

LIQUID PHASE ROUTES TO THE FORMATION
OF
ALUMINA-METAL COMPOSITES

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THESIS ABSTRACT

This thesis concerns methods of producing alumina and alumina/metal composites via routes involving the liquid phase. Two separate and distinct systems were investigated. In the first an iron matrix containing alumina/hercynite is produced by competitive combustion of iron and aluminium. In the second an aluminium-infiltrated alumina is produced by self-sustained catastrophic oxidation of an aluminium alloy melt. Each of the principal processes further sub-divides into two routes.

An iron/steel matrix containing alumina has been produced by:-

[a] an aluminothermic lance made up of concentric tubes of aluminium and steel through which oxygen is blown. To produce the composite the lance is fired into a steel mold such that the reaction is submerged in the melt.

[b] a crucible of molten ferro-aluminium into which is injected a non-consumable oxygen lance.

In both [a] and [b] a highly reactive aluminothermic slag is continuously produced which enables the ignition of aluminium by fluxing the alumina which may otherwise stop the reaction by forming a solid alumina coating around the aluminium. The iron behaves catalytically.

An alumina-matrix/aluminium-infiltrated composite has been produced by two routes. In the first [i] an alloy of aluminium, silicon, and magnesium is heated in a muffle furnace under atmospheric air. After an incubation period during which a molten glass is formed by magnesia, silica, and alumina, at the top of the crust, the growth of the ceramic crust results from the gas phase reaction of pore-transported aluminium over the tops of the pores. [ii] The second route utilises a molten top-glass formed out of the three oxides directly applied as powders prior to heating the aluminium charge. The resulting product is the same for each route.

PREFACE

This thesis examines two separate and distinct composite systems: alumina dispersals in steel on the one hand, and aluminium-infiltrated corundum on the other.

The work done on the steel/alumina system was initiated at Hong Kong University in the Department of Industrial Engineering. The aluminothermic lance which will be discussed was a by-product of an environmental programme aimed at energy and materials recovery at a Hong Kong Government waste incinerator. The original aims were to increase the output of the incinerator thermoelectric generators. The lance was developed as a convenient way to demonstrate that aluminium can be made to burn stably in the presence of iron and was based upon the industrial technique of flame cutting aluminium plate, which is made possible by the entrainment of iron powder in the oxy-acetylene torch flame.

Since the lance is also, in effect, a combination of the oxy-iron thermic lance on the one hand and of the so-called thermit welding on the other, many useful applications of the lance, in its own right, suggested themselves [see patent application appendix 2]. Some of these are:-

- # The cutting and boring of concrete and rock at speeds several times those of conventional oxy-iron lances.

- # The underwater cutting of steel and concrete afforded by the abundant exothermic heat available.

A simple solid state substitute for thermit welding powders.

A cheap, self-heated, source of cast steel [and, perhaps, of molten alumina].

This last application led to the discovery that the turbulence associated with firing the lance into a casting mold, entrapped finely dispersed alumina particles created as a by-product by the combustion process.

Thus, the major part of the work done on the lance was on the technological development of the lance rather than a study of an alternative route to metal matrix composites. Nevertheless, the unanticipated discovery that such composites were produced led to the inclusion of the process within the present investigation and, in the event, has contributed further perspectives to knowledge concerning alumina-metal composite formation via liquid phase routes.

The other main area of the work done for this thesis concerns an investigation of the mechanisms of alumina formation by growth on an aluminium alloy melt. [This process has been patented by "Lanxide Corp.", a U.S. company. See appendix I1].

The two systems have some common factors and have been found to share, in some respects, similar mechanisms. The breadth

of the approach has unavoidably placed some constraint upon the depth to which the some of the experimental work has been taken.

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CHAPTER 1. INTRODUCTION

1.1 AIMS

1.1.1 Primary Research Objective

1.1.2 Secondary Research Objective

1.2 IRON-MATRIX/ALUMINA PARTICLE SYSTEMS

1.2.1 The Aluminothermic Lance

1.2.2 The Bessemer Reaction

1.3 ALUMINA MATRIX/Al-FILLED PORE SYSTEMS

1.3.1 Aluminium Alloy Route

1.3.2 Aluminium Top-Dust Route

1.1 Aims

This thesis concerns methods of producing alumina and alumina/metal composites via routes involving combustion of liquid phase metals. Figure 1.1 shows how the research has been organised.

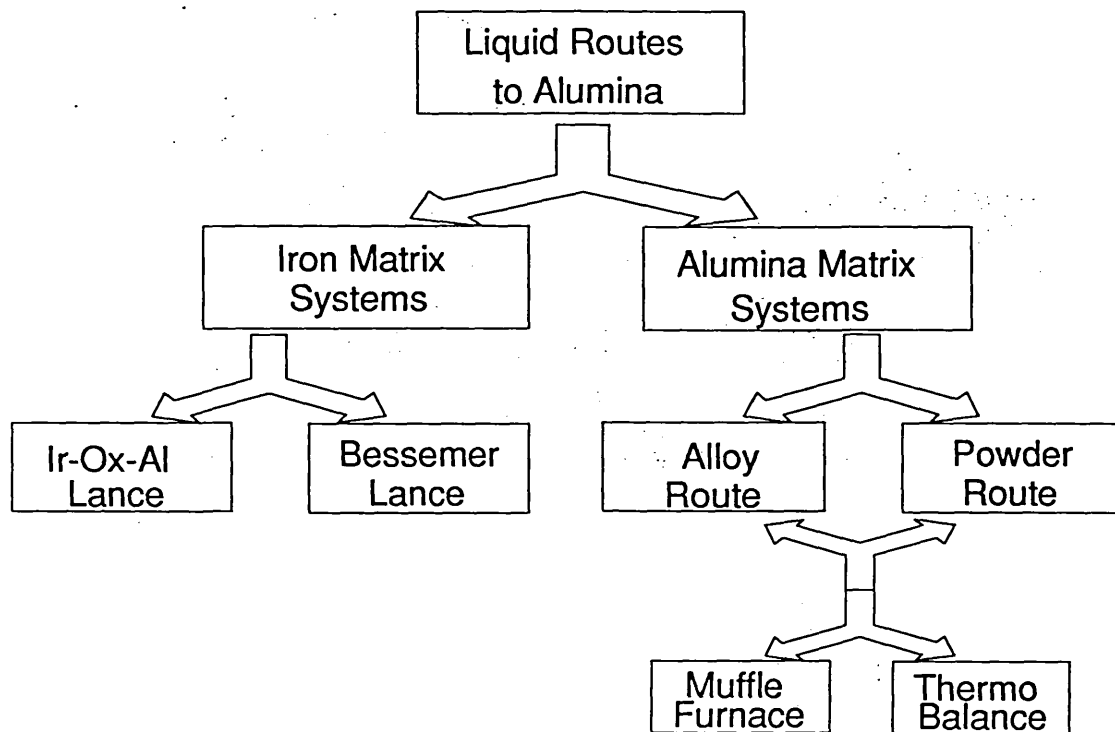


Figure 1 The Organisation of the Research

Four novel systems are examined, each of which represents a new way of approaching the formation of ceramic-metal composites. They involve the combustion of metals, directly or by redox reactions, to create ceramics *in situ* with metals.

1.1.1 Primary Research Objective

The major objective of the research reported here is to determine the actual mechanisms by which aluminium can be made to experience rapid and controlled oxidation. It is well known that aluminium exposed to oxidising atmospheres rapidly develops a thin dense impermeable oxide skin which prevents further oxidation. However several systems of rapid and continuous oxide formation have been devised or examined here which show some promise of eventual usefulness as methods of composite production. In particular the research concerns systems in which the reaction rate is so high as to render the aluminium oxide in the liquid phase, either as a slag component or alone, but at mean temperatures which are generally well below its melting point.

1.1.2 Secondary Research Objective

The strength of a composite system lies in its weakest link. In general this means the *cohesive* strength of the weaker component. The *adhesive* strength of a properly adhered joint is given by the geometric mean of the adherends [ie. the square root of the product of the cohesive strengths]. This is of course always larger than the cohesive strength of the weakest member. However in practice perfect adhesion is rarely achieved. The principal reason for this is that the adhesive strength

is directly related to the wettability of the solid member by the liquid component. Thus proper bonding means proper wetting, and vice versa.

Hence the present research is also in part directed towards methods of overcoming wettability problems, in particular those which arise between solid alumina and iron on the one hand and between solid alumina and aluminium on the other. In the first case the problem is to introduce and maintain within the iron a dispersal of alumina crystals. In the second case the problem is to explain how aluminium is infiltrated into pores permeating a crust of alumina grown upon liquid aluminium surface. [see patent abstract appendix II]

1.2 Iron Matrix/Alumina Particle Systems

The difficulties which normally arise when attempts are made to disperse fine powders of ceramic materials in a metal melt may be ascribed to several factors viz:-

- # The increase in surface energy associated with the creation of new surfaces. Powders have very large specific surfaces.
- # The poor, or non-wettability of solid ceramics by liquid metals.
- # The problem of even particle distribution within the melt.
- # The buoyancy of the dispersed particles.

Chemical reactions between particles and the suspending liquid.

Antagonistic phase relationships between particle and matrix such as widely disparate coefficients of thermal expansion, volumetric changes on solidification, or hot shortness due to the presence of a low melting point eutectic.

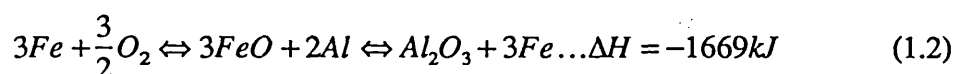
One approach is to blow powdered ceramic into the melt using a gas transport system in which the powder is entrained. Such a system is described by Quigley [1982] *et al.* Another method involves stirring the melt to form a vortex. The paraboloid surface so formed enables the powdered ceramic to spread right down through the levels of the rotating melt. Centrifugal forces generated by the rotation of the liquid establish atmospheric pressure all the way down the vortex surface. Within the melt the agitating paddle creates local turbulence causing the powder to be invested. Thus a circulating system is set up with the powders falling down the vortex surface until they are ingested by the local melt/paddle disturbance and are subsequently dispersed by the forced convection pattern. Such a programme is reported by Rohatgi [1979] *et al.*

The present research has pursued other routes involving the formation of liquid alumina by thermochemical means, *in situ*, with forced mixing and dispersal by bubble agitation. The this method goes some way towards avoiding

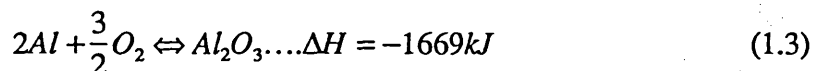
the problems, outlined above, encountered in powder injection techniques. In the two systems tried here liquid alumina is produced within slags in the initial stages, the exothermic heat consequently raising the temperature of the system until actual combustion of the aluminium occurs. The so-called "Thermit" welding and casting process provided a model for the methods presented here, but whereas the thermit method has *solid* reactants and proceeds by the equilibrium:-



[the iron oxide being in the form of haematite flakes or particles] the present reaction uses *gaseous* oxygen and proceeds as either:-



[ie. as consecutive reactions] during the transient conditions of flame ignition or flame instability, or directly as:-



.....in the case of steady state combustion. [the iron being assumed to pass through un-reacted in the casting mode]

This reaction was brought about by two separate and distinct methods:-

a consumable aluminothermic lance blown below the surface of an iron melt. [See appendix I, for patent description].

a non-consumable oxygen lance blown under the surface of a ferro-aluminium melt.

In each case the intention was to produce alumina crystals in an iron matrix *at mean temperatures below that of the melting point of alumina*, by the localised and controlled combustion of aluminium. In each case the even distribution of alumina particles was facilitated by agitation arising from the injection of oxygen bubbles.

1.2.1 The Aluminothermic Lance

An aluminothermic lance was devised which in effect replicates the so-called thermit process but which involves oxygen gas for direct as well as indirect oxidation.

In this approach a lance was constructed consisting of concentrically mounted tubes of steel and aluminium.

Oxygen, controlled by a valve, was passed through the tubes and the lance ignited by means of an oxy-acetylene torch.¹

The lance is fired into a mold in a way such that the fire-ball at the lance tip is immersed in the molten iron products. This creates a billet of steel in which there is dispersed an alumina particle phase.

1.2.2 The Bessemer Reaction

To afford better means of measurement and control a crucible system was devised wherein a continuous reaction was provided between the aluminium in a ferro-aluminium melt and oxygen bubbled beneath the surface through an alumina tube array.

This crucible based system was more easily monitored than the consumable aluminium/iron lance. Moreover the reaction took place within a ferro-alloy melt having a melting point substantially lower than that of steel.

1.3 Alumina Matrix/Al-filled Pore Systems

An interesting discovery by Dizio [1985] [working with Lanxide Corp. in the U.S.] has revealed that under special conditions some alloys of aluminium may be

1 The intense combustion reaction which results has found many uses including rock boring and underwater cutting, welding and casting as well as the present use. This process is the subject of a patent application by the author and Hong Kong University.

induced to undergo catastrophic oxidation in a controlled manner. The product of the process is a dense corundum matrix infiltrated with the aluminium alloy. This is claimed to be a system of pores the walls of which are a series of high energy grain boundaries. The determination of the mechanism by which this occurs forms a major part of this thesis.

Two methods of achieving the Lanxide composite have been examined here. The first replicates the conditions described in a patent taken out by Dizio *op.cit.* and the Lanxide Corporation of the U.S. [appendix II], whereby an alloy of aluminium silicon and magnesium is taken through a thermal cycle in air within a muffle furnace. The second method produces similar results via the same thermal cycle but from a specimen of pure aluminium top-dusted with silica and magnesia powder.

1.3.1 Aluminium Alloy Route

In this series of experiments specimens containing various combinations of aluminium, silicon and magnesium, [including zero values for the latter two components] were thermally cycled in a thermo-gravimetric apparatus under a flow of air at temperatures in the range 1100-1400°C. Rates of reaction at a series of process temperatures within these limits were assessed from the results. Metallographic studies were made of the

crust-like oxide products in order to assess the effects of temperature and of alloy content upon crystallographic structure, and the pore and surface morphology.

1.3.2 Aluminium Top Dust Route

The conditions of the alloy route experiments were replicated but using "super-pure" aluminium specimens top dusted with various admixtures of silica and magnesia as controls and using various dopants [such as calcium fluoride, soda and potash, as bicarbonates, and haematite] to see if their influence, if any, could throw light upon the mechanisms by which the composite was formed. Comparisons between the two routes revealed that the composites [for those conditions and compositions for which useful corundum crusts were in fact produced] were virtually identical.

CHAPTER 2. LITERATURE SURVEY

2.1 GENERAL BACKGROUND

2.2 METAL OXIDATION

2.2.1 General Theory of Metal Oxidation

2.2.2 Self Diffusion and Chemical Diffusion

2.2.3 Oxygen Diffusion Through Slags

2.2.4 Catastrophic Oxidation

2.2.5 Breakaway Oxidation in Al/Mg Alloys

2.2.6 Composites by Metallothermic Reactions

2.2.7 Calculation of Aluminothermic Balances

2.2.8 Combustion of Metals

2.2.9 Thermodynamic Properties of Al-Si-Mg and their Oxides

2.2.10 In Situ Formation of Alumina in Iron

2.1 General Background

The development of modern ceramics is an area of great importance, particularly in those circumstances in which the properties of high temperature and wear resistance are paramount, as for example in the technology of heat engines. Many contemporary applications are given by Parker [1985]. Considerable efforts are being made to develop ceramic-metal composites which improve the toughness and tensile strength of what are normally brittle and weak ceramic materials, or which improve the high-temperature wear resistance, the elastic modulus and the creep resistance of metals.

Two main classes of ceramic-metal composites may be identified: those which attempt to modify the performance of ceramics, and those which aim to improve the properties of metals. The former are termed ceramic matrix composites and the latter, metal matrix composites. Both metal matrix and ceramic matrix systems have been in use for some time. Bearing metals have been formulated from soft load-spreading matrices such as white metal and given wear resistance by mixing with various inter-metallic compounds such as antimony-tin cuboids. Aluminium oxide and carbides of tungsten and titanium have been hot-sprayed, using plasma arc or oxy-acetylene flames as carriers, to bond with steel substrates. Several methods involving diffusion are used to form sub-surface nitrides, borides and carbides. One

such is the formation of aluminium nitride from aluminium-bearing steels utilising ammonia within a muffle furnace. Perhaps the oldest and best known amongst such processes is the case hardening of steel or the infolding forge carburising process which has been reported by Tylcote [1976] as the process of Damascening in 13th.century Islam and by Needham [1955] as the process of co-diffusion used in T'ang Dynasty China; in both cases used to produce swords of great toughness and yet with the ability to take a hard cutting edge. Some modern metal-cutting tools are made from carbide matrix-metal composites in the sense that they generally employ a metallic binder such as cobalt, nickel or their alloys. These may in turn be coated with alumina to add superior wear resistance to the tough "cermet" body material.

The term ceramic has traditionally been used to describe substances akin to natural rock, which is principally made up of metallic oxides, but synthesised from clay "slips". Nowadays however the term embraces mixtures, aggregates and products sintered from metallic carbides, nitrides, and borides, as well as oxides. Some very effective complex compounds have been formulated such as Sialons [made from Silicon-Aluminium-Oxygen-Nitrogen, Jack [1978] which show significant improvements over traditional ceramic materials.

Sintering involves high temperature diffusion bonding of material powders, often at high pressures and for periods of many hours. More convenient methods have been investigated such as the infiltration of ceramic particles by metals Urquhart [1987]. However this approach is made difficult by the fact that ceramics are difficult to wet by metals since the surface free energy of metals is, in general, much greater than that of ceramics. Hence, although the interfacial surface energy favours the wetting of liquid or solid metal by liquid "ceramics", ie. slags, it does not normally favour the wetting of solid ceramics by liquid metals. If capillary attraction is to be invoked to infiltrate ceramic matrices then some means of increasing the surface free energy of the ceramic has to be used. This may be made possible by surface activating techniques such as doping the solvent metal with a more reactive metal such as Mg, or Ca [a comprehensive review of such techniques is made by Rohatgi et al [1986] and/or by creating a grain boundary "sandwich" of more compatible layers of material the outer layer of which is wettable by metal. For an example of this approach see Tokisue and Abbaschian [1978]. A method of high speed electro-deposition of multiple coatings of metals on SiC fibres is reported by Lashmore [1987].

An effective means of improving the properties of aluminium is termed S.A.P.- which refers to the dispersion hardening of aluminium by sintering surface

oxidised aluminium powders. This method relies upon the anchoring of slip planes by sub-micron alumina particles. The particles result from the dispersion of the oxidised surface layer initially coating the aluminium powder

2.2 Metal Oxidation

The routes to the formation of ceramic-metal composites followed here all involve catastrophic oxidation of one or more of the metals in a melt to form a ceramic component. The general approach is to initiate chemical reactions and invoke kinetic mechanisms which in unison give rise to situations which allow rapid formation of stable ceramic-metal systems. Generally research into the occurrence of catastrophic oxidation has had the aim of prevention. Nevertheless much data which is relevant to this programme does exist in the literature.

2.2.1 General Theory of Metal Oxidation.

In the theory of metal oxidation that according to Wagner [1933] is the most generally accepted. In his schema the following assumptions are made:-

Migration of electrons or of ions is the rate controlling process.

Thermodynamic equilibrium is established at both the metal-oxide and the oxide-gas interfaces.

The oxide layer shows only small deviations from stoichiometry.

Thermodynamic equilibrium is established locally throughout the oxide.

Oxygen solubility in the metal may be neglected.

It then follows that activity gradients are set up across the oxide. Consequently, metal ions and oxygen ions will tend to migrate across the oxide in opposite directions. Because the ions are charged, this migration will cause an electric field to be set up across the oxide resulting in consequent transport of electrons across the oxide from metal to atmosphere. In summation the net force acting upon each particle resulting from both chemical and electrical gradients will be given by Equation 2.1.

$$Force = 1/N_A \left(\frac{\partial \mu_i}{\partial x} + Z_i F \frac{\partial \phi}{\partial x} \right) \text{joules} \cdot \text{particle}^{-1} \text{cm}^{-1} \quad (2.1)$$

Where "N" is Avogadro's number, "F" is the Faraday constant in coulomb per mole and the partials are the chemical and electrical potential gradients at any value of "x".

The relative migration rates of cations, anions, and electrons are therefore balanced such that no net charge transfer occurs across the oxide layer as a result of ionic migration. Being charged particles, ions will respond to both chemical and electrical potential gradients which together provide the net driving force for ionic migration. Knowledge of these factors together

with the impedance to ion mobility allows us to assess the flux of species across the oxide and hence the maximum rate to which the oxidation reaction is limited.

2.2.2 Self Diffusion, and Chemical Diffusion

The impedance to ion mobility through an oxide layer is defined experimentally in terms of the diffusion coefficient " D ". In general, the value of " D " relates to the following factors:-

- # The diffusing ion [or atom or molecule] charge and radius.
- # The structural configuration of the solvent.
- # Any deviations from stoichiometry.

The diffusion of ions in a potential gradient, ie. "chemical diffusion", differs from that of neutral atoms or molecules such that the transport rate is around two orders of magnitude greater. The term "self diffusion" is used to describe the transport of atoms by random dispersal mechanisms, through their own medium. In this work the term diffusion generally refers to chemical diffusion.

In general, the steady state species flux, " J ", is related to the concentration gradient by the diffusion

1 In fact the so-called diffusion "constant" varies strongly with temperature [via an Arrhenius relation] and, over a certain value, with the concentration also.

coefficient, "D", such that:-

$$J = D_0 \left(\frac{\partial c}{\partial x} \right) \quad (2.2)$$

Which is Fick's First Law [1855].

For solids the variation of "D" with temperature "T" is given by:-

$$D^* = D_0 \exp \left(-\frac{E}{kT} \right) \quad (2.3)$$

Where "k" denotes Boltzmann's Constant, and "E" the activation energy.

The relationship between the chemical diffusion coefficient $\bar{D}$ and the self diffusion coefficient is given by:-

$$\bar{D} = D^* \left(\frac{\partial \ln a_m}{\partial \ln c_m} \right) \quad (2.4)$$

As the thermodynamic differential in this term in non-stoichiometric compounds can have large values, it follows that the chemical diffusion coefficient can be many orders of magnitude greater than the self diffusion coefficient. It should also be noted that the chemical diffusion coefficient is a function of composition. This is illustrated below in Figure 2.1 taken from Steele [1973]

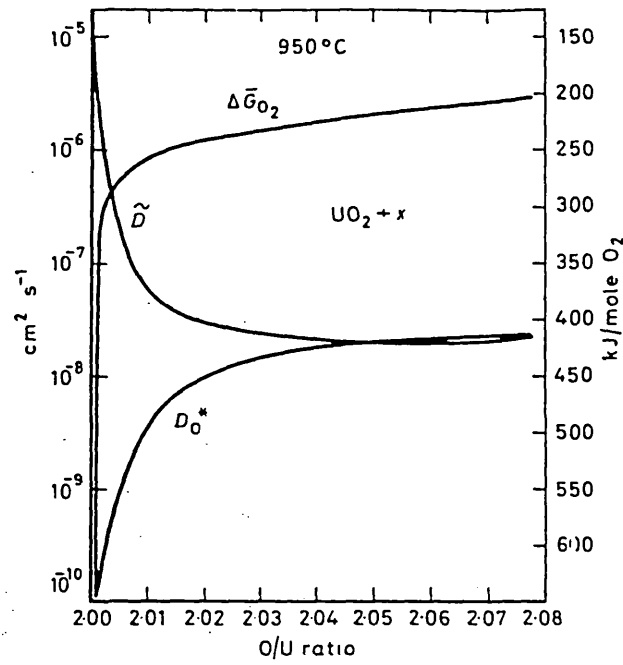


Fig. 2.1 Oxygen self (D_O^*) and chemical ($\tilde{D}$) diffusion coefficients in UO_{2+x} as a function of composition. Relevant $\Delta\bar{G}_{O_2}$ values also included

Figure 2.2, depicts the dramatic difference between the self and the chemical diffusion coefficients in wustite.

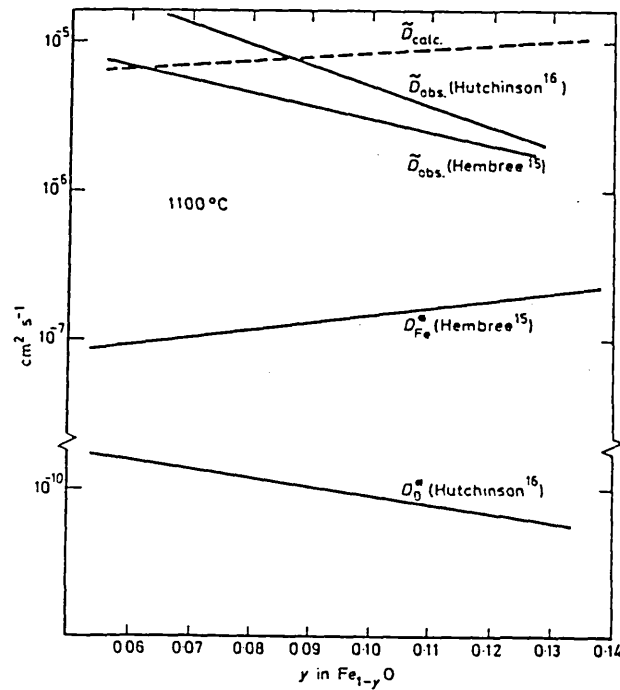


Fig. 2.2 Self (D^*) and chemical diffusion coefficients ($\tilde{D}$) in $Fe_{1-y}O$

Thus, the diffusion flux permeability through molten slags is dramatically improved by the addition of dopants¹ which can alter the diffusion mechanism from the physical mode to the chemical mode. One such example is given by Sasabe and Jibiki [1983] who have claimed increases in permeability amounting to ten to the tenth power by adding iron oxide to a C-S-A melt. In general diffusion is enhanced by basic additions to glassy melts which act to break the chains of silicate tetrahedra. Magnesia is one such chain breaker and alumina is basic relative to silica.[ie. it is amphoteric]

2.2.3 Oxygen Diffusion Through Slags and Glasses

Of particular importance in this research is the diffusion of oxygen through slags. This has been found in the present work to be the key mechanism by which combustion of aluminium is initiated and stabilised. At ambient temperatures below the melting point of alumina [2050°C] the oxidation of aluminium proceeds logarithmically to a point where the aluminium is essentially protected from further oxidation by a dense impermeable layer of alumina. In some molten alloys of aluminium however, slags of the oxides of the component metals may be formed providing that the ambient temperature is above the relevant slag eutectic temperature. Oxidation can therefore occur at a much faster rate through the liquid environment. Even so the rates are insufficiently high to

¹ And in particular, dopants having oxides of more than one valency ie. the transition metals eg. Fe, Mn, V, Ti.

be useful in the formation of ceramic bodies. For the necessary oxide growth rates more rapid and continuous oxidation should be made to occur by the invocation of further mechanisms. The harnessing of mechanisms known to cause catastrophic oxidation is the approach adopted here¹. These phenomena generally involve gas phases as well as condensed phases.

2.2.4 Catastrophic Oxidation

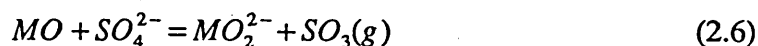
Harmful catastrophic oxidation and metal loss are known to occur in certain circumstances. One example, cited by Birks and Meier [1983], is the impoverishment of chromium in chrome oxide-forming alloys at high temperatures. This is caused by the breakdown of the chromium oxide to its volatile sub-oxide which is subsequently lost. This is also known to occur generally when an alloy contains a refractory metal such as molybdenum, tungsten, and vanadium. In the case of molybdenum, Gulbransen and Meier [1979] report that vapour species evolve in significant amounts at temperatures over 725°C. A similar situation has been mentioned by Gulbransen et al [1966] in which

¹ Another approach, not investigated here is the use of dopants to increase oxygen permeability. Sasabe and Jibiki [1983] have found that the permeability of oxygen through molten C-S-A slag containing iron oxide increases the permeability by a factor of ten to the tenth power. This is ascribed to the transport mechanism changing from physical to chemical diffusion. The potential usefulness of this phenomenon in the production of ceramics is discussed under "Future Work".

silicon consumption was 300 times faster in oxygen partial pressures below a critical value given by Wagner [1958] as:-

$$p_{O_2}(crit) = \frac{1}{2} \sqrt{\left(\frac{D_{SiO}}{D_{O_2}} \right)} p_{SiO}(eq) \quad (2.5)$$

Goebel et al. [1970 & 1973] have noted that the oxidation of alloying elements, molybdenum, tungsten, or vanadium in nickel-aluminium alloys in the presence of sodium sulphate on the surface, decreases the oxide activity of the flux by virtue of the reaction :-



.....and dissolves the protective layers NiO and Al₂O₃. Away from the flux-metal interface, cations Ni²⁺ and Al³⁺ react with the molybdate anions, resulting in the liberation of volatile MoO₃, and the precipitation of NiO and Al₂O₃ particles near the gas-flux surface. This oxidation process is catastrophic because, once initiated, Mo in the alloy insures the continued presence of the acidic flux and prevents the formation of a protective oxide layer.

Peters et al [1976] found that Ni-15Cr-Mo alloys with Mo contents in excess of 3% were catastrophically attacked in static oxygen at 900°C, but in an oxygen flow a

protective scale was formed. Apparently the evaporation of MoO_3 in the flowing atmosphere prevented sufficient accumulation of Mo oxides to cause severe corrosion.

Turkdogan [1980] has generalised the conditions for catastrophic oxidation thus:-

"For the onset of self sustaining catastrophic oxidation, three conditions are necessary and sufficient:-

- #1 Single application of a low melting point non-volatile flux,
- #2 oxidation and dissolution of alloying elements that render the flux acidic,
- and, #3 vaporisation of the oxides of the alloying elements at the gas-flux interface".

Two more preconditions for very high rates of catastrophic oxidation, including combustion, can be added here:-

So-called "Metal Fog" formation, a transport process in which the metal vapour reacts with the oxygen diffusing towards the vaporising surface to form an oxide mist. "PdV" changes enhance the counterflux of metal vapour and oxygen by creating "sink" conditions. This phenomenon was first reported by Delavault [1936] in his PhD thesis [Univ. Paris 1936] in connection with

magnesium vaporisation [and by Krupowski and Balicki [1937]. Gulbransen et al [1966] reported vaporisation enhancements of some three hundred times that which would normally be expected at a particular temperature.

Turkdogan, Grieveson and Darken [1963] quantified the systems occurring over copper and over iron and provided a rigorous theory for the phenomenon [see Figure 5.12]. The enhanced vaporisation rates resulting from the formation of a metal fog approached those formed *in vacuo*. This would have the effect of lowering the boiling point of aluminium below 1000°C which would have a pronounced effect on the reactions occurring in the present work. [see Table 2.1 Chapter 2. section 2.2.7 *ibid*]

Ignition of the metal to initiate spontaneous combustion after a period of accelerating reaction as exothermic heat raises the temperature of the flux, and consequently raises the vapour pressure of the metal which has diffused up to the gas liquid interface.

To anticipate the results of this work, we have just such a situation occurring in the initial stages of the alumina crust formation on the top of an aluminium-silicon-magnesium alloy. In the initial stages of the growth reaction, a ternary glass of the respective oxides is formed which is essentially non-volatile and acidic. This sets up an accelerating reaction as the exothermic heat raises the flux temperature and as the cation diffusion rate increases correspondingly, according to " $RT \ln p$ ". Aluminium vapour and its sub-oxides are evolved at the

glass-air interface. In this particular case, in still air, these oxidise and the flux is thus continuously replenished with dissolved alumina [via the combustion/condensation "fog-forming" reaction, see Turkdogan and Grieveson and Darken [1963 *op.cit*]]. Precipitation of the alumina onto the corundum surface away from the pores occurs and process continues until the metal is finally exhausted.

2.2.5 Breakaway Oxidation in Aluminium-Mg Alloys

The phenomena by which the presence of magnesium creates conditions for breakaway oxidation to occur in aluminium-magnesium alloys have been reviewed by Drouzy and Mascré [1966], and examined by Delavault [1936], Balicki [1958], Balicki and Leitzl [1959], and von Thiele [1962] and more recently by Haginoya and Fukusako [1983] and by Cochran *et al* [1977] [see Fig.2.3]. Of particular relevance to the work reported here on oxygen blowing is that of Wightman and Fray [1983], who performed experiments upon aluminium alloy melts in which the system was agitated by the passage of oxidising gas bubbles resulting in very rapid reactions.

All investigators appear to be in close agreement concerning the sequence of events occurring and, in general, with their interpretation of the phenomena. Cochran *et al* [1977] *op cit* provide the following sequence of events and their controlling factors.

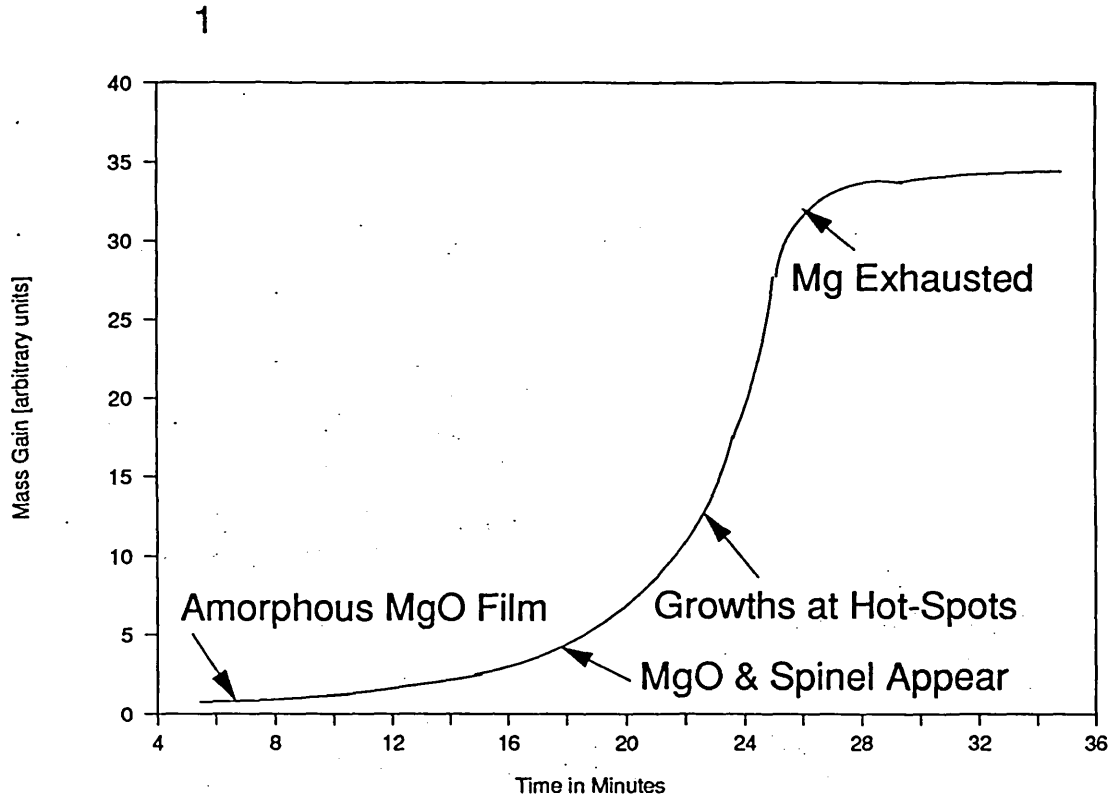


Fig.2.3 Spinel Formation Al-Mg Alloy Melts

[according to Cochran et al op.cit]

Stage 1. At temperatures above the melting point of the alloy, an amorphous film of MgO appears on the surface after an interval which is determined as:-

Decreased by:

- (1) increasing temperature or Mg concentration.
- (2) adding crystalline MgO, or spinel from previous oxidation.
- (3) slow melting.

Increased by:

- (1) adding Be or Na or by dusting B on the surface.

(2) using atmospheres containing carbon dioxide and nitrogen.

(3) fast melting and homogenisation of the solid.

Stage 2. Crystalline MgO and spinel appear, creating fragmented clusters infiltrated with aluminium metal.

Stage 3. Growths form at "hot spots".

Stage 4. Weight gain ¹

Stage 5. End of growth as Mg is exhausted.²

The authors note that, under certain conditions, actual combustion of the magnesium has been seen to occur.

2.2.6 Composites Via Metallothermic Reactions

This topic has been surveyed in view of certain similarities which it shares with the present work. These include:-

¹ Now determined by the present research as Log/Linear ie., $W = A \cdot \exp(kt)$

² The present research finds that, in the presence of silicon, not all of the Mg is reacted, some remaining to form a ternary glass of silica, alumina, and magnesia. This may be due to the remaining presence of di-magnesium silicide which partly structures the alloy melt [Mondolfo[1976]]. This lowers the magnesium activity and, by definition, the Mg partial pressure over the melt.

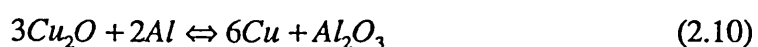
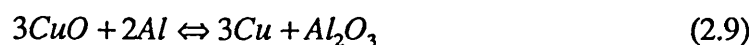
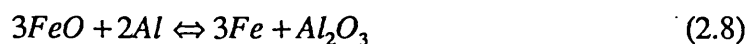
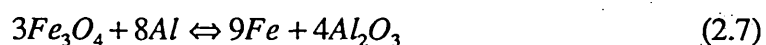
Coupled oxidation/reduction reactions at high temperatures.

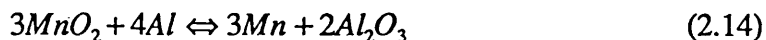
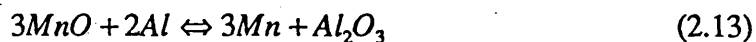
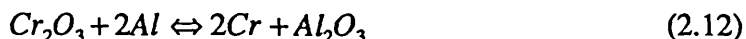
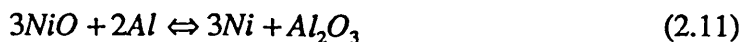
The formation of liquid alumina.

The fluxing of alumina in the initial stages of ignition.

The formation of alumina-metal mixtures.

Powerful exothermic reactions can be made to occur between metal powders and oxides. Perhaps the best known industrial example is the so-called thermit welding process which utilises the reaction [Eqn.1.1] which occurs between aluminium and iron oxide. This was first introduced by H.Goldschmidt [at the convention of the German Electro-chemical Society held in 1898]. He later developed the process as a welding and casting process for large masses of steel [under the trade name, "Thermit"]. The advantage of this process is that it provides an *in situ* melting system. In welding the joint members themselves form the mold walls. Many other metals can be reduced from their oxides utilising similar exothermic reactions. Some examples reviewed by Fricke [1978] are:-





Although all of the reactions listed above have Al as the reducing metal, [and are hence termed "Aluminothermic"] other combinations are used also. The criterion of technical practicability is whether or not the difference in the enthalpy of formation is sufficient to accomplish the melting of the oxide product, although this may be fluxed.

Sheppard [1986] has reviewed contemporary efforts to produce cermets by "self-propagating high-temperature synthesis". Work principally pioneered in the U.S.S.R. by Merzhanov [1974], has been carried out on some two hundred different ceramics, cermets, carbides, nitrides, borides, and their composites. A comprehensive report of this work is to be found in **"Gasless Combustion Synthesis."** Frankhauser et al [1985]. A description of the formation of SiC by **"Self-propagating High-temperature Synthesis"**, can be found in Yamado et al [1986]. Some early work at Georgia Tech. in the USA by Walton and Poulos [1959] describes the formation of cermets by way of thermit/alu-

mina mixtures, the alumina being used as a chemically passive thermal damping agent to control reaction propagation rates and to limit the temperatures reached.

The metallothermic reaction is often referred to as "liquid combustion" notwithstanding the absence of a flame, the rationale being that the temperatures, luminosity, and reaction rates, are similar to those found in flames. In the majority of cases however the reaction front moves outwards from the ignition point in a spherical shell leaving the products behind within the sphere. ie. the reaction is three-dimensional. This differs radically from the situation in which most flames are propagated in which the reaction is stationary at a series of two dimensional planes and through which the reactants proceed **one-dimensionally** [ie. orthogonal to the plane in which the reaction is occurring]. Such a situation has been set up in the present work where the aluminothermic lance simulates flame conditions.

2.2.7 Calculation of Aluminothermic Balances

Normally exothermic reaction temperatures are calculated by assuming adiabatic conditions and equating the heat of formation to that gained by the products, after making

due allowance for heats of phase transition and the variation of specific heat with temperature.

Thus:-

$$\Delta H = \Delta H_{form}^{298} + \int_{(T_1)}^{(T_2)} (\Delta C_p) dT + \Delta H_{trans} \quad (2.15)$$

Where values of C_p with temperature are taken from the literature as:

$$C_p = a + bT + cT^{(-2)} \quad (2.16)$$

"a", "b" & "c", being experimentally determined constants specific to certain ranges of "T".

At high temperatures it is often necessary to take into account dissociation and, since the equilibrium constant itself depends upon temperature, a process of successive approximation is called for. One first assumes a reasonable value for temperature and from this a value for the equilibrium constant is obtained. This gives a lower figure for the available enthalpy and hence a new value for the temperature. This in turn necessitates the recalculation of the equilibrium constant, and so on until the values converge at the adiabatic temperature. One such method is given by Weinberg [1956b]. For the combustion of aluminium in oxygen at one atmosphere, Grosse [1952] *op.cit.* gives a temperature of 3500°C. This is rather too close to the decomposition temperature of

alumina [given by Brewer & Searcy [1951] *op.cit* as 3575°C] since the production of exothermic heat would drop towards zero at this point. Moreover, in high temperature reactions adiabatic conditions are seldom in evidence since radiation losses are proportional to the fourth power of the temperature. A method of calculation of metal combustion is outlined in Chapter 5 below.

For thermite type reactions involving only the condensed phases typified by the production of chromium and manganese, procedures have been adopted which take into account crucible losses and the necessity of providing preheat to ensure that the products are molten. Often non-stoichiometric compositions are employed to lower the viscosity of the alumina-rich slags which are formed. Two examples are cited here.

If manganese dioxide is mixed with aluminium as a starting mixture, the reaction is explosive whereas if the monoxide is used, insufficient heat is evolved. A balanced charge of predetermined Mn/O is therefore made by mixing the two oxides so that a reasonable heat balance is achieved. This is illustrated in Figure 2.4 below.

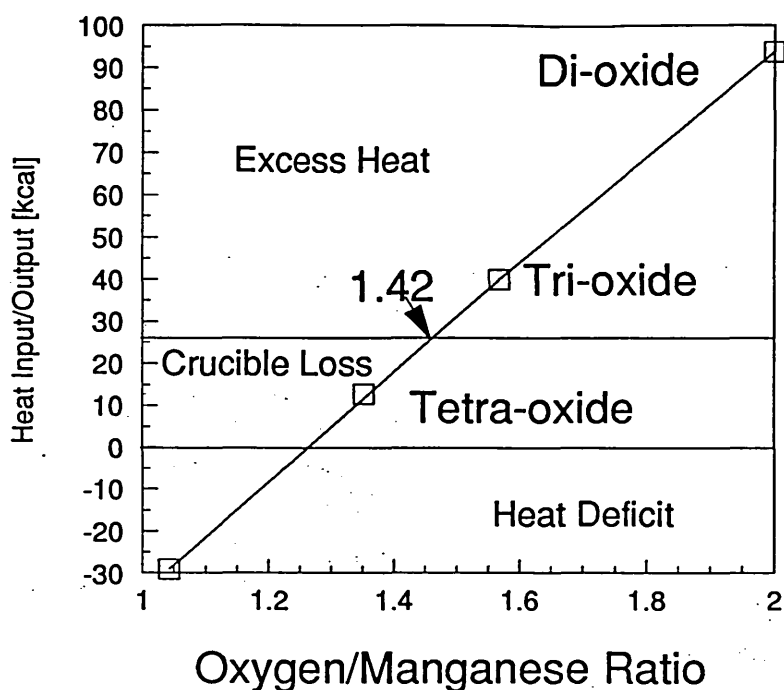
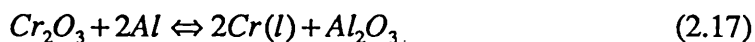


Fig.2.4 Aluminothermic Production of Manganese
[heat balance vs Manganese/Oxygen ratio]

In the case of chromium oxide, there is not sufficient heat available from the reaction;



..and the deficiency is met by preheating the charge to about 500°C, or by adding sodium di-chromate. The addition of CrO_3 , is not practical on the industrial scale because the solid is hygroscopic and stores badly.

The standard heat change for the reduction of chromium tri-oxide by aluminium is -130kcal/mole. Since the reaction involves one mole of oxide for every 2g atoms of aluminium, the heat capacity of this amount of material is about 49 cal per degree, and there are seven g atoms

involved. To raise the temperature of this mass by 2200°C, which is 150°C above the melting point of alumina, requires 108 kcal. The heats of transformation and melting total 26 kcal per mole of alumina and about 10 kcal for 2 g atoms of chromium making a total of 144 kcal. Since this quantity is 14 kcal larger than the heat change for the reaction which produces chromium, it follows that a pre-heat of 500 degrees must be provided as well as the heat losses by conduction and radiation from the reactor assembly. This amount is then 24 kcal which is the heat capacity of 49 cal per degree for the reaction formula multiplied by the pre-heat temperature. The heat loss due to radiation and conduction is therefore about 10 kcal/mole. See Figure 2.5 below.

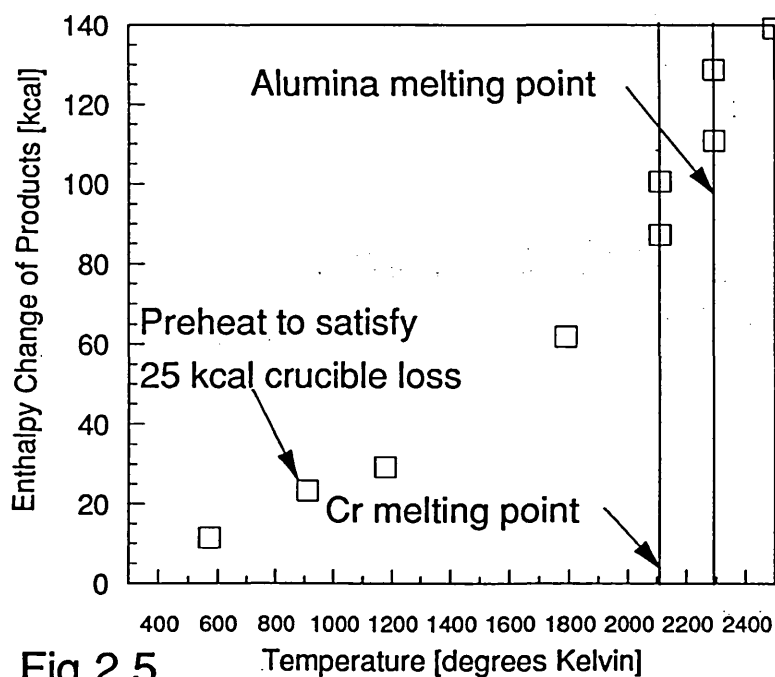


Fig.2.5

Aluminothermic Production of Chromium
[heat to melt products]

Referring back to the manganese production, we can now estimate what metal/oxygen ratio would be required in the original charge to raise the reacted mass to the melting point of alumina. For the reactions involving each oxide; monoxide [-124 kcal], tetroxide [-152 kcal], and dioxide [-214 kcal] the approximate heat capacities, using the Kopp-Neumann law, are then 56, 50.8, and 45.5, cal/degree. The heats then required to melt the charge are then 160, 145, and 131 kcal. This suggests that the choice should be to operate with as high a Mn/O ratio as possible. However, the Mn/Al ratios are 1.5, 1.125, 0.75 and since aluminium is expensive the correct choice would be the lowest Mn/O ratio. In practice the operator must choose a compromise, taking into account the costs of pre-heating and the problems of using flux's.

In the present case, the calculation of the process temperature is necessary since direct measurement is complicated by the fact that the actual reaction occurs at minute hot spots at the pore tops. The mean field temperature is measurable by both thermocouple and optical pyrometer and rough estimates can be made by considering the ratio of hot to cool areas. However estimates of flame emissivities are prone to errors resulting from light scattering by the sub-micron sized alumina particles. cf Wolfhard and Parker [1949] *op cit*.

2.2.8 Combustion of Metals

Flames are spontaneous self-propagating steady state reactions, generally¹ between oxygen and a gaseous hydro-carbon fuel. The high rate at which exothermic heat is liberated together with the low specific heat capacity of most gases, ensures that the thermal equilibrium [in which radiation losses exactly balance the heat generated] occurs at high temperatures. Flames are most often highly luminous when condensed phases exist as products.

Flames, being high-temperature chemical reactions, are generally kinetically rate limited. The rate-limiting step may be either the fuel supply or the oxygen supply. In natural flames [as distinct from man-made premixed "Bunsen" type flames] oxygen delivery is via gas diffusion. Gas fuel is most often evaporated from the liquid phase via thermal coupling. Some portion of the heat liberated goes to provide the enthalpy of evaporation of the liquid fuel². Thus the rate of burning

1 Other oxidants such as the halogens also provide exothermic reactions at rates sufficiently high to enable a self-sustaining combustion.

2 This can be envisaged mathematically as a coupling of the van't Hoff equation to the Clausius-Clapeyron equation via the Stefan-Boltzman equation. Thus the nett heat gained by radiation from the flame to the melt, results in evaporation of the fuel as given by the integral of the Clausius-Clapeyron equation. This is the fuel input of the flame, the chemical potential $[-RT \ln p]$ of which is given by the integral of the van't Hoff equation.

can be effected by the heat transfer characteristics of the flame/liquid. Factors which determine steady state conditions are:-

- # Flame luminosity and liquid surface reflectivity¹. [high for metals]
- # Flame temperature and thermal generating capacity. [high for metals]
- # The dissociation constant of the combustion reaction.
- # Specific heat capacity of the liquid.
- # Vapour pressure/enthalpy of evaporation of the liquid.

The thermal coupling effect, together with the balance between oxygen diffusion downwards towards the flame and the upwards vaporisation of the fuel towards the flame, determine the distance at which the flame stands over the liquid surface and is another interactive self-regulating feature of flame systems. This is particularly so for the flat thin "flames" associated with metals combustion. Bouriannes & Manson [1970] have observed burning aluminium droplets with superimposed HF heating. They measured the diameter of the flame sphere around a droplet of known diameter for a range of auxiliary heat inputs and interpreted them in terms of the vaporisation rate. The surface area of the flame bottom increases with the square of the radius, thus a

¹ Monochromatic emissivity is equal to absorptivity, hence reflectivity determines the proportion of the received radiation which actually heats the melt. For aluminium this is estimated to be less than 10%.

new equilibrium elevation is established for each value of heat input. In this way the velocity of flame propagation can be measured together with the latent heat of vaporisation.

The combustion of metals differs from that of hydrocarbons in that the products are in general in the condensed phase rather than the gas phase, either liquid or as is most often the case, solid. This has fundamental kinetic consequences since the "flames" involved are **neg-entropic** and hence **thin, flat, and collapsing** in nature, resulting in steep partial pressure gradients and in diffusion "wells" or sinks. Although apparently not investigating combustion as such, Turkdogan et al [1963] *op.cit.* report that an **oxide fog** or mist may appear over a volatile metal melt, and that this has the effect of increasing the rate of metal evolution up to that normal for the *free vaporisation* of the metal *in vacuo*.¹ In near-vacuum conditions, as Table [2.1] shows, boiling occurs at temperatures much below 1000°C. Later we will some examine evidence experimentally determined in this work which indicates that, under certain conditions,

¹ One way of considering this is that the boiling point *in vacuo* is considerably reduced below that normal at atmospheric pressure. eg. aluminium boils below 1000°C in a near vacuum. This would enable combustion to occur [after ignition and fog formation] very stably at the temperatures used in the present series. The Hertz-Knudsen Eqn. gives the maximum rate of both adsorption and desorption [vaporisation ie. free vaporisation] as:-

$$\mathcal{R}_{\max} = \frac{P_{\text{vap}}}{\sqrt{2\pi MRT}} \text{ reducing to, } \mathcal{R}_{\max} = 44.3 \frac{P_{\text{vap}}}{\sqrt{MT}} \text{ mole cm}^{-2} \text{ sec}^{-1}$$

aluminium combustion is maintained down to the solidification temperature of the *metal* rather than that of the oxide.

TABLE 2.1

<i>Boiling Points At Low Vapour Pressures</i>			
<i>Al Si Mg</i>			
PRESSURE	VAPOUR	VAPOUR	VAPOUR
atmos	PRESSURE	PRESSURE	PRESSURE
TEMPERATURE	10 ⁻³	10 ⁻⁶	10 ⁻⁹
Celsius	atm	atm	atm
ALUMINIUM	1509	1060	790
SILICON	2067	1476	1154
MAGNESIUM	584	365	236

Metal combustion also differs from hydrocarbon combustion in that the products may contaminate the reaction surface and, in some cases block the reaction soon after it commences. A precondition for spontaneous and sustained combustion is that the exothermic heat generated must be capable of maintaining the oxide formed in a liquid or gas state so that oxygen/metal counter-diffusion can occur rapidly enough. For example pure aluminium can normally only be made to burn at temperatures above that of the melting point of the oxide [2050°C]. Furthermore combustion is normally only possible if the metal is in

the form of particles small enough not to chill the reaction. Particulate aluminium combustion aids the performance of solid fuelled rockets by raising the flame temperature and thus the specific impulse. Aluminium foil is a further way to improve the surface area-to-volume ratio, and it takes this form in some photo-flash bulbs. Bouriannes *op.cit* and Bouriannes and Manson [1970] have investigated the detachment of aluminium flames from droplets subjected to ancillary HF heating in order to separate the chilling effect of the aluminium mass. Grosse and Conway [1952] have fed aluminium into a furnace in which previous combustion had raised the temperature above the oxide melting point. The same workers have demonstrated an aluminium-particle oxygen-blown cutting flame capable of rapidly boring a hole 10cm in diameter, through one metre of rock. Flame temperature measurement is complicated for both aluminium and magnesium by spurious brightness readings. One problem encountered in the measurement of magnesium flame temperature is that its apparent colour temperature does not indicate the true temperature of the actual flame. Wolfhard and Parker [1949] for example measured the apparent flame temperature of magnesium as 3900 K, however they point out that this cannot be the true temperature since it exceeds the boiling point of the oxide and the latent heat of vaporisation of the oxide is in fact far too large for this to occur. Hence they propose that the high temperature colour is due to the small size of the condensed oxide particles, which causes

the emissivity to be wavelength dependent. Surface flames of the diffusion type have been observed by Markstein [1963] at temperatures as low as 720°C. This may well be an example of diffusion-limited enhanced vaporisation [ibid. Turkdogan et al] which has been reported to produce [in the limit as a critical partial pressure of oxygen is achieved] virtually free vaporisation ie. as *in vacuo*] and for which the boiling temperature is substantially depressed. Table 2.1 shows that at 10⁻⁹ atmospheres the boiling point of magnesium is 750°C.

Whilst it can be explained how metal combustion is maintained in terms of the high enthalpies of formation when sufficiently high surface-to-volume ratios obtain such as in powder systems, it is not at all clear how *bulk* metals such as iron and aluminium melts can be made to burn spontaneously. Initially hot melts such as those found in oxygen steel-making, are pre-heated and hence capable of sustaining fast oxidation reactions which then become, to an extent, self-sustaining combustion systems. In the lance system examined here preheating iron by means of an oxy-acetylene flame and preheating aluminium by the resultant iron combustion is sufficient to initiate self-sustaining aluminium combustion [probably with the assistance of the fluxing action of the iron oxide]. The Lanxide system requires pre-heat temperatures between 1100-1400°C. This leads to the formation of oxides in the vapour phase to form fumes. Subsequent absorption of the fumes by a slag covering the corundum surface

occurs and, in turn, saturation of the alumina in the slag causes precipitation to occur at the bottom of the slag where both lower temperatures and favourable nucleation sites obtain.

Third components either in the gas phase or the liquid phase may prevent rapid oxidation. Emi and Pehlke [1975] have shown that for stagnant conditions dilutants to the oxygen gas as low as 1% reduce the oxidation rate by as much as 50%. They explain this phenomenon as the action of a gas/metal film impoverished in oxygen and forming a diffusion impedance to oxygen transport. The same authors, as well as Baker [1967] and Robertson *et al* [1970], report that Si in excess of 6%, and Al in excess of 8% create passivating layers and inhibit further oxide growth. However, oxygen jets and oxygen bubble formation are likely to disrupt any protective layers, provided that they are molten. Chen and Faeth [1983], using a chlorine gas jet submerged in a sodium melt, confirm that even in such a volumetrically "collapsing"¹ reaction, vapours arise which maintain the bubble well into the melt. Such is the case in both the iron/aluminium/oxygen reactions and the aluminium alloy Bessemer process investigated in the present work. Oxy-acetylene² flame

¹ "Collapsing" in the sense that, whilst at least one of the reactants is a gas, the products are in the condensed phase.

² The acetylene fuelling only the preheating of the steel to its melting point.

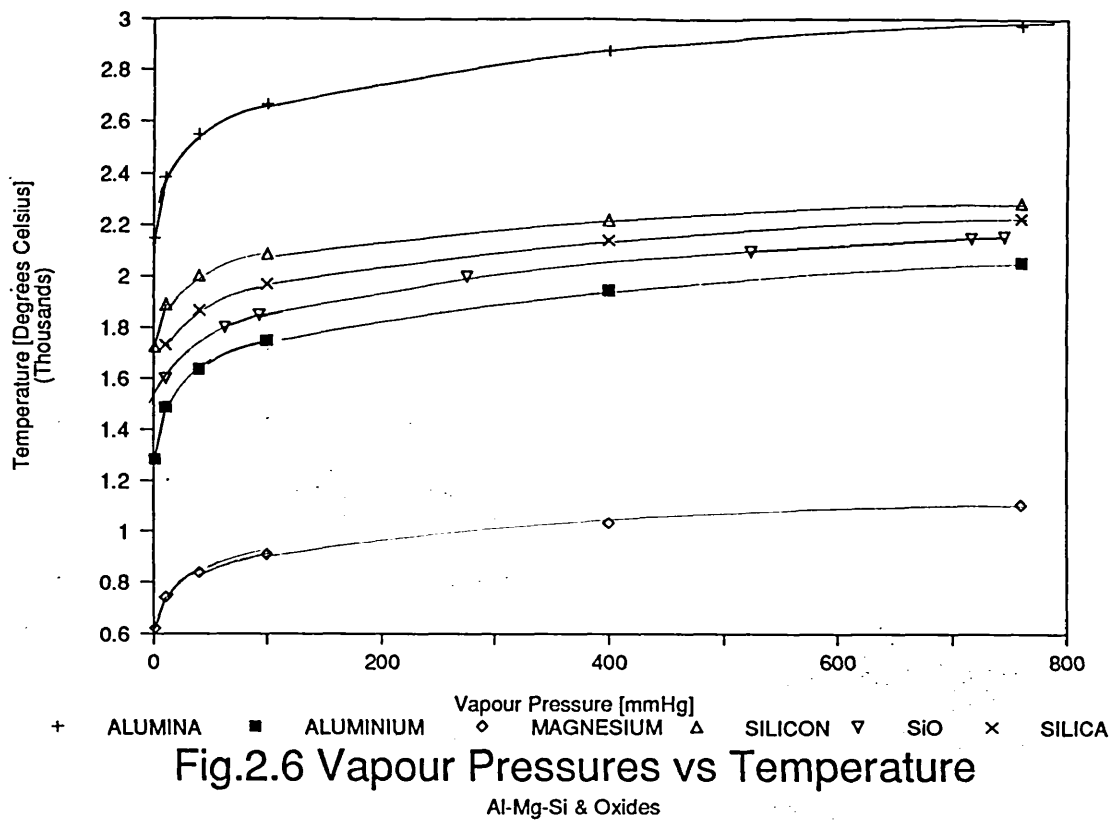
cutting of steel depends upon oxygen jets to accelerate the reaction, clear away dross, and compensate for heat-sink losses.

2.2.9 Thermal Properties of Al, Mg, Si, & Oxides

TABLE 2.2

<i>Phase Transition Data for Al Mg Si and Oxides</i>				
Species	Melting Point °C	Enthalpy of Melting kJ/mol	Boiling Point °C	Enthalpy of Boiling kJ/mol
Aluminium	660	11	2327	284
Silicon	1414	46	2360	297
Magnesium	650	9	1120	132
Aluminium Oxide	2050 corundum	109	dec 2977 [3527] ¹	
Silicon Dioxide	1703 tridymite	15	dec 2250 [2590]	
Magnesium Oxide	2800 periclase	77	dec3600 [3193]	

¹ Brewer, L. and Searcy, A.W. 1951 J. Amer. Chem. Soc., 73, 5308



2.2.10 In Situ Formation of Alumina in Iron

Leaving aside the phenomenon of "internal oxidation" which proceeds by way of the metal surface, a relevant source of *in situ* alumina formation comes from the work done on de-oxidation of steels by aluminium in Bodsworth and Bell [1972] *op.cit.*, who note the free energy data of several different experimenters as well as values for the

equilibrium constant. They give their assessment of the best values for the formation of alumina from dissolved aluminium and oxygen in iron as:-

$$\Delta G^0 = -287,560 + 89.32T \frac{\text{cal}}{\text{mol}} \quad (2.18)$$

and,

$$\log K_{Al-O} = \log \left\{ \frac{(a_{Al_2O_3})}{((a_{Al})^2 (a_O)^3)} \right\} = \frac{62870}{T} - 19.53 \quad (2.19)$$

Although one of the aims of *in situ* alumina dispersoid formation is to avoid the problems of getting the particles into the melt against anti-pathetic surface tensions, nucleation of the alumina within the melt still poses problems. For nucleation to proceed, the nuclei have to mount a free energy barrier. Bulk negative free energy has to exceed the surface free energy of the particle. The former follows the cube law whilst the latter follows the square law. Initially the latter exceeds the former, and excess work has to be done to overcome the deficit and allow the critical radius to be achieved and exceeded. Excess pressures resulting from the evolution of small "bubbles" of alumina are given by the Laplace equation:-

$$P_{inner} - P_{outer} = \frac{2\gamma}{r} \quad (2.20)$$

Alternatively, this may be independently arrived at by free energy considerations, viz:-

$$\Delta G^{\circ} = 4/3\pi r^3 \Delta G_{vol} + 4\pi r^2 \gamma \quad (2.21)$$

[Where "gamma" represents the interfacial free energy and "r" the bubble radius.]

Table 2.3. shows the values calculated for the excess pressure acting upon alumina "bubbles" forming in the melt.

TABLE 2.3

Excess Pressure on Alumina Inclusions [twice surface tension/r]		
Interfacial Tension [dyne/cm]	Spherical Radius [cm]	Excess Pressure [atmos]
500	10^{-2}	10^{-1}
500	10^{-4}	10
500	10^{-6}	10^3

2.2.10.1 Dopants to Reduce Interfacial Free Energy

Interfacial free energy may be reduced to an extent by doping the solvent with surface active agents. The surface tension of iron, for example, may be reduced from 1750dyne/cm to 1100dyne/cm by the addition of a mere 0.03% selenium, and that of aluminium from 900 dyne/cm to

450 dyne/cm by adding 5% bismuth [Korol'kov in Richardson [1974] *op cit* p428-430]. Swisher and Turkdogan [1967] have reported the surface tension of iron with 0.1% dissolved oxygen is lowered to 1000 dyne/cm. Thus doping creates conditions favourable to the wetting of alumina by aluminium but the interfacial energy for iron/alumina remains large since the surface tension of alumina remains lower than that of even selenium-doped iron. This is exacerbated as temperature rises. Swisher and Turkdogan (1967) *op cit.* report an increase in surface tension values with temperature in melts in which the values had been initially lowered by the introduction of surface-active agents. However for un-doped surfaces the surface tension generally relaxes with temperature by a factor of about $[-0.2]$ [dyne/cm/K].¹

The patentees [Lanxide] of the alumina matrix composite investigated here cite high-energy alumina grain boundaries as being the agency of aluminium infiltration and it is worth noting here that whilst this is undeniable it has been found that the presence of magnesium or MgO [as spinel] is a much more effective

¹ This gives a reversal of the wetting characteristics of aluminium on alumina at about 950°C. Over this inversion temperature aluminium wets alumina. However, as shall be pointed out later, the pore surfaces in the present investigation show evidence of very strong wetting indeed and, to anticipate the findings, the raising of the surface free energy of the pores results from the activity of magnesia. It should also be noted that for surface tension reductions achieved by the use of surface active components increases in temperature can actually increase surface tension values.

means of reducing interfacial energy via the formation of a surface layer of the spinel in solid solution with alumina.

CHAPTER 3. IRON/ALUMINA COMPOSITE FORMATION

3.1 THE ALUMINOTHERMIC LANCE

3.1.1 Experimental Procedure

3.1.2 Results

3.1.2.1 The Alumina Sheaf

3.1.2.2 The Composite Ingot

3.1.2.3 Problems of Study

3.2 THE BESSEMER REACTION

3.2.1 Experimental Procedure

3.2.2 Results

3.3 PRELIMINARY DISCUSSION

3.1 The Aluminothermic Lance

The aluminothermic lance typically consists of an array of concentrically mounted tubes and rods of iron and of aluminium. Since all the components of the lance are of uniform cross-sectional area it is convenient to use the relative areas of the iron and the aluminium as the means of varying stoichiometry. For example, the area ratio which gives the stoichiometric composition is approximately 1:1.25. Oxygen was supplied from a commercial cylinder and regulated by a two stage regulator and finally throttled through a manually operated valve which forms part of the lance-to-hose connection. Appendix I includes the patent application and contains details of the lance arrangement.

Melt off rate

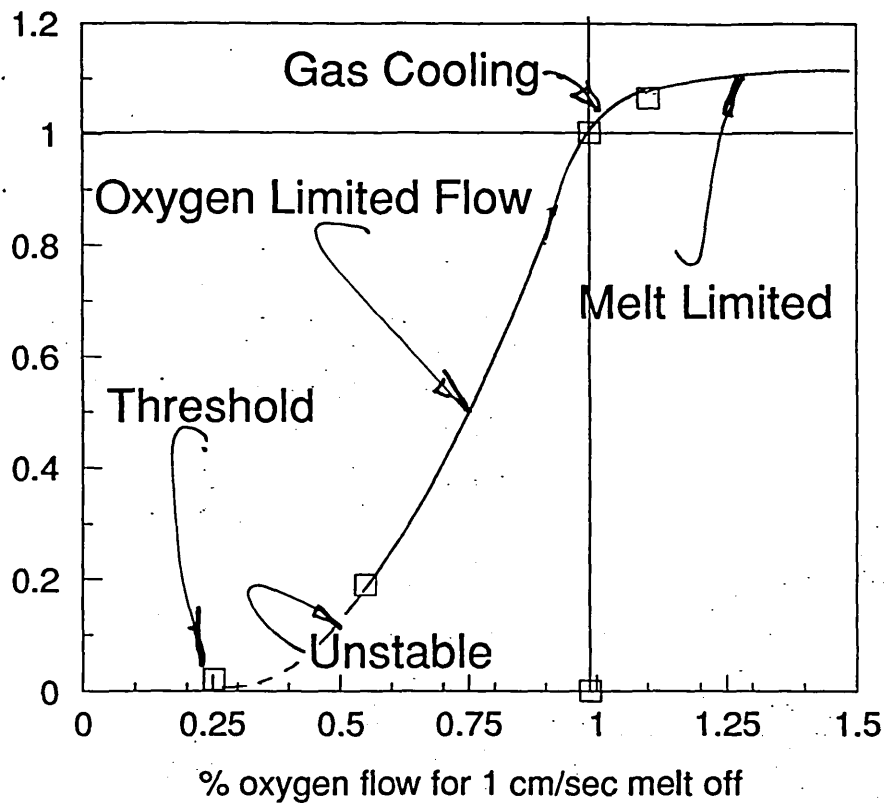


Fig.3.1 Lance Burnoff Characteristics
[melt rate vs oxygen flow rate]

The rate at which the lance is consumed, ie the burnoff rate, is a complex function of both the oxygen supply rate and the rate at which a proportion of the heat generated is transferred to the lance tip. This is illustrated qualitatively in Figure 3.1. A certain minimum flow is needed in order to establish temperatures at which the ignition temperature can be reliably maintained. As the flow rate is increased the combustion zone grows to cover the entire area of the lance tip. Further increases in supply result in a sensibly proportionate rise in the burnoff rate. However, eventually a limiting rate is reached beyond which

further increases in oxygen supply have little effect upon the rate of consumption of the lance. This limiting rate of oxygen supply appears to be related to a certain value of power intensity, and thus, by inference, to a particular steady state. Since melt off rate is clearly a function of heat transfer to the iron [Since the melting temperature of iron is considerably greater than that of aluminium] and in turn the equilibrium temperature at the lance tip, it must be assumed that isothermal combustion obtains. Since the limiting value of thermal intensity has been found to be the same for a broad range of powers and conditions it appears that it is a critical condition.

Under steady state operating conditions the lance produces molten iron, alumina and/or iron oxide as it melts back under the influence of the combustion of aluminium. The melt-off rate is not a direct function of the chemical reaction rate but is affected by a complexity of factors including:-

- # a balance of heat transfer from the combustion zone to the iron and aluminium tubes. [and to a lesser extent, that from the tubes to the oxygen flow within them]
- # their thermal conductivities.
- # their specific heat capacities.
- # their melting temperatures.
- # the relative cross-sectional areas.

The thermal intensity of the lance lies between that of an oxyacetylene welding torch and that of a typical welding arc. Table [3.1] gives comparative thermal flux intensity data for a range of industrial heat sources. The picture is complicated by the differing heat generating zone configurations. In particular the nature of a hydro-carbon flame is dominated by the thermally expanding gasses which reduce the heat "densities" and hence the temperatures achieved. This is in contrast with the conditions in a metal flame in which the products of combustion are generally in the condensed phase and in which therefore, the thermal density [and its conjugate, temperature] is higher.

The thermal power of the lance can readily be calculated from the cross-sectional area, the burn-off rate, and the thermodynamic data. For stoichiometric lances burning in the casting mode the thermal flux intensity is around 60kw/cm^2 . However, in the submerged casting [or boring] condition it is more accurate to consider the thermal flux intensity using an estimation of the surface area of the submerged bubble¹.

¹ In the rock boring application, the hole size may be estimated by consideration of the power density within the hemispherical bore front. The diameter of the hemisphere, and hence that of the bore-hole, will depend upon the thermal equilibrium established at the surface of the melting front. This, in turn, is a function of the specific heat and the melting point of the rock material on the one hand, and the thermal flux on the other.

TABLE 3.1

Thermal Flux for Some Industrial Heat Sources		
Industrial Process	Industrial Uses	Thermal-Flux watt/sq.cm
Electron Beam	Welding/Cutting	10^9
Laser Beam	Weld/cut/ht.trtm	10^9
Plasma Arc	Welding/Cutting	10^6
Open-Arc	Welding	10^5
Ir-Ox-Al Lance	Wldg/Ctng/Castng	$6 \cdot 10^4$
Oxyacetylene	Welding/Cutting	10^3

In the free spray condition the reaction occurs not only at the melting tube ends but also along the spray of detached droplets carried away by the gas stream. Figure 3.2 shows the spray of burning droplets streaming away from the melting lance. The different burning characteristics of aluminium [white] and the iron [red] can clearly be seen.



Figure 3.2 Free-burning Lance. [100 KW]

The velocity of the spray can be estimated by measuring the length of the drop path traversed during the time for which the camera shutter was open [1ms]. The red streaks are burning iron, and the white streaks are burning aluminium.

The energy density and the resultant heat transfer depends very much upon the reaction path and the kinetic history of the droplets. In an enclosed situation such as that which occurs in bubbles below the surface of the melt in the casting mode, more of the heat released is used in increasing the burn-off rate of the lance and overall heat transfer efficiency is maximised.

The ratio of the alumina to the iron which is produced is fixed by the ratio of the areas of aluminium to iron selected for the lance tube array. The supply of oxygen is hyper-stoichiometric to that needed for the combustion of the aluminium in order to minimise the occurrence of

aluminium in the composite and to ensure sufficient bubbles are formed within the melt to cause vigorous agitation and thorough dispersal of the alumina particles. The iron behaves as a thermal diluting agent during steady state combustion and so limits the upper temperature reached by the melt.

3.1.1 Experimental Procedure

A water-cooled steel mold was constructed in order to produce ingots of composite material. This is shown in Figure 3.3.



Figure 3.3 Water-cooled Steel Mold

High heat transfer is achieved by copper finning and a cooling water flow-rate of 80l/min for a lance of 100KW. The inner mold is 6mm wall thickness. Separation of the ingot is enabled by a sheaf of chilled-out alumina of some 2mm in thickness.

Insulation of the melt from the mold walls was fortuitously provided by a thin alumina shell some 2mm in thickness which subsequently chilled out of the melt during the firing of the ingot. An alternative arrangement which reduced the severity of chill was an

air-cooled steel mold of sufficient thickness to provide a pre-calculated degree of thermal dilution and to lower the thermal gradient across the alumina sheaf.



Figure 3.4 Lance Ignition Procedure

Ignition of the lance commences with the preheating of the iron tube by an oxy-acetylene torch. When a local spot melts the main oxygen supply is opened and the iron begins to burn. Very shortly afterwards the aluminium ignites.

Ignition of the lance was brought about by bringing a small spot at the end of the iron tube up to the melting point using an oxy-acetylene flame whereupon the main reaction could be initiated by turning on the oxygen supply through the lance. [see Figure 3.4]

The burn-off rate was raised by increasing the oxygen flow rate until a maximum was achieved and then increased further to provide excess momentum to the spray and

consequently to provide bubbles to disperse the alumina particles formed in the melt.

TABLE 3.2

Typical Lance Burnoff Characteristics					
Lance Geometry Fig.3.5	Condition	Metal Cross-Section cm	Measured Power kw #	Burnoff Rate cm/sec	Thermal Flux watt/cm ²
A	Boring Firebrick	4.14	230	1.2	55.55
B	Casting Steel	1.95	108	1.0	55.38
C	Free Burn	2.23	132	1.1	59.19
D	Under Water	1.96	97	0.8	49.48

Note: "#"= Measured calorimetrically.

"*" = Stoichiometric ratios of Fe/Al [This corresponds to an area ratio of 1.25/1 Al/Fe.]

"\$" = Superabundance of oxygen flow of about 1.5-2 times stoichiometric requirements in all cases. [This was measured once for a fully opened valve condition using a "gasometer" type apparatus consisting of a steel drum

containing water. Oxygen was collected over water in an inverted plastic drum].

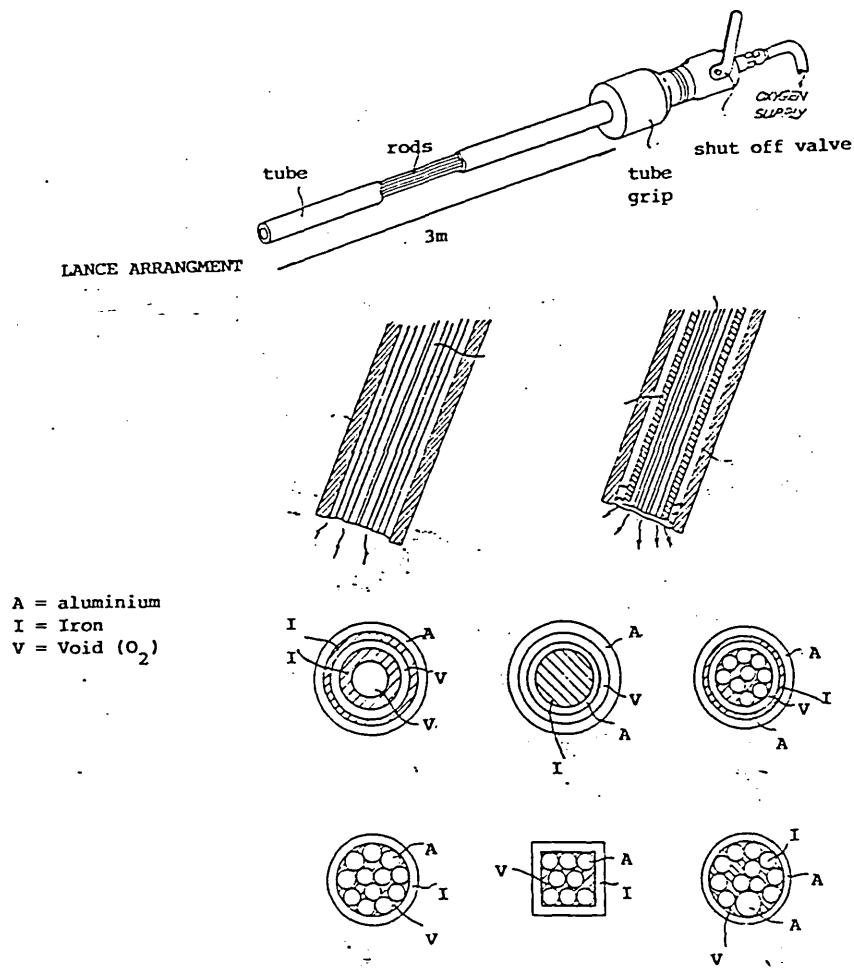


Fig. 3.5 Details of Lance Makeup Geometry.

Alternative lance configurations are shown in Figure 3.5. Free burn-off rate was measured in the open spray condition, and the gas flow rate noted. The limiting burn-off rate was found to be essentially constant at about 1.0 cm/sec in the open spray condition and 1.2 cm/sec in the submerged condition where the heat transfer to the melting lance tip is enhanced by liquid phase

contact on the one hand, and by the intensification of the reaction by its containment within a bubble on the other.

The ignited lance was up-ended into the vertical position and fired into the mold. [see Figure 3.6]



Figure 3.6 Charging an Ingot

Charging into a massive air-cooled mold. Note the suprisingly moderate conditions. The protective alumina sheaf around the ingot was similar to that of the water-cooled mold.

Firing was continued until a charge weighing about 1kg had been deposited, then the shut-off valve was closed,

and the remaining part of the lance removed. After allowing sufficient time for the ingot to cool the mold was inverted and the solidified contents tipped out.¹

3.1.2 Results

The ingot produced using the water cooled mold detached easily from the mold walls along with the non-adhering fragments of the protective alumina sheaf which had been formed by chilling out of the turbulent melt onto the mold walls². Subsequent firings using the air cooled steel molds often stuck in the mold when filamentary connections occurred through cracks in the alumina sheaf. Such specimens were less homogeneous and so unsuitable for experimental purposes.

3.1.2.1 The Alumina Sheaf

In appearance the alumina was of a uniform grey colour, shiny on the ingot face and rough on the mold side. Figure 3.7 shows the grain structure at the ingot interface.

1 a. The composite castings were in fact, only a part of an experimental programme, which also included attempts to weld railway rails [as an alternative to the thermit process], and rock and concrete boring [at a much faster rate of penetration than the oxy-iron so-called "thermic lance"].

2 The walls being the preferential location for nucleation at any temperature.

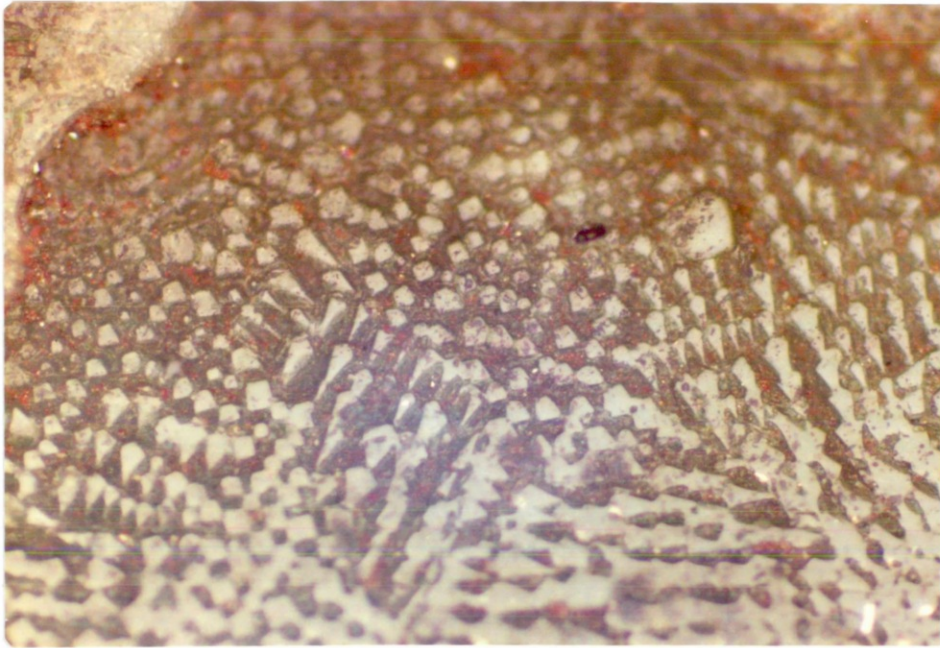


Figure 3.7 Inner Surface of the Alumina Sheaf $\times 500$

The scale-like appearance of the inner surface of the sheaf is common to both the water-cooled and the air-cooled systems. The mold-side surface was rough and contaminated with iron and iron oxide.

The grain morphology is in the form of "fish-scales" of uniform size. Electron microscope x-ray analysis gives a gradient of corundum purity [judged from the aluminium element reading] ranging from better than 99% at the shiny inside face to less than 90% at the mold face. This was confirmed by powder x-ray crystallographic analysis as alpha-alumina [corundum]. Alumina is much more likely to come out at the system boundary than it is in the melt. [a] due to nucleation considerations and [b] due to the chilling of the alumina by the mold walls. This presents a problem. The amount of the alumina actually remaining in the steel will be only a small fraction of the total produced. Furthermore it would not appear possible to control that fraction. The solidification of

the alumina occurs at 2050°C, which is far above the range of temperatures useful for the melt. This precludes us from externally heating the mold in an attempt to prevent the alumina chilling out.

3.1.2.2 The Composite Ingot

The bottom 5mm of the ingot exhibited gross porosity, the average pore size being about 1mm in diameter. The main body [about 5cm diameter by 10cm in length] was pore-free. The surface was smooth in appearance and of a dull grey lustre. The top 1.5cm contained cavernous pores of greater than 1cm diameter covered by adhering remnants of slag. The pores at the top were clearly formed by expanding oxygen bubbles whereas, those at the bottom are likely to be caused by the evolution of dissolved nitrogen and excess oxygen together with CO/CO₂ gas evolving from the oily mold surfaces and/or any carbon which was contained in the lance material itself.

The specific gravity of the pore-free bulk of the ingot was found by Archimedes' method to be approximately 6.24 gm/cc. That is to say, less than 80% of that of steel [confirmed later by SEM X-ray analysis]. This indicates a considerable concentration of aluminium and/or alumina. The residual aluminium may be due in part to the very high temperatures of combustion and consequently low values of the equilibrium constant. Back-reaction could have been precluded by the sudden chilling in the very steep temperature gradients prevailing around the

reaction zone. Alternatively, and more likely, the aluminium may not have had time to react completely.

Microscopic examination of specimens cut, polished, and etched with 2% Nital solution, revealed [see Figure 3.8] a medium-to-coarse grain structure.

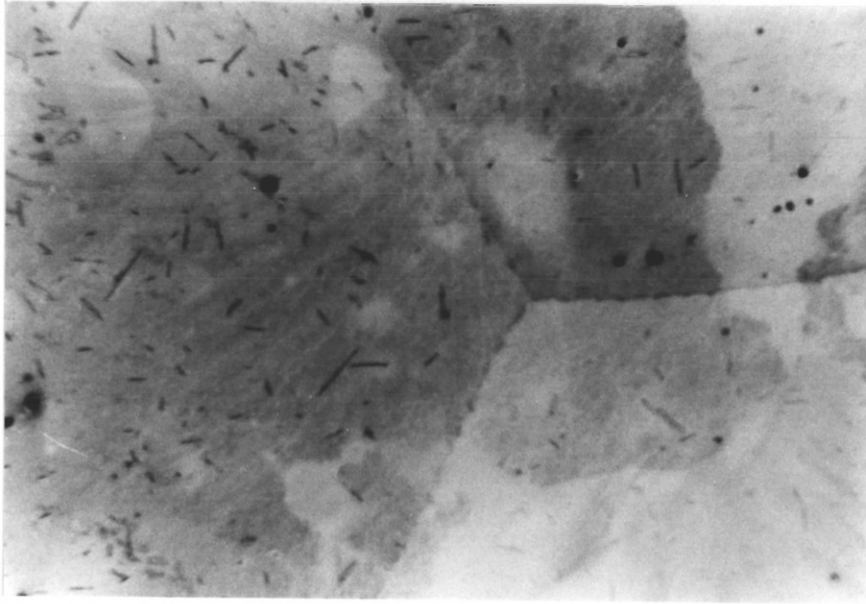


Figure 3.8 Steel Composite Grain Structure $\times 500$

Specimens were characterised by irregular grain sizes due to heterogenous cooling resulting from the severe agitation of the cooling melt.

White acicular inclusions of alumina of average size 2 microns by 15 microns were in evidence both within the grains and at the grain boundaries. Electron-micrographs [see Figure 3.9] show that the ceramic needle inclusions are seriously flawed by jagged re-entrants which create severe stress concentrations. Alumina inclusions in aluminium deoxidised steel are known to take a dendritic

form and although direct analysis is difficult owing to the minute size and embeddedness of the needles it is deduced that they are alumina primary dendrites.

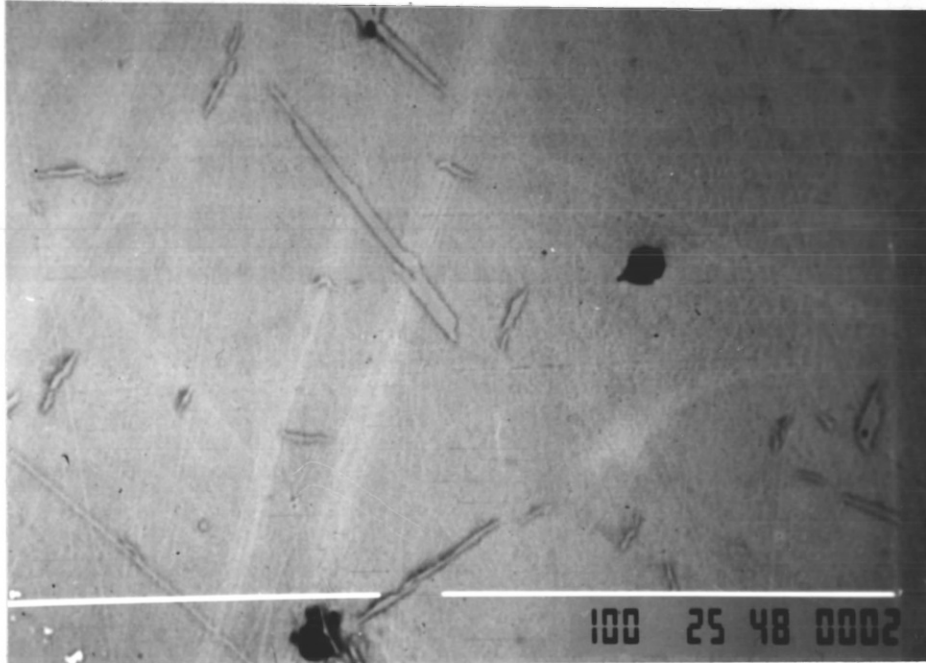
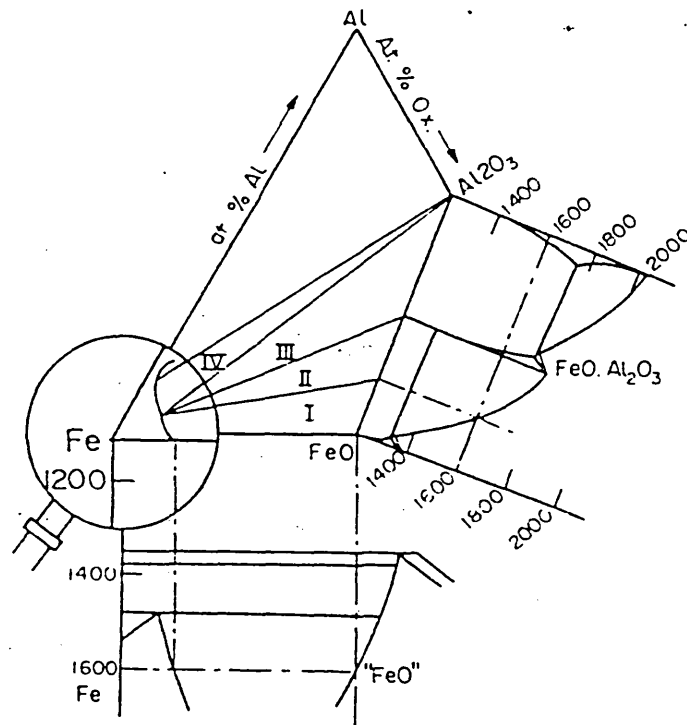


Figure 3.9 Primary dendrites of alumina.

The alumina inclusions were typically 15-20 microns in length and 1.5-2.5 microns in diameter. The alumina formed by a reaction fed by diffusion processes within the melt. The ragged shape of the needles presents problems of high stress concentration.

Analysis of the metal matrix indicated that some 20% of the elemental count is aluminium. This is made up off less than 10% alumina inclusions and the remainder being the dissolved element or intermetallic compounds of which the system Fe/Al contains a fair number [see Figures 3.10 and 3.13].



- Equilibria in the system Al-Fe-O
- I. (Fe, O, Al) - (FeO, Al₂O₃);
 - II. (Fe, O, Al) - (FeO, Al₂O₃) - <FeO . Al₂O₃>
 - III. (Fe, O, Al) - <FeO . Al₂O₃> - <Al₂O₃>
 - IV. (Fe, O, Al) - <Al₂O₃>

Figure 3.10 Fe-O-Al Ternary Phase Diagram

The fields of the many and various phases are close together and complex. In order to yield pure alumina the process would have to be strictly controlled to maintain a reaction path which consistently terminated in the alumina field.

Tensile test specimens were prepared and subsequent tests gave tensile strength values of less than half those typical for mild steel. Elongation at break was negligible, the fracture surface indicating brittle failure.

3.1.2.3 Problems of Study

Whereas the lance system shows some promise of being a useful tool for the "instant" production of molten steel,

alumina, and high intensity heat [for welding, rock cutting and boring for example] it is far from being an ideal research vehicle. The reaction is heterogeneous. Combustion takes place in a complex and essentially uncontrollable manner. Some of the heat goes to melt the iron and the aluminium at the lance tip [the primary reaction zone]. The majority however, is evolved in the free stream [the secondary reaction zone] in the spray condition or at the melt surface [the tertiary reaction zone] in the casting mode [or the boring mode].

The role of the iron in the combustion of aluminium in both of the iron-matrix systems studied is a major focus of interest since it is *sine qua non*, ie. aluminium will not burn in its absence. In the lance system it is not easy to see how the iron interacts with the aluminium and, in particular, whether it undergoes mixing in the elemental or in the oxide form.

To go some way in reducing these problems another system was devised which both uncouples the oxygen flow from the melting rate of the metals and ensures that the metals are mixed in a predetermined ratio.

3.2 The Bessemer Reaction

In this system a crucible containing a premixed iron/aluminium melt ^{at} a predetermined temperature is reacted with a controlled flow of oxygen bubbles injected

below the melt surface from a non-consumable alumina tube array. This in effect the inverse of particle combustion the reaction taking place on the inside rather than the outside of a sphere. This enables the heat transfer to the melt to be calculated since it will be total.

Ignition is spontaneous on the commencement of the oxygen supply. The melt is preheated and maintained by a high-frequency induction furnace. [see Figure 3.11].



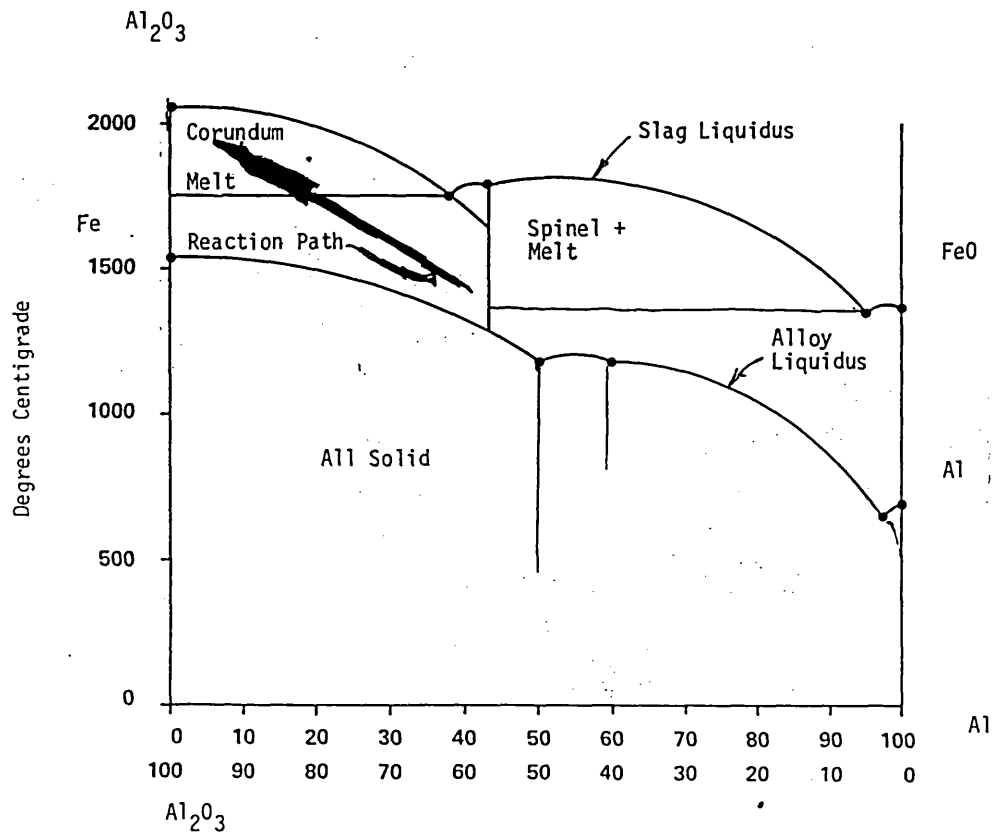
Figure 3.11 The Bessemer Experiment

An attempt to improve the control of the process by means of an alumina lance providing oxygen bubbles at a controlled rate. Submerged combustion occurs within the bubbles. This is in contrast with the combustion of the droplet spray of the consumable metal lance.

Using a binary melt allows start up temperatures well below that of the melting point of iron. As the reaction proceeds the mean melt temperature may be controlled to

stay at a fixed degree of superheat above the liquidus as the aluminium concentration is progressively lowered.

[see Figure 3.12].



Superimposition of slag phase diagram onto alloy diagram.

Figure 3.12 Reaction Path of the Bessemer Reaction

In this system an attempt is made to reduce the mean process temperatures by the use of a ferro-aluminium melt. The reaction path is intended to follow the liquidus until the aluminium is totally converted to alumina.

The dominant equilibrium is Eqn.3.1:-



Alumina is formed in the solid phase although, initially at least, it is fluxed by wustite around slag-skinned oxygen bubbles rising through the melt. It was anticipated that as the reaction proceeded the iron concentration would rise towards 100% and the aluminium concentration would diminish towards zero. Vigorous agitation resulting from the bubbling of oxygen would ensure that homogenisation of melt was maintained and that the corundum particles were evenly dispersed.

3.2.1 Experimental Procedure

A graphite susceptor surrounding an alumina crucible was wrapped in a "Kaowool" blanket and placed within the coils of a high frequency furnace. The alumina crucible was charged with granulated 50/50% ferro-aluminium. The charge was brought to a molten condition at 1250°C, measured by means of a Pt/Pt.13%Rh thermocouple. A bundle of fine bore alumina tubes were bound together to form a non-consumable lance array. This was connected to a regulated and metered flow of oxygen supplied from a commercial cylinder. Initial pressure settings were estimated from a model in which air was bubbled through an equivalent head of water. The alumina lance was preheated to minimise thermal shock and slowly introduced

through a leathery skin of aluminium-infiltrated oxide, and into the ferro-aluminium melt. The reaction ignited spontaneously but after only a brief period of combustion it was extinguished by its own products. The procedure was once again attempted but with the lance being circled in a stirring action. This had the desired effect of creating a continuously renewed supply of reactants and the combustion remained steady. The submerged flame was surprisingly quiescent but emitted blinding white luminosity, presumably through bubbles opening at the surface although these could neither be seen nor heard¹. [see Figure 3.11]. Combustion was continued until it extinguished itself by depletion, though not by the exhaustion, of the aluminium. Since the flame did not appreciably alter its colour towards the end of the reaction it was assumed that the iron had not at that stage been attacked. However, to anticipate later results, subsequent powder X-ray analysis revealed the presence of hercynite as well as that of alumina. Moreover there was also some aluminium carbide which was traced to a crack in the alumina crucible and consequent contamination via the reaction:-



¹ Another interpretation of this is that "liquid combustion" is occurring. This is similar in conception to the thermit type of reaction which is typically gasless, silent, and highly luminous.

..or by way of the reduction of alumina or its sub-oxides by carbon monoxide gas. The kinetics of the process are complex and the products cannot be predicted with any certainty by thermodynamic considerations alone. In fact the appearance of hercynite and aluminium carbide indicates that equilibrium was not achieved throughout the melt. These phases will not have appeared in the same region of the specimen.

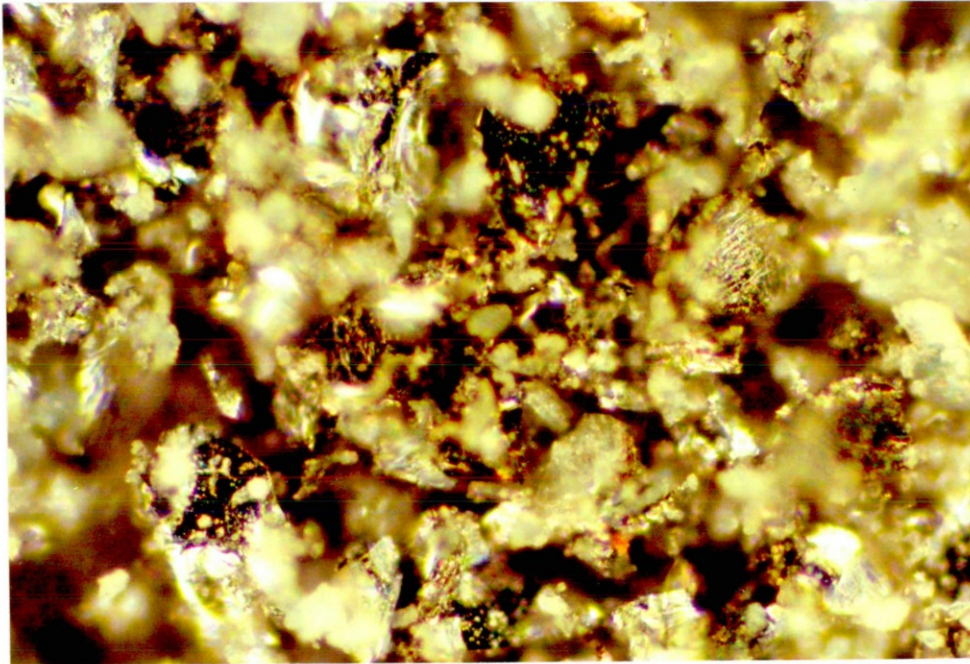


Figure 3.13 Powder Products of the Bessemer Reaction

The "ingot" formed by the reaction was friable at finger pressures. The powder was glassy as formed. Devitrification and x-ray analysis revealed a complex of oxides and their solid solutions together with unreacted ferro-aluminium.

After a suitable cooling period the furnace arrangements were dismantled and the alumina crucible, which was found to be cracked, broken up to reveal what at first appeared to be an ingot of composite. Subsequently this proved not

to be the case since, on being lightly struck with a hammer, the substance crumbled to a fine even grey dust made up of particles about 50 microns in diameter. [see Figure 3.13].

Preliminary X-ray powder analysis indicated amorphous glassy structures. Heat treatment in argon and in air at 1400°C was performed in order to de-vitrify the powder for re-examination of the crystal structures.

3.2.2 Results

Powder x-ray analysis of the products of the crucible reaction identified the following species:-

#Alumina

#Hercynite

#Aluminium carbide

#Iron oxides

#Intermetallic compounds of aluminium and iron

TABLE 3.3

Powder Products of the Crucible Reaction					
Code	Form	Heat Treatmnt Celsius	Argon Atmos l/h	Time	Location in Cast
A1	240 mesh HCl cleaned	970	0.5 tube furnace	18	centre
A2	240 mesh HCl cleaned	1400	0.5 tube furnace	3	centre
A5	as cast 240 mesh	1400	muffle	18	centre
A6	as cast 240 mesh	1400	muffle		bottom
A7	as cast 240 mesh	as cast	as cast	as cast	top
A8	coarse powder	1400	0.5		bottom

Analysis below.

Note: specimens A1-A4 were immersed in hydrochloric acid to remove the metallic phases to facilitate the analysis of the ceramic phases.

ANALYSIS.

A1 & A2.

The major phase was Al_2Fe_2 [plus possible presence of corundum]

A5

The main phase was corundum Al_2O_3 with some spinel FeAl_2O_4 and an intermetallic phase [probably Al_3Fe_4]. In addition there is a fourth phase which is isomorphous with Mn_2AlO_4 this is thought to be Fe_2AlO_4 or $\text{Fe}_4\text{Al}_2\text{O}_8$ [by multiplying by two] made up of $\text{FeO} \cdot \text{Fe}_3\text{O}_4 \cdot \text{Al}_2\text{O}_3$. The Al_2O_3 lines occur as doublets. This is because alumina of two different structures is formed. The alumina with the higher unit cell dimensions probably has iron dissolved in it. Indeed the alumina-hematite phase diagram shows evidence of this as hematite dissolves in alumina. This sample contained more of the $[\text{Al}_2\text{Fe}]_2\text{O}_3$ phase than Al_2O_3 .—Hence the brown colour of the powder.

A6

The major phase here was Al_2O_3 with some $[\text{Al}_2\text{Fe}]_2\text{O}_3$ present. The colour of the powder was light brown. An intermetallic compound is also present.

A7

The major phase here was Al_3Fe_4 . Alumina is also present.

A8

FeAl_{12} was the major phase.

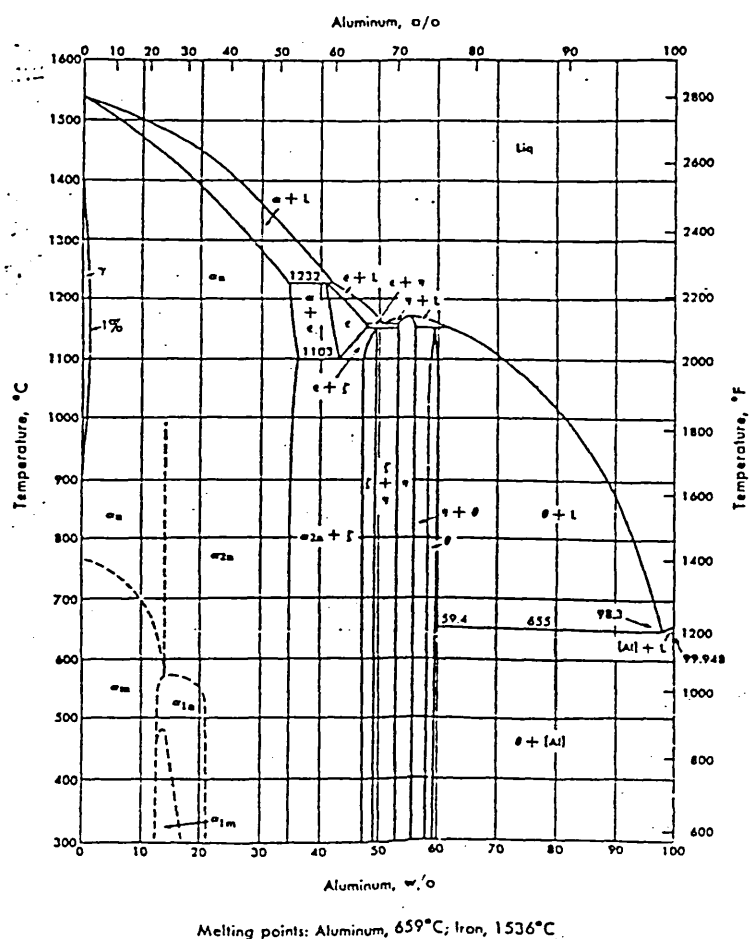


Figure 3.14 Iron-Aluminium Phase Diagram

The reaction path of the process follows a locus some 50°C above the liquidus. This ensures that the mean temperature of the process is minimised. On exhaustion of the aluminium the oxygen supply is discontinued. Oxygen bubbles serve both to provide the exothermic reaction heat and to agitate the melt to distribute the alumina/hercynite crystals.

Consideration of the relevant phase diagrams [see Figure 3.14, Figure 3.15 and Figure 3.16] [neglecting the aluminium carbide], shows that the regimes of the various fields are narrow and lie close together hence, in view of the likelihood of heterogeneity caused by bubble agitation, it appears unlikely [in retrospect] that the

products would be simple alumina in an iron matrix. Furthermore, in the experiment the reaction was not taken to completion.

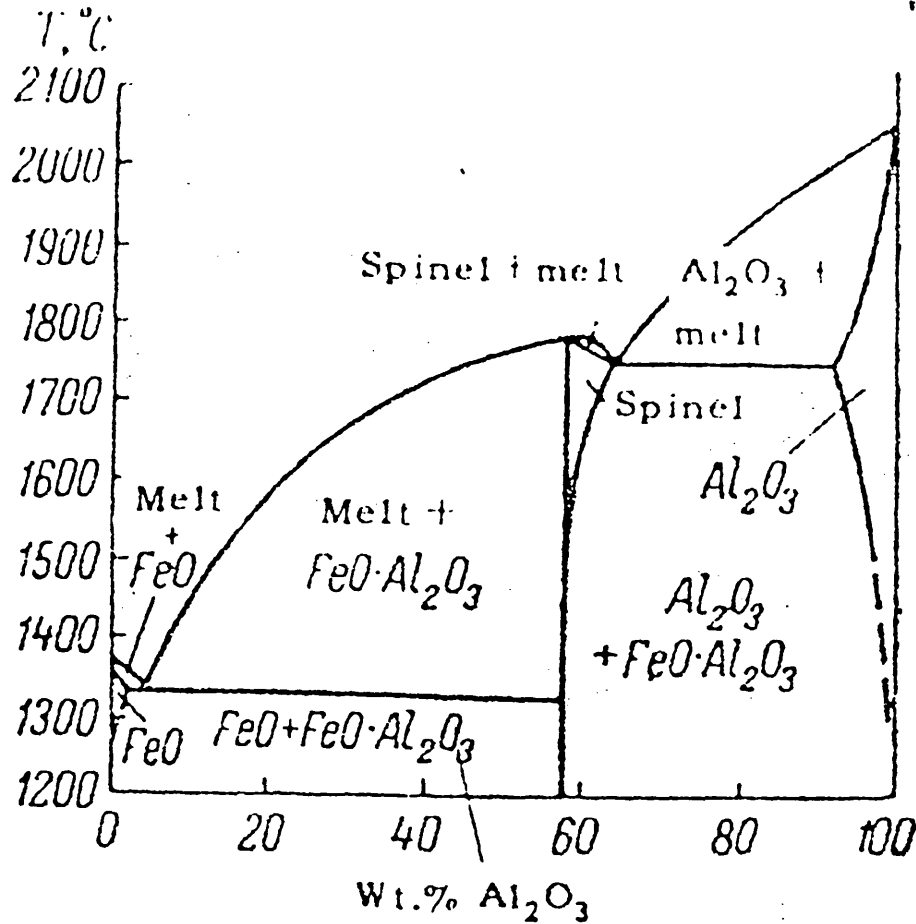


Figure 3.15 Iron Oxide/ Aluminium Oxide Phase Diagram FISCHER 1954
'Physical Chemistry
of Steelmaking'

The complex distribution of the narrow phase fields demands very close control over the reaction path if only pure corundum crystals are to be produced.

3.3 Iron-Matrix Composite Routes- Preliminary

Discussion

Neither of the routes to iron-matrix alumina composite formation examined above show promise of their immediate adoption as useful methods in their present form. However

each offers useful and interesting insights into the mechanisms occurring in multi-phase melts at very high self-generated temperatures. These in turn may well suggest more reliable processes based upon similar approaches. For example, further oxygen bubbling through by means of a non-consumable auxiliary lance could lower the presently high residual aluminium content of the consumable aluminium/iron lance which is seen to be the major fault in the first process. Conversely less oxygen could be provided to the second [crucible] route described. This may have the effect of ensuring that the reaction is maintained in the corundum field [see Figure 3.15]. Alternatively since the actual products of the second reaction are already in a useful powder form they may thus form the basis for a wettable [and reactive] powder technique. All of these possibilities as well as others will be discussed later in Chapter 6.

Before final conclusions are made concerning the iron-matrix processes just reviewed a description of the second major direction of this thesis will be made after which more generally relevant arguments will be put on the theory of alumina-containing composites produced by self-propagating redox reactions.

The next section deals with alumina as the matrix material of ceramic-metal composites.

CHAPTER 4. ALUMINA/ALUMINIUM COMPOSITE FORMATION

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4.1 The Lanxide Patent

The Lanxide Patent [Appendix II] describes the method by which a massive thick crust-like layer of alumina is made to form continuously under certain circumstances on the top of an aluminium alloy melt. Silicon and magnesium

solutes in quantity varying between 1%-10% are heated in air or oxygen to temperatures within an upper bound of 1400°C and a lower bound of 1100°C. During a period measured in hours, the aluminium oxidises catastrophically forming a thickening crust of corundum permeated with aluminium-filled pores through which the reaction is supplied. The process is self-propagating, only terminating when the aluminium melt is totally converted to alumina or when the temperature has dropped below the operational threshold. The patent describes in part the mechanism as resulting from the "wicking" of aluminium up through pores in the crust. The formation of the pores is said to be the result of an initial spinel forming stage. The aluminium having passed up through the pores from the melt reacts with oxygen at the top surface to form alumina.

4.1.1 The Problems

The patentees, either by ignorance or by design, do not attempt to explain the various mechanisms which must take place in order to bring about formation of the ceramic-matrix composite which they describe. The patent system, of course, does not require that they should. The onus of the applicants is merely that they disclose sufficient details to enable replication of the claims by a reasonably competent practitioner of the field of art

or science in which the invention lies. Thus the questions which this part of the study sets out to answer are:-

How does the spinel forming process occur, and how does it create conditions in which the pore forms continuously despite the fact that the spinel-rich pore-initiating layer remains behind at the crust-melt interface?

How is the [nominally] alumina pore-surface wetted by the aluminium, bearing in mind the unfavourable surface free energy situation?

How does the aluminium react swiftly and continuously to form alumina when at the temperatures claimed for the process it would normally be solid thus precluding a sufficient rapid supply of oxygen for the reaction to proceed as it does?

How does the corundum become evenly distributed over the growing surface of the crust in view of the fact that the aluminium arrives at the surface via the pore system which accounts for only a small fraction of the surface area?

What is the role of the silicon?

What is the role of the magnesium?

What factors determine the upper process-tempera-

ture boundary which occurs at about 1400°C?

What factors determine the lower process-temperature boundary which occurs at about 1100°C?

Additionally it would be of interest to know more about the effects of process conditions:-

What is the rate of the reaction, and what factors determine this rate.

What is the effect of background temperature.

Can any other dopants be used which would enable the process temperature to be lowered. [the patent mentions other Group IVB elements]

Can pore and grain morphology be controlled¹. [the patent describes the effect of temperature on pore diameter]

Finally, although the effects of various conditions upon the cermet produced were considered to be of some importance, the primary research strategy was to determine the *mechanisms* by which the process worked rather than to arrive at a pattern of reactants and conditions which would effect the production of the cermet crust.

¹ Capillarity is inversely related to the pore diameter, [Laplace's Equation Eqn.29 *ibid*] hence there will be a limiting crust thickness, where the gravitational forces approach those due to surface tension. Thus the finer are the pores, the greater is the limiting thickness. In the present work it will be shown that there are, in any crust produced, a range of pore diameters. The larger are exhausted before the smaller.

4.1.2 Experimental Design

The nature of the reaction system poses some difficult observational problems. The reaction is heterogeneous, occurring in part at hot-spots at microscopically small pore exits and at very high temperatures. Preliminary assessment of the temperatures which were likely to exist at the hot-spots indicated that the reaction could take place in the gas phase and at rates high enough to initiate combustion. It was anticipated that indirect methods of temperature assessment would have to be adopted. The measurement of the reaction rates in terms of the weight gain could be accomplished with some degree of accuracy using thermogravimetric apparatus. Estimates could be made of the cross-sectional area of critical sections at which the reaction was considered to occur. These were considered to be closely related to the pore exit areas. Taking into account the reports in the literature that metallic "flames" are thin and flat [as are the so-called fog reactions, *ibid* Section 2.2.7] temperature values could be derived from considerations of radiation flux intensity. These derivations proceed by way of the Stefan-Boltzmann radiation law on the assumption that radiation heat transfer is dominant at the high temperatures which are likely to occur.¹

¹ At 1200°C thermal conductivity is less than one sixth that at room temperature. Mean temperature drop across the thickness of the crust is only 100°C. On the other hand the radiation losses from the reaction hot spots is driven by a temperature differential of about 600°C and the losses are proportional to the fourth power of the temperature.

With the questions posed in the previous section in mind, the following experimental approach was adopted. Rates of reaction were measured for small specimens using thermogravimetry. To reduce the influence of any boundary effects occurring as a result of the large surface to volume ratio of the small thermogravimetric specimens, parallel experiments were conducted on batches of specimens of larger size in a muffle furnace. The muffle furnace experiments were more suitable for running pilots for both varying compositions and varying conditions. One furnace run could be used to test a whole range of compositions. A range of alloy compositions were selected from within the "Lanxide" window as well as others beyond the reported boundaries. To reduce the large combinatorial number of possible experiments some pilot trials were run using temperatures which were varied with time. Speculative experiments were performed using dopants which might enable the Lanxide process window to be circumvented and in particular to see if the process could be made to occur at lower temperatures [for example by the application of slags of lower melting point].

A most powerful variant method which afforded a substantial reduction in the number of experiments, was the use of the powdered oxides of silicon and magnesium on the top surface. This circumvented the initial MgO and spinel formation stage. It also separated the capillary mechanisms which otherwise supplied the magnesium and silicon reactants, from those occurring at the reaction

zone. The fact that this route was found to produce virtually identical results to those of the alloy route pointed the way to the eventual formulation of the proposed kinetic model by forcing a convergence of attention upon the role of the dopants as slag forming agents. The formation of such a slag is thought to be a precondition for the initiation of combustion reactions at the top surface.

The main series of experiments were all conducted with the specimens buffered on all but the top surface by alumina powder. This allowed air access over most of the specimen. To test the effects of confining the reaction to the top surface, a run was made with the melt in an alumina crucible without buffering. The results of this experiment, although atypical, were also of crucial significance in the construction of the kinetic model.

It is worth noting here that the optical microscopy was considerably enhanced by the use of darkfield objectives. Without these very little detail could be made out and most of the conclusions drawn could not have been arrived at. Normal brightfield objectives showed very little contrast between the oxide phases which appeared to be of a uniform grey tone.

4.2 The Alloy Route

In this approach the model conditions provided by the Lanxide patent [Dizio 1985] were replicated. These are fully detailed in appendix II but substantially the temperature window lay between 1100°C and 1400°C, and the alloying compositions of both silicon and magnesium were from 0% to 12%. Aluminium-Si-Mg alloys were subjected to various thermal cycles within a muffle furnace to obtain specimens for phenomenological examination of the pore morphology and the grain structure. The most fruitful of these experiments were later replicated in a thermogravimetric tube furnace in order to investigate the dynamics of the process.

4.2.1 Experimental Procedure

Various alloys of aluminium-silicon-magnesium including zero values of each of the solutes were made up from "superpure" aluminium, silicon, magnesium, Al-8% Mg [H8], and Al-12.5% Si [the eutectic composition] in combination. For the thermogravimetric experimental series these were first cast into multiple 6mm diameter holes drilled through a 30mm thick steel block and then sawn into 6mm long cylindrical specimens in order to minimise the surface to volume ratio. Further casts were made onto a thick alumina disc to produce specimens for the muffle furnace series. These were approximately 80mm in diameter and 10mm in thickness.

4.2.1.1 Muffle Furnace Experiments

The disc shaped specimens were weighed and placed on a thick alumina disc and put into a muffle furnace. The temperature was raised at the rate of 250°C/h until the desired value within the "envelope" [taken from the Lanxide patent] was attained. Dwell times were selected to yield specimens at various stages in the formation of the ceramic. Temperatures were monitored by means of a Pt/Pt.13%Rh thermocouple shielded by an alumina sheaf. Spot checks of the temperature at the specimen surface were made by sighting a total radiation optical pyrometer through a shuttered hole prepared in the furnace roof. After each run the specimen was weighed and then cut using a diamond impregnated slitting disc into convenient sizes and then prepared for subsequent optical and electron microscopy and for x-ray analysis.

4.2.1.2 Muffle Furnace Series Results

The specimens which were doped with both silicon and magnesium became coated with a crusty skin of dark grey oxide at around 800-1000°C, the lower limit corresponding to a zero silicon value. This was subsequently found to consist of spinel and alumina. Specimens withdrawn from the furnace after times during which temperatures exceeded 1100°C [that is to say, after the second reaction had occurred] were coated with a crust of grey alumina the thickness of which was directly related to the time. In general a typical rate of growth in thickness was

about 3mm/h. Specimens which were allowed to go to completion, ie. until the aluminium was completely exhausted, were found to contain a cavernous void conforming exactly with the original shape of the specimen, [Figure 4.1] even to the extent of showing on the corresponding inner surface precise replicas of the file marks which had been made prior to the experiment. Specimens were prepared for x-ray analysis and micrography.

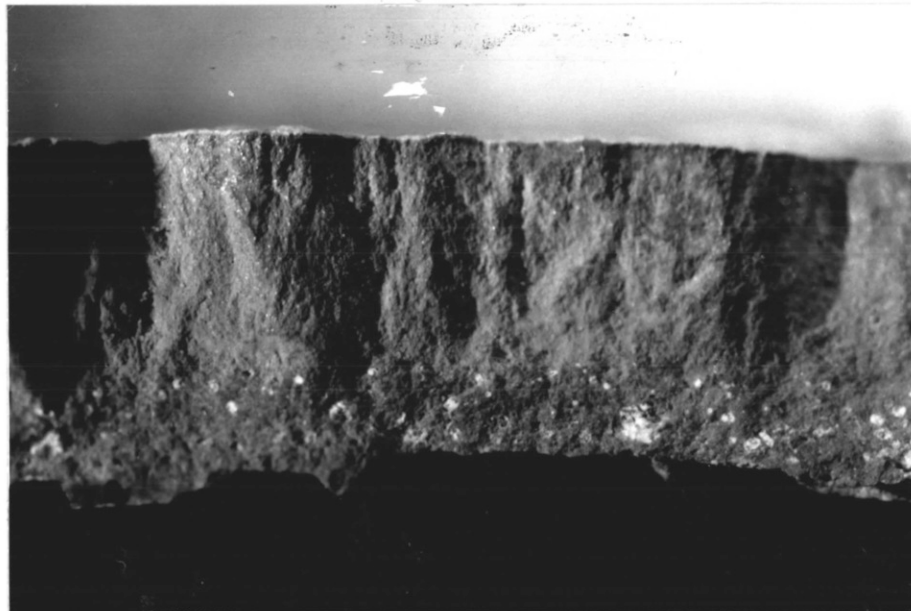


Figure 4.1 The Cermet Crust

The crust consists of alumina permeated with two types of pore. The larger pores, or voids, are the result of impingement of growing fractals whilst the fine aluminium-infiltrated pores are maintained by the metal melt. The blue colour is thought to be due to the presence of di-magnesium silicide.

Micro examination revealed a grey coloured matrix infiltrated by a fine tracery of pores amounting

generally to around 15% but up to 30% of the cross-sectional area. The pores were of two types. Some 70% of the pores were fine [about 5% microns] in diameter which were generally aluminium-filled. The 30% remaining pores were coarse ranging from around 30 microns to around 90 microns¹. These latter were often empty in those specimens taken to completion [see Figure 4.2]

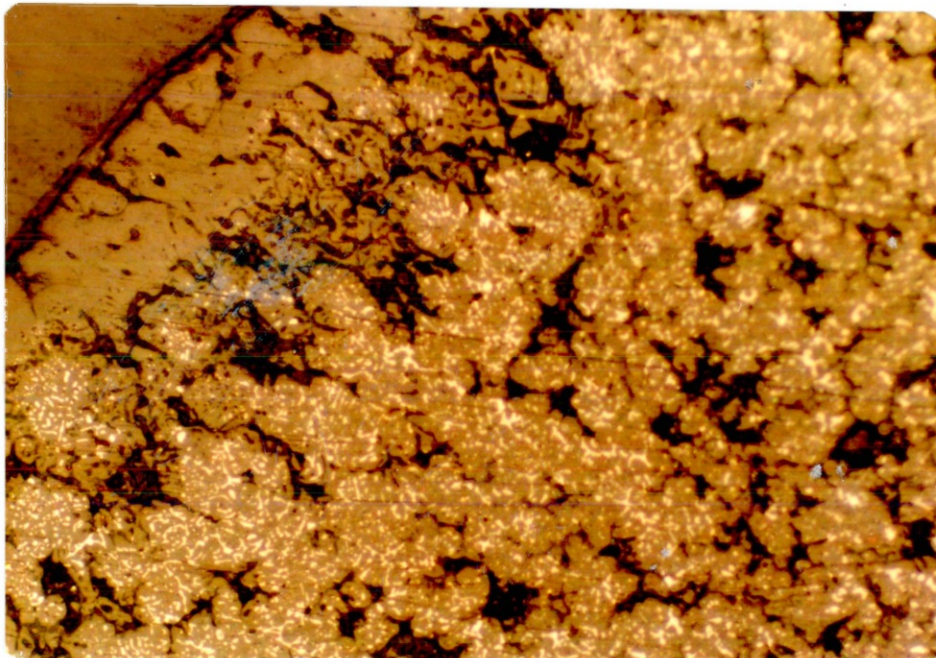


Figure 4.2 Empty Voids and Filled Pores [X100 Brightfield]

The figure shows a vertical section through an alloy route specimen taken to termination. The top of the crust is coated with a glassy oxide which is principally magnesia.

¹ Although the pores accounted for up to 30% of the cross sectional area an imaginary slice taken normal to the pore direction would show something like a tenth part of this. This is of significance when calculating the thermal flux intensity at the pore tops.

The top surface of the resulting crust was found to be coated intimately with a thin [500 micron] layer of a transparent glassy substance [see Figure 4.3]. This was assumed to be of a composition which was close to the eutectic of alumina-silica-magnesia and suggested that the mechanism of alumina formation was via a reactive slag involving the initial reduction of the silica by the aluminium to form alumina at the hot reaction surface followed by alumina precipitation at cooler regions as saturation occurred. The silicon would, in turn, become re-oxidised at the atmospheric surface thus providing for the continuation of the reaction.

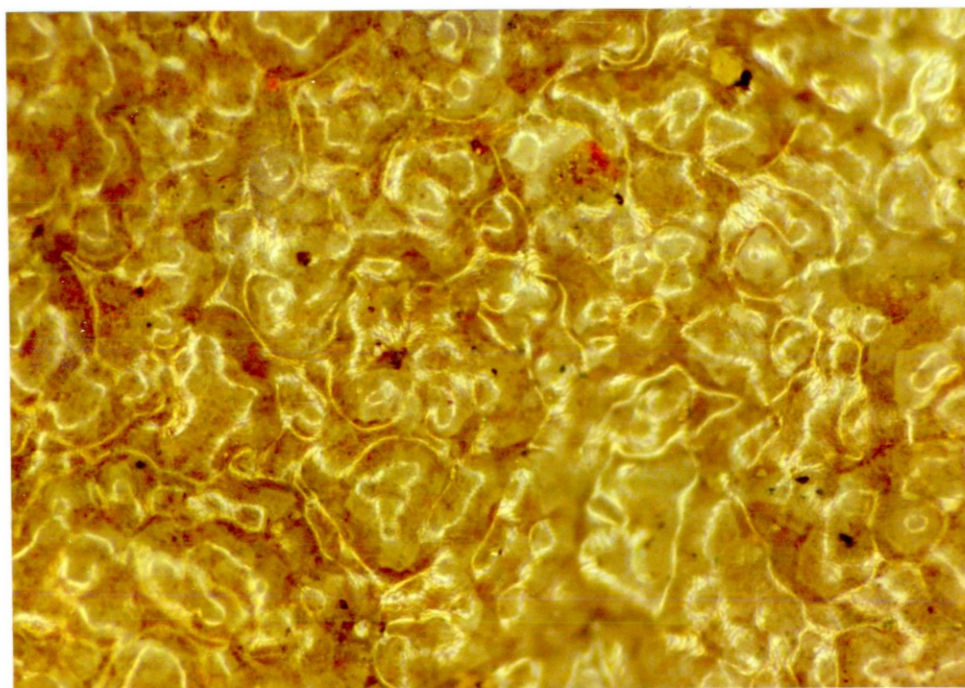
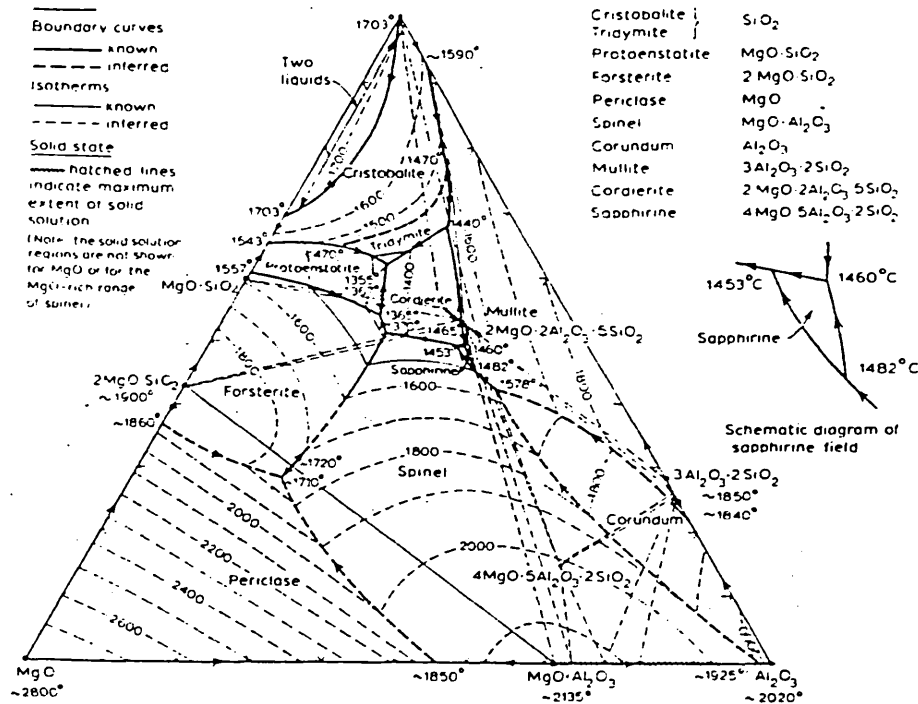


Figure 4.3 Glassy Overlayer [X200 Darkfield]

Plan view of the typical appearance of the glassy coating found at the top surface of the specimens.



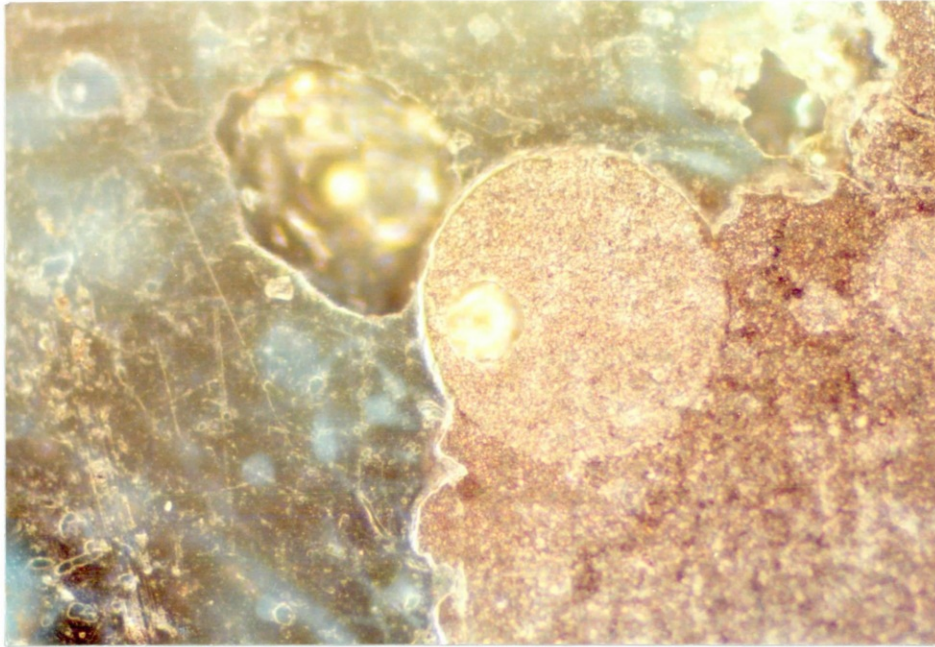
DRF West 1982
 Ternary Phase
 Diagrams

Figure 4.4 Ternary Phase Diagram [alumina-silica-magnesia]

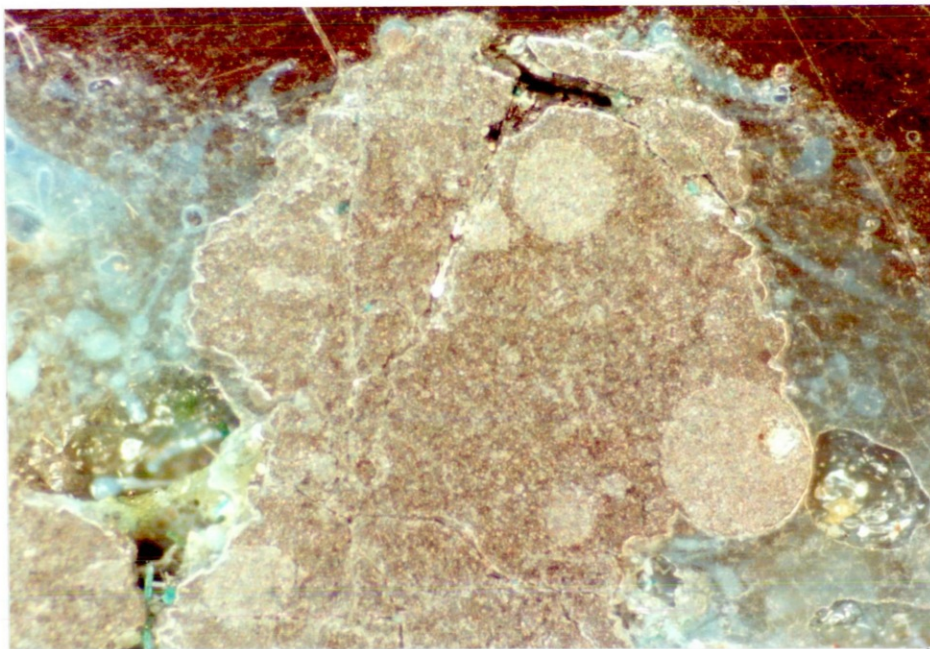
Examination of the phase diagram [see Figure 4.4] for alumina-silica-magnesia shows the eutectic temperature is 1347°C. The heat needed to raise the specimen from the furnace temperature [1250°C] could be supplied initially exothermically by the aluminothermic reduction of the silica.

TABLE 4.1

Experimental Programme: Muffle furnace series. [alloy route]				
Alloy Constitution	Spinel Forms [R1]	Alumina Forms [R2]	Temp [C] [R1/R2]	Time [R1-R2] minutes
Aluminium	NR	NR	NR	NR
Al/12.5% Si	NR	NR	NR	NR
Al/5% Mg	Yes	NR	856	NA
Al/8% Mg	Yes	NR	780	NA
Al/5% Mg +5% Si	Yes	Yes	900 1230	NA 80
Al/6% Si+ 4% Mg	Yes	Yes	950 1223	NA 67
Al/Fe50%	NR	Slight	1400	60



[a] X50 Darkfield



[b] X50 Darkfield

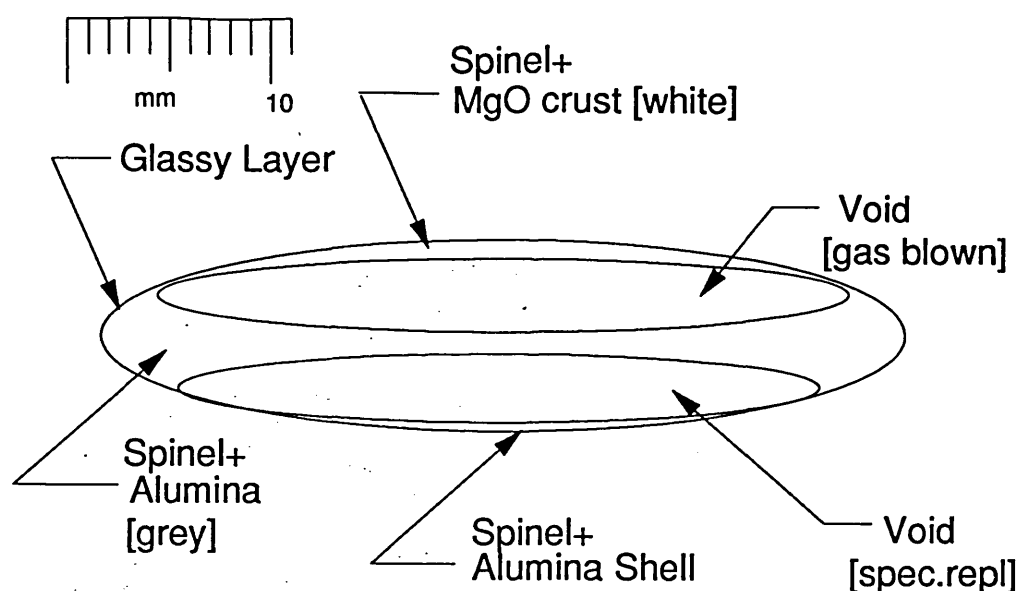
Figure 4.5 Alumina Spheres Formed in the Presence of Silica

The substrate upon which the main series of specimens was heated was aluminium oxide. However other substrates were tried to gauge their effect upon the reaction. These

included "Siffil" wool since initially it was considered to be close to the composition of the oxides to be formed from the alloy. In the event the excess silica deriving from the wool had significant effects upon the ceramic produced.¹ The presence of excess silica had an interesting and ultimately informative effect. A dome of white substance later found to be spinel and alumina covered most of the top surface [see Figure 4.6]. Normal alumina growth was confined to the edges and shaped botryoidally. On the white dome being broken away, the inner surface of the alumina crust was found to be coated with a fine white layer of MgO. In some cases this powder had built itself into supporting walls within the dome effecting partitions. This phenomenon served to aggravate the problem of finding the general mechanism involved. It was clear however that the spinel/magnesia dome had been plastic at some stage during the course of its creation and this was in all probability due to the presence of silica and the resulting ternary eutectic.

1 The silica was transported from the bottom to the top of the specimen. The mechanism involved is likely to be :-

*#reduction of the silica by the aluminium melt.
 #dissolution of the silicon into the melt at the bottom.
 #oxidation to silica once more at the top of the growing alumina crust.*



Typical for quartz powder on 5%Mg alloy & Ca4 on "Siffil"
[but NOT for pure Al+[powder-mix], or Al-12%Si+MgO]

Fig.4.5 Magnesia-choked Furnace Specimen
[over-doped]

Further but contrasting evidence of the influence of silica in the formation of the cermet is shown in Figures 4.5 [a]&[b] which are micrographs of an area at the bottom of the specimen adjacent to the "Siffil" wool. Spheres of alumina-infiltrated fine porous alumina are shown, some in the process of being engulfed. Figure 4.7 shows a pair of impinging spheres, one having been transformed to the cermet and the other [of silica] as yet un-influenced by aluminium. Their spherical shape is further clear evidence that they were formed out of the liquid phase before the main alumina-forming sequence engulfed them.

The significance of these phenomena will be discussed in Chapter 5 in conjunction with evidence gleaned from other

experimental series. At this stage it is sufficient to note that the formation of aluminium-filled pore permeated alumina is possible through an aluminothermic reduction of silica route. And that the product appears to be finer and morphologically more homogeneous than that normally produced.

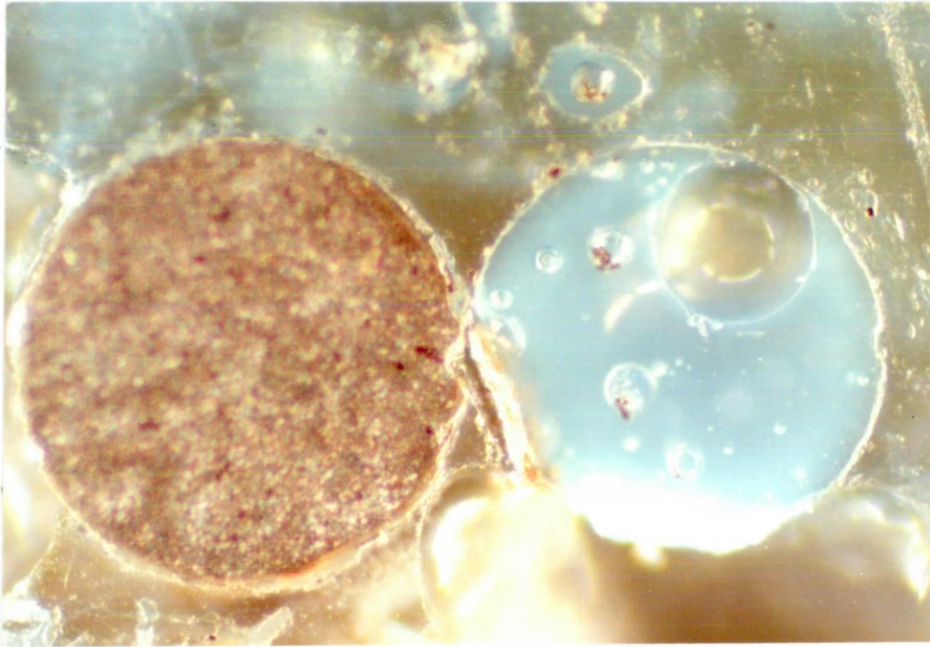


Figure 4.7 Free-forming Sphere of Cermet Impinging Upon Silica Sphere [X200 Darkfield]

The actual process of engulfment is shown in progress in Figure 4.8. Whilst Figure 4.9 shows a totally engulfed sphere. The similarities between the general morphology are such that they could share a common history with the alumina formed under normal circumstances.

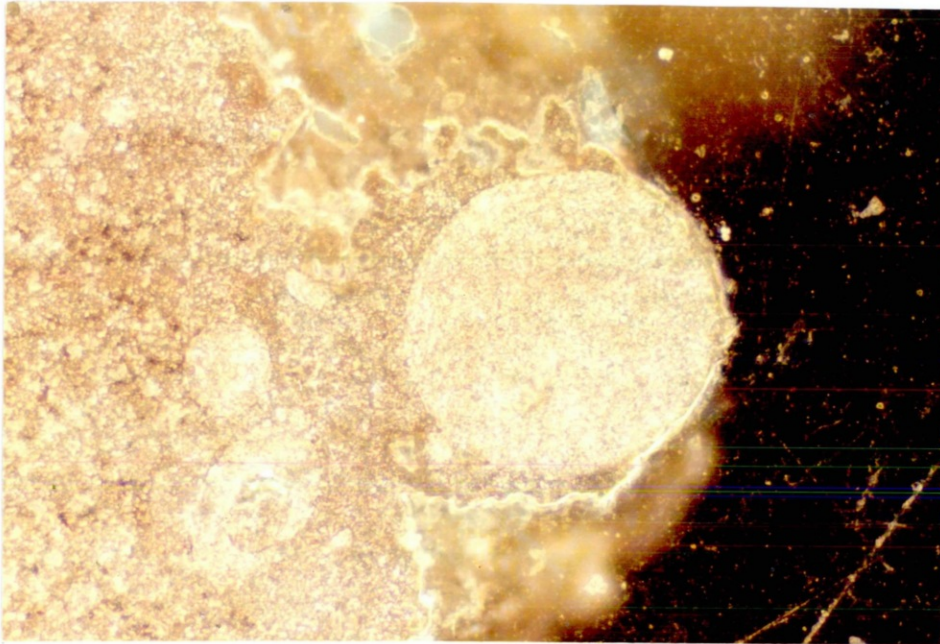


Figure 4.8 Free-formed Sphere in the Process of Engulfment [X100 Darkfield]

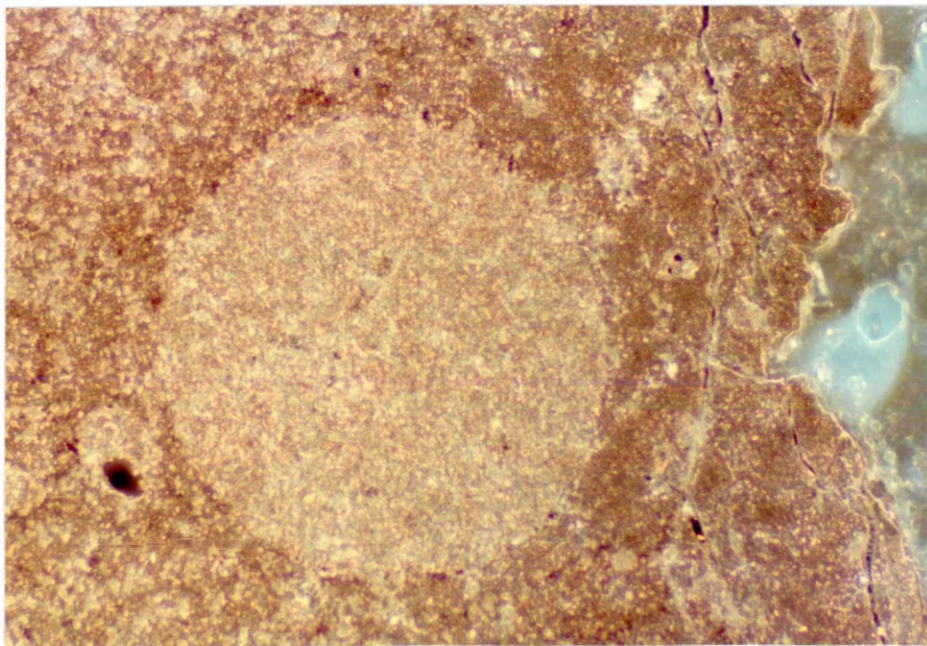


Figure 4.9 Free-formed Engulfed Sphere [X200 Darkfield]

4.2.1.3 Thermogravimetric Experiments

Special conditions were needed to prevent contamination from causing spurious reactions at the high temperatures used. The cylindrical specimens were embedded in fine alumina powder so that only the top surface was exposed to the atmosphere. Mineral [principally MgO/alumina] crucibles were thoroughly dried in a furnace for ten hours at 800°C during which test weighings were made to monitor the dehydration process until all weight loss had stopped.

The dried crucibles were initially alumina-wash coated to seal them. However problems were encountered when flaking occurred during some of the experimental runs and consequently this procedure was abandoned.¹

A platinum wire gondola was fashioned to hold the crucible and to enable it to be suspended from the thermogravimetric apparatus within the tube furnace. [see Figure 4.10]

¹ The protection afforded by the wash layer having been lost, some experiments were in fact contaminated by the crucible material and breakaway oxidation of the specimen occurred, even in the pure aluminium control series. This added further insights.

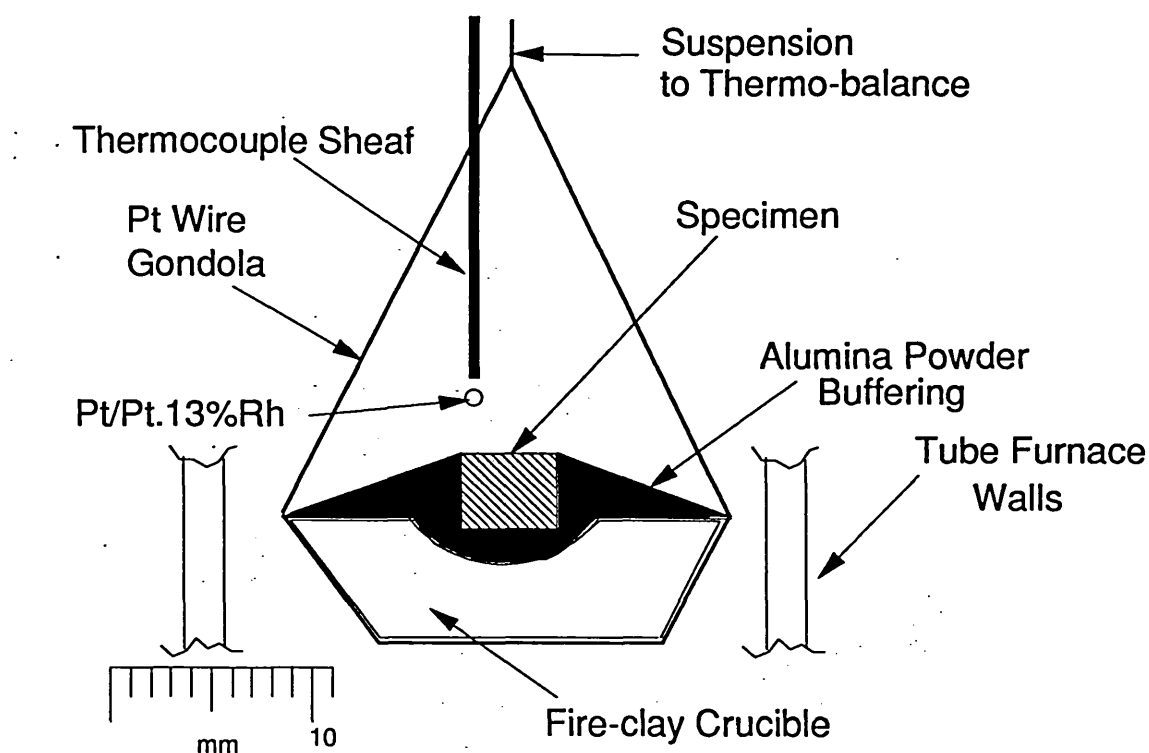


Fig.4.10 Specimen Containment Arrangements

The whole assembly including the alumina powder-embedded specimen was carefully weighed both before and after each run. In addition the specimen was weighed separately.

The test atmosphere was provided by an array of glassware which included: a rising-bubble flowmeter, dessicators [silica gel], and valving arrangements for switching argon, oxygen, and air.

The thermal profile of the heating cycle was controlled by a micro-chip operated proprietary furnace driver. Two Pt/Pt-13% Rh thermocouples were employed to monitor respectively, the furnace temperature [and also to provide negative-feedback for the driver], and the

specimen itself. The specimen thermocouple was suspended at a height of some 3mm over the specimen's top surface. The output of the thermocouples was recorded on a chart-recorder.

A gas flow-rate of 200cc/min was selected to provide super-abundant oxygen but without creating turbulence around the crucible. [the tube diameter was 35mm and the crucible 25mm]

The main series of experiments were conducted using:-

- # air as the oxidising medium,
- # an Al-5%Si-5%Mg alloy,
- # a mid-window temperature of 1250°C,
- # and a temperature-rise rate of 250°C/h.¹

¹ However, after the initial run was made it was discovered that two separate and distinct reactions occur, the first at about 950°C and the second at over 1100°C. Subsequently, dwell periods were held at each of these temperatures to maintain isothermal conditions until the reactions were completed.

TABLE 4.2

Experimental Programme: Thermogravimetric Series [alloy route]					
Alloy Constitution	Spinel Forms	Alumina Forms	Temp. [C]	Time [min]	Mass gain rate mg/sec /cm ²
Aluminium	NR	NR	NR	NR	NR
Al/12.5% Si	NR	NR	NR	NR	NR
Al/5% Mg	Yes	NR	860	NA	NR
Al/8% Mg	Yes	NR	770	NA	NR
Al/5% Mg/ 5% Si	Yes	Yes	890 1240	NA 73	NR 0.33
Al/6% Si/ 4% Mg	Yes	Yes	950 1223	NA 65	NR 0.53
Al 50%/Fe 50%	NR	Slight	1400	60	NR

4.2.1.4 Thermogravimetric Series Results

A pilot run was made to establish the peculiar characteristics of the reaction in terms of weight-gain profile. Three significant weight-gain events occurred [see Figure 4.11].

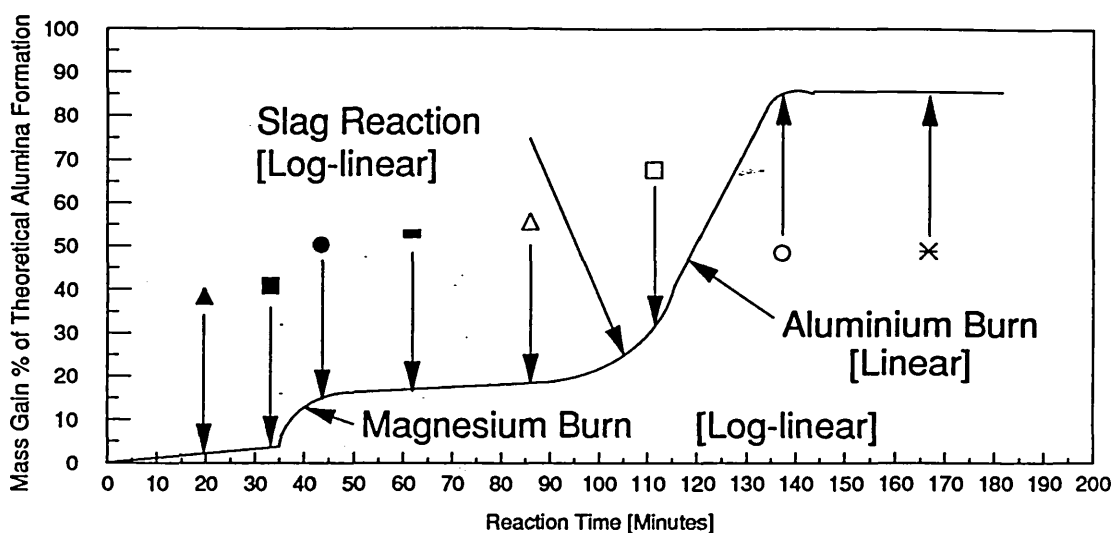


Fig.4.11 Mass Gain vs Time Al/Si/Mg Alloys

The first reaction occurred at around 950°C and was attributed primarily to the oxidation of the magnesium which has an appreciable partial pressure at that temperature, and a second more sustained reaction occurred at 1250°C clearly corresponding, in the main, to the continuous formation of alumina itself.

The first reaction paths for two alloys having silicon/magnesium ratios of 1:1 and 1.5:1 respectively are plotted in Fig 4.12. Each shows a sharp initiation [take-off] point followed by an exponential rise for the major part of the weight gain, and finally a terminal period during which the rate falls off smoothly during what is thought to be a glass formation stage.

Both the initial and the terminal period differ from that reported by Cochran et al [op cit] being reversed in their nature [cf Figure 2.3]. The results reported for their work related to experiments conducted upon aluminium-magnesium alloys. A control run using an 8% Mg alloy was carried out in the present series and the result is depicted in Fig 4.13 and again as a Log/Linear plot in Fig 4.14. In this case the results were in close agreement with those of Cochran et al [1966] having an initial exponential weight gain which was abruptly terminated by the exhaustion of the magnesium.

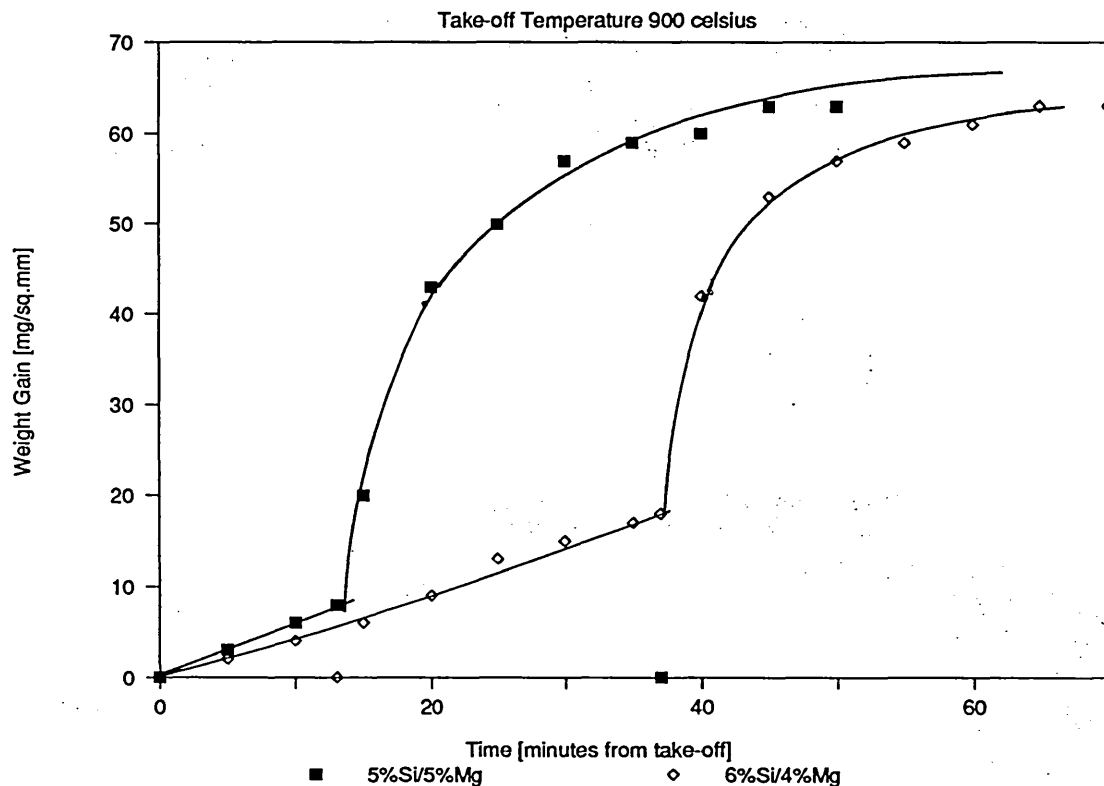


Fig.4.12 Spinel Formation Rate [Al-Si-Mg]

The sharp initiation points which occurred for the magnesium burn in those alloys which contained silicon is

thought to correspond to the abrupt occurrence of magnesia saturation in the glassy layer being formed over the spinel pore-initiating layer. The precipitation of magnesia giving rise to the formation of spinel pores and the enhancement of air supply to the reaction. The alloy which was the richer in silicon was relatively tardy in its take-off but its initial rate of weight gain was correspondingly greater. Alternatively, the melting point of the intermetallic compound Mg_2Si is approached at around $1000^{\circ}C$ [Mondolfo *op.cit*] and the sudden evolution of Mg vapour may be due to the resulting increase in the activity of the magnesium. The tail-off in the reaction rate during the final part of the burn is ascribed to the reducing activity of magnesium as its concentration drops in the alloy being supplied. The specimens which were withdrawn from the furnace immediately after the first reaction were found to be covered with an alumina/spinel layer. The quantity of magnesium as spinel was estimated to be about half that originally contained by the specimen, the remainder being available for the second [alumina-forming] reaction.

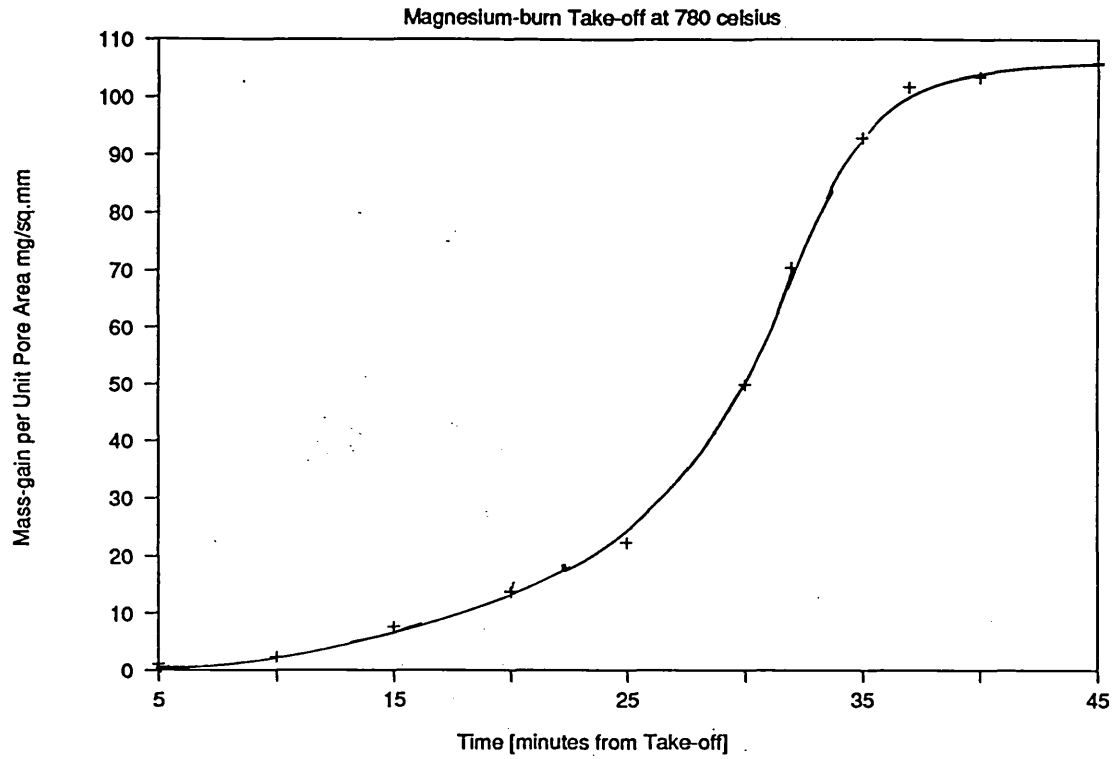


Fig.4.13 Spinel Formation Rate [Al-8%Mg]

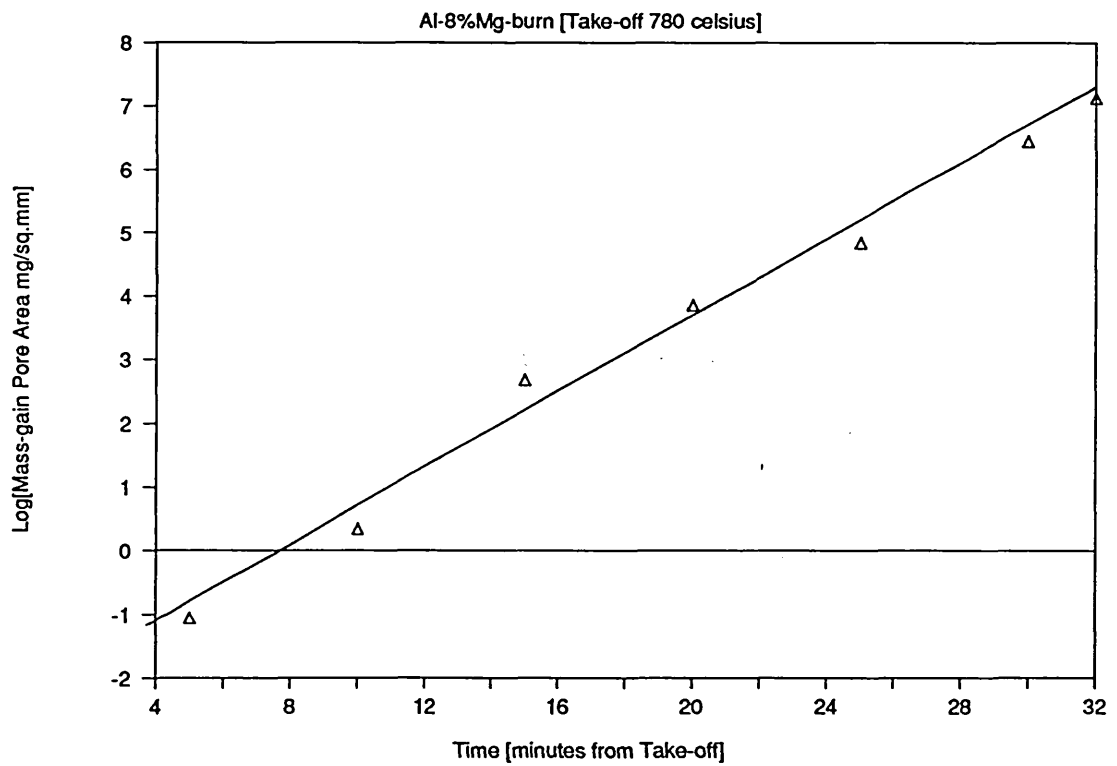


Fig.4.14 Log.[Spinel Formation Rate]

The second reaction [or aluminium-ignition reaction] occurred after an incubation period of an hour and whilst the furnace temperature of the furnace was rising through 1150°C. Subsequent runs were carried out after an isothermal dwell time of 30 minutes at 1000°C. The second reaction was then deliberately triggered by rapidly raising the temperature to 1250°C. This reaction occurred in two stages, the first [the ignition reaction] being indicated by an exponential rise in weight over 25 minutes, and the second being a linear increase in weight which continued until the aluminium was exhausted. Figures 4.15 and 4.16 show the ignition reaction as a function of the weight gain, and as the log of the weight gain respectively. [these figures also contain information about the powder route]

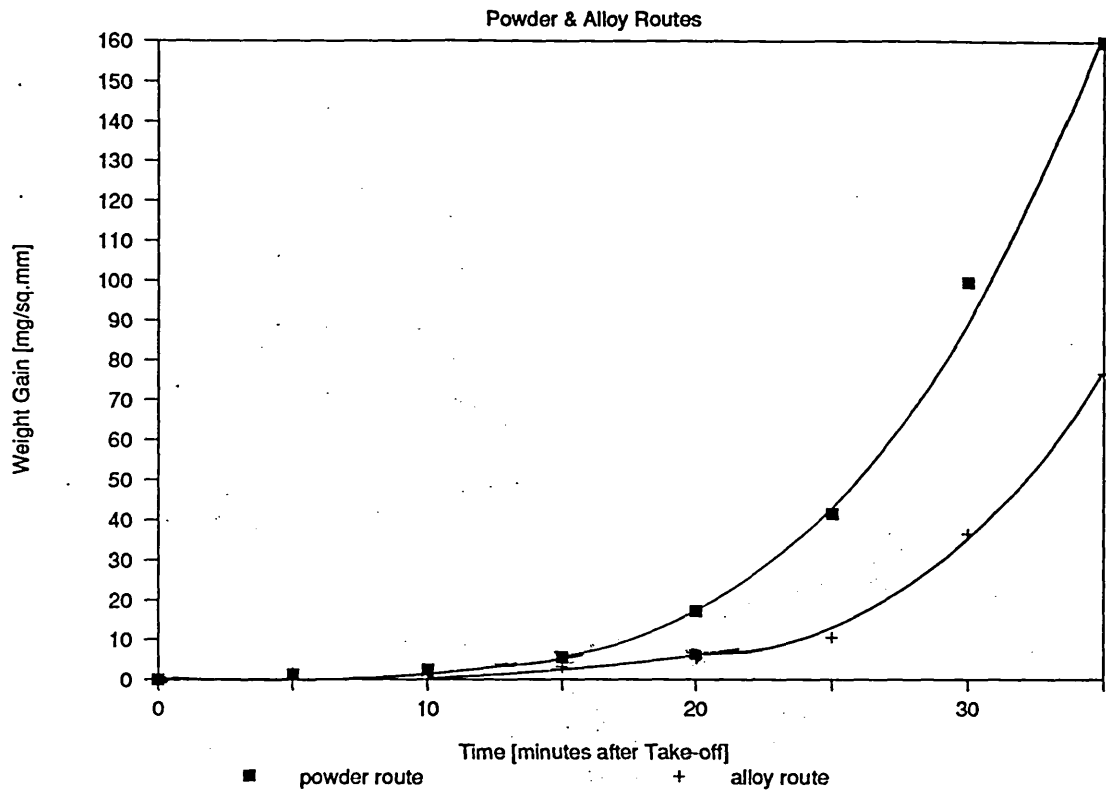


Fig.4.15 Alumina Reaction Initiation [Ignition]

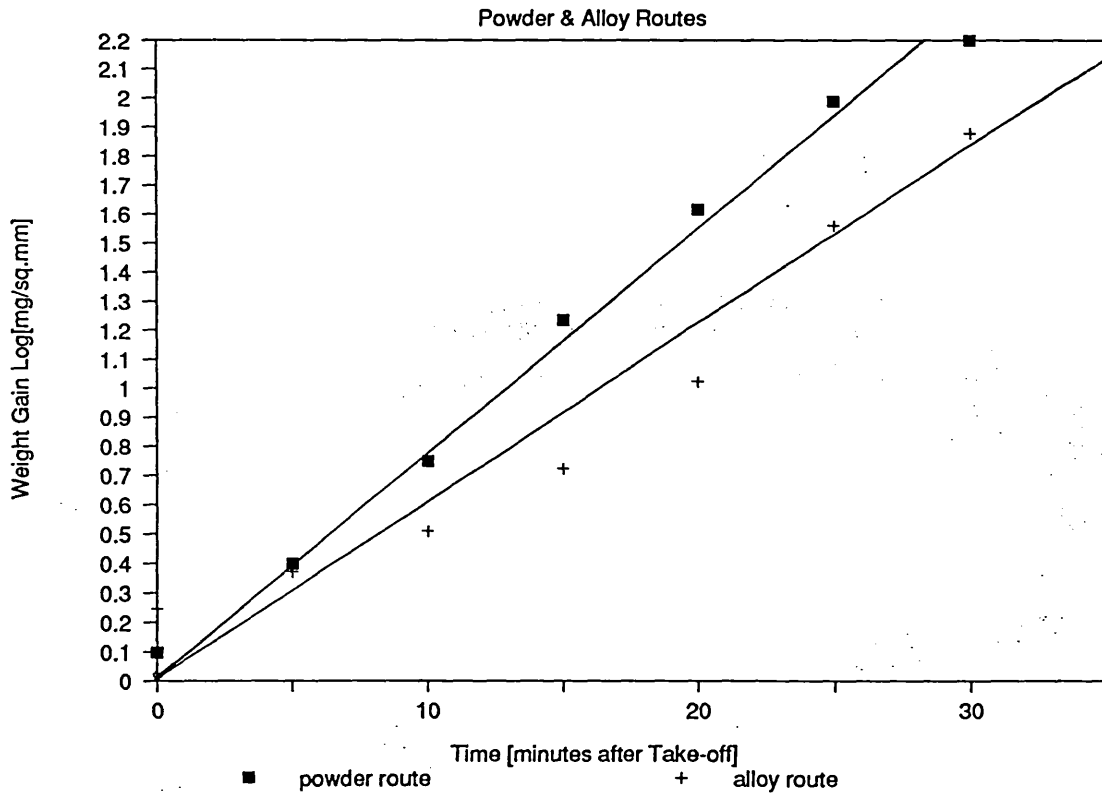


Fig.4.16 log[Alumina Reaction Initiation]

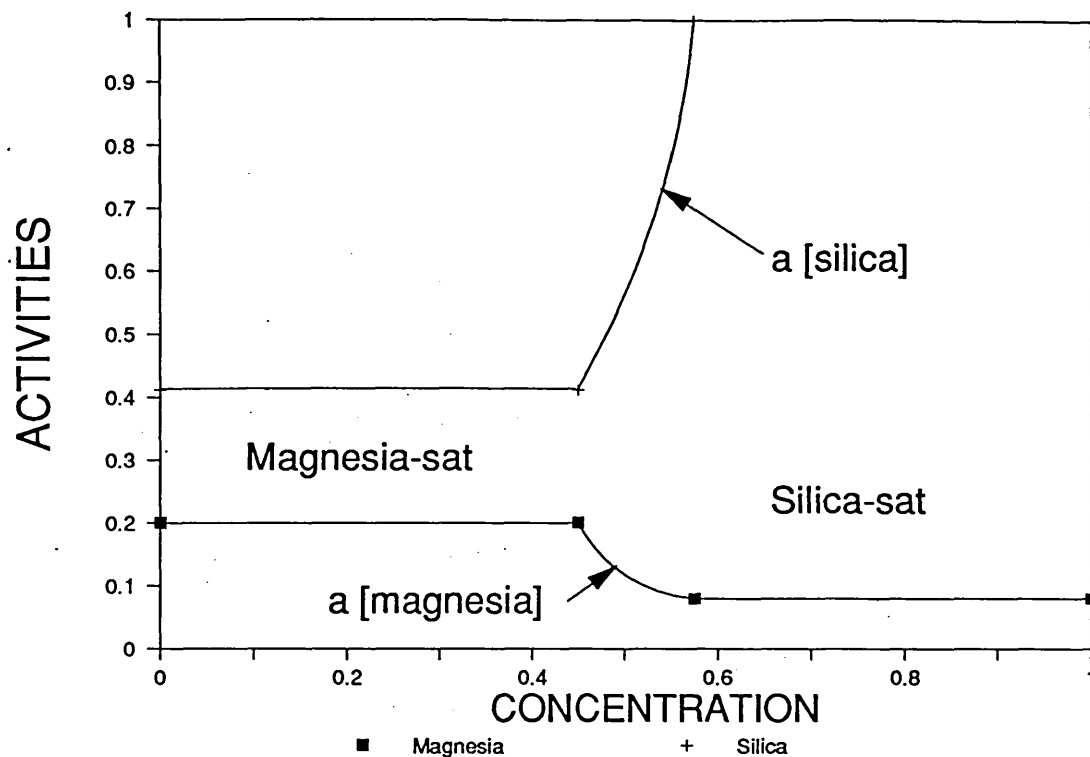


Fig.4.17 Activities of Magnesia and Silica
[Melt at 1650 Celsius]

4.3 The Powder Route

Since the mechanism of the process clearly involved the oxides of the elements of the alloy in some manner [and in all probability, as a ternary glass], a muffle-furnace test was made using pure aluminium with a top-dusting of the oxides of magnesium and silicon. As it had been assumed that the exothermic heat of alumina formation provided by aluminothermic reduction of silica played an essential role in the system, alumina was omitted from

the powder make-up. This yielded a cermet crust which was in all respects superior to [and more reliable than] those resulting from the muffle-furnace alloy route.

4.3.1 Experimental Procedure

Various powder combinations were formulated from fine powders of magnesia and silica evenly mixed and barrelled. Typically these were spread in an even layer some 2mm thick over the top surface of the specimen. The main series was conducted using "super-pure" aluminium. Other runs were made on; Al-Mg and Al-Si alloys. In particular silica powder was put onto Al-Mg alloys and magnesia powder was put onto Al-Si alloys.

During the alloy route series some specimens had become contaminated by inadvertent contact with the crucible bottom. This had caused weight gain reactions even were the specimen was the pure aluminium control. Hence further tests were made here after deliberate and measured contamination with ground-up crucible material [mainly alumina-magnesia but with trace silica].

The powder route also enabled other dopants to be investigated such as calcium fluoride, iron oxide, soda, and potash as well as other glass formers such as vanadium and lead oxides. However these were not made a part of a systematic search for alternative dopants but rather as *ad hoc* experimentation to test the evolving

theory of the mechanism which will be presented here. This will be further elaborated on in the theoretical arguments put forward in Chapter 5.

4.3.1.1 Muffle Furnace Experiments

With the notable exception of experiments concerned with the magnesium burn [which did not occur since clearly in the absence of elemental magnesium the reaction would consist only of the alumina formation stage], those conducted with a powder overlayer replicated those of the alloy route previously described.

TABLE 4.3

Experimental Programme: Muffle furnace series [powder route]				
Specimen Top Powders	Spinel Forms	Alumina Forms	Temp [C]	Time [min]
Aluminium	NR	NR	NA	NA
Al/MgO	Yes	NR	780	NA
Al/Silica	NR	NR	NR	NA
Al/MgO Silica	Yes	Yes	900 1200	55
/Vanadium PbO	NR	Yes [sponge]	650	NA
/Hematite	NR	NR	NA	NA
/Calcium Flouride	NR	NR	NA	NA
/Sodium Carbonate	Yes [calcine]	[sponge] Yes	851 900	NA
/Potassium Carbonate	Yes [calcine]	[sponge] Yes	891 891	NA

4.3.1.2 Muffle Furnace Series Results

The most striking difference between the results of this series and those of the alloy route was the reliability with which a crust of smooth flat appearance could be produced. The one exception to this occurred when silica powder was used to coat an Al-Mg specimen and small domes of spinel/magnesia appeared. This suggested that the phenomenon of the white crust was due, not as would be anticipated, to an excess of magnesium but, conversely, to an excess of silicon.

The microstructure was typically finer than those specimens produced by the alloy route, fewer large pores or voids being in evidence.

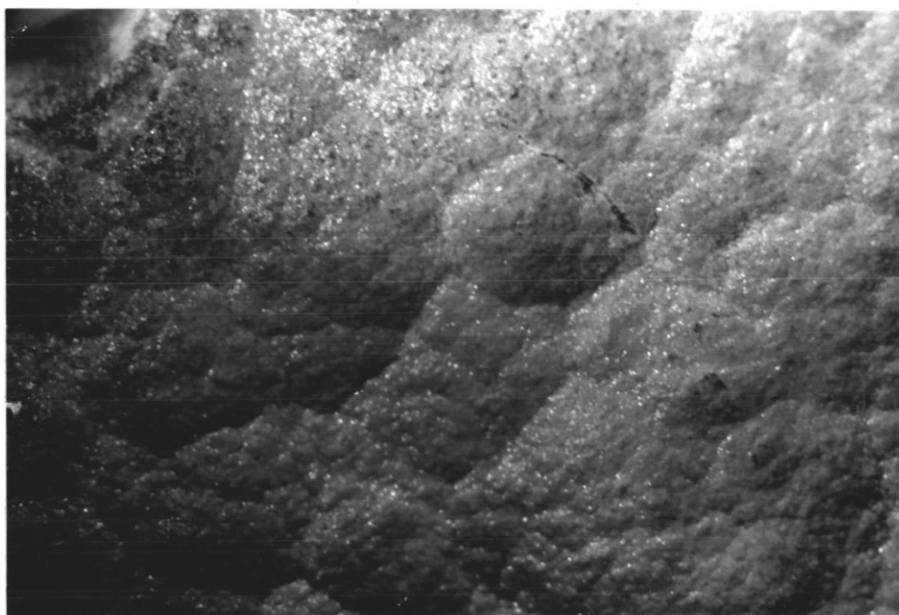


Figure 4.18 Powder Route Crust

4.3.1.3 Thermogravimetric Series Results

The principal difference between these results and those of the alloy series was the complete absence of the magnesium burn since the elemental magnesium had been substituted by the powdered oxide. Otherwise the results differed only in terms of the apparent superior quality of the powder route products.

TABLE 4.4

Experimental Series: Thermogravimetric Series [powder route]					
Specimen /powder	Spinel Forms	Alumina Forms	Temp [C]	Time [mins]	Mass Gain Rate [mg/sec /cm ²
Al/MgO	Yes	NR	860	NR	NA
Al/Silica	NR	NR	NR	NR	NA
Al/MgO Silica	Yes	Yes	770	45	0.43
Crucible Scrapings	NR	Yes	1140	75	0.0145
/Hematite	NR	Slight	1223	NA	0.0008
/Calcium Flouride	NR	Slight	1250	NA	0.0004

4.4 The Unbuffered Crucible Experiment

This experiment was a one-off test made to gauge the effects of dispensing with the alumina powder buffering typical of the main series. Phenomenologically however it yielded some the most important results of the entire programme. Although the experiment did not produce a useful cermet crust material the phases that were produced showed clear separation and gave important insights into the mechanisms probable during successful crust production. These are discussed more fully in Chapter 5.

4.4.1 Experimental Conditions

A cylindrical crystallised alumina crucible 3cm in diameter and 5cm in depth was filled to a depth of 3cm by a molten aluminium alloy containing 5% each of magnesium and silicon, this being the standard mid-window composition. The crucible was placed in the muffle furnace and taken through a thermal cycle essentially the same as for the main series:-

250°C/h temperature rise to 1250°C

10 hours dwell period at 1250°C

Air cooling outside the furnace

4.4.2 Crucible Experimental Results

On cooling the crucible contents separated easily from the crucible walls as a metal ingot capped by what appeared to be a 3mm thick grey crust, but which proved on slitting with a diamond impregnated wheel to consist of a very distinctive multi-layered structure as shown in Figure 4.19. These layers are thought to result from a surfeit of dopant-formed oxides forming on the top-face. In the normal circumstances where oxygen access is provided to the side and bottom through the powdered alumina the resulting oxides would be distributed over the entire surface of the alloy but in this case they can only appear at the atmospheric interface at the top surface. The significance of this is that the quantity appearing there will be some six times that which is

normal. This apparently is the cause of the choking of the process since the resultant glass layer will be too thick to allow diffusion at rates which are sufficient to maintain the process dynamics.

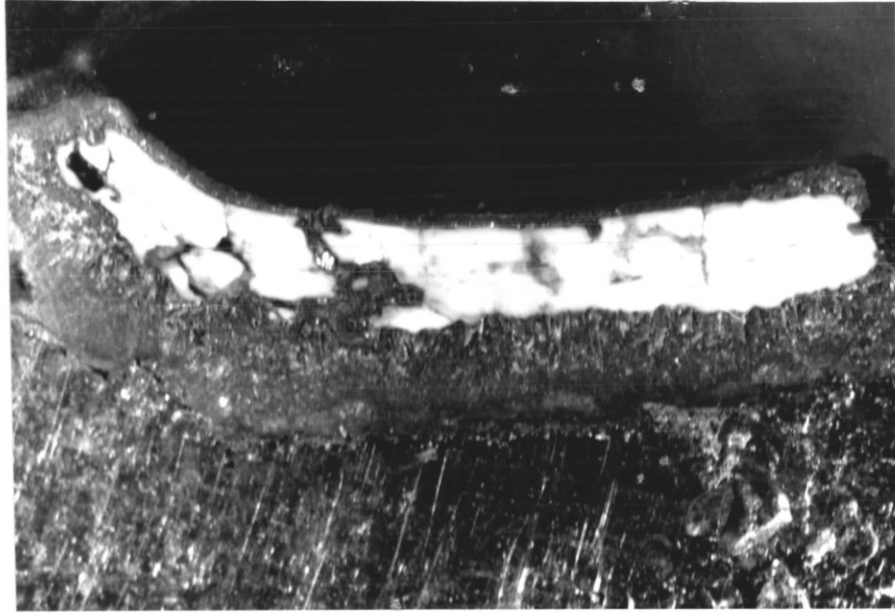


Figure 4.19 Cross-Section of Crucible Specimen

Specimen from an experiment without an alumina buffer. The experiment was aborted when it became clear that after an initial fast reaction no further weight gain occurred. This was attributed to the over-thick glassy coating resulting from the confinement of the reaction to the top-face.

The layers were analysed by X-ray SEM to reveal that the thin top layer consisted of MgO and spinel, the broad layer of white substance is MgO and the thick grey layer consists of spinel infiltrated by aluminium at distinct planar crystal boundaries.

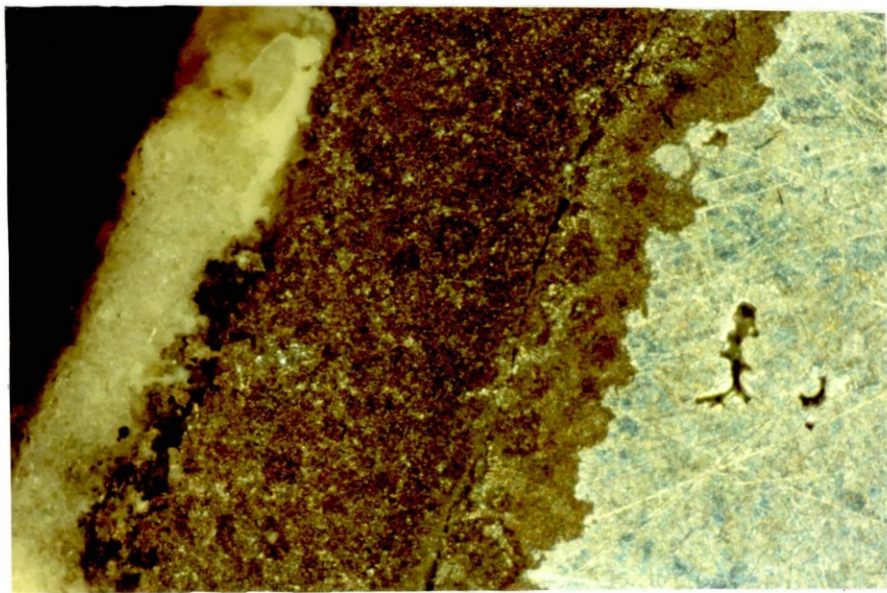


Figure 4.20 Layered Structure of Crucible Specimen

The stratifications are, in top down order, alumina [grey], magnesia [white], and spinel [grey]. The overall thickness is approximately 3mm. The spinel phase is actually translucent. This is clear under brightfield lighting at higher magnification. [see Fig.4.21]. The reaction appears to have been suffocated by an overthick layer of magnesia at the top of the specimen resulting from the blocking of air access to the sides and the bottom of the reaction.

Closer examination of the phase boundaries between the alloy and the spinel crystal faces reveals the high degree of wetting which has occurred. This has implications in the analysis of the pore wetting phenomena which obtain in the main series. To anticipate the final analysis here, it is probable that the favourable interfacial conditions apparent in the main series is connected to the occurrence of spinel on [or in solution with] the pore walls. The transparent nature of the spinel crystals is shown together with a closer view

of the infiltrated metal and the magnesia overlayer in Figure 4.21 taken with polarised light at 500X magnification and a darkfield objective.

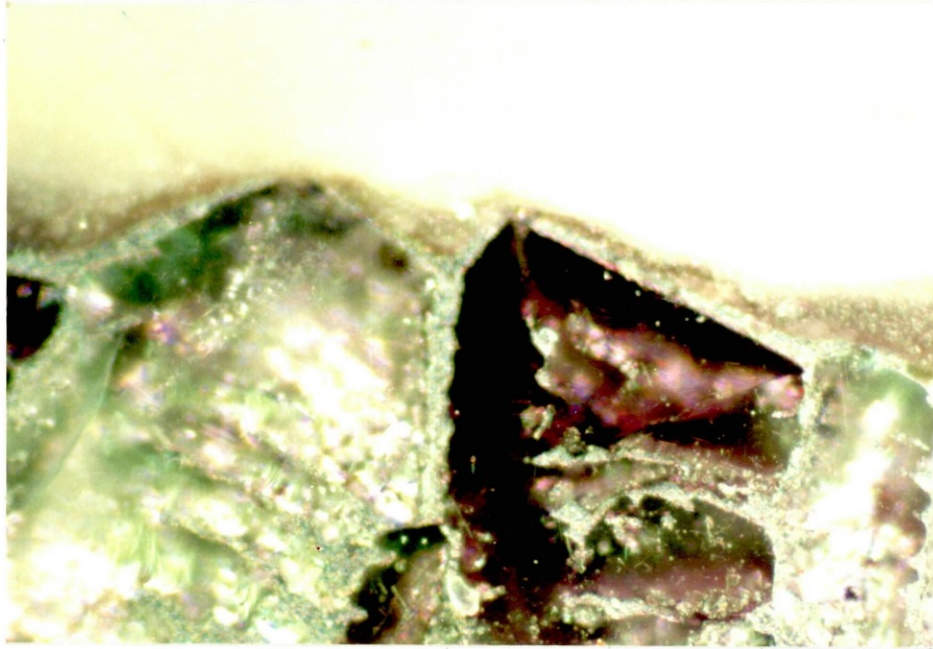


Figure 4.21 Interface of Spinel-Magnesia-Metal Phases
[500X polarised light darkfield objective]

This figure clearly shows the excellent wetting of the spinel by the aluminium melt. The spinel and magnesia phases result from the superabundance of magnesia. The experiment was performed in an alumina crucible without the normal alumina powder buffering. This prevented air access to the sides and the bottom of the specimen which would have distributed the magnesia/spinel over about six times the area of the topface.

4.5 Preliminary Discussion: Alumina-Matrix

Routes

From a review of the results gleaned from the various experimental methods employed in the investigation of the

formation of the Lanxide crust a picture emerges of a string of four mutually dependent phenomena acting in series. These are:-

The preconditional pore formation mechanism which initiates the process by rupturing the normally passivating alumina skin.

The capillary system which carries the aluminium through the corundum crust and to the reaction interface with the oxidising atmosphere.

The reaction system which produces the alumina in a transferable form.

The material transfer system which carries the alumina from the reaction and deposits it more or less evenly over the surface of the growing crust.

In addition to these mechanisms which describe the continuous steady state process, it is apparent that there is a vitally important transient ignition event. This is made evident by the occurrence of the period of exponentially increasing weight gain which has been found in all cases to occur immediately prior to the steady state growth stage.

4.5.1 Pore Formation and Capillary Transport

There is little doubt concerning the events which take place during the pore formation stage. These have been reported in the literature by several independent workers such as Cochran et al [1977], Sasabe & Jibiki [1983], Delavault [1936], and von Theile [1962].

The sequence of events commences with the formation of MgO at temperatures at which the vapour pressure of Mg is appreciably high, that is to say above 750°C. The reduction in volume on oxidation is around 20% hence the MgO forms a fragmented granular substrate constituting a seed bed for the growth of spinel dendrites which allow oxygen access to the aluminium which in turn rises up through the pores by capillary attraction. The necessarily low interfacial free energy appears to result from the continuing presence of MgO/spinel in at least trace quantities at the pore surface and throughout the pore system as it grows [although this requires further examination]. The propensity for the infiltration of aluminium metal along high energy grain boundaries which is made much of in the Lanxide patent is merely a invocation of a truism ie. that high energy grain boundaries have high energy. It may be however that deposition of surface active agents is facilitated by the irregular lattice ends which could have the same effect of increasing wettability.

4.5.2 Ignition, Reaction, and Alumina Distribution

These three events represent the core phenomena which are held to be responsible for the peculiar characteristics of the process. The models which will be presented in the theoretical arguments put forward in Chapter 5 centre on the proposition that there must be a gas phase reaction system in order to account for the resulting rates of reaction which have been measured. Also it is apparent that the alumina distribution over the crust surrounding the pores involves the gas phase. That combustion could occur it is first necessary to explain how ignition could occur. For ignition to occur it is in turn necessary to explain how the normally passivating layer of solid alumina is disrupted. The explanations in each case involve the proof that a liquid phase slag is generated out of solid oxides of silica, magnesia and alumina and that the powerful exothermic reactions necessary to produce such a liquid phase are at the same time sufficient to raise the temperature of the slag to the ignition condition.

The explanation of the mechanism by which alumina is transferred and distributed must also account for the characteristics of the growth pattern and surface morphology encountered. This is explained in terms of a "micro-climate" which is powered by an exothermic vaporisation-oxidation [fog forming] reaction which it is

argued must stand above the aluminium emerging as a vapour at the top of the pores. Alumina is formed via its volatile sub-oxides. This is absorbed into the surface of a glassy slag laying on the plane occupying the areas around the flame-spots. Alumina is finally precipitated from the bottom of the glass onto the cooler solid surface of the growing crust.

CHAPTER 5. DISCUSSION

5.1 Liquid Alumina Formation

5.1.1 Temperature Estimations:The Iroxal Process

5.1.2 Temperature Estimations:The Lanxide Process

5.1.3 Phase Relationships

5.2 Kinetic Models of the Iron Matrix System

5.3 Kinetic Models of the Alumina Matrix System

5.3.1 Pore Formation

5.3.2 Initiation Reactions

5.3.3 Vaporisation-oxidation Reaction

5.3.4 Fume Formation

5.3.5 Crust Formation

5.3.6 Terminal Conditions

5.4 Summary of Crust Formation Mechanisms

5.5 Combustion Routes to Composite Formation

5.1 Thermodynamics of Liquid Alumina Formation

The thermodynamics of production, dissolution and decomposition of alumina is of crucial importance in the understanding of alumina-based composite formation. This involves knowledge of temperatures, transformations, solubilities and activities.

Much of the information required can be had from the literature provided that the temperature and the composition is known. The most difficult problem to solve is the determination of the temperature since in this case it cannot be measured directly.

5.1.1 Temperature Estimations: the Iroxal Process

The task of estimating the temperature of the Iroxal processes is problematical. In the case of the Lanxide process it was possible to consider the local reaction at the pore-top to be two-dimensional thus simplifying the calculation of thermal flux intensity. However, in the case of the Iroxal processes the question is complicated by the fact that [notwithstanding the thin nature of the combustion system] the reacting surface is distributed in complex ways. In the spray condition the combustion zone is a spherical shell on the surface of the droplets, whilst in the submerged modes the combustion takes place within the spherical bubbles. Furthermore the radii of the spheres are likely to vary significantly. Thus we are

constrained to consider models of the combustion system on which to make our assessments of the regime of reaction temperature. Fortunately we can base our estimates upon knowledge of the enthalpy of formation of the products and the rate of their formation. We can then make educated guesses about the size of the reaction surface. For example we can measure the diameter of the bore hole made when the lance is used to pierce firebrick. Our estimate is then based upon the area of the advancing hemi-spherical surface of the hole front and upon our knowledge of the material properties eg. specific heat capacity and melting point. From these factors we may first calculate the resulting flux intensity generated by the lance [the power being a known value] and then make an estimate of the reaction temperature.¹

5.1.2 Temperature Estimations:Lanxide Process

Knowledge of the temperatures at which the Lanxide process operates is an essential prerequisite for the determination of the mechanisms involved. In the present circumstances it is not possible to measure the actual temperatures of the alumina formation directly. In the corundum matrix process the reaction occurs at a large

1 There remains an important consideration which is best understood by studying the borehole shown in Figure 5.16. It is evident from this view that the slag issuing from the hole is still reacting since it has continued to bore down through neighbouring bricks. Thus due allowance must be made for the incomplete utilisation of the enthalpy of formation in melting the original brick.

number of very small hot-spots. The apparent mean field temperature has been measured directly by pyrometry and by thermocouples. Both of these techniques gave a temperature reading of 1350°C. This was barely high enough to allow the formation of the ternary eutectic [1347°C] necessary for the observed glassy top covering. On phenomenological grounds the true value must be higher. The temperature readings made by both methods are considered to be unreliable. On the one hand the thermocouple is a relatively massive heat sink when compared to the thin glass layer, and on the other hand the emissivity of the surface read by the pyrometer is an unknown grey body value. In both of these cases the readings made are certain to give spuriously low values.

The temperature above the surface is unevenly distributed. Hot spots must exist above the pores. Although we cannot measure the hot spot temperatures directly we can crudely define the temperature window in which the actual temperature must lay. We know that since the reaction is exothermically driven the upper limit must lay considerably below the point at which the free energy of formation is zero¹. Furthermore since boiling conditions

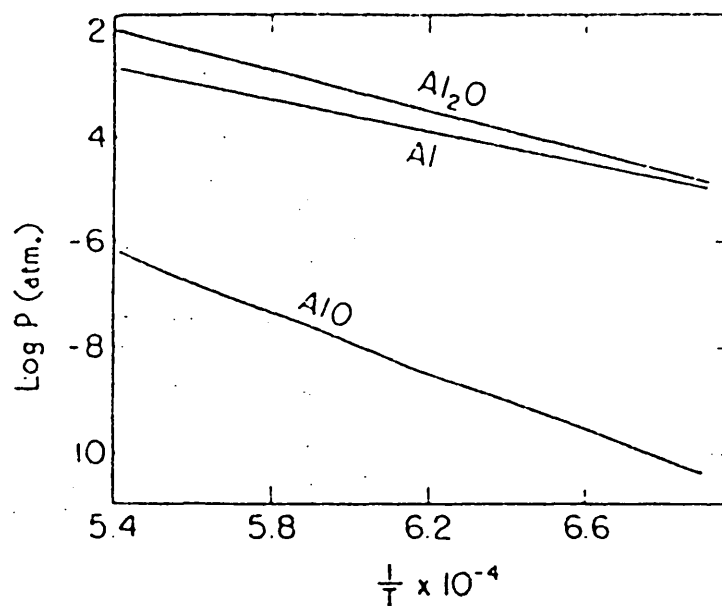
¹ The fact that the reactants are preheated does not affect the limiting temperature. The limiting temperature is that at which the change in Gibb's Energy for the reaction is zero. At this condition the equilibrium constant is unity. The amount of exothermic heat available will fall with the equilibrium constant logarithmically. This will only effect the quantity of heat available appreciably for values of $1 < "k" < 100$. Thus the temperature band for this to occur is narrow and locatable.

would be disruptive, we may place the temperature regime well below the boiling point of aluminium even at the reduced pressures considered to obtain. We know that the lower limit must lay above the eutectic temperature necessary for the observed glassy slag to form [see Figure 4.4 ternary phase diagram and Figure 5.2 isoactivities of S-A-M at 1600°C]. On phenomenological grounds this brackets the temperature very broadly between 1547°C and about 1800°C. The actual boiling point of aluminium [2367°C-at atmospheric pressure] is likely to be significant since the enthalpy of boiling is moderately high [284kJ/mol]. This phase change represents an isothermal plateau in that it consumes a large amount of heat. It will be argued later that evaporation from the aluminium melt surface elevates the vapour phase reaction to an equilibrium position above the surface, analogous to the common phenomenon encountered with flames emanating from liquid.

Temperature calculations based upon adiabatic conditions are not truly representative of the processes occurring here. Since they are high temperature surface reactions much heat is freely radiated out of the system. In fact the system is a steady state process which is characterised by a dynamic balance between the heat generated on the one hand and the equivalent amount dissipated [principally] by radiation from the sum of the hot spots and cooler zones on the other. It is this which allows us to estimate the temperatures by equating the

rate of heat known to result from the reaction [measured in terms of weight gain rate] with that radiated via the Stefan-Boltzmann radiation equation. The heat radiated from the cooler zones results from the mass transport of the products from the hot spots. These calculations lead to temperature values at which it is virtually certain that the alumina is being formed out of a complex gas phase vaporisation-oxidation reaction over a total area which is several times that of the total pore area, and that fumes are absorbed into the glassy slag to be finally evenly precipitated at the crust surface.

The equations describing the method of temperature estimation will be developed later in Section 5.3.3



5.1.3 - System Al- Al_2O_3 ; gaseous species over liquid Al and solid Al_2O_3 mixture.

Leo Brewer and Alan W. Searcy. *J. Am. Chem. Soc.* 73.

Figure 5.1 Vapour Pressures of Aluminium and its Sub-oxides

5.1.3 Phase relationships

Alumina once formed can also be dissolved into many oxide melts over a broad range of temperatures below its actual melting point and caused to precipitate by lowering the melt temperature generally or along temperature gradients or preferentially at chilled surfaces. Finally, alumina may be formed as the product of a self-propagating aluminothermic reaction within a reactive slag system. It is proposed that all of these mechanisms occur at some stage in the reactions examined here.

5.2 Kinetic Models for the Iron-Matrix/Alumina Systems

The spontaneous occurrence of a thin layer of alumina on the surface of newly produced aluminium and its effect as a protection against further oxidation is well known. However by the same token it prevents the use of conventional oxy-acetylene cutting techniques¹. The thermal cutting of aluminium plate is nowadays accomplished by plasma-arc cutting which overcomes the protective alumina layer by the application of a very high temperature [20,000K] constricted arc. Prior to the introduction of plasma technology [c1960] several rather crude techniques were devised to enable oxygen cutting. One of these was a precursor of plasma cutting using a continuous wire-fed electric arc at very high current densities. Other approaches were thermochemical and throw some light upon the combustion of aluminium-iron systems. Historically the first of these techniques employed a thin sheet of steel placed on top of the aluminium plate. An oxy-acetylene torch was applied to the steel sheet which produced iron oxide at very high temperatures and [it is here assumed] triggered a thermit-type reaction

1 Conventional oxy-acetylene cutting is essentially confined to cutting low carbon ferritic steels. The higher carbon steels and cast iron set up conditions which produce CO at a higher oxygen potential than wustite. Chromium bearing steels produce a protective layer of refractory oxide. Other metals have unfavourable ratios between their heats of formation and their thermal capacities. Other unfavourable factors include high thermal conductivity eg. copper and high melting point eg. tungsten.

thus causing the aluminium to ignite. Significantly the steel so-called "waster-plate" was not in stoichiometric ratio with the aluminium. This is evidence that the iron-aluminothermic reaction served merely to trigger the combustion of aluminium by slagging the alumina covering. However the cutting could only proceed if the waster plate was laid completely along the length of the intended cut implying the continuing need for stabilisation [implying a continuous liquid sink for alumina] and re-ignition should the aluminium flame fail.

The Iroxal [**IR**on-**OX**xygen-**AL**uminium] lance devised here essentially shares the sequence of events of waster-plate cutting. Ignition of the aluminium is achieved by means of the oxy-acetylene reaction via the intermediary step of iron combustion. Experience also shows that the iron continues to be necessary after ignition takes place. It was confirmed in a trial experiment that it was not possible to maintain the lance in a free burning condition when the outer iron sheaf was withdrawn from the lance during combustion.

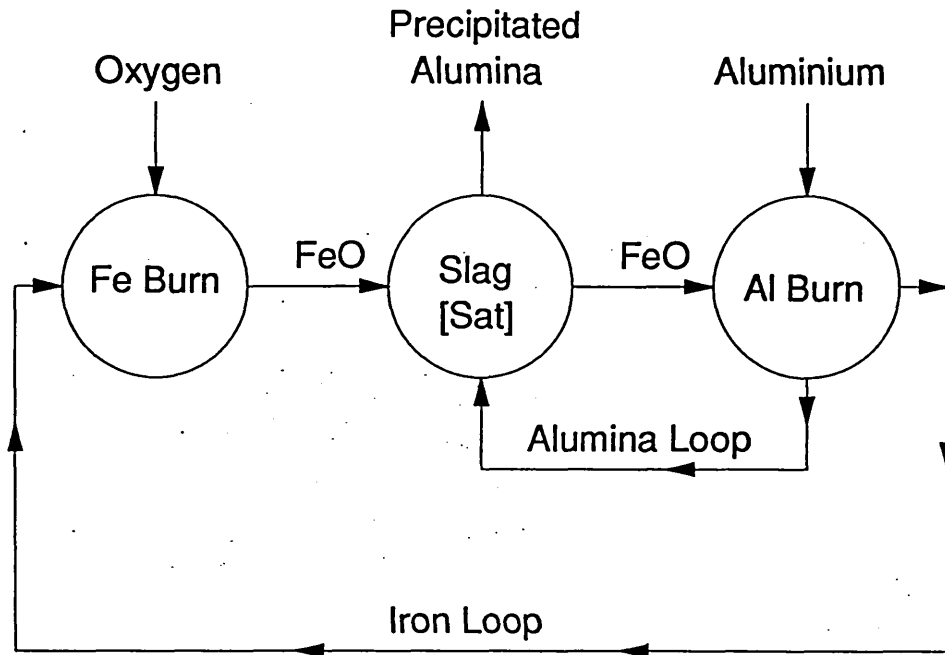


Fig. 5.2 Aluminium Ignition Conditions
[Iron Auto-Catalysis]

However Grosse and Conway *op.cit* have demonstrated that aluminium combustion can be maintained, once ignited, without catalytic support providing that the surface of the aluminium melt is held at temperatures exceeding the melting point of alumina. The "flame" observed under these conditions is localised in what the authors describe as the "skating sun" phenomenon. This implies that the aluminium evaporation rate was sufficient to support an island of combustion over the total area only by means of a travelling or "scavenging" action. Such mobility is possible at the lance tip. Additionally free burning droplets also occur, apparently in circumstances where the surface area to volume ratio is high enough to ensure temperatures higher than the melting point of the inevitable alumina skin. It is therefore concluded that

iron is involved in the combustion of the Iroxal lance both in the ignition stage and during the steady state production of alumina. It is also concluded that stabilisation of the process is continually provided by the slag formed from alumina and iron oxide.

A schematic representation of the system is shown in Figure 5.2.

5.3 Kinetic Models for the Alumina/Al Systems

The Lanxide process is extremely complex and up to the present time no logical explanation has been presented in the literature. Several observations made in the present investigation have allowed a reaction scheme to be proposed. The following requirements are necessary for the process to work:-

1. Additives are required to prevent the formation of a coherent alumina film on the surface of the liquid aluminium.
2. The initial oxide film must be of such a structure as to allow the penetration of liquid aluminium through the oxide film for further oxidation.
3. It is necessary that the alumina produced grows as large crystals and provides a material of low porosity.

It is proposed that several mechanisms are necessary to account for the above criteria:-

1. The initial oxide should be non-coherent. This is accomplished by the introduction of MgO which forms spinel and so creates fragmentation of the oxide skin covering the melt.
2. The interfacial tension between the aluminium and the oxide should allow capillary flow - in this respect it is considered that this is influenced by dissolved MgO.
3. Aluminium at the surface of the capillaries should oxidise without forming a coherent film - it is proposed that the mechanism of oxidation occurs by a vaporisation-oxidation process involving volatile aluminium oxides.
4. The growth of the alumina ceramic is controlled by a liquid slag film, containing magnesia and silica, at the surface of the ceramic. This is fed by the alumina formed from the vaporisation-oxidation process and a temperature gradient established by the exothermic oxidation of the aluminium.

Figure 5.9 depicts the reaction schema. This complex sequence explains the many necessary conditions for the process.

The results indicate that several of the mechanisms are interrelated, viz:-

Spinel is formed from magnesia and alumina, the magnesia having been either formed by oxidation of the metal or directly applied as a powder.

It is well known that liquid aluminium does not wet alumina. Work on the production of composite materials has shown that the presence of small quantities of MgO strongly affects the interfacial tension in this case allowing the capillary rise of the aluminium metal. The slag film at the top of the ceramic is also enabled by the MgO.

Evaporation of the liquid aluminium at the top of the pores leads to gas phase reactions producing alumina. The oxidation process proceeds [at least in part] by way of the volatile sub-oxides of aluminium which further react with oxygen to produce alumina. This concept is supported strongly by the observation of alumina whiskers at the surface of the oxidised specimen [see Figure 5.14]. The whiskers also provide the source of alumina for the growth of the alumina grains. The process occurs by dissolution of the alumina which was formed from the gas phase into the slag. Deposition of the alumina on the alumina grains is promoted by a temperature gradient through the slag.

The presence of silicon in the metal or an addition of silica as a powder on the surface of the melt is essential for the formation of the slag and the alumina growth mechanism.

This complex process requires that these several mechanisms propagate the growth of large granular alumina

at a fast rate. It is considered that the proposed complex procedure adequately answers all the questions that the Lanxide process posed.

Both powder and alloy routes to the formation of the material described in the Lanxide patent share the same mechanism for the ignition and the steady state regimes. They differ only in the preconditional stages. The alloy route commences with a magnesium burn to form MgO and then spinel. In the powder route the MgO is extrinsically applied but has to form spinel with the alumina formed initially.

The incubation period events are also common to both routes. In this stage slow diffusion between the powder components eventually results after a period of about 30min in a thin-film liquid phase around the powder granules. This accelerates the process of complete liquid formation and brings on the ignition stage.

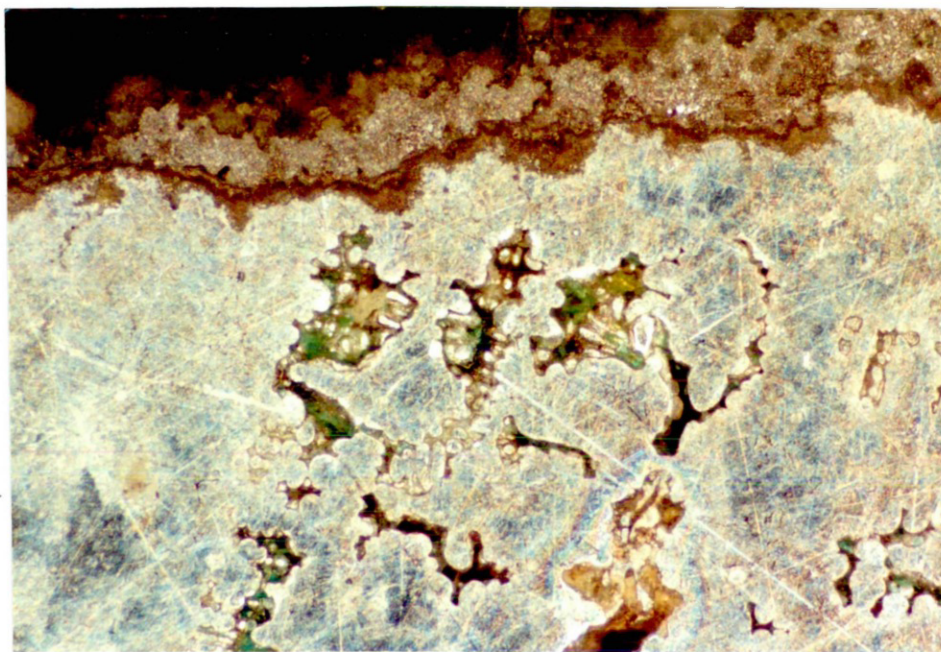


Figure 5.3 Cavities Formed by Evacuating Eutectic

The figure shows that the eutectic is being drawn from the cooling metal melt indicating that the reaction is continuing at these low temperatures.

The ignition stage is a period in which liquid diffusion transport takes place in an ionic melt driven by chemical potential differences created by chemical reactions. At the bottom of the slag some of the rising aluminium reduces silica to form alumina. The balance of the aluminium becomes ionised and chemically diffuses to the top of the slag to capture oxygen. The slag becomes locally saturated with alumina. Precipitation occurs as the temperature falls radially away from the pore top reaction zone. The silicon cation so released chemically diffuses towards the top surface of the slag where it oxidises to replenish the silica. The aluminothermic reaction of aluminium with silica may be so vigorous that

turbulence could occur thus creating conditions for rapid mass transport and further increasing the reaction rate. Figure 5.4 shows the occurrence of the so-called Bernard cell pattern characteristic of bottom heated convection in thick fluids [Bernard 1901]. Figure 5.5 indicates that aluminium can on occasion flow beneath the slag as well as permeate through it. However these are considered to be isolated events which occur only in the cases where the vaporisation-oxidation system momentarily fails. In any event the process temperature increases exponentially over a period of about 20min until at a limiting rate of reaction steady state conditions prevail.

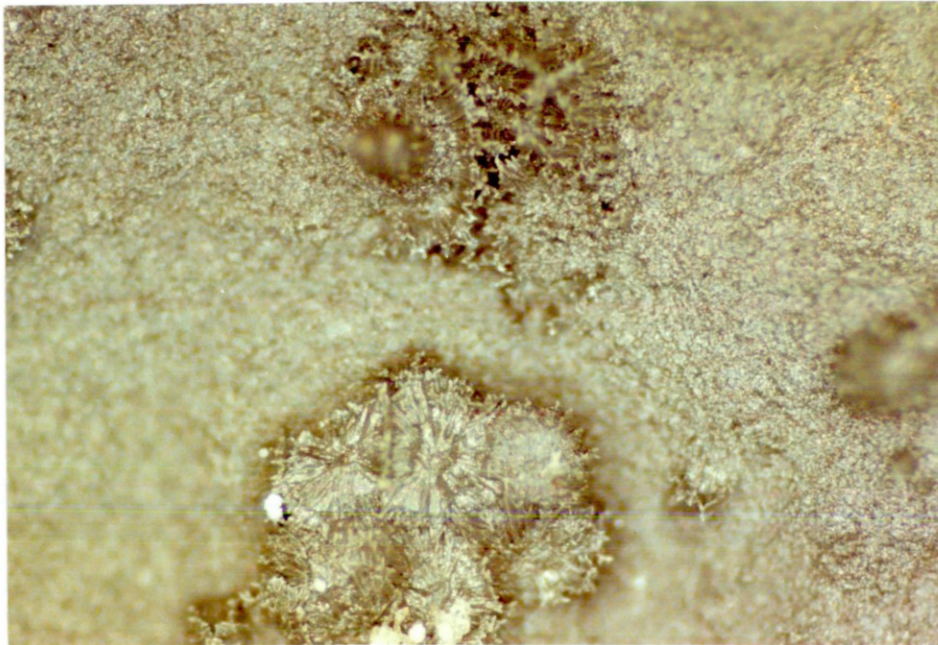


Figure 5.4 Bernard Convection Cell

Hexagonal shaped convection cells form in viscous liquids when heated from the bottom. This phenomenon was first reported by Bernard [1901]. In the present study the occurrence is regarded as exceptional.

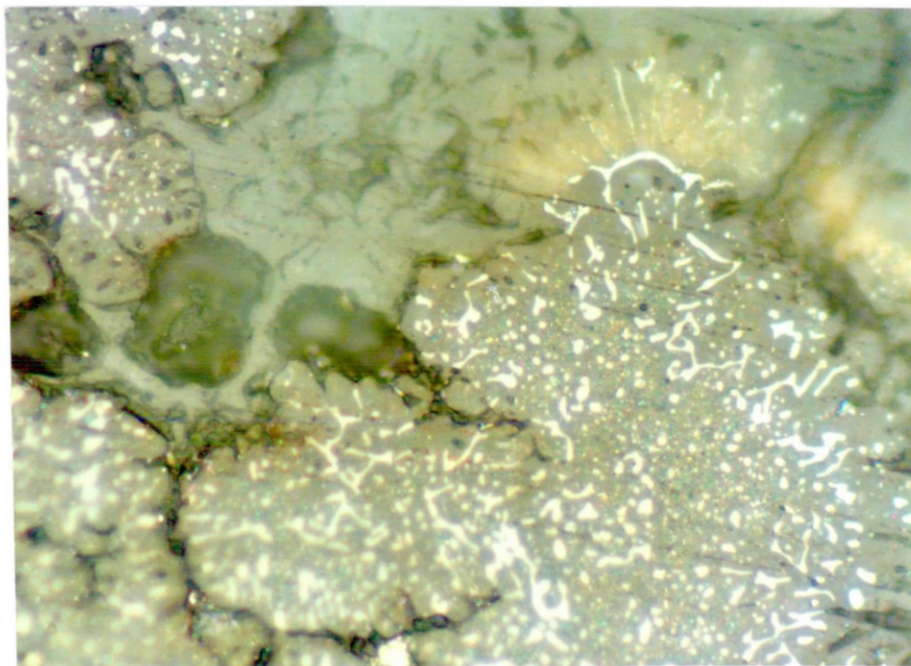


Figure 5.5 Aluminium at Slag/Crust Interface
[showing aura of aluminium vapour over]

Exceptionally aluminium metal may spread locally between the slag and the crust. When this occurs it is associated with an aura of what appears to be aluminium vapour in the glassy layer above the reaction. At the interface aluminium reduces silica producing heat and alumina and Bernard cell formations.

The steady state period continues until the supply of aluminium is exhausted or until the specimen is withdrawn from the furnace and allowed to cool well below 1000°C.

The fact that the process does continue to react at temperatures well below its ignition temperature is a measure of its autostability. There is evidence that the reaction is still occurring when the ambient temperature has fallen below the liquidus of the alloy. Figures 5.3 & 5.6 show that the liquid eutectic of the alloy is still being consumed as the alloy solidifies causing cuspid cavities in the cooling metal¹. This would be below 660°C. This is consistent with the fact that **free evaporation** of the aluminium can take place in **combustion** or in **metal fog** conditions.

¹ In some cases large spherical voids are formed out of coalescing cuspid voids vacated by the intergranular eutectic liquid. This would require that air was let into the void through the spinel fragmented sidewalls. There is photographic evidence that this is the case. Figure 5.3 shows cavities which are clearly connected with the side walls. Figure 5.6 Also shows that air has oxidised some of the eutectic liquid which was close to a region of short open pores.

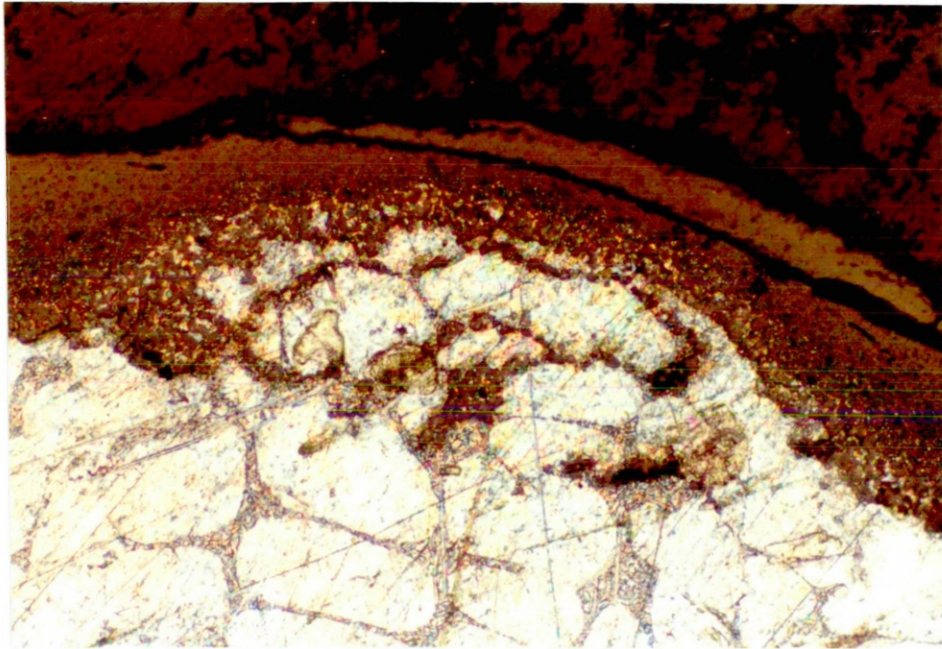


Figure 5.6 Oxidation of the Eutectic Liquid via Pores

Evidence that the pore system remains open is shown by the oxidation of the metal eutectic. This demonstrates that the reaction is still occurring at temperatures at which the metal eutectic can exist.[ie. below the liquidus]

5.3.1 Pore Formation

In a study of the oxidation of Al-Mg alloys by Haginoya and Fukusako [1983] *op.cit* the authors conclude that :-

"The oxides produced in molten Al-Mg alloys were magnesia, spinel, and an amorphous substance. MgO was produced in an early stage of oxidation, increased for a short period and then gradually decreased. Correspondingly spinel increased with the decreasing amount of magnesia. Much of the amorphous substance which was

observed in the early stages crystallised into spinel."
and,

"..the oxidation mechanism of the molten Al-Mg alloy is inferred as follows. First, Mg around the surface of the molten alloy is selectively oxidized, producing MgO granules in the area. By the production of the granules, pores are formed in the molten alloy, and they introduced air into the molten alloy producing MgO granules even more [sic]. Therefore, the MgO granules are irregularly dispersed at the surface of the molten alloy. When a large amount of MgO is formed near the surface of the molten alloy, the Mg content in the alloy around there decreases, and spinel is formed from the surface side toward the inside gradually, by the reaction of MgO, Al around it and oxygen from the air. Spinel is constructed as more minute particles than those of MgO by crystallisation of an amorphous oxide, and the homogeneously mixed layer composed of metal (mainly Al) and [out of] the minute oxide particles (spinel) is formed."
[Transactions of the Japan Institute of Metals vol.24, No9 (1983) pp613-619]

This has been quoted at length because it makes mention of an "amorphous layer" which crystallises into spinel and which may well be identical with that found at all stages in the reactions investigated in the present study. Nowhere in the report do the authors infer from this that there are temperatures high enough to produce the glassy substance to which they refer. This is

puzzling in view of the significance of high temperatures [perhaps as high as 3000K *ibid*] in the determination of the thermodynamic and the kinetic event sequences which they describe. Direct observation of combustion occurring at the surface of Al-Mg alloys has been reported by Cochran [1977] *op.cit* who take proper account of the strong exothermic nature of the reactions involved.

5.3.1.1 Spinel Formation

Table 5.1

Reaction	Gibbs Free Energy kJ		
	923K	1023K	1123K
#1. $\text{Mg} + 1/2\text{O}_2 = \text{MgO}$	-28.9	-28.3	-27.7
#2. $\text{Mg} + 2\text{Al} + 2\text{O}_2 = \text{MgAl}_2\text{O}_4$	-108.6	-107.1	-103.7
#3. $\text{MgO} + 2\text{Al} + 3/2\text{O}_2 = \text{MgAl}_2\text{O}_4$	-79.7	-78.7	-76.0
#4. $\text{MgO} + \text{Al}_2\text{O}_3 = \text{MgAl}_2\text{O}_4$	-0.574 (at 803K)		

5.3.1.2 Pore-Wall Wetting

The conditions for wetting to take place between liquid aluminium and solid alumina are only marginally favourable at the temperatures for which the process works. There is strong phenomenological evidence which indicates that the good wetting which does in fact occur is the result of the formation of a surface active layer on the pore walls. This surface is thought to be in the form of either spinel or a solid solution of spinel and alumina. The experimental evidence for this comes from the unbuffered crucible run. This is described above in Section 4.4.2, but briefly the experiment yielded a specimen made up of layers of differing oxides and double oxides. Amongst these was a layer of spinel crystals which were extensively penetrated by aluminium along the grain boundaries. See Figure 5.7 below. It is clearly evident that the spinel is very thoroughly wetted by the alloy.

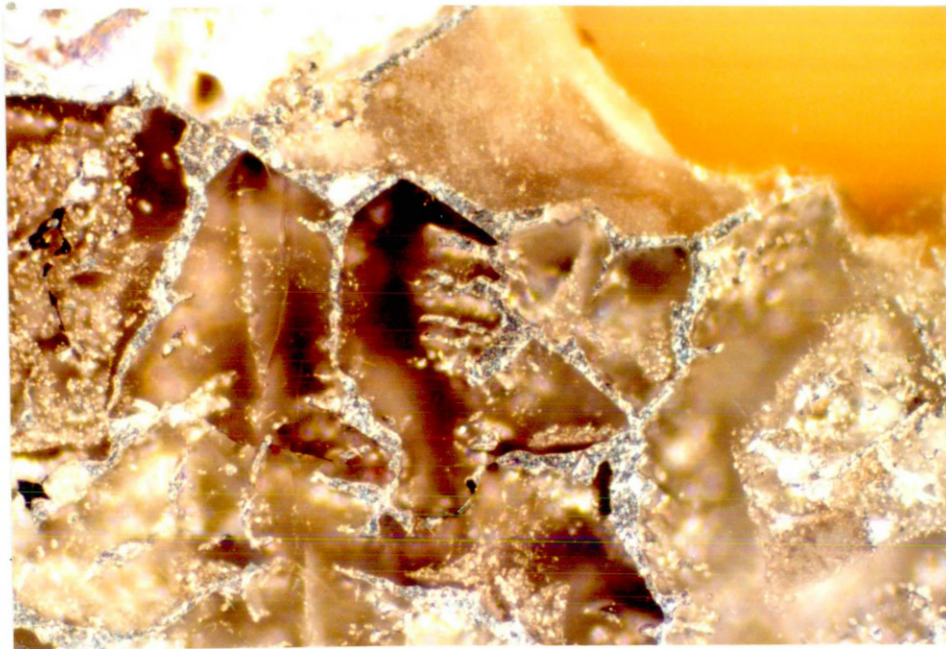


Figure 5.7 Layered Specimen Showing Spinel Crystals
Strongly Wetted by Aluminium

*Evidence of the high interfacial free energy
between spinel and molten aluminium.*

The influence of additions of magnesia in the sintering of alumina is well known [see for instance Coble [1961]]. The beneficial effect of MgO on the density of sintered alumina is due to the fact that it eliminates discontinuous grain growth during the late stages of sintering. Discontinuous grain growth means that the grain boundaries break away from the pores, thereby entrapping the pores within the new large grains.

Interestingly MgO is only marginally soluble in alumina to the extent of 600ppm and it is just this concentration which has been determined by Peelen [1975] as being optimal for the production of higher strength alumina ceramics. It should be noted that for surface active materials, complete surface coverage can be produced in

equilibrium with very small concentrations in solution. eg. sulphur in iron gives complete surface coverage with a concentration in solution of only 0.01 wt%

The fact that the presence of MgO tends to eliminate pores on the one hand is offset on the other hand by the fact that it enhances wetting by the formation of spinel. Thus whilst low energy grain boundary adhesion is promoted by the absence of micro-pores, the larger pores at high energy grain boundaries are more strongly infiltrated by aluminium metal which ensures that they remain open. It should also be noted that the greatest capillary forces will be in the smallest pores. We may infer from this the capillary forces serve an intermediary or bridging purpose.¹ This being the case pore transport is one possible mechanism to consider in the search for the rate limiting step. The other candidates are the various diffusion mechanisms of the reactants. At these high temperatures we may dismiss both the chemical reaction rate and adsorption desorption mechanisms as possible rate limiting steps since they are very rapid. However the engine for the mass transport is aluminium vapourisation coupled with the chemical

¹ There in fact will be a small overall energy gain resulting from the temperature gradient which will tend to draw the liquid upwards as interfacial energy lessens [and the work of adhesion therefore increases]. This phenomenon is well known to braziers who thus apply the spelter to the joint at the side opposite to that of the heat source.

reaction and not, as the patent implies, the capillary mechanism *per se*. However, the pore radius will determine the maximum crust thickness which is attainable.

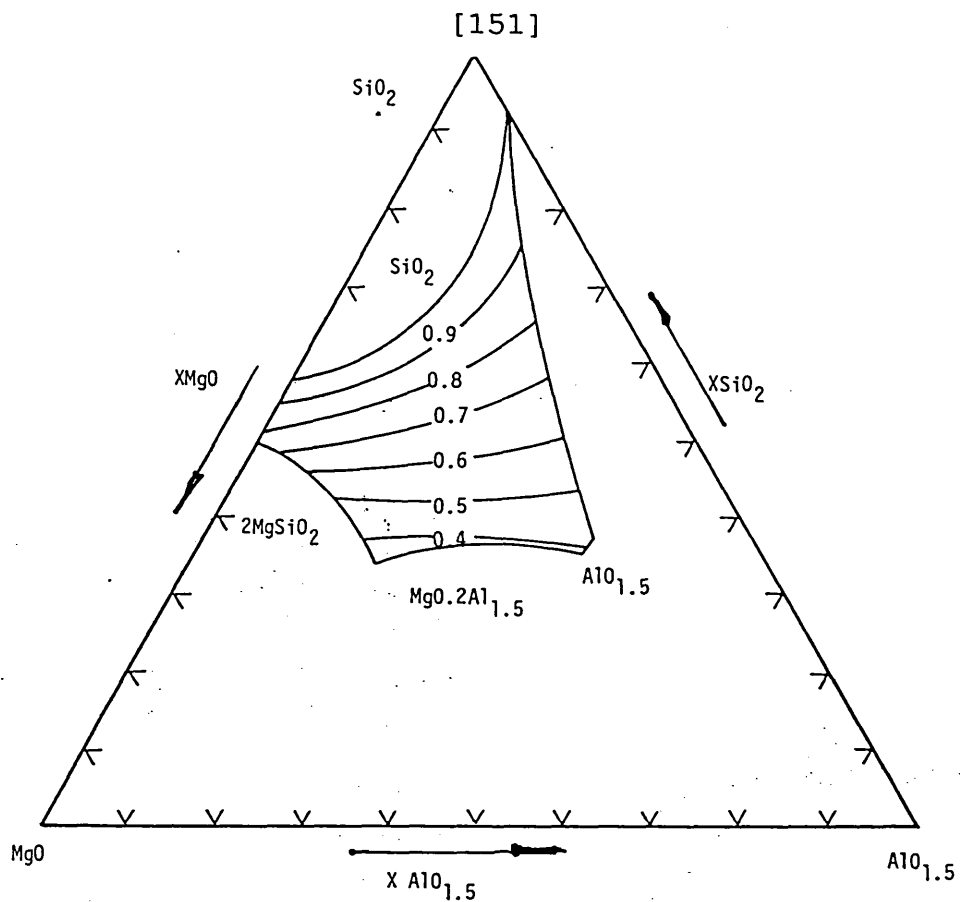
5.3.2 Initiation Reactions

The operation of the process is dependant upon a series of stages. Similarly the initiation of the process depends upon a series of events. Of fundamental importance is the establishment of conditions leading to steady state operation. This is the result of a set of preconditions beginning with the formation of a eutectic/glass phase which is brought about [in the case of the alloy route] exothermically by a series of redox reactions. Conditions are set up which progressively raise the system temperature up to the point at which steady state is achieved.

5.3.2.1 Glass Formation

The first process in a series of processes is the formation of a reactive slag/glass phase. The initial constituents of the glass are the oxides of aluminium, magnesium and silicon. In the alloy route these oxides result from oxidation by the atmosphere thus providing some of the heat necessary to form the glassy slag. The eutectic temperature of the system is 1347°C, which is about 100 degrees above the furnace temperature. The powder route also experiences the exothermic reaction of the formation of the double oxide spinel from its

constituent oxides but this is not in itself sufficiently energetic to heat the system to the eutectic temperature. It would seem that in either case the necessary heating results initially from the reduction of the silica by the aluminium and to a lesser extent on the slower solid-diffusion limited processes taking place at impinging points in the oxide powders analogous with the formation of water from ice and solid road salt. This accounts for the observed incubation period between the spinel formation reaction and the commencement of catastrophic oxidation of the aluminium itself for the alloy route and the marginal weight-gain period which is seen to occur prior to the take-off event in the powder route.



Activity of SiO_2 in $\text{SiO}_2\text{-MgO-Al}_2\text{O}_3$

slags at 1600°C [Rhein and Chipman].

Figure 5.8 Liquid field phase diagram for the System
A-S-M [and silica activities] at 1600°C

5.3.2.2 Exothermic Temperature Rise

When the glass has formed sufficiently to create conditions for rapid liquid diffusion a feedback situation is set up such that the increases in the reaction rate raise the reaction temperature and in turn the reaction rate. This is shown to be the case by the log-linear nature of the weight gain versus time curve

shown in Figure [4.16]¹. For the purpose of determining the mechanism of the reaction the fact of exponential change in weight gain rates is most significant. It indicates that the exothermic reaction which was anticipated does indeed take place and that it takes place at a rate which is sufficient to raise the temperature exponentially until an external rate-limiting situation comes into being whereupon the rate becomes linear. The supply of the aluminium vapour to a gas phase reaction over the glass is governed by the limiting heat transfer rate from the exothermic reaction to the aluminium melt surface. Since the thermal flux results from the exothermic reaction it is clear that the rate limiting step is the supply of oxygen.

5.3.2.3 Preconditions for the Steady State

The conditions preceding those under which the weight gain rate becomes constant can be defined as a spontaneous self-propagating but **unsteady** state reaction. Such a system is auto-stable [or metastable] and constitutes a dynamic equilibrium which **self-heated** undergoes internal changes which automatically attempts to re-establish a new equilibrium. This is little more than a re-statement of Le Chatelier's Principle but it is

¹ The previous figure [4.15] depicts the actual weight gain rate variation and appears to show that the powder route creates conditions favourable to a more rapid take-off of the alumina formation reaction. However the log-linear plot shows the initial rates to be identical although the alloy route specimen was more tardy in establishing exponential weight gain conditions.

rephrased in **dynamic** terms in order to emphasise that the complex and interactive nature of the process under investigation makes it particularly well suited to systems approaches. In particular the eventual achievement of steady state conditions illustrates that the system **automatically** moves towards thermal and mass transport equilibrium. By generating heat exothermically the operating point is raised to a temperature at which the heat generated by a particular rate of reactant consumption becomes equal to the heat lost across the system boundary.

The slope at any point on the mass gain rate curves shown in Figure 4.15 is related to the rate of exothermic heat generated by the process. When this slope becomes constant [ie. when steady state has been achieved] the system is in thermal equilibrium with its surroundings ie. heat generated is equal to the heat lost. To satisfy this condition the rate of reaction must have become constant. At high temperatures the **chemical** reaction rate is very high and it is virtually certain that the rate is kinetically limited by impedance to the supply of one or more of the reactants [assuming that the products do not affect the reaction adversely]. The kinetic circumstances under which the exponential rise becomes linear are of crucial interest here. Since the supply of aluminium vapour to the reaction is conditional upon the reaction itself, ie. higher reaction rates stimulate greater rates of evaporation, the rate limiting factor would appear to be the supply of oxygen. This has been shown by

Turkdogan, Grieveson and Darken [op cit] to be governed by the oxygen partial pressure. Thus the limiting rate in the Lanxide case where the atmosphere was the atmospheric partial oxygen pressure.

In summary: steady state conditions are preceded by increasing temperatures which raise the rate of the reaction exponentially until the limit of oxygen counter-diffusion is reached. At moderate rates of reaction a vaporisation-oxidation reaction system is established. At higher rates the fog forming reaction will become a combustion reaction. This is one of the principal differences between the iroxal reaction, performed at high oxygen pressures, and the Lanxide process. The distinction between the exothermic vaporisation-oxidation ["fog"forming] reaction and that of combustion is in any case arbitrary.

5.3.3 Vaporisation-oxidation Reaction Temperatures

In order to estimate the level of the reaction temperatures which exist during the alumina formation stage we can start by measuring the rate of weight gain for a typical specimen and estimating the area over which this reaction is actually taking place. Thermodynamic

tables will give the enthalpy of formation of the products. From which the rate of heat generated exothermically is [Eqn.5.1]:-

$$\left(\frac{\partial q}{\partial t}\right) = \Delta H_{form} \cdot \left(\frac{\partial m}{\partial t}\right) \quad (5.1)$$

As a first approximation we may then equate the rate of heat formation to that of its radiation since at these temperatures radiant heat loss will account for the greatest part of the heat lost by the system. The radiant heat loss is given by the Stefan-Boltzmann equation [eqn.5.2]:-

$$\left(\frac{\partial q}{\partial t}\right) = \sigma \epsilon (T_2^4 - T_1^4) \quad (5.2)$$

[Where sigma is the Stefan-Boltzmann constant and epsilon is the grey-body emissivity]

These are re-arranged to give:-

$$T_2 = \left\{ \left(\frac{\partial q}{\partial t} \right) \cdot \frac{1}{(\sigma \epsilon)} + T_1^4 \right\}^{\left(\frac{1}{4}\right)} \quad (5.3)$$

and

$$T_2 = \left\{ \left(\frac{\partial m}{\partial t} \right) \cdot \frac{(\Delta H_{form})}{(\sigma \epsilon)} + T_1^4 \right\}^{\left(\frac{1}{4}\right)} \quad (5.4)$$

and by rearrangement also,

$$\left(\frac{\partial m}{\partial t}\right) = \frac{(\sigma \epsilon)}{(\Delta H)} (T_a^4 - T_b^4) \quad (5.5)$$

Hence we can predict the weight gain rate at any "T_{eq}"

In the case under investigation the system is heterogenous. We have the hot spots in the vicinity of the pore tops which are radiating heat. Mass transfer of the products out of the hot spot carries away the balance of the heat in the form of fumes¹. This is given by the product of the Kirchoff Equation eqn.5.6 and the mass flow rate. For the steady state situation the mass flow rate is identical to the rate of product formation. Hence we may write the heat balance between the hot and the cool zones as equation 5.9. This is developed as follows:

Rate at which heat is transported away in the fumes:

$$\left(\frac{\partial m}{\partial t}\right) \left(\int_{(T_1)}^{(T_2)} (\Delta C_p) dT + \Delta H_{trans} \right) \quad (5.6)$$

[Where values of C_p with temperature are taken from the literature as:

$$C_p = a + bT + cT^{(-2)} \quad (5.7)$$

1 The heat carried away in the form of fumes will, in turn, lose heat by both radiation and by conduction to the glassy melt on condensation. This aspect of the heat transfer system is difficult to quantify adequately.

"a", "b", and "c", being experimentally determined constants.]

Thus :

"rate of heat generated [Eqn.5.1]" = "rate of heat radiated [Eqn.5.2]" plus "rate at which heat is absorbed to heat up the products [Eqn.5.5]"

$$\Delta H_{form}^{298} \frac{\partial m}{\partial t} = \sigma \epsilon (T_2^4 - T_1^4) + \left(\frac{\partial m}{\partial t} \right) \left(\int_{(T_1)}^{(T_x)} (\Delta C_p) dT + \Delta H_{trans} \right) \quad (5.8)$$

"T₂" represents the temperature of the hot spots, and "T_x" is the mean temperature of the fume products. The mean temperature of the fumes is not determinable directly and must be estimated on phenomenological grounds. The presence of whiskers of alumina on the crust [see figure 5.12] is one such phenomenon.

The heat of formation is not entirely available at high temperatures and account must be taken of the degree of dissociation occurring. In the case of the oxidation of aluminium the reaction goes substantially to completion within the range of temperatures which are likely in this work. This is illustrated by the Gibb's energy function [eqn 5.9] and the equilibrium constant function [eqn 5.10] given by Bodsworth and Bell [1972]

$$\Delta G^0 = -287,560 + 89.32T \frac{\text{cal}}{\text{mol}} \quad (5.9)$$

$$\log K_{Al-O} = \log \left\{ \frac{(a_{Al_2O_3})}{((a_{Al})^2 (a_O)^3)} \right\} = \frac{62870}{T} - 19.53 \quad (5.10)$$

The parameters which have to be measured or estimated from the experimental results are: The mass gain rate and the reaction area. The steady state mass gain rate can be measured fairly precisely from thermogravimetric traces¹. The measurement of the actual reaction area is more problematical. For the steady state combustion stage it has been assumed that the reaction area is approximately equal to ten times the pore area. The pore area is a very small fraction of the actual crust area. Cross-sectional micrographs of specimens taken **normal to the reaction face** show a relative pore area typically about 10%. However consideration of the geometry of any section taken **normal to the pores** gives a value around the square root of this say 3%. Errors made in the assessment of the reaction area lead to errors in the calculation of the temperature which are proportional to the fourth root less serious. For example, if the error made in the estimate of the area is as high as 20% the error in the calculation of the temperature will be only 4.6%.

1 It is important to note that the thermogravimetric traces record the increase in mass-gain with time, the mass-gain rate is really a function of the temperature. Temperature is of course time dependant hence the employment of the partial notation.

2 For an ideal example we may take the case of square pores of 5 microns side pitched 20 microns apart. A section parallel to the pores gives a relative pore area of 25%, however a section taken across the pores gives a relative pore area of about 6%. In general the relative pore reaction area is about the square root of the relative pore area taken from a section parallel to the pore.

Thus we can estimate the temperature of the reaction **at any steady state** by using Equation.5.3 derived above as a function of the measured weight-gain rate and the furnace temperature.¹ Estimations [see appendix II] of the localised chemical reaction occurring in the vicinity of the top of the pores give temperatures above 1700°C.

This gives rise to the question of whether or not the hot spots can be described as zones of "combustion". Under normal circumstances combustion zones of such microscopic size would not be possible owing to the thermal severity imposed by the relatively massive heat-sink surrounding the system. However in the present circumstances there is a considerable amount of pre-heat from the furnace. Under these controlled conditions steady state combustion can be initiated and maintained. This is an important precondition for the process. Bouriannes and Manson [1970] *op.cit* report that the combustion of aluminium droplets could be maintained by the superimposition of electrical HF heating even when the oxygen partial pressure was reduced to lower the rate of exothermic heat production. We have here a similar situation in the sense that the furnace preheat will reduce the chilling due to

¹ It would still be possible to estimate the temperature of the reaction at any time "t" during an unsteady state such as the take-off to ignition period whilst the temperature is rising with time but the errors introduced by the lag time caused by the thermal reservoir [mass] effect are likely to be such that this would merely be an academic exercise.

the metal melt. Combustion is therefore easier to initiate and to maintain even at reduced oxygen partial pressures.

If we propose a model such as that shown in Figure 5.9 we can account for much of the behaviour observed experimentally.

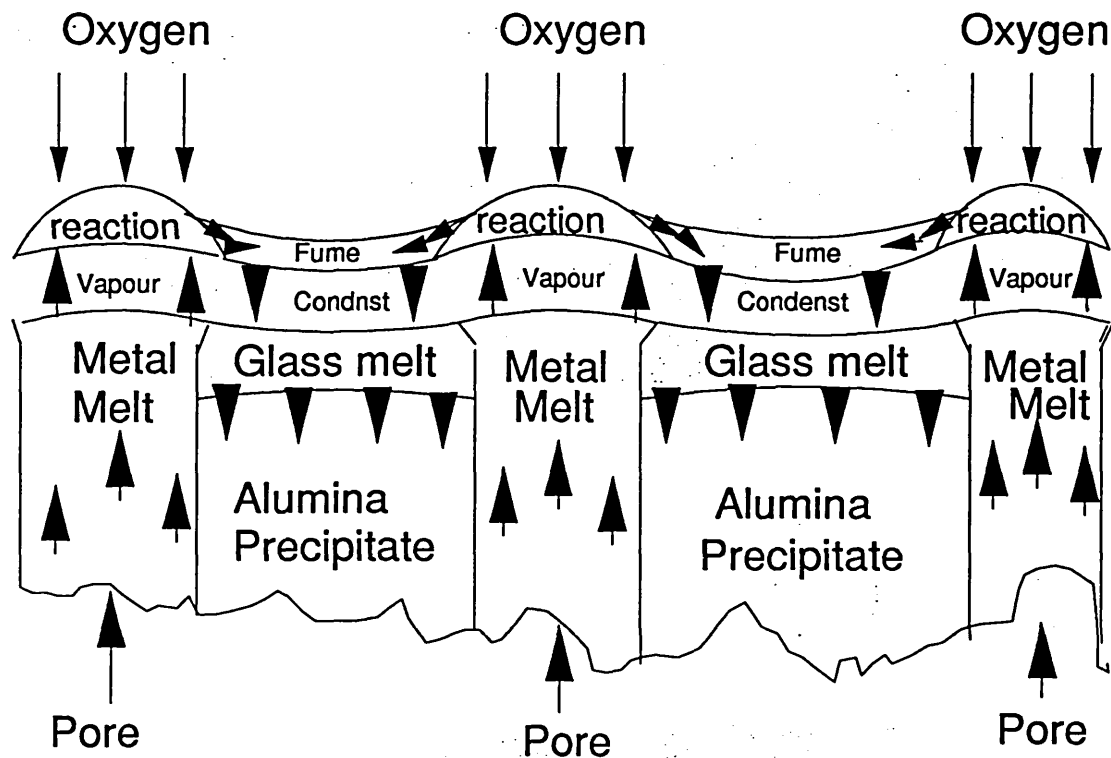


Fig.5.9 Top-Face Reaction System

The model depicts a steady state process in which a proportion the heat of combustion occurring in the the form of a thin flat metallic hot spot reaction above the melt provides the input to the metal melt enabling sufficient vapour transport to maintain the combustion. Initially the reaction rate will tend to increase

exponentially as a result of temperature increases until thermal equilibrium is established at a temperature at which the net heat losses from the reaction zone balance the chemical reaction rate. This infers that the rate limiting factor is either:

#[a] the supply of oxygen to the top of the reaction zone [by diffusion and perhaps in turn by convection-induced turbulence].

#[b] the evaporation rate of the aluminium melt [this is related to the heat transfer by radiation from the bottom of the reaction. This in turn is moderated by the emissivity of the flame and the reflectivity of the melt]. Since "flame" emissivities are known to be low and the reflectivity of the melt is high only a very small fraction of the heat generated ends up supplying the enthalpy of evaporation of the aluminium melt.

Argument I

If #[a] were to be the rate limiting step then it would be expected that the effect of reducing the furnace temperature would have little effect upon the reaction rate since the diffusion rate of oxygen down to the reaction is less effected by a background temperature change than are events on the under-side of the combustion reaction¹. At the metal pool below the reaction

¹ This is because the oxygen is diffusing towards a very high temperature reaction compared to which small changes in background temperature are marginal. On the other hand an increase in the furnace temperature has a direct and powerful consequence on the melt evaporation rate.

however the effect on the evaporation rate of a [say] 100oC temperature rise is immediately and powerfully felt and we would expect that the reaction rate would increase quite significantly [see Figure 2.6 which gives aluminium vapour pressures with temperature at this range of temperatures] and in fact the rate changes brought about by varying the temperature are rather large, actually doubling for 100oC rise. This supports the hypothesis that the system is acting in positive feedback in which the fuel supply is thermally coupled to the reaction. Figure 5.10 shows the argument.

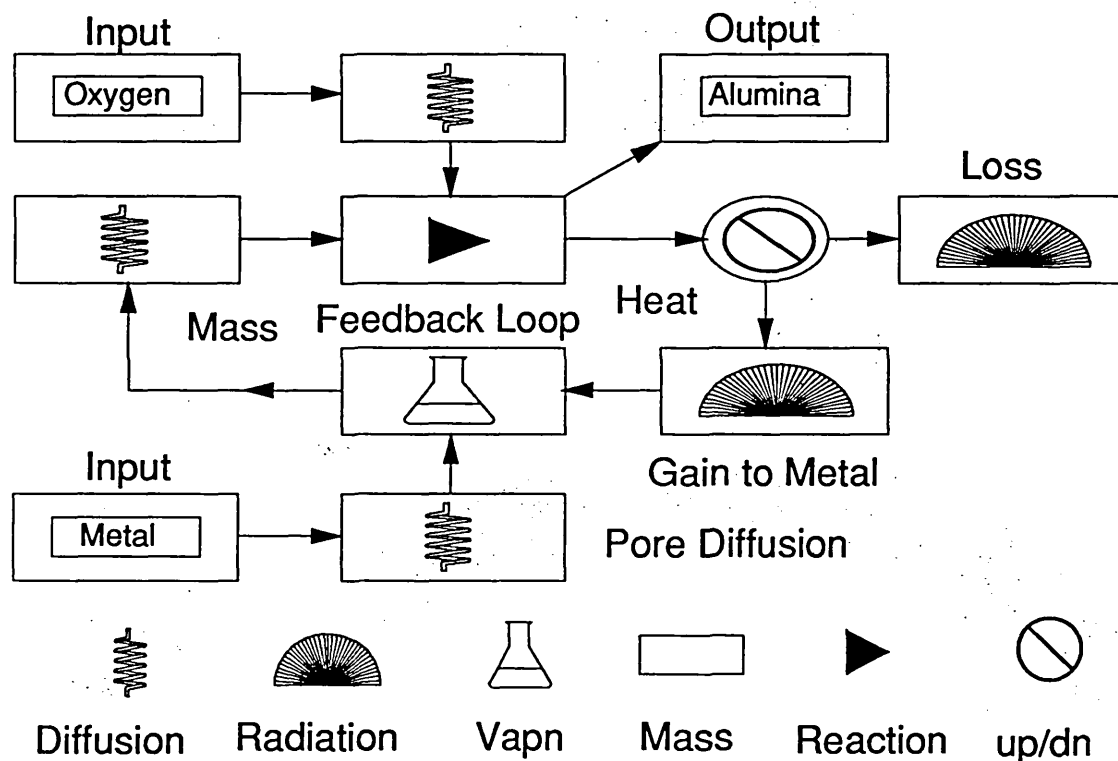


Fig.5.10 Autocatalytic Feedback System

Argument II

The argument for the alternative hypothesis #b is briefly that: [i] The fuel supply results from the evaporation of aluminium vapour. [ii] The aluminium vaporisation rate is controlled by the radiant heat transfer to it from the combustion reaction. [iii] The heat transfer is in turn governed by the temperature of the combustion reaction which itself is controlled by the fuel supply and inf. Put in terms of governing thermodynamic laws:-

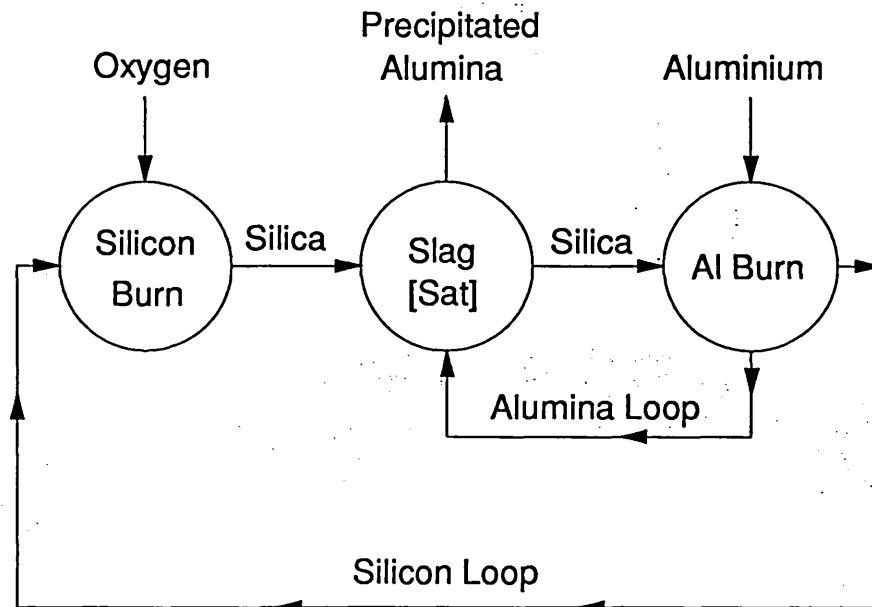
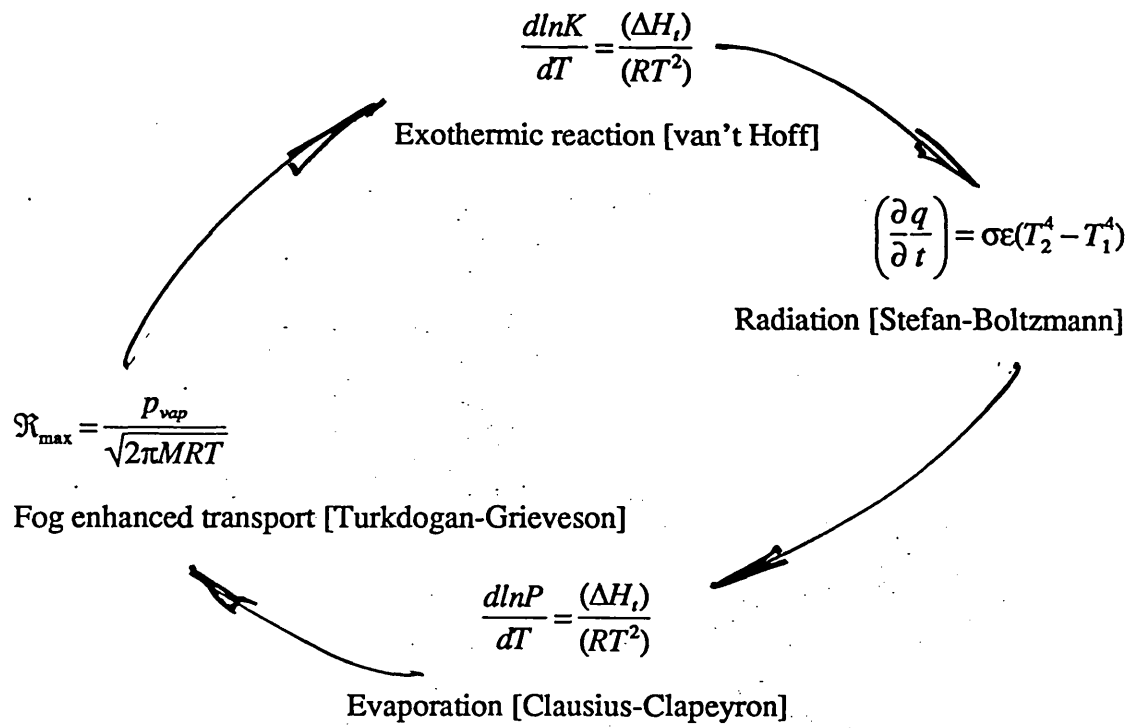


Fig. 5.11 Aluminium Ignition Conditions
[Silicon Auto-Catalysis]

The figure depicts conditions prior to ignition. A reactive slag consisting of alumina, magnesia, and silica, is fed with aluminium. A continuing aluminothermic reaction produces heat which progressively raises the reaction temperature until combustion occurs. During this pre-ignition period the alumina content is kept in the super-saturated condition, the alumina being continuously precipitated at cooler areas away from the pores. Note the similarities between this schema and that proposed for the iroxal system in Figure 5.2.

[Note the similarities between the scheme above and that describing the iroxal system]

SYNTHESIS.

The alternative hypotheses #a and #b concerning the rate limiting step are [i] the oxygen supply, and [ii] the aluminium vapour supply.

It has been tentatively suggested above that since temperature change has a more marked effect on the rate of aluminium vapour evaporation than upon oxygen diffusion, then the rate limiting step would appear to be [ii]. However, at any given temperature, the evaporation rate is determined by the reaction rate through a heat transfer coupling. Thus, since the reaction rate is, at any temperature, controlled by the oxygen supply, this must be the true rate limiting step.

5.3.4 Fume Formation

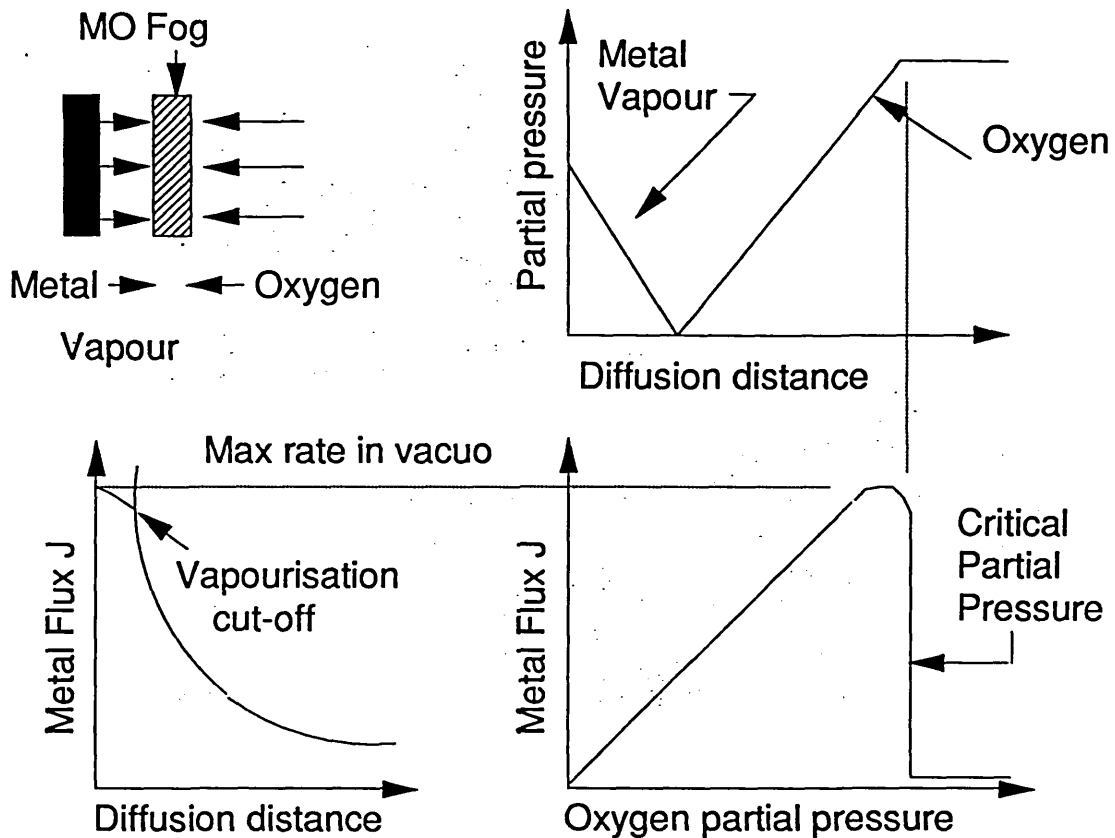


Fig.5.12 Metal Oxide Fog Vaporisation Enhancement
[after Turkdogan & Grieveson]

The figure is reproduced from Turkdogan [1980] p254. and is from Turkdogan, Grieveson, and Darken [1963]. "The formation of an oxide in the gas phase provides a sink for the metal vapour and oxygen resulting in the counterflux of these two gaseous species." This counterflux enhances the vaporisation rate of the metal. in the present work this condition is represented by a "collapsing" flame. The volume of the oxides is very much less than that of the vapour species from which they are formed. This is in contrast with normal hydrocarbon flames in which moderate reductions in the volume of the gaseous products are more than offset by their thermal expansion.

Metallic vapours and metallic oxide fogs are thought to be amongst the critical kinetic agents acting in the cycle of events which are proposed here to account for the formation of corundum in the Lanxide process. It is well established that metal and metal oxide fogs are to be observed above many industrial melts. Wagner (1958) and Gulbransen et al (1966) have reported great enhancement of the rate of silicon oxidation by smoke formation above the surface from the combustion of silicon monoxide.

Turkdogan et al (1963) have described the mechanism by which metal oxide fogs are generated. This is depicted in figure 5.12 above. The rate of metal vapour evaporation is enhanced by the localised depression of the total pressure of a thin layer over the melt. The depression results from the formation of metal oxides from the metal vapour over the melt [termed here a **collapsing reaction**]. In the limit this raises the evaporation rate up to a rate approaching that which would occur *in vacuo*. This acts as a diffusion pump to enhance both oxygen and metal vapour diffusion. In the case of the work cited the reaction rate could be increased by raising the oxygen partial pressure up to the point at which the evaporation of the metal achieved a maximum [ie as *in vacuo*] at which point further increases in the oxygen partial pressure pushed the fog down onto the metal surface and terminated the reaction by choking the surface with the oxide. See Figure 5.12 above. In the present case there are certain

differences, the principal amongst which is the higher temperatures involved. This results from a much higher ratio of the enthalpy of formation of alumina to its specific heat capacity than was the case for the cases cited above for copper and iron oxide fogs. This has the effect of creating conditions in which the evaporation rate becomes so high that the fog reaction remains standing above the metal surface¹.

5.3.4.1 Alumina Transport

One of the most difficult questions to resolve was how to account for the fact that whilst the reaction probably took place locally at hot spots above the pores, the alumina growth takes place more or less uniformly over the entire crust surface. The experimental results showed that a glass coating covered the top of specimens removed from the furnace and this looked like a good candidate for the transport agent. During the ignition stage aluminium reacts with the silica to form alumina and process heat. This also gives rise to a reactive slag which swiftly becomes saturated with alumina causing precipitation to occur away from the hot spots as temperatures fall radially. This appeared to have the

¹ This metastable configuration is a familiar combustion phenomenon and may be observed over bunsen burners. The flame front remains still relative to the observer when the velocity of flame propagation is identical to that of the gas jet. Self adjustment occurs as a result of the conical spread of the gas jet. Increases in gas flow rate at the tube exit have the effect of moving the flame front up the cone to maintain the same local flow rate per unit area.

necessary characteristics to explain both the steady state mechanism of alumina formation and its even distribution. However it could not even nearly account for the very large rates of oxygen transport to the local hot spots which would be necessary to maintain the process. At some stage the oxygen would have had to enter into the liquid slag [unless the aluminium welled up and spilled over the slag surface¹] in order to get to the aluminium², and the maximum rates possible for diffusion through the slag are insufficiently high. Furthermore any diffusion inwards along radii emanating from the hot spots would have to fight an uphill battle against the thermal gradient.

One other fact that tends to disqualify the aluminothermic slag hypothesis is the absence of any significant amount of silica from the experimental specimens. This does not prove that silica does not play some vital and continuing role throughout the process. It does mean however that at some stage the silicon and the silica must have reacted to form silicon monoxide gas which subsequently escaped³. At the temperatures calculated the vapour pressure of silicon and its oxide and sub-oxide

1 An unlikely event since the surface tensions and the relative densities the wrong way around.

2 This is not entirely impossible. There appears to be evidence that it may have happened at some stage during the formation of the layered specimen which came from the unbuffered crucible run. [see Figure 5.7]

3 The evaporation of silicon monoxide from molten slag with reduced silicon di-oxide activity is substantially proportional to the elemental silicon.

are all appreciably high [see Figure 2.6]. Whereas the combustion hypothesis does not invoke silica as a necessary agent in the direct steady state alumina formation stage [apart from a role in its even distribution by a slag] the reactive slag hypothesis requires the presence of silica as a **chemical reactant** throughout the entire process.

This leaves the alumina distribution problem to be solved. Figure 5.9 depicts a cyclic process which is thought to be the mechanism by which the alumina is evenly distributed over the surface. Heavy fumes of alumina and its sub-oxides coming horizontally out of the reaction zone not only carry heat away from the hot zones but also continue to produce heat via the further oxidation of the sub-oxides. This leads to the ready formation, in the gas phase, of alumina particles, often in the form of whiskers. These particles or whiskers dissolve into the slag film overlayer. [Figure 5.13 shows the appearance of alumina fumes as they are formed around burning aluminium droplets in the Iroxo lance process. Figure 5.14 below shows whiskers of what is considered to be alumina which is known to produce such forms under similar conditions. These seem to have been formed in the gas phase by direct oxidation]. Precipitation of the alumina occurs at the cooler crust/slag interface. X-ray SEM analysis of the glassy looking substance which covers

the surface shows that it contains more or less equal amounts of magnesium and aluminium presumably as solid solutions of oxides and the double oxide.

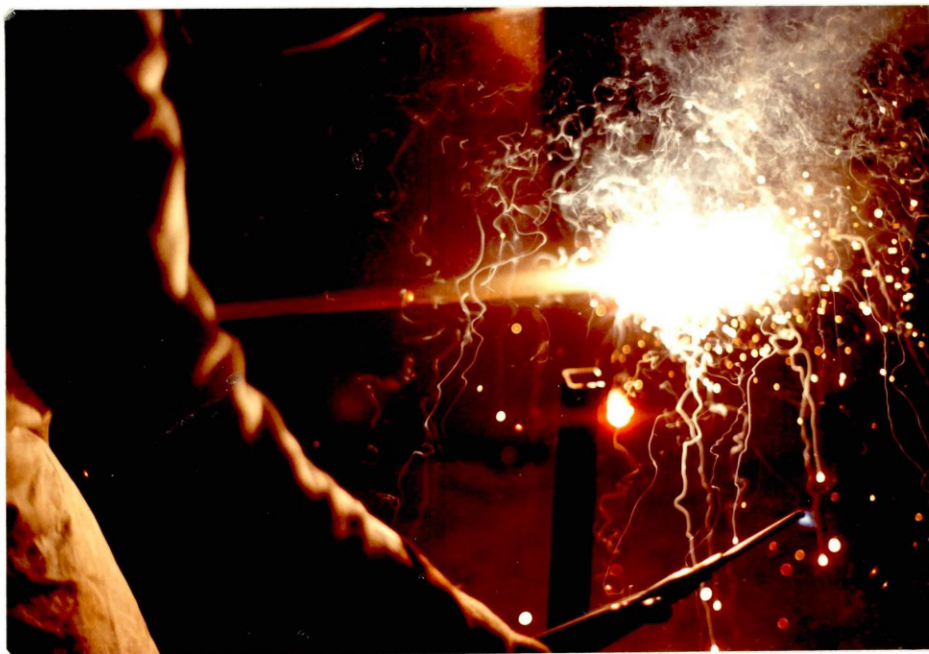


Figure 5.13 Alumina Fumes from Burning Droplets.

Dense alumina fumes are formed out of a vaporisation-oxidation zone above the surface of molten aluminium. Note the high integrity of the smoke trails.

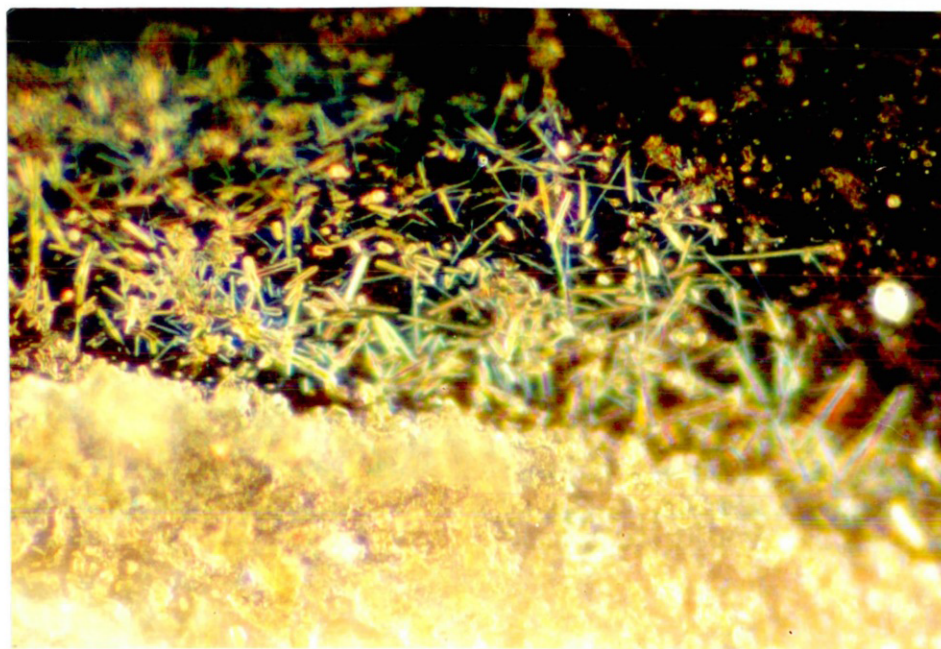


Figure 5.14 Whiskers at the Top of the Glass Layer

Whiskers of alumina formed in the gas phase and absorbed into the glassy slag covering the top surface of the specimen.

5.3.5 Crust Formation

Crust formation is thought to occur by precipitation from a ternary slag. Figure 5.15 shows the iso-activities of alumina silica and magnesia at 1600°C. The continued production of alumina pins the precipitation reaction in the corundum cusp [valley] and incidently gives the composition of the silica and the magnesia in the distributing slag [at 1600°C].

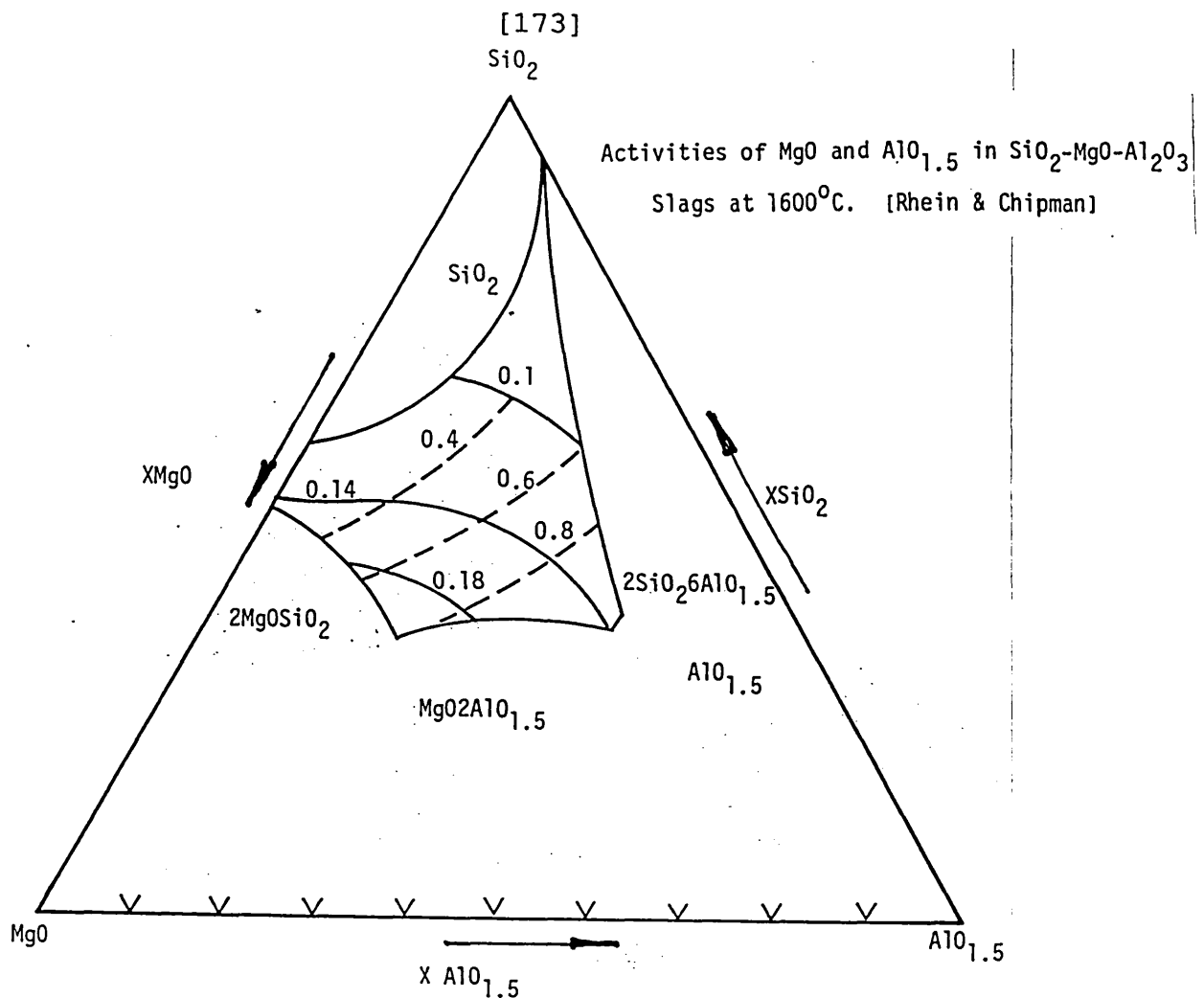


Figure 5.15 Iso-activities: A-S-M System

Aluminium supplied by the pore system continually drives the alumina into saturation and precipitation as corundum. At any fixed temperature the activities of the other constituents, magnesia and silica are fixed by the appropriate iso-activity line above.

This describes the general thermodynamic pattern but says nothing about the actual growth morphology of the expanding surface. Microscopic examination reveals not a flat featureless plain surface but rather a coral garden

of polyp or raspberry [recursive spheres¹] shaped growths in a sea of glass [see Figure 5.5]. The growths are about 100 microns across and roughly spherical. They consist of alumina radially permeated with alumina filled pores in cross-section suggesting a river delta. Between the impinging spheres are voids which may sometimes contain glass but never aluminium. The size of the voids is related to the size of the raspberry-like growths. These are related to the speed of growth which in turn is related to the furnace temperature.

The finest structures [ie those with the smallest raspberry growths] are obtained by way of the powder route. It is likely that the fineness of the pores can be controlled to an extent by the fineness of the powder employed in the powder route. The fineness of the pores also determines the limiting thickness of the crust. The finer the pore the greater will be the capillary forces which balance gravitational forces.

5.3.6 Terminal Conditions

Terminal conditions occur in two stages. The first is when the reservoir of aluminium is exhausted and the

*1 It is interesting to note that recursive clusters of spheres [a common "fractal" phenomenon] are the inverse three-dimensional analogue of dendrites. In the former case agglomerative growth occurs optimally when the surface/volume ratio of the **liquid** is a maximum and in the latter case dendritic growth is promoted when heat transfer away from the **solid** is optimised at the maximum surface/volume ratio. In the present case the liquid is better able to precipitate alumina when the shape of the liquid is dendritic.*

second is during the depletion of the aluminium-containing pores. The difference between the stages lies in the capillary effect. In the first stage the input attraction is very nearly balanced by the output impedance [due to the same attractive force]. Any marginal difference between input and output forces is due to the frictional drag acting upon the flow of aluminium through the pore. However, when the reservoir of aluminium becomes depleted the net force on the aluminium within the pores acts to retain the metal in the pores. The driving force acting to bring out the metal is the "pumping" action of the vaporisation process. Thus the combustion process behaves as if it were a heat engine drawing out the liquid and is more heavily loaded in the final stage.

Should the process be interrupted before the reservoir is exhausted, for example by removing the specimen from the furnace, the combustion continues since the reaction system has become self-sustaining. Evidence for this is shown in Figure 5.3 which depicts a void in the solidified metal. The eutectic liquid has been drawn out during the process of solidification of the alloy. This must occur between the liquidus and the solidus of the alloy. The eutectic temperature is 615°C and the melting point of aluminium is 660°C . This means that the combustion process is still in operation when the temperature has dropped to this region of temperature.

5.4 Summary of Crust Formation Mechanisms

The crust formation mechanism relies upon a series of events. Catastrophic oxidation begins with the preferential formation of MgO at around 700°C. The volume of the oxide is some 20% less than the element and is therefore fragmented allowing oxygen access to the virgin metal through fissures or pores.

When the magnesium content [or more accurately the activity coefficient] has fallen sufficiently spinel forms from the MgO and alumina. This ensures the development of self sustaining pores. The pore surface is probably a solid solution of spinel in alumina. This has a high surface energy and promotes the capillary ingress of the metal melt.

The steady state stage of continuous formation of alumina at the top of the pores is preceeded by an initiation stage where oxidation takes place in a reactive oxide slag. The slag is driven to and held at alumina saturation by the rising metal. During this stage alumina is continuously precipitated on the cooler surface of the crust thus sustaining the reaction. The system is not however in a state of thermal equilibrium. The rate at which exothermic heat is produced exceeds that at which it is transferred away, hence the temperature rises. Before thermal equilibrium can be achieved the rising

temperature alters the system conditions by creating metal vapours which undergo oxidation in the gas phase immediately above the melt.

Eventually a limiting condition is encountered at which the oxygen diffusion rate is only just sufficient to oxidise the aluminium vapour at that temperature. Thus a dynamic equilibrium, or steady state, is achieved wherein the heat supplied by the reaction of the vapour with the limiting supply of diffusing oxygen is just sufficient to produce the requisite rate of vapour formation. However, transport of the sub-oxides of aluminium away from the oxygen impoverished hot zones create further exothermic heat as they are transported over the glass layer where fresh oxygen supplies exist. This is the principal driving mechanism by which the alumina crust is formed. This state is characterised by a constant rate of weight gain. Hence, the diffusion rate of oxygen is the rate limiting step. The limiting rate of aluminium vapour supply is the result from the limiting heat transfer rate from the isothermal vaporisation-oxidation reaction to the melt. This is in turn governed by the rate of diffusion of the oxygen to the reaction. Since the transport of aluminium sub-oxides away from the hot zones causes further exothermic reaction some heating occurs over the entire surface

The smoke or fumes [condensed alumina] from the reaction, emanate in the horizontal plane from the reaction zone

and are deposited upon the surface of the glassy slag as a form of condensate by which they are absorbed. Finally alumina is precipitated at the bottom of the slag onto the cooler crust. This model is depicted in Figure 5.9.

The evidence for combustion or hot spot-fog reaction being the principle reaction mode is drawn from the estimation of the reaction equilibrium temperature. These calculations are based upon experimentally obtained figures of weight gain rate per unit area and the associated thermal flux [Appendix II].

5.5 Combustion Routes to Composite Formation

All of the routes to composite formation investigated here involve alumina in the liquid phase. In each case the alumina is, at some stage, fluxed by other oxides. The reaction rate per unit area in all cases yields thermal flux values corresponding to temperatures above that at which metal ignition is known to occur.

During the crucial ignition stage catalysis occurs. In the case of the iroxal process iron oxide behaves autocatalytically as depicted in Figure 5.2. In the Lanxide process silicon dioxide and/or magnesium oxide behave autocatalytically; see Figure 5.11.

There are both advantages and disadvantages to combustion routes. On the one hand we have processes which are

spontaneous and self-propagating and fast. On the other hand we have to contend with the problems of very high reaction temperature and the heterogeneity arising through turbulence in the lance systems and the pore field nature of the Lanxide process.

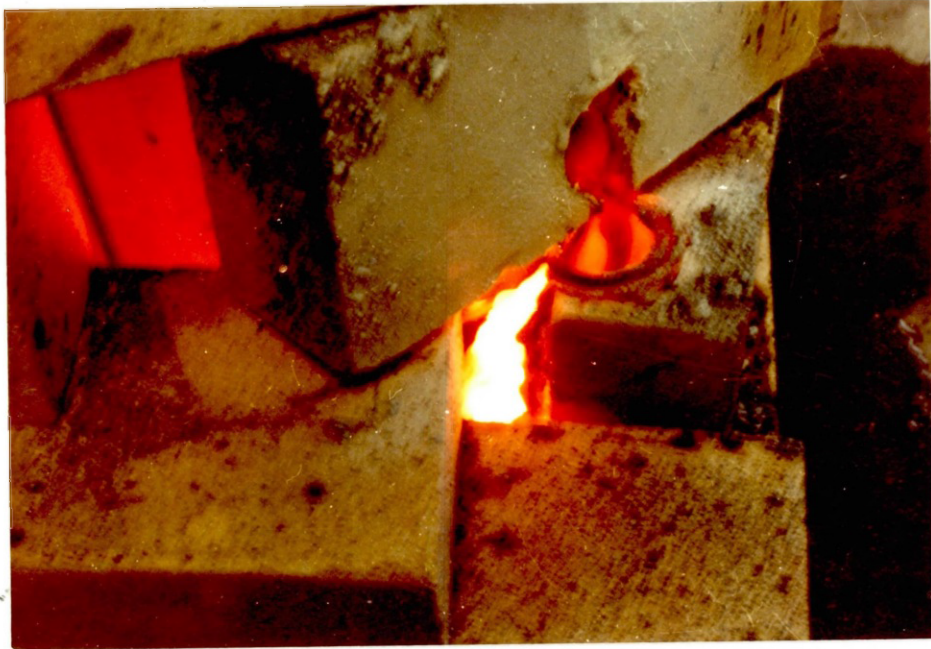


Figure 5.16 Borehole in Firebrick: note the still reacting slag.

CHAPTER 6. CONCLUSIONS

The principal goals of the research were:

to assess the feasibility of developing metallothermic routes to the production of alumina dispersals in an iron matrix.

to study the mechanisms by which the Lanxide process produces aluminium-infiltrated alumina composites.

6.1 The Iroxal Processes

The Iroxal process involves free combustion of aluminium and iron. This has been studied by means of two approaches. In the first a consumable oxygen lance was devised in which concentric tubes of aluminium and iron were burned in a controlled manner. The reaction took the form of a spray of burning droplets. In the casting mode the spray was directed into a mold. Hence the combustion mode was semi-submerged. In this mode combustion could take place either on the outside of droplets or alternatively on the inside of bubbles. Since the rates of reaction would be different in the contrasting heat sink conditions a second method, termed here the "Bessemer" method, was devised such that combustion could be constrained to the inside of a train of bubbles.

The products of the iroxoal lance consisted of a fine dispersal of about 2% alumina needles [or primary dendrites] in a matrix of iron heavily contaminated with aluminium. The needles which were produced were ragged in form giving rise to potential stress concentrations. The level of remaining aluminium is so high as to produce brittle type fracture under applied stresses of less than half those typical for mild steel. It is concluded from these disappointing results that the process, in its present form, is not suitable for producing useful composites. However, if it can be shown that combustion is still stable, it may be possible to blow oxygen into the melt from an auxiliary non-consumable lance until equilibrium has been established at the point at which the aluminium is just exhausted.

On the other hand the Bessemer reaction system shows some promise of eventual usefulness. The technique is more easily controlled, it is less violent, and it has produced ceramic crystals [after heat treatment] of convenient size. These crystals could be blown into a steel melt to provide a desirable wear resistant steel composite. The problems of wetting appear to have been reduced by the presence of the spinel [hercynite] probably in solid solution with alumina.

6.2 The Lanxide Processes

The results of this programme have lead to the conclusion that the primary mechanism by which alumina is produced in the lanxide method is a complex series of interconnected processes viz:-

The pore structure is brought about by the formation of spinel which by yielding a fragmented surface, causes catastrophic oxidation to occur.

Aluminium is transported up the pores by capillary forces. The favourable wetting conditions at the pore walls are the result of surface activity phenomena resulting from the presence of a small amount of dissolved magnesia and /or spinel.

The vaporisation-oxidation of aluminium vapour over the top of fine pores. The evaporation of the aluminium is enhanced by the so-called fog reaction phenomenon.

The distribution of heat and the alumina over the whole surface of the crust is by way of heavy oxide fumes of alumina together with still reacting aluminium sub-oxides. These emanate from the reaction hot-zones often having formed whiskers in the gas phase, and are eventually absorbed at the top of a glassy slag which has been shown to coat the top of the growing alumina crust.

A temperature gradient exists through the slag such that the alumina supersaturates close to the bottom of the glassy layer. Precipitation occurs giving rise to a characteristic fractal growth morphology consisting of large alumina grains interconnected at their low energy faces.

The precipitation reaction at the growing crust surface produces corundum. The ternary phase diagram for the oxides of Al-Si-Mg shows the eutectic point=1357°C. The continual supply of alumina to the melt ensures that the operating point is coincident with the corundum "valley". There is an invariant reaction at a temperature of 1547°C above which pure corundum forms. Precipitation of pure corundum can however occur at temperatures below this dependant on the requirements for supersaturation.

The temperatures required to form a liquid slag system result from the combination of the furnace temperature and that arising from exothermic reactions. The slag is thought to have been initiated via the oxidation of the metallic vapour phase in the case of the alloy route, and initially in the case of the powder route by the exothermic reduction of the silica by aluminium.

The entire process relies upon the transportation of the metal melt up the pores and it is concluded from the evidence of the results that the wetting of the pore

walls by the melt is enhanced by the presence of MgO either as spinel or in solid solution with the alumina. The pores are formed in the first place by the volumetric changes which occur as magnesium forms its oxide and the subsequent formation of the spinel. The presence of magnesium is known to prevent discontinuous grain growth by reducing the tendency of the grain boundaries to break away from the pore phase. This is well reported in the literature. In this study it is concluded that pore initiation is assisted by the evolution of magnesium vapour, and that the continuation of the pore structure results from the pores being filled with aluminium as well as the forementioned agency of magnesium as an inhibitor of discontinuous grain growth.

A second approach to the process was investigated which involved the sprinkling of silica and magnesia powder onto the top surface of the pure aluminium specimen. This produced identical results to those obtained starting from the alloy. In this case the reactive slag is a ternary oxide system including alumina. The system is continuously driven into alumina saturation by a sustained exothermic reaction driven by the rising aluminium from the pores.

Initially, the rate of formation of alumina is exponential. Temperature rises increase the reaction rate and vice versa. Steady state conditions are ultimately realised when the limiting rate of oxygen diffusion is

achieved. Combustion, once initiated, is both self-sustaining and self-regulating. This is so even when the environmental temperature is reduced to below 700°C, as attested by the leaching of the metal eutectic below the liquidus.

6.3 Lanxide Process Background Temperature Limits

The Lanxide patent delimits the operational temperature regime as having an upper bound of about 1400°C and a lower bound of about 1100°C. The lower limit coincides with the boiling point of magnesium and it is likely that below this the spinel forming mechanism necessary to produce the pore system is inoperative. The upper bound is associated with the additional temperature rise brought about exothermically and the combination of heating sources gives rise to temperatures at which the mechanisms of alumina formation are likely to break down due to vapour [and perhaps silicon monoxide] losses from the slag.

6.4 Reaction Temperature Estimation.

Knowledge of the reaction temperature is of crucial significance if we are to come to conclusions concerning the physical chemistry of the systems investigated.

The problems inherent in measuring the temperature of combustion are aggravated by the nature of the systems under investigation. On the one hand we have the problem

of the involved reaction path of the Iroxal processes looked at here. Amongst these the most severe constraint on observation is due to the immersion of the reaction in the melt. On the other hand we are confronted by the problem of the minute size of the combustion system at the top of the pore system in the Lanxide process. This problem has been circumvented to an extent by the estimation of reaction temperature by way of calculation of the flux intensity resulting from reactant mass consumption rate [or product mass formation rate]. However it is still necessary to estimate the actual reaction area and this is more problematical. The smaller the reacting area, the hotter will be the operating temperature. The lower limiting value of the reaction area occurs at the upper limit of temperature at which stable conditions obtain. This area is approximately twice that of the pore. This condition yields temperatures approaching that of alumina dissociation and may be considered as the upper boundary of the process. Once ignition has occurred the system becomes self-stable, even at much lower temperatures. Hence, if the reaction tends to become more diffuse by spreading out over the neighbouring slag, combustion is still maintained. In any event, if the system reverts to a slag reaction, metallothermic heating would lead once more to a vapour phase reaction.

It is argued that the dynamic open system method of estimating the reaction temperature such as that adopted

here is more appropriate than that which utilises the Kirchhoff product-enthalpy equation. The latter assumes closed system adiabatic conditions which cannot in fact be realised [especially at these high temperatures]. In this study on the other hand, a dynamic mathematical model has been developed which takes account of the unavoidably high rate of radiant heat transfer across the system boundary in order to estimate the temperature at which the heat losses equate to the rate of heat generation. However, further knowledge concerning the size and the nature of the reaction area will have to be established before valid and reliable calculation of the operating temperature can be achieved. A plot of the relationship between the reaction area and the resulting temperature can be found in Appendix II.

This leaves us with the more difficult task of estimating the temperature of the Iroxal processes. In the case of the Lanxide process it was possible to consider the flame at the pore-top to be two-dimensional thus simplifying the calculation of thermal flux intensity. However, in the case of the Iroxal processes the question is complicated by the fact that [notwithstanding the thin nature of the flame] the flame surface is distributed in complex ways. In the spray condition the flame is a spherical shell on the surface of the droplets, whilst in the submerged modes the combustion takes place within the spherical bubbles. Furthermore the radii of the spheres are likely to vary significantly. Thus we are constrained

to consider models of the combustion system on which to make our assessments of the regime of reaction temperature. Fortunately we can base our estimates upon knowledge of the enthalpy of formation of the products and the rate of their formation. We can then make educated guesses about the size of the reaction surface. For example we can measure the diameter of the bore hole made when the lance is used to pierce firebrick. Our estimate is then based upon the area of the advancing hemi-spherical surface of the hole front and upon our knowledge of the material properties eg. specific heat capacity and melting point. From these factors we must first calculate the resulting flux intensity generated by the lance [the power being a known value] and then make an estimate of the reaction temperature¹. Figure 6.1 depicts the result of a typical boring operation. In this case the bore is into an aluminosilicate firebrick. Note that the slag, having produced the hole, continues to react so vigorously that it has gone on to pierce the brick below.

¹ There remains an important consideration which is best understood by studying the borehole shown in Figure 6.1. It is evident from this view that the slag issuing from the hole is still reacting since it has continued to bore down through neighbouring bricks. Thus due allowance must be made for the incomplete utilisation of the enthalpy of formation in melting the original brick.



Figure 6.1 Reacting Slag Pouring From Lanced Firebrick

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CHAPTER 8. APPENDICES.

Appendix 1 concerns the so-called Iroxal process. The patent application has been reproduced in full since it contains descriptions of some of the intended uses of the process which have not been detailed elsewhere.

Appendix 11 concerns the so-called Lanxide process. The data which appears in the patent application has been included. Calculations based upon the present work are recorded.

Appendix 111 Is a collation of ancilliary micro-photographs which show puzzling or interesting phenomena referred to in the text.

8.1 Appendix 1.

The work on this process is largely of a technological nature. Prior to this doctoral programme work had been directed towards the development of a range of working processes. Some of the practical results of these are included here for the purpose of general perspective.

8.1.1 Iroxal Patent Application

(12) UK Patent Application (19) GB (11) 2 151 530 A

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(51) INT CL⁴

B23K 35/00 B28D 1/00 E21C 37/16

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B3V 4B2

B3R 18X 32G 37X 9

B5E X6

C7D 15

E1F 5

F4B 105 121 126 E

U1S 1792 2316 B3R B3V B5E C7D E1F F4B

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GB A 2101510

GB 1536107

US 3487791

(58) Field of search

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B3R

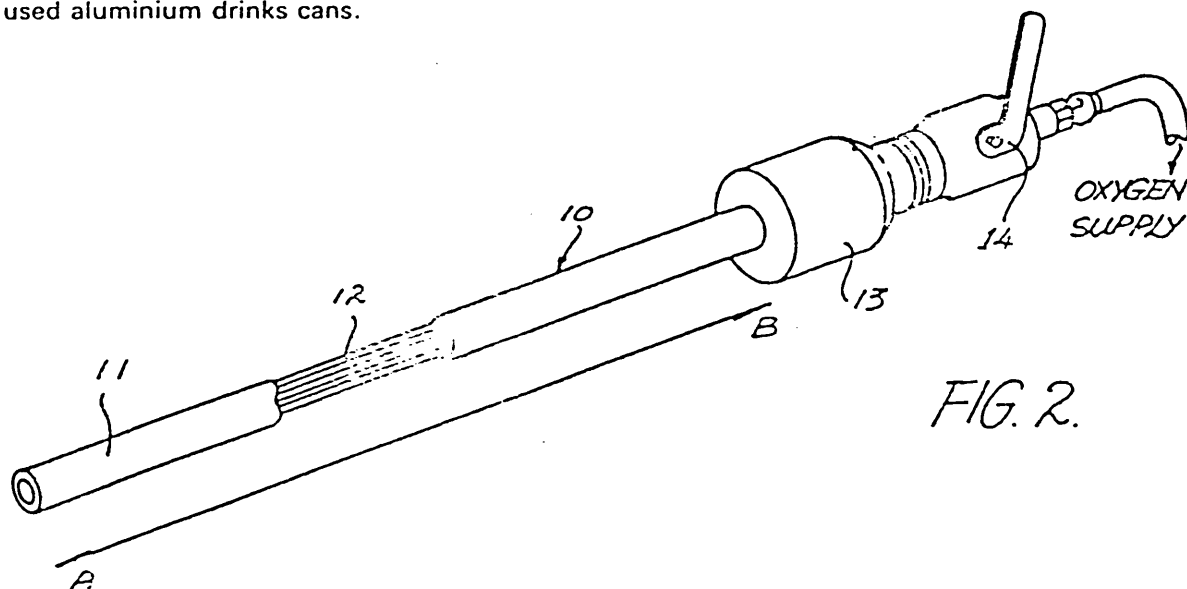
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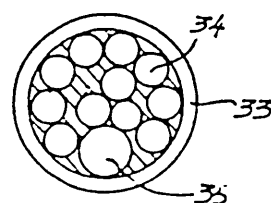
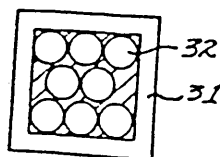
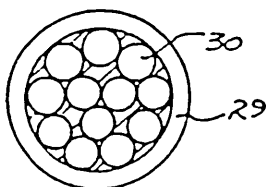
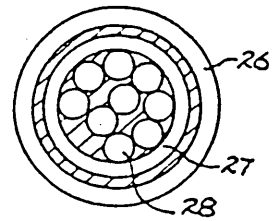
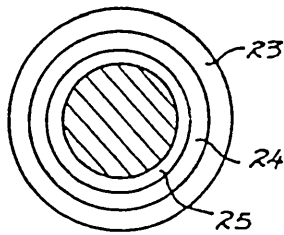
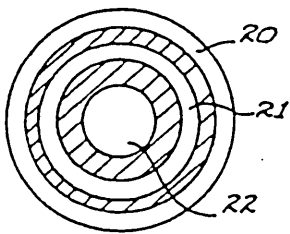
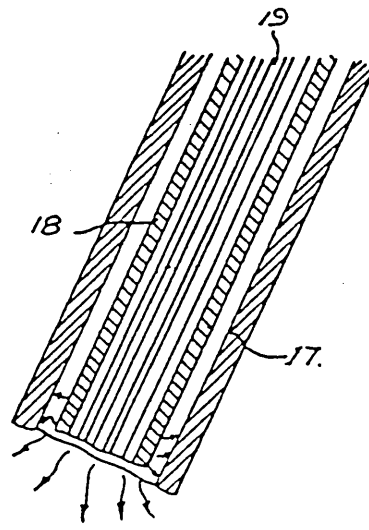
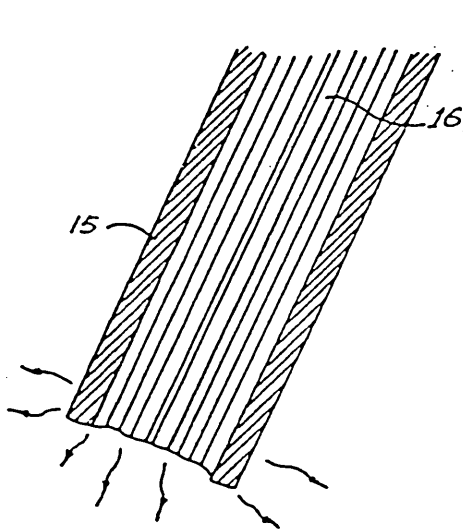
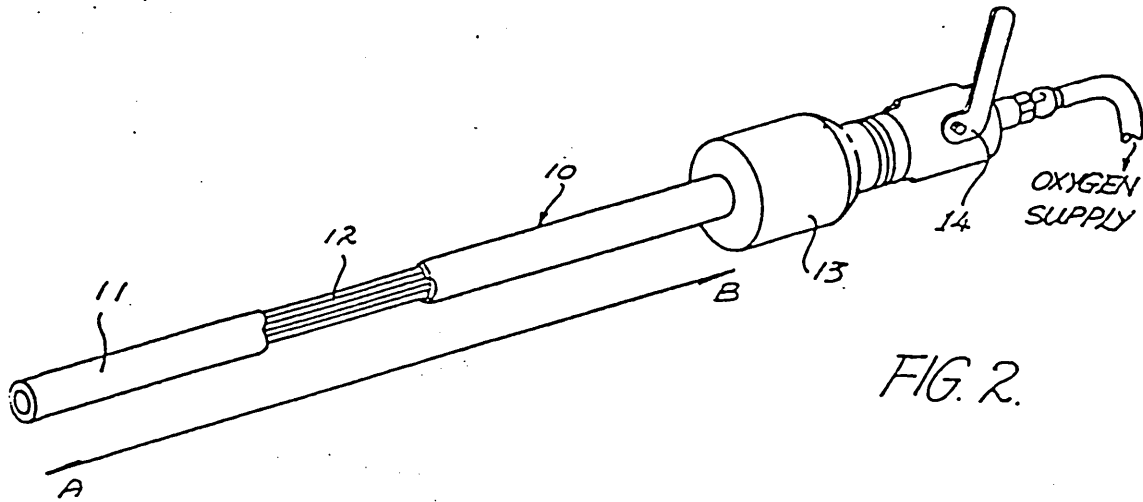
(54) Thermic lance and dual-stage combustion system

(57) A thermic lance comprises a tube 11 of Al, Fe or Fe alloy and an inner tube and/or rods 12 of Al, Fe or Fe alloy, at least one tube or rod being of Al and at least one of Fe or Fe alloy, in a holder 13 including a valve 14 for controlling the supply of oxygen. The lance may be used for cutting or goging metal, rock, brick etc. It may also be used for forming thermic weld material or for providing heat or weld metal directly to a weld site.

A two-stage combustion system uses iron, aluminium and oxygen inputs with outputs of alumina, refined iron or steel and heat energy. In the first stage iron or steel is burnt, using free oxygen, to produce iron oxide particles and heat. The iron oxide is blown by the force of combustion to the second stage where it reacts with aluminium. The aluminium captures the bound oxygen from the iron oxide thus releasing the iron and producing further exothermic heat. Hence, three valuable and useful products are created: molten alumina, molten iron and heat. The starting materials may be scrap steel and used aluminium drinks cans.



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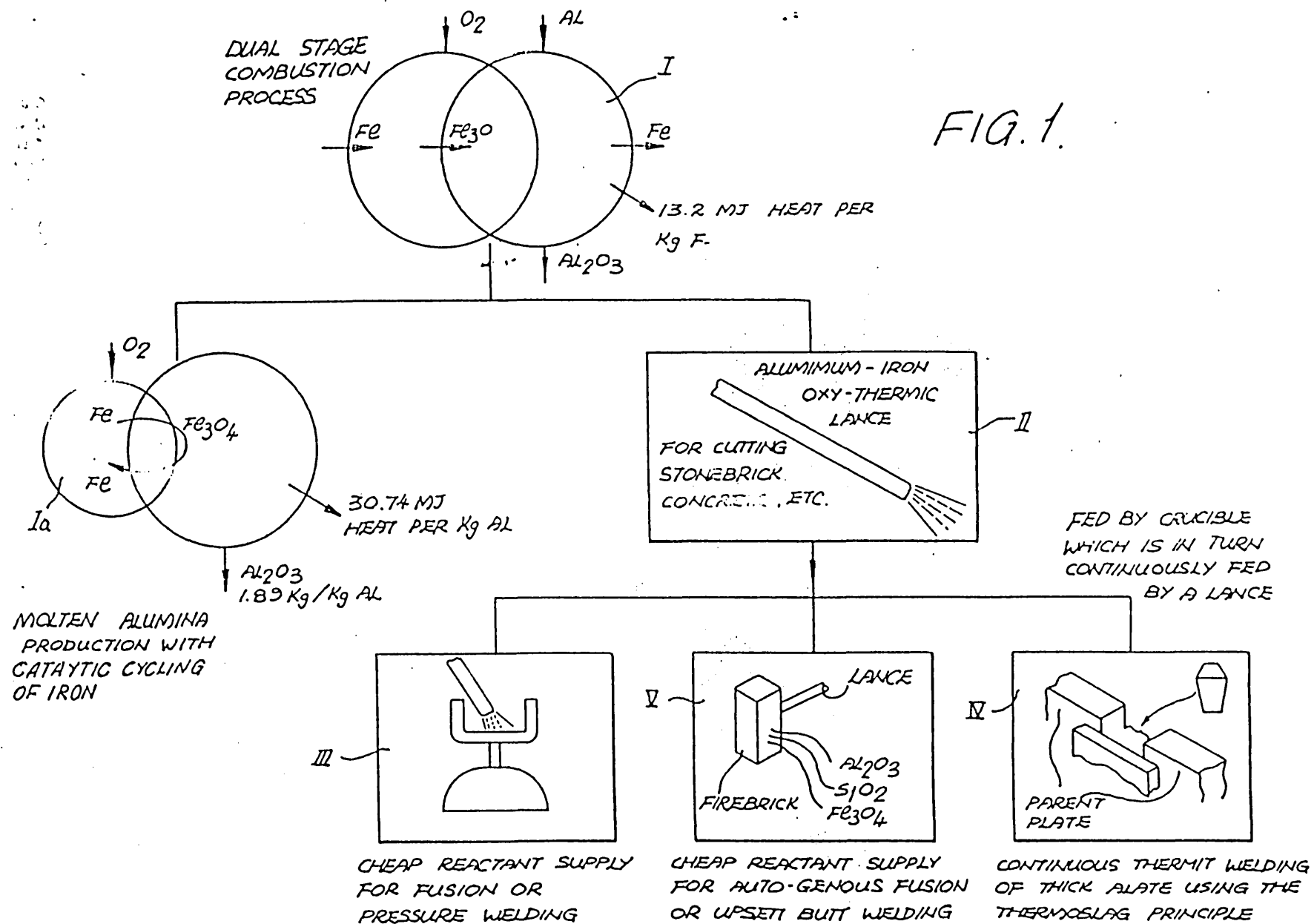


FIG. 1.

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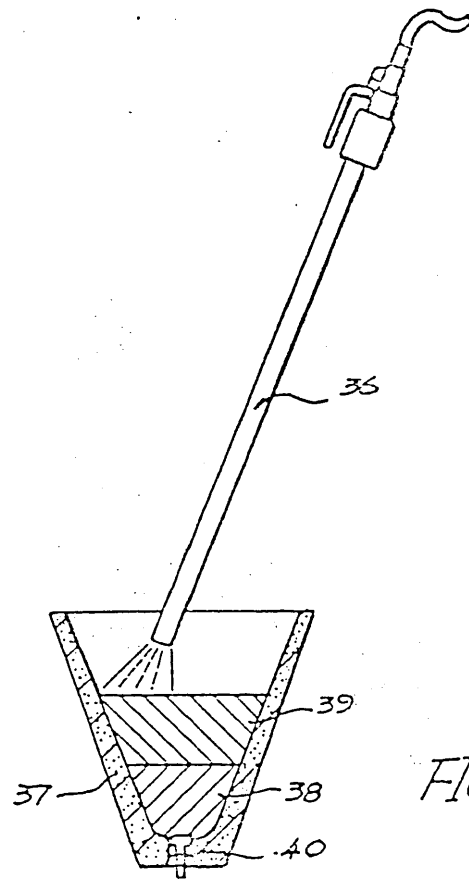


FIG. 5

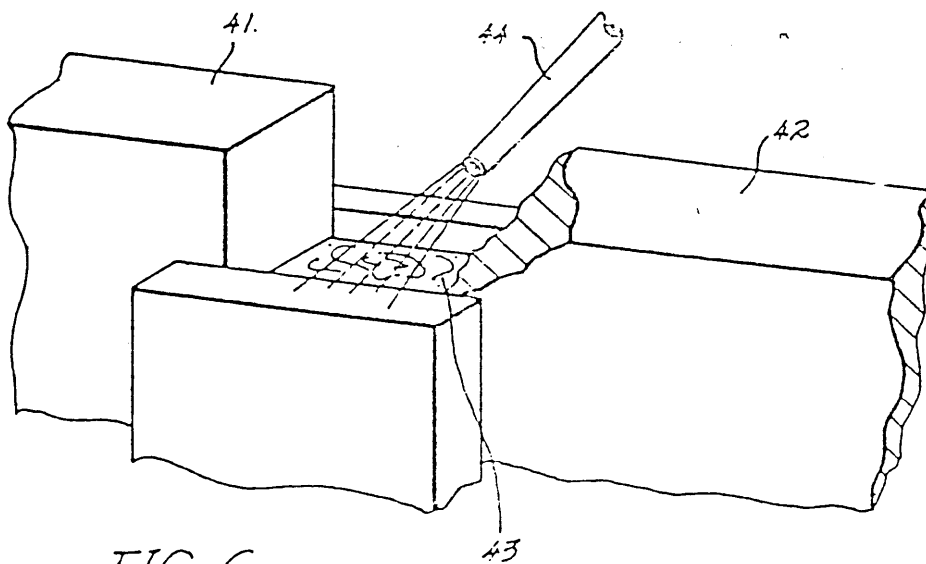


FIG. 6.

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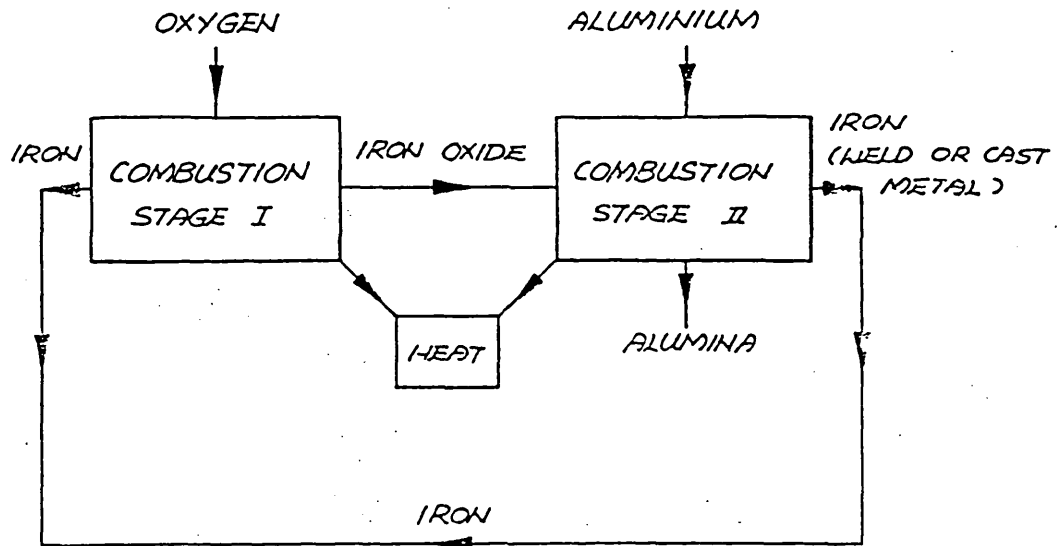


FIG. 7.

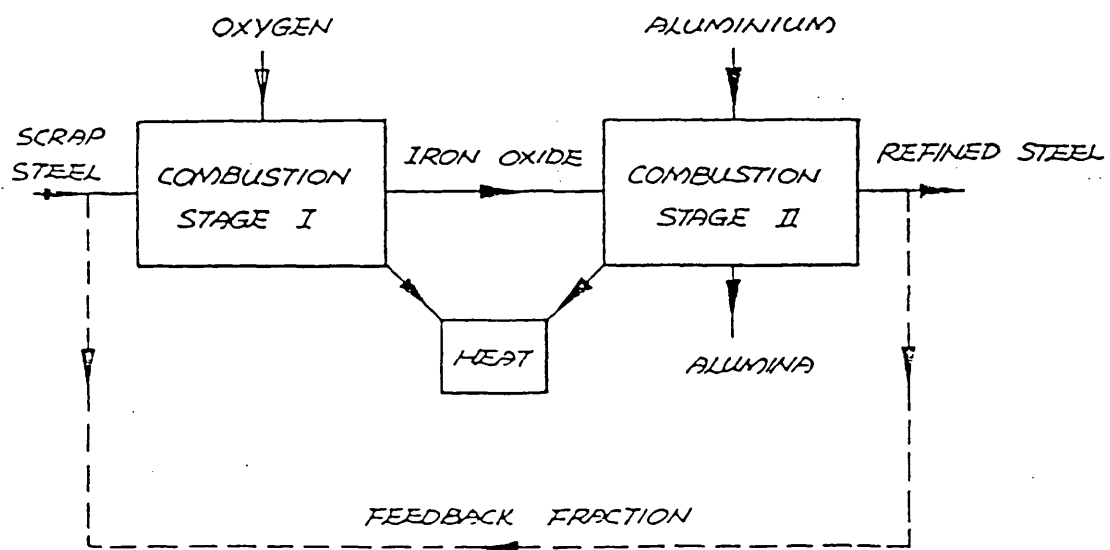


FIG. 8.

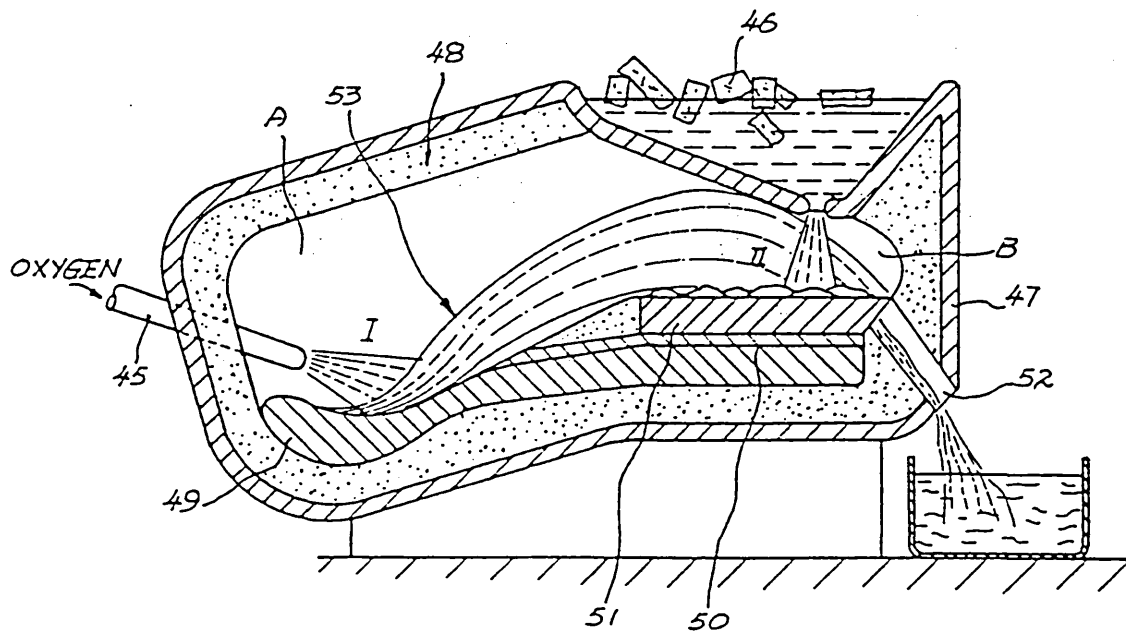


FIG. 9

SPECIFICATION

Dual-stage combustion system

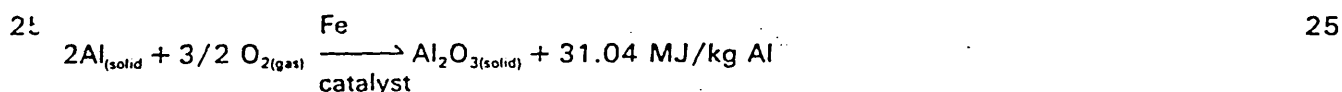
- 5 The present invention relates to dual-stage combustion and in particular to an improved thermic cutting lance and to a process and plant for producing alumina and other desirable products such as energy from steel and aluminium which utilize dual-stage combustion. 5

The two-stage combustion system uses iron, aluminium and oxygen inputs with outputs of alumina, refined iron or steel and heat energy. In the first stage, iron or steel is burnt using free oxygen to produce iron oxide particles and heat. The iron oxide is blown by the force of combustion to the second stage where it reacts with aluminium. The aluminium captures the bound oxygen from the iron oxide thus releasing the iron and producing further exothermic heat. Hence, three valuable and useful products are created: molten alumina, molten iron and heat according to the following equations: 10

Stage I: $\text{Fe} + 2/3 \text{O}_2 \rightleftharpoons 1/3 \text{Fe}_3\text{O}_4 + 6.69 \text{ MJ heat}$
(reversible) 15

Stage II: $8/9 \text{Al} + 1/3 \text{Fe}_3\text{O}_4 \rightarrow 4/9 \text{Al}_2\text{O}_3 + \text{Fe} + 6.64 \text{ MJ}$
(nett) 20

Since the heat released in the first stage is neutralised by its equivalent in dissociation, the free heat gain is due to combustion of aluminium only. Thus the process can be represented as:



An oxy-thermic lance consists of an iron or steel conduit or tube which may have inserted through it a number of steel rods or wires. A stream of oxy-acetylene gas mixture is passed through the conduit or tube and ignited at the end remote from the gas supply, ignition being sufficient to initiate the iron/oxygen combustion which is thereafter self-sustaining. The oxy-thermic lance has numerous cutting and boring applications. 30

We have sought to provide an improved thermic lance.

35 Accordingly in one aspect the present invention provides a thermic lance comprising an outer metal conduit being made of either aluminium or iron or an alloy containing predominantly iron, an inner metal conduit and/or a number of metal rods located within the outer metal conduit, the inner metal conduit and/or metal rods being made of either aluminium or iron or an alloy containing predominantly iron such that at least one of the conduits or one of the rods is made of aluminium and at least one of the conduits or one of the rods is made of iron or an alloy containing predominantly iron; the lance including a holder at one end, the holder being provided with a valve through which, in use, oxygen may be admitted to pass through the lance to the other end for ignition. 40

The conduits or rods made of an alloy which is predominantly iron may be steel.

45 In a preferred embodiment of the lance, an aluminium conduit surrounds a steel conduit and a number of iron rods are located with the steel conduit such that oxygen can pass down the lance between the aluminium and the steel conduits and past the iron rods. 45

In another embodiment of the lance, an iron or steel conduit surrounds a number of aluminium rods such that oxygen can pass through the conduit.

50 If the lance is constructed with an outer conduit made of iron, this should have a minimum thickness of 1mm since otherwise the lance does not perform satisfactorily since the iron conduit burns away before the aluminium is ignited. 50

The shut-off valve controls the rate of flow of oxygen through the lance. The rate of flow of oxygen must be sufficient to sustain burning and should generally be between 1.5 gm/sec and 6 gm/sec to achieve lance burn-off rates (in air) of between 4 gm/sec (Fe) and 16 gm/sec (Fe) (using stoichiometric ratio of Fe, Al, O₂) yielding 50 Kw and 200 Kw, respectively. In general, an increase in oxygen flow rate will speed up the burning rate. For reasons which are not understood, whilst boring non-metallic materials, the iron output is itself oxidised and in these confined conditions, burn-off rate is approximately doubled. Boring rates for fine brick are about 60 2 gm of aluminium per cm³ of brick melted but the melting efficiency may be considerably higher if the effluent slag is contained rather than spilled out of the hole. 60

Using the above lance, the burning rate is automatically stabilized and the percentage utilization of aluminium is virtually 100%. It is not necessary to construct the lance with an amount of iron which is equivalent to the stoichiometric amount set out in the equation above

65 However, sufficient iron must be present to

is fast enough to produce sufficient iron oxide in stage I and sufficient iron in stage II to maintain the oxidation of aluminium, in other words the rates of the two reactions of the dual stage combustion which is taking place at the end of the lance must be complementary and to give and maintain a sufficiently high temperature for the ignition and oxidation of aluminium and the vaporization of the alumina formed. The iron is in effect continuously recycled within the flame boundary as shown by the above equations and so the lance need only be constructed with a small quantity of iron to ensure combustion of the aluminium and the production of heat. In practice, the lance should be constructed with at least 50% of the stoichiometric quantity of iron.

10 Combustion is initiated by means of an oxy-acetylene flame or by connection to an electrical power source, e.g. a welding transformer or by use of a pyrotechnic igniter. 10

The thermic lance of the present invention produces a much greater quantity of heat than that produced by known thermic lances and the temperatures reached by using the lance of the present invention are in excess of 3500°C as compared with temperatures of less than 2500°C reached using known lances.

15 Known thermic lances produce 6.67 MJ per kilogram of iron consumed whereas the thermic lance of the present invention is capable of producing in excess of 30 MJ per kilogram of aluminium consumed and if the iron is also completely burnt (which is the case when boring non-metallic materials) in excess of 45 MJ per kilogram of aluminium consumed. 15

The lance of the present invention yields heat at energy densities in excess of 10^4 watts/cm² at powers of from 50 to 200 kw for manual operation. The temperatures resulting are well in excess of the melting points of most common materials (2500 to 3500°C). Thus, the lance may be used to slit, gauge or bore metal, natural synthetic ceramics such as rock, concrete and brick. In boring rocks generally, lower slag melting temperatures are achieved due to the formation of a three (or more) phase system e.g. Al_2O_3 , Fe_3O_4 , SiO_2 . The three (or more) phase system produces lower eutectic temperatures than the two-phase system encountered with the oxy-iron lance. Hence, even greater speeds of boring are achieved. 20

The lance of the present invention is an improvement on existing oxy-thermic boring lances which are conventionally used to bore large castings or brick, rocks or concrete. Since an extra stage of combustion has been added by providing a thermit-type reaction slightly downstream of the iron oxygen burn, the thermal intensity of the process has effectively been doubled thus providing a faster cutting system. Furthermore, in the boring of siliceous rocks (which constitute the majority), the alumina and the iron oxide form a three-phase equilibrium system with the silica thus reducing the melting point well below that of iron oxide and silica in the conventional oxy-thermic lance. This increases the speed of boring. Although the addition of the aluminium tube increases the consumable cost quite considerably, the cost per heat unit produced is almost identical. Moreover, there are savings in cutting time. The real value of the lance is its speed. In cases where time is limited, for example in freeing people from collapsed buildings or liberating money from jammed safes or time vaults, the extra cost of the aluminium tube would be insignificant. 30

Another use is the splitting of boulders and large rocks. The products of the lance are deposited in a hole which has been drilled vertically. Heat from the products then fractures the rock by thermal shock via differential expansion proportional to the high temperature gradient produced by the extremely hot slag. 35

45 The lance also has application in underwater situations. 45

The thermic lance of the present invention is also of value in conventional thermit welding and casting equipment.

In this use of the lance of the present invention, an inexpensive consumable supply system for thermit welding and casting is provided. At present, thermit welding uses finely ground aluminium and ferric oxide particles together with an igniter substance. A great hazard of the process is contamination by water which, on reaction, produces hydrogen which can then cause an explosion. By using the lance of the present invention, the process is both safer and made cheaper in that cheaper iron and aluminium in the form of the lance is substituted—thermit ignition is spontaneously accomplished by the first-stage reaction and so an igniter is not required. 50

The advantages of this system are:

(a) It is unnecessary to purchase special thermit welding powder or igniter powder. The tube rod or wire forms of alumina and iron are easily and universally obtained. 55

(b) Storage problems presently encountered with storing powdered material are overcome by using the lance. In particular, the hazard of hydrogen explosion from water-contaminated powder is avoided. 60

(c) The process is cheaper, even when the added cost of oxygen is considered, as special thermit welding powder is not needed and the amount of aluminium consumed per kilogram of iron is roughly halved from about 40% of the total input to less than 25%. This is due to the doubling of the available heat. 65

(d) The process is more reliable and safer.

(e) Because of the additional stage of combustion, more heat is produced thus facilitating the use of more steel "make-up" than the presently used thermit process permits. Since with the present invention a much greater quantity of extra iron may be added since the extra heat from combustion stage I (of the dual-combustion process) is available. Generally, the increase in yield of weld or cast metal is 100% since the extra heat adds 100% to the thermit stage. 5

All situations in which the conventional thermit process is used, i.e. railway line welding, reinforced concrete bars welding, heavy section ship frame parts welding, repair of heavy castings and forgings and mill roll repair would be more cheaply and easily carried out by using the lance of the present invention as a consumable supply system for thermit welding and casting. 10

Pressure butt welding with the lance as an external heat source is accomplished by two different methods. In each case, since no lance iron is used in the actual weld, the purity of the iron output is irrelevant and since this is the case, both ferrous and non-ferrous welds may be accomplished as well as certain combinations of dissimilar metals (providing no fusion occurs) such as stainless steel to carbon steel, high speed steel to carbon steel. In both upset methods, the present lance provides considerably more heat than the crucible thermit reaction. Firstly, it is at least twice as calorific, secondly the charge is applied directly to the weld reservoir thus minimising losses. 15

The lance of the present invention can be used in alumina shell-mould autogenous welding in which the prismatic components to be welded (such as railway lines) are butted closely together have been passed through suitably shaped holes located at opposite ends of the thermal reservoir chamber. The molten products from the consumption of the lance are sprayed directly or poured into the chamber, immersing the components. Another method is to conduct the molten products from boring a fire brick (SiO_2 , Fe_3O_4 , Al_2O_3) into the chamber to improve flow and heat transfer since they form a three-phase low melting point eutectic system. Since the components are initially at room temperature, some of the alumina solidifies out onto those parts of the surfaces which are inside the reservoir. Conductive and convective heat transfer from the reservoir melt raises the component metal adjacent to the butting faces to a temperature either just above or just below that of fusion. In the first condition, the abutting faces fuse together heat transfer along the axis of the parts and across the boundary of the reservoir chamber provides a temperature gradient calculated to ensure that any slight melting takes place only locally at the centrally positioned joint faces. In the latter case, where melting is not required such as in the welding of dissimilar metals, the heat transfer provides a temperature gradient such that the zone closest to the abutting faces reaches hot plasticity. A lateral force is then provided (for example by screws, wedges or hydraulically) to cause the plastic material to deform so as to produce a plastic deformation weld—conventionally known as upsett butt welding. The remaining liquid charge is then teemed away before it has time to solidify. In another method, the parts to be welded are separated by between 10mm and 30mm depending upon the massiveness of the parts. The sides of the gap are enclosed by dam molds. The lance charge is deposited in the reservoir thus formed. Initially, some of the alumina will solidify out on the exposed faces thus protecting them from the remaining melt when sufficient heat has been transferred to the parts. To ensure their plastic state, the parts are brought together by mechanical means and the molten melt is first ejected followed by the formation of sufficient upset to ensure that the alumina is broken and extruded from the weld interface. 20 25 30 35 40 45

+ 17 Mullite
+ 5 Sph
30mm

Any of the thin alumina shell mould remaining is then shattered by a suitable tool such as a chipping hammer.

Aluminium is now extensively used to manufacture beer and soft drink cans and the disposal of such used cans constitutes a considerable pollution and environmental problem. Similarly, the disposal of low grade scrap steel is a problem since in both cases the monetary incentive for their collection is very low. 50

We have sought to provide a process which utilizes steel and aluminium to produce alumina and energy in the form of heat which can be used to generate electricity by means of steam-driven gas turbines. It is considered that such a method will be sufficiently economically attractive to provide greater incentives than at present to collect scrap aluminium and scrap steel. A by-product of the process is pure iron. 55

Accordingly in another aspect, the present invention provides a dual-stage combustion process in which in the first stage iron or an alloy containing predominantly iron is burned by a jet of oxygen in a first combustion chamber to produce ferric oxide and heat energy, the ferric oxide thus produced is sprayed by the force of combustion into a second combustion chamber into which liquid aluminium is fed, the relative proportions and high temperature of the aluminium and ferric oxide being such that spontaneous combustion takes place to produce iron and aluminium oxide, heat energy being obtained from the aluminium oxide on cooling. 60

The process can utilize scrap steel and/or scrap aluminium. The iron produced in the second stage may be recycled to the first stage. 65

Iron/oxygen combustion is achieved by using an oxy-acetylene gas mixture to initiate the iron/oxygen combustion which is thereafter self-sustaining. The main oxygen supply for the iron/oxygen combustion is obtainable from liquid oxygen supplied in gaseous form to the combustion chamber through a regulating valve via a water-cooled lance. The iron at this stage of the process is generally fed in as liquid scrap steel or liquid iron obtained from the second stage of the process and fed back to the first stage input through refractory channels. In the present system, both stages of combustion takes place in a closed chamber and the heat generated is removed and may be used either to generate electricity by means of steam-driven turbines or as process heat or to melt scrap steel (which is now generally performed by an electric arc furnace at high energy cost) which can be used as stated above as the source of iron for the reaction.

The whole of the ferric oxide or a proportion thereof passes to the second stage of the process.

The ferric oxide obtained from the first stage of the process is either in the form of red hot slag or as a dense spray of particles.

In the second stage, aluminium is fed into the combustion process in the form of relatively pure aluminium liquid, having been pre-melted by first stage combustion, preferably utilizing some of the process heat. In the second stage, the relative inputs of liquid aluminium and ferric oxide are so synchronized that spontaneous combustion takes place and steady state conditions prevail. The combustion of aluminium and ferric oxide yields liquid iron which can be removed from the bottom of the chamber. The liquid iron so produced can either be recycled to the first stage of the process or removed as iron as weld or cast metal, with the alumina also formed being removed from the surface of the molten iron on which it floats by means of a spillway or other suitable means, so the process or invention can also be considered as a refining process for scrap steel since the second stage reaction is conventionally used to produce weld metal in the so-called thermit welding and casting process. Suitable alloying ingredients may be added to the molten iron and the process used for the continuous casting of steel. The combustion of aluminium and ferric oxide also yields heat at very high temperatures (over 3000°C) and this heat can also be utilized to raise steam to generate electricity in addition to the first stage combustion stage of the process, or both can be used as process heat. Aluminium oxide is a most commercially valuable product and can be used for abrasives and refractory manufacture. It is noted that no free oxygen is necessary for the second stage combustion since it is liberated from the ferric oxide fed in from the first stage of the process.

The process can be a continuous process if a fixed amount of iron is constantly recycled and has the advantage that since the two stages take place in an enclosed environment, no significant gaseous emissions occur. By adjusting the relative inputs of oxygen and aluminium it is possible, if desired, to obtain (in addition to heat energy) iron, iron oxide (if a greater quantity of oxygen than is needed to oxidise all the aluminium is added) and aluminium oxide. If desired, the process can be operated batchwise.

The process is particularly suitable for developing nations with ready access to scrap steel and aluminium, e.g. metal-cutting swarf, the only other input and consumable cost being oxygen in the form of liquid oxygen. Aluminium is generally to be obtained at nominal cost in the form of crushed and bailed soft drink and beer cans. The process of the invention is particularly attractive in a world where fossil fuels are expensive but scrap steel and scrap aluminium is cheap. Whilst the total energy derived from the process is less than that required to reduce bauxite to aluminium or iron ore to iron, the process has potential usefulness in that it may utilize waste products of the industrial system.

Listed below are the various aspects and advantages of the present invention.

The process produces alumina which has many potential uses, principal amongst which are for use as abrasives, use as refractory insulation manufacture, use in ceramic cutting tools and electrical insulation.

The output value of the alumina for abrasives is some three or four times the input value of the consumables.

A further advantage is that alumina is produced in liquid form, hence it may be sprayed or poured to produce hard surfaces, particles of controlled size, and cast forms.

The system is self-energizing so does not rely on fuel or electricity supplies and this may improve price stability and independence from fuel market fluctuations.

The system is a nett producer of energy.

The process can be continuous-running and so provides economic, thermodynamic and technical benefits.

The process has size-flexibility. Small units may be tailored to suit existing demands or resources (such as municipal incineration complexes).

The process yields improved refinement of steel as in the "thermit" welding process.

The high temperatures of combustion affords higher thermodynamic efficiency if the process is utilized for electrical energy generation via steam turbines.

The process provides an incentive for waste collection.

Minimal gaseous emission occurs during the process, thus less harm is done to the environment than by hydrocarbon combustion and less heat is lost since no gaseous exhaust is produced.

5 The present invention is further illustrated in the accompanying drawings, wherein: 5
Figure 1 is a block diagram illustrating the various aspects of the present invention;
Figure 2 shows one embodiment of a thermic lance in accordance with one aspect of the present invention;

10 *Figures 3(a) and 3(b)* are partial longitudinal cross-sections through two embodiments of a thermic lance in accordance with the present invention; 0

Figures 4(a) to 4(f) are transverse cross-sections through various embodiments of a thermic lance in accordance with the present invention;

Figure 5 shows a thermic charging lance in accordance with the present invention charging a crucible of a thermit welding arrangement;

15 *Figure 6* shows an improved thermo-slag welding system which can be used for upset butt welding or fusion-welding any metal or for upset butt welding dissimilar metals; 15

Figure 7 is a flow sheet showing the continuous dual-stage combustion system with iron feed back; and

Figure 8 is a flow sheet showing refined steel output in addition to alumina output.

20 Fig. 1 is a block diagram illustrating how various of the different aspects of the invention are linked to one another. 20

The embodiment labelled I relates to the method of producing molten alumina iron and heat in the dual-stage combustion process—this is detailed below. The alumina is initially in a molten stage and this has special advantages such as facilitating casting and spraying and the greater ease of producing particles of alumina. 25

The embodiment labelled Ia illustrates how the dual-stage combustion process can be used in a continuous fashion with iron feedback.

The embodiment labelled II illustrates the thermic lance which can be used for cutting high melting point metals and non-metals and non-ferrous as well as ferrous metals.

30 The embodiment labelled III utilizes the thermic lance of embodiment II as a reactant supply for fusion or pressure welding. 30

The embodiment labelled IV utilizes the thermic lance of embodiment II to feed a crucible which in turn provides the feed for continuous thermit welding of thick plate using the thermoslag principle.

35 The embodiment labelled V utilizes the thermic lance of embodiment II as a cheap reactant supply for autogenous fusion or upsett butt welding. 35

The embodiment of the thermic lance of the present invention of Fig. 2 is shown generally as 10 and comprises an iron pipe 11 surrounding a bundle of aluminium wires 12. The iron pipe 11 and aluminium wires 12 are connected at one end to a holder 13 which in turn is connected to an oxygen supply by means of a valve 14. The length of the lance from A to B is approximately three metres.

40 Figs. 3(a) and 3(b) show two further embodiments of the thermic lance in accordance with the present invention. In Fig. 3(a), a steel tube 15 surrounds a bundle of aluminium wires 16. In Fig. 3(b), an aluminium tube 17 surrounds a steel pipe 18 which in turn surrounds a bundle of iron wires 19. 45

Figs. 4(a) to 4(f) show further embodiments of the thermic lance in accordance with the present invention.

In Fig. 4(a), a steel pipe 20 surrounds an aluminium pipe 21 which in turn surrounds an iron rod 22.

50 In Fig. 4(b), a steel pipe 23 surrounds an aluminium pipe 24 which in turn surrounds a second steel pipe 25.

In Fig. 4(c), an aluminium pipe 26 surrounds an iron pipe 27 which in turn surrounds a bundle of iron wires 28.

55 In Fig. 4(d), an iron pipe 29 surrounds a bundle of aluminium wires 30 (this is identical to the embodiment shown in Fig. 2).

In Fig. 4(e), a square iron conduit 31 surrounds a bundle of aluminium wires 32.

In Fig. 4(f), an iron pipe 33 surrounds a bundle of aluminium wires 34 and an iron rod 35.

In all of the embodiments 4(a) to 4(f), the areas cross-hatched represent gaps through which the oxygen flows.

60 In Fig. 5, a thermic charging lance in accordance with the present invention is used to provide the consumables for welding using the thermit process. The lid of a crucible 37 is removed and a lance 36 is inserted into the chamber of the crucible 37. When charging of the chamber by the lance is complete, the lid of the crucible 37 is replaced, the reaction completed and a layer of molten iron 38 is formed with a layer of alumina 39 on top. The iron is then run off through a spout 40 into a mould (not shown). Extra iron may be added at around 100% of 65

that yielded by the normal stoichiometric process since the extra heat supplied by the iron/oxygen combustion is also a 100% addition. That is an extra 524 grams of iron in addition for each kilogram of lance in the improved process.

Fig. 6 shows the continuous welding of two thick plates 41 and 42 using a conventional electro-slag welding arrangement but with filler 43 being provided by a thermic lance 44 in accordance with the present invention.

The process illustrated in Figs. 7 to 9 uses low grade scrap metal and aluminium to provide heat at high temperatures (which may be subsequently used to generate electricity via steam raising heat exchangers and turbo-electric generators) to produce alumina and refined steel. The type of scrap converted could be steel and aluminium cans or alternatively metal-cutting swarf.

The process consists of two stages of combustion which can take place within one furnace. The thermo-chemistry is outlined in Fig. 7.

In stage one, liquid steel is oxidized by an oxygen lance 45 (see Fig. 9) to produce heat. The product of this combustion, iron oxide, is blown into a spray of molten aluminium where spontaneous combustion occurs producing more heat, refined steel and alumina. The purified iron is fed back to the liquid steel pool which fuels the first reaction. Thus the inputs are aluminium and oxygen from which alumina and process heat are obtained. In this version of the process the steel charge is continually recycled and the valuable output is liquid alumina or corundum. However, the process may be extended to operate additionally as a producer of refined steel by supplying a greater quantity of scrap steel than is fed back and then taking off this excess—this is illustrated in Fig. 8. Of course, extra aluminium would be necessary to provide for the increased throughput. The feedback fraction can be reduced to zero provided the steel pool at the input is of sufficient thermal capacity to pre-melt the scrap input prior to combustion.

A furnace arrangement of the combustion system is shown in Fig. 9. A furnace 47 lined with fire brick 48 is constructed as two semi-chambers A and B and is used to accommodate the two stages of the dual-combustion process.

Oxygen supplied to the lance 45 is preferably from a bulk liquid supply. After ignition of the lance 45, pure oxygen is blown into steel premelt 49 producing a red hot spray 53 of iron oxide which impinges on liquid aluminium in semi-chamber B. The aluminium is preferably pre-melted by some small fraction of the process heat and aluminium premelt 46 is gravity-fed to the appropriate location in the furnace 47. The iron 50 produced during the second stage of combustion flows down into the steel pre-melt 49 under the influence of its own weight, the alumina produced during the second stage of combustion forming a floating slag 51. As the alumina is continuously produced by the second stage combustion, it is drawn off at 52 to provide a desirable product for use in abrasives applications or refractory products. Since the alumina is in a molten state, it may be sprayed or poured to produce (a) hard surfaces, (b) particles of controlled size, (c) cast forms. Heat is also a valuable by-product.

In this method, scrap aluminium may be utilized, for example soft drink cans or swarf which has been pre-melted by a portion of the heat of combustion. Process heat may be obtained by water-cooling the furnace.

CLAIMS

1. A thermic lance comprising an outer metal conduit being made of either aluminium or iron or an alloy containing predominantly iron, an inner metal conduit and/or a number of metal rods located within the outer metal conduit, the inner metal conduit and/or metal rods being made of either aluminium or iron or an alloy containing predominantly iron such that at least one of the conduits or one of the rods is made of aluminium and at least one of the conduits or one of the rods is made of iron or an alloy containing predominantly iron; the lance including a holder at one end, the holder being provided with a valve through which, in use, oxygen may be admitted to pass through the lance to the other end for ignition.
2. A thermic lance as claimed in Claim 1, in which the alloy containing predominantly iron is steel.
3. A thermic lance as claimed in Claim 1, in which an aluminium conduit surrounds a steel conduit and a bundle of iron wires are located within the steel conduit.
4. A thermic lance as claimed in Claim 1, in which an iron or steel conduit surrounds a bundle of aluminium wires.
5. A thermic lance as claimed in Claim 1, in which a steel conduit surrounds an aluminium conduit which in turn surrounds an iron rod.
6. A thermic lance as claimed in Claim 1, in which a first steel conduit surrounds an aluminium conduit which in turn surrounds a second steel conduit.
7. A thermic lance as claimed in Claim 1, in which an aluminium conduit surrounds an iron conduit which in turn surrounds a bundle of iron wires.
8. A thermic lance as claimed in Claim 1, in which an iron conduit surrounds a bundle of aluminium wires and an iron rod.

9. A thermic lance as claimed in any of Claims 1 to 8, in which at least 50% of the stoichiometric quantity of iron is present.
10. A thermic lance as claimed in Claim 1, substantially as herein described with reference to the accompanying drawings.
- 5 11. A method of thermit welding or casting in which a thermic lance of the type claimed in any of Claims 1 to 10 is used to produce the molten iron for the welding or casting. 5
12. A method of autogenous welding in which the heat produced by burning a thermic lance of the type claimed in any of Claims 1 to 10 is used to produce (a) a plastic deformation weld or (b) a fusion weld within a self-formed alumina shell mould.
- 10 13. A method of continuous welding in which a thermic lance of the type claimed in any of Claims 1 to 10 is used to produce the weld metal. 10
14. A dual-stage combustion process in which in the first stage iron or an alloy containing predominantly iron is burned by a jet of oxygen in a first combustion chamber to produce ferric oxide and heat energy, the ferric oxide thus produced is sprayed by the force of combustion into a second combustion chamber into which liquid aluminium is fed, the relative proportions and high temperature of the aluminium and ferric oxide being such that spontaneous combustion takes place to produce iron and aluminium oxide, heat energy being obtained from the aluminium oxide on cooling. 15
- 15 15. A process as claimed in Claim 14, in which the alloy containing predominantly iron burned in the first stage is scrap steel. 15
- 20 16. A process as claimed in Claim 14 or 15, in which the aluminium burned in the second stage is scrap aluminium. 20
17. A process as claimed in Claim 14 or 16, in which the iron produced is recycled to the first stage.
- 25 18. A process as claimed in any of Claims 14 to 16, in which alloying ingredients are added to the molten iron to produce cast steel on cooling. 25
19. A process as claimed in any of Claims 14 to 16, in which both stages of combustion take place within a single furnace.
- 30 20. A process as claimed in Claim 14 substantially as herein described and with reference to the accompanying drawings. 30

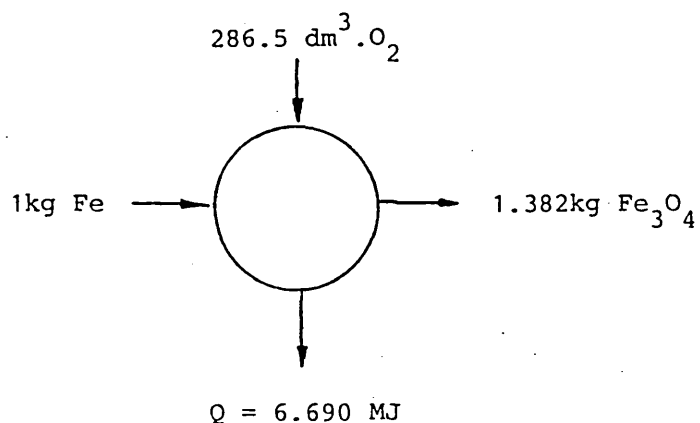
8.1.3. Economic Considerations

Iron (Black mild steel) = \$ 2.2/kg

Aluminium (cold drawn tube) = \$21.6/kg

Oxygen (bottle gas) = \$0.1235/litre

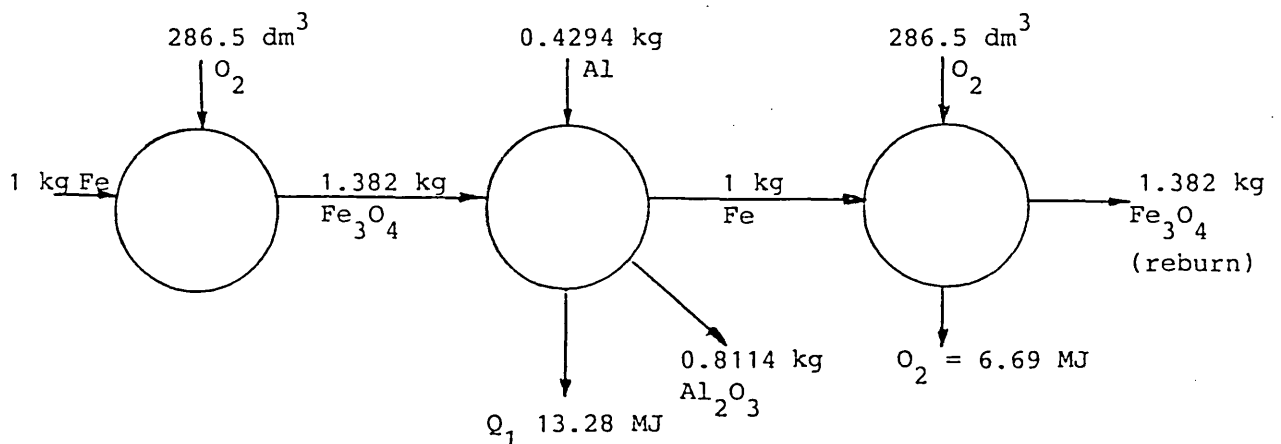
1) Conventional Lance (iron oxygen)



Cost of heat output (6.690 MJ/kg Fe) =

$$\begin{aligned} \text{Cost of 1 kg Fe} + \text{Cost of } 286.5 \text{ dm}^3 \text{ O}_2 &= \$2.2 + \$3.6 = \$5.8/6.69 \text{ MJ} \\ &= \$0.867 \text{ MJ} \end{aligned}$$

2) Iroxal Lance



$$\begin{aligned} \text{Cost of 1 kg Fe} + \text{Cost of 0.4294 kg Al} + 2(\text{Cost of } 286.5 \text{ dm}^3 \text{ O}_2) \\ = \$2.2 + \$9.28 + \$7.1 = \$18.6 \end{aligned}$$

$$\begin{aligned} \text{Cost per MJ} &= \frac{\$18.6}{(13.28 + 6.69) \text{ MJ}} = \$0.93/\text{MJ} \end{aligned}$$

8.2 The Lanxide Patent

NOVEL CERAMIC MATERIALS AND METHODS OF MAKING SAME

The present invention generally relates to a novel class of ceramic materials and methods of producing them. The ceramic materials of this invention possess a dense, polycrystalline microstructure which is unusually strong and fracture-tough as compared with conventional ceramics.

The method by which the ceramic materials of this invention are formed is based upon the discovery of conditions which produce a surprising oxidation behavior of a metallic material. When an appropriate metal or alloy (as will hereinafter be described) is exposed to an oxidizing atmosphere within a particular temperature envelope above the melting point of the metal or alloy, the liquid metal oxidizes from its surface outward, progressing toward the oxidizing atmosphere by wicking along channels which form in place of high energy grain boundaries in the otherwise impermeable oxide structure. New oxide material is continually formed by reaction of the liquid metal with the oxidizing vapor, thus "growing" a ceramic oxide structure interconnected primarily along low energy grain boundaries. The resulting material also contains some or all of the constituents of the parent metal or alloy dispersed in metallic form throughout the microstructure in either interconnected or isolated arrangement, and present to a greater or lesser degree depending upon process conditions as shall be elaborated further herein. The uniformly dispersed metallic material and dense nature of the oxide-metal structure appear to account for the high fracture toughness of the resultant ceramics.

The materials of this invention can be grown with substantially uniform properties throughout their cross-section to thicknesses heretofore unachievable by conventional processes for producing dense ceramic structures. The process which yields these materials also obviates the high costs associated with fine uniform powder preparation and pressing techniques, characteristic of conventional ceramic production methods.

3% Si / 0 - 10% Mg WEIGHT GAIN vs
SET POINT TEMPERATURE

10% Mg / 3% Si
7% Mg / 3% Si
5% Mg / 3% Si
3% Mg / 3% Si
2% Mg / 3% Si
0% Mg / 3% Si
0% Mg / 0% Si
1% Mg / 3% Si

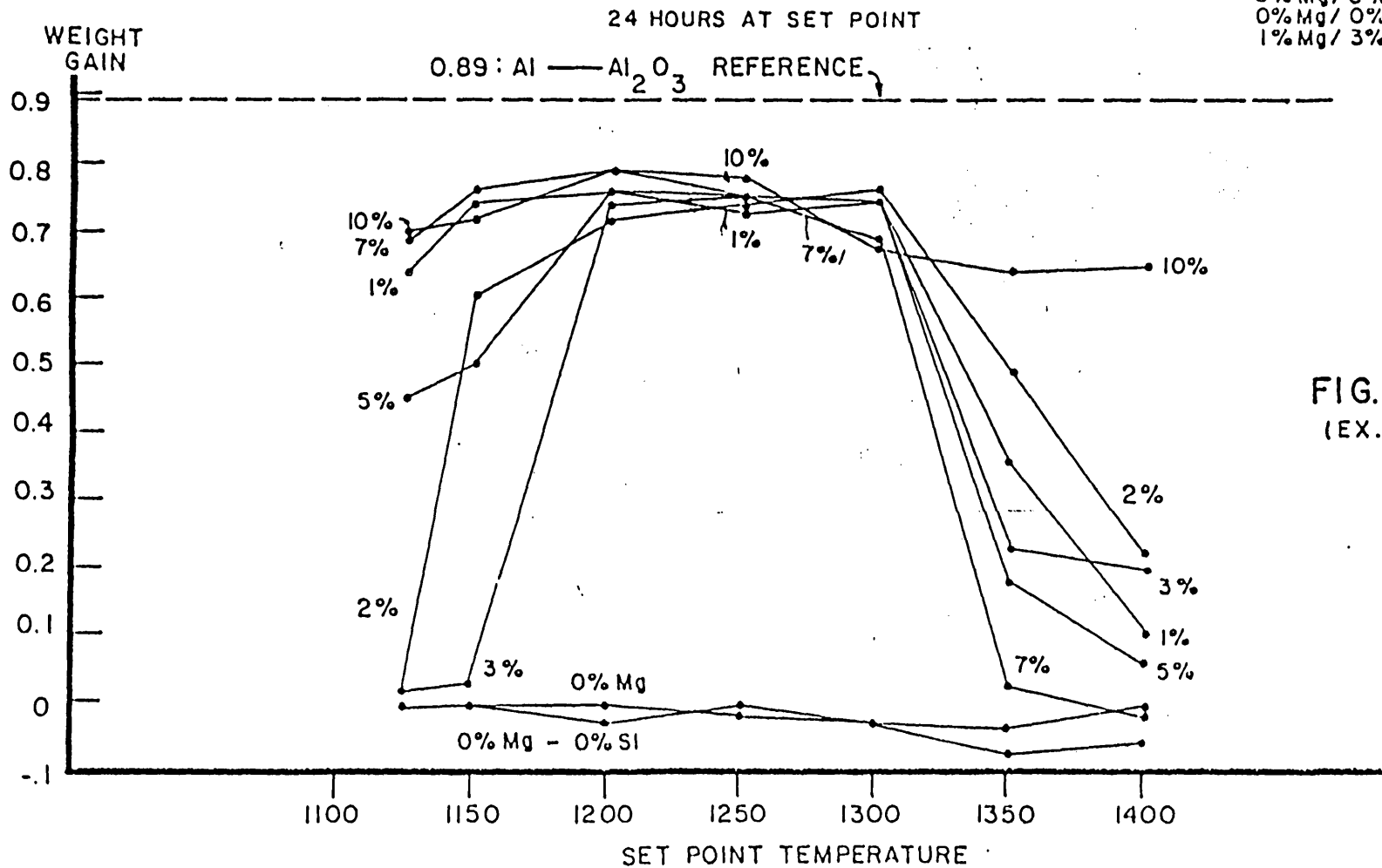


FIG. 1
(EX. 1)

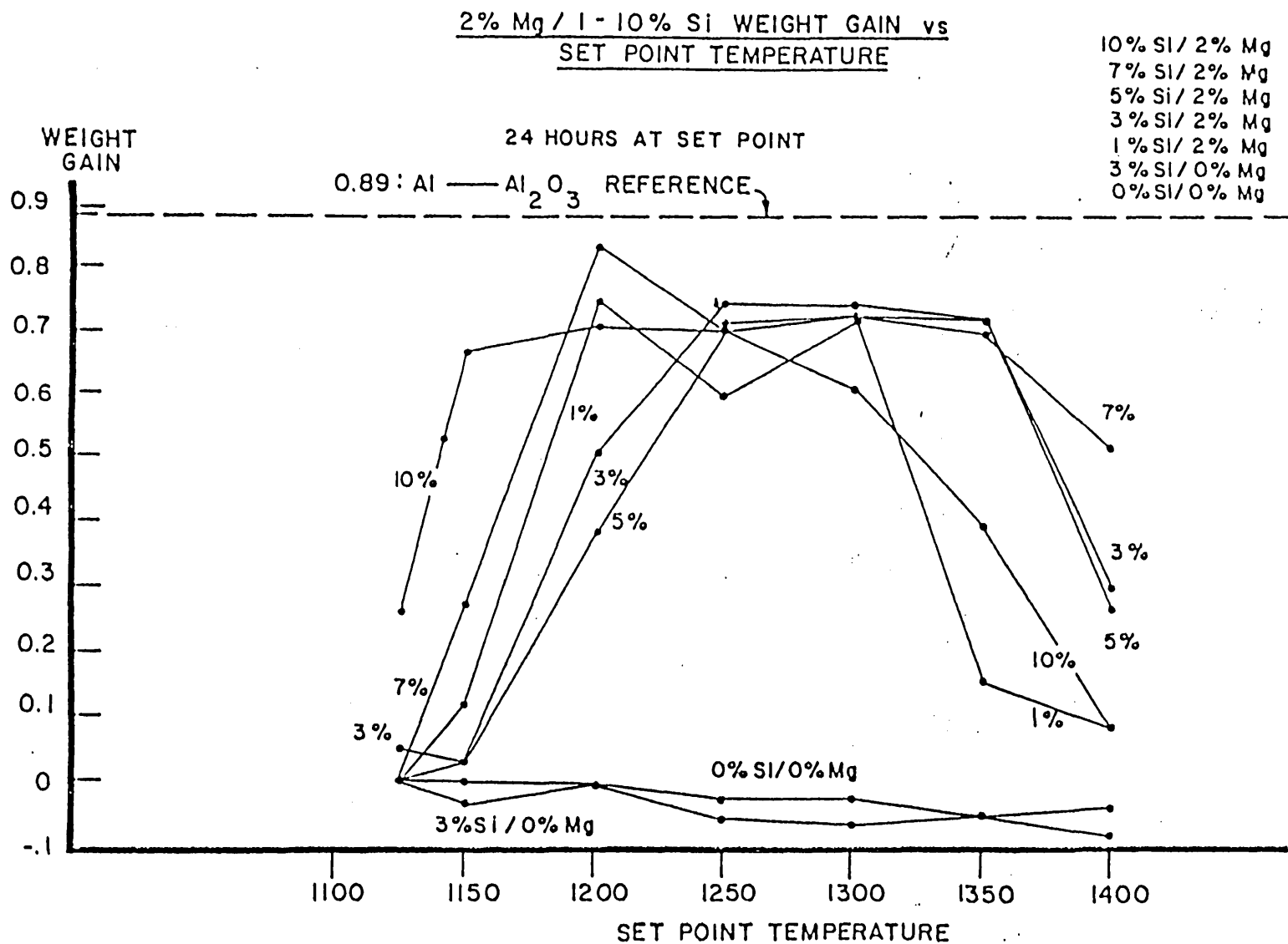


FIG. 2
(EX.2)

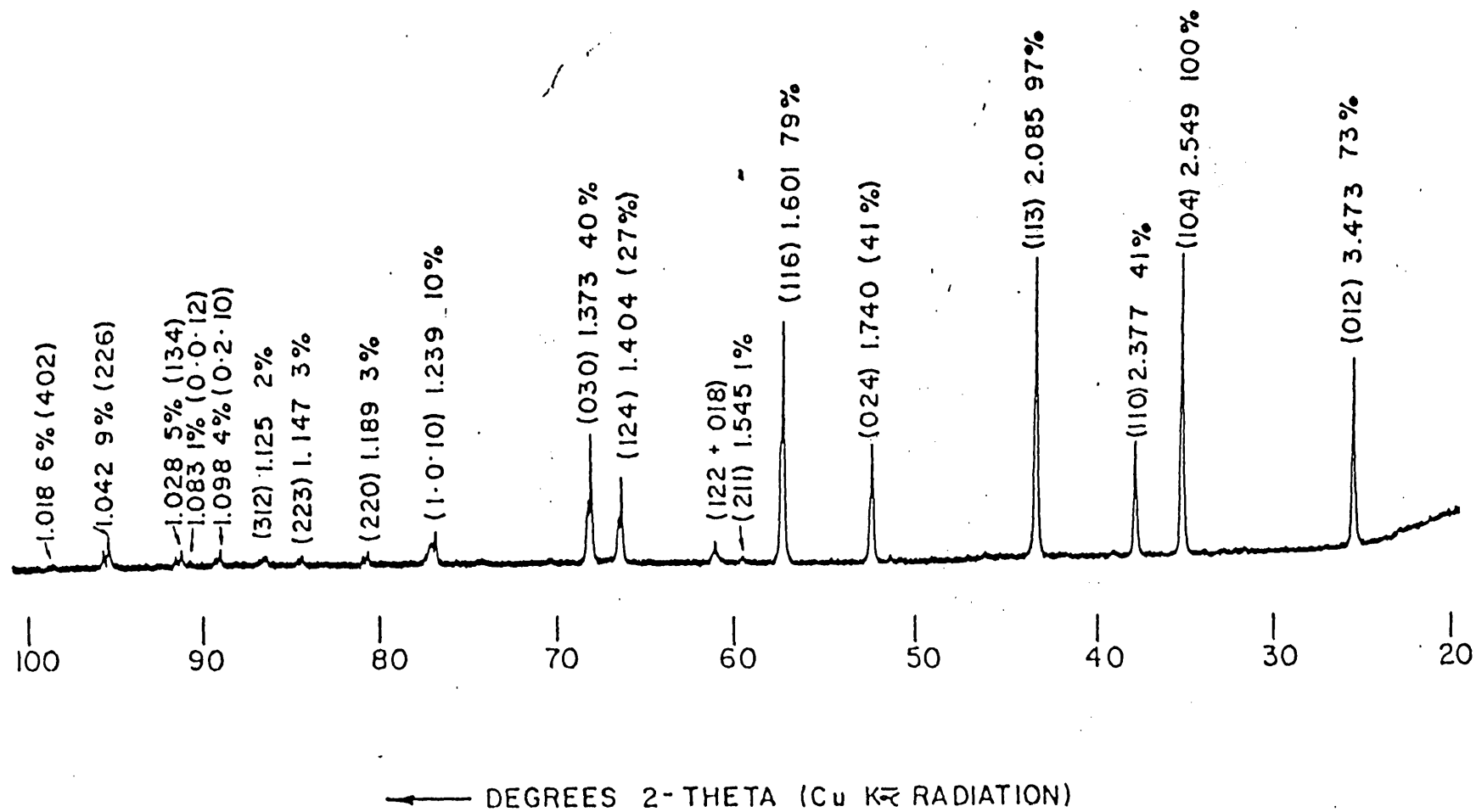
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FIG. 9a

0.3 MICRON α Al_2O_3
(LINDE A)

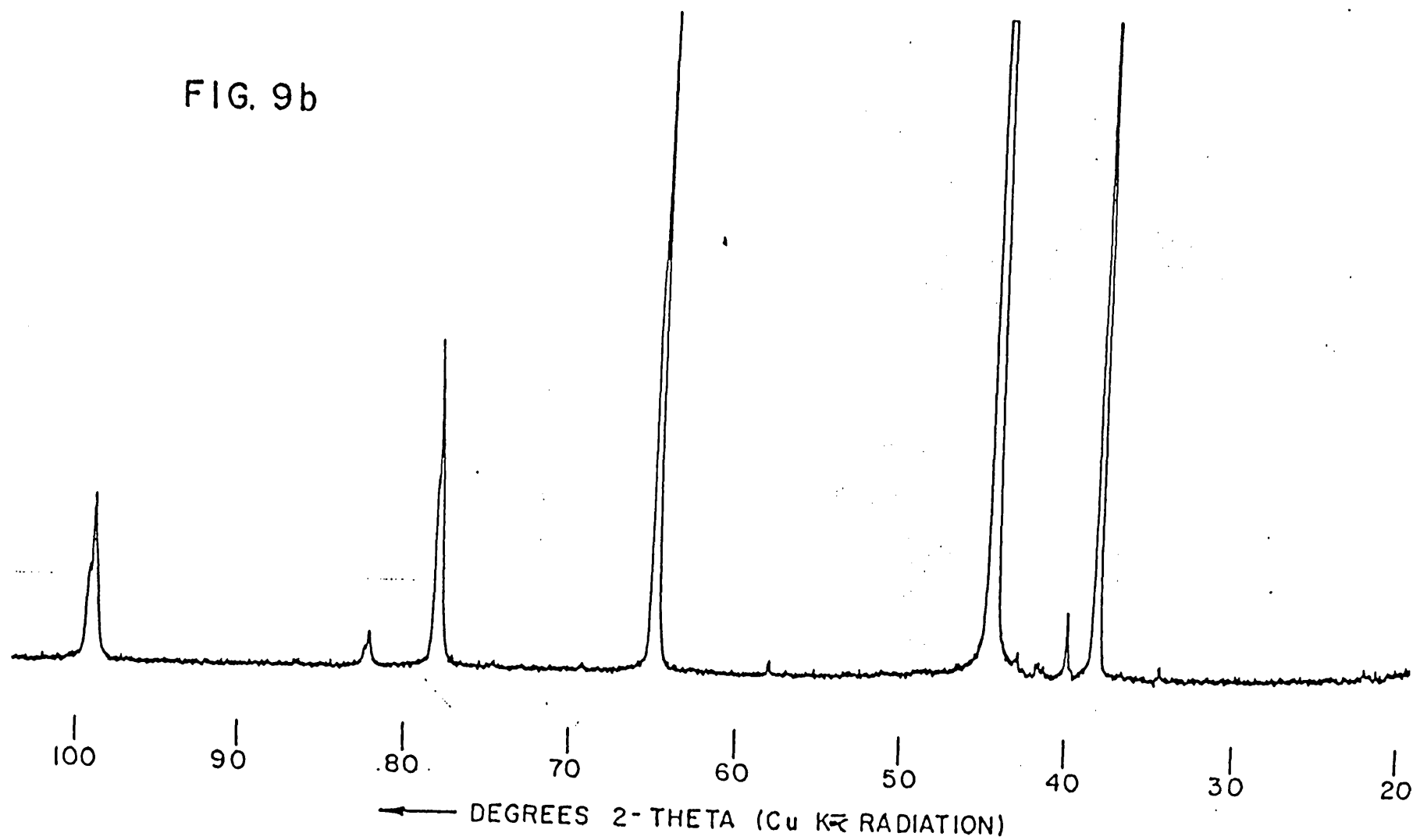


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FIG. 9b

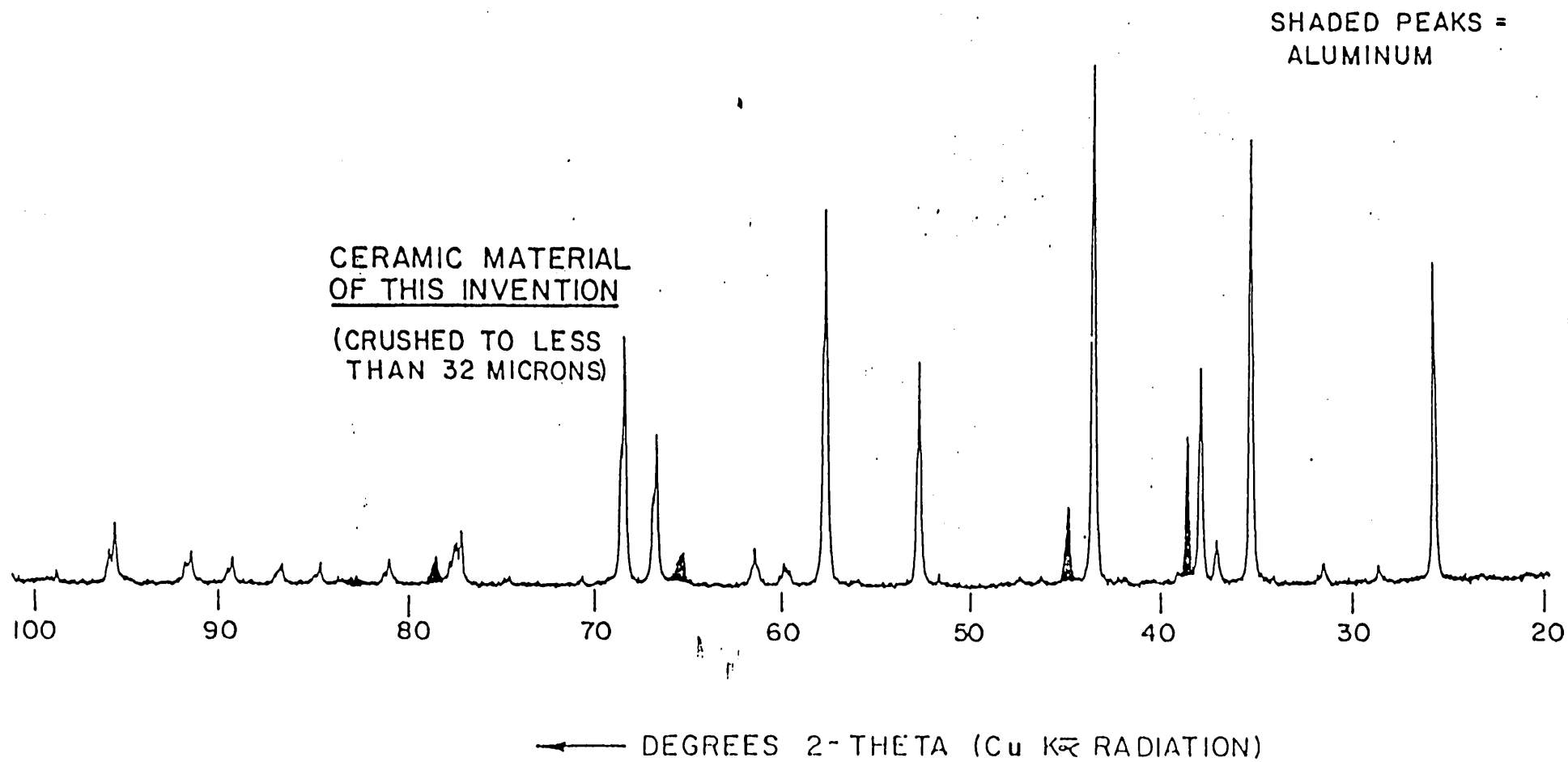


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FIG. 9c



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8.2.2 Calculation of Thermal Flux Intensity

The calculation of the reaction temperature of the Lanxide process assumes that the reaction occurs in an essentially two dimensional stratum above the pore exit. It is reasonably assumed that, at the elevated temperatures under consideration here, that radiant heat transfer dominates, hence the Stefan-Boltzmann relation has been utilised. Thus as a first approximation the reaction is considered to take place entirely at hot spots above the pores. The thermal flux [power intensity] is directly related to the rate [per unit area] at which total conversion of the aluminium metal vapour to its oxide occurs. [N.B. this is a simplifying assumption since intermediate reactions involving the sub-oxides of aluminium are also present. The sub-oxides are considered to be one of the principle agencies by which heat is transferred to the regions over the glassy film.]

VARIABLE LABELS: 'a' = total specimen area [a fixed value]

'p' = a selected reaction area factor related to the pore area [being the reciprocal % of total area and yielding a linear relation]

'H' = specific enthalpy [for the conversion of one gram Al]

'm' = mass gain rate [experimentally determined]

'Q' = radiation flux intensity Watt/cm²

VARIABLE LABEL VALUES:

'a' = $5.026 \cdot 10^{-2}$ cm²

'p'; if reactions above the pores make up in total, x% of the crust area 'a', then 'p' = 100/x. eg. if the reaction is presumed to occupy 25% of the entire top surface of the specimen then 'p' = 4

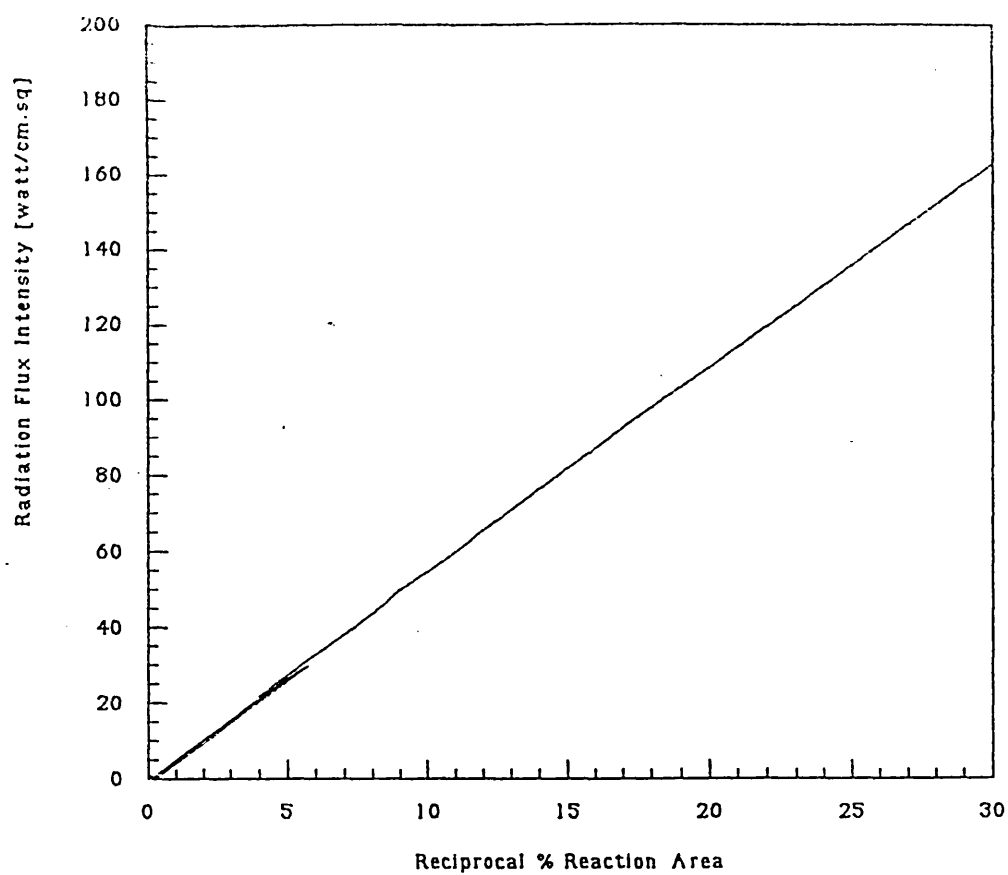
'm' = $1.667 \cdot 10^{-4}$ gm/sec

'H' = $1.667 \cdot 10^{-8}$ Joules/gm

FUNCTION:

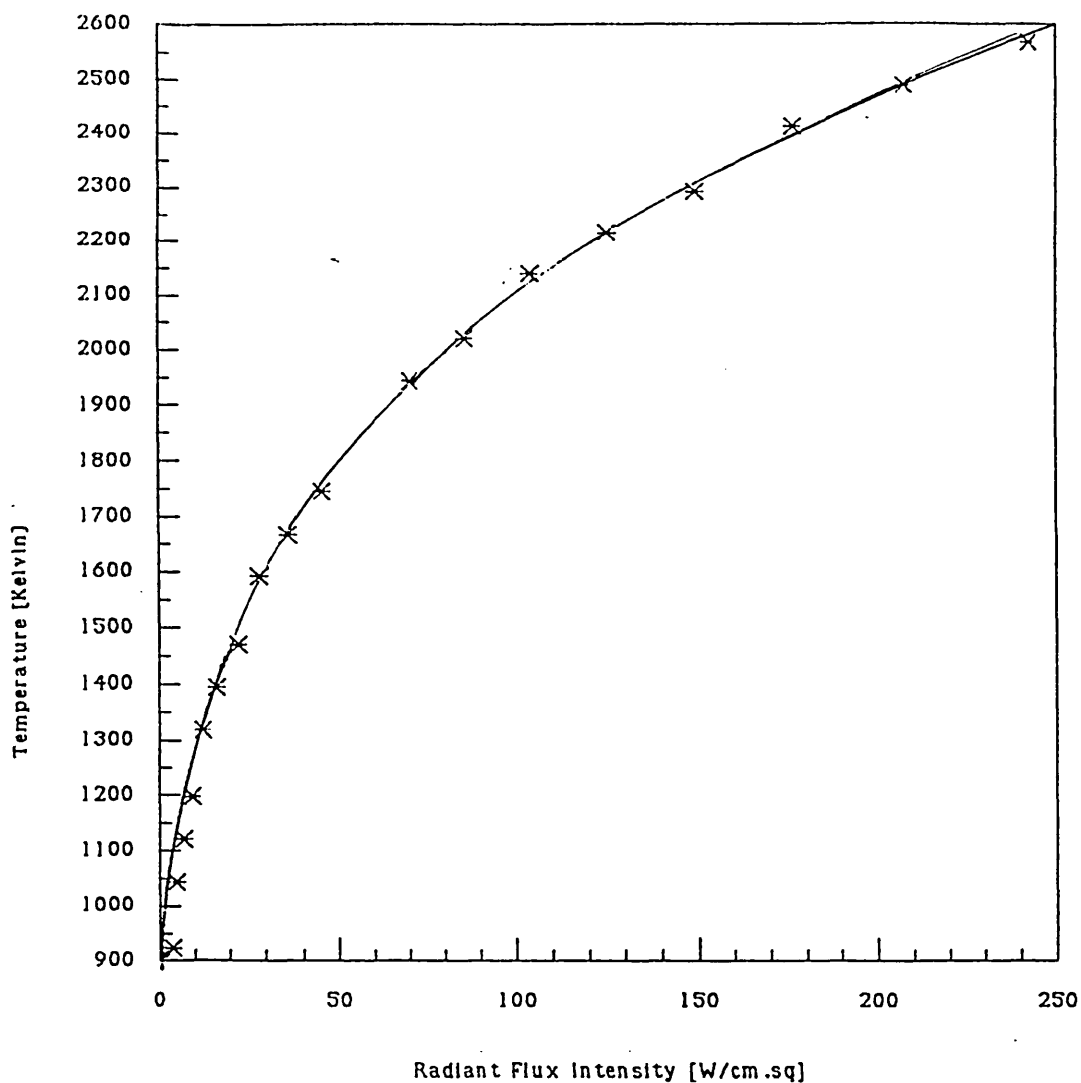
$$Q = [H \cdot m \cdot p] / a$$

Radiant Flux Intensity vs Reaction Area [reaction area as inverse pore factor]



8.2.3 CALCULATION OF REACTION TEMPERATURES

Reaction Temperature vs Radiant Flux Intensity



$$\left(\frac{\partial q}{\partial t}\right) = \sigma \epsilon (T_2^4 - T_1^4) \quad (5.2)$$

Where:-

$$\left(\frac{\partial q}{\partial t}\right) = Q$$

[The Radiation Flux]

The second figure enables the estimation of reaction temperatures to be obtained from the corresponding radiation flux

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intensity data drawn from the previous graph.