THE SULPHIDATION PROPERTIES OF Fe-10WT% A1 ALLOYS AT 1173 K IN H_2S/H_2 ATMOSPHERES

BY

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ABSTRACT

The sulphidation properties of Fe-lowt% Al alloys at 1173 K in $H_2S\chi H_2$ atmospheres were studied in the range of $P_{S_2} = 1 \times 10^{-2}$ atm to 1×10^{-6} atm with special reference to the morphological development in the sulphide scale. Nodular growth of Fe_{1-x}S has been observed at $P_{S_2} = 1 \times 10^{-4}$ atm to 1×10^{-3} atm with extensive internal sulphidation beneath these nodules.

Sulphidation kinetics of the Fe-lowt% Al alloys were approximated to a two-stage parabolic rate. A duplex scale is observed with an outer layer of $Fe_{1-x}S$, an inner layer composed of $Fe_{1-x}S + FeAl_2S_4$ having a pearlitic appearance and Al_2S_3 platelets or needles at the alloy/scale interface. At long exposure, a film of $FeAl_2S_4 + Al_2S_3$ develops at the alloy/scale interface. Two models are advanced for the growth of this film. The presence of Al_2S_3 platelets or needles beneath the continuous Al_2S_3 film is interpreted to result from morphological breakdown of the Al_2S_3 /alloy interface and internal sulphidation. Platinum markers were found between the outer and inner layers suggesting growth of the outer layer by outward iron migration and growth of the inner layer by jnward sulphur migration.

A schematic ternary Fe-Al-S isotherm is constructed using the alloy sulphidation results and available thermodynamic data with respect to the binary sulphide phases. Various virtual diffusion paths representative of the sulphidation kinetics and scale microstructures for Fe-10wt% Al and Fe-15wt% Al alloys are indicated on this schematic diagram.

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CHAPTER 1

INTRODUCTION

Development of high temperature sulphur and H_2S resistant materials has gained considerable importance at present because of the degradation of reactor materials used in coal gassification systems^{1,2}. A promising way of utilizing coal is to convert it to synthetic natural gas (SNG) and petroleum type products. The typical operating temperatures of the reactors used for coal-gassification (1123 K-1273 K) and high operating pressures lead to severe corrosion of reactor materials. The off-gas from the gassifier contains H_2 , H_2O , CO and H_2S , of which H_2S is quite corrosive³. The presence of other gases like CO₂, CH₄ and NH₃further complicate the situation.

On the other hand, oil industries have been presented with the problem of high temperature sulphur corrosion in a number of their processes due to the presence of sulphur in the crude oil. During the processing of crude oil, sulphur is released primarily as hydrogen sulphide.

The development of corrosion resistant alloys is of considerable importance because of the focus on the use of high temperature combustion and energy conversion systems, including fluidized bed coal combustors, coal gassifiers, gas turbines etc., in which alloys constitute a major fraction of the structural components that are exposed to corrosive atmospheres at elevated temperatures. Quite often stainless steels and other alloys are used to obtain useful life times for petroleum processing vessels (temperature of operation 473 to 873 K)^{4-6,9} and gassifiers

respectively. Therefore it would be of considerable interest if less expensive, H₂S resistant Fe-based alloys could be developed at the temperature of concern. * ·<u>*</u> - ·

The use of aluminium in a number of metals and alloys to reduce the oxidation behaviour at elevated temperatures or as an external coating is well known ⁷, because of the preferential formation of a protective aluminium oxide film. It has been found also, that aluminium addition to iron reduces the sulphidation of pure iron by two orders of magnitude in pure sulphur vapour in the range of temperatures from 774 K to 973 K ⁸⁻¹¹ In view of the above facts, sulphidation studies of Fe-Al alloys in H_2/H_2S atmospheres at elevated temperatures is a matter of basic importance.

The sulphidation behaviour of metals and alloys is also a subject of academic interest, since it would be hoped that fundamental studies of this phenomena might ultimately lead to a more complete understanding of the process, for the development of better sulphidation resistant materials. The growth of multilayered scales (usually observed in CO/CO_2 and H_2/H_2S atmospheres) is not well understood because of the corrosion processes are generally complex owing to the oxide/sulphide solid solutions and multicomponent compounds, concurrent diffusion in the alloy, internal oxidation/sulphidation respectively. There is also a lack of fundamental data concerning metal-sulphur and the binary alloy-sulphur systems in respect of sulphide defect structures, phase diagrams, diffusion data.

Materials considered for application in the high temperature corrosive gaseous environment must possess good structural integrity and inherrent resistance to the corrosive atmosphere. For the present investigation Fe-10wt% Al was chosen because of its good resistance to high temperature oxidation¹² as well as good room temperature mechanical properties¹³⁵.

In the following chapters, a general outline of the theory applicable to alloy sulphidation, a literature survey, experimental and analytical techniques will be discussed followed by a presentation and discussion of the results obtained in the present study.

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CHAPTER 2

PRINCIPLES OF SULPHIDATION OF METALS AND ALLOYS

2.1 INTRODUCTION:

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Elementary sulphur and its compounds constitute a major problem of corrosion in many essential branches of modern industry. Although sulphur and oxygen are the elements of the same group of the periodic table, environments containing sulphur or its compounds are generally more aggressive than oxygen environments. First, the degree of disorder of the crystal lattice of sulphides exceeds considerably the disorder of corresponding oxides, in consequence of which the mobility of reactants in sulphide scales is many times higher than in oxide scales. In addition, eutectic temperatures for metal-sulphide systems are considerably lower compared to the eutectic temperatures for corresponding oxide systems. Catastropic corrosion, caused by the formation of liquid corrosion product, appears therefore in sulphur or H_2S environments at lower temperatures than in oxygen atmospheres. Also the high dissociation pressures of sulphides compared to oxides lead to a high partial pressure of sulphur at the sulphide-core interface which favour rapid intergranular corrosion.

Table 2.1 shows the melting point of several sulphides and sulphide eutectics¹³. Nickel for example, exhibiting the greatest oxidation resistance among the iron group, has at the same time the lowest sulphur resistance¹⁴, which is a consequence of the lowest eutectic point in the Me-Mes system among these metals (Table 2.1). A reverse situation exists in the case of refractory metals. Molybdenum and tungsten are

Chemical	Melting,	Sulphide	Melting
Compound	Point K	Mixtures & Eutectics	Point K
La2S3	2372	Mn0-MnS	1673
Ce ₂ S ₃	2273	`	
ThS2	2198	FeS-MnS	1454
ZnS	2073		
CdS	2023	Fe0-FeS	1213
MnS	1818	Fe-FeS	1258
HgS	1823	· •	000
FeS .	1470	3 ⁵ 2	908
MoS	1458	co-co ₄ s ₃	1153
CuS	1403		4
PbS	1385		
CoS	1373		
A1 ₂ S ₃	1373		
sis ₂	1373		
Na ₂ S	1251		
Nis ·	1083		
Ni ₃ S ₂	1060		
BiS .	948		
Sb ₂ S ₃	823 ·		

Melting point of some sulphides and sulphide eutectics

TABLE 2.1

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rapidly corroded in oxygen atmosphere, whereas in sulphur environment, even above 1373 K they exhibit scaling resistance properties¹³. Therefore, the reaction kinetics in both of these processes differ in magnitude and in the nature of rate controlling steps which are different in high temperature oxidation and sulphidation reactions.

In this chapter, the theories of oxidation and the general observations in the metal-sulphur system have been outlined. For a detailed aspect of oxidation and a more comprehensive review relating to specific metal-sulphur systems written by Strafforod¹⁵, the reader is refered to many standard works^{13,16-21} and recent reviews^{22,23}.

2.2 THERMODYNAMICS OF SULPHIDATION:

A consideration of the elementary thermodynamic principles provide an initial guideline to establish the likelihood of forming a sulphide from a metal in a given sulphidizing environment (elemental sulphur or \dot{H}_2S).

Where $\mathrm{H}_{2}\mathrm{S}$ is the principal species, the reaction would be of the type

$$M + H_2 S = MS + H_2$$
 (2.1)

The driving force for the above reaction is the free energy of this reaction ΔG , which can be expressed in terms of the standard free energy of this reaction and the activities of the reactants and products.

$$\Delta G = \Delta G^{0} + RT \ln \frac{a_{MS} p_{H_{2}}}{a_{M} p_{H_{2}}S}$$
(2.2)

where ΔG = free energy of the reaction (2.1)

 ΔG^{0} = standard free energy of the reaction (2.1)

R = gas constant

If ΔG is negative, then the reaction can be assumed to occur spontaneously.

The standard free energy values of the reaction of type (2.1) are generally not reported in the literature. Therefore the standard free energy for reaction (2.1) can be obtained by adding the ΔG^{O} of two following reactions,

$$M + 1/2 S_2 = MS$$
(2.3)

$$H_2S = H_2 + 1/2 S_2$$
 (2.4)

since the free energy is independent of the reaction path. References (15) and (24) describe the standard free energy versus temperature diagrams for the formation of various sulphides.

2.3 KINETICS OF SULPHIDATION:

Oxidation of different metals generally follow different kinds of rate laws. The oxidation product eventually covers the metal surface completely so that subsequent reaction will be controlled by the physicochemical properties of the oxide scale. Table 2.2 summarizes the integrated form of rate laws. However, during sulphidation of pure metals under isothermal conditions, three kinds of rate laws are generally observed (linear, parabolic and mixed parabolic).

TABLE 2-2

Integrated Forms of Rate Law

Linear	$\frac{\Delta W}{A} = k_{\ell} t + C_{\ell}$
Parabolic	$\left(\frac{\Delta W}{A}\right)^2 = k_p t + C_p$
Mixed parabolic or	
General Paraboic 🏅	$\left(\frac{\Delta W}{A}\right)^2 + \frac{\Delta W}{A} k_{\ell} = k_{\rm p} t + C_{\rm Mp}$
Cubic	$\left(\frac{\Delta W}{A}\right)^3 = k_c t + C_c$
Logarithmic	$\frac{\Delta W}{A} = k_{ln} \ln(t + t_0) + C_{l}$
Inverse Logarithmic	$\left(\frac{\Delta W}{A}\right)^{-1} = C_{i\ell} - k_{i\ell} \log t$
(AW) is the second state of	

where $\left(\frac{\Delta W}{\Lambda}\right)$ is the weight change per unit area of the specimen.

The sulphidation of a pure metal takes place in different stages. These stages are described individually and are in general applicable to metal oxidation and sulphidation.

2.3.1 Adsorption of gas molecules

The adsorption of gas on a solid surface is the accumulation of gas molecules on the surface. In the reaction between a metal and a gas, this adsorption is a very initial process. On an average there are about 10^{15} adsorption sites per square cm of a clean metal surface. From kinetic theory of gases, it may be estimated that if all the molecules that impinge on a clean metal surface are adsorbed, a monolayer of adsorbed gas will be formed in about 2 seconds at a pressure of 10^{-9} atmosphere and room temperature. Therefore diffusion in the gas phase is not rate controlling.

The adsorption process results in a decrease of the surface free energy. The reactive gas molecule initially adsorbed on the surface forms a Vander Waals (physical adsorption) type of bond. The physical adsorption of molecules generally proceeds without any activation energy (like liquefaction) and occurs as fast as molecules impinge on the surface. The next step is the formation of a chemical bond between the adsorbed species and the surface atoms. In this step (chemisorption), the reaction may proceed slowly involving an activation energy (activated adsorption) and eventually an oxide nucleus is formed. In contrast to physical adsorption, chemisorption may at this stage control the reaction kinetics. Chemisorption is dependent on crystallographic orientation, ledges and point defects in the surface etc. and is supposed to predominate at "active" sites on the surface. However, the work of Germer and MacRae²⁵ and that of Ramasubramanian²⁶ have shown that the initial oxide forms at random positions on the surface after the surface had become fully covered with chemisorbed oxygen.

2.3.2 Nucleation and growth of oxide Particles

The initial oxide formation on the surface of a pure metal generally appears at random sites as isolated oxide nuclei. The nature of the nucleation sites is still a matter of conjecture, but they may possibly constitute surface imperfections, impurity atoms, grain boundries etc. The nucleation of NiO and its orientation on Ni surface has been found to occur preferentially on the (111) and (100) planes of Ni²⁷. After the formation of random oxide nuclei, the oxidation proceeds through a growth of individual crystallites until the whole surface is covered with oxide.

Evans²⁸ has considered oxidation processes involving lateral growth of three dimensional oxide crystals on the surface. For such

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lateral growth, the fraction f of the total surface area covered at time t is given by

$$f = [1 - exp(-kt^{n})]$$
 (2.5)

where n is given by the nucleation rate. If nuclei appear simultaneously and the density of nuclei remains constant, n = 2; if the nucleation rate is constant, n = 3. If nuclei grow simultaneously at a linear rate normal to the surface, by a rate controlling phase boundry process for example, the reaction rate will initially increase and eventually become linear when the surface is completely covered. Alternatively, if the oxide growth normal to the surface is parabolic (diffusion controlled for example), the oxidation rate will initially increase and eventually decrease according to a parabolic rate. The latter type of kinetics is described by a sigmoidal curve and has been observed in the sulphidation of Ni-13a/oAl alloy²⁹.

2.3.3 Oxide Whiskers and Platelet Formation

Oxide crystals have been observed in numerous gas-metal reactions to grow in the shape of whiskers, columnar crystals, blades and platelets $^{30-35}$, in addition to the growth of oxide nuclei and crystallites in the form of mounds and polyhedra. Such growth has never been found to occur during the initial stage of oxidation but is perhaps associated with oxide films or scales. Oxide whiskers are single crystals. Example of such whisker growth has been observed by Gulbransen and Copan³⁵ in the oxidation of iron.

The growth and the shape of the oxide crystals are functions of temperature, time and atmospheric composition. In the oxidation of iron in $H_20 + 0_2$ mixture at 400°C whiskers were observed during the first

few hours of reaction and after 14 hours, whiskers were absent. The presence of water vapour was found to have a critical effect on the shape and size of a crystal. Gulbransen et al.³⁴ have suggested that the metal structure itself determines the localized crystal growth, but it is more widely believed that the whiskers have their nucleation sites and origin in the oxide base film^{30,31}. It has been found that when a metal forms more than one stable oxide during oxidation, whiskers always consist of the highest oxide. This suggests that whiskers are not in direct contact with the metal.

The amount of oxide contained in whiskers and platelets represents a minor part of the total surface oxide. Although such crystal growth greatly increases the total surface area of the specimen, there is no unequivocal evidence that such crystals have any marked effect on the reaction behaviour. At this stage the total reaction rate appears to be governed by the growth of the base film, and the whisker growth is probably a result of secondary effects and changes in the oxide film. Fig. 2.0 shows some typical shapes of wustite whiskers obtained in CO_2/CO atmosphere at high temperatures.

2.3.4 Scale Formation

Oxide films greater than 10,000Å in thickness are assumed to be electrically neutral when formed rapidly at high temperatures and after extended periods of time at intermediate temperatures. In most cases, scales exhibit parabolic growth behaviour. Other growth relationships like linear, asymptotic and logarithmic are also observed depending on the type of rate control and occurrence of additional processes such as spalling of oxide film and a short circuit diffusion of reactants in the oxide films.

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(a) needle-like whisker formed at 1243 K for 2 hours,

(b) prism-like whisker formed at 1123 K for 18 hours,

(c) ribbon-like whisker formed at 1273 K for 1 hour,

(d) pagoda-like whisker formed at 1123 K for 48 hours

- Fig. 2.0 .

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For the growth of thick oxide films, Wagner³⁶ has formulated a quantitative theory for the parabolic growth which has since been tested in many systems and by several investigators. He postulated that the diffusing species in the oxide scales are ions and electrons which migrate independently. The prerequisite for an ionic species to be mobile is that its sublattices contain point defects such as interstitial ions and vacancies. Reactions at the oxide-gas and oxide-metal interfaces are considered to be sufficiently rapid for local equilibrium to be established at these interfaces. Wagner defined a rational reaction rate constant, $\boldsymbol{k}_{r},$ by the equation

$$\frac{dx}{dt} = V_{eq} \cdot \frac{k_r}{x}$$
(2.6)

where

 $\frac{dx}{dt}$ = rate of thickening of the oxide scale

t = time $V_{eq} = Equivalent volume of the oxide.$

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The expression for the rate constant k_r involving diffusion coefficient is given by _(s)

$$k_{r} = \varepsilon_{i} \begin{cases} a_{X}^{T} (D_{MZ_{X}}^{T} + D_{X}) d \ln a_{X} \\ a_{X}^{(m)} \end{cases}$$
(2.7)

or

$$c_r = C_i \int_{a_M}^{a_M} (D_M + \frac{Z_X}{Z_M}) dlna_M$$
(2.8)

where $C_i = Z_M C_M = Z_X C_X$ is the concentration of metal or non-metal ions in the oxide in equivalents per cubic centimeter, a_x and a_M are the thermodynamic activities of the nonmetal, and metal respectively. D_{M} and D_{χ} are the self-diffusion coefficients of the metal and non-metal respectively. The superscripts (m) and (s) refer to the oxide-metal

and oxide-gas interfaces respectively.

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In Wagner's parabolic oxidation theory it is assumed that the oxide is homogenous and does not contain structural irregularities such as pores, grain boundries or dislocations. Investigations on oxide layers by electron microscopy, X^{\downarrow} -ray diffraction techniques and studies of nucleation of oxide on metal surfaces show that these assumptions may often be an over simplification. Smeltzer et al.³⁷ have proposed a theory to describe the non-parabolic oxidation kinetics of titanium, hafnium and zirconium. In this theory, lattice diffusion and diffusion along low resistance paths, which decrease in density with time, were assumed to occur simultaneously. Irving³⁸ proposed a model for nonparabolic oxidation based upon a combination of grain boundry diffusion and lattice diffusion. Perrow, Smeltzer and Embury³⁹ have employed the above concepts based upon short-circuit diffusion of reactants to explain the non-parabolic oxidation kinetics of nickel. In their analysis the contribution of grain boundry diffusion to the effective diffusion coeffi- ~ cient, D_{off} , was weighted according to the grain size.

It has been shown by Fishbeck⁴⁰ that oxidation can occur by phase boundry control at the oxide/gas interface when experimental conditions satisfy the relation that diffusion of reactants through the scale is much more rapid than the surface reaction steps. Petit et al.^{41,42} and Smeltzer^{43,44} have shown that this condition applies to the oxidation of iron in CO/CO₂ atmospheres at high temepratures. Smeltzer has obtained a functional dependence of the linear reaction rate constant on the partial pressure of CO₂ in the atmosphere for iron oxidation and applied this mechanism to the oxidation of Fe-Ni alloys in CO₂/CO atmospheres.

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A simplified approach to one such case of oxidation of a metal or an alloy in CO_2/CO atmosphere is outlined below.

For a reaction of type

$$M_{\text{solid}} + CO_2(g) = MO_{\text{solid}} + CO_{\text{gas}}$$
(2.9)

the steps involved can be written as

$$s + co_2(g) \xrightarrow{k_1} co(g) + o_{ads}$$
 (2.10)

$$0_{ads} \xrightarrow{k_2} 0_{inc} + S$$
 (2.11)

$$CO_2(g) \longrightarrow CO(g) + O_{inc}$$
 (2.12)

where S represents a vacant surface site and 0_{ads} represents chemisorbed oxygen and 0_{inc} represents oxygen incorporated in the oxide MO. Under the assumption that number of vacant surface sites is constant, a detailed mass and surface site balance predicts a simple linear relation between the linear oxidation constant k_{g} and the partial pressure of $C0_{2}$ in the ambient i.e.

$$k_{g} = A(P_{CO_{2}} - P_{CO_{2}}^{*})$$
 (2.13)

where A is a constant, whose magnitude depends on the forward and backward rate constants k_1 , k_1' and k_2 , k_2' . $P_{CO_2}^*$ is the partial pressure of CO_2 corresponding to the dissociation pressure of the oxide. Equivalent expressions have been derived by Kobayaski⁴⁶ and Turkdogan, et al.⁴⁷.

Linear kinetics will also be observed if diffusion through a barrier film of constant thickness is the rate determining process. If

a compact scale becomes converted into a porous scale during the sulphidation process, and the porous scale grows at a rate equal to the rate of conversion of compact to porous scale, paralinear kinetics will result. Also a transition from linear to parabolic kinetics occurs as a scale thickens and transport process becomes the rate controlling step.⁴⁵

The initial sulphidation of steel has been studied in pure H_2S-H_2 atmosphere⁴⁸. The data were analyzed by the graphic-kinetic technique of Fishbeck⁴⁹ and Wagner⁵⁰. According to this method, the corrosion reaction is assumed to proceed by two consecutive reaction steps: a linear interface reaction, followed by a diffusion through the scale.

Each of these reaction steps has its own resistivity defined as $1/k_1$ for the interface reaction where k_1 is a linear reaction constant, and as y/k_2 for the diffusion step, where k_2 is the parabolic rate constant, and y is the thickness of the reaction product scale through which diffusion occurs. The total reaction rate is then given by

$$\frac{dy}{dt} = \frac{C}{\frac{1}{k_1} + \frac{y}{k_2}}$$
(2.14)

where C is a constant. Integrated and rearranged, this becomes,

$$\frac{t}{y} = \frac{1}{Ck_1} + \frac{y}{2Ck_2}$$
(2.15)

Consequently, a plot of t/y vs. y should be linear, with 1/Ck₁ as the intercept, and 1/Ck₂ as the slope. Thus the initial kinetics may be explained in terms of two consecutive rate-limiting steps: a linear step, presumably limited by an interface reaction and a proabolic step, probably controlled by the rate of diffusion of the reactants through the sulphide layer.

2.4 OXIDATION OF ALLOYS:

Oxidation and sulphidation of alloys are more important in practical terms. It is necessary accordingly to develop at least a comprehensive understanding of the mechanisms involved in order to predict their reaction rates and to design alloys that are more oxidation or sulphidation resistant.

When an alloy AB is oxidized, the oxides may produce an oxidesolid solution or they may be completely or partly immiscible, producing simple or multiphase scales. In the case of partly or completely immiscible oxides a simple classification for a range of alloys AB in which A is the more noble and B is the less noble metal may be made and the following categories exist:

- (i) A relatively narrow composition range near pure A where A0 is produced almost exclusively, at least in the external scale.
- (ii) A relatively wide composition range near pure B where BO is produced almost exclusively.
- (iii) An intermediate composition range where both BO and AO are produced.

In composition ranges (i) and (ii), it is often possible to find doping of the major oxide by an element having a different valency, changing its defect structure and thereby its growth rate.

In the following a classification has been made⁵¹ on the different types of oxidation and scale morphologies.

Class I

a) As a minor element B oxidizes in the following manner:

(i) Internally producing BO particles in the matrix element A

(Fig. 2.1(a)). The ϕ xygen pressure in the atmosphere is less than the equilibrium dissociation pressure of AO.

- (ii) Exclusively externally, giving a single layer of BO above an alloy matrix depleted in B (Fig. 2.1(b)). The oxygen pressure in the atmosphere is again less than the dissociation pressure of AO. A special case however exists when both alloying elements can oxidize but the conditions permit B to be highly selectively oxidized e.g. Fe-Cr and Ni-Cr alloys rich in Cr produce essentially Cr₂0₃ scales, especially when oxidized at low partial pressures of oxygen.
 - (b) The element A is now the major element and oxidizes exclusively:
 - (i) leaving the non oxidizable metal B dispersed in AO, e.g.Cu-Au alloys rich in copper (Fig. 2.1(c)).
 - (ii) leaving the non-oxidizable metal B in a B-enriched zone beneath the AO scale e.g. Ni-Pt alloys (Fig. 2.1(d)). Fe-Cr alloys richer in Cr than those in Class I (a)(ii) fall in this category, as do certain Fe-Ni alloys Under appropriate conditions.

<u>Class II</u>

Both alloying elements oxidize simultäheously to give AO and BO, the oxygen pressure in the atmosphere being greater than the equilibrium dissociation pressure of both oxides.

- (a) AO and BO react to give a compound.
- (i) AO and BO give a single solid solution (A,B)O, e.g. Ni-CO alloys (Fig. 2.1(e)). In practice some internal (A,B)O richer in B than the surface scale is found in the alloy.

- (ii) A double oxide is formed, often as a spinel, which may give

 a complete surface layer of variable composition (Fig. 2.1(e))
 as for certain Fe-Cr alloys, or particles incorporated into
 a matrix of A0 if the reaction is incomplete, as for certain
 Ni-Cr alloys (Fig. 2.1(f)).
- (b) AO and BO are virtually insoluble in each other.
- (1) The less noble metal B is the minor component. An internal oxide BO lies beneath a mixed layer of AO and BO, e.g. certain @u-Ni, Cu-Zn, Cu-Al alloys and many other examples (Fig. 2.1(g)).
- (ii) The less noble metal is the major component so that no internal oxidation is now observed (Fig. 2.1(h)). In practice, the second phase BO in Figure (g) may not be present in the outer regions of the scale containing the oxide AO as the matrix phase. The outer regions may be oxidized to higher oxides, e.g. a CuO layer is found outside Cu₂O on Cu-Si alloys. Conditions may develop so that the internal oxide particles link up to give a complete healing layer of BO at the scale base.

2.4.1 Theories of Alloy Oxidation

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Most alloys are thermodynamically unstable in an oxidizing atmosphere. The level of oxidation rate is generally achieved by the formation of a scale which acts as a barrier to the reactants, and must have the following properties.

(a) The concentration of ionic defects which effect transport,
 must be low, and the oxides must remain nearly stoichiometric.

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b.









Figure 2.1 Schematic representation of modes of oxidation of alloy AB of variable composition where B is the less noble metal.

- (b) The vapourisation rate of the oxides forming the scale must be insignificant.
- (c) The scale must be practically free of pores, cracks or other paths for short circuit diffusion.

Concentration of point defects in a semi-conducting oxide or sulphide (AO or AS) is affected by the addition of oxide or sulphide of heterovalent metal (B_2O_3 or B_2S_3) respectively if it forms a solid solution. If dissolution of a metal (of higher valence) sulphide produces vacancy and holes, diffusivity of A will increase. However, if interstitial diffusion of metal ions is predominant, diffusivity of A will decrease, since the concentration of metal interstitials is reduced by the "Frenkel reaction".

If the defect is on the anion sublattice, production of anion interstitials will increase its diffusivity but will decrease the diffusivity of anions through anion vacancies. Similarly, predictions can be made for the addition of lower valent metal sulphides.

Thus one has a choice of alloying the parent metal to control the sulphidation. However, this has a limited use because conditions such as simultaneous sulphidation and good mutual solid solubility of the sulphides must be satisfied.

2.4.2 Selective Oxidation:

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Neglecting internal oxidation, mutual solubilities of oxides and assuming the formation of a p-type oxide BO in which B diffuses by a vacancy mechanism and electrons by postive holes, Wagner⁵² showed that the diffusion controlled growth of BO (Fig. 2.2) on the alloy AB (Fig. 2.1(b)) followed a parabolic rate lower than that on the pure



Figure 2.2 Wagner's⁵² oxidation models (a) Selective

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metal B as given by

$$\frac{k}{k_{o}} = \frac{p_{a}^{1/n} - p^{1/n}}{p_{a}^{1/n} - p_{o}^{1/n}}$$
(2.16)

here k and k_0 are the parabolic rate constants for BO growing on the alloy and pure B respectively, p_a is the pressure of oxygen, p_0 is the dissociation pressure of oxide in equilibrium with pure B. n is a constant, usually in the range of 3 to 6, which is determined by the defect equilibrium established locally within the oxide BO. Selective oxidation takes place in alloys for which the oxides of the alloying components show a great difference in stability for example iron alloys with Si, Al, Cr and copper alloys with beryllium or silicon. The occurrence of preferential oxidation is dependent not only on the alloying element but also on the composition of alloy, reaction atmosphere and temperature.

2.4.3 Competing Oxides

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In an alloy AB of which B is a solute element and if A is not totally unreactive, the kinetic processes may introduce A into the oxide phases, either as AO or as a mixed (AB)O oxide. If local depletion or enrichment effects could be avoided (as by very high interdiffusion in the alloy), the more stable oxide (taking account of the activities of A and B in the alloy) must eventually form in contact with the alloy owing to its ability to replenish the active element in the alloy phase as it oxidizes. In real cases, the metallic element that is oxidized at a faster rate is depleted from the alloy.
Wagner⁵³ examined the case in which BO has a lower dissociation pressure than AO, but AO grows faster on pure A, than BO grows on pure B. If diffusion in the alloy is much faster than in oxide BO; the stable BO must eventually come to occupy the alloy-oxide interface region. Alloys containing nearly equal A and B concentrations may form continuous layers of fast growing AO with particles of the slower growing BO embedded in it (Fig. 2.3(b)). BO may nucleate first, then becomes surrounded by AO (Fig. 2.3 (a)(b)); further formation of BO particles could be by a combination of direct reaction on the B-enriched alloy layer and by chemical displacement of the type:

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 $AO + B (alloy) \longrightarrow BO + A (alloy)$ (2.17)

Levin and Wagner⁵⁴ showed that this reaction continues even if the oxygen supply is cut off but annealing is continued. Price and Thomas⁵⁵ showed that selective oxidation of the reactive element could be ensured from the start by keeping the oxygen pressure so low that only BO can form.

BO particles formed as a dispersed phase can grow to give a continuous layer, otherwise they act as a blocking layer and restrict the active diffusion area through AO. The critical concentration for the formation of a continuous BO blocking layer lies near the A-rich side than the B-rich side (Fig. 2.3(d)).

Under the conditions of compact scale formation, three main cases for oxidation of alloy A-B can be considered:

(i) At low concentrations of B, only A oxide is formed and



ITA RTA AB alloy



b.

AB alloy

BO





d.

 $\xi_2 \gg \xi_2 - \xi_1$, $\xi_2 \gg W$

С.

Fig. 2.3 Model for the early stages of simultaneous growth of immiscible oxides AO and BO

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B will diffuse into the alloy from the alloy/oxide interface. As oxidation proceeds, the concentration of B in the alloy will increase, and formation of B oxide will take place when the concentration of B at the interface reaches the equilibrium concentration, X_B^* , for the mixture (alloy + A oxide + B oxide). The concentration of B in the bulk alloy X_B^i , is originally smaller than X_B^*

(11) For sufficiently high concentrations of B in the alloy $X_B^{"}$, only B oxide will be formed and A will diffuse into the alloy from the alloy/oxide interface. Formation of A oxide will take place only when the concentration of A at the interface reaches the critical concentration $X_A^{*} = 1 - X_B^{*}$ corresponding to the equilibrium (alloy + A oxide + B oxide).

(iiî) At concentrations ranging from X'_B to X''_B , both B and A oxide will be formed simultaneously. A possible reaction scheme for this case, assuming that cations are the mobile species and AO grows more rapidly than BO is shown in Fig. 2.3(c).

Based on the oxidation reaction controlled by diffusion processes, Wagner showed that the critical concentration $X_B^{"}$, above which only B oxide is formed is given by:

$$X''_{B} = \frac{V}{Z_{B}M_{O}} \left(-\frac{\pi k_{O}}{D_{AB}} \right)^{\frac{1}{2}}$$
(2.18)

where V is the molar volume of the alloy, Z_B is the valence of the B^{ZB} ion and k_0 is the parabolic growth rate constant of pure BO on metal B and M_0 is the atomic weight of oxygen. Rapp⁵⁶ has found a good agreement

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with the above theory in his investigation of Ag-In system whereas $Maak^{57}$ found large discrepancies for Cu-Be alloys at $850^{\circ}C$ in air, owing to sub-scaling and porosity growth in the cuprous oxide. The Cu₂O scale had an inner two-phase Cu₂O-BeO layer, along with internal BeO in the alloy phase.

2.4.4 Interface Stability

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Wagner⁵³ suggested that if interdiffusion in the alloy is fast compared with the rate at which B is consumed by scale growth $(D_{AB}^{>>k})$, B cannot become depleted in the alloy to any great extent. A ripple in the alloy-oxide interface develops rapidly at the advanced position shown in Fig. 2.4 and labelled (1), because the concentration gradient through the oxide is steeper at that point. Hence the ripple decays and a planar interface tends to be restored.

However, when diffusion in the alloy is much slower, the oxide growth rate k drops well below k_0 . Ripples in the alloy-oxide interface now grow more rapidly at deepest positions, labelled (2), because the steepest concentration gradient in the alloy exists at such points. So instability of the phanar interface is favoured by slow intermetallic diffusion and easy diffusion through the oxide. This is not subscaling as oxygen dissolution and diffusion through the alloy and discontinuous alloy phases are not involved. Lateral diffusion of B in the alloy spikes is contributes to the overall rate of oxide growth.

Wagner⁵⁸ found that the necessary condition for instability of a planar interface is given by



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Fig. 2.4 (a) Interface stability model of the wave, decays if diffusion through the oxide is slow and grows if diffusion through the alloy is slow.

(b) Fully developed alloy spikes.

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$$\frac{X_{B}}{1-X_{B}} = \frac{(D/V_{a})alloy}{(D^{*}/V_{o})oxide} < 1$$
(2.19)

where X_B is the mole fraction of B in the bulk alloy, D^* is the selfdiffusion coefficient of cation in the oxide at the alloy interface, and V_a and V_o are the respective molar volume of alloy and oxide phase and D is the interdiffusion coefficient in the alloy. The spikes are favoured by dilute B and small diffusivity in the alloy relative to the oxide. The more extended tips of the alloy spikes tend to spheroidize and may give rise to isolated particles embedded in the external scale as observed in the oxidation of Fe-Ni alloys by Wulf⁵⁹ et al. The above Wagner criterion is limited under the assumption that solubility of oxygen in the alloy and of the more noble alloy component in the oxide are negligible.

Coates and Kirkaldy 60 in their paper have analyzed the conditions for the stability of planar phase interface in isothermal ternary systems making no assumption about phase constitution with the alloyoxide interface as a special case. Later Whittle, et al.⁶¹ examined the effects of removing the two solubility restraints introduced by Wagner on the criterion for planar interface stability and demonstrated that oxygen dissolution into the alloy with or without diffusional interactions leads to a less restrictive criterion for planar interface stability.

2.4.5 Formation of Complex Oxides

Formation of a pure less-noble metal oxide as the protective layer on an alloy gives rise to the depletion of the alloy by oxidation and causes the system to have poor self-healing properties in the event of mechanical rupture of the protective film. Therefore, the situation where a complex oxide containing both alloying components forms on the alloy may be desirable. Diffusion rates in complex oxides are very often appreciably lower than in the single oxides^{19,62,63}.

The best known examples of complex oxides are 'spinels' consisting of compounds with the general formula $AO \cdot B_2 O_3$ where A-B is the alloy. Generally spinels have a cubic structure. Schmalzried and Wagner⁶⁴ have studied the lattice defect phenomenon in Fe-Ni spinels and demonstrated that the diffusion parameters are smaller than in single oxides. On Fe-Cr alloys FeCr₂O₄ spinel is formed, whilst NiCr₂O₄ is formed on Ni-Cr under certain experimental conditions. A review of the kinetics and mechanism of solid state spinels has been made by Armijo⁶⁵. Oxide, sulfide and iodide spinels are technologically important as computer memory cores and as protective scales formed during the oxidation of high temperature alloys. Non-cubic oxides and sulphides also form double oxides or double sulphides in a similar way to that of spinels.

2.4.6 Internal Oxidation

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Internal oxidation is a process whereby oxygen diffuses from the phase boundry of the alloy into its interior depending on the solubility and mobility of oxygen in the metals, to form oxide particles of the less noble metal within the alloy matrix. This is often termed subscale formation. For internal oxidation to occur, the diffusion rate of oxygen in the alloy must be much faster than the alloying element. If this among other conditions⁶⁶ are satisfied, an oxygen gradient is established in the alloy and the dissolved oxygen will react to form oxide of the less noble oxidizing element in a zone below the alloy surface. The internal oxide zone extends to a depth at which the concentration of dissolved oxygen becomes too low to support oxide formation.

Various features of this type of reaction behaviour have been described by Rhines, et al. 67,68 Darken⁶⁹, Bohm and Kahlweit⁷⁰, Wagner⁷¹ and Rapp^{56,72,73}. If diffusion control is maintained, the depth ξ , of the internal oxidation zone is a parabolic function of time, 't', and may be expressed as:

$$\xi = 2_{\rm Y} (D_0 t)^{\frac{1}{2}}$$
 (2.20)

while the velocity of the reaction front motion $d\xi/dt$ is given by:

$$\frac{d\xi}{dt} = \gamma \left(\frac{D_0}{t}\right)^{\frac{1}{2}}$$
(2.21)

where, $D_{\rm O}$ is the diffusivity of oxygen in the base metal and γ is a dimensionless parameter.

By the application of Fick's second law to the one-dimensional diffusion of oxygen in the base metal and assuming that previously precipitated particles do not interfere with this diffusion of oxygen,

$$\frac{\partial N}{\partial t} = D_0 \frac{\partial^2 N}{\partial x^2}$$
(2.22)

which may be solved for the following boundry conditions.

$$N_0 = N_0^{(s)}$$
 for x = 0, t = 0 (2.23)

$$N_0 = N_0$$
 for x > 5, t > 0 (2.24)

where N_0 is the mole fraction of oxygen in the base metal, $N_0^{(s)}$ is the mole fraction of oxygen at the external surface and x is the distance from the external surface. Analogously, the solution of the diffusion for the less noble alloying element B, namely

$$\frac{\partial N_B}{\partial t} = D_B \frac{\partial N_B}{\partial x^2}$$
(2.25)

is obtained with the boundry conditions

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$$N_{B} = N_{B}^{(0)}$$
 for x > 0, t = 0 (2.26)

$$N_{B} = 0$$
 for x < ξ , t > 0 (2.27)

where N_B is the mole fraction of B at x and $N_B^{(o)}$ is the mole fraction of B in the bulk alloy.

Wagner⁷¹ obtained the following solutions of equations (2.22) and (2.25) for the given boundry conditions as

$$N_{0} = N_{0}^{(s)} (1 - \frac{\operatorname{erf}[x/2(D_{0}t)^{\frac{1}{2}}]}{\operatorname{erf} y})$$
(2.28)

$$N_{B} = N_{B}^{(0)} (1 - \frac{\operatorname{erfc}[x/2(D_{B} \cdot t)^{2}]}{\operatorname{erf}_{\gamma\phi^{2}}})$$
(2.29)

where $\phi = D_0/D_B$, erf is the error function and erfc is complimentary error function and x is the distance from the outer surface of the alloy.

Since the flux of oxygen is equal to the flux of B atoms at the front of the internally oxidized zone:

$$\sum_{\epsilon \to 0} \lim_{\epsilon \to 0} \left[D_{0} \left(\frac{\partial N_{0}}{\partial x} \right)_{x} = \xi_{-\epsilon}^{2} - \nu D_{B} \left(\frac{\partial N_{B}}{\partial x} \right)_{x=\xi+\epsilon} \right]$$
(2.30)

where v is the number of oxygen ions per B ion in the oxide BOv.

It can then be shown that

$$\frac{N_{0}^{(s)}}{N_{B}^{(o)}} = \frac{\exp(\gamma^{2})\operatorname{erf}\gamma}{\phi^{\frac{1}{2}}\exp(\gamma^{2}\phi)\operatorname{erfc}(\gamma\phi^{\frac{1}{2}})}$$
(2.31)

from which γ can be determined.

The mass balance condition at the precipitation front of the internal oxidation zone can be used to find an expression for γ .

Two limiting cases exist. For $_{Y}$ << 1 and $_{Y}\phi^{\frac{1}{2}}$ >> 1 which is equivalent to

$$\frac{D_{B}}{D_{0}} << \frac{N(s)}{N_{B}^{(o)}} << 1, Equation (2.20; 2.21) may be$$

simplified to

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$$\xi \approx \left[\frac{2N_0^{(s)}D_0^{t}}{\sqrt{N_0^{(o)}}}\right]^{\frac{1}{2}}$$
(2.32)

Equation (2.32) is expected to hold under conditions where the movement of the precipitation front is completely determined by the diffusion of oxygen in the base metal. A shematic drawing of the concentration profiles under these conditions is given by Fig. 2.5(a).

In a second limiting case, if $\gamma << 1$ but $\gamma \phi^{\frac{1}{2}} << 1$, conditions which are equivalent to $\frac{N(s)}{N_{R}^{(0)}} << \frac{D_{B}}{D_{O}} << 1$, then

$$\xi = \frac{N_{0}^{(s)}}{\nu N_{B}^{0}} (\pi \phi D_{0} t)^{\frac{1}{2}}$$
(2.33)
$$\phi = \frac{D_{0}}{D_{B}}$$

where

In this case, the rate of outward diffusion of the alloying element, as well as the inward diffusion of oxygen are important in determining the kinetics of oxygen. A schematic representation of the concentration profiles under these conditions is given by Fig. 2.5(b).

Similar treatments for simultaneous scale formation and internal oxidation have been given by Rhines, et al.⁶⁸ and Maak⁵⁷ for parabolic growth of scale. Rapp⁷⁴ has treated the situation when scale growth is linear. Bohm and Kahlweit⁷⁰ have made a detailed analysis of oxide formation at the internal oxidation front. For the assumptions of diffusion control and a finite solubility product (K_{sp}) of the precipitated B0 oxide in the matrix, they derived the following equation for the number of precipitates per unit volume as a function of the distance from the surface x.

$$Z(x) = \beta \left(\frac{N^{(s)}}{x}\right)^{3}$$
 (2.34)

where β is a function of $\frac{D_o}{D_B}$, $N_B^{(o)}$, K_{sp} and $(N_o^*)(N_B^*)$ (the critical concentration product necessary to form a nucleus of critical size).

Wagner⁷⁵ utilized the solutions of diffusion equations for oxygen and the alloying element B to obtain an expression for the product $N_B N_0^{\nu}$ at any point. The gradient of this product can be related to the diffusion parameters in the alloy, the bulk alloy composition,



Fig. 2.5 (a) Concentration profiles for the exclusive internal oxidation of alloys.

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Fig. 2.5(b) Concentration profiles for the exclusive internal oxidation of alloys.

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composition of the alloy at the scale/alloy interface and the rate of thickening of the external scale. Wagner evaluated the following parameter in the alloy

$$g_{s} = \left(\frac{\partial \ln N_{B} \cdot N_{O}^{\circ}}{\partial x}\right)_{x} = x_{O}$$
(2.35)

where  $x_0$  is the co-ordinate of the scale-alloy interface. At the scalealloy interface, the alloy is saturated with respect to the oxide BO<sub>0</sub>, i.e. the product  $N_B N_0^{\nu}$  equals to the solubility product K at x =  $x_0$ . Thus one has the following cases:

- (a) If the value of  $g_s$  in equation is negative, the alloy next to the scale is undersaturated with respect to oxide 80, and no internal oxidation can occur.
- (b) If conversely  $g_s$  is positive, the alloy next to the scale is supersaturated with respect to oxide  $BO_v$  and internal oxidation may occur. Accordingly, the limiting condition

for possible internal oxidation is  $g_s > 0$ . Qualitatively, it is readily understood that internal oxidation is favoured by a flat oxygen concentration profile due to a high value of  $D_o$  and further by a steep positive gradient of  $N_B$  corresponding to a high value of the corrosion constant and low value of  $D_B$ . Wagner applied the criterion  $g_s > 0$  to the oxidation of Cu-Pd alloys and obtained a value of statisfied.

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#### 2.4.7. The Concept of Diffusion Path

In the oxidation or sulphidation of binary alloys, the independent concentrations of the solute element B and oxygen or sulphur are functions of the time and distance co-ordinates. However, if it can be shown that  $N_B$  and  $N_o$  are parametric solutions to the diffusion equations, i.e. for all values of time, t, and distance, x

$$N_{B} = N_{B}(\lambda) \qquad (2.36)$$

and 
$$N_0 = N_0(\lambda)$$
 (2.37)

where  $\lambda = \lambda(x,t)$  of the form  $x = \lambda t^{\frac{1}{2}}$  (2.38) A relation between N<sub>B</sub> and N<sub>o</sub> can be obtained which is independent of time and distance. That is,

$$N_{\rm B} = N_{\rm B}(N_{\rm o}) \tag{2.39}$$

This relation can be plotted on the pertinent A-B-O isotherm and the locus obtained is termed as the "VIRTUAL DIFFUSION PATH". This path is unique for the given terminal compositions and a given set of experimental conditions e.g., temperature, pressure, etc. The diffusion path concept is a very compact means of representing a ternary diffusion behaviour, especially in multiphase systems.

Kirkaldy and Brown<sup>76</sup> have developed seventeen useful theorems relating to the construction of diffusion paths in ternary multi-phase systems. The path obtained by plotting the relation (2.39) is defined as a virtual diffusion path because it is calculated on the assumption that all the interfaces are planar and stable and that there is no internal precipitation. Using the virtual diffusion path in conjunction with a knowledge of the thermodynamic and diffusion parameter of the system, o

one can find whether or not to expect the morphological breakdown or internal oxidation. To describe the actual configuration one must take into account such phenomena and solve the diffusion equation with a reformated set of boundry conditions. A relationship of the form Eqn. (2.39) then obtained will be referred to as the "actual diffusion path".

Figure 2.6 shows a ternary isothermal section of a hypothetical phase diagram (A-B-O) on which two possible diffusion paths and corresponding schematic microstructures are shown. Path (1) enters into a two phase region coinciding with a tie line showing a planar interface between the oxide and alloy. Path (2) crosses the tie lines in a two-phase region which implies the existence of a constitutionally super-saturated zone in front of the planar alloy/oxide interface. Relief of this super-saturation can occur through morphological breakdown of planar alloy/ oxide or sulphide interface and/or through internal precipitation of oxide within the alloy phase adjacent to the interface. The oxidation behaviour of Ni-Fe and Ni-Cr alloys have been interpreted by Dalvi and Coates using the diffusion path concept<sup>77</sup>.

It is worthwhile to mention the role of ternary diffusion interactions in producing internal oxidation. The criterion for defining the onset of internal oxidation is when conditions exist at the alloy side of the scale/alloy interface for the product of the metal and oxygen concentrations to exceed the solubility product of the binary oxide. By this means a minimum composition of the less noble metal in the binary alloy, above which internal oxidation will not occur, can be ascertained in terms of the metal and oxygen diffusivities in the alloy and the parabolic rate constant for external scale growth. Recently Smeltzer and Whittle<sup>78</sup>



VIRTUAL DIFFUSION PATH (2)

DIFFUSION PATH (1)

DIFFUSION PATH FOR METAL AND OXYGEN SUPER-IMPOSED ON THE A-B-O TERNARY ISOTHERM. PATH (I) CORRESPONDS TO THE FORMATION OF AN EXTERNAL BO SCALE AND PATH (2) CORRESPONDS TO THE CASE OF AN EXTERNAL SCALE FORM-ATION ACCOMPANIED BY INTERNAL OXIDATION. expanded this analysis by treating the binary alloy plus oxygen as a ternary system to include the effect of both metal and oxygen gradients in the alloy on the oxygen flux. The limiting bulk concentration of the solute oxidized selectively is ascertained in terms of metal and oxygen diffusivities in the alloy, the Wagner interaction coefficient between oxygen and solute and the parabolic rate constant of recession of the alloy/oxide front.

#### CHAPTER 3

#### LITERATURE REVIEW

### 3.1 INTRODUCTION:

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During the past 15 to 20 years there has been an increasing concern in the petroleum and petrochemical industries with the elevated temperature corrosion problems. Stainless steels are not immune to attack by  $H_2-H_2S$ , although the rate of scaling is generally low. Therefore alternative alloying elements like Al and Cr were added to plain carbon steel for petroleum refinery applications to resist high temperature  $H_2-H_2S$  attack. This chapter reviews the available data on ironaluminium, iron-sulphur and aluminium-sulphur systems which will be useful later in designing the experiments and to analyze the experimental results. A thorough quantitative interpretation of the experimental results of the Fe-Al-S system will only be possible if informations such as phase equilibria, activity coefficients, diffusion coefficients, ternary phase extents, interaction coefficients are available.

Sulphidation behaviour of pure iron and plain carbon steel has been investigated by numerous workers in  $H_2-H_2S$  atmospheres in a range of temperatures. Unfortunately not much information is available on the kinetic and thermodynamic properties of aluminium sulphidation resulting in a very limited knowledge on iron-aluminium sulphidation properties.

### 3.2 PROPERTIES OF Fe-A1 ALLOYS:

### 3.2.1 Crystal and Defect Structures

The phase diagram of Fe-Al (Fig. 3.1) is quite well known  $^{79,80}$ . Unlike other f.c.c. metals Al is a ferrite («) stabilizer, the atomic radious being 12% larger than iron. Miscibility with  $\alpha$ -Fe extends to more than 50 atomic percent aluminium. Within this b.c.c. region there are two superlattices with wide solubility limits. In AlFe ( $\beta_2$ ), Fe occupies the cube curners and Al the centres, the CSCl (B2) structure and AlFe<sub>3</sub> ( $\beta_1$ ) where Al occupies alternate cube centres, the BiF<sub>3</sub>(DO<sub>3</sub>) structure. Ordered AlFe<sub>3</sub> disorders at T  $\sim$  830 K while disordering temperature of FeAl is above 973 K as the alloy quenched from that temperature is ordered. Four intermediate phases are formed:  $\theta(A1_3Fe)$  has a very complex end-centered monoclinic structure,  $n(A1_5Fe_2)$  has an end-centered orthorhombic structure,  $\zeta(Al_2Fe)$  has a complex rhombohedral structure and  $\varepsilon$  forms pertectically at 1504 K which decomposes eutectoidally at about 1367 K. Solid solubility of Fe in Al based on lattice parameter measurement<sup>81</sup> has been found to be 0.052 wt% Fe at 928 K, 0.025% at 873 K, 0.006% at 773 K, and practically nil at 673-723 K. The lattice parameter of alloys in the range 0-50 at % Al and structural changes connected with order-disorder transformation were studied by Bradley<sup>82</sup> and et al.

# 3.2.2 <u>Directional Decomposition of e-FeA1</u>

The  $\varepsilon$ -FeAl phase which has been suggested to be b.c.c. with 16 atoms per unit cell is formed peritectically at about 1503 K. The FeAl-FeAl<sub>2</sub> eutectoid as most eutectoids has a lamellar morphology<sup>83</sup>.



Al-Fe Aluminum-Iron

Figure 3.1 Fe-Al phase diagram

The unit cell and the lattice parameter of FeAl<sub>2</sub> have been recently studied by Bastin et al. $^{84}$ 

#### 3.2.3 Thermodynamic Properties

The activity of Al and Fe in solid iron-aluminium alloys have been determined by various co-workers<sup>80,85,86,118</sup>. Heats of formation of solid Fe-Al alloys have been determined calorimetrically by Blitz and Haase<sup>87</sup>, Oelsen and Middel<sup>88</sup>, and Kubaschewski and Dench<sup>89</sup>. Radcliffe, Averbach and Cohen<sup>86</sup> have determined the thermodynamic properties of Fe-Al alloys between 1173 K and 1273 K by electromotive force measurements, using a molten chloride electrolyte. Fig. 3.2 represents a plot of the activity of Fe and Al vs. atom fraction of aluminium at 1173 K. The activity of aluminium in these alloys shows a strong negative deviation from Raoult's law at low concentrations but increases rapidly above 40 atomic percent aluminium. The thermodynamic properties of Fe-Al alloys have been reported in reference 80.

### 3.2.4 Diffusion Properties

The diffusion in the  $\alpha$ -phase of the Fe-Al system has been investigated by Sato<sup>115</sup>, Hirano et al.<sup>116</sup> and Nishida et al.<sup>117</sup>. Sato has studied the diffusion of Al into  $\alpha$ -iron at 1123 K and obtained the following results.

$$\tilde{D} = 8.2 \times 10^{-10} \text{ cm}^2/\text{sec.}$$
  
 $D_{A1} = 9.7 \times 10^{-10} \text{ cm}^2/\text{sec.}$   
 $D_{Fe} = 1.73 \times 10^{-10} \text{ cm}^2/\text{sec.}$ 

A detailed investigation on the interdiffusion in the  $\alpha$ -solid solution of the Fe-Al system has been made by Nishida et al.<sup>117</sup> in the range of



Figure 3.2 Fe and Al activities in Fe-Al system at  $1173^{\circ}$ K.

temperature 1073 K to 1373 K. The chemical  $\tilde{D}$  was found to be strongly dependent upon the Al concentration of the  $\alpha$ -range in the Fe-Al system and each  $\tilde{D}$  showed a peak value for a certain concentration of Al and these peaks corresponded to the order-disorder boundry of the alloy ( $\alpha$ ) (Fig. 3.3).

Figure 3.4 shows an Arrhenius plot of D vs. 1/T at critical compositions from which the activation energy Q was evaluated by Nishida and et al.<sup>117</sup>. This activation energy was found to vary with the aluminium concentration within the  $\alpha$ -phase field. Figure 3.5 represents the change in intrinsic diffusivities with temperature in the range of 35.0 to 42.8 at % Al.

Ryabov and et al.<sup>119</sup> reported the following approximate diffusion coefficients of  $Fe^{55}$  in Fe-Al compounds at 1223 K as determined by a thin-layer radioactive tracer technique:

| Fe in | FeA13              | D ~ | $1.25 \times 10^{-10}$  | <sup>)</sup> cm <sup>2</sup> /sec. |
|-------|--------------------|-----|-------------------------|------------------------------------|
|       | Fe2A15             | D ~ | $20 \times 10^{-10}$    | cm <sup>2</sup> /sec.              |
|       | FeA12              | D ~ | $0.63 \times 10^{-10}$  | <sup>)</sup> cm <sup>2</sup> /sec. |
|       | FeA1               | D ~ | 6.3 x 10 <sup>-10</sup> | cm <sup>2</sup> /sec.              |
|       | Fe <sub>3</sub> A1 | D ~ | $20 \times 10^{-10}$    | $cm^2/sec.$                        |

Recently Fellner<sup>120</sup> and et al. have measured the chemical diffusion coefficient D in the low and intermediate temperature range for 25 at % of Al-Fe.

In the range of temperature 473 to 673 K the D value was found to be



Figure 3.3 Variation in chemical diffusion coefficient (D) with Al concentration.







FIGURE 3.5 Change in intrinsic diffusivities  $(D_{Fe}, D_{11})$  with temperature in the range of 35.0 to 42.8 atomic % Al.

$$\tilde{D} = 6.518 \times 10^{-11} \exp^{(-2685 \text{ K/T})}$$

while at 673 K to 873 K

 $\tilde{D} = 6.567 \times 10^{-6} \exp^{-(10466 \text{ K/T})}$ 

3.3 PROPERTIES OF Fe-S SYSTEM:

### 3.3.1 Crystal and Defect Structure

The equilibrium diagram of Fe-S (Fig. 3.6) is well established<sup>79</sup>. The different phases existing in the Fe-S system and their crystal structures are tabulated in Table 3.1. Out of the various sulphides pyrrhotite (Hexagonal Fe<sub>1-x</sub>S) and pyrite (FeS<sub>2</sub>) are stable sulphide phases. The FeS<sub>2</sub> phase decomposes on heating at 1 atmospheric pressure and 970 K.

| TABL | E | 3. | 1 |
|------|---|----|---|
|------|---|----|---|

| Phase | Formula                          | Symmetry     |
|-------|----------------------------------|--------------|
| ζ     | FeS (Troilite)                   | Hexagonal    |
| ε     | Fe <sub>l-x</sub> S (Pyrrhotite) | Hexagonal    |
| ٤     | Fe <sub>l-x</sub> S (Pyrrhotite) | Monoclinic   |
| η     | FeS <sub>2</sub> (Pyrite)        | Cubic        |
|       | FeS <sub>2</sub> (Marcasite)     | Orthorhombic |

The troilite phase is stoichiometric, whereas the hexagonal pyrrhotite due to the presence of Fe vacancies (NiAS structure) exhibits nonstoichiometry ranging upto 25 atomic percent. Its





Figure 3.6 Phase diagram of Fe-S<sup>90</sup>.

nonstoichiometry or phase extent as a function of sulphur activity and temperature have been the subject of many recent investigations 91-95.

Iron sulphide is a metallic-type electrical conductor at temperature exceeding 411  $K^{96}$ , and the magnitude of the conductivity is practically independent of sulphur activity<sup>97</sup>. A point defect structure model for this solid based on the existence of interacting iron vacancies exhibiting strong repulsive forces has been advanced by Libowitz<sup>94</sup> to account for the dependence of non-stoichiometry on sulphur activity and temperature. It has been suggested also that different types of defects can exist near stoichiometry, namely Frenkel defects<sup>94</sup> or iron in sulphur sites<sup>95</sup>, but direct experimental evidence has not been found to the present for their existences<sup>98</sup>.

The phase diagram<sup>99</sup> for  $Fe_{1-x}^{S}$  is represented in Fig. (3.7), which shows the presence of various phases. The sulphur-rich boundry is moved to increasingly higher sulphur content as the temperature is increased. The dotted lines represent the variation of non-stoichiometry with temperature in iron sulphide at various sulphur <del>p</del>ressures.

#### 3.3.2 Thermodynamic Properties

The standard heat of formation of FeS has been obtained by numerous workers and summarized in Reference 100. The effect of composition on the standard heat of formation of  $Fe_{1-x}^{S}$  has been determined by Ariya et al.<sup>101</sup>. Gronvold et al.<sup>102</sup> determined the heat capacity of  $Fe_{1-x}^{S}$  and determined the standard entropies  $S_{298}^{o} = 14.415$  Cal/mole.K. Rosenqvist<sup>103</sup> has determined the free energy of formation of



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Figure 3.7 Fe-S phase diagram in the  $Fe_{1-\delta}^{S}$  S region<sup>99</sup>.

FeS between 773 K and 1261 K (eutectic temperature) by using a mixture of  $H_2S$  and  $H_2$ . A detailed calculation of these data are represented in Appendix I. The equilibrium diagram for Fe- $H_2S/H_2$  system in Fig. 3.8 is drawn by Rosenqvist<sup>103</sup>. The heavy curves correspond to different two-phase equilibria, and the slope of these curves correspond to the heat of the corresponding reaction eq.

$$Fe + H_2S = FeS + H_2$$
(3.1)

The fine curves correspond to constant compositions within a homogeneous phase, and the slope of these curves corresponds to the heat of solution of sulphur referred to hydrogen sulphide as reference, e.g.,

$$H_2S = S(in FeS) + H_2$$
 (3.2)

This type of diagram (Fig. 3.8) is quite useful in anticipating the reaction products at a given temperature and  $H_2S/H_2$  ratio.

The dissociation pressures of FeS over a range of temperature has been described by McCabe et al.<sup>108</sup> and recently by Nagamori et al.<sup>92</sup>. In the region of temperature from 1073 K to 1373 K, the pressure temperature relationship is given by<sup>92</sup>

$$\log P_{S_2} = -1.528 \times \frac{10^4}{1} + 5.48$$
 (3.3)

Figure 3.9 shows such relationship.

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The compound pyrite  $\text{FeS}_2$  can exist in one of two forms (marcasite at low temperature and pyrite at high temperature) with a transformation temperature of about 635 K.  $\text{FeS}_2$  decomposes around 980 K, yielding a monosulphide and elemental sulphur. The thermodynamic properties of FeS<sub>2</sub> have been reported in Reference 100. The standard free energy



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Figure 3.8 Plot of  $H_2S/H_2^{4}$  vs. 1/T for the system Fe-S<sup>103</sup>.



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of formation of FeS<sub>2</sub> is given by

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$$Fe(S) + S_2(g) \longrightarrow FeS_2(g)$$
(3.4)  
$$\Delta G^0 = -334,700 + 240.5 \text{ T } (+800)\text{J.Mole}^{-1}$$
(3.5)

## 3.3.3 Diffusion Properties

The diffusivity <sup>109</sup> and solubility <sup>110</sup> of sulphur in  $\alpha$ -Fe are well known and are given as follows

$$D_{S}(in \alpha - Fe) = 1.68 \times exp - \frac{48,900}{RT}$$
(3.6)  
wt%S<sub>max</sub>(in  $\alpha$ -Fe in equilibrium with FeS)  
= 7.85 x 10<sup>3</sup> x exp - \frac{28,900}{RT} (3.7)

Diffusional investigations on FeS are rather limited. Until 1974 iron and sulphur diffusivities were inferred from the scaling kinetics. Condit et al.<sup>99</sup> in 1974 using the radiotracer technique demonstrated that iron diffusion occurs by a vacancy mechanism and at rates dependent on the crystallographic direction,  $D_c = 1.8$  Da, (C+ prismatic direction, a + Basal direction). Furthermore they found that sulphur diffuses at rates several orders of magnitude lower than for iron (Table 3.2). Fryt and et al.<sup>111</sup>, recently determined the chemical diffusivity and nonstoichiometry as a function of sulphur pressure and temperature.

Using the interrupted sulfidation kinetics method originally derived by Rosenberg<sup>112</sup>, Fryt, et al.<sup>111</sup>, calculated the chemical diffusion coefficient and found it to be independent of the degree of nonstoichiometry at a given temperature. Its temperature dependence has been given as

$$\tilde{D}(\text{cm}/\text{sec.}) = (6.7 \pm 2.0) \times 10^{-2} \exp \frac{-30,900 \pm 600}{\text{RT}}$$
 (3.8)

Figure 3.10 shows the variation of chemical D with temperature. Using a point defect model involving a large repulsive interaction between iron vacancies to interpret their results, Fryt,<sup>111</sup> et al. obtained a correlation yielding an expression to evaluate the self diffusion coefficient of iron from chemical D, and obtained good agreement with the iron tracer diffusivity in the a-direction obtained by Condit, et al.<sup>99</sup>.

Recently Daniełewski<sup>113</sup> has studied the self-diffusion of Fe in Ferrous sulphide and using the tracer diffusivity results by Condit et al.<sup>99</sup>, the K<sub>p</sub> value was calculated and found to agree satisfactorily with the published results. However, at higher sulphur pressures experimental pressure dependence differs from that predicted by the calculated K<sub>p</sub> values and was attributed to the dependence of the diffusion coefficient on the iron sulphide crystal orientation<sup>114</sup>.

# 3.3.4 Kinetics and Mechanism of Fe Sulphidation

The kinetics of iron sulphidation have been studied by various authors<sup>121-129</sup>. The kinetics of Fe sulphidation<sup>123,124</sup> have been shown to be parabolic at sulphur pressures in the range  $1.31 \times 10^{-4}$  atm to  $6.58 \times 10^{-1}$  atmosphere for the range 673 K to 1073 K. Hauffe and Rohmel<sup>123</sup> and Meussner and Birchenall<sup>124</sup> considered that the growth of FeS occurred by an outward diffusion of Fe ions via cation vacancies in the FeS lattice. Most of the investigations have utilized pure sulphur vapour with P<sub>S2</sub> ranging from 10<sup>-4</sup> atmosphere to 1 atmosphere and parabolic kinetics have been observed at pressures as low as 10<sup>-8</sup> atm utilizing H<sub>2</sub>S-H<sub>2</sub><sup>130</sup> and

| Temperature<br><sup>O</sup> K | Iron<br>deficit x | D <sub>a</sub><br>a-axis | D <sub>c</sub><br>c-axis |  |  |
|-------------------------------|-------------------|--------------------------|--------------------------|--|--|
| 550                           | 0.003             | 9.6 x 10 <sup>-13</sup>  | 1.7 x 10 <sup>-12</sup>  |  |  |
| 570                           | 0.003             | $1.6 \times 10^{-12}$    | $6.1 \times 10^{-12}$    |  |  |
| 625                           | 0.003             | $1.2 \times 10^{-11}$    | $2.2 \times 10^{-11}$    |  |  |
| 723                           | 0.060             | 5.9 x 10 <sup>-10</sup>  | $1.2 \times 10^{-9}$     |  |  |
| 861                           | 0.066             | $6.3 \times 10^{-9}$     | - 8.3 × 10 <sup>-9</sup> |  |  |
| 970                           | 0.031             | $1.5 \times 10^{-8}$     | $4.3 \times 10^{-8}$     |  |  |
|                               |                   |                          |                          |  |  |

TABLE 3.2 (a) Iron self diffusion in  $Fe_{1-x}^{99}$  in cm<sup>2</sup>/sec.

|         |      | TABLE 3.2 (b) |    |                       |    |         |
|---------|------|---------------|----|-----------------------|----|---------|
| Sulphur | self | diffusion     | in | Fe1_x S <sup>99</sup> | in | cm/sec. |

| Temperature<br><sup>O</sup> K | Iron<br>deficit x | D <sub>a</sub><br>a-axis | D <sub>c</sub><br>c-axis                                                                                               |
|-------------------------------|-------------------|--------------------------|------------------------------------------------------------------------------------------------------------------------|
| 1168                          | 0.065             | $3.2 \times 10^{-12^*}$  | , <u>والمحالية من والمحالية من والمحالية في المحالية المحالية من المحالية من المحالية المحالية المحالية المحالية ا</u> |
| 1223                          | 0.065             | $6.4 \times 10^{-12^*}$  |                                                                                                                        |
| 1270                          | 0.052             | 2.2 x 10 <sup>-9</sup>   | $1.22 \times 10^{-9}$                                                                                                  |
| 1330                          | 0.098             | $8.4 \times 10^{-9}$     |                                                                                                                        |
|                               | *<br>\            |                          |                                                                                                                        |

\*Orientation not determined.




$COS-CO-CO_2$  mixtures<sup>128</sup>. However, there is a general agreement that scale growth involves iron migration by iron vacancies in Fe<sub>1-x</sub>S but the sulphur pressure dependence is unusual in that the parabolic rate constants show a P<sub>S2</sub><sup>1/n</sup> dependence where n ranges from 3 to 7.

The two general features that have prevented a rigorous comparison of measured and parabolic sulphidation rates were the dependence of the value of the iron self-diffusion coefficient on the directionality in NiAS structure of  $Fe_{1-x}^{99}$  and the fact that the scales exhibit a texture with the preferred growth direction dependent on sulphur pressure<sup>111,114</sup>. Recently Fryt, et al.<sup>131</sup> have systematically examined the sulphidation kinetics of pure iron over a wide range of sulphur activity,  $10^{-11} < P_s < 10^{-2}$  atm. They calculated the parabolic scaling constants in relation to the scale texture, the iron self diffusion coefficient and the defect structure of iron sulphide using Wagner equation for scaling by iron diffusion and the Libowitz point defect model involving a strong repulsive interaction between the iron vacancies. The expression yielding the parabolic rational rate constant is given by

$$K_{r} = \frac{\tilde{D}\Delta\delta}{\tilde{v}}$$
(3.9)

where  $\tilde{D} = (6.7 \pm 2.0) \times 10^{-2} \exp^{-(20,900 \pm 600)/RT}$ 

and 
$$\sigma = P_{s_2}^{\frac{1}{2}} \exp - \frac{\mu_{FeS} + qV_{Fe} + 4\xi V_{Fe}^{\delta(2-\delta)}}{RT}$$
 (3.10)

where  $\tilde{D}$  = chemical diffusion coefficient in Fe<sub>1-x</sub>S

 $\sigma$  = Non-stoichiometry in FeS

 $\mu_{\text{FeS}}^{=}$  Free energy of formation of stoichiometric FeS

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qV = Free energy of formation of Fe vacancies with respect fe to pure solid iron.

 $\xi V_{Fe}$  = Free energy of interaction between iron vacancies. The predicted values for these rate constant were found to be in good agreement with the experimental results obtained by Fryt, et al.<sup>131</sup>. They have also found that the sulphur pressure dependence of K<sub>r</sub> (vary-ing from P<sub>s</sub><sup>1/3</sup> to P<sub>s</sub><sup>1/7</sup>) is not accidental but directly arises from the predicted influence of sulphur pressure and temperature on stoi-chemctry caused by the strong repulsive interaction between iron vacancies. The activation energy for parabolic sulphidation varies with the sulphur pressure ranging from 16.5 and 2.0 KCal/mole at P<sub>s</sub> = 10<sup>-2</sup> and 10<sup>-8</sup> atm. respectively.

Sulphidation of pure Fe in  $H_2S/H_2$  atmospheres often leads to a duplex layer growth at temperatures less than 873 K. According to marker measurements it is suggested that sulphur can be supplied to the iron substrate by perforations resulting from dissociation of the inner part of the outer layer of iron sulphide<sup>132-134</sup>. Several kinetic equations involving the growth of a two-layer scale on iron in  $H_2S/H_2$  atmospheres have been described by Haycock<sup>135</sup> and Dravnicks et al.<sup>136</sup>. Haycock has described the growth of FeS in  $H_2S/H_2$  atmospheres to occur at a slower rate than in pure sulphur vapour because of an effective barrier by 'E' centers to the migration of metal ions. These 'E' centers are formed by the interaction of cation vacancies and hydrogen incorporated into the FeS lattice.

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Summary of Crystal Structures of  $\mathrm{Al}_{2}\mathrm{S}_{3}$ 

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|                                   |                           | •                                                              |                                                                                            |                                                                  |            |
|-----------------------------------|---------------------------|----------------------------------------------------------------|--------------------------------------------------------------------------------------------|------------------------------------------------------------------|------------|
| Description                       | Crystal System            | Density<br>(gms/cm <sup>3</sup> )                              | Lattice Parameters                                                                         | Comments                                                         | References |
| a- Al <sub>2</sub> S <sub>3</sub> | Hexagonal                 | $\rho_{\rm m}^{\rm A} = 2.33$<br>$\rho_{\rm m}^{\rm A} = 2.32$ | $a_{c}^{a} = 6.423$<br>$c_{c}^{c} = 17.83$<br>$c_{o}^{o}/a_{o}^{c} = 2.776$                | Stable at room<br>temp. and 1 atm<br>pressure                    | 136,137    |
| B- Al <sub>2</sub> S <sub>3</sub> | Hexagonal                 | p = 2.55<br>m = 2.5                                            | a = 3.579<br>$c^{0} = 5.829$<br>$c^{0/a} = 1.629$                                          | Stable in the<br>presence of Al4 <sup>C</sup> 3<br>1000 - 1100°C | 136,137    |
| r- Al <sub>2</sub> S <sub>3</sub> | Hexagonal<br>Rhombohedral | p = 2.37<br>m = 2.36<br>m                                      | a = 6.47<br>$C^{0} = 5.829$<br>$C^{0}/a_{0} = 2.669$<br>$a_{R} = 6.86$<br>$= 56^{0}16^{1}$ | Stable from<br>1000 - 1100 <sup>0</sup> C,<br>1 atm              | 137        |
| Tetragonal<br>defect spinnel      | Tetragonal                | ı                                                              | $a_0 = 7.026$<br>$C_0 = 29.819$<br>$C_0/a_0 = 4.244$                                       | Prepared at<br>2-65 Kbar<br>1000 - 1200 <sup>0</sup> C           | 140        |
| Cubic defect<br>spinnel           | Cubic                     | x = 2.71                                                       | a = 9.94<br>o                                                                              | Prepared at<br>40 Kbar<br>400 K                                  | 139        |
| Cubic defect<br>spinnel           | Cubic                     | x = 2.78<br>m = 2.80                                           | a = 9.93                                                                                   | 2% As substituted<br>for Al                                      | 138        |
| $*_{\rho_{\chi}}$ is the calculat | ed density from t         | he lattice p                                                   | arameter; $ ho_{\rm m}$ is the n                                                           | neasured density.                                                |            |

#### 3.4 PROPERTIES OF THE A1-S SYSTEM

#### 3.4.1 Crystal and Defect Structure

In the Al-S system, Hansen and Anderko have reported that AlS(S) and Al<sub>2</sub>S<sub>3</sub>(S) exist and Ficalora, et al. have identified AlS(g), Al<sub>2</sub>S<sub>2</sub>(g) and Al<sub>2</sub>S(g) in the vapour phase.

The structure of  $Al_2S_3$  has been investigated by Flahaut<sup>136,137</sup>, who reported three structural modifications, each of which is hexagonal. Later studies showed that it can also have a cubic defect spinel structure when prepared with either 2% As substituted for  $Al^{138}$ , or when prepared at high temperature and pressure<sup>139</sup>. A tetragonal defect spinel structure has also been reported for synthesis at high temperature and pressure<sup>140</sup>. This structural in formation is collected in Table 3.3.

A hypothetical phase diagram of Al-S is given by Hansen, et al.<sup>79</sup> and is based on the cooling curve data and examination of sulfidation products of Al at various temperatures (Fig. 3.11).  $Al_2S_3$  melts at 1373 K. The solubility of sulphur in Al ranges from 1 atomic percent at 973 K to 9 atomic percent at 1273 K.

## 3.4.2 Thermodynamic Properties

The reported values of the heat of formation of  $Al_2S_3$  show wide divergence<sup>100</sup>. However, the value  $H_{298}^0 = -172.9$  KCal/mole of  $Al_2S_3$  or 115.26 KCal/mole of  $S_2$  has been chosen in the literature to be more accurate The standard entropy of formation of  $Al_2S_3$  has been reported to be  $(29.5 \pm 5)$  Cal.mole<sup>-1</sup>.K<sup>-1</sup>. The heat capacity of  $Al_2S_3$  in the range of 298 to 1300 K is reported to be<sup>100</sup>:

 $C_p = [24.42 + 8.62 \times 10^{-3} \text{T}] \text{ cal.mole}^{-1} \text{K}^{-1}$  (3.10)



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Figure 3.11 Al-S phase diagram (hypothetical).

AlS is extremely unstable and decomposes in air.  $Al_2S_3$ , being a salt of very weak base and weak acid, hydrolyses slowly in moist air, generating  $H_2S$  and  $Al(OH)_3$  or perhaps  $Al_2O_3 \cdot Al_2S_3 \cdot H_2O^{141}$ 

## 3.4.3 Diffusion Properties

The diffusion properties of the sulphide phases in Al-S system are not reported in the literature.

# 3.4.4 Sulphidation kinetics of pure aluminium are not reported in the literature.

#### 3.5 PROPERTIES OF THE Fe-Al-S SYSTEM

## 3.5.1 Crystal and Defect Structure

The existence of a ternary compound of composition  $\text{FeAl}_2S_4$ is reported in the literature by several authors <sup>137,142,143</sup>. Nishida and Narita<sup>143</sup> have reported its structure to be hexagonal with the lattice parameter as  $a_0 = 3.659 \pm 0.004$  Å and  $C_0 = 36.17 \pm 0.03$  Å and found a good agreement with the lattice parameters obtained by Flahaut<sup>137</sup>.

## 3.5.2 Thermodynamic Properties

The thermodynamic properties of Fe-Al-S system are not available in the literature.

#### 3.5.3 Diffusion Properties

Diffusion data in the Fe-Al-S system are not available in the literature.

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## 3.5.4 Sulphidation Properties

Strafford, et al.<sup>144</sup> have studied the sulphidation properties of Fe based alloys containing 5 wt% of Ni, Co, Cr or Al in sulphur vapour at 773 K. They observed approximately linear kinetics and the Fe-Al alloys exhibited a substantially lower reaction rate relative to pure Fe. In their subsequent work<sup>8</sup> they have reported the scaling behaviour of Fe-5 wt% Al in pure sulphur vapour in the rangé of temperature 773 to 973 K. The outer scale was found to be FeS and the inner scale a mixture of FeS and  $Al_2S_3$ .

High temperature corrosion behaviour of Fe-Al alloys have also been investigated by Nishida, et al. 10,145, in 1 atm sulphur vapour in the temperature range 773 to 1173 K. The reaction rate constant (in mm·hr<sup>-1</sup>/<sub>2</sub>) was found to decrease continuously at various temperatures with the increase in Al content. The platinum wire  $40\mu\phi$  welded on to the surface at first was found at the outer/inner scale interface after corrosion. Most of the aluminium was found to be concentrated in the inner layer.

Subsequent work by Nishida, et al.  $^{145}$  on Fe-2%C-A1 alloys (Al upto 25 wt%) has shown an increase in corrosion rate upon small additions of A1 to Fe-2 wt%C. However, additions of aluminium more than 7 to 8 wt% increased the corrosion resistance of the alloy markedly.

#### 3.6 SUMMARY:

Sulphidation behaviour of pure Fe, both in sulphur and  $H_2^{S/H}_2$ atmospheres are well established with a diffusion controlled growth of iron sulphide. However the sulphidation behaviour of pure aluminium is not reported in the literature. A limited work on binary Fe-Al ' alloys show their parabolic sulphidation behaviour in sulphur vapour and a linear behaviour in early stages of sulphidation in  $H_2^S + H_2$ , atmospheres. However, the established beneficial effect of Al to the corrosion resistance of Fe in sulphur and  $H_2^S$  bearing atmospheres demands a complete investigation. A thorough literature search does not reveal any useful data on the defect structure and diffusion properties of the sulphides in the Al-S and Fe-Al-S systems which can be used to rationalize the observations and experimental results to be obtained in this investigation.

For practical purposes, high temperature alloys like Ni-Al and Ni-Cr are generally unsuitable in sulphur and  $H_2S$  atmospheres because of liquid sulphide formation at 973 K. Therefore, Fe based alloys containing Cr and Al are currently being developed <sup>146-152</sup>.

## CHAPTER 4

## EXPERIMENTAL TECHNIQUES AND PROCEDURE

## 4.1 <u>INTRODUCTION</u>:

In this chapter, descriptions of sample preparation, sulphidation apparatus, procedure and various metallographic and analytical techniques are made.

## 4.1.1 Specimen Preparation

Alloys of Fe-Al were made by melting weighed quantities of Fe (99.996% purity) and Al (99.99% purity) with a nominal composition of 10wt% and 15wt% aluminium in an argon arc furnace. Alloys were remelted several times for a homogenous composition and finally cast into small ingots (of size 6 cm in length and approximately 1 cm in diameter) and cooled in the furnace. The exact chemical analysis of these two alloys are given in Table 4.1.

These alloy ingots were annealed at 1473 K for 12 hours in a furnace with a continuous argon flowing system. To remove oxygen from the incoming argon and furnace atmosphere, zirconium chips were introduced at the entrance of the horizontal furnace tube. From the ingot, specimens were cut into small buttons of approximately 1.5 mm thick and 1 cm in diameter, using a fast speed diamond cutter. A hole of 1 mm diameter was drilled into each specimen for suspension purpose. The samples were then polished on all sides through a series of silicon carbide papers (220,320,400 and 600 grit) using water as a lubricant. A vacuum anneal (at  $900^{\circ}$ C for 18

hours) was then given by placing the samples in an alumina tube, sealed in a quartz tube under vacuum to relieve the internal stresses introduced during cutting and polishing. Final polishing was carried out on napless cloths impregnated with 6  $\mu$ m and then 1  $\mu$ m diamond paste with kerosene as the lubricant. The samples were finally washed with petroleum ether and methyl alchohol and then dried with acetone. Sample dimensions were accurately measured by using a micrometer and the surface area was calculated by using a magnified image of the sample. The specimens were then stored in <sup>a</sup> dessicator under vacuum.

## TABLE 4.1

Chemical Analysis of Fe-Al Alloys

| Norminal Composition | · · · | Actual Comp<br>wt% Al | osition<br>Atomic % Al | <u> </u> |
|----------------------|-------|-----------------------|------------------------|----------|
| Fe - 10 wt% A1       |       | 9.71*                 | 18.2                   | 3        |
| Fe - 15 wt% Al       | · · · | 13.43*                | 24.3                   | . •      |
| : `                  | s 4   | •                     | •                      | •        |

<sup>\*</sup>Average of two readings

4.2 SULPHIDATION APPARATUS:

The apparatus used for the sulphidation experiment is shown schematically in Fig. 4.1. This assembly is used to measure the weight gain in which the elongation of a McBain balance is followed by means of a cathetometer. This assembly is similar to the one described by Morris and Smeltzer<sup>153</sup> and modified by Romeo, Smeltzer and Kirkaldy<sup>154</sup>. The details of this setup has been described elscwhere<sup>155</sup>.

Figure 4.1 Kinetic Assembly

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Absorption flask filled with caustic soda. Molybdenum wire 23. Exhaust channel Spring chamber 20. Platinum wire 22. Thermocouple 19. Cathetometer Specimen 21. Furnace Spring ,14. Target Motor 17. 24. 13. 15. 16. 18. Inlet for H<sub>2</sub>S and H<sub>2</sub>S + H<sub>2</sub> mixtures  $H_2$  +  $H_2S$  inlet to the Matheson rotameter: Mercury manometer 0. By-pass channel Helium channel Oxygeh inlet Inlet for H<sub>2</sub> Mullite tube Mtxing Bulb Văcium punp Gas sampler



A mixture of hydrogensulphide and hydrogen gas was used to control the partial pressure of sulphur in the furnace chamber. The furnace chamber consists of a 73 cm x 6 cm dia mullite tube (12) surrounded by a kanthal element furnace (21). The temperature of the furnace was controlled to an accuracy of  $\pm 3^{\circ}$ C by a Honeywell temperature controller using a chromel-alumel thermocouple (22). This thermocouple was calibrated against a standard chromel-alumel thermocouple by lowering it in steps at the center of the furnace to locate the hot zone. A stream of helium gas was flown into the reaction chamber from the bottom, in order to simulate the conditions during the actual experiment.

The McBain balance consists of a winch with positioning forks, a spring (18) connected to the winch by a molybdenum wire (16) and a target (14) attached to the bottom of the spring. The sample (13) was suspended from the target by means of a platinum wire. An electric drive (17) was connected to the winch to raise or lower the specimen. During the reaction, the extension of spring was followed through the target movement by a cathetometer (19). Helium gas was used for purging the upper portion of the reaction chamber, thus avoiding condensation of sulphur in the spring chamber (15). The flow rate of helium was kept low as not to dilute the  $H_2S-H_2$  atmosphere and was controlled by a Matheson rotameter. The method of preparation of the Ni-span-C spring has been described elsewhere<sup>156</sup> and its composition is tabulated in Table 4.2(a). A similar material called "Elinvar extra" of composition listed in Table 4.2(b) is available with Hamilton-watch company, Pennsylvania and currently springs are being prepared from it for future purpose. The spring was calibrated with the help of small weights and the spring constant for various springs varied from

# <u>TABLE 4.2 (a)</u>

Material: Ni-Span-C

Composition in weight percent:

| Ni <sup>*</sup> | Cr . | Mn   | S    | Ti   | C    | A1   | Si   | CO | Fe   | Cu   |
|-----------------|------|------|------|------|------|------|------|----|------|------|
| 42.25           | 5.33 | 0.40 | 0.02 | 2.58 | 0.03 | 0.55 | 0.50 | -  | 48.8 | 0.05 |

\*Plus cobalt.

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# TABLE 4.2 (b)

Material: Elinvar-Extra

Composition in weight percent:

| Ni | Cr | Ti   | C    | · A1 | Si   | CO   | Fe   |
|----|----|------|------|------|------|------|------|
| 43 | 5  | 2.75 | 0.04 | 0.30 | 0.50 | 0.35 | 48.6 |

25 to 29.5 mgs/cm during the course of this entire work.

## 4.3 SULPHIDATION PROCEDURE:

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A prepared specimen was attached to the platinum wire (20) and then raised into the spring chamber (15) by means of the motor (17). After sealing the joints by high vacuum silicon grease, the furnace chamber was isolated from the gas mixing bulb and evacuated by means of the vacuum pump (6). Ultra high purity helium (composition listed in Table 4.3) was then introduced slowly through a rotameter for a short while to the spring and furnace chamber and again vacuum was drawn. This process was repeated several times in order to completely replace the existing trace of air by helium in the furnace. Next, for a required sulphur pressure calibrated flow rates (tosbe described later) of ultra high purity hydrogen (composition listed in Table 4.3) through a DEOXO catalyfic purifier and  $H_2^{S}$  or  $H_{2}S + H_{2}$  mixtures were passed through the mixing bulb (3) via channel (10) to the exhaust to achieve a flow stablization. Helium gas was then introduced into the furnace chamber via channel (8) and (14), allowed to leave the furnace through the exhaust channel (23). Once the required temperature in the furnace was achieved, the  $H_2S + H_2$  mixture was diverted through channel (11) into the furnace chamber and allowed to leave the furnace through the exhaust channel (23). The by-pass channel (10) was then closed. Subsequently a low flow rate of helium was maintained, such as not to dilute the atmosphere but to protect the spring and the motor from sulphur deposition and the highly corrosive  $H_{\rho}S$  gas. After equilibrating for twenty minutes the specimen was lowered to the hot zone of the furnace with the help of the motor and the extension of the spring was followed by a cathetometer through a target. The cathetometer readings were later converted to

## TABLE 4.3

I. Composition of ultra high purity Helium

Minimum purity - 99.998%

# Typical Analysis

| H <sub>2</sub>   | 0.1  | ppm  |
|------------------|------|------|
| CH <sub>4</sub>  | 0.0  | ppm  |
| H <sub>2</sub> 0 | 1.5  | ppm  |
| Neon             | 8.0  | ppm  |
| N <sub>2</sub>   | 5.0  | ppm  |
| 0 <sub>2</sub>   | 0.6  | ppm  |
| Ar .             | 0.05 | ppm  |
| co <sub>2</sub>  | 0.05 | ppng |

II. Composition of hydrogen (U.H.P.)

Purity - 99.99%

| °2                   | 1   | ppm by volume |
|----------------------|-----|---------------|
| co + co <sub>2</sub> | 1 - | ppm           |
| Hydrocarbons         | 0.8 | ppm           |
| Helium               | 50  | ppm           |
| Moisture             | 5   | ppm .         |

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III. Composition of  $H_2S$ 

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| Typical Analysi   | s in % |
|-------------------|--------|
| H <sub>2</sub> S  | 99,.7  |
| cs <sub>2</sub>   | 0.09   |
| co <sub>2</sub>   | 0.13   |
| Methyl mercaptan  | 0.02   |
| Carbonyl sulphide | 0.01   |
| \$0 <sub>2</sub>  | 0.05   |

weight gain from the calfbration curve of the spring. The spring constant was checked from the weight gain data and cathetometer readings.

## 4.4 CALCULATION OF SHIPHHR PRESSURE:

When hydrogen gas and  $H_2S$  gas are mixed at room temperature and that this mixture is heated to 1073 K to 1373 K, several gaseous species such as  $S_2, S_4, S_6, S_8$ , atomic S, HS form. Among these only the species  $S_2$  and HS will reach a substantial amount at temperatures 1073 K to 1373 K and  $P_{s_2}$  ranging from  $10^{-2}$  atmosphere to  $10^{-8}$  atmosphere<sup>104</sup>. Considering  $P_{H_2}^0 + P_{H_2S}^0 = 1$  atmosphere at room temperature and

$$H_2(g) + \frac{1}{2}S_2(g) = H_2S(g)$$
 (4.1)

Nagamori and et al.<sup>92</sup> have derived a relation between  $P_{H_2S}$ ,  $P_{s_2}$  and  $K_1$  (the equilibrium constant for reaction 4.1) neglecting the species HS. The relation is given by

$$P_{H_2S} = \frac{2K_1 n_{s_2}^{3/2} + 2n_{s_2} (1 + n_{s_2})^{1/2} + K_1 n_{s_2}^{1/2}}{K_1 n_{s_2}^{1/2} + (1 + n_{s_2})^{1/2}}$$
(4.2)  

$$K_1 n_{s_2} = P_{s_2} / (1 - P_{s_2})$$
(4.3)

and

where  $n_{s_2}$  is the equilibrium mole number of  $s_2$  species at high temperature. The value of  $K_1$  can be calculated from the free energy data:

$$\Delta G^{O}_{(4.1)} = -RT \ln K_{1} = -21,580 + 11.805T \text{ cal/mole} \quad (4.4)$$
  

$$\ln K_{1} = \frac{21,580 - 11.805 T}{RT}$$
  

$$k_{1} = \exp(\frac{21,580 - 11.805 T}{RT}) \quad (4.5)$$

From equation (4.2) through (4.5), for a known value of  $K_1$  (at a specific temperature), the partial pressure of sulphur  $P_{s_2}$  was calculated for various

values of  $P_{H_2S}$  using a computer programme. At a particular temperature, P<sub>sp</sub> increases with increase in  $P_{H_2S}$ .

In the present sulphidation set-up, calibration of flow-rates were made by soap-bubble method for various gases (Helium, pure  $H_2$ ,  $H_2S + H_2$ mixtures of various proportions). The flow rate of gases were calibrated against the float height in the rotameter. A total flow rate of 750 c.c./min. was found to vary linearly with the rotameter readings in most of the cases. Hence, for a particular  $P_{s_2}$ , the corresponding  $P_{H_2S}$  was taken from the table (computed earlier) to calculate the flow rate of pure hydrogen and hydrogen sulphide or a  $H_2S$  and  $H_2$  mixture. For a low  $P_{s_2}$ , pure hydrogen was generally blended with  $H_2S + H_2$  mixture of a low  $H_2S$  content. From the rotameter calibrations, the flow rates of various gases were converted to rotameter readings.

Another method was used to check the validity of the above calculations. Since sulphur is produced from the dissociation of  $H_2S$  by the reaction

$$H_2 S = H_2 + \frac{1}{2} S_2$$
 (4.6)

where equilibrium constant K is given by

$$K = \frac{P_{S_2} P_{H_2}}{P_{H_2}S}$$
(4.7)

Knowing K = exp  $\left(\frac{-21,580 + 11.805 \text{ T}}{\text{RI}}\right)$  and the  $P_{\text{H}_2}/P_{\text{H}_2\text{S}}$  ratio,  $P_{\text{s}}$  was calculated. At a total flow rate of 750 c.c./min. the ratio of  $H_2^2/H_2^2$  flow rates corresponded to the ratio of  $P_{\text{H}_2}/P_{\text{H}_2\text{S}}$ .

#### 4.5 EXPERIMENTAL TECHNIQUES USED FOR ANALYZING THE SULPHIDATION PRODUCTS:

## 4.5.1 Optical Metallography

The sulphidized specimens were cold mounted vertically in epoxy resin within 25 mm outer diameter plastic rings. They were polished in cross-section, on various silicon carbide papers and finally on polishing cloth by 1 µm diamond paste with kerosene as the lubricant. The micro structure of specimens were examined and photographed using a Zeiss microscope, as this equipment gave the best resolution at high magnification. The external and subscale thicknesses on each specimen were measured with the help of a calibrated cross-wire eye-piece attached to the microscope.

## 4.5.2 Scanning Electron Metallography

To study the morphological features of the sulphide scale a Cambridge scanning electron microscope was used. The samples were mounted in the cold epoxy resin and coated with carbon by vapour deposition to avoid electrical charge build-up and to allow electron conduction smoothly. Some of the samples were fractured in liquid nitrogen and examined in the SEM after carbon coating. An energy dispersive X-ray analyzer attached to the SEM was used to identify the elements present and their distribution in various parts of the scale. The results obtained from the EDAX were purely qualitative in nature.

## 4.5.3 X-Ray Analysis

The X-ray analysis of the constituents of the sulphidation product was carried out using a Philips X-ray diffractometer. Samples from various part of the scale were crushed into powder in a mortor and mounted on a glass slide by compacting it under just sufficient pressure to cause cohesion

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and smoothing off the surface. Some specimens with a very thin sulphide or oxide on it were directly mounted on the glass slide. A voltage of 30KV and 20 mA and CuK $\alpha$  radiation were used for this purpose. The results (Relative peak intensity and diffraction angle 20) obtained from the samples were compared with the standards.

## 4.5.4 Electron Probe Micro Analysis

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A cameca MS-64 electron microprobe was used to determine the phases and their composition in the sulphide scales. Repeated attempts to analyze the finely dispersed inner layer of the scale failed because of the limitation on the probe size. Therefore, several profiles of Fe, Al and S were made by scanning the probe continuously in different directions to show their distributions. This was particularly useful in identifying the internal precipitates at the alloy/scale interface, because of their fine size and distribution.

## CHAPTER 5

## EXPERIMENTAL RESULTS AND ANALYSIS

## 5.1 INTRODUCTION:

Sulphidation results for the Fe-10wt% Al alloy and some preliminarly analyses of these results are presented in this chapter. The kinetic results were obtained at 1173 K and sulphur pressures ranging from 1 x  $10^{-2}$  atmosphere to 1 x  $10^{-5}$  atmospheres. No weight gain was detected at P<sub>S2</sub> = 1 x  $10^{-6}$  atm and below (even upto 18 hours), within the minimum limits of the measurement. Kinetic results at P<sub>S2</sub> = 1 x  $10^{-2}$  atm could not be obtained beyond 3000 seconds because of sulphur deposition on the spring and glass tube. The specimens were exposed to H<sub>2</sub>S-H<sub>2</sub> atmospheres at a total pressure of 1 atmosphere.

## 5.2 SULPHIDATION KINETICS:

The sulphidation kinetics of Fe-10wt% Al alloy were determined thermo-gravimetrically using a McBain balance described earlier. The results are plotted as weight gain per unit area of the specimen vs. corrosion time, and shown in Fig. 5.1 for various sulphur pressures at 1173 K. The size of each individual point shows the maximum possible error involved in the experimental measurements. In a more informative way, the kinetic results are represented in parabolic co-ordinates  $(\Delta W^2/A^2vs. time)$  in Fig. 5.2. These plots show a complex type of kinetic behaviour. At two sulphur pressures of 1 x 10<sup>-3</sup> and 1 x 10<sup>-4</sup> atm



FIGURE 5.1 Linear plots of sulphidation kinetics.

three distinct zones in the kinetic curve were observed. Following a brief initial period (200 seconds), the kinetic curves approximately followed two different rates  $K_1$ ,  $K_2$  and  $K_1'$ ,  $K_2'$  respectively. The transition from one rate to the other at 1 x 10<sup>-3</sup> atm sulphur pressure was found to be different than at  $P_{S_2} = 1 \times 10^{-4}$  atm In subsequent text, the distinct linear sections of the reaction curves and limiting tangents (Fig. 5.2) when the sulphidation kinetics are plotted in parabolic coordinates are described as representing parabolic rates. The rate constants determined from the slopes of these lines are designated parabolic reaction rate constants (Table 5.1).

The kinetics of sulphidation during the initial period (upto 1000 seconds) of reaction are plotted in Figures 5.3 and 5.4 for various sulphur pressures. Figure 5.4 shows that, the Fe-lowt% Al alloy sulphidizes parabolicly at  $P_{S_2=3} = 1 \times 10^{-2}$  atm during the initial period. The kinetics at  $P_{S_2} = 1 \times 10^{-3}$  atm show a complex behaviour with the slope of the curve changing continuously over a range of time. The kinetics, studied over the range of  $P_{S_2}$  were reproducible. For the sake of comparison, kinetics of sulphidation of pure iron at two different sulphur pressures but same temperature are plotted in Fig. 5.5.

From the above graphs and figures it can be stated in summary that, sulphidation kinetics of Fe-10wt% Al alloy are complex and reproducible in  $H_2S/H_2$  atmospheres at 1173 K. At  $P_{S_2} = 1 \times 10^{-3}$  and  $1 \times 10^{-4}$  atm the final corrosion rate constants ( $K_2$  in Table 5.1) have similar values which are an order of magnitude less than the first parabolic rate constants ( $K_1$ ). Alloying with Al reduces the sulphidation rate of pure



FIGURE 5.2 Parabolic plots of sulphidation kinetics.

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| Ps2                      | к <mark>*</mark>         | к2*                      | к <sup>*</sup> р       |
|--------------------------|--------------------------|--------------------------|------------------------|
| x 10 <sup>-5</sup> atm   |                          | -                        | $2.9 \times 10^{-7}$   |
| $1 \times 10^{-4}$ atm   | 1.69 x 10 <sup>-6</sup>  | 4.948 x 10 <sup>-7</sup> | · _                    |
| 1 x 10 <sup>-3</sup> atm | 3.27 x 10 <sup>-6</sup>  | 4.916 x 10 <sup>-7</sup> | -                      |
| 1 x 10 <sup>-2</sup> atm | -                        | -                        | $2.424 \times 10^{-6}$ |
| * in g                   | $m^2 cm^{-4} sec^{-1}$ . | · ·                      |                        |

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# TABLE 5.1

Corrosion rates of Fe-10wt% Al at 1173  $\mbox{K}$ 



Initial sulphidation kinetics of Fe-10wt%Al alloy in  $H_2S/H_2$  atmospheres.

FIGURE 5.3





FIGURE 5.4





iron. Higher P results in higher sulphidation rates at the same  $S_2$  temperature and composition of the alloy.

## 5.3 METALLOGRAPHY:

Specimens once sulphidized were cross-sectioned and prepared. for metallographic observation. Figure 5.6 shows an optical photomicrograph through a cross-section of the scale, obtained on Fe-10wt% Al alloy at 1073 K and  $P_{S_2} = 1 \times 10^{-2}$  atm. The micrographs show three distinct regions with alternate white and dark phases in region 2. An intermediate region between 1 and 2 shows a different texture than the outer layer in region 1. Needle type internal sulphidation is observed beneath the single phase regions (3). Figure 5.7 shows a crosssection of the scale on the alloy sulphidized at 1173 K in  $H_2S/H_2$  atmosphere of  $P_{S_2} = 1 \times 10^{-2}$  atm. Similar to Figure 5.6, three distinct regions of the scale are observed. Regions 1, 2 and 3 will be shown in subsequent sections to contain  $Fe_{1-x}S$ ,  $Fe_{1-x}S + FeAl_2S_4$  and  $FeAl_2S_4 + Al_2S_3$  respectively.

Figures 5.8 to 5.14 represent the metallographic observations on the Fe-10wt% Al alloy sulphidized at 1173 K and  $P_{S_2} = 1 \times 10^{-3}$  atm. Some specimens were etched with dilute hydrochloric acid and observed in SEM after coating with carbon. Figures 5.11 and 5.12 represent these observations.

To study the details of the corrosion mechanism, the alloy was subjected to different times of reaction at 1173 K and  $P_{S_2} = 1 \times 10^{-3}$ atm. Optical photo micrographs of the scale cross-sections are shown in Figure 5.13. These micrographs show the interface region between the

FIGURE 5.6 Fe-lowt% Al sulphidized at 1073 K in  $H_2S/H_2$  atmospheres ( $P_{S_2} = 1 \times 10^{-2}$  atm.). There are three regions of scale viz. the outer scale in region 1, the lamellar two phase structure in region 2 and single phase structures in region 3 with internal sulphidation beneath it.

FIGURE 5.7 Fe-10wt% Al sulphidized at 1173 K in  $H_2S/H_2$  atmospheres ( $P_{S_2} = 1 \times 10^{-2}$  atm.). The cross-section of the scale distinctly shows a three-layer morphology with the second layer having a lamellar structure.



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FIGURE 5.8 Fe-10wt% Al sulphidized at 1173 K in  $H_2S/H_2$  atmospheres ( $P_{S_2} = 1 \times 10^{-3}$  atm.). Pictures a, b and c are scanning electron micrographs showing the outer surface of the scale with large crystals on the top and fine crystallites at the base.



Fig. 5.8

FIGURE 5.9 Cross-section of the sulphide scale (observed in optical microscopy) on Fe-l0wt% Al alloy at 1173 K and  $P_{S_2} = 1 \times 10^{-3}$  atm showing a distinct three-layer morphology.





FIGURE 5.10 Fracture cross-section of the scale (observed in SEM) on Fe-lOwt% Al alloy sulphidized at 1173 K in  $H_2S/H_2$ atmospheres ( $P_{S_2} = 1 \times 10^{-3}$  atm).

- a) shows an intermediate layer developed between regions
   (1) and (2) as in Fig. 5.9.
- b) shows region (2) as in Fig. 5.9.
- (c) and (d) show region (3) of the alloy and inner layer interfaces.


FIGURE 5.11 <sup>d</sup> Cross-section of the sulphide scale obtained at 1173 K and  $P_{S_2} = 1 \times 10^{-3}$  atm. after etching with dilute HCl (observed in SEM).

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Etched in dilute HCl for  $\frac{1}{2}$  hr.

FIGURE 5.12 Cross-section of the sulphide scale at 1173 K and  $P_{S_2} = 1 \times 10^{-3}$  atm. after etching with dilute HCl (observed in SEM). Rod like precipitates :

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are revealed in the inner layer.

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1 Q 101 ۵ FIGURE 5.13 Optical photomicrographs showing the interface regions between the alloy and inner layer at  $11/3^3$ K,  $P_{S_2} = 1 \times 10^{-3}$  atm for different time periods of ? ٩ )( reaction during the initial stage. 2 .





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FIGURE 5.14 Optical (i) and scanning electron micrographs (ii) of the interface regions between the inner most layer and the alloy showing platelets growing into the alloy. The conditions were: temp. 1173<sup>°</sup>K,  $P_{S_2} = 1 \times 10^{-3}$  atm., time 180 minutes.

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alloy and the inner layer for the initial period (upto 15 minutes) of reaction. There are platelets or needles of a sulphide phase extending into the alloy from the rods of the sulphide phase in the inner layer of the external scale. After a longer time (180 minutes) a continuous film appears at the advancing front (Fig. 5.14(i)) and needles or platelets of a sulphide are shown to extend from the continuous phase into the alloy. These features are distinctly observed in Figures 5.14(i) and (ii). It will be shown in later sections that the rods are  $FeAl_2S_4$ and the small platelets extending into the alloy from the rods or the continuous films of Region (3) are  $Al_2S_3$ .

Figures 5.15 and 5.16 show the layer thickness measurements on a Fe-lOwt% Al alloy sulphidized for various time period at 1173 K and  $P_{S_2} = 1 \times 10^{-3}$  atm. In other words, Figure 5.15 represents the growth velocity of various interfaces (gas/scale and scale/alloy). A parabolic plot of Fig. 5.15 is drawn in Fig. 5.16 which shows a two stage kinetics as observed in weight gain measurements.

At a lower pressure of sulphur ( $P_{S_2} = 1 \times 10^{-4}$  atm ) and 1173 K, nodular growth has been observed. The nodules are nucleated at isolated sites on the surface of the alloy; some of them form on the alloy grain boundries. Figure 5.17 represents SEM pictures showing the nucleation of nodules on the surface. Figure 5.18 shows the surface of the alloy covered with sulphides at places other than the nodule sites. These nodules are observed to grow laterally and vertically and finally coalesce to form a continuous outer layer. The density of such nodules is found to be higher near the edges and corners of the specimen. The outer sulphides of these nodules have a morphology similar to oxide plates



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FIGURE 5.16

FIGURE 5.17 Nucleation and growth of nodules on Fe-10wt% Al alloy at 1173 K and  $P_{S_2} = 1 \times 10^{-4}$  atm. during the initial stage of reaction.

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Nodular growth of sulphides



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FIGURE 5.18 Surface of the alloy covered with different sulphides when exposed to  $H_2S/H_2$  atmospheres ( $P_{S_2} = 1 \times 10^{-4}$  atm, temp. 1173 K) during the initial period of reaction. In Figure (a) the alloy grain boundry shows a larger density of needle like sulphide crystals.



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FIG. 5.18

and whiskers formed on iron (Fig. 5.17 (d) and (e)). The fracture cross-section of these nodules are shown in Fig. 5.19 (e) and (d). Polished cross-sections of these nodules are represented in Fig. 5.20 (a) and (b) at two different sulphur pressures ( $P_{s_2} = 1 \times 10^{-3}$  atm and 1 x 10<sup>-4</sup> atm) respectively. The outer layer of the scale was porous (Fig. 5.19 (b)) because of the whiskers and plate formations during the initial period (Fig. 5.20 (b)) of reaction. This porous nature of outer layer was observed during the entire experimental work at 1173 K and 1 x 10<sup>-2</sup> to 1 x 10<sup>-4</sup> atm sulphur pressures.

To reveal the morphology of the inner layer at  $P_{S_2} = 1 \times 10^{-4}$  atm , scale cross-sections were etched with dilute HCl acid. Figure 5.21 represents a scanning electron micrograph of the inner two-phase layer showing rod like precipitates.

The Fe-10wt% Al alloy sulphidizes parabolicly in  $H_2S/H_2$  atmospheres at  $P_{S_2} = 1 \times 10^{-5}$  atm (Figs. 5.2 and 5.3). Figures 5.22(a) and (b) show the top view of the scale obtained by SEM. On the other hand  $P_{S_2} = 1 \times 10^{-6}$  atm, no weight gain was detected. However, Figure 5.22(c) shows a thin layer of scale (dark area) on the alloy and a region (white area) from which the scale has spalled.

## 5.4 MARKER EXPERIMENT RESULTS:

Several platinum markers of 25  $\mu$ m diameter were welded to the specimen surface prior to the sulphidation experiment. Figure 5.23 shows the results of such an experiment. The markers are seen to rest in between the inner and outer layer of the scale. This suggests that the outer layer grows by the outward diffusion of iron (perhaps through FIGURE 5.19 SEM pictures showing various features as follows:

- a) Preferential nucleation of nodules at the edges and corners of the specimen.
- b) Enlarged view of the outer layer at point 1 inFigure (a).
- c) Fracture cross-section of a nodule in Figure 5.18.
- d) Enlarged view of the nodule/alloy interface.



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FIG. 5.19

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FIGURE 5.20 (a) and (c) Polished cross-sections of the nodules at  $1173^{5}$ K, P<sub>S2</sub> = 1 x  $10^{-3}$  atm.

(b) A cross-section of the nodule at 1173  $\rm \check{K},$ 

$$P_{S_2} = 1 \times 10^{-4} \text{ atm.}$$

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(d) Another view of the scale at  $1173^{3}$ K,

 $P_{S_2} = 1 \times 10^{-3}$  atm showing the outer and inner layers.







FIGURE 5.21 Fe-lowt% Al alloy sulphidized in  $H_2S/H_2$  atmospheres at  $P_{S_2} = 1 \times 10^{-4}$  atm.

- a) Cross-section of the inner two-phase layer
- b) EDAX analysis on a point A (dark phase) inFig. (a).
- c) An angular top view of the inner two-phase layer after etching with dilute HCl for 60 seconds.
- d) Rod precipitates were completely etched leaving behind circular shaped holes.

(e) and (f) Rod precipitates in the inner layer.



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FIG. 5.21

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FIGURE 5.22 (a), (b) Scanning electron micrograph showing the top view of the scale on Fe-10wt% Al alloy sulphidized in  $H_2S/H_2$  atmospheres ( $P_{S_2} = 1 \times 10^{-5}$  atm.). (c) Scanning electron micrograph showing the top view of the scale on Fe-10wt% Al alloy sulphidized in  $H_2S/H_2$  atmosphere ( $P_{S_2} = 1 \times 10^{-6}$  atm.).

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FIG. 5.22

platinum marker residing at the inner and outer layer interface after sulphidation at  $1173^{\circ}$ K,

FIGURE 5.23 Scale cross-sections on Fe-lowt% Al alloy with inert  $P_{S_2} = 1 \times 10^{-4} a tm.$ 

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FIG. 5.23

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Fe vacancies) and the inner layer grows by the inward migration of sulphur.

## 5.5 PHASE IDENTIFICATION:

The phases present in the sulphide scale were identified with the help of EDAX, microprobe analysis and powder X-ray diffraction.

## 5.5.1 Electron Probe Microanalysis

Microanalysis was performed on various parts of the scale using a Cameca-MS-64 electron microprobe. Spot analysis were made to establish the composition of the scale. An operating voltage of 20 KV was used in this work. However, because of a fine distribution of two phases in the inner layer and loss of optical contrast due to carbon coating, the point counting method was considered inadequate to ascertain the composition of the scale. Therefore, X-ray intensities displayed on a chart were obtained with the help of a pen recorder, when the specimen moved giving a line scan. The specimen movement was recorded, as a motor drove the specimen stage.

Figure 5.24 shows microprobe traces of various elements across a nodule formed on the alloy at 1173 K and  $P_{S_2} = 1 \times 10^{-3}$  atm. during the initial period of reaction. The inner layer of the nodule constitutes intense internal sulphidation as shown in Figures 5.13 and 5.20 (a) and (d). The outer layer is established as  $Fe_{1-x}$ S and perhaps doped with Al. In the internal sulphidation zone, peaks of Al correspond to the troughs of Fe and peaks of sulphur. Figure 5.25 shows the microprobe traces for Fe, Al and S across the scale formed on the alloy

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FIGURE 5.24 A microprobe trace showing the distribution of Fe, Al and S in the nodular scale at 1173 K,  $P_{S_2} = 1 \times 10^{-3}$  atm. after 5 minutes of reaction ,



FIGURE 5.25 A microprobe trace showing the distribution of Fe, Al and S in the scale (Temp. - 1173 K,  $P_{S_2} = 1 \times 10^{-1}$  atm., time - 15 minutes).

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15 minutes of reaction. From Figures 5.25 and 5.26, the inner layer is predicted to be a mixture of  $Fe_{1-x}S$ ;  $FeAl_2S_4$  and  $Al_2S_3$  with particularly alluminium sulphide at the scale/alloy interface. To confirm these results the scale was etched by dilute hydrochloric acid for about 30 minutes. The scanning electron micrograph of such a sample is shown in Figures 5.11 and 5.12. A microprobe scan across the etched inner layer is shown in Figure 5.27 showing selective etching of one of the phases. In a separate experiment the rates of chemical dissolution of FeS,  $Al_2S_3$  and  $FeAl_2S_4$  were studied. The dissolution rates as measured by the evolution rate of  $H_2S$ , decreased in the order of  $Al_2S_3$ ,  $FeAl_2S_4$ and FeS. The large counts of Al observed in Figure 5.27 arise from the undissolved  $FeAl_2S_4$  in the dilute HCl etchant as will be shown in Table 5.4 utilizing EDAX analyses.

Figure 5.28 shows a microprobe trace for elements Fe and Al across the surface scale at places other than nodular sites indicating the formation of a thin layer of  $Al_2S_3$  which hydrolyzed to  $Al_2O_3$  while handling the specimen. A complete line scan across the scale obtained at 1173 K,  $P_{S_2} = 1 \times 10^{-4}$  atm. after 180 minutes of sulphidation is represented in Figure 5.31 showing clearly an increase in Al concentration as the scale/alloy interface is approached. At the scale/alloy interface, peaks of Al and corresponding peaks of sulphur indicate the presence of  $Al_2S_3$ .

Beneath the Al and S rich zone near the scale/alloy interface, several line scans were taken across the dark needles or platelets



 $C^{*}$ 

FIGURE 5.27 Distribution of Fe, Al and S in the two-phase inner layer after etching with dilute HCl.



FIGURE 5.28 Distribution of Fe and Al across the thin scale obtained at  $P_{S_2} = 1 \times 10^{-4}$  atm. and 1173 K during the initial period of reaction



FIGURE 5.29 Distribution of Fe, Al and S in the total scale obtained at 1173 K,  $P_{S_2} = 1 \times 10^{-4}$  atm. after 180 minutes of reaction.

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FIGURE 5.30 Distribution of Al and Fe in the internal precipitation zone ahead of the inner most layer/alloy interface.

FIGURE 5.31 Distributions of Fe and S in the internal precipitation zone ahead of the inner most layer/alloy interface.

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(Figure 5.14). Such microprobe scans are presented in Figures 5.30 and 5.31. These precipitates are clearly seen to be rich in Al and S, probably constituting  $Al_2S_3$ . Because of the small size of these precipitates (< lum) spot analysis was not used. One of the important observations was the transformation of the needles in the region of alloy interface during corrosion to a continuous Al and S rich film.

It is also observed from the microprobe traces that compositions change very sharply across the scale/alloy interface.

Therefore in summary, the various microprobe scans and spot analyses made on the scales formed at 1173 K,  $P_{S_2} = 1 \times 10^{-3}$  atm. and  $1 \times 10^{-4}$  atm. indicate the formation of an outer layer rich in Fe and S (appearing yellow under optical microscope and bright under SEM) and an inner layer consisting of Fe, Al and S due perhaps to the coexistence of FeS and FeAl<sub>2</sub>S<sub>4</sub> (the dark coloured phase under both optical and SEM). The inner most layer at the scale/alloy interface was highly enriched in Al and S. Needles or platelets (appearing dark both under optical and SEM) extending into the alloy were identified to be rich in aluminium and sulphur.

#### 5.5.2 X-ray Analysis

For carrying out X-ray analyses, it was necessary to prepare the samples from various parts of the scale. The outer layer was friable and therefore it was obtained by scraping the sample surface. Samples from the two-phase region were taken after flaking the outer layer. The phases close to the alloy were identified by taking samples from that region carefully, while simultaneously observing the specimen

through an optical microscope.

The diffraction patterns of the various samples were recorded on a chart recorder. The intensity of the peaks and their positions in the chart (angle  $2\theta$ ) were recorded to evaluate the 'd' spacings by using the relation  $\lambda = 2d \sin\theta$  ( $\lambda = 1.5405 \text{\AA}$  for CuK<sub>a1</sub> radiation). For a single compound, each intensity peak was normalized with respect to the highest peak obtained in the system. Table 5.2 represents the value of d in  $\overset{\circ}{A}$  and the corresponding relative intensity (I/I<sub>1</sub> × 100) for  $Fe_{1-x}^{S}$ . Such type of tables are generally listed in ASTM cards with each intensity line emerging from a particular plane in the crystal lattice. For the sake of clarity and comparison, the standard diffraction patterns of all the three compounds ( $Fe_{1-x}S$ ,  $Al_2S_3$  and  $FeAl_2S_4$ ) are represented in Figs. 5.32 to 5.34. The compounds  $Fe_{1-x}S$  and  $FeAl_2S_4$  were prepared separately by sulphidizing pure Fe in  $H_2S/H_2$  atmosphere at 1173 K and by the method described by Nishida et al.<sup>143</sup> respectively. The lattice parameters of these compounds were calculated and compared with those available in the literature<sup>137</sup>.

To identify the various phases present in different parts of the the scale, the X-ray results were plotted on graphs (Figs. 5.35 to 5.38). For samples having more than one phase, the analysis described by Cullity  $^{157}$  was used. In this method, a known highest intensity line of a compound, present in the mixture is taken as I<sub>1</sub> and the rest of the diffraction intensity peaks are normalized with respect to it. Then, the relative intensities of the known compound are separated from the mixture and the remaining lines are again normalized with



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FIGURE 5.33

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1-36



FIGURE 5.34

# TABLE 5.2

Intensity, d spacings and hk1 indices of  $Fe_{1-x}^{S}$ 

prepared as a standard

| · · · | Peak<br>No. | d in (A) | Relative Intensity<br>(I/I <sub>1</sub> × 100) | (hk1)   |
|-------|-------------|----------|------------------------------------------------|---------|
| •• -  | 1           | 2.919    | 47                                             | 100     |
|       | 2           | 2.653    | 37                                             | 101     |
|       | 3 .         | 2,092    | . 100                                          | 102     |
|       | 4           | 1.726    | 23                                             | 110     |
| ı     | , <b>5</b>  | 1.638    | 8                                              | 103     |
| •     | 6           | 1.466    | 9                                              | ູ200    |
|       | 7           | 1.449    | 8                                              | 201     |
|       | . 8         | 1.33     | 14                                             | · 202 · |
|       | 9           | 1.316    | 8 .                                            | 104     |
|       | 10          | • 1.11   | ۰ <u>1</u> 1                                   | 200     |
|       | 11.         | 1.054    | 10                                             | 201     |

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FIGURE 5.35





obtained from the scale at 900°C, Pszwix10<sup>-4</sup>atm.







X-Ray diffraction pattern of the samples taken from the surface of the specimen after the initial period reaction at  $900^{\circ}$ C and Ps<sub>2</sub> 1 X  $10^{-4}$  atm.

FIGURE 5.38



FIGURE 5.39

respect to the highest intensity. This method provides a useful means to identify the phases present in a mixture. Using this method, the phases present in different parts of the scale were identified from Figs. 5.35 to 5.38 by comparing their relative intensities, 'd' values and lattice parameters. These diffraction patterns are from the scale formed on Fe-10wt% Al alloy at 1173 K and  $P_{S_2} = 1 \times 10^{-4}$  atm. Figure 5.39 represents a diffraction pattern of the only scale formed on Fe-15wt% Al alloy at 1173 K and  $P_{S_2} = 1 \times 10^{-4}$  atm.

The compound  $Al_2S_3$  being unstable in air, decomposes to form either hydroxides or oxide/sulphides<sup>141</sup>. Therefore, additional peaks not belonging to any of the three compounds  $(Al_2S_3, Fe_{1-x}S, FeAl_2S_4)$ were observed in the presence of  $Al_2S_3$ . Due to frequent occurrence of these intensity peaks along with  $Al_2S_3$ , they are attributed to the hydrolysis product of  $Al_2S_3$ .

Therefore, X-ray analysis of the scale formed on Fe-10wt% Al alloy at 1173 K and  $P_{S_2} = 1 \times 10^{-4}$  atm shows an outer layer consisting of Fe<sub>1-x</sub>S (pyrrohotite) and an inner layer consisting of a mixture of two phases (Fe<sub>1-x</sub>S + FeAl<sub>2</sub>S<sub>4</sub>). The layer close to the alloy scale interface is found to be a mixture of FeAl<sub>2</sub>S<sub>4</sub> and Al<sub>2</sub>S<sub>3</sub>. Immediate analysis performed after the initial period of reaction shows a simultaneous formation of Al<sub>2</sub>S<sub>3</sub> and Fe<sub>1-x</sub>S (as nodules) on the surface of the specimen.

### 5.5.3 X-Ray Energy Dispersive Analysis

Some of the samples were analyzed qualitatively to supplement the previous quantitative analyses, by using the KEVEX X-ray energy dispersive analyzer attached to the scanning electron microscope. In this system X-rays are generated by scanning an electron beam across the surface of the specimen. Also by using a stationary spot, which is the size of the beam ( $\sim 1000\text{Å}$ ), small inclusions can be pinpointed and elemental intensity across various phases can be obtained. The X-rays which are given off the sample are collected and dependeing on the energy of the X-ray they are located in the spectrum on the oscilloscope. The X-ray energy spectrum is then analyzed by a teletype computer. To obtain representive results, flat and polished and/or etched samples are used. During such analysis it was established that X-rays have a free path to the detector.

Table 5.3 shows one of the several results of point counts obtained on the Fe-10wt% Al alloy.

EDAX point analysis on Fe-10wt% Al alloy

| NO.        | ECL | CENTROID     | FWHM | AREA    | LEFT | RIGHT | ELEMENT |
|------------|-----|--------------|------|---------|------|-------|---------|
| 1          | 1.  | 1.48         | 0.09 | 380.70  | 26   | 47    | A.1     |
| <b>2</b> . | 1   | <b>6</b> .39 | 0.14 | 7009.48 | 412  | 432   | Fe      |
| 3          | 1   | 7.03         | 0.14 | 1230.45 | 462  | 483   | Fe      |

TABLE 5.3

Tables 5.4 and 5.5 show some results of point count analysis on the outer layer and the inner layer of an etched (by dil. HCl) sample obtained at 1173 K and  $P_{S_2} = 1 \times 10^{-3}$  atmosphere respectively.

| TABL | Ε | 5. | 4 |
|------|---|----|---|
|------|---|----|---|

EDAX point analysis on the outer layer

| NO. | ECL | CENTROID | FWHM | AREA     | LEFT | RIGHT | ELEMENT |
|-----|-----|----------|------|----------|------|-------|---------|
| 1   | 1   | 2.30     | 0.13 | 15683.98 | 102  | 123   | S       |
| 2   | 1   | 6.39     | 0.16 | 18087.95 | 409  | 430   | Fe      |
| 3   | 1   | 7.03     | 0.14 | 2250.25  | 458  | 478   | Fe      |

TABLE 5.5

EDAX point analysis on the inner layer

|     |     | ويوري والمتحربين وادلا متعقي بالمترجب |        |          |      |       |         |
|-----|-----|---------------------------------------|--------|----------|------|-------|---------|
| NO. | ECL | CENTROID                              | FWHM   | AREA     | LEFT | RIGHT | ELEMENT |
| . 1 | 1 - | 1.50                                  | · 0.13 | 6502.23  | 39   | 59    | AJ      |
| 2   | 1   | 2.33                                  | 0.13   | 13434.36 | 101  | 121   | S       |
| 3   | 1   | 2.65                                  | 0.12   | 1576.23  | 126  | 146   | C1      |
| 4   | 1   | 6.41                                  | 0.15   | 9606.25  | 407  | 427   | Fe      |
| 5   | 1   | 7.07                                  | 0.17   | 1382.96  | 456  | 477   | Fe      |
|     |     | •                                     |        |          |      |       |         |

To analyze the process of nucleation and growth of nodules, several point counts were taken on the surface of the specimen after an initial period of sulphidation at 1173 K and  $P_{S_2} = 1 \times 10^{-4}$ atmosphere. Tables 5.6 and 5.7 show the results of point count analysis on the surface of the specimen indicated in Fig. 5.17 (e) and Fig. 5.40. Care was taken to analyze at those points from which X-rays were collected by the detector without any obstacle.

Apart from nodular sites, several other points on the specimen surface were also analyzed. The areas under the peaks of the various spectra are found to vary from point to point for a given element. Table 5.8 shows some of the EDAX analysis at various points on the specimen surface. From the analysis of these results (Table 5.8) and metallography (Fig. 5.18), formation of a thin film rich in aluminium and sulphur at the initial stage of reaction cannot be completely ruled out. The inner Tayer of the scale formed on this alloy consists of a fine dispersion of two phases. EDAX analysis on a point on the dark phase shows the presence of Fe, Al and S (Fig. 5.21(b) and Table 5.9) whereas a point on the bright phase indicates the presence of Fe and S with a very small amount of Al (Table 5.10).

At low sulphur pressures ( $P_{S_2} \le 1 \ge 10^{-5}$  ātm.) the complex twolayer scale was absent and instead, a thin layer of needle like corrosion product is formed as shown in Fig. 5.22. EDAX analysis at a point on the scale surface Fig. 22(a), (b) is shown in Table 5.11(a), whereas Table 5.11(b) represents some results of the analysis at different points B and C (Fig. 5.22(c)) on the specimen surface at

## TABLE 5.6

EDAX analysis at a point on the peripherry of

the nodule (Fig. 5.40)

| NO. | ECL | CENTROID | FWHM | AREA     | LEFT | RIGHT | ELEMENT |
|-----|-----|----------|------|----------|------|-------|---------|
| 1   | 1   | 1.47     | 0.13 | 21935.09 | 40   | 60    | Al      |
| 2   | 1   | 2.29     | 0.13 | 21391.70 | 101  | 122   | S       |
| 3   | 1   | 6.38     | 0.17 | 7482.2   | 407  | 428   | Fe      |
| 4   | 1   | 7.04     | 0.12 | 702.75   | 457  | 478   | Fe      |
|     | •   |          |      |          |      |       |         |

## TABLE 5.7

EDAX analysis at a point on a crystal protruding

from the nodule (Fig. 5.40)

| NO. | ECL | CENTROID | FWHM | AREA    | LEFT | <b>/</b> RIGHT | ELEMENT |
|-----|-----|----------|------|---------|------|----------------|---------|
| 1   | 1   | 2.30     | 0.13 | 7506.71 | 102  | 122            | S       |
| 2   | 1   | 6.39     | 0.14 | 8779.5  | 408  | 428            | Fe      |
| 3   | 1   | 7.04     | 0.15 | 1249.98 | 456  | 477            | Fe      |
|     |     |          |      |         |      |                |         |





Point B

FIG. 5.40

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# TABLE 5.8

EDAX analysis at various points on the specimen surface

at 1173 K,  $P_{S_2} = 1 \times 10^{-4}$  atm. (Fig. 5.18)

(a)

| _ |     |     |          |      |         |      | <u>`````````````````````````````````</u> |         |
|---|-----|-----|----------|------|---------|------|------------------------------------------|---------|
|   | NO. | ECL | CENTROID | FWHM | AREA    | LEFT | RIGHT                                    | ELEMENT |
| - | 1   | 1   | 1.54     | 0.18 | 8072.48 | 45   | 65                                       | A1      |
|   | 2   | 1   | 2.35     | 0.17 | 9819.08 | 106  | 126                                      | S       |
|   | 3   | ]   | 6.43     | 0.17 | 2847.97 | 411  | 431                                      | Fe      |
|   |     |     |          |      |         |      |                                          |         |

# (b)

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| 1   1   1.48   0.11   1083.21   40   61   A1     2   1   6.39   0.16   19499.95   408   429   Fe     3   1   7.05   0.15   3251.49   457   477   Fe | NO. | ECL | CENTROID | FWHM | AREA     | LEFT | RIGHT | ELEMENT |
|-----------------------------------------------------------------------------------------------------------------------------------------------------|-----|-----|----------|------|----------|------|-------|---------|
| 2 1 6.39 0.16 19499.95 408 429 Fe<br>3 1 7.05 0.15 3251.49 457 477 Fe                                                                               | 1   | 1   | 1.48     | 0.11 | 1083.21  | 40   | 61    | A]      |
| 3 1 7.05 0.15 3251.49 457 477 Fe                                                                                                                    | 2   | 1   | 6.39     | 0.16 | 19499.95 | 408  | 429   | Fe      |
|                                                                                                                                                     | 3   | 1   | 7.05     | 0.15 | 3251.49  | 457  | 477   | Fe      |

|     |     | ·····    |      |         |      |       | ·····   |
|-----|-----|----------|------|---------|------|-------|---------|
| NQ. | ECL | CENTROID | FWHM | AREA    | LEFT | RIGHT | ELEMENT |
| 1   | 1   | 1.48     | 0.13 | 8720.73 | 40   | 61    | Al      |
| 2   | 1   | 2.30     | 0.13 | 5040.72 | 101  | 122   | S.      |
| 3   | 1   | 6.39     | 0.16 | 3467.75 | ,408 | 428   | Fe.     |
| 4   | T   | . 7.04   | 0.14 | 462.20  | 457  | 478 · | Fe      |

| NO. | ECL | CENTROID | FWHM | AREA /   | LEFT | RIGHT | ELEMENT |
|-----|-----|----------|------|----------|------|-------|---------|
| ]   | 1   | 1.48     | 0.12 | 4742.23  | 45   | 66    | A1      |
| 2   | 1   | 2.30     | 0.12 | 10648.08 | 109  | 129   | S       |
| 3   | 1   | 2.62     | 0.11 | 2288.45  | 1.33 | 154   | S       |
| 4   | 1   | 6.40     | 0.14 | 11157.21 | 424  | 445   | Fe      |
| 5   | 1   | 7.04     | 0.15 | 1446.46  | 474  | 495   | Fe 🐟    |
|     |     |          |      |          |      |       |         |

TABLE 5.9

EDAX point analysis on the dark phase of the inner layer

TABLE 5.10

EDAX point analysis on the bright phase of the inner layer

|     |     |          |       |                 |        | •     |         |
|-----|-----|----------|-------|-----------------|--------|-------|---------|
| NO. | ECL | CENTROID | FWHM  | AREA            | LEFT   | RIGHT | ELEMENT |
| 1   | 1   | 1.4      | 0.09  | <b>,</b> 246.42 | . 18 • | 38    | A1      |
| 2   | 1   | 2.22     | 0.13  | 15069.84        | 82     | 102   | S       |
| 3   | ٦   | 6.33     | 0.15  | 16576.10        | 404    | 424 . | Fe      |
| 4   | 1   | 6.98     | 0.14' | 2355.35         | 455    | \$75  | Fe      |
|     |     |          | -     |                 |        | Þ     |         |

 $P_{S_2} = 1 \times 10^{-6}$  atm. and 1173 K. No sulphur could be detected at or below this sulphur pressure.

Figures 5.41 and 5.42 show the AlK X-ray mappings of the inner layer and the total scale respectively. The dark phase is rich in alumninium with most of the aluminium present in the inner layer. Fig. 5.42 shows enrichment of Al at the scale/alloy interface.

## 5.6 RESULTS OF QUENCHING EXPERIMENT:

A rod morphology is observed in the inner layer of the scale on Fe-10wt% Al alloy in the present work. Lamellar morphologies have also been observed in the sulphidation of Ni-Mo<sup>168</sup>, Ni-Al<sup>29</sup> and in the oxidation of Zr-Nb<sup>169</sup> alloys. A similar morphology is also observed in various phase transformations in alloys viz. discontinuous precipitation, eutectic and eutectoid decompositions. In the case of pearlite transformation in steels, supersaturation of austenite is brought about by cooling and a relation between the growth velocity and lamellar spacing can be obtained from irreversible thermodynamics<sup>170</sup>. In the case of oxidation-sulphidation phenomenon, however, the growth velocity of the lamellar scales may be controlled either by an interfacial reaction at the gas/scale interface or by the diffusion of oxidizing species through the scale under isothermal conditions.

In the present work a separate experiment was carried out to confirm whether the lamellar or rod type morphology is obtained isothermally or as a result of cooling the sample. The results of this experiment were also useful in determining whether the continuous  $Al_2S_3$ 

EDAX point analysis on the scale at  $P_{S_2} = 1 \times 10^{-5}$  atm., 1173 K NO. ECL CENTROID FWHM ARÉA LEFT RIGHT ELEMENT 0.12 6861.97 1 1.46 24 A1 1 45 2 1 2.28 0.13 699.70 89 110 S 6.36 0.15 3952.95 409 430 Fe 3 1 4 1 7.00 0.10 322.77 459 479 Fe

TABLE 5.11 (b) EDAX point analysis on the scale at  $P_c =$ -6 1 x 10

| ,<br>3 | EDAX | point analys | is on the | e scale at | <sup>P</sup> S2 <sup>=</sup> | 1 x 10  | atm., 1173 | K |
|--------|------|--------------|-----------|------------|------------------------------|---------|------------|---|
| NO.    | ECL  | CENTROID     | FWHM      | AREA       | LEFT                         | · RIGHT | ELEMENT    |   |
| ï      | ]    | 1.49         | 0.11      | 812.10     | 27                           | 47      | AJ         |   |
| 2      | 1    | 6.39         | 0.15,     | 8968.88    | 412                          | 432     | Fe .       |   |
| 3      | Ţ    | 7.04         | 0.15      | 1184.22    | 463                          | 483     | Fe         |   |

TABLE 5.11 (c)

| •   | ••• | •        |        | •              |      |       |         |
|-----|-----|----------|--------|----------------|------|-------|---------|
| NO. | ECL | CENTROID | FWHM . | AREA           | LEFT | RIGHT | ELEMENT |
| 1   | 1   | 1:46     | 0.12   | 6378,84        | 25 ~ | 45    | , A1    |
| 2   | .1  | <u> </u> | .0.15  | 4136.22        | -410 | 431   | Fe      |
| 3   | 1   | 7.01     | 0.14   | <u>665.4</u> 入 | 460  | 181   | Fe.     |

FIGURE 5.41 AlK mapping of the inner layer showing the dark phase rich in aluminium.

FIGURE 5.42

5.42 AlK mapping of the total scale formed at 1173 K,

 $P_{S_2} = 1 \times 10^{-4}$  atm.



layer and morphological breakdown in combination with internal sulphidation ahead of it, occurred isothermally or due to cooling.

Alloy samples were sulphidized at 1173'K and  $P_{S_2} = 1 \times 10^{-4}$ atm under similar conditions for 1/2 hour and 4 hours. Two samples were sulphidized simultaneously of which one was quenched from the reaction chamber by a stream of helium gas injected through a mozzle at a velocity of 125 cm/sec towards the specimen and the other sample was allowed to furnace cool in He atmosphere after flushing the  $H_2S/H_2$ gas mixture from the reaction chamber. The photomicrographs of specimen cross-sections are shown in Figures 5.43 and 5.44. It is established from all the four micrographs that the inner two-phase layers and the inner most FeAl<sub>2</sub>S<sub>4</sub> + Al<sub>2</sub>S<sub>3</sub> layer have formed isothermally and not due to cooling.

Some special features of the sulphidation reaction are exemplified in the micrographs of Figures 5.43 and 5.44. The degree of internal sulphidation (growth of  $Al_2S_3$  platelets or needles beneath the  $Al_2S_3$ film) was less at the peak regions of the serrated alloy interface where the external sulphide scale was of largest thickness (Figures 5.43 (a) and (b)). Also the furnace cooled specimens tended to exhibit a greater thickness of the Fe  $Al_2S_4 + Al_2S_3$  inner layer and a. deeper penetration of  $Al_2S_3$  platelets (Figures 5.44 (a) and (b)). This behaviour resulted from the continuation of the sulphidation reaction during the combined flushing of the  $H_2S$  atmosphere by He and the slow cooling process.

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FIGURE 5.43 Optical micrographs of:

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a) Scale microstructure of the quenched sample after
1/2 hour of sulphidation (Specimen A)

157

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b) Scale microstructure of the furnace cooled sample after 1/2 hour of sulphidation (Specimen B).



158

FIG. 5.43

- FIGURE 5.44 a) Quenched from reaction temperature after 4 hours of sulphidation.
  - b) Furnace cooled after 4 hours of sulphidation.



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b) Furnace cooled

FIG. 5.44

### CHAPTER 6

#### DISCUSSION

6.1 INTRODUCTION:

Sulphidation of Fe-10wt% Al alloy in  $H_2^{S/H_2}$  atmospheres may be said to occur in two stages after a brief initial period; namely a first parabolic stage of decreasing reaction rate followed by a final parabolic rate, particularly at two sulphur pressures of  $1 \times 10^{-3}$  and  $1 \times 10^{-4}$  atm. At two other sulphur pressures ( $P_{S_2} = 1 \times 10^{-3}$  atm and  $1 \times 10^{-5}$  atm ) studied at present, the reaction continued parabolically with growth of multilayer and single layer corrosion products respectively. Henceforth, most of the discussion will refer to the mechanism of sulphidation at two sulphur pressures of  $1 \times 10^{-3}$  atm and  $1 \times 10^{-4}$  atm.

The sulphidation mechanism is complex due to the occurrence of a number of complicated processes. During the initial reaction stage both Fe and Al sulphidize simultaneously resulting in formation of an  $Al_2S_3$  film and FeS nodules at the defect sites present in the film. The FeS nodules grow laterally and vertically and the alloy beneath these nodules is sulphidized internally. Since the diffusivity of sulphur in Fe<sub>1-x</sub>S is negligible, sulphur supply for growth of the inner layer must have originated at the Fe<sub>1-x</sub>S/alloy interface.

During the first parabolic growth of the scale, outer  $Fe_{1-x}^{S}$  formation, internal precipitate formation and their conversion from  $A1_2S_3$  to a  $Fe_{1-x}^{S}$  and  $FeA1_2S_4$  conglomerate take place. The second

parabolic stage leads to the formation of a continuous  $Al_2S_3$  film at the alloy/scale interface. Once the  $Al_2S_3$  film covers the alloy surface, further corrosion proceeds at a rate approximately an order of magnitude less than the initial rate (Table 5.1). These metallographic observations will be discussed along with the kinetic results in separate sections in order to present a growth model for the corrosion products. A ternary Fe-Al-S phase diagram is constructed which is consistent with these observations and mechanisms for the growth of the sulphide phases.

#### 6.2 SULPHIDATION KINETICS

The kinetics of Fe-Al sulphidation are complex but generally reproducible. The sulphidation rates are higher at higher sulphur pressures. It is apparent from the kinetic results that parabolic behaviour begins after an initial brief reaction period of  $\sim 100$  seconds (Figures 5.3 and 5.4). Relatively thick scales are observed at high partial pressures of H<sub>2</sub>S (P<sub>H2</sub>S  $\sim 0.2$  to 0.7) with diffusion control across the sulphide scale. Because of the complex morphologies of the sulphide phases, diffusion in the inner two-phase layer (Fe<sub>1-x</sub>S + FeA1<sub>2</sub>S<sub>4</sub>) may be due either to iron migration through the two phases or to the inward migration of sulphur along the long channels and boundaries between the two phases (diffusion of S in Fe<sub>1-x</sub>S is negligible and in FeA1<sub>2</sub>S<sub>4</sub> the rate is unknown) or through microscopic pores in the inner layer, as suggested by the inert marker experiments.

The fact that sulphidation kinetics are parabolic clearly shows that the total scale is thick during early stages of the reaction. Since both the outer and inner layers grow simultaneously, the increase in sample weight  $\Delta W$  represents the total weight gain due to both layers. Corrosion rate constants are found to be lower than pure Fe at 1173 K for all sulphur pressures used in the present study. FeS is a metallic conductor above 411 K and one might expect partial dissolution of  $Al_2S_3$ to give an alteration of its defect structure according to the defect model,

$$A1_2S_3 = 2 A1_{Fe}^x + V_{Fe}^x + 3 S_s^x$$
 (6.0)

Because of the creation of additional neutral iron vacancies, diffusion of Fe in Fe<sub>1-x</sub> S would be increased, thereby increasing its growth rate. However, the present work shows that this first stage of parabolic sulphidation for the alloy is less than the sulphidation rate of pure Fe.

The decrease in the sulphidation rate after the first stage of parabolic sulphidation can be explained in one of two ways. Firstly, the growth of outer FeS scale is dependent on the rate of movement of Fe outwards from the alloy through the inner two-phase layer. Therefore the effective area for bulk diffusion of Fe is decreased by the blocking effect of the FeAl<sub>2</sub>S<sub>4</sub> rods which increase in diameter with increasing exposure time (Fig. 5.13). Also it can be suggested that the supply of iron may be insufficient to maintain the appropriate concentration at the inner and outer layer interfaces to allow normal parabolic diffusional scale growth as observed with pure Fe under the same conditions. This was evidenced quite clearly in all the micrographs by the presence of pores and fissures in the outer layer. It was only during the initial period of time (first 500 to 1000 seconds) in the high P<sub>S<sub>2</sub></sub> range (=  $1 \times 10^{-2}$  and  $1 \times 10^{-3}$  atm ) that a solid compact

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FeS layer was formed.

Secondly, the reduced rate of sulphidation of the alloy may be associated with the creation of localized strain fields in the  $Fe_{1-x}^{S}$ due to the incorporation of Al (the ionic radii of  $Fe^{++}$  and Al<sup>3+</sup> are 0.76 Å and 0.5 Å respectively) which may act to exert attraction force on the iron vacancies. Hence the vacancy diffusion rate may be decreased leading to a reduction of the reaction rate constants.

### 6.3 NODULAR SCALE GROWTH:

The scale growth on Fe-10wt% Al alloy in the  $P_{S_2}$  range 1 x 10<sup>-3</sup> and 1 x 10<sup>-4</sup> atm takes place by the mechanism discussed next.

Due to the difference in stability of  $Al_2S_3$  and  $Fe_{1-x}S$  at 1173 K, initially a thin layer of  $Al_2S_3$  is formed on the alloy (Fig. 5.18) and with time this film dissolves the residual oxide film formed on the alloy prior to sulphidation. The  $Al_2S_3$  film is highly defective, imperfect and has a number of leakage paths where FeS nucleates readily to grow as hemispherical nodules with circular base and mushroom shape. This is similar to the situation where an imperfect and discontinuous  $Al_2O_3$  film is formed on Ni-6wt% Al alloy in oxygen atmosphere<sup>163</sup>. Since the sulphur activity is small at the alloy/ $Al_2S_3$  interface corresponding to the dissociation pressure of  $Al_2S_3^{1}$  it is reasonable to assume that Fe is transported relatively rapidly by preferential diffusion paths in the  $Al_2S_3$  film. The number of these leakage paths are a function of alloy composition, surface finish, sulphidation temperature and the specimen geometry. The last factor is readily illustrated in Figure 5.19 (a) at the edge and corner of the sample where the density of nodules are high.

 $Fe_{1-x}S$ , which is not the most favoured phase thermodynamically, forms at a faster rate (depending on the sulphur pressure) than  $Al_2S_3$  and tends to cover the surface. No data on the growth of  $Al_2S_3$ is available at high temperature. However, at 673 K the growth rate of FeS is  $10^4$  times faster than the growth rate of  $Al_2S_3^8$ . Upon nucleation of each nodule they spread laterally and grow vertically to coalesce with other nodules and finally form a continuous  $Fe_{1-x}S$  scale having extensive porosity (Fig. 5.17). Since certain preferred sites act as nucleation centres during the initial period, the fractional coverage of the surface 'a' at time 't' can be expressed as,

 $\alpha = 1 - \exp^{(-\beta t^2)} = \frac{A}{A_0}$  (6.1)

where  $\beta$  is the lateral growth parameter of the nodules, and A, A<sub>0</sub> are the surface coverage of nodules and original surface area of the alloy respectively<sup>28</sup>. Since the volume and area of the nodules increase with time, a relationship between the total weight gain due to the vertical growth of Al<sub>2</sub>S<sub>3</sub> and lateral and vertical growth of the Fe<sub>1-x</sub>S nodules can be obtained. One such relationship was previously derived and verified in the case of wustite-fayalite nodules formed on Fe-1.5wt% Si alloy in CO<sub>2</sub>/CO atmospheres when the oxide phases were assumed to grow according to linear kinetics<sup>158</sup>.

The average size of the nodules obtained in the present case varied from 100 to 150 µm before they coalesced with other nodules;

the smallest size observed was about 25 to 30 µm. At times some of the nodules nucleated at the alloy grain boundries. Internal sulphidation beneath these nodules has been observed (Fig. 5.20) concurrent with the Fe<sub>1-x</sub>S nodular growth. This is due to the fact that the Fe<sub>1-x</sub>S/alloy interface is exposed to a much lower sulphur potential corresponding to its sulphide dissociation pressure. Consequently the internal precipitates in the alloy are  $Al_2S_3$ . The higher thermodynamic activity of Al at this point also favours the formation of  $Al_2S_3$ . This mechanism of nodular growth is found to be similar to that for the growth of wustite-fayalite nodules on Fe-1.5wt%Si alloy in  $CO_2/CO$ atmospheres<sup>158</sup> and NiO-NiAl<sub>2</sub>O<sub>4</sub> nodules on Ni-6wt%Al alloy in oxygen<sup>163</sup>. Oxide nodular growth has also been observed on Ni-Cr<sup>159</sup>, CO-Cr-Al<sup>160</sup> and Fe-Cr<sup>161,162</sup> alloys.

It appears that the nodular sulphide phenomenon during sulphidation of the Fe-lOwt%Al alloy is governed by the large difference in  $^{2}$  the diffusion and thermodynamic properties of the sulphides. Nodules of the less stable sulphide (Fe<sub>l-x</sub>S) appear at the localized regions of the more protective and stable sulphide (Al<sub>2</sub>S<sub>3</sub>).

## 6.4 MECHANISM OF SULPHIDATION:

5.4.1 Introduction

When Fe-Al.alloy is exposed to a  $H_2S/H_2$  atmosphere, the following reactions can take place:

$$H_{g}S(g) = H_{g}(g) + S_{ade}$$

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(6.2)

Since FeS is a metallic conductor at temperatures above 411 K, adsorption of sulphur produces a neutral iron vacancy in the sulphide lattice and growth of the scale takes place by the diffusion of Fe through Fe vacancies.

$$S_{ads} = S_{s}^{X} + V_{Fe}^{X}$$
(6.3)

$$(v_{Fe}^{X})_{outer} = (v_{Fe}^{X})_{inner}$$
 (6.4)

$$(V_{Fe}^{X})_{inner} + Fe_{alloy} = Fe_{Fe}^{X}$$
 (6.5)

Adding equations (6.2) through (6.5), the overall reaction is given by:

$$H_2^{S(g)} + Fe_{alloy} = FeS + H_2^{(g)}$$
 (6.6)  
onsidering the free energy of formation of FeS and  $Al_2S_3^{O_3}$  ( $\Delta G_{FeS}^{O_1173} K$   
-42 KCa//mole of S<sub>2</sub> and  $\Delta G_{Al_2S_3}^{O_1173} K = -79.4$  KCal/mole of S<sub>2</sub>),  $Al_2S_3$   
s also formed during the initial reaction period,

 $2 \text{ Al}_{alloy} + 3 \text{ H}_2 \text{ S} = \text{Al}_2 \text{ S}_3 + 3 \text{H}_2$  (6.7)

The dissociation pressure of FeS in contact with pure Fe can be calculated by using Equation (3.3)  $(P_{S_2}^{diss. FeS} = 1.49 \times 10^{-8} \text{ atm} \text{ at 1173 K})$  and its value in contact with Fe-lowt% Al alloy can be calculated using the following equation.

$$K = \frac{a_{FeS}^2}{a_{Fealloy}^2 S_2}$$
(6.8)

where  $P_{S_2}$  is the dissociation pressure of FeS in contact with the alloy and K is the equilibrium constant for the reaction,
$$2Fe + S_2 = 2FeS$$
 (6.9)

defined by the equation,

$$K = \exp \frac{-\Delta G_{FeS}}{RT}$$
(6.10)

 $a_{Fes}$  is determined from the composition of the scale if in solid solution with Al<sub>2</sub>S<sub>3</sub> and a is determined from thermodynamic measurements plotted in Fig. 3.2.

# 6.4.2 Formation of Outer Layer

Formation of the outer  $Fe_{1-x}^{S}$  layer proceeds by the outward migration of Fe through iron vacancies. The initial iron sulphide layer exhibited whiskers or plates supplying a large surface area for the subsequent adsorption of sulphur in comparison to a solid compact FeS layer. Counts of the number of whiskers per unit area have been made by Fischmeister and et al.<sup>164</sup> and it has been reported that a surface area increase of 50 to 1000 percent is possible due to whisker formation. However, this only would be of importance when chemisorption of the gaseous reactant is the rate determining.

The outer layer of  $Fe_{1-x}^{S}$  is doped with Al (Fig. 5.24) but very high levels of Al were found by the microprobe analysis in localized regions (Figs. 5,25, 5.29). This is perhaps associated with the conversion of the Al<sub>2</sub>S<sub>3</sub> film sections buried beneath the growing  $Fe_{1-x}^{S}$ . phase to FeAl<sub>2</sub>S<sub>4</sub> via reaction of the type,

 $FeS + A1_2S_3 = FeA1_2S_4$ 

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(6.11)

# 6.4.3 Formation of Inner Layer

The mechanism for the growth of the inner layer containing  $Fe_{1-x}^{S} + FeAl_2S_4$  was ascertained from the marker experiments. It is inferred that the outer  $Fe_{1-x}^{S}$  layer grows by outward diffusion of Fe through Fe vacancies and the inner layer by the inward diffusion of sulphur. Since sulphur diffusion is too low in FeS (3.2 x  $10^{-12}$  Cm<sup>2</sup>/sec. at 1168 K), the source of sulphur supply for the growth of inner layer is by direct penetration of H<sub>2</sub>S if the outer scale is porous, or sulphur along the grain boundries from the source of adsorbed sulphur if the scale is compact. However, because of the compact nature of  $Fe_{1-x}^{S}$ at the base of the whiskers in the initial period and neglecting the inward diffusion of sulphur (from the source of adsorbed S) through grain boundries in the outer layer, the only source of sulphur supply will be from the dissociation of Fe<sub>1-x</sub> S at the Fe<sub>1-x</sub> S/alloy interface.

$$3 \operatorname{Fe}_{1+y}$$
S = 3(1-x)Fe + 3S (6.12

and

$$2 \text{ A1}_{(alloy)} + 3S_{alloy} = A1_2S_{3alloy}$$
 (6.13)

Reaction (6.13) is possible in the alloy beneath the  $Fe_{1-x}$  S/alloy interface because the high dissociation pressure of  $Fe_{1-x}$  S is sufficient to supply sulphur for the growth of  $Al_2S_3$  precipitates. The iron released from reaction (6.12) migrates outwards whereas sulphur diffuses inward through boundries between  $Al_2S_3$ /alloy or in the alloy phase by an interstitial mechanism: For each sulphur atom consumed through internal sulphidation, one iron atom is simultaneously removed from the  $Fe_{1-x}S_3$ layer at the  $Fe_{1-x}S$ /alloy interface. Due to the dissociative mechanism, vacancies condense, creating micropores and is counteracted by the increase in volume in the internal sulphidation zone (Expansion coefficient  $\Delta_{A1-A1_2S_3} = 3.7$ ,  $\Delta_{Fe-FeS} = 2.7$ )<sup>147</sup>. Addition of Equations (6.12) and (6.13) gives the displacement reaction of type (6.14).

$$3Fe_{1-x}S + 2A1_{alloy} = 3(1-x)Fe + A1_2S_3$$
 (6.14)  
alloy

However, such a solid state displacement is only possible when the path of Fe (released by reaction 6.14) is not hindered by the formation pores due to the condensation of vacancies close to the FeS/alloy interface and in the neighbourhood of  $Al_{2}S_{3}$  precipitates. If such pore formation exists, Fe flow to the growing outer layer becomes increasingly lean and the equilibrium sulphur pressure rises at the external pore surface. Because of the difference in sulphur pressure across the pore, dissociation of outer FeS (lean in Fe) occurs and sulphur is transferred to the Fe rich inner interface. At the dissociation sites, the excess Fe formed maintains the normal iron flux towards the outer  $Fe_{1-x}S/gas$ interface. The sulphur liberated from the dissociation reaction moves inward to form fresh  $Fe_{1-x}$ S in the inner scale in the vicinity of the internal precipitates. The inner layer grows at a low partial/ pressure of sulphur which perhaps favours the growth of the small sulphide crystallites (Fig. 5.10(a)). These crystallites may in turn bridge the crack and re-establish partial contact with the scale. In this way small pores remain within the scale (Fig. 5.10(a)). Thus formation of pores or cavities contribute considerably for the formation of  $Fe_{1-1}$ in the inner layer. The aluminium solubility in  $Fe_{1-x}^{1-x}S$  is low <sup>164</sup>.

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16- 6<sup>3</sup> AG < 1%, and therefore  $Al_2S_3$  precipitates will react with FeS in its vicinity to form a mixed sulphide of FeAl\_2S\_4 through reaction (6.11).

The FeAl<sub>2</sub>S<sub>4</sub> precipitates grow as rods in both inward and outward directions. This is suggested by the thickness of the inner layer protruding outward from the original gas/alloy interface as shown by 👒 the inert marker position several microns above this original inter-The shift of marker position can also be explained due to the face. formation of a porous layer consisting of fine  $Fe_{1-x}^{2}S$  crystallites at the base of the outer layer (Fig. 5.23) as observed in the sulphurization of copper  $^{167}$ . The growth of FeA1<sub>2</sub>S<sub>4</sub> rods can be interpreted as follows. Since the defect structure of  $FeA1_2S_4$  is unknown, it must be assumed that Al ions are mobile in it as in the case of NiAl  $20_4^{163}$ . From the sulphidation kinetics and scale microstructures, it is obvious that the  $FeAl_2S_4$  phase in the inner layer gives protection to the alloy by reducing the effective area for Fe diffusion through  $Fe_{1-x}^{3}S$ . It is therefore reasonable to make the assumption that Fe exhibits a very low mobility in FeAl<sub>2</sub>S<sub>4</sub>. At the Fe<sub>1-x</sub>S/FeAl<sub>2</sub>S<sub>4</sub> interface the following reaction can take place:

$$4FeS + 2A1^{3+} = FeA1_2S_4 + 3Fe^{++}$$
(6.15)

At the  $FeAl_2S_4/Al_2S_3$  interface,

$$4AI_{2}S_{alloy} + 3Fe_{alloy} = 3FeAI_{2}S_{4alloy} + 2AI_{alloy}$$
(6.16(a))

and in the alloy reaction 6.16(b) can take place:

 $^{2A1}alloy + ^{3S}alloy = ^{A1}2^{S}_{3alloy}$  (6.16(b))

Iron released through reaction (6.15) diffuses outward through Fe vacancies in Fe<sub>1-x</sub>S and Al released through reaction 6.16(a) is enriched near the alloy/scale interface. This is in qualitative agreement with the microprobe results (Figs. 5.25 and 5x29). Reaction 6.16(b) takes place at the interface since the activity of Al is high in this region. The alloy in between the FeA1<sub>2</sub>S<sub>4</sub> or A1<sub>2</sub>S<sub>3</sub> precipitates is sulphidized gradually by the sulphur released from the dissociation of FeS at pores in the inner layer. The inner layer is generally porus which may be attributed to the volume change associated with the formation of FeA1<sub>2</sub>S<sub>4</sub> rods. The more rapid formative rate of the inner layer (Fe<sub>1-x</sub>S + FeA1<sub>2</sub>S<sub>4</sub>) is perhaps associated with the rapid diffusion of gaseous sulphur species released through the dissociation reaction (6.12) to form sulphides by reactions (6.15) and (6.16).

The FeAl<sub>2</sub>S<sub>4</sub> rods are dense and do not have any sign of porosity (Fig. 5.21). The overall reaction rate at this stage decreases because the effective area for diffusion of Fe is reduced due to the limited supply of Fe through  $Fe_{1-x}$ S and from reaction (6.15). During this reaction stage, the  $Fe_{1-x}$ S/alloy interface moves inward by the formation of fresh  $Fe_{1-x}$ S in the inner layer.

6.4.4 Rod Morphology in the Inner Layer

The inner layer of the scale in Fe-lOwt%Al has been found to be a mixture of two phases,  $Fe_{1-x}^{S}$  and  $FeAl_2S_4$  (having a rod morphology Fig. 5.21). Rod morphology is observed generally in a certain volume fraction range of precipitates. Higher volume fraction of precipitates

leads to its continuous formation and a lower volume fraction leads to isolated precipitation. In this Fe-Al-S system, the Al percentage in the alloy is a deciding factor for determining the morphology of FeAl<sub>2</sub>S<sub>4</sub>. This consideration arises because for a given FeAl<sub>2</sub>S<sub>4</sub> volume fraction, the precipitate morphology will adjust to its stable configuration or shape when the total free energy is at a minimum.

# 6.4.5 <u>Formation of a Continuous A</u>l<sub>2</sub>S<sub>3</sub> <u>Layer at the Alloy/Scale</u> Interface

Growth of the inner  $Fe_{1-x}S + FeAl_2S_4$  layer as plotted in Figs. 5.15 and 5.16, decreases to a very low scaling rate (2.136  $\times$  10<sup>-8</sup>  $cm^2/sec.$ ) after 1/2 hour of sulphidation at  $P_{S_2} = 1 \times 10^{-3}$  atm. This phenomenon initially occurs at isolated places during first 1/2 hour near the alloy/scale interface and it is attributed to the formation of FeAl<sub>2</sub>S<sub>4</sub> and Al<sub>2</sub>S<sub>3</sub> layers. Contact between the inner heterophase layer ( $Fe_{1-x}S + FeAl_2S_4$ ) and alloy is isolated at these sites, once the  $Al_2S_3$  layer develops at the scale/alloy interface. The preferential sites for  $Al_2S_3$  formation at the interface could not be ascertained in the present work. However, it was a general observation that the impingment of FeAl<sub>2</sub>S<sub>4</sub> rods at isolated sites near the alloy/scale  $_{2}$ interface (Figs. 5.12 and 6.1) leads to a decrease in sulphidation rate due to the partial blockage of Fe supply from the bulk alloy to the inner and outer scale layers. Further corrosion leads to the growth of existing  $Al_2S_3$  precipitates at the FeAl\_2S\_4/alloy interface to form a continuous  $Al_2S_3$  film as will be shown in Fig. 6.4. It is appropriate to mention here that, it takes approximately 3 hours for the

# FIGURE 6.1 Scale cross-section showing impingement of FeAl $_2$ S $_4$ rods at random sites.

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FIG. 6.1 175

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 $Al_2S_3$  film to appear throughout the scale/alloy interface, thereby decreasing the corrosion rate by an order of magnitude (Table 5.1). Lateral growth of an  $Al_2S_3$  film is possibly initiated at these regions of rod impingement if aluminium enrichment occurs in the alloy between the  $Al_2S_3$  needles by reaction 6.16(a).

$$4A12^{S}3_{alloy} + 3Fe_{alloy} = 3FeA12^{S}4_{alloy} + 2A1_{alloy}$$
 (6.16(a))

Formation of an  $Al_2S_3$  film at the alloy/scale interface does not necessarily involve direct impingement of the FeAl $_2$ S $_4$  rods. The aluminium concentration at a particular site near the three phase (Alloy,  $Fe_{1-x}S$ ,  $FeA1_2S_4$ ) region (Fig. 6.3) is increased during the reaction period by two processes. In the first process,  $Fe_{1-x}^{S}$  acts as a low resistance path for Fe diffusion in comparison to its original path through the alloy ( $\tilde{D}$  in Fe<sub>1-x</sub>S is 9 x 10<sup>-6</sup> Cm<sup>2</sup>/sec. whereas  $\tilde{D}$  in  $\alpha$ -Fe-Al alloy is 5.2 x 10<sup>-10</sup> Cm<sup>2</sup>/sec. at 1173 K). Therefore, Fe is released through  $Fe_{1-x}$ S at a rate approximately 4 orders of magnitude higher than the interdiffusion in the alloy. Since Al diffusion is negligible in  $Fe_{1-x}S$ , the aluminium concentration will increase at the  $Fe_{1-x}S - FeAl_2S_4$  - alloy region (Fig. 5.24). In the second process Al is released into the  $Fe_{1-x}$  -  $FeAl_2S_4$  - alloy region by reaction 6.16(a). Consequently, the aluminium activity can attain a sufficiently high value to react with sulphur in the alloy to form Al<sub>2</sub>S<sub>3</sub> by reaction 6.16(b). These precipitates would continue to grow laterally by these two above processes to ultimately lead to Al<sub>2</sub>S<sub>3</sub> film bridges across the original  $A1_2S_3$  platelets. The electron probe traces shown in Figs. 5.24 and 5.25

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showing an increase in the Al concentration of the alloy possibly give support to these considerations. The lateral growth of the innermost  $Al_2S_3$  film would involve the simultaneous growth of a FeAl\_2S\_4 layer on its upper surface in accordance with the following reaction.

$$FeS + A1_2S_3 = FeA1_2S_4$$

Careful compositional and structural analysis demonstrated the occurrence of this  $\text{FeAl}_2S_4$  layer (Fig. 5.37). Simultaneous diffusion of iron and aluminium would cause its continual growth. It was not possible, however, to distinguish the relative the thicknesses of  $\text{FeAl}_2S_4$  and  $\text{Al}_2S_3$  in the innermost sulphide layer.

In the present work it was not possible to establish conclusively whether the nucleation and growth of the  $Al_2S_3$  film was due either to the impingement of favourably oriented  $FeAl_2S_4$  rods leading to the bridging of  $Al_2S_3$  platelets under these sites or to the relieve of supersaturation arising from the difference in Fe diffusion coefficient in the  $Fe_{1-x}S$  phase and alloy. However, in the present case a combination of both mechanisms is suggested for the growth of  $Al_2S_3$  layer at the alloy/scale interface.

## 6.5 SULPHIDATION MODEL: .

A model for the sulphide scale growth and internal sulphidation of the Fe-lowt%Al alloy exposed to  $H_2S/H_2$  atmospheres at  $P_{S_2}$ between 1 x 10<sup>-3</sup> and 1 x 10<sup>-4</sup> atm. is suggested in the following. This model is illustrated by referring to the previously presented and described photomicrographs and schematic models shown in this section.

During the initial reaction stage a discontinuous  $Al_2S_3$  layer was formed rapidly (in view of its thermodynamic stability) by dissolving the residual aluminium oxide on the alloy surface (Figs. 5.18 and 6.2(a)).  $Fe_{1-x}S$  then nucleated at the defective sites (or leakage paths) of this film to form well defined mushroom shaped nodules. These nodules exhibit whiskers and plates of pyrrhotite and grow at a faster rate than  $Al_2S_3$ . The alloy beneath these nodules is simultaneously sulphidized internally producing  $Al_2S_3$  precipitates. Growth of  $Fe_{1-x}S$  during the initial reaction stage in the outer compact layer below the whiskers (Fig. 5.20) suggests that formation of the  $Fe_{1-x}S$ +  $FeAl_2S_4$  inner layer and internal precipitation of  $Al_2S_3$  is as a result of diffusion and displacement reactions. Following the initial nodular growth period, as illustrated in Figs. 6.2(b) and (c), a continuous outer and inner layer is formed over the entire alloy surface (Figs. 5.20(d) and 6.2 (d)).

The model for the outer layer growth involves diffusion of Fe from the bulk alloy, and from reaction 6.15 through iron vacancies in the Fe<sub>1-x</sub>S, the flux of which is given by  $^{134}$ ,

$$j_{Fe} = -C_{Fe} D_{Fe} \frac{d \ln a_{Fe}}{dx}$$
(6.17)

where  $C_{Fe}$ ,  $D_{Fe}$ ,  $a_{Fe}$  are iron concentration, self-diffusion coefficient and activity respectively. The parabolic rational rate constant for the Fe<sub>1-a</sub>S layer is given by<sup>131</sup>,

$$K_r = \tilde{D} \cdot \frac{\Delta S}{\tilde{L}}$$

(6.18)



(Cont'd ... 181)

where v is the equivalent volume of  $Fe_{1-\delta}^{S}$  and  $\delta$  (referred to 'x' earlier) is the non-stoichiometry in  $Fe_{1-\delta}^{S}$  S which increases asymptotically with sulphur pressure (Equation 3.10). A direct variation of K<sub>r</sub> with the non-stoichiometry (Equation 6.18) and asymptotic dependence of  $\delta$  on the P<sub>S2</sub>, leads to higher reaction rates at higher P<sub>S2</sub> for the Fe-10wt%A1 alloy. This is because, the major volume fraction of the scale is  $Fe_{1-\delta}^{S}$ . However, this is merely a qualitative interpretation because, the double sulphide (FeAl<sub>2</sub>S<sub>4</sub>), Al<sub>2</sub>S<sub>3</sub> and micropore formations in the inner layer effect the kinetics of Fe<sub>1-x</sub>S scale growth in the outer layer.

The nodules grow laterally and vertically to coalesce with other nodules (Figs. 5.17, 5.20, 6.2(b)(c)). A continuous outer and inner layers is formed over the alloy after a certain period of time (Figs. 5.20(d), 6.2(d)). The FeAl<sub>2</sub>S<sub>4</sub> rods grow in both inward and outward directions by sulphur and aluminium diffusion, respectively as described in Section 6.4.3 through reactions 6.15 and 6.16. The  $Fe_{1-x}S + FeAl_2S_4$  zone always extends parallel to the growth direction and independent of alloy grain orientation (Fig. 5.12).

Figure 6.3 shows a schematic growth model for the two-layer scale growth during the first parabolic period following rates  $K_1$  and  $K_1^i$  at different sulphur pressures (Fig. 5.2). No attempt has been made to show the presence of a small volume fraction of porosity (Fig. 5.21) in these schematic models. The rods of FeAl<sub>2</sub>S<sub>4</sub> (average diameter 3  $\mu$ m) are aligned perpendicular to the alloy/scale and gas/ scale interfaces with an average spacing of 4.5  $\mu$ m. The incorporation

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FIGURE 6.2



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FIGURE 6.3

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of FeAl<sub>2</sub>S<sub>4</sub> rods into the alloy upto the three phase region of Al<sub>2</sub>S<sub>3</sub>, FeAl<sub>2</sub>S<sub>4</sub> and alloy was not verified due to the limitation of the measurement techniques used in the present work. The schematic models shown in Figs. 6.2 and 6.3 describing the above sulphidation features do not completely describe the sulphidation kinetics. In some samples an Al<sub>2</sub>S<sub>3</sub> layer formed beneath the internal sulphidation zone of the nodules (Fig. 6.2(b)) during the transient period, perhaps by the lateral diffusion of Al from the neighbouring sites where a continuous Al<sub>2</sub>S<sub>3</sub> layer had formed at the gas/alloy interface.

The formation of a partial continuous layer of  $Al_2S_3$  near the alloy/scale interface was described in Section 6.4.5 and attributed to the impingement of FeAl\_2S\_4 rods at random sites and supersaturation of Al at  $Al_2S_3$ , FeAl\_2S\_4 and alloy regions leading to its precipitation as  $Al_2S_3$ . A schematic growth model showing the impingement of FeAl\_2S\_4 rods at isolated sites leading to a continuous  $Al_2S_3$  film at the alloy/scale interface is shown in Figure 6.4. The model for the final reaction stage will be shown in Figure 6.5.

The Al<sub>2</sub>S<sub>3</sub> film perhaps acts as an effective barrier permitting at most only a very small supply of iron from the alloy to the inner layer. The Al<sub>2</sub>S<sub>3</sub> layer is always associated with a layer of FeAl<sub>2</sub>S<sub>4</sub> on its upper surface (by reaction 6.11) which separates it from the inner Fe<sub>1-x</sub>S + FeAl<sub>2</sub>S<sub>4</sub> heterophase layer. This final sulphidation process reaches a final parabolic reaction stage after which corrosion takes place in the presence of a complete Al<sub>2</sub>S<sub>3</sub> layer at the alloy/scale interface. The model for this reaction stage is shown in Fig. 6.5. FIGURE 6.4 Schematic representations showing the impingement of  $FeAl_2S_4$  rods at isolated sites. Beneath the thin  $FeAl_2S_4$  layer a continuous  $Al_2S_3$  film and platelets or needles form. The model for the final morphology is shown in Figure 6.5.

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SCHEMATIC MODEL FOR THE SCALE GROWTH DURING THE FINAL PARABOLIC PERIOD ON THE Fe-IOwt%AI ALLOY AT 900°C PS2 \* 1x10-401m

FIGURE 6.5

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The continuous  $Al_2S_3$  and internal sulphidation zone is clearly seen in Figs. 5.14 and 5.44. Precipitation of  $Al_2S_3$  as needles or platelets beneath the  $Al_2S_3$  layer suggests that S is mobile in FeAl\_ $2S_4$  and  $Al_2S_3$ and supplied from the dissociation of FeS in the inner layer. Outward growth of the FeAl $_{2}$ S<sub>4</sub> layer at this stage would take place by outward diffusion of Al to react with FeS by reaction (6.15). Growth of  $Al_2S_3$ . layer as well as  $Al_2S_3$  precipitates may take place concurrently by the outward diffusion of Al and inward diffusion of sulphur in the alloy. The high levels of internal sulphidation beneath the  $Al_2S_3$  layer could be due to the rapid ionic diffusion of sulphur inwards at the experimental temperature of 1173 K which is about 0.85  $T_m$  of Al<sub>2</sub>S<sub>3</sub> (melting point of  $Al_2S_3$  is 1373 K). The protective property of  $Al_2S_3$  is therefore decreased. The average width of the  $Al_2S_3$  platelets or needles beneath the  $Al_2S_3$  film range from 0.8 to 1  $\mu$ m in a total sulphidation time of 14,000 seconds. Generally these platelets grow in a direction normal to the original alloy surface and to the reaction front, their orientation being independent of the prior alloy grain structure.

It is possible that  $Al_2S_3$  needles or platelets beneath the continuous  $Al_2S_3$  film have formed as a result of both morphological breakdown of the  $Al_2S_3/alloy$  interface and internal sulphidation. These features are suggested by the morphologies shown in Figs. 5.14 and 5.44 where precipitates of  $Al_2S_3$  are shown to emerge from the  $Al_2S_3$  layer into the alloy and also as isolated needle or platelet precipitates in the alloy. In the former case, the tips of the alloy in between two  $Al_2S_3$  precipitates have spherodized and give rise to isolated alloy

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particles (rich in Fe) embedded in the continuous  $Al_2S_3$  scale (Fig. 5.44). In the latter case further growth of the  $Al_2S_3$  internal precipitates takes place due perhaps to the inward diffusion of sulphur and lateral diffusion of Al from the alloy. The Wagner criterion for planar interface instability,

$$\frac{X_{A1}}{1-X_{A1}} = \frac{\begin{pmatrix} D_{A1}/V \\ alloy \\ (D_{A1}/V) \\ sulphide(Al_2S_3) \end{pmatrix}}{\begin{pmatrix} D_{A1}/V \\ alloy \\ black \\ sulphide(Al_2S_3) \end{pmatrix}} < 1$$

and the more comprehensive model for interface stability proposed by Coates and Kirkaldy<sup>60</sup> could not be tested due to the lack of experimental data.

# 6.6 CORRELATION OF SULPHIDATION MODEL TO THE FE-A1-S ISOTHERM:

The ternary Fe-Al-S isotherm has never been reported in the literature. However, from the binary phase extents (from Figs. 3.1, 3.6 and 3.11) at 1173 K and results from this investigation, one can speculate as to the form of the ternary isotherm as shown in Fig. 6.6(a).

Pure Fe and Al dissolve upto 0.05 and 5 to 5.5 atomic percent sulphur respectively at 1173 K. These concentrations and the sulphur solubility in the alloy are presented by a dotted line and a solid line on the isotherms as shown in Figs. 6.6(a) and 6.8 respectively. The solubility of Al and Fe, respectively in  $Fe_{1-x}S$  and  $Al_2S_3$  is unknown at present. A ternary phase based on the composition of FeAl\_2S\_4 has been reported in the literature 137,143. Its method of preparation and structure have also been described in Section 3.5.1. The phase extents of  $\text{FeAl}_2S_4$  by equilibrating the alloy with FeS and 'Al\_2S\_3 have not been determined. Accordingly, the construction of three-phase triangles and two-phase regions shown in Fig. 6.6(a) is intended to be schematic, since the actual terminal compositions are unknown.

The isothermal diffusion controlled formation of a sulphide scale of uniform thickness on the planar surface of a binary alloy can be considered as a three phase (vapour-sulphide-alloy) ternary diffusion couple. The corresponding diffusion path can be calculated (using Equation 2.39) and then plotted on the appropriate ternary isotherm as illustrated in Fig. 6.7. Two possible  $^{60}$  configurations are shown in this figure. In the first case (dotted line MN), a region of supersaturation isolated from the AS/alloy interface is indicated by the calculated diffusion path. This leads to the precipitation of sulphide within the alloy phase upon relief of supersaturation and is referred to as internal sulphidation. In the second case, solid line KN, a region of supersaturation in contact with the interface can relieve supersaturation through a transition from planar to non-planar morphology by the growth of AS precipitates emerging from the As scale. If the calculated diffusion path associated with the second possibility cuts deeply into the two-phase field, internal sulphidation as well as morphological breakdown will result.

Sulphidation of the Fe-Alalloys led to complicated sulphide morphologies which evolved to a final structure containing a multilayer



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Virtual diffusion paths and corresponding scale microstructures (schematic) on Fe-IOwt%AI and Fe-I5wt%AI alloys at 900°C and  $p_{S2} = 1 \times 10^{-4}$  atm FIGURE 6.6(b)

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FIGURE 6.7 Isothermal section of a phase diagram ABS relevant to alloy sulphidation. The lines MNOPQ and MNOPQ are two possible calculated diffusion paths corresponding to uniform sulphidation of a binary alloy AB of composition given by a point M to form a sulphide AS.

scale and an internal sulphidation zone. The sulphidation rates continually decreased and it was found that two regions in each reaction curve could be approximated to different rates of parabolic sulphida-The scale microstructures for these two regions of parabolic tion. sulphidation of the Fe-lOwt% Al alloy and also for parabolic growth of an  $Al_2S_3$  scale on the Fe-15wtwt% Al alloy are schematically shown in Fig. 6.6(b). Virtual diffusion paths on the ternary Fe-Al-S isotherm corresponding to these stages of parabolic sulphidation and microstructures are shown in Figs. 6.6(b) and 6.8. For Fe-10wt% Al two paths are shown. (path X and 1) in Fig. 6.8. The path X (path AXMOPQRSTU in Fig. 6.8) represents the diffusion path during the initial period, during which there is a greater depletion of Al from the bulk and no continuous formation of FeAl<sub>2</sub>S<sub>4</sub> and Al<sub>2</sub>S<sub>3</sub> occur. Two regions of virtual supersaturation (AXM 'and 'RST in Fig. 6.8) are shown on the isotherm leading to the precipitation of  $A1_2S_3$  in the alloy and  $FeA1_2S_4$  in  $Fe_{1-x}S$ . In these cases the virtual path cuts tie lines in two-phase fields and crosses three phase fields.

When a final parabolic reaction stage is reached due to the development of a continuous inner layer containing FeAl<sub>2</sub>S<sub>4</sub> and Al<sub>2</sub>S<sub>3</sub>, the diffusion path representing the sulphidation reaction is given by Path 1 (path A1BCDEF in Fig. 6.8). This path enters well into the two phase region (alloy + Al<sub>2</sub>S<sub>3</sub>) at cn angle to the tie lines and exits coincident with one of them: The two phase zone contains isolated needles and/or plates of Al<sub>2</sub>S<sub>3</sub> (due to internal sulphidation) and non-isolated plates of Al<sub>2</sub>S<sub>3</sub> rooted in the parent phase (continuous Al<sub>2</sub>S<sub>3</sub> layer) due to



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morphological breakdown of the  $Al_2S_3$ /alloy interface. This path is represented in both Figures 6.6 (b) and 6.8.

The diffusion path for Fe-15wt% Al alloy which exhibits a thin layer of  $Al_2S_3$  is shown by Path 2 ( $A_2B_2C_2D_2E_2$  in Figs. 6.6(b)). Insignificant depletion of Al occurs by the formation of an outer  $Al_2S_3$  layer.

6.7 SUMMARY:

The sulphidation properties of Fe-lOwt% Al alloy at 1173 K and in  $H_2S/H_2$  atmospheres were studied with respect to the kinetics and sulphide scale growth. The sulphur pressures ranged from 1 x  $10^{-2}$  to 1 x  $10^{-5}$  atm.

The kinetics were approximated to parabolic in all cases. The sulphidation curves at two sulphur pressures  $(1 \times 10^{-3} \text{ and } 1 \times 10^{-4} \text{ atm})$ , were approximated to two-stage parabolic behaviour in which the final corrosion rate was approximately an order of magnitude less than the initial corrosion rate. In the initial exposure stages,  $\text{Fe}_{1-x}$  S nodules were formed at isolated sites in the  $\text{Al}_2\text{S}_3$  film. The scale microstructures were complex with an outer layer of  $\text{Fe}_{1-x}$ S,  $\text{FeAl}_2\text{S}_4$  (having a rod morphology) and  $\text{Al}_2\text{S}_3$ . From inert marker experiments it was established that the outer layer grows by outward Fe diffusion and inner layer by inward sulphur diffusion. During the later stage of reaction, a continuous layer of  $\text{Al}_2\text{S}_3$  covered the alloy surface completely.

It was shown that the co-operative growth of two phases  $(Fe_{1-x}^{S} + FeAl_2^{S}S_4)$  in the inner layer occurred through the conversion

of the internal sulphidation zone (alloy +  $Al_2S_3$ ) due to sulphidation by sulphur released from the dissociation of  $Fe_{1-x}S$  at the scale/alloyinterface. At this reaction stage, the decrease in sulphidation rate of the alloy was interpreted as being caused by the combined effect of a decrease in effective area of  $Fe_{1-x}S$  for Fe diffusion and a reduction in the diffusion rate of iron by a vacancy mechanism in  $Fe_{1-x}S$  due to localized strain resulting from a small Al solubility in  $Fe_{1-x}S$ .

The growth of the inner film containing  $\text{FeAl}_2S_4$  and  $\text{Al}_2S_3$  layers was interpreted in one of the two ways. Firstly, the impingement of  $\text{FeAl}_2S_4$  rods at isolated sites leads to the growth of existing  $\text{Al}_2S_3$  precipitates beneath the  $\text{FeAl}_2S_4$  layer. Secondly, the supersaturation of Al in the  $\text{Fe}_{1-x}S$ ,  $\text{FeAl}_2S_4$  and alloy region (due to 4 orders of magnitude difference in the values of iron diffusion coefficients in  $\text{Fe}_{1-x}S$  and in the alloy) leads to massive precipitation of  $\text{Al}_2S_3$  and  $\text{FeAl}_2S_4$ .

The morphological breakdown of the Al<sub>2</sub>S<sub>3</sub>/alloy interface accompanied by internal sulphidation was attributed to a high diffusivity of Al in Al<sub>2</sub>S<sub>3</sub> than in the alloy and inward diffusion of sulphur respectively. Rapid diffusion of sulphur inwards and a concurrent diffusion of Al outwards through Al<sub>2</sub>S<sub>3</sub> is suggested to increase the thicknesses of this film and of the internal sulphidation zone in the alloy as well as the FeAl<sub>2</sub>S<sub>4</sub> layer beneath the inner Fe<sub>1-x</sub>S + FeAl<sub>2</sub>S<sub>4</sub> scale layer.

During the final slow sulphidation stage of the Fe-10wt% Al alloy, the overall reaction was associated with several processes involving diffusion mechanisms in the fully developed scales containing layers

of  $Fe_{1-x}^{S/Fe}_{1-x}^{S} + FeAl_2^{S}_4/FeAl_2^{S}_4/Al_2^{S}_3$  and the internal sulphidation zone containing  $Al_2^{S}_3$  precipitates.

A ternary Fe-Al-S isotherm was constructed from the respective binaries and present experimental findings. Virtual diffusion paths were shown on this isotherm consistent with the development of the scale microstructures.

#### CHAPTER 7

#### CONCLUSIONS

- 1. The sulphidation kinetics of Fe-10wt% Al alloy at 1173 K in  $H_2S/H_2$  atmospheres are slower than pure Fe at all sulphur pressures (1 x 10<sup>-2</sup> atm to 1 x 10<sup>-5</sup> atm). The kinetics approximate to parabolic behaviour and increase with increasing P<sub>S2</sub>. At two sulphur pressures (1 x 10<sup>-3</sup> atm and 1 x 10<sup>-4</sup> atm) the kinetics transformed from an initial parabolic stage to a much slower final parabolic stage.
  - 2. During the initial period of sulphidation a thin layer of  $Al_2S_3$ is formed on the alloy by selectively dissolving the thin residual oxide film on the metallographically polished alloy specimens.  $Fe_{1-x}S$  nodules nucleate at defective sides (leakage paths) of the  $Al_2S_3$  film and grow (by the migration of Fe through iron vacancies in  $Fe_{1-x}S$ ) laterally and vertically at  $P_{S_2} = 1 \times 10^{-3}$  atm and  $1 \times 10^{-4}$  atm. The alloy beneath the nodule is sulphidized internally by the precipitation of  $Al_2S_3$  in the alloy matrix.
- 3. The formation of internal sulphides has a direct bearing on the sulphidation rate, since the sulphur required to form internal sulphide is produced by the dissociation of  $Fe_{1-x}S$  at the alloy/  $Fe_{1-x}S$  nodule interface.

- 4. The internal sulphidation zone is converted to a  $Fe_{1-x}S + FeAl_2S_4$  layer by further sulphidation due to the inward diffusion of sulphur. A final parabolic stage is obtained corresponding to the growth of a film containing layers of  $FeAl_2S_4$  and  $Al_2S_3$  at the alloy/scale interface.
- 5. The formation of a film containing  $\text{FeAl}_2S_4$  and  $\text{Al}_2S_3$  layers at the alloy/scale interface is explained by an impingement model due to which impingement of  $\text{FeAl}_2S_4$  rods at random sites aid in the growth of the existing  $\text{Al}_2S_3$  precipitates to form a continuous layer underneath these impingement sites and by the supersaturation of Al in the alloy beneath the  $\text{Fe}_{1-x}S + \text{FeAl}_2S_4$  inner layer interface due to large difference in magnitude of Fe diffusivities in the Fe<sub>1-x</sub>S and the alloy.
- 6. The sulphidation rate of the Fe-l0wt% Al alloy during the final reaction stage was dependent on several factors, such as: dissociation of FeS in the inner scale layer, several growth and diffusion processes taking place in the Fe<sub>1-x</sub>S/Fe<sub>1-x</sub>S + FeAl<sub>2</sub>S<sub>4</sub>/FeAl<sub>2</sub>S<sub>4</sub>/Al<sub>2</sub>S<sub>3</sub> zones. Therefore a rate controlling step could not be suggested.
- 7. From the present experimental results and the data from the respective binaries in the Fe-Al-S system, a ternary Fe-Al-S isotherm was constructed at 1173 K. Consistent with the scale microstructures, virtual diffusion paths were shown on this isotherm.

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#### CHAPTER 8

#### SUGGESTIONS FOR FUTURE WORK

An investigation has been completed on the sulphidation kinetics and morphological development of the corrosion products on Fe-lowt% Al alloy at 1173 K. Since the defect structures and diffusional properties of the various sulphide phases containing Fe, Al, S and Al, S are unknown, quantitative or at least a semi-quantitative interpretation of the sulphidation mechanism was not possible. An attempt must therefore be made to determine the transport properties of different species in various Fe-Al sulphide phases.

The Fe-10wt% Al alloy developed an  $Al_2S_3$  film at the alloy/ external scale interface in the final reaction stage, in the presence of which corrosion proceeded at a very slow rate. Therefore, in future, the transition from internal  $Al_2S_3$  precipitation to a continuous  $Al_2S_3$ film formation at the alloy/external scale interface should be determined by studying the kinetics, microstructure and diffusional properties of Fe-Al alloys having less than 10wt% Al.

Since an external protective scale of  $Al_2S_3$  is solely formed on Fe-Al alloys containing Al greater than 15 wt%, attempts should be made to study the sulphidation kinetics of alloys containing larger Al contents and diffusional properties for metal and sulphur in the  $Al_2S_3$ phase.

Possibility of using various intermetallic phases of Fe-Al system could possibly serve as constituents of protective coatings for sulphidation resistance. The sulphidation properties of these Fe-Al intermetallic phases should be explored. Addition of a third element (Ti, Mn, Mo) to Fe-Al alloys could also be considered to determine if appropriate concentration influences the subsequent sulphidation kinetics, mechanism and scale microstructures.

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The Fe-Al-S isotherm is not quantitatively known. The presently advanced isotherm requires verification using equilibrated phases and results from structural determinations and quantitative compositional estimations from diffusion couple measurements.

## APPENDIX I

1. Calculation of thermodynamic data for FeS: Between 773 and 1261 K (eutectic temperature) the gas ratio  $H_2^{S/H_2}$ , for the reaction,

$$Fe + H_2 S = FeS + H_2$$
 (I-1)

is given by the following expression.

$$\log(H_2S/H_2) = \frac{-3100}{T} + 0.179$$
 (I-2)

The corresponding Gibb's free energy is given by,

$$\Delta G^{\circ} = RT \ln\left(\frac{H_2 S}{H_2}\right)$$
(I-3)

$$\Delta G^{0} = 4.576 T(\frac{-3100}{T} + 0.179)$$
  
$$\Delta G^{0} = -14.186 + 0.00082KCa1$$
 (I-4)

From the work of Richardson and Jeffes 104, the free energy for the reaction,

$$2H_2 + S_2 = 2H_2S$$
 (I-5)

is given as,

$$\Delta G^{\circ} = -43.16 + 0.02361 \text{ T KCal/mole of S}_2 (I-6)$$

Therefore, the free energy for the reaction

$$2Fe + S_2 = 2FeS \qquad (I-7)$$

is given by,

 $\Delta G^{\circ} = -71.532 + 0.02525 T KCal/Mole of S<sub>2</sub>$ 

There are other available data from Sudo<sup>105</sup> given by,

$$\Delta G^{\circ} = -71.25 + 0.02462 \text{ T KCal/mole of S}_2$$
 (I-8)

and Alcock and Richardson<sup>106</sup>,

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$$\Delta G^{\circ} = -71.82 + 0.02512$$
 T KCal/mole of S<sub>2</sub> (I-9)  
The recent paper by Jacob et al.<sup>107</sup> reviews the Fe-S binary system  
and established the standard free energy for the reaction,

$$(1-x)Fe(S) + 1/2S_2(g) \longrightarrow Fe_{1-x}S(S)$$
 (I-10)  
 $\Delta G^0 = -151.500 + 54.1 T(+1500) \text{ Joules/mole of FeS}$  (I-11)

From the work of Nagamori and et al.<sup>92</sup>, the standard free energy for the reaction (I-10) in the range of 1073 K to 1373 K is given by  $\Delta G^{0} = -34.95 + 0.01254 \sqrt{(\pm 0.5)}$ KCal/mole of sulphide (I-12)

# 2. Calculation of dissociation pressures:

For the following reaction at 1173 K

$$2Fe + S_2 = 2FeS$$
 (I-7)  
 $\Delta G^0 = -42 \text{ KCal/mole of S}_2$ 

The equilibrium constant for reaction (I-7) is given by,

$$K = \exp \frac{-\Delta G^{O}}{RT} = \frac{a^{2} FeS}{a^{2} Fe^{2} P^{*}_{S_{2}}}$$

where  $P_{S_2}^{\star}$  is the dissociation pressure of FeS on pure Fe. At 1173 K,  $P_{S_2}^{\star} = 1.49 \times 10^{-8}$  atm. (I-13)

For Fe-10wt% Al alloy,

and

 $^{2\text{Fe}}$ alloy +  $^{5}$ <sub>2</sub> = 2FeS
$$K = \exp \frac{-\Delta G^{O}}{RT} = \frac{a_{FeS}^{2}}{a_{Fealloy}^{2} \cdot P_{S2}^{P}}$$

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Using the Fe-Al activity data  ${}^{a}_{Fe} = 0.61$  for Fe-lowt% Al alloy the dissociation pressure of FeS is calculated as follows, assuming the  ${}^{a}_{FeS} = 1$ .

$$6.7114 \times 10^7 = \frac{1}{0.37 \times P_{S_2}^{diss.}}$$

$$P_{S_{2_{j}}}^{\text{diss.}} = 4 \times 10^{-8} \text{ atm.}$$
(I-14)

From the free energy data for  $Al_2 S_3^{100}$ ,

$$\frac{4}{3} A1 + S_2 = 2/3 A1_2 S_3$$
 (I-15)

 $\Delta G^{0} = -79 \text{ KCal/mole of } S_{2} \text{ at } 1173 \text{ K from which}$   $P_{S_{2}}^{\star} \text{ is calculated.}$   $K = \exp \frac{-\Delta G^{0}}{RT} = \frac{a_{A1_{2}}^{2/3}}{a_{A1_{2}}^{4/3} P_{S_{2}}^{\star}}$ 

at 1173 K for pure A1,  $P_{S_2}^* = 1.9 \times 10^{-15}$  atm. (I-16) For Fe-10wt% A1 alloy with  $a_{A1} = 2.2 \times 10^{-3}$ ,

$$P_{S_2}^{diss} = 6.657 \times 10^{-12} \text{ atm.}$$
 (I-17)

Similarly, for  $Al_2O_3$  on pure Al at 1173 K the dissociation pressure is given by,

$$P_{0_2}^* = 6.636 \times 10^{-39} \text{ atm.}$$
 (I-18)

On Fe-10wt% Al alloy the value is

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$$P_{0_2}^{\text{diss.}} = 2.215 \times 10^{-35} \text{ atm.}$$
 (I-19)

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