**STRENGTH AND TOUGHNESS OF CERAMIC-METAL COMPOSITES
PREPARED BY REACTIVE HOT PRESSING**

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APR 04 2000
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ABSTRACT

Metal-reinforced Al_2O_3 -matrix composites were prepared using reactive hot pressing. The volume fraction of the reinforcing phase was controlled by the stoichiometry of the particular displacement reaction used. Dense Al_2O_3 -Ni and Al_2O_3 -Nb composites were fabricated using this technique. The best combination of strength, 610 MPa, and toughness, $12 \text{ MPam}^{1/2}$, was found for the Al_2O_3 -Ni composites. Indentation cracks and fracture surfaces showed evidence of ductile deformation of the Ni phase. The Al_2O_3 -Nb composites had high strength, but the toughness was lower than expected due to the poor bonding between the Nb and Al_2O_3 phases.

INTRODUCTION

Metal-reinforced ceramics offer the potential for improved strength and toughness compared to monolithic ceramics. These composites combine the high elastic modulus, hardness and low density of the ceramic phase with the high ductility of the metallic phase to produce composites with properties unattainable from either pure ceramics or pure metals. Of the ceramic-metal systems studied, Al_2O_3 -Al composites have probably received the most attention. A number of processing techniques have been developed to fabricate Al_2O_3 -Al composites, including directed metal oxidation [1], reactive metal penetration [2], displacement reactions between Al and SiO_2 [3], and the pressure infiltration of Al into porous Al_2O_3 preforms.[4] The most significant factor limiting the use of Al_2O_3 -Al composites is its low use temperature due to the relatively low melting temperature of aluminum. Many of the potential applications for ceramic-metal composites require higher use temperatures than are attainable in the Al_2O_3 -Al

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system. Thus, there is a need for processing techniques to make composites that contain more refractory metals.

Many other reinforcements have been investigated for Al_2O_3 -matrix composites, including Ni and Nb. Al_2O_3 -Ni composites have received considerable attention [5-12]. A number of processing techniques have been developed to form Al_2O_3 -Ni composites, including free sintering of Ni and alumina powders [5], displacement reactions between Al and NiO [8], and reduction of NiO or NiAl_2O_4 . [6, 7, 10, 11] Free sintering routes are complicated by the tendency of Ni flow out of Al_2O_3 powder compacts during sintering.[5] Fabrication of Al_2O_3 -Ni composites by the reduction of NiO or NiAl_2O_4 , followed by subsequent free sintering or hot pressing avoids the wetting issue, but complicates densification.[6, 7, 10, 11] Also, the hot pressing of sol-gel derived powders has been successfully used to form Al_2O_3 -Ni composites with Ni contents up to 50 vol.%. [12] In fact, one of the highest reported toughness for any of these methods was $8.3\text{MPa}\cdot\text{m}^{1/2}$ for a composite containing 50 vol.% Ni prepared by hot pressing sol-gel derived powders. [5]

Although they have received less attention, composites of Al_2O_3 and Nb are particularly interesting due to a near thermal expansion match between the two. Al_2O_3 -Nb composites have been formed by sintering of attrition milled Nb and Al_2O_3 powders in vacuum at 1550°C . [13, 14] A composite consisting of 30 volume percent Nb had a strength of 530 MPa, a hardness of 15 GPa and a toughness of $4.5\text{MPa}\cdot\text{m}^{1/2}$. In these composites, the cracks tended to propagate along the Nb- Al_2O_3 interface, forming few bridging ligaments. With few bridging ligaments the composite's toughness was lower than expected based on the metal content and the ductility of Nb.

This work briefly describes the processing of Al_2O_3 -Ni and Al_2O_3 -Nb composites by reactive hot pressing. The elastic modulus, hardness, strength and toughness were measured and the mechanical performance was correlated with the observed microstructures. The high strength and toughness of the Al_2O_3 -Ni composites are of particular note.

PROCESSING

Al_2O_3 -Ni and Al_2O_3 -Nb composites were prepared by reactive hot pressing metal and ceramic powder mixtures. Two different displacement reactions were used to form these alumina-based composites. Each reaction was thermodynamically favorable; that is, the Gibbs energy change associated with conversion of the reactants to the products was strongly negative. It was important to maintain a very low partial pressure of oxygen during the reaction to

limit oxidation of the Al. In addition, heat input to the reactants during processing was regulated to prevent the ignition of a self-propagating high-temperature synthesis reaction. The stoichiometries of the displacement reactions are given in Reactions 1-2.

The milling, drying, and hot pressing procedures were the same for all compositions.

Precursor powders were mixed and ground by attrition milling (Model 01-HD, Union Process, Akron, OH) in methanol with 3 mm zirconia media for one hour at 600 rpm. The slurry was air-dried and then lightly ground using a mortar and pestle, after which the powders were passed through a 35 mesh sieve.

The precursor powders were hot pressed in graphite dies that were spray-coated with BN (Cerac, Inc., Milwaukee, WI) to limit reaction with the powders. The hot press chamber was evacuated to 10^{-2} torr and back-filled with ultra high purity argon gas. This process was repeated three times. The hot press was heated at $1^\circ\text{C}/\text{min}$ to 1450°C , after which a pressure of 34.5 MPa (5000 psi) was applied to the die. The temperature was held at 1450°C for 30 minutes, then the furnace was cooled at $20^\circ\text{C}/\text{min}$. The pressure was released after the die temperature was less than 300°C .

In general, dense composites that were completely reacted did not adhere to the graphite. The density of the hot pressed billets was calculated using Archimedes' technique with water as the immersion/saturation fluid. Billets were machined (Chand Kare Technical Ceramics, Worcester, MA) into size B (3 by 4 by 45 mm) bend bars. Strength was determined in four-point loading. Fracture toughness was measured using the single edge v-notch beam method.[15] Size B beams were fractured in four-point loading. Modulus was measured using a pulse-echo technique, and hardness was determined by Vicker's indentation with loads ranging from 5 to 10 kg. Polished cross sections, indented samples, and fracture surfaces were examined by scanning electron microscopy.

RESULTS AND DISCUSSION

Al₂O₃-Ni Composites

Al₂O₃-Ni composites were prepared by the reactive hot pressing of NiO and Al powders batched with the stoichiometry of Reaction 1. From Reaction 1, a composite composition of 56 vol.% Al₂O₃ and 44 vol.% Ni was predicted. However, the actual metal contents were less because a small amount of Ni squeezed out of the die during hot pressing. Knowing the initial mass of the reactants, the predicted final composition and the mass of Ni exuded, the composites were estimated to contain around 35 vol.% Ni. The predicted density of this composition is 5.70 g/cm³, based on a Ni density of 8.9 g/cm³ and an alumina density of 3.98 g/cm³. The composite density measured, by Archimedes' technique was 5.52 g/cm³, or 97 % relative density. The mechanical properties of Al₂O₃-Ni composites are summarized in Table I. This composite has an unusually high combination of strength and toughness with strength values of 610 MPa and toughness of 12.1 MPa•m^{1/2}.

Examination of polished cross sections revealed a bimodal size distribution for Ni inclusions. Ni ligaments approximately 5 μm in width were observed as were smaller Ni inclusions of ~1 μm. Indentation cracks show evidence of bridging by intact Ni ligaments (Fig. 1). Cracks are not seen to travel preferentially along the Ni-Al₂O₃ interface, as has been observed in previous works.[6, 7, 10] The formation of bridging ligaments indicates a relatively strong bond between the Ni and Al₂O₃. SEM examination of the fracture surfaces shows that the Ni ligaments have been ductily deformed resulting in knife-edges (Fig. 2). Knife-edging is another indication that the Ni reinforcement produces bridging ligaments during crack propagation. The bridging ligaments reduce the stress intensity at the crack tip, thus enhancing the material's toughness.

Al₂O₃-Nb Composites

Nb₂O₅ and Al powder mixtures were hot pressed to produce Al₂O₃-Nb composites. From the stoichiometry of Reaction 2, a composite composition of 34 vol.% Nb and 66 vol.% alumina is predicted. The predicted density of these composites is 5.52 g/cm³ based on densities of 3.98 g/cm³ for alumina and 8.57 g/cm³ for Nb. The density of hot pressed composites was 5.45 g/cm³, or about 98% of theoretical. The composite properties are summarized in Table I. This composite had a moderately high strength, 525 MPa, but a toughness of only 6.2 MPa•m^{1/2}. The toughness was lower than expected, based on results of the Ni containing composites.

Figure 1. SEM micrograph showing an indentation crack in a composite of Al_2O_3 and Ni.

Figure 2. SEM micrograph showing the fracture surface of an Al_2O_3 -Ni composite.

Examination of the microstructure of a polished cross section after hardness testing (Fig. 3) revealed that the indentation crack traveled preferentially along the ceramic-metal boundary. Few bridging metal ligaments were found, indicating poor adhesion at the ceramic-metal interface. Poor adhesion is probably the reason for the lower toughness. With such poor adhesion bridging metal ligaments do not form, thus the metal phase is not deformed and does not absorb energy during fracture. Such preferential propagation of cracks along the ceramic-metal interfaces has been observed for low toughness composites in previous studies.[5-13]

Table I. Mechanical Properties of Composites.

	V_f Metal (%)	Strength (MPa)	Toughness (MPa·m ^{1/2})	Modulus (GPa)	HV (GPa)
Al ₂ O ₃ -Ni	35	610	12.1	292	5.3
Al ₂ O ₃ -Nb	34	525	6.2	284	9.4

SUMMARY

Thermodynamically favorable displacement reactions were used to form ceramic-metal composites using reactive hot pressing. Metal and ceramic powder mixtures were attrition milled and then hot pressed at 1450°C and 34.5 MPa. Composites had relative densities of 95% or greater. Al₂O₃-Ni composites had an impressively high combination of strength and toughness. Examination of indentation cracks and fracture surfaces showed evidence of ductile deformation of Ni ligaments during fracture. Al₂O₃-Nb composites had high strength, although toughness values were lower than expected, possibly due to poor adhesion at the ceramic-metal interface.

ACKNOWLEDGEMENTS

The authors wish to thank John Geiske of Sandia National Laboratories for performing the modulus measurements. This work was supported by the Advanced Industrial Materials Program in the Office of Industrial Technology at the U.S. Department of Energy (DOE). Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U.S. DOE under contract number DE-AC04-94AL85000.

Figure 3. SEM micrograph showing an indentation crack in a composite of Al₂O₃ and Nb.

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