CERAMIC-METAL COMPOSITE FORMATION BY REACTIVE METAL PENETRATION

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ABSTRACT

Ceramic-metal composites can be made to near-net-shape by reactive penetration of dense ceramic preforms by molten metals. Reactive metal penetration is driven by a strongly negative Gibbs energy for reaction. For Al, the general form of the reaction is $(x+2) \text{Al} + (3/y) \text{MO}_y \rightarrow \text{Al}_2\text{O}_3 + \text{M}_{3/y}\text{Al}_x$, where MO_y is an oxide that is wet by molten Al. In low PO_2 atmospheres and at temperatures above about 900°C , molten Al reduces mullite to produce Al_2O_3 and Si. The Al/mullite reaction has a $\Delta G_r^\circ(927^\circ\text{C})$ of -338 per mole of mullite and, for fully dense mullite, the theoretical volume change on reaction is less than 1%. Experiments with commercial mullite containing a silicate grain boundary phase average less than 2% volume change on reaction. In the Al/mullite system, reactive metal penetration produces a fine-grained alumina skeleton with an interspersed metal phase. With ≥ 15 vol.% excess aluminum, mutually interpenetrating ceramic-metal composites are produced. Properties measurements show that ceramic-metal composites produced by reactive metal penetration of mullite by Al have a Young's modulus and hardness similar to that of Al_2O_3 , with improved fracture toughness ranging from 4.5 to $10.5 \text{ MPa}\cdot\text{m}^{1/2}$.

Other compositions also are candidates for in-situ reaction synthesis, but they exhibit differences in reaction kinetics, most probably due to different wetting behavior. For example, Mg reacts with mullite to form multi-phase composites. These reactions occur at lower temperatures ($675^\circ\text{--}750^\circ\text{C}$) than those for Al/mullite ($1100^\circ\text{--}1500^\circ\text{C}$). In addition, Mg wets mullite more readily than does Al, and Mg more readily infiltrates porous ceramic preforms. The absence of a passivating oxide layer on Mg can account for this behavior.

1.0 INTRODUCTION

Ceramic-metal composites are being developed because they can exhibit combinations of properties that are unobtainable in single-phase materials, for example, high stiffness, high toughness and oxidation

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resistance combined in a single material (1). A number of processing routes are being studied for ceramic composites, including physical mixing of ceramic powders or whiskers in molten metals (1), metal infiltration of fibrous or porous ceramic preforms (2), in-situ reaction routes (3), in-situ oxidation of molten metals, (4, 5), and in-situ displacement reactions (6-9). The reactive forming techniques have a number of advantages, including the prospect of near-net-shape forming. In this paper we review the preparation and properties of composites formed by the process we call reactive metal penetration (6).

2.0 COMPOSITES BY MOLTEN METAL REACTION

2.1 Reactive Metal Penetration

Reactive Metal Penetration (RMP) forms ceramic-metal composites by reaction between oxide ceramics and molten metals such as Al and Mg. The two most important criteria that determine materials selection for RMP are: (1) the metal must wet the ceramic; and (2) the thermodynamics for reaction must be favorable. The RMP process is driven by a negative Gibbs energy for reaction and thus the candidate metals are those that are strong reducing agents for the oxides of interest. Wetting is required to form an interface so that the species will be close enough to react at useful rates. The result of the redox reaction typically is a composite microstructure of mixed metal and ceramic phases. Reaction can be by contact of a ceramic preform with a molten metal bath, or by heating mixtures of ceramic and metal powders. Compositions we have studied react relatively rapidly and composite reaction fronts penetrate dense ceramic preforms at rates approaching 5 mm/hr. The process occurs readily with dense ceramics under the appropriate conditions, and thus it is distinguished from other techniques involving capillary infiltration of porous materials.

2.2 Reactions and Thermodynamics

The general oxidation-reduction reaction to form the composite can be written as $(y + b) M + a AO_x \rightarrow M_yO_{ax} + M_bA_a$. Typical reactive metals are Al and Mg. Ceramics we have studied most extensively are aluminosilicates such as mullite and kaolinite. For reaction of Al with a generic oxide, the reaction can be written as $(y + 2) Al + 3/x AO_x \rightarrow Al_2O_3 + Al_yA_{3/x}$. The corresponding reaction with Mg can be written as $(y + x) Mg + AO_x \rightarrow x MgO + Mg_yA$. Gibbs energies for reaction of Al and Mg with mullite are presented in Table 1. Other ceramics and metals have been identified as candidates for RMP based on thermodynamic calculations and reaction experiments (6). The reactions in Table 1 have been verified experimentally by x-ray diffraction and electron microprobe analysis (6).

2.3 Wetting Behavior

RMP reactions of ceramics with molten Al require temperatures of 900 to 1500°C, which is well above the 660°C melting point of the metal. Wetting of ceramics by Al is limited by the tendency of the metal to form a passivating oxide layer by reaction with any available oxygen in the environment (10).

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Table 1: Gibbs Energies for Reaction of Molten Metals With Mullite

Reaction	Temperature, °C	ΔG°_R , kJ
$3 \text{ Al}_6\text{Si}_2\text{O}_{13} + 8 \text{ Al} \rightarrow 13 \text{ Al}_2\text{O}_3 + 3 \text{ Si}$ (1)	927	-1014
$\text{Al}_6\text{Si}_2\text{O}_{13} + 6 \text{ Mg} \rightarrow 2 \text{ MgSi} + 4 \text{ MgO} + 3 \text{ Al}_2\text{O}_3$ (2)	660	-695

The oxygen partial pressure in equilibrium with Al at 900°C is approximately 10^{-37} atm., so even very low PO_2 atmospheres are capable of forming an oxide surface layer. Such layers inhibit wetting of the ceramic by Al; thus, reaction rates are extremely slow unless the reaction temperature is $>900^\circ\text{C}$, where the oxide layer begins to break up. Another consequence of high wetting angles is that Al has to be heated to $\geq 1400^\circ\text{C}$ before it will spontaneously flow into porous ceramics by capillary infiltration (11). Figure 1 shows typical wetting behavior of Al on a dense, kaolinite-based aluminosilicate ceramic, that has the chemical formula $\text{Al}_2\text{Si}_2\text{O}_5$ after firing. Typical of reactive wetting systems, Al contact angle decreases with time at temperature on kaolin. Similar curves have been obtained for Al on mullite (6). At times less than ~15 min. and temperatures $\leq 1100^\circ\text{C}$ the Al contact angle on $\text{Al}_2\text{Si}_2\text{O}_5$ is greater than 90° (i.e., non-wetting), so a higher reaction temperatures is desirable for RMP composite formation.

Figure 1. The contact angle of molten aluminum on fired kaolin as a function time and temperature. Temperatures $\geq 1100^\circ\text{C}$ are required to achieve wetting (i.e., $\theta < 90^\circ$) and RMP composite formation.

Experiments with Mg, which is reactive but does not form a passivating oxide coating, provide a test of the importance of surface oxide layers to reaction. Our studies showed that Mg readily wets and spreads on oxide ceramics at temperatures just above its 649°C melting point. Figure 2 is a cross-section of a wetting experiment in which a sheet of Mg was heated between two pieces of mullite at 700°C for 30 min. in oxygen-gettered Ar. The upper piece was a fully dense mullite tube, whereas the lower piece was a cylinder of porous mullite with a relative density of 70%. The Mg wet and spread on both pieces of mullite, rising up the inner surface of the tube and infiltrating the pores of the lower cylinder. This behavior contrasts that of Al on mullite, where at 700-750°C, the contact angle is greater than 140°, there is no penetration of porous mullite by Al, and there is no reaction at the interface. The logical inference is that the surface oxide on Al controls its wetting and reaction behavior.

2.4 Microstructure and Mechanisms

Reactive metal penetration can produce ceramic-metal composites with a range of compositions. In the Al/mullite system, composite composition can be approximated by Reaction 3, where x accounts for the Al content in the final composite.

Figure 2. Wetting of mullite by Mg after 30 min. at 700°C. The dark region on the lower part is from Mg penetration of the porous mullite.

Reactive penetration also produces composites with a range of microstructures. In all of the cases we have studied, the ceramic phase in the composite is continuous in three dimensions. At the lower range of composite metal contents, as can be obtained by heating powder mixtures, the metal phase is observed to be dispersed in the continuous ceramic matrix. For higher metal contents typical of those obtained by reacting a ceramic preform with excess (i.e., $x > 0$) molten metal, both the metal and ceramic phases are co-continuous and mutually-interpenetrating (Figure 3).

A number of techniques, including SEM, TEM, x-ray diffraction, and energy dispersive spectroscopic analysis, show that the ceramic phase in the fully-reacted regions is Al_2O_3 , whereas the metal phase is predominantly Al with occasional inclusions of Si. Quantitative stereology measurements have been used to relate metal and ceramic volume fractions in the composite to particular processing conditions (12) and to develop process maps that allow us to obtain specific compositions and microstructures.

The mechanism(s) that control microstructure formation in these composites are not completely understood at present; however, a number of important facts are known (6). Wetting experiments show that there is an initial period, on the order of 5 min. at 1100°C , where there is no wetting or reaction between molten Al and mullite. After this induction period the Al begins to wet the mullite and penetrate the grain boundaries. TEM analysis of early stage reaction shows small Al_2O_3 precipitates surrounded by Al between the mullite grains (13). The reaction proceeds by reducing the mullite grains and forming a rigid Al_2O_3 skeleton that defines the overall shape of the composite.

Figure 3. A typical, interpenetrating phase composite microstructure formed by reacting Al with a dense mullite substrate at 1100°C for 2 hr. in oxygen-gettered Ar.

During the reaction, Al diffuses into the developing composite, and there is a counter current diffusion of Si out of the composite and into the surrounding Al bath. Experiments with Al-Si alloys showed that the reaction stops when the Al bath becomes saturated with Si. At the conclusion of a typical experiment with nominally pure Al and mullite, Al has replaced essentially all of the Si, and the Al in the composite contains ~1.5 at.% Si (i.e., the approximate solubility of Si in Al at the eutectic temperature of 577°C). The Al remaining in the surround bath is full of Si precipitates.

When the composite is made by heating powder mixtures, the Si produced on reducing the mullite remains in the composite; thus, the overall composition of the composite is set by the initial stoichiometry in Reaction 3. Reactive sintering of powders is useful for making precisely-defined composite compositions for property measurements; however, the Si contents in composites made in this manner are higher than in composites made by reacting a ceramic preform with molten Al. We recognize that the physical properties of the composite may be influenced by the Si content.

2.5 Net-Shape Reactions

One of our most interesting observations is that reactive metal penetration produces composites to near-net-shape for a wide range of processing conditions, aluminosilicate compositions, and relative densities of ceramic preforms. For example, for Reaction 1 in Table 1, the molar volumes (V_m) of mullite reactant and composite product(s) are nearly the same. The relevant values in cm^3/mol are: $\text{Al}_6\text{Si}_2\text{O}_{13}$ (135.26), Al (9.99), Al_2O_3 (25.62), and Si (12.00). The calculated volume change on completion of the reaction is $-0.72 \text{ cm}^3/\text{mole}$. The fractional volume change on reaction is given by:

$$\frac{\Delta V_m(\text{composite} - \text{mullite})}{V_m(\text{mullite})} = \frac{13 V_m(\text{Al}_2\text{O}_3) + 6 V_m(\text{Si}) - 3 V_m(\text{Al}_6\text{Si}_2\text{O}_{13})}{3 V_m(\text{Al}_6\text{Si}_2\text{O}_{13})} = -0.0018$$

Thus, based solely on molar volumes, Reaction 1 is net-shape to within 0.2 vol.%.

The volume change on reacting Al with aluminosilicate ceramics with different SiO_2 to Al_2O_3 ratios, such as kaolinite, sillimanite, or a ceramic with a silicate second phase, can be calculated in a similar way by assuming that the molar volumes of the aluminosilicate and silica phases in the preform are additive. Because Al reduces the silica part of aluminosilicate ceramics, the metal content in the composite is expected to increase with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the preform. Figure 4 is a plot of such a calculation. Our experimental observations are that reactions with a range of aluminosilicate compositions produce composite parts that differ in volume from the ceramic preforms by less than 2% (12).

With a controlled excess of Al such as obtained by reaction of metal and ceramic powder mixtures, RMP produces a composite of Al_2O_3 , Al, and Si whose molar volume depends on the specific x value in Reaction 3. Net-shape composites also can be obtained with $x > 0$ compositions by adjusting the porosity of the ceramic preform to accommodate the increased volume of Al present in the composite

Figure 4. Predicted metal content in an RMP composite as a function of the silica content in the ceramic preform.

For x excess moles of Al, the relative density, ρ_r , of the mullite preform required for no volume change on reaction is:

$$\frac{3 V_m(\text{Al}_6\text{Si}_2\text{O}_{13})}{13 V_m(\text{Al}_2\text{O}_3) + 6 V_m(\text{Si}) - x V_m(\text{Al})} = \frac{406.2}{405.5 + x}$$

The above equation assumes that the Al content of composites made by RMP of molten Al can be varied at will. However, our observations indicate that it is difficult to exceed ~30 vol.% Al in composites made by penetration of dense mullite preforms. If, as the TEM studies suggest, a rigid Al_2O_3 skeleton is formed before the RMP reactions are complete, the final Al content will be constrained by the geometry of the skeleton. Thus, composite formation will be an inherently near-net-shape process because the interconnected Al_2O_3 framework locks in the original preform shape before reaction is complete. Verifying that this explanation is correct will require further experiments.

2.6 Composite Properties

Physical and mechanical properties of ceramic-metal composites can vary significantly with metal content (6, 14, 15). For example, fracture toughnesses of an $\text{Al}_2\text{O}_3/\text{Al}$ composites formed by RMP range from 4.5 to 10.5 $\text{MPa}\cdot\text{m}^{1/2}$, and toughness increases with Al content (Figure 6). As anticipated, composite fracture toughness is also greater than that of the monolithic ceramic preform from which it was made.

Figure 5. Predicted composite metal content as a function of preform porosity for reaction of aluminum with mullite.

Figure 6. Fracture toughness of Al₂O₃ composites formed by RMP as compared to dense mullite.

The ceramic skeletal framework in RMP composites controls many of its physical properties such as hardness, modulus, and expansion coefficient. Like toughness, these properties also can be systematically controlled by controlling metal content (15). Thus, RMP provides a useful method for making application-tailored composites with desirable property combinations; for example, tough materials with high stiffness for automotive applications.

3.0 SUMMARY

At temperatures $>900^{\circ}\text{C}$, molten Al reduces aluminosilicate ceramics in-situ to produce Al_2O_3 and Si. The Al content of reactively-formed $\text{Al}_2\text{O}_3/\text{Al}$ composites can be varied systematically by controlling the silica content and/or porosity of the ceramic preform. In turn, composite properties are systematically determined by the Al content. Mutually interpenetrating ceramic-metal composites containing 15 - 55 vol.% metal have been produced to date.

Composites produced by in-situ reaction of Al with aluminosilicate ceramic preforms have improved mechanical properties and increased stiffness relative to the ceramic preform, and have desirable property combinations relative to pure Al_2O_3 or Al. A rigid alumina skeletal structure dominates such composite physical properties as Young's modulus, hardness, and coefficient of thermal expansion, while the interpenetrating ductile Al phase contributes to improved composite fracture toughness. Composite fracture toughness increases with increasing aluminum content.

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