SYNTHESIS AND PROCESSING OF COMPOSITES
BY REACTIVE METAL PENETRATION

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Abstract

When molten aluminum is placed in contact with a dense mullite preform it infiltrates the ceramic and converts it to a composite. Analysis showed that their composite consisted of a co-continuous network of Al₂O₃ ceramic and Al-Si alloy. Further work revealed that this technique is a general route to composite synthesis with the prospect for near-net-shape processing.

Generally, reactions between Al and oxides are of the form:

\[(2 + x) \text{Al} + (3/y) \text{MO}_y \rightarrow \text{Al}_2\text{O}_3 + \text{Al}_x\text{M}_{3/y} \]

(1)

where \(\text{MO}_y\) can be either a simple binary or complex oxide, and the residual metal phase can take a variety of forms as determined by the phase equilibrium relations of the given system. Reactive penetration has been found in a number of oxide-metal systems for which there is both favorable wetting of the oxide by the molten metal (i.e., contact angle \(\theta < 90^\circ\)) and a negative Gibbs energy for reaction.

In the Al/mullite system, molten aluminum reduces mullite to produce alumina and elemental silicon according to the reaction,

\[3 \text{Al}_6\text{Si}_2\text{O}_{13} + (8 + x) \text{Al} \rightarrow 13 \text{Al}_2\text{O}_3 + 6 \text{Si} + x \text{Al} \]

(2)

For the reaction with \(x=0\), \(\Delta G_r(1200K) = -1014 \text{ kJ}\) and \(\Delta G_r(1600K) = -828 \text{ kJ}\).

With excess aluminum present (i.e., \(x > 0\)), a composite of alumina, silicon, and aluminum is formed. When the mullite preform is in contact with a large external source of molten Al, the Si produced from the reaction diffuses outward into the Al source, leaving only a small concentration in the composite. Thus, the process naturally avoids leaving significant amounts of Si that could embrittle the composite.

Metal-ceramic composites have been produced by reactive penetration of dense and porous ceramic preforms with molten metal and by reactive sintering or hot pressing mixtures of ceramic and metal powders. Experimental results on different compositions of metal-ceramic reaction couples indicate that reactive metal penetration can be a general route to composite synthesis. Additionally, in many systems, reactive metal penetration affords near-net-shape forming capability. Because composite formation by reactive metal penetration appears to be a
diffusion controlled process with parabolic reaction kinetics at short times, metal-ceramic composite coatings can be made by controlling the penetration time.

Making composites with physical properties optimized for particular applications is one of the potential benefits of the reactive metal penetration process. For composites in the Al/Si/Al₂O₃ system, improvements in Young's modulus, fracture strength, density, hardness, fracture toughness, and specific modulus are apparent as compared with the pure mullite preform. The fracture toughness of reactively-formed metal-ceramic composites increases with increasing Al concentration, while modulus and density remain relatively constant, making it possible to make materials that are both tough and have a high specific modulus (i.e., modulus/density). Mechanical and physical property data, as well as microstructural evidence, indicate a three-dimensional, alumina skeletal structure is formed during reactive penetration. For higher Al concentrations the Al phase also is continuous, resulting in a composite with mutually-interpenetrating metal and ceramic phases. Results also indicate that, relative to the ceramic preform, the composites are more flaw tolerant; that is, the strength degradation from crack formation and propagation appears to be less severe in the metal-ceramic composite than in the mullite preform.

With further development, improvements in strength and fracture toughness can be expected.

Properties of Metal-Ceramic Composites Formed by Reactive Metal Penetration Compared to the Properties of the Ceramic Preform

<table>
<thead>
<tr>
<th>Property</th>
<th>Mullite</th>
<th>Al₂O₃-Al-Si Composite</th>
</tr>
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<tbody>
<tr>
<td>Bend Strength (MPa)</td>
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INTRODUCTION

Ceramic-metal composites are being developed as engineering materials because of their high stiffness-to-weight ratios, good fracture toughness, and because their electrical and thermal properties can be varied through control of their compositions and microstructures. Wider use of ceramic-metal composites requires improvements in synthesis and processing so that high-performance parts can be produced more economically. Over the past three years reactive metal penetration has been shown to be a promising technique for making ceramic and metal-matrix composites to near-net-shape with control of both composition and microstructure. It appears that reactive metal penetration could be an economical process for manufacturing many of the advanced ceramic composites that are needed for lightweight structural and wear applications for transportation and energy conversion devices. Near-net-shape fabrication of parts has the additional advantage that costly and energy intensive grinding and machining operations are significantly reduced, and the waste generated from such finishing operations is minimized.

The goals of this research and development program are: 1) to identify compositions favorable for making composites by reactive metal penetration; 2) to understand the mechanism(s) by which these composites are formed; and 3) to control and optimize the process so that composites and composite coatings can be made economically.

TECHNICAL PROGRESS: FY 1995

Summary

This work is based on the discovery by R.E. Loehman of SNL and A.P. Tomsia of Pask Research and Engineering that when molten aluminum is placed in contact with a dense mullite preform it infiltrates the ceramic and converts it to a composite. Analysis showed that their composite consisted of a co-continuous network of Al₂O₃ ceramic and Al-Si alloy. Further work revealed that this technique is a general route to composite synthesis with the prospect for near-net-shape processing.

Generally, reactions between Al and oxides are of the form;

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where $\text{MO}_y$ can be either a simple binary or complex oxide, and the residual metal phase can take a variety of forms as determined by the phase equilibrium relations of the given system. Reactive penetration has been shown to produce composites in a number of oxide-metal systems for which there is both favorable wetting of the oxide by the molten metal (i.e., contact angle $\theta < 90^\circ$) and a negative Gibbs energy for reaction.

In the Al/mullite system, molten aluminum reduces mullite to produce alumina and elemental silicon according to the reaction,

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For the reaction with $x=0$, $\Delta G_r(1200K) = -1014$ kJ and $\Delta G_r(1600K) = -828$ kJ. With excess aluminum present (i.e., $x > 0$), a composite of alumina, silicon, and aluminum is formed. When the mullite preform is in contact with a large external source of molten Al, the Si produced from the reaction diffuses outward into the Al source, leaving only a small concentration in the composite. Thus, the process naturally avoids leaving significant amounts of Si that could embrittle the composite.

Ceramic-metal composites have been produced by reactive penetration of dense and porous ceramic preforms with molten metal and by reactive sintering or hot pressing mixtures of ceramic and metal powders. Experimental results on different compositions of ceramic-metal reaction couples indicate that reactive metal penetration can be a general route to composite synthesis. Additionally, in many systems, reactive metal penetration affords near-net-shape forming capability. Ceramic-metal composite coatings can be made by controlling the penetration time.

Making composites with physical properties optimized for particular applications is one of the potential benefits of the reactive metal penetration process. For composites in the $\text{Al}_2\text{O}_3/\text{Al}/\text{Si}$ system, improvements in Young's modulus, fracture strength, density, hardness, fracture toughness, and specific modulus are apparent as compared with the pure mullite preform, as shown in Table 1. The fracture toughness of reactively-formed ceramic-metal composites increases with increasing Al concentration, while modulus and density remain relatively constant, making it possible to make materials that are both tough and have a high specific modulus (i.e., modulus/density).

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Mechanical and physical property data, as well as microstructural evidence, indicate a three-dimensional, alumina skeletal structure is formed during reactive penetration. For higher Al concentrations the Al phase also is continuous, resulting in a composite with mutually-interpenetrating metal and ceramic phases. Results also indicate that, relative to the ceramic preform, the composites are more flaw tolerant; that is, the strength degradation from crack formation and propagation appears to be less severe in the ceramic-metal composite than in the mullite preform. With further development, improvements in strength and fracture toughness can be expected.

Milestones:

Work this year has focused on Tasks 1, 2, 3, and 5 of the Field Work Proposal.

Task 1. Evaluate Mechanisms of Composite Formation in the Al/Mullite System

We have continued our experiments to understand the mechanism for reactive metal penetration. By combining TEM results on microstructural development with previously obtained thermodynamics and kinetic data, we have been able to develop a likely reaction mechanism for reactive metal penetration. As reported previously, the concentration of oxygen in the system (PO₂) during reaction plays a critical role. At 1200K, there is a large thermodynamic driving force for reaction (2) to proceed as written (i.e., ΔGᵢ = -1014 kJ). However, there is also a large thermodynamic driving force for reaction of aluminum with atmospheric oxygen to form alumina at 1200K (i.e., ΔGᵢ = -1163 kJ/mole). The Ellingham diagram for Al/Al₂O₃ indicates that Al and alumina will be in equilibrium at a PO₂ of 10⁻²⁸.₅ atm., which is a condition favorable for wetting. Thus, to limit Al oxidation by atmospheric oxygen and to ensure the Al/mullite reaction proceeds as written in reaction (2), a system PO₂ of ≤ 10⁻²⁸.₅ atmospheres is required. It seems likely that the molten Al itself acts as an O₂ getter during the reaction to reduce the PO₂ of the mullite grain boundaries to ≤ 10⁻²⁸.₅ atmospheres, which will make conditions favorable for wetting and reaction. The optically-visible reaction layer formed during partial penetration can be attributed to the localized oxygen deficiency and initial precipitation of metal particles at the grain boundaries. The time required to reduce grain boundary oxygen concentration to ≤ 10⁻²⁸.₅ atmospheres can explain the 5 - 10 minute delay in penetration at the start of an experiment. Finally, localized grain boundary reduction also explains the difference in penetration of dense and porous mullite preforms. It appears that, because oxygen diffusion through an interconnected pore structure is faster than along grain boundaries, it is more difficult to achieve a favorable PO₂ condition for wetting and reaction in a porous mullite body.

To characterize wetting and penetration in the Al/mullite system, sessile drop experiments were conducted with high purity, molten aluminum on dense mullite at 900, 1000, and 1100°C. Contact angles decrease with time at 900°C and above. Because of metal penetration and reaction, the molten Al drop decreases in volume during the experiment. The absence of a steady-state contact angle is indicative of an on-going chemical reaction. XRD analysis shows the infiltrated specimens contain Al₂O₃, Al, and, usually Si, demonstrating that
the reaction is the same whether the product is formed by reaction of mixed powders or by
penetration of Al into the dense ceramic. Sessile drop experiments conducted on nominally
100%, 99.5%, and 99% pure, dense mullite (with the remainder as SiO2) at 1100°C reveal no
significant differences in wetting behavior with minor compositional variations in the ceramic
preform. Wetting (i.e., 0 < 90°) is not observed at 900°C and it occurs only after ~30 minutes at
1000°C in the Al/mullite system. Aluminum penetration and composite formation are sluggish
below ~1000°C, indicating that both wetting and a negative Gibbs energy of reaction are required
to make ceramic-metal composites by reactive metal penetration.

To more quantitatively determine the kinetics of ceramic-metal composite formation in
the Al/mullite system, an apparatus was designed and constructed for making ceramic-metal
composites by controlled dipping of ceramic preforms in molten aluminum. Reaction times were
accurately controlled by dipping a dense ceramic preform into molten aluminum at 900-1500°C
for a prescribed time, and then removing it. The reacted samples were sectioned, and the
thickness of the composite layer formed was measured by optical microscopy. There is a 5-10
min. induction time for Al penetration and reaction with mullite. The rate of ceramic-metal
composite formation in the Al/mullite system is proportional to the square root of time for short
reaction times (<1 hr) and is linearly proportional to time for longer reaction times. As expected,
composite formation rate also increases with temperature up to 1150°C but then exhibits a
surprising decrease with increasing temperature between 1150 and 1500°C. The exact
temperature of the maximum rate of composite formation depends on the preform density.
Based on the measured penetration distances at given times for different temperatures, an
activation energy for composite formation of ~200 kJ/mole was calculated. Although the exact
mechanism has yet to be determined, the rate controlling step for reactive metal penetration
appears to be the interface reaction.

Scanning and transmission electron microscopic analysis of Al/mullite reaction couples
revealed that silicon diffuses out of the mullite ceramic during reactive metal penetration. This
observation is also supported by X-ray diffraction analysis and scanning electron microscopy
with electron dispersive spectroscopy, which indicated that composites produced by reacting
aluminum with mullite are silicon deficient.

In summary, TEM, thermodynamic, and kinetic analyses suggest the following 4-stage
reaction mechanism for reactive metal penetration: 1) the metal melts and wets the ceramic
preform surface; 2) oxygen diffuses out of the ceramic preform grain boundaries to lower the PO2
to a favorable wetting condition; 3) molten metal penetrates the ceramic preform grain
boundaries; and 4) the metal on the grain boundaries reacts with and reduces the individual grains
of the ceramic preform.

Impact: By evaluating reactions to understand the mechanisms of composite formation by
reactive metal penetration, we are establishing guidelines to control composite formation, and to
control the structure and properties of composites formed by reactive metal penetration. These
guidelines will be the basis for developing a commercial process for manufacturing ceramic-metal
composites with tailored properties.

Task 2. Evaluate Other Ceramic-metal Systems

As discussed briefly above, the reactions other than Al/mullite that may produce ceramic-
metal composites by reactive metal penetration include:
We, as well as others, have proposed that refractory ceramic-metal composites can be synthesized in-situ in the Al/TiO₂ and Al/NiO systems according to the reactions listed above. Ti or Ni formation is predicted when x = 0 in the third and fourth reactions above. For x = 1, TiAl or NiAl formation is expected. According to equilibrium thermodynamics, when Al reacts with TiO₂ or NiO, the reactions proceed as written above. However, little is known about the kinetics or microstructural mechanisms of the reactions between Al and either TiO₂ or NiO. Likewise, the possibility of using these reactions to form refractory ceramic-metal composites by melt penetration or reactive hot pressing has not been explored in detail.

The contact angle of Al on TiO₂ was determined as a function of temperature. Figure 1 shows that the contact angle decreases as temperature increases from 1000°C to 1400°C. At 1200°C the contact angle approaches 90° while at 1400°C it reaches 80°, indicating that aluminum partially wets the ceramic. After an equilibration time of less than 10 minutes, the contact angle varies little with time, indicating no further significant reaction at the interface. Figure 2 shows the cross-section of an Al drop on TiO₂ after heating at 1400°C for 75 minutes. No reaction layer was observed for any of the Al/TiO₂ reaction couples, indicating that reactive metal penetration of TiO₂ by Al does not occur under these conditions. Despite not forming a discernible reaction layer, the Al drop strongly adhered to the surface of the substrate. This was true even for contact angles above 90°.

No contact angles were observed for Al on NiO because the aluminum did not become fluid enough to form a uniform sessile drop. Apparently, contact with Al reduced the NiO substrate, and then, due to reaction with the oxygen liberated during the NiO reduction, a thick, stable oxide layer formed on the Al drop during the wetting experiment. The Al, however, did penetrate and react with the NiO. As shown in Figure 3, an appreciable reaction layer developed during the 1400°C contact angle experiment. Samples heated at 1000°C, 1100°C, and 1200°C also showed distinct reaction zones, though penetration depth decreased slightly with decreasing reaction temperature. The reaction layer at the ceramic-metal interface shows that reactive metal penetration is possible in the Al/NiO system; however, much more work needs to be done to develop sufficient understanding for process control.

Al/TiO₂ and Al/NiO powder mixtures were reactively hot-pressed at 1200-1300°C and 34.5 MPa (5000 psi) for 1/2 hr in graphite dies. A compositionally homogeneous, but porous composite of Al₂O₃ and Ti was produced by hot pressing an Al/TiO₂ powder mixture containing x = 0 Al at 1200°C. Preliminary results indicate that it may be possible to produce a dense composite with a higher hot-pressing temperature.

A phase-segregated composite consisting of a central metallic core surrounded by a ceramic shell was produced by reactively hot pressing Al/NiO powder mixtures containing x = 0 and x = 1 Al at 1200°C and 1300°C. X-ray diffraction analysis showed that the metallic core was Ni and NiAl for the x = 0 and x = 1 samples, respectively. The ceramic shell was Al₂O₃ in both cases. The phase segregation of the ceramic and metal phases indicates poor wetting of the Al₂O₃ by the metallic and intermetallic reaction products. A temperature/pressure program was
designed to minimize phase segregation and produce a more favorable condition for wetting so that interpenetrating ceramic-metal composite microstructures can form.

The extension of reactive metal penetration and reactive hot pressing to systems that form alumina-intermetallic composites allows for the preparation of novel composites for a variety of high temperature applications. The advantages of these techniques over existing technology include lower raw material and fabrication costs and a finer-scale, interpenetrating microstructure.

![Al Contact Angle on TiO₂](image)

**Figure 1.** Contact angle as a function of time for Al in contact with TiO₂ at 1000°C, 1100°C, 1200°C, and 1400°C.

![Optical micrograph](image)

**Figure 2.** Optical micrograph of the cross-section of an aluminum drop on TiO₂ after heat treatment at 1400°C for 75 minutes, note the absence of a reaction layer.
Cost is perhaps the most important factor in determining the commercial potential of new materials. Advanced composites may offer marked improvement in performance and reliability, but any increase in cost as compared to traditional materials usually prevents significant market penetration. One potential barrier to commercialization that so far has not been addressed in detail in our program is that of raw material cost. Due to the availability, purity, and batch-to-batch consistency of mullite powder as compared to other aluminosilicates, the majority of our work on reactive metal penetration has been carried out using phase-pure mullite preforms. The absence of second phases and trace impurities greatly simplifies the study of reaction mechanism and kinetics as well as the volume and mass balance calculations and thermodynamic predictions. Typically, phase-pure mullite powder sells for $25/kg. In a previous technical advance, SD5484 at Sandia, we discussed the advantages of using kaolin, $0.10/kg, as a low-cost alternative to mullite.

As with the Al/mullite reaction, initiating the Al/kaolin reaction depends on first forming a ceramic-metal interface. Recent results show that aluminum wets dense kaolin better than mullite, as indicated by a reduced contact angle. The lower contact angle should produce a more uniform ceramic-metal interface and, therefore, a more stable reaction front as the metal reacts with and penetrates into the preform. One indication that the Al/kaolin reaction is kinetically more favorable is that complex shapes are more easily formed from kaolin preforms as compared to mullite. For porous preforms, aluminum must physically infiltrate the pores prior to reaction with the matrix. In this case, the reduced contact angle in the Al/kaolin system means that physical infiltration of the pores can proceed at much lower temperatures than in the Al/mullite system.

Kaolin, \(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\cdot2\text{H}_2\text{O}\), dehydrates to meta-kaolin, \(\text{Al}_2\text{Si}_2\text{O}_7\), when heated to 800°C. When heated to the sintering temperature, crystalline mullite, \(\text{Al}_6\text{Si}_2\text{O}_{13}\), nucleates and grows within a glassy matrix. A fired kaolin preform is similar to a mullite preform but with a continuous glassy grain boundary phase. The sequential conversion of kaolin to meta-kaolin and then to mullite/silica is detailed in Reactions 3 and 4.
Fired kaolin preforms react with aluminum in much the same way as does phase-pure mullite. The reaction is near-net-shape and silicon diffuses away from the reaction front and out of the preform/composite, to produce an Al$_2$O$_3$/Al composite. Due to the higher silica content of the preform, composites prepared from kaolin preforms contain more aluminum than those prepared from mullite. The Al/kaolin reaction can be represented as the reaction of aluminum with mullite and silica:

\[(8 + x) \text{Al} + \text{Al}_6\text{Si}_2\text{O}_{13} + 4 \text{SiO}_2 \rightarrow 7 \text{Al}_2\text{O}_3 + 6 \text{Si} + x \text{Al}\]  

Mass and volume balance equations show that stoichiometric reaction of dense kaolin with aluminum produces a composite that contains approximately 30 vol.% Al and 70 vol.% Al$_2$O$_3$. This corresponds to an x value of \( \sim 7 \) in Reaction 5. The predicted composite density is 3.62 g/cm$^3$.

As in the Al/mullite reaction, aluminum reacts with porous kaolin to produce dense ceramic-metal composites through a combination of physical infiltration and reactive penetration. Kaolin preforms fired at 1100°C for 3 hours are \( \sim 61\% \) of theoretical density. After reaction with aluminum, the resulting composite contains 56 vol.% Al, 13 vol.% Si, and 31 vol.% Al$_2$O$_3$. The predicted composite density is 3.05 g/cm$^3$. The volume and density calculations for reaction of aluminum with dense and porous kaolin are summarized and compared to mullite in Table 2.

<table>
<thead>
<tr>
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<th>Dense Mullite</th>
<th>Porous Mullite</th>
<th>Dense Kaolin</th>
<th>Porous Kaolin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al Content (vol.%)</td>
<td>17</td>
<td>54</td>
<td>28</td>
<td>56</td>
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<tr>
<td>Density (g/cm$^3$)</td>
<td>3.75</td>
<td>3.15</td>
<td>3.62</td>
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Figures 4 and 5 plot the contact angle of aluminum as a function of temperature on dense and porous kaolin, respectively. As shown in Figure 4, the contact angle for aluminum on dense kaolin generally decreases with increasing time and temperature, except at 1100°C. At 1100°C, the aluminum drop rapidly penetrates the preform, indicating a maximum in reaction rate near this temperature. Increased reaction is often accompanied by a decreased contact angle. For aluminum on dense kaolin at T \( \geq \)1100°C, the contact angle is less than 90°, indicating partial wetting. In comparison, the aluminum contact angle on mullite between 1100 and 1400°C is around 140°. The implication is that aluminum forms a stable interface more rapidly with kaolin than with mullite.
The contact angle of aluminum on kaolin increases with increasing preform porosity. Figure 5 shows that the contact angle of aluminum on kaolin containing 39 vol.% porosity (61% dense) is significantly higher than on dense kaolin. As with dense kaolin, the contact angle decreases with increasing temperature except at 1100°C. At 1100°C, aluminum only partially wets porous kaolin, but it rapidly infiltrates the preform and completely within 30 minutes. For porous mullite, the aluminum contact angle is $\sim 140^\circ$ at 1100°C, with no penetration or reaction. A temperature of at least 1500°C is required for aluminum to wet and infiltrate porous mullite.
The 400°C reduction in processing temperature using a kaolin preform will result in significant energy savings during processing, as well as a process more favorable for commercialization. It is curious that wetting and penetration are best at 1100°C for both dense and porous kaolin. Generally, contact angle decreases with increasing temperature. The fact that contact angle increases above 1100°C for both dense and porous kaolin may be due the formation of a reaction layer between aluminum and kaolin above 1100°C. Further study is required to determine why 1100°C is such a favorable temperature.

**Impact:** The discovery that kaolin can be used as a raw material may have enormous impact on the commercialization of ceramic-metal composites. Kaolin, the main mineral constituent of common clay, is a low-cost raw material that is available in nearly unlimited quantities. The ceramic industry prepares huge quantities of clay-based products at a nominal cost per piece. In raw material cost alone, there is nearly a three order-of-magnitude savings for kaolin as compared to mullite, with additional savings due to the fact that kaolin is easier to handle, requires fewer organic processing aids, and requires lower firing temperatures. Combined with the ease of conversion from preform to ceramic-metal composite, the low raw material and processing costs suggest that Al₂O₃/Al composites will be cost-competitive with traditional materials, while offering superior strength and fracture toughness. We are extremely excited about the potential of the Al/kaolin reaction system and are actively pursuing its development.

**Task 3. Assess Near-Net Shape Formation by Reactive Metal Penetration**

Reaction of Al with mullite can be written as stated in Reaction 2 in the Summary section. The change in volume, ΔV, on reaction can be calculated from the molar volumes, Vₘ, of reactants and products. In the Al/mullite system, the relevant values in cm³/mol are: Al₆Si₂O₁₃ (135.26), Al (9.99), Al₂O₃ (25.62), and Si (12.00). For the above reaction, assuming x = 0 and a dense mullite preform, the predicted volume change after Al penetration, ΔV, is -0.72 cm³/mole. The fractional volume change on reaction, as calculated below, is -0.0018.

\[
\frac{\Delta V}{3V_{m(Al_6Si_2O_{13})}} = \frac{13V_{m(Al_2O_3)} + 6V_{m(Si)} - 3V_{m(Al_6Si_2O_{13})}}{3V_{m(Al_6Si_2O_{13})}} = -0.0018
\]

The volume change on reacting Al with commercial mullite-SiO₂ ceramics can be calculated in a similar way by assuming that the molar volumes of the mullite and silica phases in the preform are additive.

With excess Al (i.e., x > 0), reactive metal penetration produces a composite of Al₂O₃, Al, and Si whose molar volume depends on the x value in Reaction 2. 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 after reaction. For x excess moles of Al, the relative density, \(\rho_r\), of the mullite preform required for no volume change on reaction is

\[
\frac{3V_{m(Al_6Si_2O_{13})}}{13V_{m(Al_2O_3)} + 6V_{m(Si)} - xV_{m(Al)}} = \frac{40.62}{40.55 + x}
\]
The aluminum content of ceramic-metal composites prepared by reactive metal penetration of dense preforms is controlled by the silica to alumina ratio of the preform. The predicted aluminum content of the composite as a function of the silica content of the preform is given in Figure 6. This model has been validated by reacting dense aluminosilicate preforms with 28 to 50 wt.% silica and then determining metal content by quantitative stereology and density measurements. Some of the preform compositions tested and their corresponding composite metal contents are shown in Figure 6. By calculation, the upper limit of metal content for reacting a dense silica preform with Al is ~40 vol.%; however, experimentally, 35 vol.% was found to be the upper limit.

![Figure 6. Predicted composite metal content as a function of preform silica content.](image)

Reaction of porous preforms was explored in order to produce composites with higher metal content. Aluminum physically infiltrates the pores of porous mullite preforms and then reacts with the ceramic matrix. The predicted composite metal content increases as the porosity of the preform increases, as shown in Figure 7. This calculation assumes that the reaction is net-shape and that the pores are completely filled with metal. The bulk of our experimental work has been carried out with mullite preforms of 62% relative density, which produce composites that contain 55 vol.% metal. Examination of composite cross-sections by scanning electron microscopy shows that much of the silicon generated during reaction is retained in the composite. This case contrasts with reactive metal penetration of dense preforms in which the silicon diffuses out of the composite during processing.

**Impact:** The ability to react porous preforms allows us to prepare ceramic-metal composites with controlled metal content, ranging from near 0 to 55 volume percent. This compositional flexibility
will allow the design of composites with properties tailored to specific applications. The compositional range demonstrated for reactive metal penetration is far greater than for other reactive forming techniques used to prepare ceramic-metal composites.

![Graph showing the predicted composite metal content as a function of preform porosity for reaction of aluminum with mullite.](image)

**Figure 7.** Predicted composite metal content as a function of preform porosity for reaction of aluminum with mullite.

**Task 5. Evaluate Ceramic-metal Composite Microstructure and Properties.**

The average four-point bend strength for composites with 55 vol.% metal is ~300 MPa, and the Young's modulus is 160 GPa. The strengths of these high metal-content composites are comparable to those of other, lower metal-content composites prepared by reactive metal penetration of dense preforms. The strength is impressive for a composite with such a high metal content, and is attributed to the continuous alumina skeleton. The modulus is significantly lower than the lower metal content composites due to the increased size of the metal ligaments. The increased connectivity of the metal phase can be seen when comparing the fracture surface of a composite containing 55 vol.% metal to one with a lower metal content, as shown in Figure 8. The metal phase is continuous on the fracture surface of the higher metal content composite whereas isolated metal ligaments are seen in the 25 vol.% metal material. In both microstructures, knife-edging is evident, indicating that the toughness of these composites is enhanced by ductile metal toughening. A toughness as high as 9.0 ± 1.1 has been calculated from work of rupture measurements on ceramic-metal composites containing 30 vol.% Al. Work is in progress to determine more precise toughness values for both types of composite.
The wear properties of a ceramic-metal composite prepared by reactive hot pressing were evaluated by the U.S. Bureau of Mines. The composite was found to have a wear rate of $1.94 \times 10^{-3}$ mm$^3$/N*m, which is slightly less than the values for alumina and silicon nitride. Additionally, the reactively-formed ceramic-metal composite exhibits less brittle microfracture on the abraded surface. These are very positive results since many of our proposed applications require good abrasion resistance.

**Impact:** We have established a property data base for ceramic-metal composites prepared by reactive metal penetration that will be useful for making comparisons to composites formed by other techniques. The property data base also will be useful in demonstrating the versatility of the reactive metal penetration process for making composites for commercial application.

**PUBLICATIONS AND PRESENTATIONS (1/1/95 - 12/1/95)**

**Journals**


Proceedings


Presentations


HONORS AND AWARDS

None this reporting period

PATENTS/DISCLOSURES

None this reporting period

LICENSES

None this reporting period

INDUSTRIAL INPUT, TECHNOLOGY TRANSFER, AND OTHER INTERACTIONS

Collaboration with other researchers

We are continuing our collaboration with A.P. Tomsia of Pask Research and Engineering. Dr. Tomsia is the co-discoverer of reactive metal penetration and is contributing significantly to
its understanding and development. Dr. Eduardo Saiz is a visiting scientist working with Dr. Tomasia on the project, supported by Pask Research and Engineering. Dr. Y. Gao of Pacific Northwest Laboratories has continued to collaborate on TEM analysis of composites formed by reactive metal penetration. Professor Ping Lu of New Mexico Institute of Mining and Technology is also providing TEM analysis of reaction zones, supported on a subcontract to the project. Bala Lakshman is a graduate student at the University of New Mexico who is doing a Master’s thesis on reactive metal penetration under the direction of Dr. Ronald Loehman. Professor Raj Bordia of the University of Washington provided a graduate student to work on the project during the summer of 1995 at the Advanced Materials Laboratory and throughout the year at U. WA. One of UT (El Paso) Professor Art Bronson’s graduate students is working on the project as a co-op student for his MS thesis. We also continued our collaboration with researchers at the U.S. Bureau of Mines to study the wear properties of ceramic-metal composites made by reactive metal penetration. Additionally, John Kaniuk Of Zircoa, Inc. Conducted corrosion tests this year on some of our high metal content composites.

COST-SHARING

Pask Research and Engineering is contributing significant research output at no cost to the project. Pask R&E values their contributions at ~$40,000 in direct salary costs for the staff time devoted to the project. Graduate students working on the project with support from their home institutions (U. WA and UT, El Paso) accounted for an additional ~$50,000 of support for the program. Work conducted at the U.S. Bureau of Mines has an estimated value (in direct salary costs) of ~$10,000.

HIGHLIGHTS

The discovery that kaolin can be used as a raw material for the preparation of ceramic-metal composites may have enormous impact on the commercialization of such materials. Kaolin, the main mineral constituent of common clay, is a low-cost raw material that is available in nearly unlimited quantities. In raw material cost alone, there is nearly a three order-of-magnitude savings for kaolin as compared to mullite, with additional savings from the fact that kaolin is easier to handle, requires fewer organic processing aids, and requires lower firing temperatures. The reaction of Al with kaolin is similar to that with mullite, except that kaolin has a higher silica content, which is reflected in the reaction product:

\[(8 + x) \text{Al} + \text{Al}_6\text{Si}_2\text{O}_{13} + 4 \text{SiO}_2 \rightarrow 7 \text{Al}_2\text{O}_3 + 6 \text{Si} + x \text{Al}.\]

Thus, kaolin can produce composites with higher Al contents than does mullite, which extends the range of available metal contents using dense preforms. The ease of conversion from preform to ceramic-metal composite and the lower raw material and processing costs using kaolin suggest that Al/Al_2O_3 composites will be cost-competitive with traditional materials, while offering superior strength and fracture toughness.
Significant Accomplishment

Reactive Penetration Process Produces Ceramic-Metal Composites to Net-Shape Using Low-Cost Raw Materials

Problem
Ceramic-metal composites are candidate materials for advanced structures and components because of their high stiffness-to-weight ratios and excellent fracture toughness. However, their raw materials costs can be high and they generally are expensive to make in finished shapes.

Results:
Reactive metal penetration, the process by which a reactive metal penetrates a dense ceramic preform and converts it to a ceramic-metal composite, appears to be an inherently net-shape process. In the Al/mullite system the molar volumes of reactants and products are such that the stoichiometric reaction exhibits no net change in volume. However, even off-stoichiometry reactions are found to have less than a 2% volume change from reactants to products. The reason seems to be a reaction mechanism in which the dense ceramic preform maintains the overall shape of the part while the reaction proceeds.

Recently it was discovered that kaolin can be used as the ceramic preform for these reactively-formed composites. The reaction of Al with kaolin is similar to that with mullite, except that kaolin has a higher silica content, which is reflected in the reaction product:

\[(8 + x) \text{Al} + \text{Al}_6\text{Si}_2\text{O}_{13} + 4 \text{SiO}_2 \to 7 \text{Al}_2\text{O}_3 + 6 \text{Si} + x \text{Al} \]

Wetting and penetration of kaolin by Al is as favorable as with mullite. Kaolin can produce composites with higher Al contents than does mullite, which extends the range of available metal contents using dense preforms.

Contact angle of aluminum on dense kaolin.

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Significance
The discovery that kaolin can be used as a raw material for the preparation of ceramic-metal composites may have enormous impact on the commercialization of such materials. Kaolin, the main mineral constituent of common clay, is a low-cost raw material that is available in nearly unlimited quantities. In raw material cost alone, there is nearly a three order-of-magnitude savings for kaolin as compared to mullite, with additional savings due to the fact that kaolin is easier to handle, requires fewer organic processing aids, and requires lower firing temperatures than does mullite, which extends the range of available metal contents using dense preforms. (R&D performed at Sandia National Laboratories under DOE-CE-AIM support.)
Advanced Industrial Concepts (AIC) Materials Program

Work Element: Advanced Ceramics and Composites

Project Title: Synthesis and Processing of Composites by Reactive Metal Penetration

Phase: FY 1995

Performing Organization: Sandia National Laboratories

Principal Investigators: Ronald E. Loehman (505) 272-7601 and Kevin G. Ewsuk (505) 272-7620

Phase Objectives: The objectives for this year were to use results of wetting and TEM experiments to refine our model for the reactive penetration mechanism; to investigate the potential for using kaolin as an inexpensive ceramic precursor material; to investigate reactive penetration of NiO and TiO₂ ceramics; and to demonstrate net-shape forming using porous ceramic preforms that produce a wider range of composite metal contents.

Ultimate Objective: The overall objectives of the program are: 1) to identify compositions favorable for making composites by reactive metal penetration; 2) to determine the mechanisms that control the process; and 3) to optimize the process so that composites and composite coatings with commercial potential can be made.

Technical Approach: Composites are made by reacting molten metals with ceramics under controlled conditions. Cross sections of reaction fronts are examined by x-ray and electron analytical techniques to identify compositions and microstructures. Those results are compared with data from wetting and penetration experiments using the sessile drop technique and are analyzed using thermodynamic calculations and phase diagram data. We use those results to make test specimens for determining composite physical properties.

Progress: We have made ceramic composites of Al₂O₃/Ti₃Al and Al₂O₃/Ni₃Al by reactive hot-pressing. We discovered that kaolin can serve as a low-cost ceramic preform for making Al₂O₃/Al composites to near-net-shape. We learned how to improve the pressureless infiltration of molten Al into porous mullite and kaolin, which allows us to obtain composites with a much wider range of metal concentrations than when using dense ceramic preforms.

Patents: Publications: 7 Proceedings: 3
Books: Presentations: 19
PROJECT TITLE: Synthesis and Processing of Composites by Reactive Metal Penetration

CRITICAL ISSUES: The potential market for advanced ceramic-metal composites is as substitutes for existing materials. Even though their properties may be substantially better than existing materials, experience has taught us that the advanced materials are unlikely to penetrate commercial markets unless their cost is competitive with what is in current use. Because advanced materials by their nature are new, they generally lack a design history and data base on properties and reliability sufficient to persuade designers to specify the new material. Thus, the critical issues for any new material are reliability and cost. Ceramic-metal composites made by reactive metal penetration are no exception.

POTENTIAL PAYOFF: Wider use of ceramic-metal composites requires improvements in synthesis and processing so that high-performance parts can be produced more economically. Reactive metal penetration produces ceramic-metal composites that exhibit high stiffness-to-weight ratios, good fracture toughness, and their electrical and thermal properties can be varied through control of their compositions and microstructures. We are learning that reactive metal penetration could be an economical process for manufacturing many of the advanced ceramic composites that are needed for light-weight structural and wear applications. Near-net-shape fabrication of parts has the additional advantage that costly and energy intensive grinding and machining operations are significantly reduced, and the waste generated from such finishing operations is minimized.