ABSTRACT

The microstructure of Al/α-Al₂O₃ composites made by infiltrating Al into dense mullite preforms has been characterized using transmission electron microscopy. Observations revealed that the formation of the Al/Al₂O₃ composites involves three stages. Initially, Al infiltrates into a dense mullite preform through grain boundary diffusion, and reacts with mullite at grain boundaries to form a partial reaction zone. Then, a complete reaction takes place in the reaction region between the partial reaction zone and the full reaction zone to convert the dense mullite preform to a composite of α-Al₂O₃ (matrix) and an Al-Si phase (thin channels). Finally, the reduced Si from the reaction diffuses out of the MA₂O₃ composite through the metal channels, whereas Al from the molten Al pool is continuously drawn to the reaction region until the mullite preform is consumed or the sample is removed from the molten Al pool. Based on the observed microstructure, infiltration mechanisms have been discussed, and a growth model of the composites is proposed in which the process involves repeated nucleation of Al₂O₃ grains and grain growth.

INTRODUCTION

Because of the advanced and tailored properties of metal/ceramic composites, interest in commercial applications of such composites has spawned the development of a variety of techniques for synthesis of the metal/ceramic composites [1-4]. Of these techniques, a novel technology based on the directed oxidation of molten (Lanoxide's DIMOX™ Process) [2, 5, 6] has received considerable attention. This process offers the ability to produce unreinforced [7], particulate-reinforced [2], and fiber-reinforced [8] composites with a wide range of compositions and microstructures. For example, the reaction of a molten aluminum alloy with air has been used to form an Al₂O₃/metal composite with a mutually-interconnected microstructure [9].

Recently, a new method for synthesis of metal/ceramic composites by infiltrating a reactive metal into a dense ceramic preform has been reported by Loehman et al. [4]. For instance, in the Al/mullite system, molten aluminum reduces mullite (Al₆Si₂O₁₃) to produce alumina and elemental silicon according to the oxidation-reduction reaction:

\[ 3\text{Al}_6\text{Si}_2\text{O}_{13} + (8+x)\text{Al} \rightarrow 13\text{Al}_2\text{O}_3 + 6\text{Si} + x\text{Al} \]  \hspace{1cm} (1)

With excess aluminum present (i.e., \(x>0\)), a composite of alumina, silicon, and aluminum is formed. The principal criteria for successful infiltration are a negative Gibbs free energy for the reaction and favorable wetting of the ceramic by the molten metal. The microstructure of the metal/ceramic composites made by reactive metal infiltration comprises mutually interconnected networks of metal and ceramic phases, similar to that observed in the composites made by the Lanoxide™ process [6, 9]. Thus, reactive metal infiltration appears a promising new route to synthesize and process a wide range of metal/ceramic composites to near-net-shape with tailored microstructure and properties.

The objective of this paper is to characterize the microstructure and composition of the initial reaction product as well as the fully developed microstructure of the metal/ceramic composite in the Al/mullite system using transmission electron microscopy (TEM) and x-ray energy dispersive spectrometry (EDS). Primary emphasis is to understand the growth of the Al/Al₂O₃ composites made by reactive metal infiltration.
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EXPERIMENTAL PROCEDURE

Reactive metal infiltration was carried out by dipping dense phase-pure mullite preforms in molten aluminum (99.99%) contained in high-purity Al₂O₃ crucibles at 1100 °C under an atmosphere of Ar. Reaction times of 5 min to 200 min were accurately controlled by dipping the mullite preforms into molten aluminum for a prescribed time, and then removing it. It was found that there is a 5-10 min incubation time for Al infiltration and reaction with mullite at 1100 °C. The growth rate of the Al₂O₃-Al-Si composites appears proportional to the square root of time for short reaction times (< 1 hr) and increases with longer reaction times. Details of composite processing, wetting behavior, and mechanical properties of the Al₂O₃-Al-Si composites have been reported elsewhere [4].

For incompletely reacted samples, there exist two visible reaction zones: a partial reaction zone and a full reaction zone. The partial reaction zone appears light brown, and the full reaction zone is dark. Grain boundaries and interfaces of four such composites were characterized by TEM and EDS. TEM specimens have been prepared for the partial reaction zone-mullite interface, the partial reaction zone, the full reaction zone-partial reaction zone interface, and the full reaction zone. The specimens were examined in a transmission electron microscope equipped with an EDS system, operating at 200 keV.

RESULTS

Partial Reaction Zone

TEM observations of the partial reaction zone revealed small precipitates at grain boundaries of the mullite preform, as shown in Fig. 1a. The precipitates were estimated to be about 10-30 nm in diameter. A number of EDS patterns were taken from the precipitates along the grain boundaries as shown, for example, in Fig. 1b. Quantitative analysis of the EDS patterns indicated that the atomic ratio of Al to Si is about 4:1, which is larger than the value of mullite (3:1), indicating that the precipitates are Al rich. Moreover, the ratio increased as reducing the electron beam size, suggesting that the Al richness of the precipitates could be washed-out in some degree due to electron beam spreading and drifting during data collection. Note that because of the electron beam spreading and drifting, some of the data in the EDS patterns were collected from the region near the precipitates. Thus, it is believed that the precipitates are Al₂O₃.

![TEM image showing small precipitates at mullite grain boundaries in the partial reaction zone](image1.png)

*Fig. 1 (a) TEM image shows small precipitates at mullite grain boundaries in the partial reaction zone. (b) An EDS pattern taken from the precipitates indicates that the precipitates are Al-rich.*
The Al$_2$O$_3$ particles become larger at grain boundaries closer to the full reaction zone. The particle size varies from 50 nm to 100 nm, and the particles appear to form a continuous thin layer, coating the grain boundaries. EDS patterns taken from the large particles confirmed that the particles are indeed Al$_2$O$_3$. Up to the interface between the full reaction zone and the partial reaction zone, the reaction in the partial reaction zone appears to take place only at grain boundaries. No evidence has been observed for the reaction frontier to move into mullite grains to form an Al$_2$O$_3$/Al/Si composite.

Interface Between the Partial Reaction Zone and the Full Reaction Zone

It was found that the interface between the partial reaction zone and the full reaction zone is a region of about 2 μm thick (Note that the grain size of the mullite preforms is about 1 μm.). On one side of the interfacial region, the reaction occurred only at grain boundaries of the mullite ceramic as shown in Fig. 1a, whereas on the other side the reaction completed, resulting in a mutually interconnected microstructure of an Al/Al$_2$O$_3$ composite (see below). Thus the interfacial region is actually the reaction region, in which the chemical reaction of Al with mullite (see Eq. 1) completes to convert mullite ceramics to Al/Al$_2$O$_3$ composites. The reaction region normally consists of five different phases: partially reacted mullite, Al$_2$O$_3$, Al, Si-Al, and Al-Si-O phase. Fig. 2a shows an example of such a reaction region, where the five phases are indicated by M, AO, A, SA, and ASO, respectively. The infiltration direction in Fig. 2a was found from right to left. The partial reaction zone was observed just on the right-hand side of this image, while the full reaction zone was found just on the left-hand side of the image. EDS patterns of the mullite, Al, Al$_2$O$_3$, Si-Al, and Al-Si-O phase in Fig. 2a are shown in Fig. 2b, 2c, 2d, 2e, and 2f, respectively. Several interesting features in the reaction region have been observed. (1) The Al$_2$O$_3$ grains (reaction product) are connected with Al, Si-Al, or Al-Si-O phase. (2) The composition of the Si-Al phase varies from Si rich to Al rich. (3) The Al-Si-O phase is always Si rich.

Full Reaction Zone

The full reaction zone is actually a composite which comprises a mutually interconnected microstructure of Al and α-Al$_2$O$_3$. Geometric shape of the Al and α-Al$_2$O$_3$ grains changes from irregular shape near the reaction region to strongly faceted shape at a distance of about 100 μm from the reaction region. Near the reaction region, the Al grains are long and narrow (0.1 μm - 0.4 μm), and the α-Al$_2$O$_3$ grains are large, about 2 μm. The irregular α-Al$_2$O$_3$ grains then underwent grain growth to become strongly faceted. Note that the Al grains were still liquid at 1100 °C, the processing temperature. Therefore, the Al and α-Al$_2$O$_3$ grains become strongly faceted at a distance of about 100 μm from the reaction region as shown, for example, in Fig. 3. One should note that the faceted shape of the Al grains was not due to their nucleation and growth, but due to the shape of the α-Al$_2$O$_3$ grains. In addition, there is no crystallographic orientation relationship found between the Al and α-Al$_2$O$_3$ grains. This could be due to the rapid solidification of the Al grains since the samples were removed from the molten Al pool in the present experiments. The Al grains appear disconnected from each other in Fig. 3. However, the Al/α-Al$_2$O$_3$ composite is a good electrical conductor, indicating that the Al grains are interconnected in three dimensions. Therefore, the Al/α-Al$_2$O$_3$ composites fabricated by reactive metal infiltration consist of a mutually interconnected microstructure of Al and α-Al$_2$O$_3$.

It should be noted that the reduced Si from the reaction (see Eq. 1) appears missing in the final microstructure of the composites. It is believed that the reduced Si diffused out of the final microstructure through the liquid Al channels during the infiltration process, and then dissolved in the Al pools used in our dipping experiments. Examination of bulk reaction samples after infiltration shows evidence of such Si crystals in the solidified Al pools, indicating that the reduced Si diffused out of the composite into the surrounding Al [10]. The outward diffusion of the reduced Si could affect the infiltration kinetics as discussed below. One may also note that the phenomenon of removing Si from the composites is similar to zone refining.
Fig. 4 (a) The reaction region comprises five different phases: mullite, Al, Al₂O₃, Si-Al, and Al-Si-O. EDS patterns taken from these phases are shown in (b), (c), (d), (e), and (f), respectively.

Fig. 3 TEM image of the full reaction zone at a distance of about 100 μm from the reaction region shows faceted Al₃O₃ (dark) and Al (light) grains.
The present study of the microstructural features of the reaction product suggests a possible mechanism of reactive metal infiltration. The infiltration process could involve three steps. (1) Al infiltrates into mullite ceramics through grain boundaries, and then reacts with mullite at grain boundaries to form the partial reaction zone. (2) A complete reaction of molten Al with mullite takes place in the reaction region between the partial reaction zone and the full reaction zone, forming a composite of a solid Al_2O_3 phase and a liquid Al-Si phase at the processing temperature of 1100°C. Note that the solubility of Si in molten Al is about 55 at.% at 1100°C [11]. (3) The reduced Si from the reaction diffuses out of the full reaction zone (or the Al/Al_2O_3 composite), whereas Al from the molten Al pool is continuously drawn to the reaction region as required for the reaction of Al with mullite.

Our previous study of reactive metal infiltration [4] showed that initial aluminum infiltration follows a t^{1/2} rate law, which indicates diffusion-controlled kinetics. However, infiltration appears switched to linear kinetics at longer infiltration times (> 1 hr). The present results clearly show that infiltration is initiated by Al diffusion along mullite grain boundaries. The reaction of Al with mullite then occurs at the grain boundaries. The chemical reaction in the partial reaction zone, albeit limited at grain boundaries, could result in a significant contribution to wetting of the mullite ceramics by molten Al during reactive metal infiltration. Thus, it is believed that the t^{1/2} kinetics during initial infiltration is largely controlled by grain boundary diffusion of Al.

At longer times, however, existence of the well-defined partial reaction zone indicates that infiltration of Al into mullite ceramics through grain boundaries is faster than either the reaction rate in the reaction region (step 2) or the mass transport rate of the reduced Si or unreacted Al through the Al/α-Al_2O_3 composite (step 3). Thus, the infiltration process at longer times is likely controlled either by the mass transport process of the reduced Si or unreacted Al by the reaction kinetics. The reaction of Al with mullite to form Si/Al_2O_3 requires the continued supply of unreacted Al to the reaction region. This is believed to occur via the convective flow of molten Al by wicking through the Al/Al_2O_3 composite from the molten Al pool via the interconnected metal channels. If this process were rate-limiting, the infiltration rate would decrease with time since transport through the composite decreased directly with increasing thickness. However, our previous study [4] indicated that the infiltration rate is constant with time at longer times. In addition, the addition of Si into molten Al can reduce viscosity of molten Al [12]. The reaction of Al with mullite produces Si, which dissolves in molten Al, resulting in an enhancement of the convective flow of molten Al. Thus, it is inferred that mass transfer of the unreacted Al is not rate-limiting in reactive metal infiltration.

It has been reported that the mean diffusion velocity of Si in Al at 500°C is about 1.3 μm/s [13]. Thus, it is expected that the diffusion velocity of Si in molten Al at 1100°C will be higher than 1.3 μm/s because of the higher temperature. The infiltration rate was found to be about 0.5 μm/s at 1100°C [14], indicating that the diffusion process of the reduced Si is not rate-limiting during reactive metal infiltration. This fast diffusion explains very well the observed microstructure of the infiltrated Al/Al_2O_3 composites. More importantly, the fast diffusion of Si in molten Al and the rapid mass transport of unreacted Al by capillary forces may indicate that the reaction rate is the rate-limiting step in reactive metal infiltration at longer infiltration times. This is consistent with the linear kinetics at longer infiltration times observed previously [4].

The Al/Al_2O_3 composite made by reactive metal infiltration comprises mutually interconnected networks of Al and Al_2O_3, similar to that observed in the unreinforced Al/Al_2O_3 composite produced by the Lanxide™ process [9]. However, the Al_2O_3 grains in the Lanxide™ composite have a preferred orientation, while the Al_2O_3 grains in the infiltrated composite are randomly oriented. This may indicate a different mechanism of formation of the Al/Al_2O_3 composites in these two processes. Compared to the oxygen-dissolution-alumina-growth process of the oriented Al_2O_3 grains in the Lanxide™ composite [15], it is believed that the formation of
the random Al₂O₃ grains in the present composite involves repeated nucleation of Al₂O₃ grains and grain growth. The nucleation and growth of the Al₂O₃ grains take place in the reaction region. It was found that the Al₂O₃ grains in the reaction region are separated from partially reacted mullite grains by a thin layer of either Al-Si or Al-Si-O phase, which indicates that the reaction of Al with mullite may involve two steps to form the Al/Si/Al₂O₃ composite. First, the reaction converts mullite to a solution of Si, Al and O. Then, Al₂O₃ grains nucleate and grow from the solution, or precipitate on small Al₂O₃ particles formed at grain boundaries during initial infiltration. Therefore, the resultant Al₂O₃ grains have random orientations.

SUMMARY

The growth of an Al/Al₂O₃ composite in the Al/mullite system by reactive metal infiltration was found to proceed through three stages. First, Al infiltrates into mullite ceramics through grain boundaries, and then reacts with mullite at grain boundaries to form the partial reaction zone. Second, a complete reaction of molten Al with mullite takes place in the reaction region to convert mullite to a composite of α-Al₂O₃ (matrix) and an Al-Si phase (thin channels). Finally, the reduced Si from the reaction diffuses out of the composite through the metal channels, whereas Al from the molten Al pool is continuously drawn to the reaction region by capillary forces until the preform is consumed or the sample is removed from the molten Al pool.

The present results show that infiltration is initiated at mullite grain boundaries. The reaction of Al with mullite at the grain boundaries enhances wetting of the mullite preforms by molten Al during reactive metal infiltration. Thus, grain boundary diffusion of Al is believed to control the infiltration kinetics during initial infiltration. However, the well-defined partial reaction zone, the fast diffusion of Si in molten Al, and the rapid mass transport of unreacted Al by capillary forces indicate that the reaction kinetics is rate-limiting in reactive metal infiltration at longer infiltration times. The randomly-oriented Al₂O₃ grains in the infiltrated composite suggest the nucleation and growth process involved in the reaction region.

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