Composites by Directed Oxidation of Aluminum Alloys

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Make knowledge circle with the winds;
   But let her herald, Reverence, fly
Before her to whatever sky
Bear seed of men and growth of minds.

- Tennyson, 1833.
Abstract

The manufacture of ceramic composites has traditionally been a complex and often expensive process. A new processing method, the DIMOX™ process, takes advantage of the high temperature oxidation behaviour of aluminum alloys to produce a ceramic-metal composite. Although this process is fairly simple to implement, there has not been any attempt to link the starting materials and manufacturing conditions to the properties of the final composite. This work attempts to identify some critical parameters in the manufacturing process and how they affect the end product. The reaction temperature, alloy composition, and powder bed condition were optimized with respect to the growth process, final composition, and resulting microstructure. These characteristics were then related to the elasticity, strength, fracture toughness, and fracture mode of the final composite.

Aluminum-magnesium-silicon alloys were oxidized into an alumina bed of either Alcan C-70 UNG powder or Struers' 400 grit. The process conditions were optimized in air at 1120°C with a 10% silicon, 2% magnesium alloy. The growth rate was dependent on the powder bed. The material was composed of alumina, silicon, aluminum, and trace amounts of magnesium aluminate spinel. The fracture mode was dependent on the composition of the material and the alumina bed.
Résumé

La fabrication des composites céramiques a été traditionnellement un procédé complexe et souvent coûteux. Une nouvelle méthode, le procédé DIMOX™, exploite le comportement avantageux de l’oxydation à haut température des alliages de l’aluminium pour produire une composites céramique-métal. Quoique ce procédé soit assez simple à réaliser, on n’a pas encore cherché à relier les propriétés des matières premières et les conditions de mise en oeuvre du procédé avec les caractéristiques finales du composite. Dans cette recherche, on a tenté d’identifier quelques paramètres critiques dans le procédé de fabrication et de déterminer leur influence sur les propriétés du composite final. On a pu ainsi optimiser la température de réaction, la composition d’alliage, et la condition des poudres relativement au processus de croissance, à la composition finale et à la microstructure résultante. Par la suite, on a établi la correspondance entre ces caractéristiques et le module d’élasticité, la résistance, la résistance à la fracture et le mode de fracture du composite obtenu.

Des alliages aluminium-magnésium-silicium ont été oxydés dans un lit de poudre d’alumine (Alcan C-70 UNG ou Struers Grit 400). Les conditions du procédé ont été optimisées pour l’air à 1120°C et pour une teneur de 10% de silicium et de 2%
de magnésium. Le taux de croissance dépendait du lit de poudre. Le composite était composé d'alumine, de silicium, d'aluminium, et contenait des traces de spinelle d'aluminate de magnésium. On a plus déterminé que le mode de fracture était dépendant de la composition du composite et du lit d'alumine.
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Chapter 1

1. INTRODUCTION

Ceramic materials are now being considered for several applications: engine components, wear parts, and heat exchangers are only a few. In these applications, ultimate failure of a component would be catastrophic. The one reason why ceramic materials would not be selected is that they are brittle. To improve the material, ceramics are reinforced with other materials to form composites. The reinforcement can be a metal or another ceramic in the form of fibres, whiskers, or particulates. The resulting ceramic matrix composites (CMC's) have higher wear resistance and a higher fracture toughness than monolithic ceramic materials.

There are several different methods for the manufacture of CMC's. Some are based on conventional ceramic processing routes such as sintering, hot pressing, injection moulding, and tape casting. A problem is that composites with preferred volume fractions (10-30%) of reinforcement generally do not fully densify on sintering. Residual porosity, as in monolithic ceramics, act as stress concentrators and lower the strength of the material. The shrinkage associated with sintering is another difficulty. To produce a complex final shape; time, effort, and money are invested to optimize the production cycle. Reaction based processing methods, producing
a dense ceramic part to near net shape, thus requiring little or no machining, are promising alternatives.\(^2\)

Different reaction based methods include chemical vapour infiltration (CVI), gas phase and liquid phase reaction bonding, and self propagating high temperature synthesis (SHS).\(^1\) CVI into a porous preform allows control over morphology and texture of the deposit, high purity levels, and low operation temperatures. The problems are that it is difficult to achieve uniform infiltration, the reactants are toxic and explosive, and long times are needed to produce a part. The process is also very expensive. Gas phase reaction bonding has been primarily developed for producing silicon nitride (Si\(_3\)N\(_4\)) from silicon powder compacts and nitrogen gas. Disadvantages are not only residual porosity, but residual silicon in the matrix which weakens the material. Liquid phase reaction bonding has a liquid infiltrating a ceramic preform then reacting to form a ceramic material. This method is used to produce reaction bonded silicon carbide. In the SHS process, a mixed powder compact is ignited and densification occurs with the reaction and applied pressure.\(^3\) The process is relatively inexpensive as there is no need for high temperature furnaces and the reaction times are minutes rather than hours. SHS has been used to produce cemented carbides, TiC-Ni and WC-Co, as well as ceramic composites, B\(_4\)C-Al\(_2\)O\(_3\) and TiN-Al\(_2\)O\(_3\). The major disadvantage is the residual porosity, typically greater that 5\%.
A new, novel approach is the directed oxidation of molten metals where the oxidation product forms the ceramic composite. This may also include growing the composite into a porous ceramic preform. Extensively developed by the Lanxide Corporation, the process is known as the DIMOX™ process. It is relatively inexpensive and capable of producing ceramic composites near net shape. The process can be used in several metal ceramic systems, for example, metal forming an oxide or metal with respective nitride. These materials have excellent wear resistance. In rotating pin slurry erosion tests, one material has nearly 20X the wear resistance of 96% alumina. Hence, the ability to produce at or near net shape is important as the machining of this material would be difficult.

Despite the reputed low cost and ease of manufacture, very little work is being done on this material outside of the commercial developers. The majority of the articles have been published by the Lanxide Corporation. There has been no systematic study published determining the important parameters from start to finish in manufacturing the composite and their effect on the final material properties.
Chapter 2

2. BACKGROUND AND LITERATURE REVIEW

The DIMOX™ process has been described in general terms in the literature and appears to be fairly simple to implement: all that is required is an aluminum alloy, filler, and an oxidizing atmosphere furnace capable of reaching 1250°C. As this is a new technology, only some specific aspects of the process have been published to date, relating theory in the literature to experimental observations.

In this chapter, the DIMOX™ process will be reviewed. Subsequent literature pertaining to different aspects of the process will then be presented.

2.1 DIMOX™ Process

The technology of directed oxidation of molten metal to form a ceramic matrix composite has been patented and named the DIMOX™ process. Specific details of the process have been kept confidential, but a general representation is shown below. A molten alloy within a refractory container reacts with a gas phase oxidant to produce a ceramic matrix which then 'grows' into a reinforcement material. The ceramic matrix contains interconnected metal channels that supply metal to the surface via capillary flow and sustains the reaction. Different metals can be used: aluminum, zirconium,
and titanium to name a few. The reactant in the gas phase could be oxygen, or nitrogen, reacting to form an oxide or a nitride respectively. The choice of the filler material is another option. Some choices are silicon carbide, alumina (Al₂O₃), barium titanate, and aluminum nitride. The filler could be in the form of particulates, platelets, whiskers, or fibres. A technically simple system would be oxidizing an aluminum alloy in air into an Al₂O₃ bed. Typically, two dopants are required to have a reasonable growth rate: one from group IVB in the periodic table and magnesium. The process temperature depends on the alloy present: for aluminum-magnesium-silicon alloys, the temperature is in the range of

![Diagram of the DIMOX process](image)

**Figure 2.1:** Schematic of the DIMOX™ Process.
1000-1250°C. The filler material influences the growth behaviour and the material microstructure. With no filler, the material is composed of columnar grains with the c-axis parallel to the growth direction. The filler reduces this preferential orientation but does not totally negate it. The process can be split into two phenomena, infiltration and oxidation. As will become apparent, these phenomena are not mutually exclusive.

2.2 Oxidation Behaviour of Molten Aluminum Alloys

The oxidation behaviour of molten Al-Mg-Si alloys has mainly been studied at low temperature - primarily for application in foundry furnaces. Solid state oxidation has been well documented and the various mechanisms can be extended to higher temperatures where the alloy is liquid.

Aluminum alloy melts, free of volatile elements such as magnesium or zinc, oxidize very slowly due to the formation of a protective Al₂O₃ film. Magnesium additions result in rapid oxidation of the melt, a situation commonly known as "breakaway oxidation." This is understandably detrimental to aluminum melting practices, but certainly it is of primary importance to the DIMOX™ process.

Before breakaway oxidation occurs, there is an induction period which is shortened by increasing temperature, increasing magnesium content, seeding the surface with either MgO or MgAl₂O₄, and slow melting of the alloy. For Al-Mg
alloys oxidized at 900°C, the surface of the oxide growth is
covered with MgO when the magnesium content is in the range of
0.7 to 6% Mg. However, other researchers have found by in situ
observation that the surface of an aluminum-magnesium melt is
covered with a combined amorphous and crystalline film of MgO.

The role of magnesium in solution, in relation to oxidation, is to reduce the protective aluminum oxide layer to form magnesium oxide as represented by:

\[ 3 \text{ Mg}_{(\text{sol},n)} + \text{Al}_2\text{O}_3 \rightarrow 3 \text{ MgO} + 2 \text{ Al}_{(l)} \]

This breaks the protective surface film and the oxidation rate increases. (Figure 2.2) It has been found that sodium dusted on the surface lengthened the incubation period. However, sodium in the metal decreased the incubation period and increased the oxidation rate. Other elements, besides magnesium and sodium, which promoted rapid oxidation were calcium and zinc at concentrations of ~1at%. The role of silicon in the oxidation process is unclear, yet, it is required to sustain the oxidation and subsequent growth of the oxide. This is developed further below.

Some research has been published on the oxidation mechanism and how this affects the DIMOX process. For an Al-Si-Zn-Cu-Fe-Mg alloy, the oxidation rate increases with temperature. In the range of 1050-1100°C, the rate was found to be constant with time; over a range of 1125-1200°C, the rate decreased with time. The oxidation rate at 1100°C was
Figure 2.2: Action of Magnesium in initiating Breakaway Oxidation.
determined to be \(5-6\times10^{-5}\) g/cm\(^2\)s. The rate controlling step was proposed to be the transfer of the oxygen across the continuous thin MgO layer present on the oxide surface.\(^5,13,14\)

For a simpler alloy system, Al, 10\% Si, 3\% Mg, the rate at 1150\(^\circ\)C and in 100\% oxygen was \(8\times10^{-6}\) g/cm\(^2\)s. The magnesium in the starting alloy was found mainly in a spinel layer between the metal reservoir and the composite material. The reaction rate is reported to increase two to three times when oxidizing into an Al\(_2\)O\(_3\) 90 grit filler bed.\(^5\) This is thought to be due to an increase in the reactive surface area and thus an increase in the oxygen diffusion across the thin MgO film.

Some observations of the oxidation process can be supported by thermodynamic calculations. The Gibbs excess energy of mixing for the Al-Mg-Si liquid phase is available from the calculated phase diagram.\(^15\) This allows thermodynamic calculations to be performed, guided by proposed mechanisms for the real system. The Facility for the Analysis of Chemical Thermodynamics' (F*A*C*T) computational programs are available to assist in these calculations. The calculations are relevant to the bulk phases only. Surface properties, including the effect of curvature, are not considered.
2.3 Infiltration of Powder Beds

The growth of the oxidation product is a continuous process where the metal is transported to the air-oxide interface by a wicking action. In essence, the molten alloy infiltrates its own oxide and this process is not adversely affected by the presence of a filler material. Two topics should then be addressed: wetting and capillary phenomena.

2.3.1 Wetting Phenomena

A liquid will infiltrate into a porous bed depending upon the degree the liquid wets the solid. The wetting of ceramic materials by liquid metals has been extensively reviewed, addressing aspects such as the importance of wetting in composite formation\textsuperscript{16,17} to the compilation of data and theory in the literature.\textsuperscript{18} The vast majority of the literature sources determine the wettability using the sessile drop method. The results are given in terms of the contact angle $\theta$, where if $\theta<90^\circ$, the liquid wets the solid. The three surface tensions, or surface energies, can be related to the contact angle through Young's Equation:\textsuperscript{19}

\begin{equation}
\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta
\end{equation}

The above equation was derived from a force balance, as shown in Figure 2.3, neglecting the force of gravity. It was later
Non-wetting

Wetting

Figure 2.3: Wetting and Young's Equation.
The subscripts \( lv \), \( sv \), and \( sl \) refer to the liquid-vapour, solid-vapour, and solid-liquid surface energies, respectively.

derived from an energy balance by Gibbs.\(^2\) Both assumed that the three phases are in chemical equilibrium. To establish at what length scale the force of gravity can be neglected, the magnitude of the gravitational and the liquid-vapour interfacial energies can be equated and then arranged to define the capillary length, \( L_{\text{cap}} \). For dimensions much smaller than this length, gravity can be neglected. The resulting equation is:

\[
L_{\text{cap}} = \sqrt{\frac{2\gamma_{lv}}{\rho g}}
\]  

(2.2)

where \( \rho \) is the liquid density, \( g \) is the acceleration due to gravity, and \( \gamma_{lv} \) is the liquid-vapour surface energy. For pure aluminum on alumina, \( \gamma_{lv} = 0.880 \text{ J/m}^2 \) at \( 800^\circ\text{C} \)\(^2\) and \( \rho = 2.2 \text{ g/cm}^3 \),\(^2\) \( L_{\text{cap}} \) would be about 6 mm.

In multi-component systems, the surface tensions will be
affected by preferential adsorption of one or more components at the interfaces. At constant temperature, the surface tension, \( \gamma \), for dilute solutions can be related to adsorption by:

\[
d\gamma = -RT \sum_{i=2}^{n} \Gamma_i d\ln \left( \frac{a_i}{a_1} \right)
\]

(2.3)

where \( R \) is the universal gas constant, \( T \) is the temperature, \( \Gamma_i \) is the reduced adsorption coefficient, \( a_i \) is the activity of component \( i \), and \( a_1 \) is the activity of component 1.\(^{23}\) If \( \Gamma_i \) is positive, then as \( a_i \) increases, \( \gamma \) decreases. The physical meaning of \( \Gamma_i \) can be seen in the relation:

\[
\Gamma_i = \frac{n^s}{A} \frac{X}{X} \left( \frac{X}{X} \right)_i - 1
\]

(2.4)

where superscript \( s \) refers to the surface, \( n \) the number of atoms, \( A \) the surface area, and \( X \) the mole fraction. Thus, if component \( i \) is preferably adsorbed on the surface, then \( \Gamma_i \) is positive.

Contact angles for the Al-Mg-Si alloy on Al\(_2\)O\(_3\) are not available for the simple reason that they have not as yet been measured. The Al-Al\(_2\)O\(_3\) system has been studied extensively,\(^{24,25,26,27}\) but the results are inconsistent due to the interference of the oxide layer on the drop preventing liquid/solid contact. There is, however, a trend evident in
the literature. The contact angle decreases dramatically from 140° to about 75° as the temperature increases from 850 to 1150°C. This is thought to be due the rupture of the surface oxide as the oxide layer transforms from γ to α-Al₂O₃. This transformation is accompanied by a decrease in volume which would crack the oxide layer and allow solid/liquid contact. It has also been shown that the Al-Al₂O₃ contact angle is strongly dependent on the partial pressure of oxygen, decreasing from 180° to 90° as the partial pressure of O₂ goes from 10⁻¹⁰ to 10⁻⁴⁹ atm at 700°C.²⁸

Magnesium additions are known to lower the surface tension of aluminum melts,²⁹ thus resulting in improved wetting. A problem is the growth of small MgAl₂O₄ crystals at the Al-Al₂O₃ interface. These crystals have been observed in the study of metal matrix composites and correlated to the reduction in strength of metal matrix composites.³⁰ Wetting experiments for Al-Mg alloys have not been performed at higher temperatures, >900°C, due to the rapid volatilization of Mg from the alloy.

Silicon liquid will wet Al₂O₃.³¹ As mentioned above, silicon is required to allow the oxidation process to proceed. No data for Al-Si alloys on Al₂O₃ has been found, or known to exist. Just recently have some observations on the effect of the silicon on the contact angle of Al-Mg alloys on Al₂O₃ and MgAl₂O₄.²¹ The silicon, in conjunction with the magnesium, appears to be surface active and significantly lowers the
surface tension of an aluminum alloy. This synergism has been observed for silicon and carbon in steel;\textsuperscript{23} nevertheless, silicon is generally considered to be a non-surface active species.\textsuperscript{32}

2.3.2 Capillary Phenomena

The pressure change, $\Delta P$, across the liquid/vapour interface was first related to the surface tension by Young\textsuperscript{19} using a mechanistic argument and then later by Gibbs\textsuperscript{33} using thermodynamics. The equation is:

$$\Delta P = \gamma_{lv} \left[ \frac{1}{R_1} + \frac{1}{R_2} \right]$$

where $R_1$ and $R_2$ are the principle radii of curvature of the interface, shown in Figure 2.4.

![Figure 2.4: Capillary Pressure across an Interface.](image-url)
The equilibrium height, $\Delta h$, of a fluid in a circular capillary, of radius $r$, can be determined by relating the hydrostatic pressure of the fluid, $\Delta P = \rho g \Delta h$, to the pressure across the interface. The result is:

$$\Delta h = \frac{2 \gamma \nu}{\rho g} \tag{2.6}$$

A powder bed, however, is not composed of regular capillaries. Several methods have been proposed to calculate an average or characteristic radius of a porous bed from easily measured properties of the powder.\textsuperscript{34,35} Each method gives an equation of the form:

$$r \propto \frac{(1-\phi)}{S \rho \phi} \tag{2.7}$$

where $\rho$ is the density, $S$ is the surface area per gram of powder, and $\phi$ is the volume fraction of solid in the bed. The proportional constant is dependent upon the method of derivation of the equation. Using the concept of a hydraulic radius, the constant is 1.\textsuperscript{34}

In systems of capillary flow into packed beds, meniscus effects are important. From equation 2.6, the smaller the radius of the capillary, the higher the column of fluid. For a distribution of radii, then the fluid will move higher in the smaller capillaries. Furthermore, the capillaries, being
irregular, have regions of high curvature (or small radii). Where these small angles are formed by the particles, the edge of the meniscus will show a large rise over the bottom of the meniscus. This is known as the 'meniscus effect' and can be explained in terms of the pressure increase due to the increased curvature of the interface as indicated in equation 2.5. The higher the pressure difference, the greater the driving force for capillary flow, which results in these narrower regions being filled first.

2.4 Physical Characteristics of Lanxide™ Materials

The materials manufactured by the DIMOX™ without a filler material have a columnar grain structure. The Al₂O₃ grains are oriented with the c-axis aligned with the growth direction. The presence of a filler material largely disrupts this preferred orientation. This is likely due to a tortuous oxidation path and random nucleation sites; however, this has not been investigated. The phases present in a composite grown into an Al₂O₃ filler have been given as Al, Si, and α-Al₂O₃. The quantity of these phases and the composition of the starting material have not been given.

Lanxide™ materials are reported to have superior wear characteristics compared to monolithic ceramics and metals. Mechanical properties of composites with SiC (500 grit) filler have been reported, but no properties for composites with Al₂O₃ as the filler material have been published. The effect
of processing conditions on the physical and mechanical properties of a composite formed with no filler has been reviewed, and only recently have the metal phases present been reported and quantified.

The composite is 80 to 90% Al₂O₃, with the remainder being aluminum evenly dispersed through the microstructure. Considering the aluminum as spherical particles, the aluminum will put the Al₂O₃ matrix into hoop tension since the aluminum has the higher coefficient of thermal expansion. As cracks propagate normal to tensile stresses, the crack will be attracted to the sphere. If the matrix is in hoop compression, the crack may be deflected as cracks propagate parallel to compressive stresses. This is shown schematically in Figure 2.5. To be effective, the crack must pass within the stress field generated around the particle. To achieve optimum crack-particle interaction, the shape, size distribution, and volume percent of particles must be controlled. The metal deforms behind the crack front, work being done on the metal to plastically deform it. The additional work increases the fracture toughness of the ceramic over that of the monolithic material. The reinforcement particles should be less than the critical flaw size, typically 20 to 40 μm for Al₂O₃, or they will be strength controlling. For the same reason, the spaces between the reinforcement should be smaller than the flaw
Figure 2.5: Schematic of Crack-Particle Interaction.39
size. In practical terms, this means that the particles should be small and that there be lots of them.

The toughening mechanism has been successfully modelled using a simple, two dimensional strain model modified to account for the clamping effect of the ductile ligaments. The metal effectively retards the opening of the crack as shown in Figure 2.6. Under applied stress, \( \sigma_a \), the crack opening width \( w_o \) is retarded by the metal ligaments. A more fundamental approach has noted the importance of the debonding between the metal and matrix on the plastic deformation of the ligament, and thus on the fracture toughness. The effect of alloy composition was also noted as the unexpected precipitation hardening due to the presence of intermetallics will increase the flow stress of the ligaments.

![Figure 2.6: Schematic of a Crack in a Ceramic/Metal Composite](image)

(Dashed line represents a crack in the monolithic ceramic.)
2.5 Summary

The DIMOX™ process is used to produce ceramic matrix composites, but there is a lack of systematic study linking the process to the material properties. For the simple system of aluminum-magnesium-silicon alloys oxidizing in air and growing into an alumina filler bed, not even optimum temperature or alloy compositions are known. There is also no clear link between the process: oxidation, wetting, and capillary flow, and the resulting properties of the composite.
Chapter 3

3. OBJECTIVES

As this work is in a new research field, the primary objective is to present a description of the ceramic matrix composites made by the DIMOX™ process, from raw materials to the mechanical behaviour.

Specifically, the objectives are to:

i) determine some critical parameters in the DIMOX™ process,

ii) determine the composition of the material with respect to these critical parameters, and

iii) evaluate some physical properties of the composite.

The ultimate goal is to produce a usable material from the starting materials, namely aluminum-magnesium-silicon alloys and alumina as the filler using oxygen in air as the oxidant.
4. EXPERIMENTAL

4.1 Raw Materials

The composition of the starting materials is given in Table 4.1 below. High purity materials were used to reduce any possible surface effects of the trace constituents. The concentrations of the trace elements are in weight percent and are those given by the supplier.

Table 4.1: Starting Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Purity</th>
<th>Trace Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Belmont</td>
<td>99.99%</td>
<td>Fe 0.005%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Si 0.003%</td>
</tr>
<tr>
<td>Silicon</td>
<td>AESAR</td>
<td>99.9999%</td>
<td>none given</td>
</tr>
<tr>
<td>Magnesium</td>
<td>A&amp;C Chem</td>
<td>99.5%</td>
<td>Mn 0.15%</td>
</tr>
<tr>
<td></td>
<td>Timminco</td>
<td>99.5%</td>
<td>Fe 0.035%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu 0.02%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>none given</td>
</tr>
<tr>
<td>C-70 UNG</td>
<td>Alcan</td>
<td>99.5%</td>
<td>Na₂O 0.5%</td>
</tr>
<tr>
<td>Alumina</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400 grit</td>
<td>Struers</td>
<td>96.4%</td>
<td>TiO₂ 2.6%</td>
</tr>
<tr>
<td>Alumina</td>
<td></td>
<td></td>
<td>SiO₂ 0.6%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MgO 0.4%</td>
</tr>
</tbody>
</table>

4.1.1 Metals

The aluminum was supplied in the form of 1 gram shot; the silicon as small flakes, 100 to 0.1 grams. The magnesium from A&C Chemicals was in the form of turnings; from Timminco Metals, a 1 kg ingot. The alloys for the experiments were
fabricated in a gas fired furnace using standard foundry techniques. The molten metal was chill cast into 38 millimetre diameter bars. These bars were then cut into disks of 35 to 50 grams each. The silicon and magnesium contents were confirmed by atomic absorption and emission spectroscopy. The elements present in the alloys and approximate concentrations, determined by emission spectroscopy, are given in Table 4.2. Unless otherwise stated, all compositions are given in weight percent.

<table>
<thead>
<tr>
<th>% Si</th>
<th>% Mg</th>
<th>% Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2</td>
<td>0.003</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>0.011</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0.012</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.008</td>
</tr>
<tr>
<td>10</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Iron and copper were the other trace elements in the alloys, at relatively consistent levels of 0.04% and 0.004%, respectively. The source of the iron is likely the fireclay crucible used to melt the alloys. The copper and the manganese were likely from the magnesium metal. The variable manganese content is not critical as manganese does not effect the wetting characteristics of molten aluminum on Al₂O₃ at 870°C.²⁶ The same study found that a small amount, 0.54%, of copper decreased the aluminum-Al₂O₃ contact angle. Increasing the
copper content, however, will increase the contact angle. At 950°C, pure aluminum on Al₂O₃ has the same contact angle as an aluminum 1.7% copper alloy. The effect of iron on the contact angle has not been studied. Regardless, the influence of iron and copper on wetting will not be discernable in the present study. Manganese, copper, and iron have a small effect on the oxidation behaviour of aluminum alloys relative to magnesium. As the magnesium content is high, it is assumed that the trace elements will not affect the oxidation behaviour. The first five alloys listed in Table 4.2 were used in the preliminary experiments to determine temperature and composition effects. The 7% Si, 2% Mg alloy was adopted for later experiments.

4.1.2 Alumina Powder

The filler material is a Bayer alumina: Alcan C-70 UNG. The mean particle size was found to be 5 μm by a sedimentation technique with soft agglomerates on the order of 100μm. Figure 4.1 shows the tabular form of the grains and the structure of the agglomerates. The major impurity of the powder is soda, Na₂O, resulting from the precipitation step in the Bayer process.

The tap characteristics and tap density of the C-70 alumina were determined with a 50 mL graduated cylinder. As the tap density varied somewhat with the mass and tap history

* Micrometrics Sedigraph 5000D
Figure 4.1: Alcan C-70 UNG Alumina.

Figure 4.2: Struers' 400 Grit Alumina.
of the powder, two methods were used and the results averaged. By one method, the cylinder was filled then tapped until the volume of powder remained constant. The second method involved measuring roughly 25mL of powder into the cylinder, shaking the cylinder and then tapping to constant volume. The tap density of the C-70 powder, as received, ranged from 0.95 to 1.02 g/cm$^3$, with an average of 0.98 g/cm$^3$. This corresponds to 24% of theoretical density. Milling the powder increased the tap density to 1.22 to 1.30 g/cm$^3$, with an average of 1.26 g/cm$^3$, or 32% of the theoretical. The specific surface area, 0.96 m$^2$/g, was determined by single point BET measurement.*

Another filler material, Struers' 400 grit alumina, was used in the manufacture of test bars. Figure 4.2 shows the sharp, angular particles. The tap density of the grit ranged from 1.91 to 1.96 g/cm$^3$, with an average of 1.94 g/cm$^3$ or 49% of the theoretical density. The specific surface area is much lower at 0.21 m$^2$/g.

4.1.3 Crucible Manufacture

The crucibles for this research were manufactured in house from A16SG alumina, a high purity alumina from Alcoa. A slip was prepared with a ratio of 2:1 alumina to water. HCl was used as the deflocculant and the slip was then ball milled for eighteen hours. After stabilizing the slip at pH 4, the

* Quantasorb
crucibles were drain cast to a wall thickness of 2-3 mm. The crucibles were fired at 1350°C for about three hours to 75% of the theoretical density. This low final density improved their thermal shock resistance. The final dimensions of the crucibles were 47 mm outside diameter and 38 mm high.

4.2 Composite Fabrication

The machined alloy was degreased and placed in a crucible. Alumina powder was then placed on top of the alloy and tapped level, as shown in Figure 4.3. The masses of the crucible, alloy and powder were noted.

Figure 4.3: Experimental Arrangement.
A heating cycle typical of all experiments is shown in Figure 4.4. The crucible was placed in the furnace which was idling at 570 ± 10°C. Ten minutes later, the furnace was turned to the set-point temperature which was reached in about two and a half hours. The heating rate was determined by manually setting the power level. The crucibles were maintained at the set-point temperature for either 24 or 48 hours. The furnace was turned down and the crucibles were removed three hours later, at roughly 600°C, and cooled in air to room temperature. The furnace was kept at 600°C for a practical reason: to reduce the thermal fatigue experienced by the silicon carbide elements. For the manufacture of the larger pieces used for test bars, the crucibles were placed into, and removed from, a 'cold' furnace.

At various times during the experiments, the crucibles were examined in situ to note the surface condition of the powder bed. This gave some indication of the rate of infiltration.

4.3 Material Characterization

4.3.1 Microstructure and Density

The crucibles were sectioned, and samples of the composite were cut from the resulting material. The samples, along with a section of the crucible, were mounted in epoxy resin. The specimens were ground on 220 and 600 grit diamond
Figure 4.4: Heating Cycle to 1120°C for 48 hours.
discs then polished using $6 \mu m$ and $1 \mu m$ diamond paste on silk cloth. The samples were first examined under an optical microscope and later carbon coated for analysis: using an scanning electron microscope with energy dispersive spectroscopy (EDS). Another sample was cut from the composite for density measurement by an Archimedes method. (See Appendix A)

4.3.2 Composition

The phases and quantity present in the material was determined by quantitative EDS analysis and quantitative powder x-ray diffraction (XRD).

The EDS analysis was used for determining rough concentrations of the components of the composites. These compositions were then used to select appropriate standards for XRD quantification. The mounted composite was scanned over an area of $\approx 1 mm^2$ (100X magnification). From the relative composition of Al and Si given by the standardless quantification program, the Al:O peak ratio for the area, and the Al:O peak ratio for the alumina standard, an approximate matrix composition could be calculated. This calculation assumed spinel was not present in the matrix. An alumina crucible, made from A16SG, was used as a standard. (See Appendix B)

For XRD, a sample was pulverized by milling in a cast

*Jeol JSM-840A, Tracor TN-5400.*
iron shatterbox for 15 seconds. The powder was then analyzed on a Phillips 1700 Automatic Powder Diffractometer. Standards of known composition were made from aluminum powder, C-70, and silicon. Calibration curves were plotted and were then used to quantify the phases in the composite. (Appendix C.)

4.3.3 Mechanical Properties

Bars were cut and ground from large bodies made by infiltrating a powder bed 5 x 7 x 1 cm deep. One surface was polished and the edges bevelled with a 240 grit diamond disc to remove stress concentrators. Before fracture, the Young's modulus was calculated from the measured natural frequency of vibration of the bar in flexure and assuming a Poisson's ratio of 0.3. The bars were then fractured in a four point bend test on an Instron testing machine with a crosshead speed of 0.5 mm/s. The Modulus of Rupture, MOR, was calculated using the formula:

\[
MOR = \frac{3Pa}{bd^2}
\]  

(4.1)

where P is the load, a is the moment arm, b is the width of the tensile surface of the bar, and d is the thickness of the bar. The fracture surfaces were examined optically with a low power binocular microscope. Samples were then cleaned with acetone, mounted, and sputter coated with gold for examination.

* Grindo-Sonic MK4i
A section of the test bar was mounted in epoxy resin for optical microstructural examination and Vickers hardness testing. The fracture toughness, $K_{\text{lc}}$, was calculated from the crack pattern resulting from indentation. A schematic of the crack pattern is given in Figure 4.6. Two formulae were used in this calculation. The first was:

$$K_{\text{lc}} = 0.016\left(\frac{E}{H}\right)^{1/2} \left(\frac{P}{C^{3/2}}\right)$$  \hspace{1cm} (4.2)

which was derived for half-penny crack geometry.\(^4\) The second formula was:

$$K_{\text{lc}} = 0.015\left(\frac{C-a}{a}\right)^{-1/2} \left(\frac{E}{H}\right)^{2/3} \left(\frac{P}{C^{3/2}}\right)$$  \hspace{1cm} (4.3)

which was derived for rectangular, or Palmqvist, crack
For both formulae, $E$ is the Young's modulus, $H$ is the hardness, and $P$ is the applied load. The crack geometry is represented by $c$ and $a$. After indentation, the samples were carbon coated for scanning electron microscopy to examine microstructure and crack paths from the indents.

**Figure 4.6:** Schematic of Indentation Crack Pattern.
5. RESULTS AND DISCUSSION

5.1 Effect of Temperature and Alloy Composition

The purpose of this first set of experiments was to determine a good temperature/alloy combination that achieved good growth characteristics and a consistent microstructure. For this study, 'good growth characteristics' meant a uniform growth moving from the metal reservoir upwards through the filler bed (an even growth surface) and a sharp interface between the metal reservoir and the composite matrix.

Figure 5.1: Alloy Compositions.
The experiments were performed at four temperatures: 1000°C, 1090°C, 1120°C, and 1200°C. The residence time was 48 hours. Figure 5.1 is a schematic of the composition matrix of the alloys used to infiltrate a bed of C-70 alumina. The mass of alloy used was insufficient to infiltrate the total volume of the powder bed. This was done so that the shape of the growth front could be easily observed.

The sectioned crucibles for the growth at 1000°C are shown below in Figure 5.2. In this and the following figures of sectioned crucibles, the crucibles are arranged such that the magnesium content increases moving from left to right and the silicon content increases moving from bottom to top as in Figure 5.1. The numbers at the base of the crucible denote the silicon and magnesium content of the parent alloy respectively. (e.g. 7/5 → 7wt%Si, 5wt%Mg) In the text, the notation 7/5 refers to the composite grown from the 7%Si, 5%Mg alloy. Immediately noticeable in Figure 5.2 is that only the high magnesium alloys grew into the filler bed. There is no clear delineation between the growth and the metal reservoir. The growth front is also uneven across the bed. The phases present in the 3/8 and 10/8 material, as ascertained by powder x-ray diffraction (XRD), are alumina, silicon, aluminum, and spinel (MgAl₂O₄).

The growth behaviour at 1090°C showed remarkable improvement as seen in Figure 5.3. All the metal reservoirs have almost completely reacted, resulting in a composite
Figure 5.2: Sectioned Crucibles from 1000°C.

Figure 5.3: Sectioned Crucibles from 1090°C. Note the spinel layer.
material. Note that the crucible with the 10/2 alloy is misleading; the growth occurred in one side of the crucible and what is shown is the edge of the composite. There is a clear demarkation between the metal reservoir and the composite material, appearing in some crucibles as a grey-blue region. This region was determined to be largely spinel and the thickness of the layer increases with magnesium content. For the 3% silicon alloys (3/2 and 3/8), the growth front moved up the side of the crucible and across the top of the bed, leaving an uninfiltrated region in the centre. As the silicon content increased in the alloys, the growth front appeared to move evenly through the filler bed. The phases present are aluminum, silicon, alumina, and spinel. According to the XRD analysis, the spinel content in the matrix has been significantly reduced. (See below.)

Increasing the temperature to 1120°C improved the growth behaviour of the alloys, as shown in Figure 5.4. Notably, both the 10% silicon alloys (10/2 and 10/8) have formed an even growth around the circumference of the crucible. The 3% silicon alloys (3/2 and 3/8) have again left an uninfiltrated region but not to as large an extent as at 1090°C. Also, the spinel layer thickness increased with magnesium content. The increase in temperature did not seem to affect the thickness of the spinel layer over that at 1090°C for the same alloy; however, the spinel content in the composite material did increase.
Figure 5.4: Sectioned Crucibles from 1120°C. Note the a) uneven growth front and b) diffuse spinel layer.

Figure 5.5: Sectioned Crucibles from 1200°C. Note the a) uneven growth front and b) diffuse spinel layer.
Figure 5.5 shows the sectioned crucibles for the composites grown at 1200°C. The infiltration has deteriorated: the composite has collapsed into the metal reservoir, the growth front was no longer even, and the spinel layer has extended into the matrix itself.

Several measurements are available to quantify the extent of oxidation. The most obvious is the weight gain. If the oxidation goes to completion, weight gain is clearly dependant on the original mass of alloy present: the more metal, the higher the weight gain. Expressing the weight gain as 'weight gain per gram alloy' can be misleading, especially if the oxidation is not complete. For example, if the weight gain is 15g, the weight gain per gram with an original mass of 30g metal is 0.50. If however, the original mass of metal is 45g, the weight gain per gram is only 0.33. The mass of metal varied over the temperature range, but at each temperature, the mass of the alloys used for the above experiments were within a 5g range. Table 5.1 below gives both the weight gain and the weight gain per gram alloy.

At 1000°C, the weight gains for the 8% Mg alloys are large, but the infiltration characteristics are poor. At 1120°C, the weight gain per gram alloy is approximately the same from one alloy to the next, yet the infiltration characteristics are quite different.
The percent oxidation of each of the alloys is given in Table 5.2. This was calculated as a ratio of the weight gain to the theoretical weight gain if that alloy had oxidized completely.

Table 5.2: Percent Oxidation

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Percent Oxidation At Each Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000°</td>
</tr>
<tr>
<td>3/2</td>
<td>0.6</td>
</tr>
<tr>
<td>3/8</td>
<td>72.1</td>
</tr>
<tr>
<td>7/5</td>
<td>7.7</td>
</tr>
<tr>
<td>10/2</td>
<td>17.5</td>
</tr>
<tr>
<td>10/8</td>
<td>65.8</td>
</tr>
</tbody>
</table>

The composition, density and porosity of the composite material grown from the 7-10% silicon alloys, that is, the top
three crucibles in the preceding figures, are given in Table 5.3. The microstructure of the composite from the 3% silicon alloys varied considerably throughout the bed which precluded reasonably accurate composition and density determinations. The compositions given are those determined by quantitative x-ray diffraction. The aluminum content is accurate to ±1% and the silicon content is accurate to ±2%. The method and calibration curves are presented in Appendix B. The densities, measured by the Archimedean method, are reported to two decimal places, but considered accurate to one. The percent porosity was calculated from the theoretical density, based on the matrix composition, using:

$$\rho_{th} = \%Al \cdot \rho_{Al} + \%Si \cdot \rho_{Si} + (1-\%Al-\%Si) \cdot \rho_{Al_{2}O_{3}} \quad (5.1)$$

Note that the spinel content has not been accounted for in the porosity calculations. The spinel content, dealt with only semi-quantitatively, is given as a ratio of peak intensities, I/I₀, where I is the peak height from the spinel (311) plane and I₀ is the peak height from the Al₂O₃ (110) plane.

The aluminum content in the composite is surprisingly constant at 2-3%. The silicon content, however, follows a curious pattern. At 1090°C, the silicon content for all three alloys lies within measurement error of each other. At 1120°C and 1200°C, the silicon content in both the 10/2 and 10/8 composites is roughly 5%, that is, half of that of the
starting alloy. Yet, the 7/5 composite has less than 3.5% silicon, varying between 1-2%. This difference is just at the measurement error for the silicon concentration; thus, the significance of this difference is questionable.

Table 5.3: Composition, Density, and Porosity for Growths.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Alloy</th>
<th>% Al</th>
<th>% Si</th>
<th>Q g/cm³</th>
<th>% P</th>
<th>Spinel Peak I/I₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>10/8</td>
<td>2.8</td>
<td>2</td>
<td>3.69</td>
<td>5.5</td>
<td>0.300</td>
</tr>
<tr>
<td>1090</td>
<td>7/5</td>
<td>2.0</td>
<td>2</td>
<td>3.32</td>
<td>15.0</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>10/2</td>
<td>2.2</td>
<td>3</td>
<td>3.38</td>
<td>13.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10/8</td>
<td>2.4</td>
<td>4</td>
<td>3.34</td>
<td>13.6</td>
<td>0.033</td>
</tr>
<tr>
<td>1120</td>
<td>7/5</td>
<td>2.0</td>
<td>2</td>
<td>3.44</td>
<td>12.3</td>
<td>0.141</td>
</tr>
<tr>
<td></td>
<td>10/2</td>
<td>2.4</td>
<td>5</td>
<td>3.38</td>
<td>12.5</td>
<td>0.053</td>
</tr>
<tr>
<td></td>
<td>10/8</td>
<td>2.6</td>
<td>5</td>
<td>3.43</td>
<td>11.0</td>
<td>0.457</td>
</tr>
<tr>
<td>1200</td>
<td>7/5</td>
<td>2.2</td>
<td>1</td>
<td>3.46</td>
<td>11.7</td>
<td>0.138</td>
</tr>
<tr>
<td></td>
<td>10/2</td>
<td>1.9</td>
<td>4</td>
<td>3.44</td>
<td>11.4</td>
<td>0.092</td>
</tr>
<tr>
<td></td>
<td>10/8</td>
<td>2.1</td>
<td>5</td>
<td>3.43</td>
<td>11.2</td>
<td>0.074</td>
</tr>
</tbody>
</table>

As the temperature increases for the 10/2 material, the spinel content increases. For the 10/8 material, the spinel content reaches a maximum between 1090 and 1200°C. The 7/5 material fits somewhere between these two. Possible explanations for these changes of the constitution of the composite with temperature and alloy are addressed in Section 5.3 below. The marginal increase of the density with temperature, along with the slight decrease in porosity, could indicate that a higher reaction temperature is helpful in
reducing porosity - or this is due to the increasing spinel content, overlooked in the calculations. From a mechanical standpoint, a porosity of 11-15% is too high for an engineering ceramic material. With a view of improved fracture toughness, the metal content could be increased.

The microstructures of the 7/5, 10/2 and 10/8 composites grown at 1120°C are given in Figure 5.6. In these optical micrographs, the grey phase is alumina, the white phase is primarily silicon, and the black regions are pores. Aluminum is not visible at this low magnification. The most striking point of all the microstructures is the raspberry-like structure, with clusters on the order of 100μm. The pore size distribution is bimodal: small pores in the raspberries, large pores between the raspberries. Comparing the 10% silicon alloys, the lower magnesium content in the starting alloy, the fewer the smaller pores within the clusters.

To locate the aluminum within the composite, samples were examined by EDS/SEM. As there is no difference between the x-rays emitted by Al and Al³⁺, the aluminum to oxygen peak ratio was used in conjunction with that of an alumina standard to determine the amount of aluminum metal. Spot analyses of the grey phase in Figure 5.7 produced spectra with only Al and O peaks. A spectrum is given in Figure 5.8. The Al:O ratios were in excess of that for the alumina standard. As there was no metal phase visible at the point of the analysis, some aluminum is present in the Al₂O₃ matrix as relatively pure
Figure 5.6 a: Optical Micrograph of 7/5 Composite.

Figure 5.6 b: Optical Micrograph of 10/8 Composite.
Figure 5.6 c: Optical Micrograph of 10/2 Composite.

Figure 5.7: SEM Micrograph of 10/2 Composite.
Figure 5.8: X-ray Spectrum from Spot Analysis of \( \text{Al}_2\text{O}_3 \) Matrix.

Figure 5.9: X-ray Spectrum from Spot Analysis of Silicon.
inclusions on an order of less than $1 \mu m^3$, that is, the excitation volume caused by the electron beam.\textsuperscript{45} The white phase in Figure 5.7 is primarily silicon. Spot analyses revealed aluminum metal within some of the silicon precipitates. (Figure 5.9.) These observations are consistent with the literature. Transmission electron microscopy, TEM, has revealed the presence of small aluminum inclusions on the order of 250 nm connected by narrow channels 10 to 50 nm in diameter.\textsuperscript{6,36}

Based on these experiments, a promising alloy/temperature combination would be the 7-10\% silicon alloys at 1120°C. The 3\% silicon alloys left a centre of uninfiltirated powder which may be difficult to eliminate when infiltrating larger beds. It was noticed from direct observation of the crucibles during the reaction that the largest extent of infiltration occurred within the first 23 to 26 hours. Thus, the remaining time would serve only to further oxidize the metal. Complete oxidation of the metal is not desirable as a low metal content would not result in an appreciable increase in the fracture toughness of the composite over that for pure alumina or other alumina ceramics. The components of the alloys would oxidize in the order of ascending values of $\Delta G$ of reaction; that is, magnesium, aluminum, then silicon. Thus, increasing the extent of oxidation will also increase the relative amount of silicon in the metal phase. The porosity remains a serious problem: pores are defects and act as stress concentrators,
hence weakening the material.

5.2 Microstructural Refinement

5.2.1 Effect of Time and Metal Reservoir

Figure 5.10: Sectioned Crucibles, 1120°C, Excess Metal and 24 hour Residence Time.

In an attempt to reduce the porosity and increase the metal content, an experiment was conducted using the 7-10% silicon alloys with excess metal in the reservoir for a shortened reaction time of 24 hours. The rationale is to eliminate the meniscus effects by limiting the powder bed size and providing sufficient metal to fill all the capillaries. The sectioned crucibles are shown above in Figure 5.10. The 7% silicon, 5% magnesium alloy started to develop similar
characteristics of the 3% silicon alloys discussed in the previous experiments; that is, growth up the side then across the top. The 10% silicon, 2% magnesium alloy has grown quite well: fully and evenly. The 10% silicon, 8% magnesium alloy has grown evenly, yet is considered unsuitable due to the drastic increase in spinel content. This was caused by a channel, visible in Figure 5.10 that developed in the powder bed.

The weight gains for these crucibles are given in Table 5.4 below. The weight gains were only slightly lower than for the previous experiments using a 49 hour reaction time, confirming that most of the growth occurs in the first 24 hours. Note that the two 10% silicon alloys have the same percent oxidation. This is consistent with the observation that most of the magnesium oxidizes first. The percent oxidation of the 7% silicon alloy is higher which is also consistent with the fact that the silicon will not have oxidized.

Table 5.4: Weight Gains Using Excess Metal.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>gain (g)</th>
<th>g/g alloy</th>
<th>Percent Oxid’n</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/5</td>
<td>24.25</td>
<td>0.611</td>
<td>68.2</td>
</tr>
<tr>
<td>10/2</td>
<td>22.86</td>
<td>0.639</td>
<td>63.4</td>
</tr>
<tr>
<td>10/8</td>
<td>22.49</td>
<td>0.602</td>
<td>63.2</td>
</tr>
</tbody>
</table>

A rough rate of oxidation of $2.1 \times 10^{-5}$ g/cm$^2$s was calculated for the 10% silicon, 2% magnesium alloy assuming linear kinetics
over the 24 hours. This rate is lower than the real value as the incubation period is not taken into account. For a 10% Si, 3% Mg alloy with no filler material, the oxidation rate was reported to be $8 \times 10^{-6}$ g/cm$^2$s.\textsuperscript{5} The higher rate could be explained by a higher reactive surface area, caused by the meniscus from the alloy melt wetting the particles, and thus an increase in the diffusion of oxygen across the MgO surface layer.

Figures 5.11 and 5.12 compare the weight percent of aluminum and silicon, respectively, for composites grown in this experiment and in the previous experiment at 1120°C. For the 7/5 composite, both the aluminum and silicon contents have doubled. The metal content in the 10/2 and 10/8 composites increased marginally. The higher aluminum content is beneficial as this is a ductile phase and should increase the fracture toughness of the composite. Silicon has relatively poor mechanical properties compared to the Al$_2$O$_3$ and the aluminum; thus, a high silicon content would have a detrimental effect on the mechanical properties of composite.

The microstructures and densities of the 7/5, 10/2, and 10/8 composites are given in Figure 5.13. When comparing with Figure 5.6, the smaller pores have been eliminated; however, the large pores appear larger. The elimination of the small pores has improved the bulk density of the material. The 7/5 composite showed the greatest improvement, followed by the 10/2 composite.
Figure 5.11: Aluminum Content in Composite Using Excess Metal.

Figure 5.12: Silicon Content in Composite Using Excess Metal.
Figure 5.13 a: Optical Micrograph of 7/5 Composite.
Excess Metal, $\rho = 3.51 \text{ g/cm}^3$

Figure 5.13 b: Optical Micrograph of 10/8 Composite.
Excess Metal, $\rho = 3.47 \text{ g/cm}^3$
The 10/8 composite showed no improvement at all, either in microstructure or density, over the excess filler material. The improvement of the material, as seen by lower porosity and higher metal content, is likely due to the negation of the meniscus effect. There was enough metal present to fill the capillaries. More importantly, the crucibles were removed from the furnace before the growth could continue past the top surface of the C-70 bed. This further oxidation could have removed metal from the composite body and increased the porosity.

The microstructure needs further improvement as the large pores must be eliminated to realize the full potential of the physical properties of the material. These clearly resemble bridging pores caused by hard agglomerates in the C-70 ceramic
powder bed. The silicon content should also be reduced, lessening the effect of this weak, brittle phase in the matrix. To confirm the size of the agglomerates, the C-70 powder was sieved, revealing hard agglomerates in the range of 53 to 105µm. The pores would likely be removed by milling the C-70 which would break up these agglomerates.

It appears that a silicon content of 7% or higher is required for good infiltration characteristics. Yet, with the milling of the C-70, the size of the pores should be reduced. Previous results indicate that a low magnesium content is desirable in eliminating small porosity. Thus, a new alloy composition of 7% silicon, 2% magnesium was used in an attempt to optimize the microstructure.

5.2.2 Effect of Powder Bed Condition

The C-70 powder was milled in ~30g batches in an alumina lined shatterbox for 5 minutes. After infiltration for 24 hours at 1120°C, the crucibles were sectioned and are shown in Figure 5.14. The new 7% silicon, 2% magnesium alloy infiltrated from one side, and has one small uninfiltrated region in the centre. The 7% silicon, 5% magnesium alloy had infiltrated in a similar manner to the 3% silicon alloys in the first experiments. These resulting voids would constitute the critical flaws in any manufactured part.

The weight gains for this experiment are presented in Table 5.5 below. The weight gain for the 7% silicon, 2%
magnesium alloy is low as it grew into the powder bed from one side. There is also alloy remaining in the reservoir. The gain for the 7% silicon, 5% magnesium alloy is lower than for the case with excess metal alone. A more tortuous path for oxygen diffusion to the growth front may account for this decrease as milling the powder results in a higher tap density (increasing from 24% to 32%) and hence better packing of the Al₂O₃ particles in the bed. The percent oxidation is skewed by the difference in the alloy remaining in the reservoir.

Figure 5.14: Sectioned Crucibles, Milled C-70.
Table 5.5: Weight Gains Using Milled Powder.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>gain (g)</th>
<th>g/g alloy</th>
<th>Percent Oxid'n</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/2</td>
<td>18.09</td>
<td>0.452</td>
<td>48.4</td>
</tr>
<tr>
<td>7/5</td>
<td>22.59</td>
<td>0.545</td>
<td>60.8</td>
</tr>
</tbody>
</table>

Figure 5.15: Metal content in 7/2 and 7/5 composites.

The metal content in the 7/5 composite has not changed significantly, but the 7/2 composite has a higher aluminum and lower silicon content as shown in Figure 5.15. This increase in the aluminum content was unexpected.
Figure 5.16 a: Optical Micrograph of 7/2 Composite. Milled C-70, $q = 3.51 \, g/cm^3$

Figure 5.16 b: Optical Micrograph of 7/5 Composite. Milled C-70, $q = 3.46 \, g/cm^3$
The densities of the composites are presented with the microstructures in Figure 5.16, the effect of magnesium content is clear. The 7/2 composite has a higher density and a microstructure characterized by smaller pores than the 7/5 composite. The density for the 7/5 composite did not improve with milling the C-70.

The alloy compositions that result in a reasonable growth into a powder bed are the 7% silicon, 2% magnesium and the 10% silicon, 2% magnesium alloy. The 10% silicon alloy should have better growth behaviour of the two metals. These alloys were then used to infiltrate a larger powder bed with the purpose of making test bars.

5.2.3 Infiltration Characteristics into Coarse Alumina Grit Filler

In the manufacture of test bars, 400 grit alumina was infiltrated to form a composite. The growth rate at 1120°C was much slower than for the C-70, thus requiring a longer residence time. The composites were grown over 84 hours, or 3½ days, at which point the 400 grit beds were still not completely infiltrated. The growth rate into the C-70 bed was on the order of 10mm per day, while the rate into the 400 grit was 2 to 3 mm per day. The sectioned crucibles are shown in Figure 5.17. The growth characteristics for the alloys with the 400 grit are similar to those with the C-70. The 10% silicon, 2% magnesium alloy had the thickest and most even
growth, followed by the 7/2 alloy. The composite grown from
the 7% silicon, 5% magnesium alloy was not usable for test
bars. The spinel layer acted to lift the centre of the powder
bed, resulting in infiltration up the sides, but not in the
centre. Also, the bottom surface of the 7/5 composite has a
corrugated appearance, quite reminiscent of the surface

![Image of crucibles]

**Figure 5.17:** Sectioned Crucibles for Bars, 400 Grit Filler.

presented in Figure 2.2, for the role of magnesium in the
oxidation process. The bottom surface of the 7/2 composite is
not as undulating as there was not as much magnesium in the
alloy. The lower magnesium content is preferable as this would
reduce both the machining requirements and the thickness of
the initial spinel layer.
The composition and the density of the composites are given below. The density is much higher than that of the composites made with C-70 filler. In addition, the metal content was found to be significantly higher. These values are approximate from the XRD calibration curves.

**Table 5.6: Composition of 400 Grit Material.**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>% Al</th>
<th>% Si</th>
<th>( \rho ) g/cm(^3)</th>
<th>% Pores</th>
<th>Spinel Peak I/I(_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/2</td>
<td>8</td>
<td>6</td>
<td>3.57</td>
<td>5</td>
<td>0.075</td>
</tr>
<tr>
<td>10/2</td>
<td>13</td>
<td>9</td>
<td>3.55</td>
<td>2</td>
<td>0.116</td>
</tr>
</tbody>
</table>

The microstructure of these two composites did not appear to be different. Figure 5.18 gives an optical micrograph and SEM micrograph of exactly the same region in the 10/2 composite. (The optical micrograph is a mirror image.) In the SEM micrograph, the dark grey phase is the alumina; the grey phase, aluminum; the light grey, aluminum/silicon; and the white phase, a phase of aluminum, silicon, titanium, and zirconium. No oxygen was detected. For simplicity, this phase will be referred to as the "intermetallic phase." Spot analysis of several intermetallics, using EDS standardless quantification, gives a consistent atomic composition of 8% Al, 61% Si, 29% Ti, and 2% Zr. A spectrum is given in Figure 5.19. The grit is the source of the titanium and zirconium, where they have been leached out by the alloy.
Figure 5.18 a: Optical Micrograph of Composite from 400 Grit and 10/2 Alloy

Figure 5.18 b: SEM micrograph of same region above. a is Al₂O₃, b is aluminum, c is aluminum/silicon, and d is the intermetallic.
Figure 5.19: X-ray Spectrum from Spot Analysis of Intermetallic Phase.
Comparing the infiltration of the two beds, the sectioned crucibles for C-70 are presented in Figure 5.20. The sections for the 10/2 and 7/2 alloys are next to the crucible wall and give the best representation of the growth. The 10/2 alloy provided the best growth characteristics, but the composite was marred by one small uninfiltrated region. The bed above the 7/2 alloy was not as well infiltrated, as marred by a few uninfiltrated regions. The 7/5 alloy grew into the bed in a very random manner, leaving large volumes of powder. Only two bars were cut from the low magnesium composites, none could be cut from the 7/5 composite. The density, composition, and microstructure of the composite bars were consistent with the previous experiments.

Figure 5.20: Sectioned Crucibles for Bars, C-70 Filler.
5.3 Proposed Growth Mechanisms

The growth mechanisms can be subdivided into three sections: heating, isothermal reaction process, and cooling. The effect of magnesium is primarily felt upon heating the sample to the reaction temperature. Capillary and wetting phenomena are part of the reaction process. Cooling entails solidification and thermal expansion mismatch which may have an effect on the mechanical properties.

5.3.1 Heating Stage

The spinel layer is the result of the first step in the growth mechanism: the initiation of breakaway oxidation. Here the molten alloy is covered by an intact aluminum oxide film. The magnesium in the melt reacts with the oxide film forming regions of MgO. The magnesium also has a high vapour pressure and thus some volatilizes. The magnesium reacts with the oxygen and forms more MgO. This promotes breakaway oxidation. Most of the MgO at the metal bed interface diffuses into the Al₂O₃ to form MgAl₂O₄. If the magnesium vaporizes faster than the oxygen diffuses through the powder bed, then magnesium vapour will diffuse into the bed. The result will be a thick, diffuse spinel layer. As the temperature increases, the rate of the reaction between magnesium and Al₂O₃ increases. The reaction, in the absence of oxygen, can be represented by the equation:

\[ 3Mg_{(v)} + Al₂O₃ \rightarrow 3MgO + 2Al_{(l)} \]
At higher temperatures, this reaction acts to lower the thickness of the final spinel layer. Magnesium has been detected by EDS spot analysis at the air/growth interface, but it is not certain whether this is in the form of MgO or MgAl$_2$O$_4$. This is consistent with other observations of magnesium at the air/growth interface. 13

Thermodynamic calculations based on the real metal system, that is, taking into account the excess energies of mixing, give the oxide layer above the melt to be MgAl$_2$O$_4$. (See Appendix D) The reported layer of MgO can be explained from diffusion data. The mobility of magnesium is significantly higher than that of aluminum in both Al$_2$O$_3$ at 1000°C 46 and MgAl$_2$O$_4$ between 1300 and 1450°C. 47

5.3.2 Isothermal Reaction Process

For the C-70 filler, the growth surface contained significant amounts of sodium. No sodium was detected in the composite body, nor at the air/growth interface of the 400 grit filler. The source of the sodium is the C-70 filler itself, since Na$_2$O is the major impurity at 0.05%. In an aluminum alloy, sodium has been found to increase the oxidation rate, although these studies were reported for lower temperatures. 12 It has been proposed that the diffusion of oxygen across the air/growth interface is the rate controlling step. 14 If so, then the sodium may be acting as a dopant, increasing the oxygen diffusion across the interface and hence
raising the oxidation rate.

The rate may also be increased by an increase in specific surface area resulting from the powder bed, as previously mentioned. The slower rate for the 400 grit bed may be due to the lack of sodium at the air/growth interface or the more tortuous diffusion path for the oxygen caused by the higher density of the powder bed. Doping the growth surface with sodium containing compounds may be a way of accelerating the growth process and thus reducing the time required to produce a composite part.

The improvement in the growth characteristics with the higher silicon alloy deserves some discussion. At this stage in the process, the amount of magnesium in the melt is assumed to be negligible. The aluminum-silicon eutectic occurs at 12.6% Si. (Figure 5.21) At this point, the melt has the highest superheat, and thus the highest fluidity. At 1120°C, the increase in superheat over a pure aluminum alloy is roughly 5%, so superheat is not likely the major factor in improving the growth characteristics.
Figure 5.21: Aluminum - Silicon Phase Diagram.
The aluminum-silicon system is a simple binary system. As such, the behaviour of the system is determined by physical, as opposed to chemical, interactions between atoms. There are trace elements in the alloy, namely magnesium and copper. Depending on the filler, there is also sodium or titanium and zirconium. These elements show strong compound formation with aluminum and each other. In such cases, the impurities will be surface active. These elements, combining with the silicon at the eutectic composition, could bring about a lowering of the surface energy of the metal alloy. Hence, the change in the infiltration behaviour of the alloy.

These generalizations would explain the growth of the 3% silicon alloys. The growth starts up the side of the crucible because of the temperature gradient in the crucible on heating at a rate of 5 K/min. When the alloy composition reaches the eutectic due to the oxidation of the aluminum, the growth begins to move across the top. This is also seen for the 7/5 alloy with the milled C-70. The growth starts upwards, but moves outwards after a shorter time as less aluminum must oxidize for the silicon content to reach 12.2%.

As the oxidation continues, the silicon content increases to 59% where silicon will start to precipitate at the reaction temperature. This is shown in the aluminum-silicon phase diagram (Figure 5.21). Further oxidation will increase the amount of solid silicon, as this does not oxidize in the presence of aluminum, and the liquid composition will remain...
fixed at 59% Si until the cooling stage.

5.3.3 Cooling Stage

As the composite slowly cools, primary silicon precipitates out of the liquid. When the eutectic temperature is reached, the silicon in the remaining liquid has time to diffuse to the primary silicon which results in a divorced eutectic of Si and Al. This would explain the segregation of the aluminum from the silicon as detected by EDS.

The slow cooling, 2 K/min, also minimizes the stresses caused by the coefficient of thermal expansion mismatch. Residual stresses will remain in the composite after cooling to room temperature, where the metal will be in tension and the ceramic matrix in compression. This will have an effect on the crack propagation through the composite body as previously discussed in Section 2.4.

5.4 Mechanical Testing

Powder beds of 5cm x 7cm x 1cm deep were infiltrated and test bars were cut and machined using a diamond cut-off wheel and surface grinder. The heating cycle was changed somewhat as these larger crucibles were put into, and removed from, a cold furnace. The reason for the change was to reduce the thermal shocks on the crucible on heating and the composite on cooling.

The mechanical properties determined were the hardness,
Young's modulus, fracture toughness, and modulus of rupture (MOR). The properties of the material are given below with the number of tests performed. The error given corresponds to the standard deviation of the average value. Properties of two other materials are given for comparison: a commercial monolithic alumina (Durafrax® 1542) which has previously been compared to the composite material grown at 1125°C with no filler. The composite, referred to as "Material A", was grown from Al alloy 5052; nominally Al, 2.5% Mg.

5.4.1 Young's Modulus

The Young's modulus, E, for the C-70 material was not determined. E for the 400 grit filler composites were determined using two flexural readings from each bar. For the purposes of calculation, Poisson's ratio was assumed to be nominally 0.30. Changing the value of Poisson's ratio ±0.10 changes E by less than ±4 GPa.

<table>
<thead>
<tr>
<th>Material</th>
<th>No. of Measurements</th>
<th>( \rho ) g/cm³</th>
<th>E GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 7/2</td>
<td>8</td>
<td>3.57</td>
<td>253±18</td>
</tr>
<tr>
<td>400 10/2</td>
<td>16</td>
<td>3.55</td>
<td>266±11</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>-</td>
<td>3.75</td>
<td>326±4</td>
</tr>
<tr>
<td>Material A</td>
<td>-</td>
<td>3.53</td>
<td>231±3</td>
</tr>
</tbody>
</table>

The values for E varied considerably from bar to bar. The lower values appear to be associated with bars that have
infiltration defects, that is, some region of spinel. For the defect free bars, the values of $E$ are 271 and 277 GPa for the 7/2 and 10/2 material, respectively. The deviation is ±3 GPa. The $\text{Al}_2\text{O}_3$ has the highest $E$, which is expected. The 10/2 material should have an $E$ lower than that of the 7/2 material because the 10/2 has a higher metal content. Material A has a lower $E$ due to its high aluminum content of about 19%.

5.4.2 Hardness and Fracture Toughness

Using the indentation method for determining the fracture toughness of the material is questionable for three reasons: (a) the relatively high porosity, (b) the indents being on the same scale as the microstructure, and (c) the high metal content of the material. The resulting indent will not likely have an ideal half penny, nor ideal Palmqvist crack profile. Thus, the two equations 4.2 and 4.3 are used to calculate $K_{ic}$ and the results given below.

Immediately after indentation, the indent and crack profile was observed to enlarge for 1 to 2 minutes. This indicates sub-critical stress crack growth, of which ceramics are susceptible.\(^4\) As the cracks are then longer, the value for $K_{ic}$ will be low. Another difficulty was the actual measurement of the crack length as the crack was difficult to see in the microstructure. The measurements will then be shorter than the actual crack length, giving a higher $K_{ic}$. Hopefully, these two errors cancelled each other.
The high porosity in the C-70 material made indentation difficult as the material would collapse at high loads and deform at low loads. For the composites with C-70 and 400 grit filler, the hardness increases with increasing metal content. This may be due to the relative increase in silicon content, a hard material. (Vickers Hardness of 10GPa\textsuperscript{50}) As expected, the hardness is between the Lanxide material and the Al\textsubscript{2}O\textsubscript{3}.

The fracture toughness of the C-70 composites was calculated assuming a Young's modulus of 200 GPa and was quite high. This may be explained by the fracture mode of the material. Figure 5.22 shows a crack in the C-70 7/2 composite which has propagated around the Al\textsubscript{2}O\textsubscript{3} grains. Several aluminum ligaments are visible stretching between the crack surfaces.

The \(K_{ic}\) values appear to increase with increasing silicon content. The crack path, however, is not impeded by the presence of silicon. This is shown in Figure 5.23.
Figure 5.22 a: SEM micrograph of crack path in C-70 10/2 composite showing a) intergranular fracture and b) aluminum ligaments.

Figure 5.22 b: Close-up of lower right area in above micrograph showing an aluminum ligament.
Figure 5.23: SEM micrograph of crack path in C-70 10/2 composite unimpeded by silicon.
This unexpected increasing of $K_{IC}$ may be an artifact due to the low number of tests or the fracture mode of the material. As the silicon content increases, there is a more continuous grain boundary phase through which the crack tends to propagate. The crack path becomes more tortuous and thus the measured crack length is shorter than the real crack length.

The fracture toughness for the 400 grit composite is lower than that of the C-70 composite. Unlike the intergranular cracking in the C-70 material, the 400 grit composite exhibited transgranular cracking through the filler phase as seen in Figure 5.24. As the silicon content increases in the 400 grit composite, the fracture toughness decreases. As seen in Figure 5.25, the cracks propagated through the weaker regions of the silicon and intermetallic phases.

The cracks will propagate towards the metal inclusions as the metal is in tension and the surrounding matrix in compression.39 (See Figure 2.5) Cracks in all composites had aluminum ligaments bridging the crack faces. For the crack to propagate further, additional stress must be applied to deform the aluminum. Thus, the fracture toughness of the material is increased.
**Figure 5.24:** SEM micrograph of crack path in 400 10/2 composite showing transgranular cracking.

**Figure 5.25:** SEM micrograph of crack path in 400 10/2 composite through a) silicon and b) intermetallic regions.
5.4.3 Modulus of Rupture

Table 5.9 shows the MOR values obtained for the composites. During the testing of the material, the deflection of the bars was readily visible before fracture. The C-70 7/2 material had flaws from the impingement of two growth fronts. These flaws were located near the end of the bars. The bars broke at these defects, at a bending stress significantly lower than at the centre span. The composite body, however, did survive the indicated stress. The C-70 10/2 composite broke in the mid-section of the test span and appears to have a higher MOR. This may be due to the better growth characteristics of the parent alloy and hence better properties. The low value for the MOR, compared to the 400 grit composites, is due to the high porosity and the intergranular mode of fracture. The pores are defects and lower the thickness of the material bearing the load. The crack propagates through the grain/phase boundary which is mostly silicon, the weakest phase in the material.

For the 400 grit composite, the MOR is high. The composite has a much lower porosity, and the mode of fracture is different. The silicon is no longer present as a continuous grain boundary phase as in the C-70 material, but in discrete regions within the matrix. As the cracks take the path of least resistance, the weakest constituent in the composite would then be the 400 grit. Also, the 400 10/2 material has a
porosity of 2% whereas the 400 7/2 material has 5% porosity. Again, the alloy that gives the better growth characteristics gives the higher MOR, in spite of a higher metal content.

Table 5.9: Modulus of Rupture.

<table>
<thead>
<tr>
<th>Material</th>
<th>No.of Bars</th>
<th>MOR MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-70 7/2</td>
<td>2</td>
<td>112±34</td>
</tr>
<tr>
<td>C-70 10/2</td>
<td>2</td>
<td>130±24</td>
</tr>
<tr>
<td>400 7/2</td>
<td>4</td>
<td>225±24</td>
</tr>
<tr>
<td>400 10/2</td>
<td>7</td>
<td>250±28</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>300</td>
</tr>
<tr>
<td>Material A</td>
<td>-</td>
<td>350</td>
</tr>
</tbody>
</table>

The MOR for material A and the Durafrax® 1542 is reported for a three point bend test, which will give higher values than the four point bend test used here. The lower MOR for the Durafrax® 1542, compared to material A is due to its composition: 96% Al₂O₃ bonded with a silica based glass phase. The fracture mode is intergranular, similar to the C-70 composites above. Material A is stronger as the aluminum is able to plastically deform and blunt fracture initiating flaws. It is also worthy to note that material A contains no silicon.
5.4.4 Fractography

The fracture surfaces were mounted and examined by SEM. In all cases, the fracture initiated in porous regions, as shown in Figure 5.26. Comparing the surfaces for the C-70 composites, shown in Figure 5.27, the lower silicon composite has a larger number of chisel points than the higher silicon alloy. The regions between the pulled ligaments is flat and featureless. This would indicate that the lower silicon material has a higher fracture toughness, contrary to the indentation method above. The higher the silicon content, the more continuous the grain boundary phase. Subsequently, the crack avoids the aluminum regions that would otherwise toughen the material. Thus silicon should be kept to a minimum in the composite in order to obtain a tougher microstructure. However, a low silicon content in the starting alloy would result in poor infiltration behaviour.
Figure 5.26 a: Fracture Surface of C-70 10/2 composite. Fracture initiated at the porous region.

Figure 5.26 b: Fracture Surface of 400 7/2 Composite. Fracture initiated at the pore.
**Figure 5.27 a:** Fracture Surface of C-70 7/2 Composite. (Tensile edge) Ligaments noted by arrows.

**Figure 5.27 b:** Fracture Surface of C-70 10/2 Composite. (Tensile edge) Note the absence of ligaments.
A fracture surface of the 400 7/2 composite is shown in Figure 5.28. Transgranular, or cleavage, fracture is evident. There was not an even distribution of pulled ligaments over the fracture surface area of a bar. Thus, there is no readily discernable difference between the fracture surfaces of the two 400 grit composites. There are, however, fewer ligaments than for the C-70 composite, supporting the observation above that the 400 grit composite has a lower fracture toughness. The metal content is significantly higher than in the C-70 composite, but the crack front moves through the grit and through the intermetallic/silicon phase, again avoiding the aluminum regions.

Fracture toughness is improved by aluminum ligaments stretching between the crack faces. A contribution may also be made by the aluminum debonding from the Al₂O₃. An example is shown in Figure 5.29, where the aluminum debonding is visible.
Figure 5.28: Fracture Surface of 400 7/2 Composite. (Near tensile edge)

Figure 5.29: Fracture Surface of 400 10/2 Composite. Note debonding of aluminum ligament.
6. CONCLUSIONS

Ceramic metal composites were produced by the oxidation of molten aluminum-magnesium-silicon alloys into two types of alumina powder: C-70 UNG and 400 grit. The reaction temperature, alloy composition, and powder condition were optimized with respect to the growth process, final composition, and resulting microstructure. These characteristics were then related to the elasticity, strength, fracture toughness, and fracture mode of the final composite.

1. The alloy composition influenced the growth behaviour. Infiltration was improved by the use of alloys with low magnesium and high silicon contents. A low magnesium content reduces the spinel layer and a high silicon content improves the infiltration characteristics of the alloy. The composite was composed of aluminum, silicon, Al₂O₃, and some MgAl₂O₄. The aluminum content was found to increase with a decrease in the magnesium content in the starting alloy. The high silicon content in the starting alloy resulted in a high silicon content in the final composite.
2. Porosity in the first composites made with C-70 powder filler was high at 15%. Using an excess supply of metal reduced the porosity and increased the metal content of the composite. Breaking up the agglomerates in the C-70 powder further increased the metal content and produced a finer microstructure. The porosity, however, was not reduced by the milling of the C-70 powder.

3. The size of the filler particles determines the mode of fracture of the material. With C-70 filler, the fracture mode is intergranular as there is a continuous grain boundary phase through the material. With the 400 grit filler, the fracture mode was transgranular as the alumina grit contained the critical flaws.

4. The highest fracture toughness was attained with the 7% silicon, 2% magnesium alloy and C-70 filler. This material also had a low strength, roughly 100 MPa. The 400 grit material had a higher modulus of rupture, but a lower fracture toughness due to the transgranular mode of fracture. Silicon is indeed detrimental to the fracture toughness of the composite as the silicon segregated at the grain boundaries. The crack propagates through the silicon rather than the ductile aluminum phase and the fracture toughness is lowered.
5. Changing the filler material has a pronounced effect on the growth rate and the metal content of the composite. A 1cm C-70 bed was infiltrated in one day, whereas a 400 grit alumina bed of the same thickness was not infiltrated in $3\frac{1}{2}$ days. Impurities in the 400 filler material were leached out by the aluminum and influenced the crack propagation behaviour in the composite. They formed large intermetallic precipitates, on cooling, through which crack propagation occurred.
Chapter 7

7. FUTURE WORK

There are several areas for future work. Many have been suggested in the literature, but points specifically identified in this project are as follows:

a) An improvement in the growth rate by doping the surface of the growth with compounds such as Na₂O. This assumes that the rate controlling step is the diffusion of oxygen across the air/growth interface.

b) An investigation of the effects of the filler material. The size of the particulate had a profound effect on the growth kinetics and mechanical properties. The fracture toughness and strength of the composite may be readily controlled with respect to the particle size and purity.

c) The reduction of the silicon content of the composite. A reduced silicon content would increase the fracture toughness of the material. The problem to overcome is that the silicon is required for good infiltration behaviour.
d) The measurement of the oxidation rate as a function of the grit size and partial pressure of oxygen. This would determine the extent of oxygen diffusion as the rate controlling step. In addition, changes in oxidation rate with magnesium content and time may further an understanding of the role of alloying elements in breakaway oxidation.

e) A further study of the wetting characteristics of aluminum alloys at high temperatures on alumina of varying purity. This object would be to engineer a filler such that the infiltration process will take less time, the extent of oxidation would be lower, and the metal content in the composite would be increased.

f) Examination and characterization of the interfaces and aluminum phases by transmission electron microscopy. The purity of the grit effects the extent of reaction between itself and the melt. The existence of phases at the interface and precipitates within the aluminum may effect the mechanical properties of the composite.
8. REFERENCES


41. W. Köhler, "Untersuchungen zur Benetzung von Al\textsubscript{2}O\textsubscript{3}-und SiC-Kristallen durch Aluminium und Aluminiumlegierungen." Aluminium, 51 443-447 (1975).


Appendix A

DENSITY DETERMINATION

The following method, based on ASTM C 373-88, was used to determine the bulk density and apparent porosity of the composite materials. This method can also be used to determine the water absorption and apparent specific gravity of the composite.

The test pieces were cut from the main composite body, washed in distilled water, and dried in an oven at 120°C. The mass of the samples varied with the size of the main composite body, but the samples were in the range of 4 to 6 grams. The dry mass, $D$, was measured. The samples were then placed in a beaker, isolated from the walls and each other by glass beads, and boiled in distilled water for 3 hours. The heat source (a hot plate) was turned off and the beaker allowed to cool. The samples soaked for 18 to 20 hours after the heat was removed.

The mass, $S$, of the samples was measured in distilled water while suspended in a wire basket. The samples were then patted dry with a moist paper towel. Care was taken to ensure that water was not withdrawn from the pores of the sample. The saturated mass, $M$, was measured immediately after blotting to reduce errors due to evaporation of water from the sample.

In the following calculations, 1 cm$^3$ of water was taken to weigh 1 gram. The exterior volume, $V$, in cm$^3$, was calculated from:
The bulk density, \( B \), in g/cm\(^3\), is then calculated as the dry mass divided by the exterior volume:

\[
B = \frac{D}{V}
\]

The volume of pores open to the surface, \( V_{op} \), in cm\(^3\), was calculated from:

\[
V_{op} = M - D
\]

The apparent porosity, \( P \), as a percent, is the ratio of open pores to the exterior volume:

\[
P = \frac{V_{op}}{V} \times 100
\]

Other properties that can be calculated from the above measurements are the water absorption and the apparent specific gravity. The water absorption, \( A \), as a percent, is the ratio of the water absorbed to the dry mass:

\[
A = \frac{M - D}{D} \times 100
\]

The apparent specific gravity, \( T \), of the portion of the sample that is impervious to water is calculated from:
The reported accuracy of the ASTM standard is \( \pm 0.2\% \) of water absorption based on interlaboratory testing. The ASTM standard requires specimens of at least 50 grams, whereas the above method used samples of 4 to 6 grams. As this is the only significant difference in the two methods, the accuracy will be at least an order of magnitude larger and is thus taken to be \( \pm 5\% \).
Appendix B

COMPOSITION FROM EDS ANALYSIS

This method calculates the relative quantity of the three phases present in the composite material: Al₂O₃, aluminum, and silicon metals. The scanning electron microscope and detector were set with the following parameters:

**SEM**
- Accelerating Voltage: 10 kV
- Probe Current: 3×10⁻⁹
- Working Distance: 39mm
- Magnification 100X
- Objective Aperture: open
- Image: Backscatter

**Detector**
- Detector Position: 80 mm
- Window - Ultra-thin
- Low Energy Cutoff: 0.120 keV
- Acquisition Time: 60 seconds
- Dead Time: 40%

The program package used for the spectrum analysis is called "Standardless Quantification." Relevant features of the program are the peak identification (IDENT) and quantification (QUANT) routines. The IDENT routine identifies the elemental peaks based on the energy level of the x-rays detected. The QUANT routine can give the elemental composition or the oxide composition of the material. In the latter, the oxygen content is found by difference as the routine does not have the capability of quantifying oxygen in the sample. Thus, the problem in the analysis of the material is the inability to distinguish between aluminum metal and aluminum in Al₂O₃. This
can be solved by comparing the spectra from a sample to a known standard.

With the SEM and detector set at the above conditions, three spectra representing different areas on the surface were acquired. After each acquisition, the peaks were identified and raw peak areas were calculated. QUANT was then run to find the amounts of aluminum, silicon, sodium, and magnesium present in the composite. The spectrum of an Al₂O₃ standard was then taken under the same conditions. The IDENT and QUANT routines were run to find peak heights and the error in the Si, Na, and Mg quantities. A comparison of the Al:O ratios from the composite and the standard allowed the calculation of the amount of Al₂O₃ and aluminum metal.

The fraction of aluminum metal present, \( f_{Al} \), was found by taking the aluminum peak from the composite, \( C_{Al} \), and subtracting the counts due to Al in Al₂O₃, divided by the aluminum peak:

\[
\frac{C_{Al} - \left( \frac{Al}{O} \right)_{std} \times C_0}{C_{Al}} \]

The fraction of Al₂O₃ can be found from \( 1 - f_{Al} \), or the formula:

\[
\frac{C_0 \times \left( \frac{Al}{O} \right)_{std}}{C_{Al}} \]
The composition of the composite can now be determined using the information provided by the QUANT routine, namely the atomic percent of Al and Si. The quantities of other elements calculated, namely Na and Mg, had errors approaching 100%. Thus, the relative percentage of Al and Si was first determined. For example, the relative percentage of Al was calculated from the simple formula:

\[ P_{Al} = \frac{\% Al}{\% Al + \% Si} \]

Assuming 100 moles of composite material, the mass of Al\(_2\)O\(_3\) present was calculated from:

\[ M_{Al_2O_3} = \frac{P_{Al}}{2} \times f_{Al_2O_3} \times MW_{Al_2O_3} \]

where \( MW \) is the molecular weight. The percent Al above is divided by 2 as there are 2 moles of Al in one mole of Al\(_2\)O\(_3\). The mass of aluminum was calculated from:

\[ M_{Al} = P_{Al} \times f_{Al} \times MW_{Al} \]

The mass of silicon in 100 moles of composite material is simply:

\[ M_{Si} = P_{Si} \times MW_{Si} \]

The composition, expressed as weight percent, of a phase is
then the mass of that phase over the total mass.

The accuracy of this method can not be readily determined. The QUANT program uses a Z.A.F. algorithm; correcting the peak ratios for the atomic number, Z; absorption, A; and the fluorescence, F. For the Z.A.F. method to be accurate, the material must be homogeneous and flat on the microscale (~ 5 μm), which it is not. The microstructure is on the scale of microns and the surface is not flat due to pores and relief during polishing. The effect will not be alleviated by scanning over a large area. This method then cannot be used alone: the results from these calculations were used to prepare standards for quantitative X-ray diffraction.
Appendix C

XRD QUANTIFICATION

Standards were made to the compositions determined by the EDS quantification. The standards were made from the starting materials: C-70 alumina and the silicon flakes from AESAR. The aluminum used, however, was a powder from Fisher Scientific (A559-500). The powders were weighed and then milled in an alumina lined shatterbox to grind the silicon flakes and mix the powders. The milling time was short, 15 seconds, to prevent the aluminum and silicon from smearing on the surface of the shatterbox. The scan parameters for both the samples and the standards were identical. The scan was performed in two parts: the first to scan the region of the silicon (111) peak (I/I$_{i}=100$); the second to scan the region of the MgAl$_2$O$_4$ (311) peak (I/I$_{i}=100$), the Al$_2$O$_3$ (110) peak (I/I$_{i}=40$), and the Al (111) peak (I/I$_{i}=100$).

Table C.1: Scan Parameters for XRD

<table>
<thead>
<tr>
<th>Start Angle</th>
<th>Stop Angle</th>
<th>Step Size</th>
<th>Sample Time</th>
</tr>
</thead>
<tbody>
<tr>
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<td>30.0°</td>
<td>0.01°</td>
<td>1.00 Sec</td>
</tr>
<tr>
<td>36.0°</td>
<td>39.0°</td>
<td>0.01°</td>
<td>1.00 Sec</td>
</tr>
</tbody>
</table>

The silicon phase within the standard remained as small flakes which presented some problems during the scans: the powder was not homogeneous. This was partially alleviated by further grinding the standards with a mortar and pestle before scanning. The peak height of the silicon was measured to the
nearest 5 counts. The peak heights of the MgAl$_2$O$_4$, Al$_2$O$_3$, and aluminum were given by the peak identification program in the diffractometer system.

As the standards only went up to 10% aluminum, the calibration curves were plotted as the ratio, R(Al), of Al to Al$_2$O$_3$ peak height versus Percent Aluminum for different silicon contents. Conversely, the silicon calibration curves were plotted as the ratio, R(Si), of Si to Al$_2$O$_3$ peak height versus Percent Silicon for different aluminum contents. The values of R for aluminum and silicon are given in Table C.2.

**Table C.2: Standard Calibration**

<table>
<thead>
<tr>
<th>% Si</th>
<th>% Al</th>
<th>R(Al)</th>
<th>R(Si)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>4.01</td>
<td>34.68</td>
<td>50.29</td>
</tr>
<tr>
<td>2.00</td>
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<td>69.00</td>
</tr>
<tr>
<td>2.00</td>
<td>8.00</td>
<td>28.67</td>
<td>98.13</td>
</tr>
<tr>
<td>5.00</td>
<td>4.02</td>
<td>52.31</td>
<td>47.69</td>
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<td>8.00</td>
<td>4.01</td>
<td>130.95</td>
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<td>8.00</td>
<td>5.95</td>
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<tr>
<td>8.00</td>
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<td>70.98</td>
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<td>37.89</td>
</tr>
<tr>
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<td>9.99</td>
<td>7.37</td>
<td>103.79</td>
</tr>
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<td>70.66</td>
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<tr>
<td>8.00</td>
<td>2.01</td>
<td>118.99</td>
<td>21.05</td>
</tr>
</tbody>
</table>

From the scan of the composite, the two peak ratios are calculated. The composition is determined by first finding an
approximate Al content, then determining the corresponding Si content. The process is reiterated until there is no further significant change in the two metal contents.

As can be seen from the calibration curves, the Al/Al₂O₃ peak ratio is slightly affected by the silicon content. On the other hand, the Si/Al₂O₃ peak ratio is dramatically affected by the aluminum content. Thus the error in the aluminum content will be lower than the error in the silicon content. The accuracy of the aluminum content is taken to be ± 1%; for example, (6±1)%. The accuracy of the silicon content is taken to be ± 2%.
Figure C.1: XRD Calibration Curve For Aluminum.
Figure C.2: XRD Calibration Curve for Silicon.
Appendix D

THERMODYNAMIC CALCULATIONS

The Facility for the Analysis of Chemical Thermodynamics (F*A*C*T system) was used to perform the tedious calculations required to determine the equilibrium compositions. The F*A*C*T database contains heat capacity expressions for several stoichiometric compounds. These expressions are integrated to find values of various thermodynamic properties, such as the enthalpy, $\Delta H$, and entropy, $\Delta S$, of the compound relative to 298K. For a solution, F*A*C*T can easily calculate the ideal energy of mixing. The non-ideal behaviour must be provided by the user, either by providing the activity coefficients of the components in the solution or expressions for the excess energy of mixing, $\Delta G^E$, of the system. The expressions must be in a form acceptable to the F*A*C*T system.

The aluminum-magnesium-silicon system has been modelled and expressions for the $\Delta G^E$ are available. The Al-Mg-Si model has been built up from the binary data and modified with a ternary term. For the excess energy of the binary systems, the expression is in the form of a power series:

$$\Delta G^E = \sum X_i^n X_j^n (C_1 + C_2 T)$$

where $X_i$ and $X_j$ are the mole fraction of the components in the binary system, $M$ and $N$ are exponents and must be integers, $C_1$, and $C_2$.
is an excess enthalpy term, and $C_2$ is an excess entropy term. The excess energy is in units of Joules per mole. The values of the parameters for the Al-Mg, Al-Si, and Mg-Si systems are given in Table D.1.

<table>
<thead>
<tr>
<th>Table D.1: Binary Excess Energy Terms.</th>
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</thead>
<tbody>
<tr>
<td>System</td>
</tr>
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<td>--------------</td>
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<tr>
<td>Al-Mg</td>
</tr>
<tr>
<td>Al-Mg</td>
</tr>
<tr>
<td>Al-Mg</td>
</tr>
<tr>
<td>Al-Si</td>
</tr>
<tr>
<td>Al-Si</td>
</tr>
<tr>
<td>Al-Si</td>
</tr>
<tr>
<td>Al-Si</td>
</tr>
<tr>
<td>Mg-Si</td>
</tr>
<tr>
<td>Mg-Si</td>
</tr>
<tr>
<td>Mg-Si</td>
</tr>
<tr>
<td>Mg-Si</td>
</tr>
<tr>
<td>Mg-Si</td>
</tr>
</tbody>
</table>

The binary expressions are scaled in relation to the relative amounts of the components in the ternary. The ternary term is simply:

$$\Delta G^{E,\text{tern}} = X_{Al} X_{Mg} X_{Si} (45486.3 - 75*T)$$
## Equilibrium Calculations

### Chemical Species in F*A*C*T Database Used in Calculations

<table>
<thead>
<tr>
<th>Code</th>
<th>Species</th>
<th>Phase Code</th>
<th>Heat Capacity Range</th>
</tr>
</thead>
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<td>AR[+]</td>
<td>G1 GAS</td>
<td>298.0 K - 6000.0 K</td>
</tr>
<tr>
<td>2</td>
<td>AR</td>
<td>G1 GAS</td>
<td>298.0 K - 6000.0 K</td>
</tr>
<tr>
<td>3</td>
<td>SI*O</td>
<td>G1 GAS</td>
<td>298.0 K - 2000.0 K</td>
</tr>
<tr>
<td>4</td>
<td>SI3</td>
<td>G1 GAS</td>
<td>298.0 K - 3000.0 K</td>
</tr>
<tr>
<td>5</td>
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<td>298.0 K - 6000.0 K</td>
</tr>
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<td>8</td>
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Quasichemical model for molten oxides.

60 SI*O2
61 MG*O

AL-MG-SI SYSTEMS
(FROM LUDECKE - LIQUID PHASE ONLY)

1) Calculation to determine the stable oxide on 10/2 alloy at 1390 K

Chemical Reaction (in F*A*C*T notation)

0.88 AL + 0.1 SI + 0.02 MG + 0.02 AL2O3 + 0.002 O2 + AR

This reaction represents the 10/2 alloy with some small amount of oxide and oxygen in an inert (argon) atmosphere. The EQUILIB program determines the equilibrium composition at the temperature and pressure entered below.

************************************************************
T PROD P PROD V PROD DELTA H DELTA G DELTA S
(K) (ATM) (L) MAY SPECIFY IF SUBSCRIPTS PROVIDED
************************************************************
1390 1
ENTER CODE NUMBERS, ENTER "LIST" TO DISPLAY, OR ENTER "HELP"
****(CHANGES TO EQUILIB REQUIRE THE USE OF SLASHES ABOUT
GASEOUS SPECIES)***              These are the chemical species used
in determining the equilibrium
composition. The slashes around
species denote solution phases.

/1-27/62-64/55,56,58

0.88 Al + 0.1 Si + 0.02 Mg + 0.02 Al2O3 + 0.002 O2 + Ar

1.0018 moles  (gas phase)
             ( 0.99824  Ar
             + 0.17602E-02  Mg
             + 0.21718E-05  Al T
             + 0.37021E-06  Al2O
             + 0.51104E-10  Al2 T
             + 0.53172E-11  SiO
             + 0.46161E-13  Si
             + 0.14304E-14  AlO
             + 0.25258E-16  Al2O2
             + 0.22030E-20  Si2
             + 0.32451E-21  O
             + 0.23192E-23  AlO2
             + 0.23759E-25  Si3
             + 0.16265E-30  O2
             + 0.75119E-55  O3)  
             ( 1390.0, 1.00  ,G)

             + 0.99108 moles  (alloy)
             ( 0.89428  Al  <--S
             + 0.10090  Si  <--S
             + 0.48214E-02  Mg  <--S)
             ( 1390.0, 1.00  ,SOLN 2)

             + 0.13458E-01  (MgO)(Al2O3)
             ( 1390.0, 1.00  ,S1,  1.0000)

             + 0.33888E-02  Al2O3
             ( 1390.0, 1.00  ,S1,  1.0000)

             + 0.00000E+00  MgO
             ( 1390.0, 1.00  ,S1,0.39283E-01)

DATA ON 2 PRODUCT SPECIES IDENTIFIED WITH 'T' HAVE BEEN
EXTRAPOLATED
DATA ON 3 PRODUCT SPECIES IDENTIFIED WITH ' <--S' HAVE BEEN
DRAWN FROM YOUR PRIVATE DATA COLLECTION

The calculation gives the stable oxides as Al2O3 and
MgAl2O4. Note that the activity of MgO in this system is 0.039.
2) Calculation to determine the stable oxide on 7/5 alloy at 1390 K under same conditions above.

\[ 0.88 \text{ Al} + 0.07 \text{ Si} + 0.05 \text{ Mg} + 0.02 \text{ Al}_2\text{O}_3 + 0.002 \text{ O}_2 + \text{ Ar} \]

**T PROD P PROD V PROD DELTA H DELTA G DELTA S (K) (ATM) (L) MAY SPECIFY IF SUBSCRIPTS PROVIDED**

**1390 1**

ENTER CODE NUMBERS, ENTER "LIST" TO DISPLAY, OR ENTER "HELP"

****(CHANGES TO EQUILIB REQUIRE THE USE OF SLASHES ABOUT GASEOUS SPECIES)***

/1-27/62-64/55,56,58

\[ 0.88 \text{ Al} + 0.07 \text{ Si} + 0.05 \text{ Mg} + 0.02 \text{ Al}_2\text{O}_3 + 0.002 \text{ O}_2 + \text{ Ar} \]

| (gas phase) | (mol) | Species | T | S
|-------------|-------|---------|---|---
| 1.0113      |       | Ar      |   | 0.98885
|             |       | Mg      | T| 0.11144E-01
|             |       | Al      | T| 0.22264E-05
|             |       | Al\textsubscript{2}O\textsubscript{3} | | 0.24225E-06
|             |       | SiO     |   | 0.21312E-08
|             |       | Al\textsubscript{2} | T| 0.53707E-10
|             |       | Si      |   | 0.29715E-10
|             |       | Al\textsubscript{3}O\textsubscript{3} | | 0.91301E-15
|             |       | Mg      |   | 0.91290E-15
|             |       | Al\textsubscript{2}O\textsubscript{2} | | 0.10291E-16
|             |       | Si\textsubscript{3} |   | 0.63380E-17
|             |       | O     |   | 0.20205E-21
|             |       | Al\textsubscript{2}O\textsubscript{2} | | 0.92172E-24
|             |       | O\textsubscript{2} |   | 0.63056E-31
|             |       | O\textsubscript{3} |   | 0.18133E-55

+ 0.98073

| (mol) | Species | T | S
|-------|---------|---|---
| 0.90545 | Al |   | <--S
| 0.71376E-01 | Si |   | <--S
| 0.23177E-01 | Mg |   | <--S

(1390.0, 1.00, G)

+ 0.1600E-01 (MgO)(Al\textsubscript{2}O\textsubscript{3}) | (mol) | Species | T | S
|-------|---------|---|---
| 0.00000E+00 | Al\textsubscript{2}O\textsubscript{3} |   | 1.00000
| 0.00000E+00 | MgO |   | 0.25368

(1390.0, 1.00, S1, 0.15485)

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