WETTING AND PENETRATION OF MULLITE BY REACTIVE METALS

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Abstract

Interpenetrating phase Al_2O_3/Al composites can form by reacting molten aluminum with mullite by the following reaction:

$$3\ Al_6Si_2O_{13} + [8 + x]\ Al \rightarrow 13\ Al_2O_3 + [x]\ Al + (6\text{-}y)\ Si + (y)\ Si$$

To characterize this reaction, wetting and penetration studies were conducted at 1100-1500°C in flowing deoxidized Ar. The contact angle of an Al sessile drop on dense and porous mullite was measured as a function of time at temperature. For the contact angles of Al on dense mullite at 1100 and 1200°C, the calculated liquid-solid surface tension (γ_{SL}) compare favorably with the reported γ_{SL} of Al on Al_2O_3 substrates.

The level of Al penetration and composite formation was measured on samples sectioned perpendicular to the reaction interface after cooling. Composite microstructures were characterized by using optical microscopy and an electron microprobe. Aluminum was found to wet dense mullite between temperatures of 1100 to 1500°C. Porous mullite, however, was only wetted by Al at temperatures above 1350°C. The penetration rate for Al into dense mullite preforms was 3 mm/hr with the penetration into porous mullite preforms being slightly higher at approximately 4 mm/hr.

The effect of alloying Al with Mg was evaluated by conducting comparable experiments with Al-Mg alloys 6061 and 5052 on both dense and porous mullite. It was found that the Al-Mg alloys slowed down the change in contact angles for both dense and porous mullite. The Al-Mg alloys showed a decrease in penetration into the mullite, both dense and porous, with increasing Mg content in the alloys. An additional phase, a

MgAl spinel ($MgAl_2O_4$), was identified by x-ray diffraction in composites formed from the Al 5052 alloy containing 2.5 wt% Mg.

The amounts of ceramic and metal phase in the composites can be controlled by processing temperature and preform porosity. The grain size of the composite phases increases with increasing processing temperature. Lower preform densities produce more metal phase in the composite.

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Chapter 1

Introduction

Composites are materials made up of two or more phases which together improve the combination of physical properties of the original parent materials. [1-2] The reinforcement phase consisting of particles, fibers or different phases is stronger or tougher than the matrix material which yields to the improved properties. Strength, fracture toughness and density are just some of the improved properties that make composites attractive in many applications. Composite materials have been grouped into categories based on their matrix material consisting of polymer matrix composites (PMC), metal matrix composites (MMC) and ceramic matrix composites (CMC), which have existed for some time, but just recently have come into the spot light. For example, in MMC's, ceramic fibers are added to the metal matrix to strengthen and increase toughness. Similarly with ceramics, depending on the desired properties, ceramic fibers are added to a ceramic matrix to increase strength, or a metal phase is added to the ceramic matrix to improve the ductility and fracture toughness of the ceramic. The deficiencies of composites are in their fabrication. Many composites are expensive and difficult to product. But with the increased use of these composites in the aircraft, automobile, and leisure industries, just to name a few, the field of composite fabrication has grown to help solve the deficiencies of composite processing.

This thesis investigates the process for fabricating one of these ceramic matrix composites -- alumina/aluminum composites. The

objective of this research was to determine the controlling factors in the formation of alumina/aluminum composites by the reactive metal penetration (RMP) method. In reactive metal penetration, a ceramic preform (i.e. mullite) reacts with liquid metal (i.e. aluminum) to form a ceramic matrix composite. Because liquid metal must penetrate along the pores and/or grain boundaries as well as the ceramic grains, the investigation developed into studying the contact angle, reaction front and microstructure. The contact angle between the ceramic and the liquid metal depends on the surface tension. However, the contact angle measurements are complicated because interfacial reactions are also involved between the mullite and liquid metal. The reaction front or the penetration of the liquid into the mullite depends on the reactivity of the mullite with the liquid aluminum. The microstructure of the alumina/aluminum provides a clue for evaluating the extent of the reactions. The diffusion of the reacting species is complicated by the interfaces and pores through which Si and O must transfer. In the present study, mass transfer was considered secondary compared to the effects of the surface tension and reactivity along the metal/mullite interface. Hence, the focus of the research in this thesis is the surface reactivity and the microstructural features of the liquid metal penetrating the ceramic preform.

Chapter 2

Literature Review

2.1) Background about CMC (ceramic matrix composites)

Loehman et al. [3] reported on reactive metal penetration (RMP) for processing ceramic-metal composites which are near net-shape. The process consists of a liquid metal (e.g, aluminum) reacting with a ceramic (e.g, aluminosilicate) to form an alumina/aluminum composite according to Reaction 2.1.

$$3\ Al_6Si_2O_{13} + [8 + x]\ Al \rightarrow 13\ Al_2O_3 + [x]\ Al + 6\ Si \qquad (2.1)$$

They investigated the processing of composites formed from wetting studies, similar to those which will be discussed in this thesis, and by immersing a ceramic preform into molten aluminum. Composites were also formed by hot pressing mullite and aluminum powders. Dense mullite preforms were first used to form the composites [3-5] and then later porous preforms were also used in forming the Al_2O_3/Al composites [6]. The composites that were formed from either preform density produced dense composites of a 3-D network of interconnected ceramic and metal phases. The dense mullite reacted with Al developed approximately 15% metal phase and 85% ceramic phase in the composites upon completion of the reaction. [3-5] Similarly after the reaction with the porous mullite, the composites showed 49 to 50% metal phase in the composites. [6] The bend strength of the composites was approximately

250 MPa. The additions of the metal phase to the ceramic improve the fracture toughness to ≥ 6 MPa·√m compared to 2 MPa·√m for dense mullite without a decrease in strength.

Ceramic-metal composites can also be made by pressure infiltration in which liquid metal is pressurized into the ceramic preform. [7] The ceramic reinforcement is the most difficult part of the process because the spaces between the reinforcement (e.g, fibers and particles) and the metal change with application of the infiltration pressure. In addition, the reinforcement preforms must be evacuated before the metal can be pushed into the preform so gas pockets do not form in the composite, which would affect the properties.

Lanxide has patented a liquid-gas reaction process to produce ceramic-metal composites called the DIMOX™ or direct metal oxidation process. [8] In this process, molten metal is oxidized to form the composite. A preform is placed on top of a metal pool, and metal is drawn up into the preform where it oxidizes as it grows through the preform. Lanxide has used the process to form alumina/aluminum composites from aluminum and Al alloys as well as other ceramic-metal composites such as Zr reacting with boron carbide (BC) to form ZrB_2 & ZrC. [9-11]

Matsuo and Inaba [12] and Breslin, et al. [13-14] have produced composites by reacting amorphous silica and molten aluminum. Matsuo and Inaba [12] composites are made of a mutually interpenetrating structure of about 70 wt% alumina and about 30 wt% metal phase consisting of Al and Si. Their Al_2O_3/Al/Si composites were formed at temperatures between 900 and 1000°C. Breslin et al. [13-14] also reacted Al

with amorphous silica to form Al_2O_3/Al-Si composites. Both research groups reported improvements in bend strength and other physical properties for the Al_2O_3/Al/Si composites.

2.2) Wetting & Surface Energy

To form ceramic-metal composites, wetting of the metal on the ceramic preforms is desired. A method to study wetting involves a liquid bead on the solid substrate to form a sessile drop whose equilibrium shape is determined by a balance of surface energies. The contact angle (θ) is the angle formed between the solid/liquid interface and the tangent of the liquid/vapor interface that emanates from the triple point, as shown in Figure 2.1. For wetting, the energies must favor replacing liquid/vapor interfacial area with lower solid/liquid interfacial areas. If the contact angle is less than 90°, the liquid is in a state of partial wetting or the onset of wetting the surface. Complete wetting is when the contact angle is or approaches zero (0°). At this point the liquid spreads across the surface of the solid by spreading across the substrate. Similarly if the thermodynamics of the system favor creating solid/vapor interfacial area at the expense of the solid/liquid interfacial area the liquid is non-wetting (Figure 2.2). In the non-wetting case, the contact angle is greater than 90° and the liquid moves towards the equilibrium shape of a sphere. Pask and Tomisa [15] describe wetting as when the solid interfacial energy is lowered when in contact with a liquid and the surface will tend to be covered by the liquid. If the opposite case happens, when the solid interfacial energy is increased when in contact with the liquid, the solid/liquid area is

minimized and the solid is not wetted. When the liquid and solid are in equilibrium or a steady-state condition, Young's equation (Equation 2.2) can be used to express the effect of the interfacial energies on the contact angle.

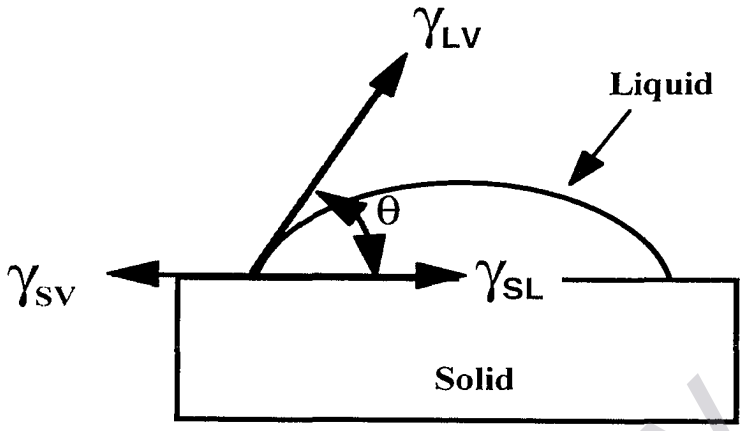
$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta \qquad (2.2)$$

The liquid surface tension (γ_{LV}) is controlled by the driving force for wetting ($\gamma_{SV} - \gamma_{SL}$). To lower the contact angle (θ) the interfacial energies in Young's equation can be manipulated. The lowering of γ_{LV} causes $(\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$ to increase, and thus a lower contact angle (θ). For the condition of $\theta < 90°$, or wetting, then γ_{SV} is greater than γ_{SL}. In a non-wetting condition for $\theta > 90°$, γ_{SV} is less than γ_{SL}. Therefore to lower the contact angle (θ) a high γ_{SV} and a low γ_{LV} are desired.

In the presence of a reaction between the liquid drop and substrate, Young's equation is modified to include the contribution of the free energy of reaction, which contributes to the driving force for wetting;

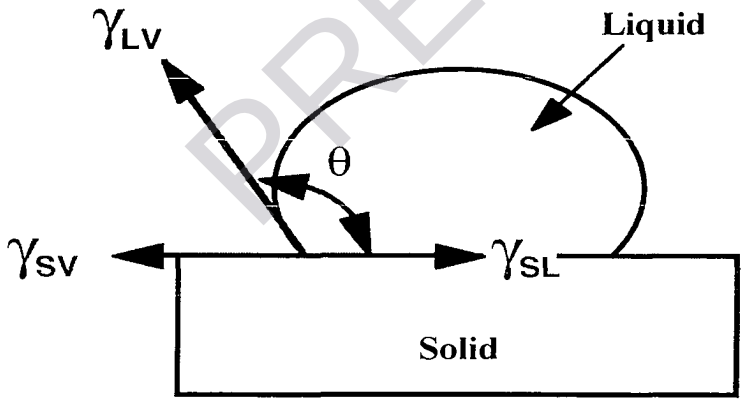
$$\gamma_{SV} - (\gamma_{SL} + \frac{\Delta G_R}{dA_s}) \geq \gamma_{LV}\cos\theta \qquad (2.3)$$

where A_s is the surface area of the drop and ΔG_R represents the Gibbs free energy of the reaction [15]. In the presence of a reaction the expansion of the liquid drop on the solid is defined as spreading. This spreading is related to the dynamic decrease in the contact angle. A reaction between the liquid and the solid can be enhanced by an increase in temperature.



$$\gamma_{SV} > \gamma_{SL} + \gamma_{LV}$$

Figure 2.1 Wetting of a solid by a liquid. [15]



$$\gamma_{SV} < \gamma_{SL} + \gamma_{LV}$$

Figure 2.2 Non-wetting of a solid by a liquid. [15]