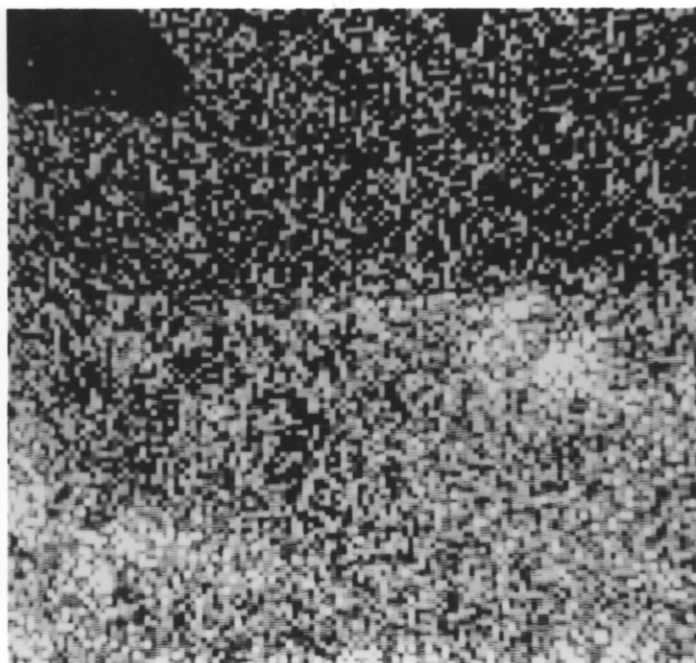
Alloy C (Fe16Cr4Al), preoxidised 1 h in air at 1100°C. Exposed 1660h, high p_{S_2} , 1123K. Weight gain 93.6 mgcm^{-2} .



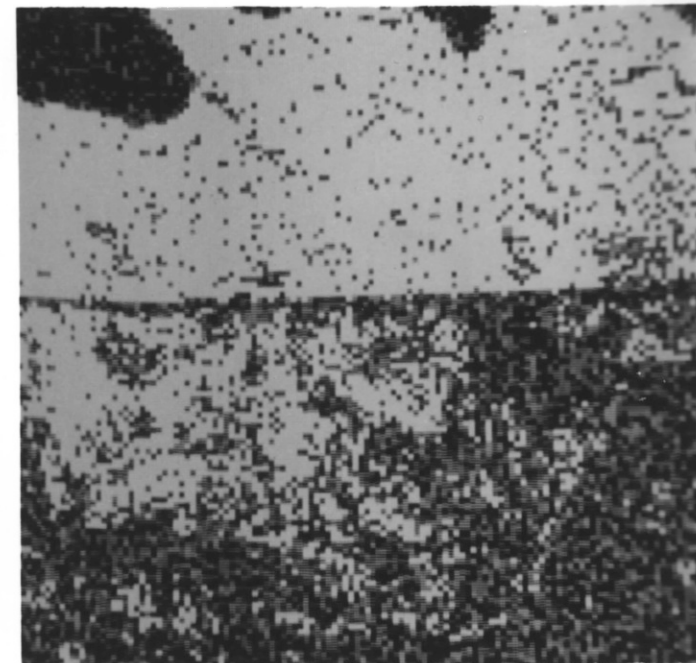
Aluminium distribution



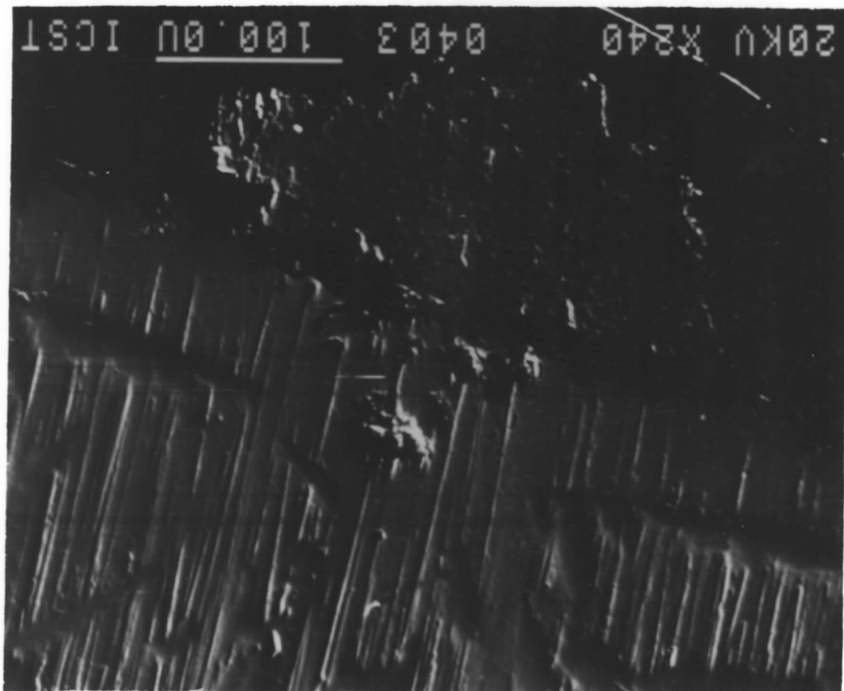
Iron distribution



Chromium distribution

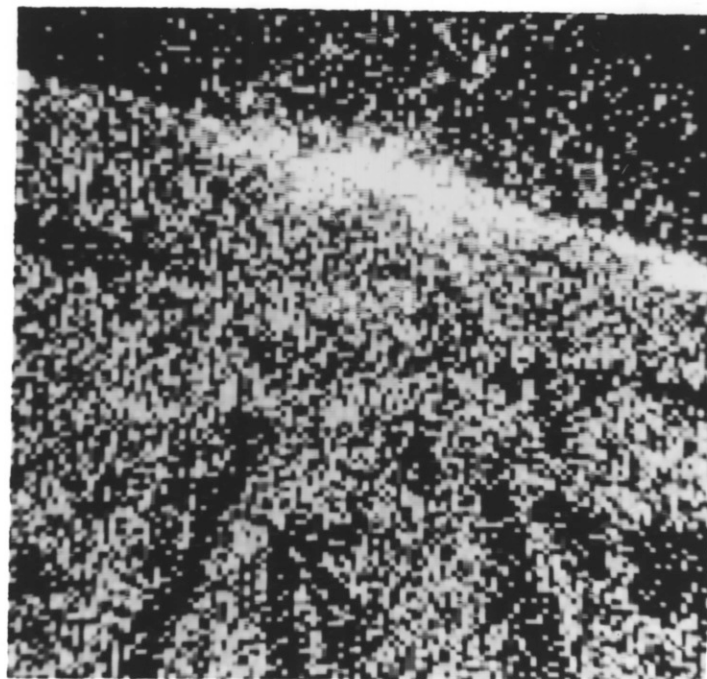


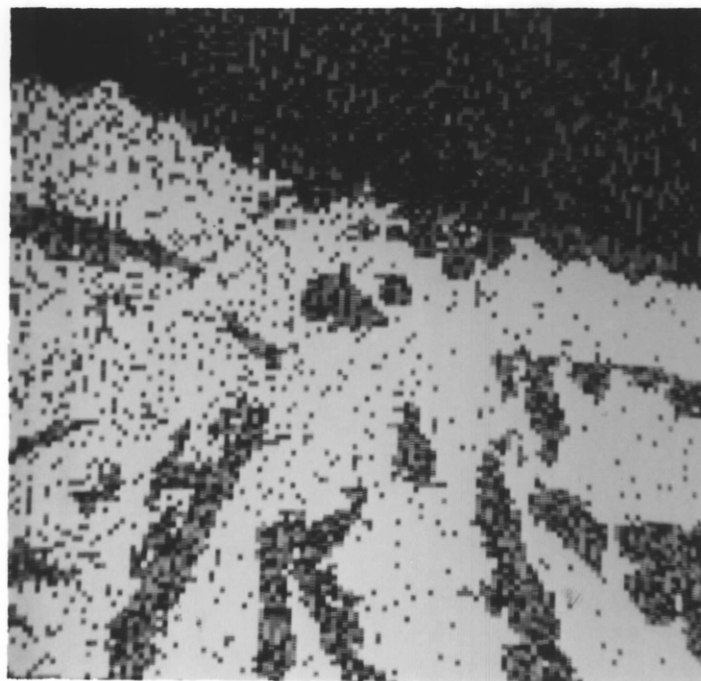
Sulphur distribution



Alloy D (Fe25Cr6.5Al), preoxidised 2h in air, 1100°C.
Exposed 1660h high pS_2 1123K.

Aluminium distribution

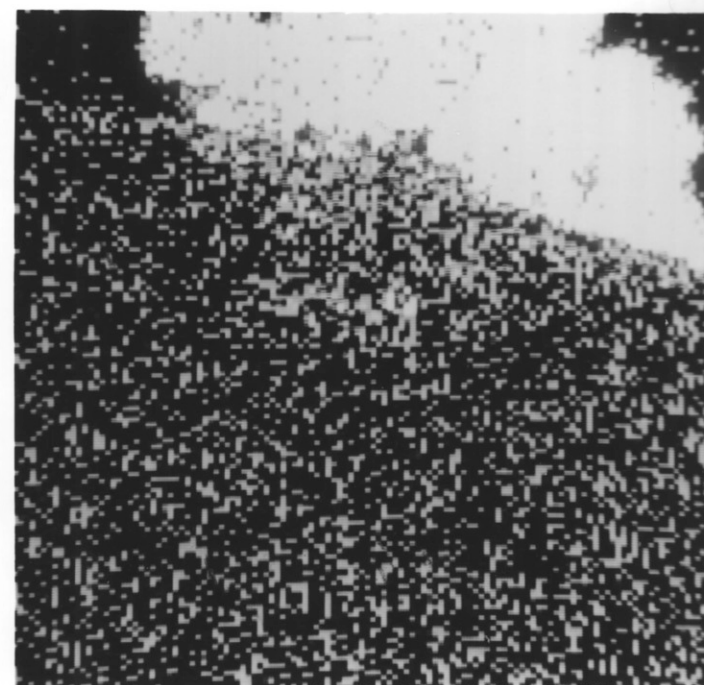




Iron distribution



Chromium distribution



Sulphur distribution

The outer scale is rich in sulphur with iron and chromium present; microprobe analysis of this layer indicates 23 ^w% Cr, 21 ^w% Fe, 37 ^w% S, 1.1 ^w% Al.

Some internal sulphidation has occurred, this is not as severe as in a non-preoxidised specimen. There is a suggestion of localised chromium enrichment in the inner scale, these areas are not always associated with sulphur.

Plate 29 shows a section of alloy D. This specimen was difficult to polish and a number of 'lath-shaped' areas were present in the matrix; these polished well but it was difficult to 'cut back' to the underlying matrix during lapping. A number of microhardness tests were made on this and other specimens of preoxidised alloy D after long exposures. The laths gave hardness values of around 600 Vickers, the matrix values were around 170 Vickers. These values must be considered to be approximate because the compliance of the mounting resin was not taken into account.

The hard areas in the matrix are clearly associated with Cr-rich, Al and Fe - depleted areas in the element distribution maps. Sulphur was almost absent from the matrix, except for a semicircular zone adjacent to the blistered area.

A thin, aluminium-rich band separates the blistered area from the main part of the specimen. The blister consists mainly of chromium and sulphur with a small amount of iron present. Microprobe analysis shows 28 ^w% Cr, 15 ^w% Fe, 36 ^w% S, 0.4 ^w% Al for the blister.

CHAPTER IV

DISCUSSION

1 Introduction

It is convenient to discuss the results under the headings: low weight gain, high weight gain and preoxidised specimens, as used in the results section.

Table 10 shows the relationship between iron activity and iron sulphide stability in the sulphur activities considered at the three test temperatures.

T/K		$pS_2/\text{atm.}$	min aFe to stabilise FeS
1123	low	3.4×10^{-8}	0.96
	med	7.3×10^{-7}	0.21
	high	8.1×10^{-6}	0.06
1223	low	1.6×10^{-7}	0.86
	med	3.6×10^{-6}	0.18
	high	3.9×10^{-5}	0.06
1323	low	6.4×10^{-7}	>1
	med	3.6×10^{-5}	0.36
	high	1.5×10^{-4}	0.14

Table 10

Iron Activity (aFe) Required to Stabilise Iron Sulphide in the Test Atmospheres Considered.

If ideal behaviour is assumed, then iron sulphide would be stable with respect to iron in all the medium and high pS_2 atmospheres used. Iron would be stable in all the low pS_2 atmospheres.

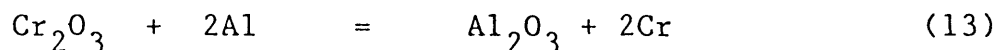
The relevant stability diagrams (Figure 1 a-c) indicate that Al_2O_3 and Cr_2O_3 would be stable with respect to aluminium and chromium.

Iron sulphide was not detected in any of the exposure conditions at 1323K and not in the med. pS_2 atmosphere at 1223K.

Kinetic considerations become significant and the interaction of alloy composition and temperature determine the scaling behaviour. Kvernes et al (1983) have demonstrated the temperature dependence of oxide morphologies on Ni 9Cr 6Al, oxidised in oxygen at 1 atm. At temperatures

from 9-1100°C the rate of weight gain increased and the alloy formed a surface spinel scale with alpha - alumina being precipitated internally. At 1200°C selective oxidation of aluminium occurred forming an alpha-alumina scale, with an associated reduction in scaling rate due to its superior protective properties.

The promotion of selective oxidation of aluminium is clearly advantageous in alloys which suffer catastrophic sulphidation once sulphide scales are formed. The presence of chromium and aluminium together has been shown to promote selective oxidation of aluminium. Wagner (1965) suggests that the presence of Cr reduces the aluminium content required to form a protective scale by gettering oxygen in the alloy and so reducing the tendency for internal oxidation of aluminium. Chromium oxide formed during gettering will subsequently be reduced to metal by aluminium:



producing a purer alumina scale. It has also been suggested that purer alumina scales will transform to alpha-alumina more readily with an increase in protective properties compared to the gamma modification.

This work has shown a distinct trend to form alumina scales at higher temperatures, even though the relative stability of iron sulphide is still high. The effect of chromium concentration in the range considered has not been marked though the 25% Cr alloy consistently outperformed its 16% Cr counterpart by a small margin. The differences would be of little practical consequence in an industrial situation.

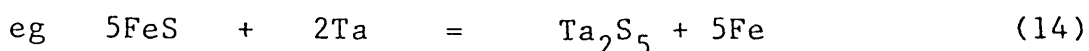
2 Low Weight Gain

These specimens generally formed aluminium - rich scales over their entire surface. There was no depletion of any of the alloys' components detected in the subadjacent matrix. Internal oxidation was not normally observed.

Sulphur was not normally detected at all in low weight gain specimens. Only in one isolated case, alloy I, was a small

(0.2 ^w%) sulphur concentration detected in the bulk alloy. Examination of the as-received alloy did not detect sulphur which suggests that it penetrated the specimen during exposure to the sulphidising atmosphere (1323K, pS_2 1.5×10^{-4} atm.).

The sulphur was mainly associated with tantalum present in the alloy. It is suggested that sulphides formed during the transient stage may have been reduced by tantalum:



Thermodynamic data is not available for this reaction but the very high stability of tantalum oxide would suggest a strong tendency to react.

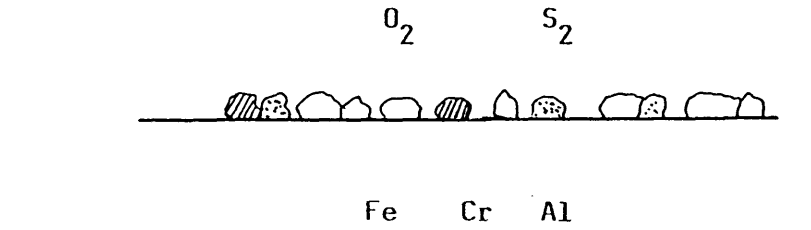
Where protective scaling has occurred, the kinetic data show a slight negative deviation from parabolic behaviour. Initially, a relatively rapid weight increase occurs, followed by a period of near parabolic kinetics which gradually slow down with increased time after about 100h.

The scales formed were found to be aluminium oxide with a trace of titanium (Plate 12). An accelerating voltage of 10kV was used in the microprobe in an attempt to restrict the probe to the scale area only. It was not possible to detect a gradient in the Ti concentration however.

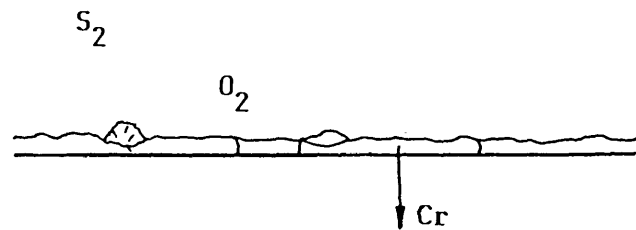
Hindam et al (1980) explain a negative deviation from parabolic growth of an alumina scale on Ni 32 ^w% Al oxidised in oxygen at 1273-1573K in terms of a reduction in the contribution of short circuit diffusion of oxygen and aluminium in the growth process. Once short circuit paths become blocked the rate of oxidation decreases.

There is general agreement in the literature (eg Golightly et al (1976, 1980), Ramanathan et al (1984a)) that the contribution of grain boundary transport is significant in the growth of Al_2O_3 .

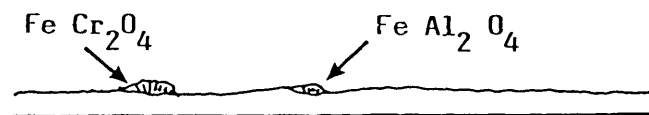
The beneficial effects of rare earth additions have been explained in terms of suppression of outward Al migration via grain boundaries, Anderson et al (1985).



i) Transient stage, nuclei of FeS , Cr_2O_3 and Al_2O_3



ii) Adjacent areas of FeS , Cr_2O_3 and Al_2O_3 react according to eqn. 15 and 16



iii) A complete alumina layer forms beneath, isolating areas of spinel

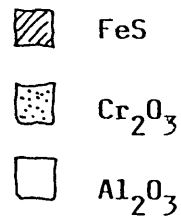
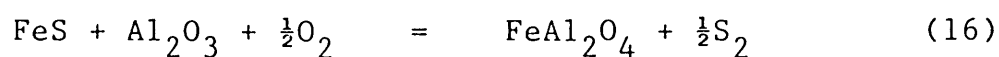
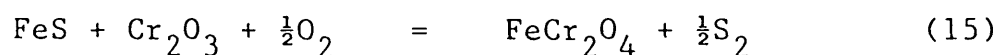


FIGURE 9

At discontinuities in the scale, yttrium, chromium and iron concentrations are higher than in the bulk scale. Sulphur has not been found in these areas. Since iron oxide would not be stable in the atmospheres used, it is probable that it is present as part of a $\text{Fe}(\text{FeCrAl})_2\text{O}_4$ spinel. This layer would be isolated from the bulk alloy by an alumina scale formed beneath it. The growth of one of these areas is represented in Figure 9. Gordon et al (1979) suggest that oxide spinel formation may not always occur readily by reaction between oxygen and metals. The presence of FeS promotes the reaction:



both these reactions are feasible in the atmospheres used.

FeS formed during the transient stage oxidation would participate in reaction 15, this would explain the absence of sulphur in the nodules. Please see Figure.

A growth mechanism for the alumina scale is represented in Figure 10(a).

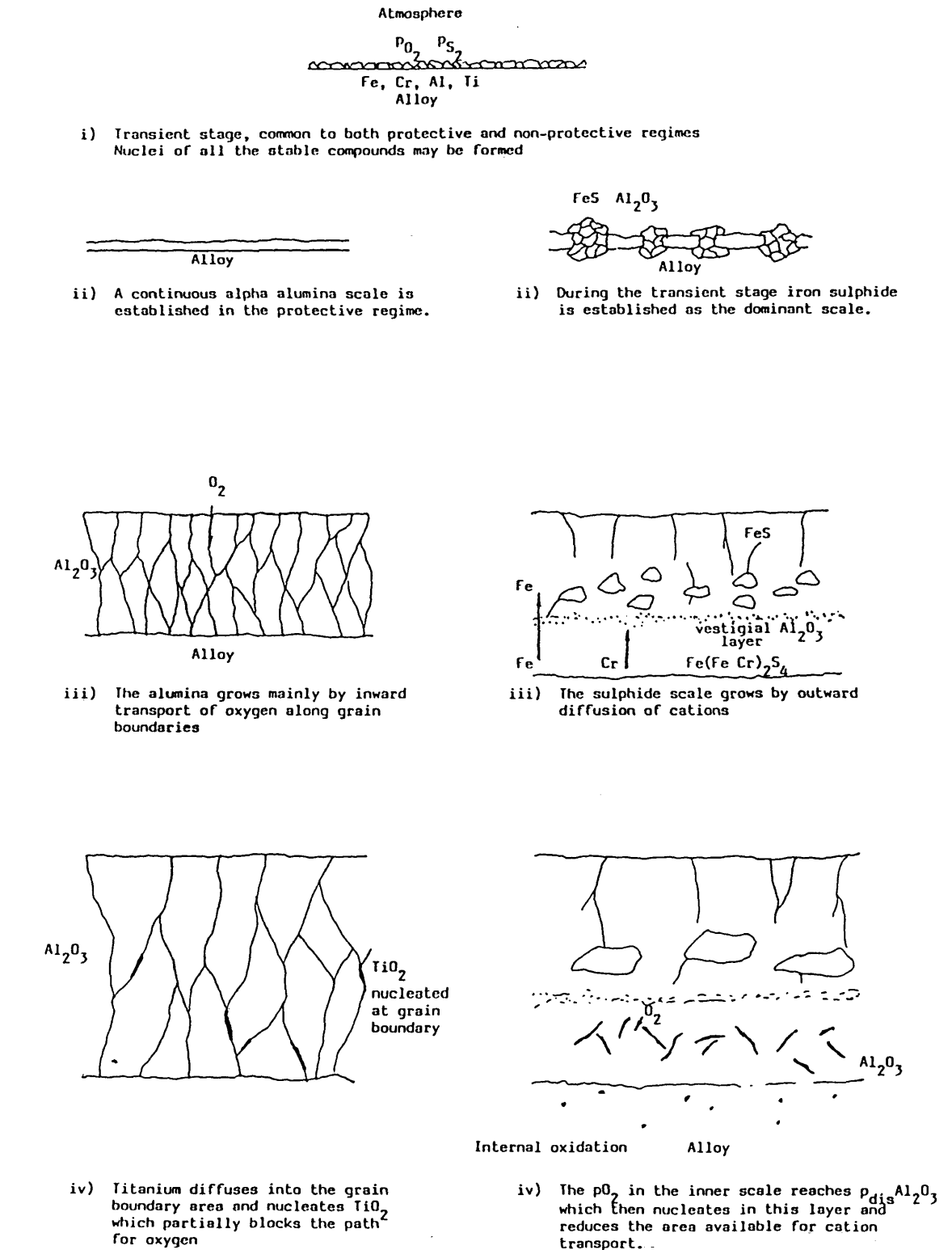
(i) Transient stage oxidation. Nuclei of all the thermodynamically stable compounds may be formed.

(ii) Alpha-alumina becomes the dominant scale. Other oxides such as Cr_2O_3 formed by gettering reactions may be reduced by aluminium (according to reaction 13).

The alumina provides an effective barrier to sulphidation.

(iii) A steady state is reached and the alumina scale thickens by a growth process involving inward ingration of oxygen via grain boundaries.

(iv) Titanium present in the bulk alloy diffuses into the grain boundary area and in some places reaches a position where $p\text{O}_2 > p\text{dis TiO}_2$ (about 10^{-30} atm.). Small areas of TiO_2 are nucleated at the grain boundaries and reduce the area of short circuit diffusion paths available for inward migration of oxygen. A reduction in scale growth rate is then observed.



A) PROTECTIVE SCALING REGIME

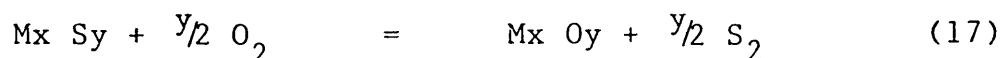
B) NON-PROTECTIVE SCALING REGIME

FIGURE 10

MA956 generally performed slightly better than the other alloys tested. MA956 is produced in industrial quantities in a 10 tonne ball mill. The pilot alloys were produced by a similar method but in a laboratory-scale mill. It is believed that these small differences in the processing method account for the difference in alloy performance.

3 High Weight Gain

Severe sulphidation only tended to occur in the higher sulphur pressure atmospheres at lower temperatures (p_{S_2} 7.3×10^{-7} - 8.1×10^{-6} atm. at 1123K and p_{S_2} 3.9×10^{-5} atm. at 1223K). Clearly the presence of oxygen in the corroding atmosphere means that some alloy components are potentially unstable with respect to sulphur and oxygen. Only one or other compound can be stable in equilibrium with a gas mixture; this is evident from the stability diagrams. Grabke (1984) comments on the possibility of simultaneous sulphide and oxide formation of the same element during the transient stage. If the rate controlling step involves a surface reaction then local equilibrium may not be reached and a banded structure may result. In effect two half reactions which represent the equilibrium.



are occurring on the same surface at different sites.

Sulphidation tended to produce a multilayered, usually duplex, scale. The outer layer was mainly pyrrhotite $Fe(1-x)S$. A wide range of stoichiometry is quoted for this sulphide; Mrowec (1984), in a review, quotes values down to $Fe\ 0.76S$. The defect concentration is a function of sulphur pressure. It has been shown by Danielewski et al (1982) that increasing the defect concentration does not have a marked effect on the self diffusion coefficient of iron in the sulphide. The self diffusion coefficient reaches a near constant value at an x value of only 0.04. This effect is explained in terms of defect site blocking (De Bruin et al (1973)) reducing their mobility.

The outer scale tended to form through-cracks and large voids at the inner edge. Some scale cracking may have occurred during specimen cooling, though cracks were present even in specimens which were cooled very slowly. The voids would have formed due to outward cation diffusion. It is very probable that gas permeation through the scale would have occurred to the level of the voids.

The inner layer of the scale consisted of a mixture of phases and an exact composition cannot be given. A Daubreelite-type sulphospinel $\text{Fe}(\text{CrFe})_2\text{S}_4$ was identified with Al_2O_3 present as 'lath' structures in the central part of this layer.

Small additions of chromium to iron have been shown to increase the sulphidation rate, this is usually attributed to doping of the p-type sulphide scale producing more cation vacancies. Zelanko et al (1974) found that additions greater than 5% Cr caused a rapid reduction in scaling rate at 540°C in H_2 0.7% H_2S . The addition of 1% Al caused a reduction of two orders of magnitude over the rate of pure iron, an explanation involving Al_2O_3 formation was suggested but this is improbable (please see Section 5 (c) Chapter 1). Reduction in the parabolic rate constant coincided with the detection of chromium sulphides in the scale.

Mrowec and Wedrychowska (1979) considered the effect of increasing additions of aluminium to an Fe 20Cr alloy corroded in sulphur vapour at 1 atm. from 923 - 1323K. The parabolic rate constant for pure iron at 1173K ranges from about 10^{-5} to $10^{-6} \text{ g}^2\text{cm}^{-4}\text{S}^{-1}$ over sulphur pressure from 1 to 10^{-6} atm. The Fe 20Cr alloy has a rate constant of $1.4 \times 10^{-6} \text{ g}^2\text{cm}^{-4}\text{S}^{-1}$ at 1 atm. p_{S_2} and the Fe 20Cr 5Al $k_p = 3.7 \times 10^{-7} \text{ g}^2\text{cm}^{-4}\text{S}^{-1}$. Marker experiments indicated that scale growth occurred by outward diffusion of cations through the scale.

The alloys formed duplex scales with similar components to those detected in this work. Aluminium is present as Al_2S_3 rather than Al_2O_3 . Diffusion of cations through the inner layer is considered to be rate limiting.

Please refer to section 5 (c) Chapter I for a further discussion of this.

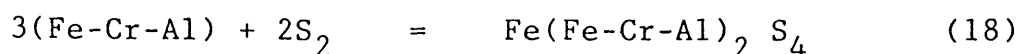
A representation of the proposed scale growth mechanism is shown in Figure 10(b).

(i) During the transient stage nuclei of all stable compounds are formed.

(ii) At lower temperatures in the higher sulphur pressure atmospheres alumina fails to form a protective scale. Iron sulphide grows around Al_2O_3 and a situation is reached where a very porous 'vestigial' layer of Al_2O_3 is rapidly outgrown by FeS. This stage resembles the final stages of the breakdown of an alumina layer formed by preoxidation, as proposed by Stott et al (1983, 1984). Once the sulphide layer is established it will grow rapidly by outward diffusion of iron.

(iii) An initially thin FeS layer is established. The presence of the vestigial alumina layer causes some reduction in growth rate due to a blocking effect. The blocking effect is similar in concept to that described by Stott and Wood (1977) in oxidation of NiAl alloys.

The p_{S_2} established at the underside of the iron sulphide layer = $p_{\text{dis FeS}}$. A reduction in local iron activity with an associated increase in chromium and aluminium activity stabilise a sulphospinel and the reaction:

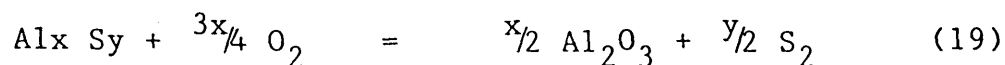


occurs.

Initial ('0'-100h) parabolic rate constants were of the same order of magnitude as those given by Mrowec (1979) for sulphidation of Fe 20Cr 5Al alloys in p_{S_2} 1 atm. suggesting that the scaling rate is almost independent of sulphur pressure over this range. This observation is in agreement with the findings of Smeltzer et al (1982) and Strafford et al (1983) who found that once $p_{\text{S}_2} > p_{\text{dis FeS}}$ the scale growth rate becomes almost independent of p_{S_2} .

(iv) Some gas permeation occurs through the outer scale and into the rather porous leading edge of the inner scale.

Oxygen pressure in the inner scale rises and reaches p_{dis} Al_2O_3 (about 10^{-40} atm. at these temperatures). Aluminium present in the inner zone is oxidised to produce the chequered lath pattern. It is not absolutely clear what reaction path is taken to form the Al_2O_3 . Aluminium is probably present as part of a sulphospinel or as Al_2S_3 . Some displacement reaction of the type



would be expected.

The formation of the 'lath' zone is accompanied by a reduction in effective cross section for outward diffusion of cations. A reduction in scale growth rate occurs and the negative deviation from parabolic kinetics is then observed.

A specimen of alloy D which was exposed to a sulphidising atmosphere (high p_{S_2} 1123K) for only 40h showed a scale of similar morphology to the longer term specimens only the 'lath' zone was not clearly visible. This observation suggests that development of the 'lath' zone occurs in the latter stages of sulphidation which is consistent with this model.

MA956 did not form a distinct 'lath' zone but tended to form areas of internal oxidation (mainly of Al) in the subadjacent matrix. It is suggested that these provide the blocking effect in this case.

In cases where very severe sulphidation occurs any blocking effects would be enhanced by a reduction of the specimen core size, which would also cause an apparent tailing-off of the scaling rate.

There is a correlation between the Cr content and the relative thickness of the inner scale, this is reflected in a reduction in scale growth rate with rising chromium content. The range of values is small and none of these alloys would be suitable for use in these atmospheres without some pretreatment. (see Table 6).

Occasionally, 'semiprotective' kinetics are observed. It is suggested that at step (ii) above alumina continues to

grow but that some isolated iron sulphide ducts still form; these areas develop sulphidation scales but adjacent areas remain unattacked. It is unlikely that the alumina film developed during storage of the specimens would be responsible for this. The film is very thin $\sim 50\text{\AA}$ (Hass (1947)) and is unlikely to participate in the high temperature corrosion process.

It is suggested that the interaction of certain surface parameters (eg degree of working) may be significant, this is beyond the scope of the present investigation.

4 Preoxidised Specimens

The formation of an alumina layer by heating in a purely oxidising atmosphere has been shown to retard or prevent sulphidation (El Majid and Lambertin (1985), Stott et al (1983 and 1984) and others, please see Section 2e, Chapter I).

The scale formed on the alloys considered here was shown to be alpha-alumina in all cases when preoxidation was carried out at 1100°C in air.

The alumina almost invariably grew as an adherent layer on the metal. In one exceptional case the scale detached and formed a low radius curl (Plate 24). Although exceptional this behaviour does suggest a residual compressive stress in the scale at the scale/metal interface. This is consistent with an inward oxygen diffusion growth model.

The underside of the curled scale was smooth and did not show any protrusions into the alloy. It is difficult to use this isolated observation as the basis of a scale adhesion theory; it is also possible that it was the absence of pegs which allowed scale detachment to occur and that all 'normal' scales grew pegs and so did not detach. Pegs were not observed in any of the sectioned scales however. It is suggested that pegging does not play a major role in the scale adhesion mechanism in these alloys.

Short (up to 10min) preoxidation treatments produced inconsistent results when the specimens were exposed to

1123K at high pS_2 atmospheres. Sulphide scales were formed and the attack was similar to semiprotective scaling of some non-preoxidised specimens.

An incubation period, during which no apparent weight increase was observed with preoxidation treatments of 20min or more. The duration of the incubation period increased with increasing preoxidation time. These observations are consistent with those reported by other workers.

The presence of a preformed oxide layer has an effect similar to a coating. Provided there are no holidays in the coating it acts as a barrier between the sulphidising gas and the underlying alloy. Because alumina is stable in the atmosphere and aluminium is present in the alloy, the scale has the advantage of being self healing, provided the underlying alloy does not become depleted in aluminium (improbable with such thin layers, generally $<5\mu\text{m}$).

In short term exposures (up to $\sim 500\text{h}$), a 1h preoxidation treatment prevented sulphidation. Longer exposures, up to 1660h at 1123K in pS_2 8.1×10^{-6} atm., caused sulphidation of alloy C, D and MA956 preoxidised for 1-3h. Areas of the alloy were still usually protected with sulphidation only occurring at isolated sites.

Localised sulphidation at corners and edges could be due to sulphur ingress or metal egress via microcracks in the oxide layer. The cracks could result from growth stresses or thermal stresses in the scale. It may be possible to design these effects out of a practical system.

Sulphidation nucleated at random sites on flat surfaces of the preoxidised specimens may be due to the nature of the scales. Through-scale ducts have formed in certain areas, possibly by a sulphur ingress mechanism via grain boundaries as proposed by Stott et al (1983, 1984).

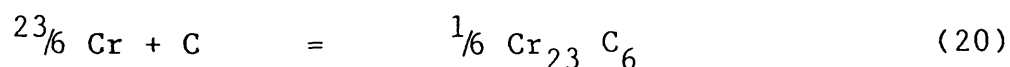
It is not clear why large areas of the specimen can remain unattacked with a few isolated blisters of sulphidation. Silicon was not found in any of the blisters analysed and it seems unlikely that they occur due to embedding of

silicon carbide during polishing though this cannot be completely discounted on the basis of this work.

Chromium has been shown to play a more important role in the sulphidation of preoxidised alloys. Blisters formed during sulphidation usually contained a higher proportion of chromium than the outer scales formed on non-preoxidised specimens. It is suggested that chromium is more mobile than iron in the sulphide ducts formed during blister development. The selective outward diffusion of a particular alloy component is not commented on in the literature.

The higher chromium content alloy D (Fe 25Cr 6.5Al) formed slipper-shaped Cr-rich islands in the alloy ahead of the corrosion front after long exposures (1660h) which produced localised sulphidation. The Cr-rich areas were found to be very hard and the morphology is similar to chromium carbides described by Tiearnay and Natesan (1982).

Thermodynamic calculations indicate that the reaction:



would require an chromium activity of 0.33 to proceed at the ambient carbon activity. Alternatively a free-carbon level of 4^w% in the alloy would be necessary to stabilise the carbide. It is improbable that this criterion would be met.

It is thermodynamically feasible for chromium nitride to form by the reaction:



Cr_2N would be stabilised by a $p\text{N}_2$ of 3.6×10^{-15} atm. which could be reached by diffusion of nitrogen into the alloy. Grabke (1984) comments briefly on nitridation arising due to gas permeation in microcracks. It is suggested that nitridation may have occurred by this mechanism.

5 Conclusions

(i) In tests at $p\text{S}_2 = 6.4 \times 10^{-7} - 1.4 \times 10^{-4}$ atm. at 1323K, $p\text{S}_2 = 3.6 \times 10^{-6} - 3.9 \times 10^{-5}$ atm. at 1223K and $p\text{S}_2 = 3.4 \times 10^{-8}$ atm. at 1123K, stable alumina layers formed spontaneously

on alloys in the range 16-25 % Al.

No evidence was found to suggest that these scales would become unstable. On the basis of this work it would be possible to recommend mechanically alloyed FeCrAl alloys for service in the chemical conditions prevailing in some coal gasification systems.

(ii) In pS_2 of 7.3×10^{-7} - 8.1×10^{-6} atm. at 1123K and pS_2 of 3.9×10^{-5} atm. at 1223K, rapid sulphidation of all alloys usually occurred. A two layered scale was formed and scale growth was controlled by outward diffusion of cations through the inner scale layer.

The formation of alumina in the inner layer caused a reduction in scaling rate.

The rate of metal loss (up to 0.5mm in 200h) would be unacceptably high for industrial service.

(iii) Preoxidation of the alloys at 1100°C in air produces an alumina layer which protects the alloy against sulphidation for several hundred hours.

Preoxidation scales always broke down in a relatively short time (<3 months) and the onset of breakdown could not be predicted accurately. It is not yet possible to recommend preoxidation as a solution to sulphidation problems in the pS_2 8.1×10^{-6} atm. at 1123K atmosphere.

(iv) No evidence was found to suggest that the presence of 4 % Ni in the alloys adversely affected their corrosion performance.

6 Comment

It should be borne in mind that the conditions used in this work are only representative of the chemical environment in a coal gasifier. The effects of physical damage to a scale due to plant operation have not been considered. These results should perhaps be regarded as optimistic in this respect.

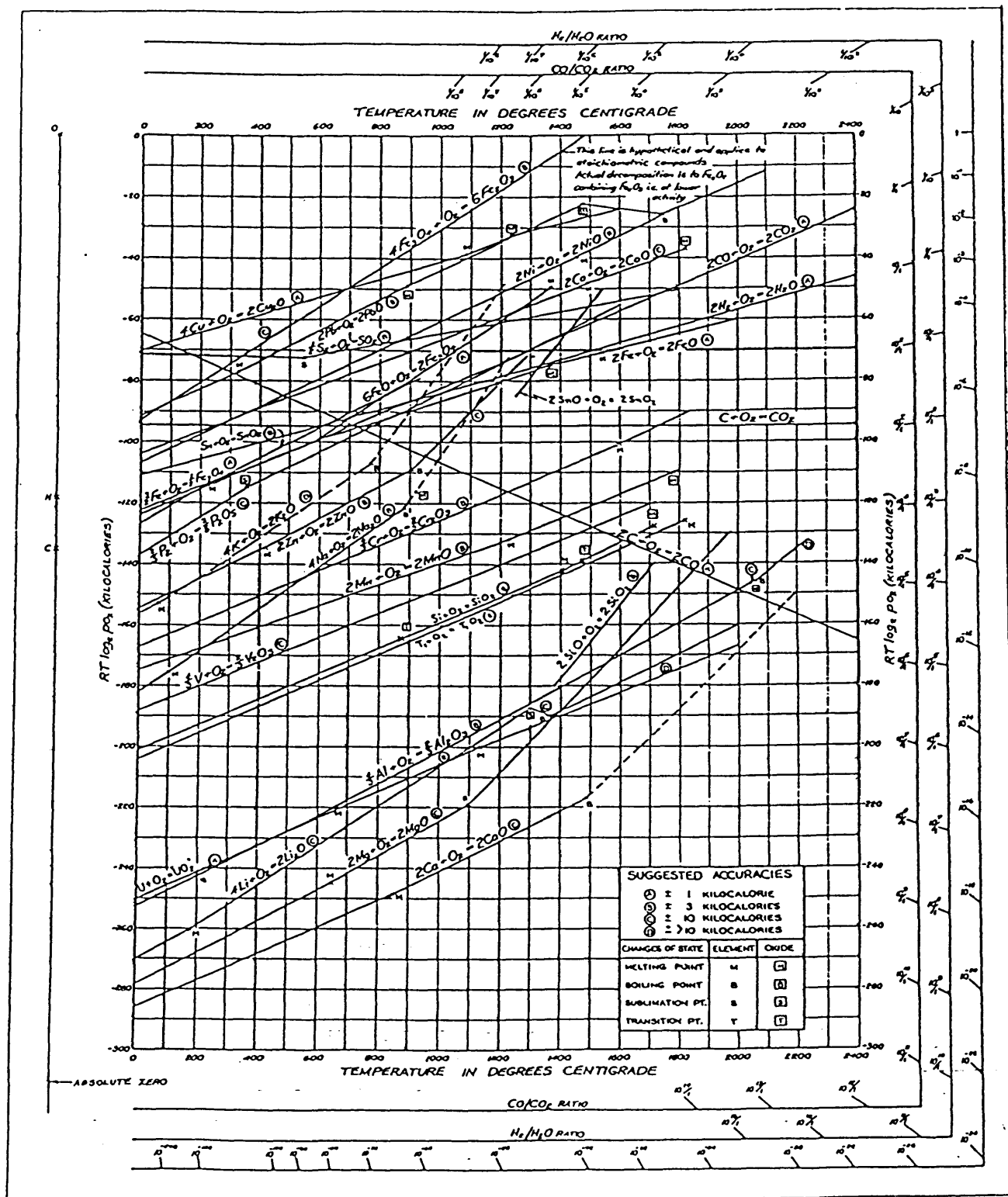
7 Suggestions for Further Work

(i) A more thorough understanding of the mechanisms leading to oxide scale penetration by sulphur and the isolated occurrence of semiprotective kinetics in high pS_2 atmospheres might suggest ways of optimising a pre-oxidation treatment.

(ii) Interference layer metallography (Buhler (1980)) could be employed in the identification of phases in the scales and subadjacent matrix. A considerable amount of preparation would be necessary in order to calibrate the equipment before this technique could be used.

APPENDICES

Appendix I



Ellingham Diagram for Oxides

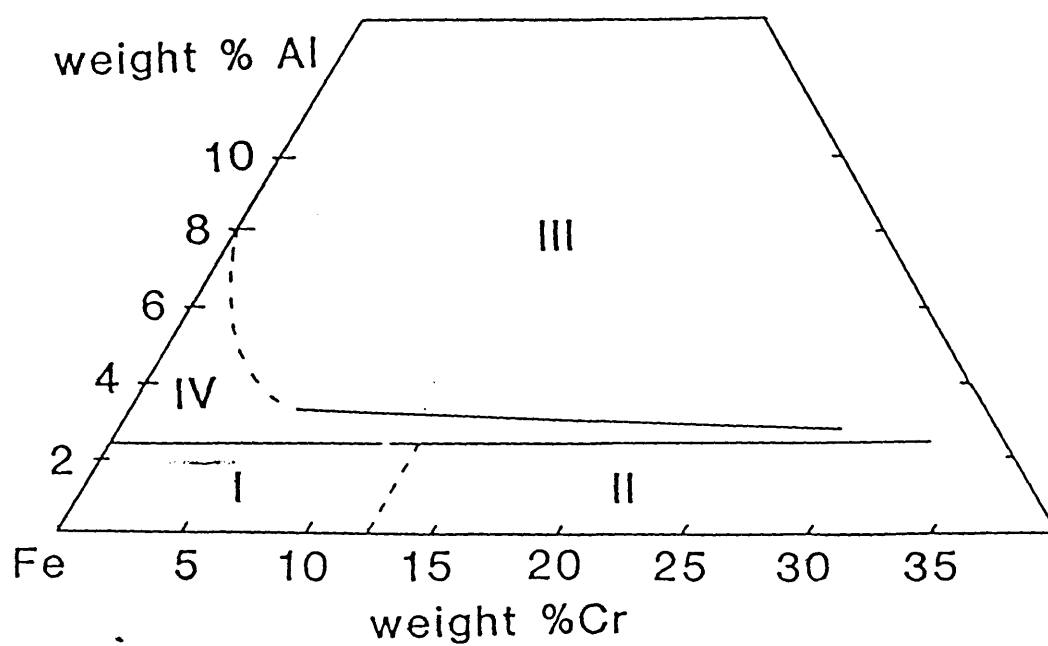
Appendix II

I Fe_2O_3 internal oxidation

II Cr_2O_3 internal oxidation

III Al_2O_3 Fe_2O_3

IV Al_2O_3

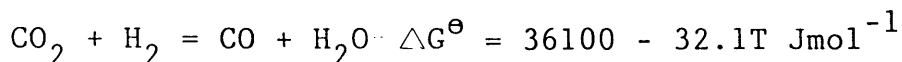


Oxide Map for Oxidation of Pure Iron-rich
Ternary FeCrAl Alloys at 800 °C $p\text{O}_2$ 0.26 atm
(from Tomaszewicz 1983)

APPENDIX III

Calculation of Gas Flow Rates to Produce the Required
Partial Pressures of Active Components at 850°C

The gas mixture was produced by mixing three of the components in the water gas shift reaction:



Nitrogen was added as forming gas (90 N₂ : 10 H₂ mixture). Hydrogen sulphide was used to produce the required pS₂. The small amount of hydrogen released by the decomposition of hydrogen sulphide does not significantly affect the gas composition.

At 1123K (850°C) the equilibrium constant for reaction is 1.0

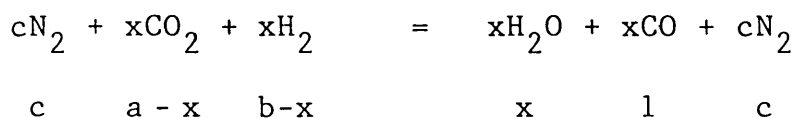
$$\therefore 1 = \frac{p_{\text{CO}} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2}}$$

The partial pressures required are:

$$\begin{array}{ll} p_{\text{H}_2} & 0.084 \text{ atm} & p_{\text{CO}} & 0.126 \text{ atm} \\ p_{\text{CO}_2} & 0.062 \text{ atm} & p_{\text{N}_2} & 0.70 \text{ atm} \end{array}$$

$$\begin{aligned} \text{hence } p_{\text{H}_2\text{O}} &= \frac{1.0 \times 0.084 \times 0.062}{0.126} \\ &= \underline{0.041 \text{ atm.}} \end{aligned}$$

From Gay Lussac's Law:



by assigning values of a, b, 1 and c to the flow rates of CO₂, H₂, CO and N₂ respectively, x = H₂O produced.

solving for x

$$\frac{p\text{CO}_2}{p\text{H}_2\text{O}} = \frac{0.126}{0.041} = \frac{1+x}{x} \quad x = 0.482$$

solving for a

$$\frac{p\text{CO}_2}{p\text{H}_2\text{O}} = \frac{0.062}{0.041}, \quad \frac{0.062}{0.041} x + x = a$$

$$a = 1.211$$

solving for b

$$\frac{p\text{H}_2}{p\text{H}_2\text{O}} = \frac{0.084}{0.041}, \quad \frac{0.084}{0.041} x + x = b$$

$$b = 1.469$$

solving for c

$$\frac{p\text{N}_2}{p\text{H}_2\text{O}} = \frac{0.70}{0.041}, \quad \frac{0.70}{0.041} x = c$$

$$c = 8.229$$

$$\begin{aligned} \text{For a total flow rate of } 100\text{cm}^3\text{min}^{-1} &= a + b + c + 1 \\ \text{hence CO}_2 \text{ flow} &= \frac{1.211}{11.909} \times 100\text{cm}^3\text{min}^{-1} = 10.2\text{cm}^3\text{min}^{-1} \end{aligned}$$

similarly flow rates of

$$\begin{aligned} \text{H}_2 &= 12.3\text{cm}^3\text{min}^{-1} \\ \text{CO} &= 8.4\text{cm}^3\text{min}^{-1} \\ \text{N}_2 &= 69.1\text{cm}^3\text{min}^{-1} \end{aligned}$$

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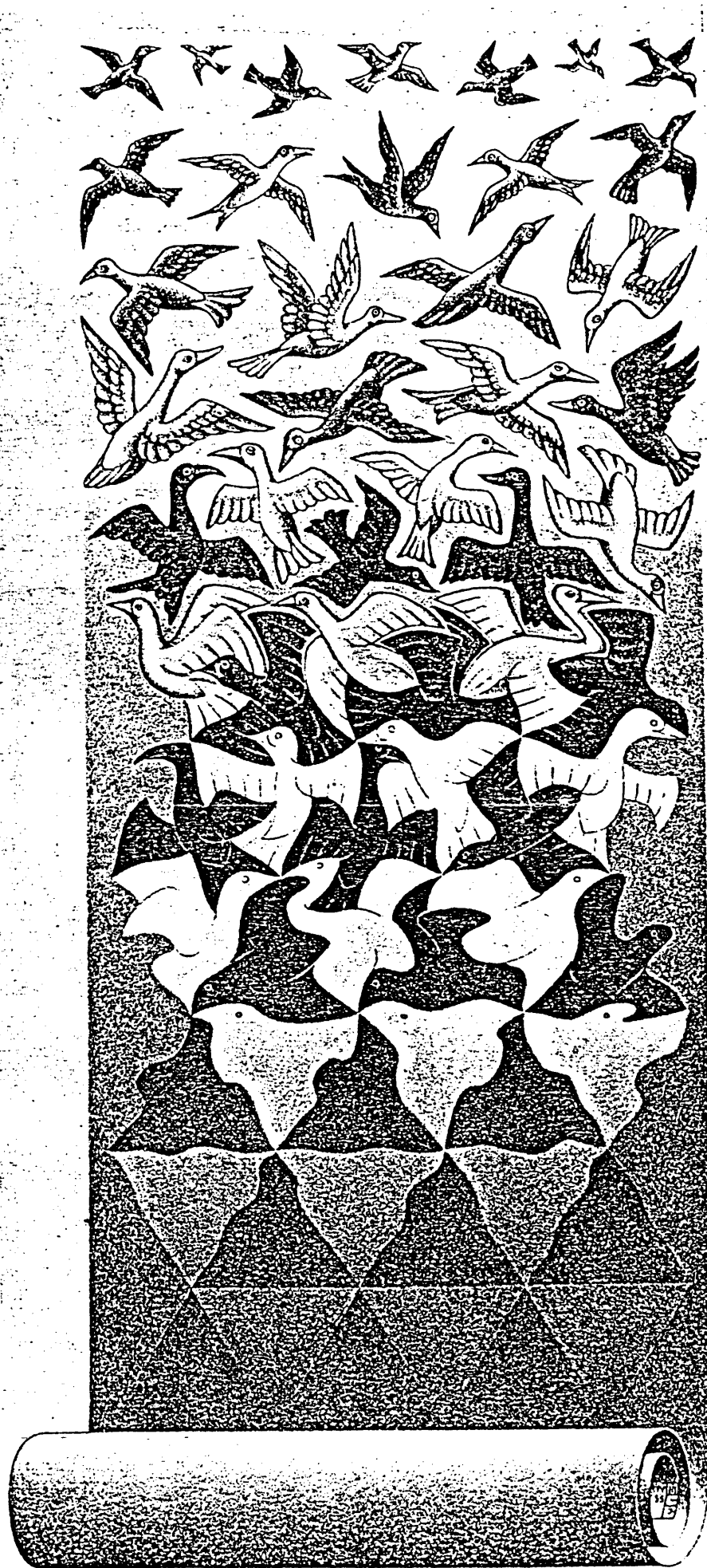
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