Preliminary studies in the processing and characterization of Al_2O_3/SnO_2 laminated composites

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All oxide composites (reinforcement and matrix both being oxides) exhibit high temperature oxidation resistance in addition to high strength and hardness. A major drawback of these materials is that the oxide fiber and oxide matrix tend to react, which strengthens the interface and therefore drastically reduces the damage tolerance. To overcome this problem, a mechanically weak interphase material, which also serves as a diffusion barrier, is generally used. One such materials system is tin dioxide (SnO_2) in alumina-based composites. Previous attempts to fabricate such alumina matrix composites have been unsuccessful due to the higher temperatures needed to densify Al_2O_3 coupled with the fact that SnO_2 decomposes to SnO in reducing environments. SnO has a relatively low melting point ($1125\,°C$). In this paper we report the successful fabrication of Al_2O_3/SnO_2, laminated composites and some observations on microstructural and mechanical characterization of the laminates. As expected from the phase diagram, no chemical compound formation was observed between Al_2O_3 and SnO_2 which means that no primary chemical bonding developed between individual laminae. TEM observations showed, however, a strong mechanical interlocking at the SnO_2/Al_2O_3 interfaces. In spite of the relatively strong interfacial bond, cracks did deflect. Our microstructural studies showed that SnO_2 served as a weak interphase material. © *1999 Kluwer Academic Publishers*

1. Introduction

There has been a growing interest in the use of oxide/oxide composites due to their high-temperature oxidation resistance [1]. One undesirable feature of these composites is the reactivity between oxide laminae or between the fiber and matrix. This reaction may prevent the composite from developing a suitable interface necessary to achieve a high damage tolerance. To avoid this chemical reaction at the interface, an interphase material that serves as a diffusion barrier is generally used [2]. Both SnO_2 and $LaPO_4$ have been proposed as interphase materials toughen to alumina-based composites vis-a-vis alumina. Alumina-based composites using $LaPO_4$ [3–5] as an interphase material have been successfully fabricated and preliminary results showed enhanced fracture toughness. An

alumina fiber-reinforced glass matrix with SnO_2 interphase also showed a damage tolerant behavior. These glass matrix composites can be processed at $900\,°C$ in vacuum where the stability of SnO_2 is not compromised. The presence of SnO_2 in glass matrix/alumina fiber composites has been shown to increase the fracture toughness if the SnO_2/alumina fiber interface is smooth (i.e. weak mechanical bonding) [6]. However, previous attempts to fabricate an alumina matrix composite using SnO_2 as an interface material, i.e., Al_2O_3/SnO_2 laminated composites, have been unsuccessful [7]. The Al_2O_3-SnO_2 phase diagram [8] shows a simple eutectic reaction at $1620\,°C$, (Fig. 1). The difficulty is that when processed in inert or reducing environments (i.e. vacuum, Ar, N_2), SnO_2 tends to decompose to SnO, which has a low melting point ($\approx 1125\,°C$). Thus processing
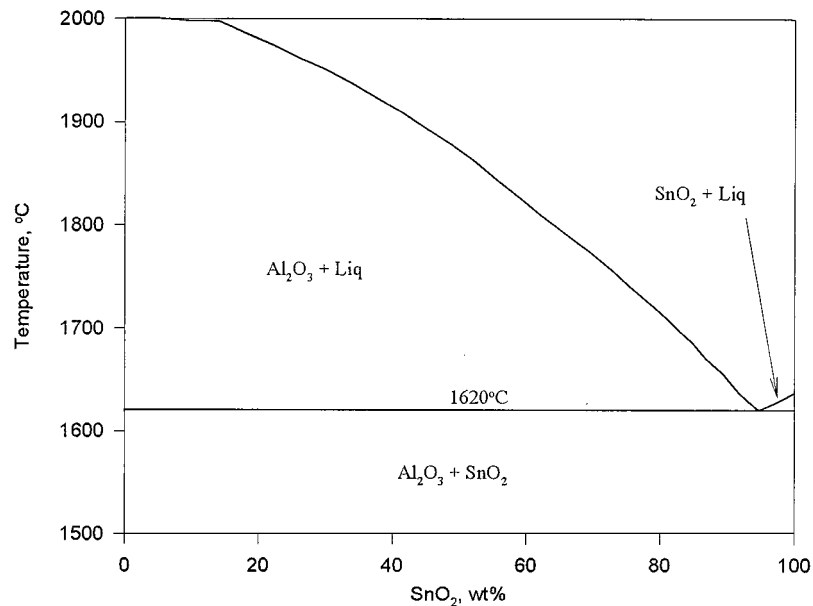
Figure 1 Equilibrium phase diagram showing a simple eutectic reaction between SnO_2 and Al_2O_3 at $1620\,°C$ [8].

at 1200–1400 °C in an inert atmosphere for alumina-based composites with SnO_2 as the interphase material is not feasible. To prevent SnO_2 from decomposing at the higher processing temperatures it is necessary to densify a crystalline ceramic matrix such as alumina in an atmosphere where there is a significant partial pressure of oxygen. Because of this processing requirement, one must also foresee the limits of application of any composite with SnO_2 as a component. Applications must be limited to high temperatures *in air* or other oxidizing environments or temperatures below 1100 °C. This excludes high temperatures used in the near vacuum of space travel as well as reducing environments.

In this paper we report the successful fabrication of Al_2O_3/SnO_2 laminated composites as well as some observations on their microstructure and mechanical properties.

2. Materials and procedure

The starting powders of Al_2O_3 and SnO_2 were purchased from Baikowski[1] and Aldrich[2], respectively. The Al_2O_3 was 99.99% pure with a grain size between 1–2 μm. The SnO_2 was 99.9% pure with a grain size <44 μm. Laminae of both SnO_2 and Al_2O_3 were prepared by tape casting aqueous slurries of the respective powders. The tapes were cut into 3.8×3.8 cm squares. Alternating sheets of each material were then stacked and laminated by pressing at 90 °C and 20 MPa. The organic materials were pyrolized at 500 °C for 5 h. The hot pressing was done *in air* at temperatures at 1400 °C and 30 MPa pressure for 35–45 min.

To obtain preliminary information on the interfacial reactions, analysis of the interface region was carried out using an electron microprobe (JEOL Superprobe 733) equipped with a Noran system for wavelength dispersive X-ray spectroscopy (WDS). SEM analysis was

carried out using a Hitachi S-800 scanning electron microscope. The specimens were coated with carbon film to prevent charging effects.

In order to obtain more detailed information on the interfacial reactions between SnO_2 and Al_2O_3, the reaction zone was investigated by means of transmission electron microscopy (TEM) using a Philips (Philips Inc., Eindhoven, The Netherlands) EM 430 (LaB$_6$ filament, 300 kV accelerating voltage). It was equipped with a Tracor system for energy dispersive X-ray spectroscopy (EDX). Thin foils of specimens were coated with carbon films to avoid charging effects.

3. Results and discussion

Fig. 2 shows the Al and Sn distribution profiles across the interface, as determined by microprobe analysis. As expected from the phase diagram, there is no detectable diffusion or compound formation at the interface. Transmission electron microscopy (TEM) together with selected area diffraction and energy dispersive X-ray analysis (EDX) shed light on both the chemical and mechanical status at the interface, (Fig. 3). The
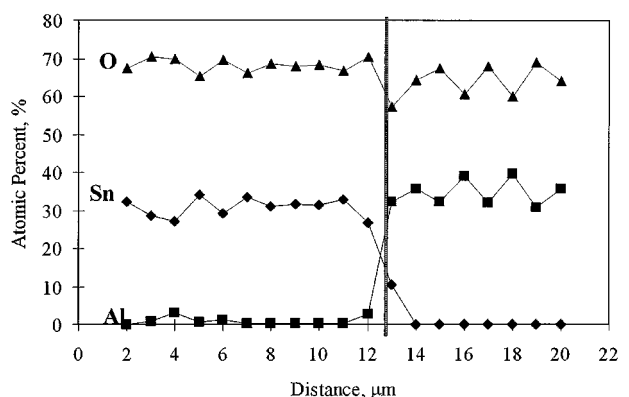

Figure 2 Wavelength dispersive X-ray spectroscopy profiles showing the atomic percent of Sn, O, and Al near the SnO_2/Al_2O_3 interface.
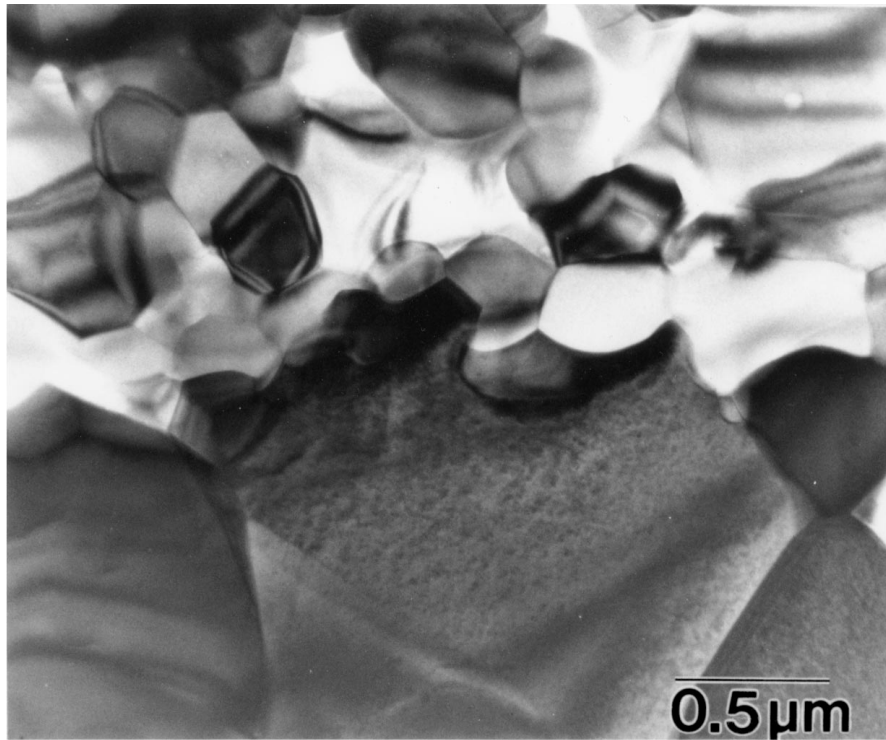
Figure 3 TEM micrograph of a SnO_2/Al_2O_3 interface. Chemical analysis indicates the presence of only SnO_2 and Al_2O_3. A mechanically strong interface can be seen because of the embedding of Al_2O_3 particles in SnO_2, shown at the arrow.
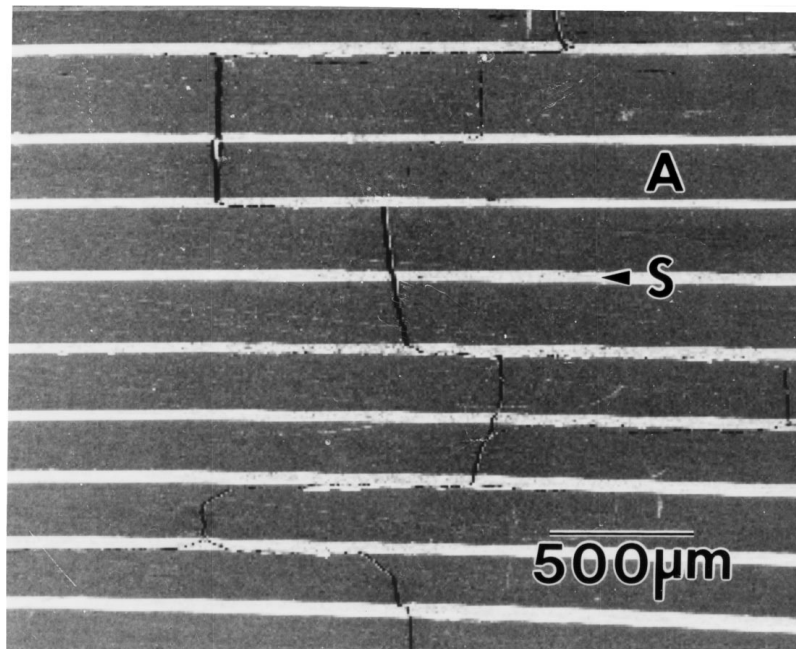

Figure 4 SEM micrograph of a SnO_2/Al_2O_3 laminated composite broken in three point bending that shows the crack being deflected within the sample.

SnO_2 layer consisted of 2–3 μm sized grains whereas the grains in the Al_2O_3 layer were distinctly smaller, (~0.5 μm). As expected from the phase diagram, no reaction product formed between SnO_2 and Al_2O_3. EDX analyses with high spatial resolution confirmed the absence of any interdiffusion between Al_2O_3 and SnO_2. However, evidence of a strong mechanical bond can be seen in Fig. 3. The tortuous nature of the interface can be noted, i.e., strong mechanical interlocking between Al_2O_3 and SnO_2 grains. This is attributed to the high temperatures and pressures used during processing. At the relatively high processing temperatures, local pressures at the interface were large enough to cause plastic deformation of the larger SnO_2 grains by the adjacent Al_2O_3.

Fig. 4 is an SEM micrograph of a SnO_2/Al_2O_3 laminated composite that was tested in a three-point bend test. The crack shows some deflection in the sample but there was no accompanying delamination between adjacent laminae of SnO_2 and Al_2O_3. Fig. 5 shows the
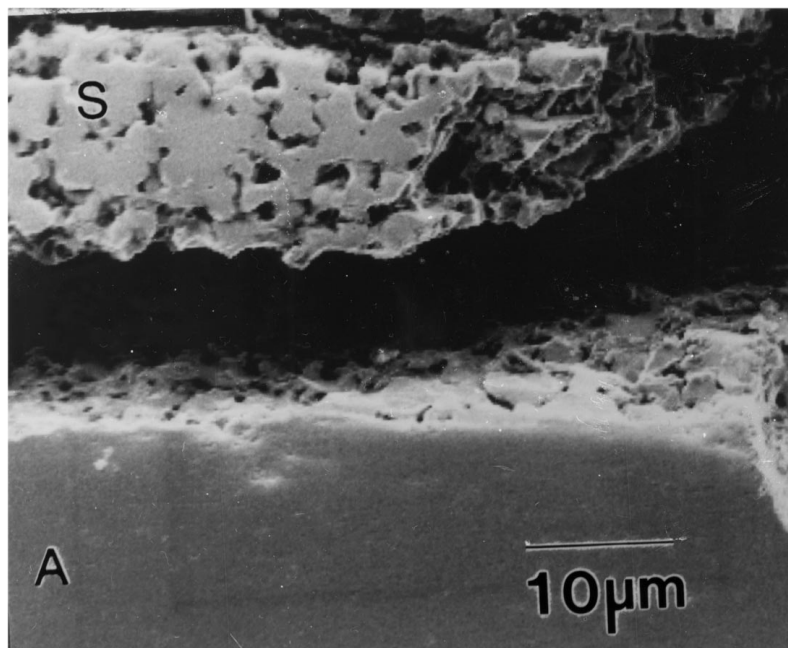
Figure 5 Delamination at the interface of a SnO_2/Al_2O_3 composite showing that some of the SnO_2 remains on the surface of the Al_2O_3 laminae.

interfacial region near where the crack was deflected. Part of the SnO_2 lamina is still seen attached to the Al_2O_3 lamina that can be explained in light of interfacial microstructure shown in Fig. 3. Even though there was no chemical bonding at the interface, the mechanical interlocking of Al_2O_3 into SnO_2 grains created a mechanically strong interfacial bond. In spite of this strong bonding, the SnO_2 layer does seem to serve as a weak interphase as can be observed from the frequent deflection in the SnO_2 layer.

There are three requirements that must be satisfied if an interphase material is to provide a weak interface and toughen a CMC. The first requirement is that the interface be thermodynamically stable during processing and under the service conditions. This will prevent diffusion and/or reaction bonding and provide a stable, chemically weak interface. The Al_2O_3/SnO_2 interface is thermodynamically stable; the obstacle is identifying the processing/application conditions so that SnO_2 will not decompose to SnO. The second condition is that the mechanical bonding must be minimized. A smooth interface will reduce mechanical interlocking and thus allow for easier delamination and crack deflection, leading to fiber pullout in fiber-reinforced CMCs. It would appear that in the present alumina/tin dioxide samples there was a strong mechanical bond (see Fig. 3) due to a rough interface between tin dioxide and aluminum, and this bonding was the reason a clean delamination was not achieved. The use of finer grained SnO_2 starting powder, and lower hot pressing pressures with a view to produce a smooth SnO_2/Al_2O_3 interface should be of help. The third requirement is the thermal stress state at the interface. Ideally, there should be a tensile stress at interface. The thermal stress at Al_2O_3/SnO_2 interface is favorable for a weak interface, since the coefficient of thermal expansion of alumina and tin dioxide are 8.5×10^{-6} and 5.3×10^{-6}, respectively. During cool-

ing from the processing conditions, an alumina particle or grain surrounded by SnO_2, will shrink more than SnO_2, generating a transverse tensile stress. The ability to delaminate at the interface will be the net result of the interaction between the mechanical interlocking and thermal stresses. When mechanical interlocking is greatest, thermal relaxation at the interface will not weaken the interface enough to cause delamination. However, in the areas where the mechanical interlocking is not as great, the contribution from the thermal stress state will be large enough to cause delamination. This will explain the fact that the SnO_2 does not cover the entire fracture surface near the Al_2O_3/SnO_2 interface in Fig. 5.

4. Conclusions

SnO_2/Al_2O_3 laminates were successfully prepared by hot pressing *in air* at 1400 °C. Electron microprobe and TEM investigations showed no chemical reaction at the interface. The mechanical bond, however, was quite strong because of the embedding of Al_2O_3 in the SnO_2 grains. The thermal stress state at the interface is favorable for a weak interface. The combined result of these factors led to a mechanically strong interface which still showed deflection and delamination at the interface. A smoother interface SnO_2 and Al_2O_3 would help in promoting interfacial delamination.

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