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Interactions between Ti and alumina-based ceramics

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Reactive metal coatings have been frequently used on ceramic materials for various purposes. However, little work was done in the past to understand the interactions between coating and ceramic substrates and their effects on the mechanical properties of the ceramics. In this study, titanium coatings were applied to single-crystal (sapphire) and polycrystalline alumina to study the interface reactions. Also, the effect of the coating on the mechanical properties of the substrates was quantified in terms of modulus of rupture (MOR) in four-point bending strength. Reactions between the coating and the Al_2O_3-based substrates at 980 °C caused the formation of a new phase, $Ti_3Al[O]$, and a significant decrease (15%–65%) in the MOR strength of the ceramic materials. This study showed that in polycrystalline alumina, interactions between titanium and the glassy grain-boundary phase in the ceramic materials were responsible for reduction in the MOR strength, while the effect of thermal expansion mismatch between titanium and the ceramic substrate appeared to be dominant for single-crystal alumina.

1. Introduction

With increased demand for polycrystalline alumina and sapphire, many applications of these ceramics require coating with metals for various purposes. For example, silicon semiconductor devices used in microelectronics are frequently mounted in alumina packages for protection from the environment. Connections from the chip to the outside world are made by depositing various metals on the alumina package [1]. In metal matrix composites, the adhesion between the metal matrix and the ceramic reinforcing fibres is critical for a strong and stable composite [2]. The physical quality and mechanical integrity of the matrix/fibre interface determine how effectively the loads are transferred from the matrix to the fibres.

The ability to be joined to other materials, particularly metals, is essential for structural ceramics to attain widespread application. Brazing is often the preferred method for joining ceramics to metals because it can provide hermetic seals, and the plasticity of the braze accommodates the differential expansion between the ceramic and metal. Braze alloys, which readily wet and bond to metals, do not usually wet ceramics without the presence of an active metal coating on the ceramic substrates. Active metal coatings are often used to promote good wetting by braze alloys to enhance the adhesion strength between the braze and ceramic.

Despite the relatively common usage of active metal coatings, little was known about the effects of the coating/alumina interaction on the mechanical properties of alumina. Previous studies [3, 4] on various silicon nitride ceramics showed that strong reactions between coatings and ceramic materials could reduce the strength of the ceramic. Titanium caused the largest reduction in modulus of rupture (MOR) strength of silicon nitride, compared to the other reactive metals studied, zirconium, hafnium and tantalum. Further, the deterioration in strength increased as the crystallinity of the grain-boundary phase decreased in silicon nitride systems. The study concluded that the titanium/amorphous grain-boundary phase interaction enhanced the crystallization of the amorphous phase and/or caused new phase formation at the grain boundaries and subsequently decreased the strength of the ceramics. Other studies with the titanium/sapphire system concentrated on the nature of the reaction at the titanium/sapphire interface [5–8]. The chemistry and kinetics of the interfacial reaction between titanium and sapphire were the main subjects of these studies.

In this paper, the following issues will be addressed.

1. Do reactive metal coatings reduce the mechanical properties of alumina in manner similar to reactive metal coatings on silicon nitride?
2. Of various coating materials, which coating will cause the most significant effect on the properties?
3. Will there be any difference if a single-crystal alumina (sapphire) is used?
4. What are the possible mechanisms to explain the observation?
5. What are the implications of these results?

In order to answer these questions, the effect of active metal coatings on the mechanical properties of alumina were quantified in terms of four-point bend strength. Also, a mechanism for the reduction in MOR strength of alumina caused by titanium coatings was investigated, based on the fracture mode of MOR bars

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and microstructure of the coating/ceramic interface. Other active coatings such as zirconium, hafnium and tantalum were used, and their effects on the mechanical properties of the ceramics were compared with that of titanium.

2. Experimental procedure

Three Al_2O_3-based ceramic materials were selected for coating. The ceramics were AL500 (95% Al_2O_3–5% silicate), AL995 (99.5% Al_2O_3), and sapphire (100% Al_2O_3). Sapphire was grown perpendicular to the R-plane $(1\bar{1}2)$ by the Czochralski technique. Titanium, zirconium, hafnium and tantalum commercial-grade metals were used for coating. The mechanical properties of AL995 were investigated with all these coating materials, while those of AL500 and sapphire were evaluated with a titanium coating.

In our previous study [3], a method was developed to measure the effects of reactive coatings on the mechanical properties of a ceramic via MOR strength tests in four-point bending, as shown in Fig. 1. MOR bars were machined (25.4 mm × 2.5 mm × 1.27 mm), the edges were chamfered, and one face of each bar was polished to an optical grade finish with 0.03 μm alumina powder. The coating material (3 μm thick) was deposited on the polished faces of the bars by electron beam evaporation at 300 °C in a 10^{-3} Pa vacuum. The coated samples were held at 980 °C for 10 min. This heat treatment simulated a typical brazing cycle with an Au–18Ni brazing alloy. Four-point bending test was done at room temperature with the coated side of the MOR bar in tension. As a control for the experiments, MOR bars were prepared and heat treated exactly the same as above without any coating. MOR tests were done using a hydraulic tension/compression machine with a strain rate of 0.5 mm min^{-1}.

In order to study the effectiveness of the coatings in promoting the wetting behaviour of a braze alloy, the sessile drop method was used to measure the contact angle of a liquid Au–18Ni braze alloy on the coated alumina. The substrate surface was polished to an optical finish, and coatings were applied using an electron beam evaporator at 300 °C in 10^{-3} Pa vacuum. About 0.5 g braze alloy was melted on the coated substrates at 940 °C in an argon atmosphere. Contact angles between substrates and the liquid braze were measured as a function of time at 1000 °C.

Fracture surfaces of the ceramics were studied using a scanning electron microscope in order to identify crack initiation sites and fracture mode. Cross-section samples of the titanium-coated alumina were prepared for transmission electron microscopy study. Two MOR bars were glued with the coated sides facing each other, using a high-temperature epoxy. Three mm discs were obtained by core-drilling and dimpled down to a thickness of 10 μm. The discs were ion-milled to perforation with 4–5 keV Ar^+ ions at an incident beam angle of 15°. Analytical TEM was performed with a Phillips EM 400T operating at 120 keV. The reaction products between the titanium-coating and alumina were identified by electron energy loss spectroscopy and electron diffraction analysis.

3. Results

3.1. Wetting test

Fig. 2 shows the results of the wetting tests at 1000 °C of a typical brazing alloy (i.e. Au–18%Ni) on various coating materials. All reactive coatings provided excellent wetting within 100 s. The braze alloy did not wet the uncoated alumina, resulting in a contact angle of > 90°. The alumina substrate used for this wetting study was AL995. Zirconium and tantalum demonstrated faster wetting responses than other coating materials. Titanium responded relatively slowly to the presence of an Au–Ni alloy even though the contact angle went below 10° after 170 s. However, the titanium coating provided a consistent and excellent wetting behaviour for different compositions of molten metals or substrate ceramics [3]. Experiments with an Ag–28%Cu braze alloy and a silicon nitride substrate [3] showed that contact angles measured on zirconium, hafnium and tantalum coatings were highly dependent on the braze alloy composition and substrate material.

3.2. Mechanical testing

The strengths of 99.5%, 95% polycrystalline alumina and sapphire MOR bars are shown in Figs 3 and 4. 99.5% alumina were coated with titanium, zirconium,

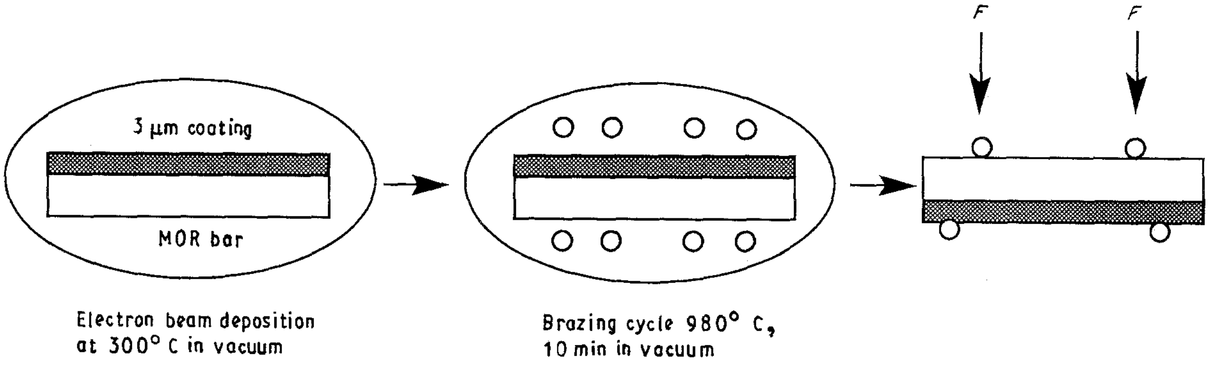

Figure 1 Procedure to evaluate the effect of coating on the MOR strength of ceramic materials. Coated samples were heated at 980 °C for 10 min prior to four-point bend test.

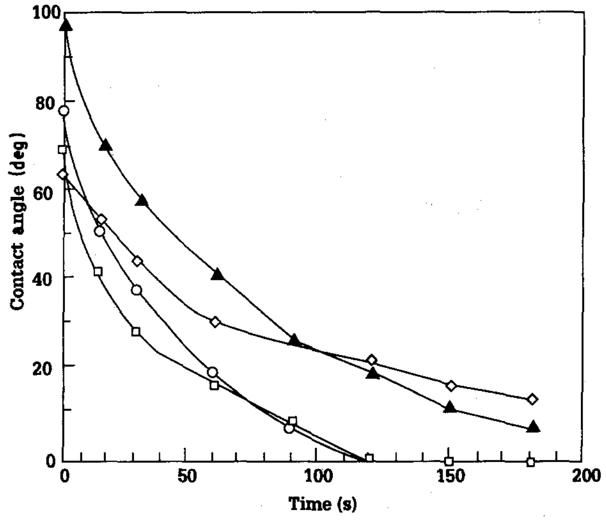

Figure 2 Wetting angles versus time at 1000 °C with an Au–18% Ni alloy: alumina with reactive coatings showed the improved wetting behaviour of an Au–18% Ni alloy compared to the uncoated alumina (> 90°). Coating (▲) titanium, (□) zirconium, (○) tantallum, (◇) hafnium.

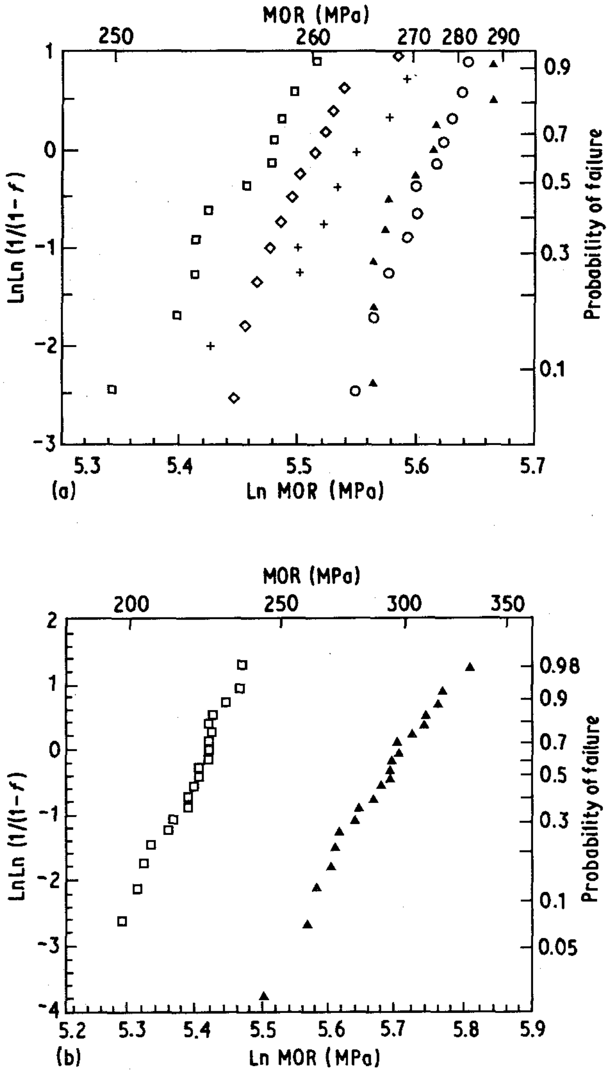

Figure 3 Weibull distribution of the MOR strength of (a) 99.5% and (b) 95% polycrystalline alumina. The presence of reactive coatings reduced the MOR strength of the alumina by 15%–25%. Coatings; (▲) uncoated, (□) titanium, (○) zirconium, (◇) hafnium, (+) tantalum.

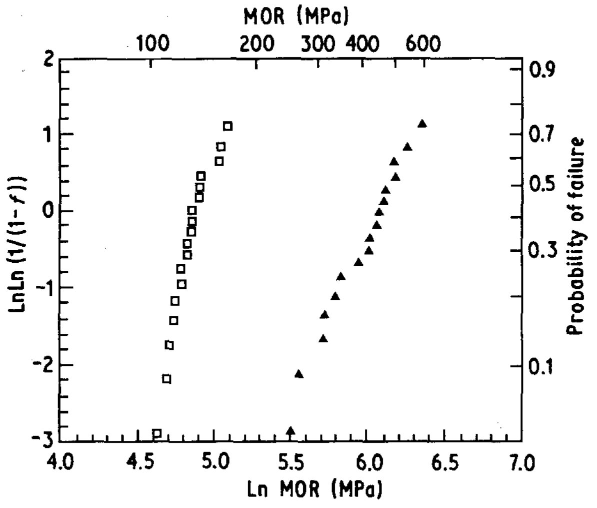

Figure 4 Weibull distribution of the MOR strength of sapphire. Titanium coating reduced the MOR strength of the sapphire by 65%. (▲) uncoated, (□) titanium coated.

hafnium or tantalum, whereas the experiments were done only with titanium coating for 95% alumina and sapphire. These results were compared with the strengths of uncoated bars of each ceramic. In all cases, uncoated bars were heat treated under the same conditions as the coated bars. The heat treatment of the coated bars of all ceramics in this study at 980 °C for 10 min caused a noticeable reduction in average MOR strength (15%–65%) of the bars, compared with uncoated bars.

In the case of 99.5% alumina (Fig. 3a), only zirconium coating did not cause any change in the MOR strength. Zirconium, tantalum, hafnium and titanium coatings reduced the MOR strength of the alumina in the order listed; zirconium decreased the strength the least. The Weibull moduli of the coated bars were not much different from those of uncoated bars. Similar effects of reactive coatings such as titanium, zirconium, hafnium and tantalum on the MOR strengths of Si_3N_4-based ceramics have been reported [4]. Fig. 3b shows that the MOR strength of 95% alumina was significantly reduced by titanium coating. As expected from a previous study [4], 95% alumina experienced more damage (25% reduction) in the MOR strength than 99.5% alumina (15% reduction) which had less grain-boundary phase. Again, there was little change observed in the Weibull modulus of 95% alumina after heat treatment.

The effect of the titanium coating on the strength of sapphire was the most detrimental among these Al_2O_3-based ceramics under study, Fig. 4. The average reduction in the MOR strength of sapphire due to the presence of the coating was 65%. This result was unexpected because sapphire is single crystal and does not contain any grain boundaries. The Weibull modulus of the uncoated sapphire was significantly lower than other polycrystalline aluminas. This indicates that sapphire was highly sensitive to the presence of any defects. The titanium-coated sapphire had a higher Weibull modulus than the uncoated sapphire. The results of all MOR tests are summarized in Table I.

3.3. Fracture surfaces

In order to understand the degradation in the mechanical properties, the microstructure and fracture surfaces of each ceramic were examined. This was correlated with the mechanical behaviour and the prevailing mechanisms responsible for the degradation.

3.3.1. Polycrystalline alumina

Fig. 5 shows fracture surfaces of tested MOR bars of uncoated polycrystalline alumina. Both 99.5% and 95% alumina failed intergranularly, with the fracture surfaces covered by grain-boundary phases. Voids of similar size, under 10 µm, were found on the fracture surfaces of both aluminas. It was noted that 99.5% alumina contained more pores than 95% alumina. The difference in porosity and grain size between these aluminas was attributed to the amount of grain-boundary glassy phase present in the ceramics.

Fractographs of coated 99.5% Al_2O_3 MOR bars were taken in the vicinity of the coating in order to study the effect of the coating on the initial stage of cracking. The failure of coated and uncoated samples occurred along the grain boundaries as shown with uncoated samples. The fracture surfaces of the uncoated and coated bar were similar. The titanium coating was observed to adhere very well to the alumina (Fig. 6a). The small volume fraction of grain-boundary phase in this alumina made it difficult to evaluate the effect of the titanium/grain-boundary phase interaction. However, the titanium/alumina grain interaction did not seem to cause any difference

TABLE I Summary of MOR test results of polycrystalline alumina and sapphire

	95% Al_2O_3	99.5% Al_2O_3	Sapphire
Average strength without coating (MPa)	290 (16.9)[a]	270 (22.7)	400 (4.3)
Average strength with titanium-coating (MPa)	217 (19.8)	232 (19.6)	131 (8.0)
Reduction in strength (%)	25	15	65
Grain size (µm)	10–15	20	∞

[a] Weibull modulus.

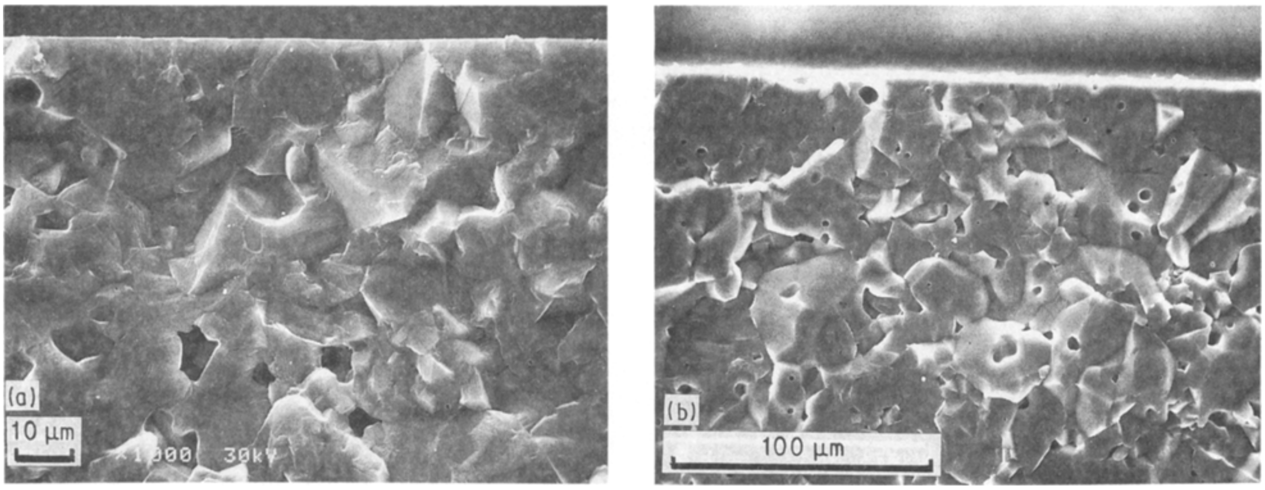

Figure 5 Fracture surfaces of uncoated polycrystalline alumina, (a) 95% and (b) 99.5%. Both alumina failed intergranularly.

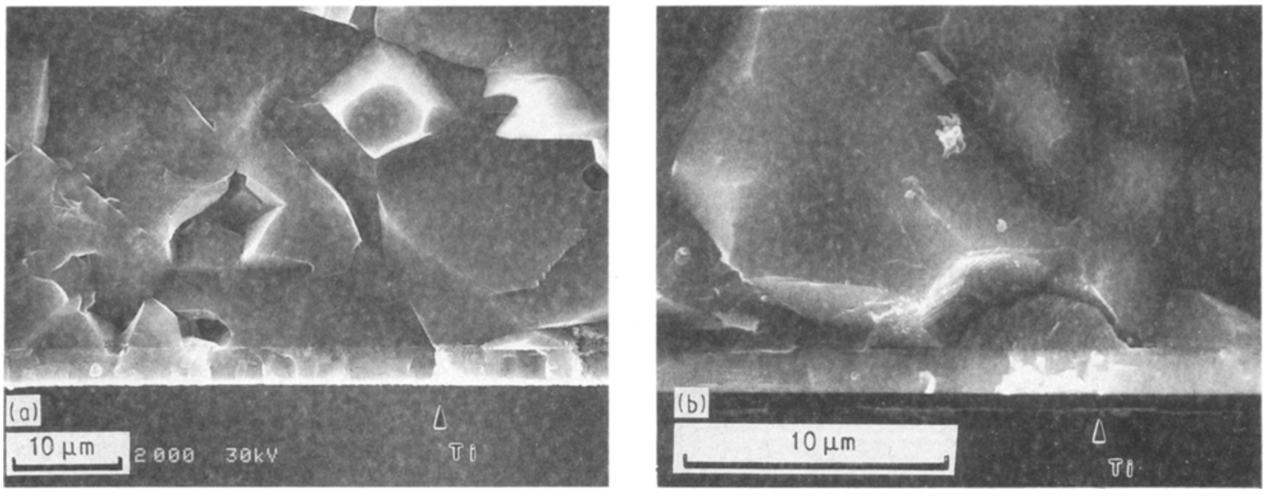

Figure 6 Fracture surfaces of titanium-coated polycrystalline alumina, (a) 99.5% and (b) 95%. The fracture surfaces of the coated and uncoated bars were similar. Note the strong adhesion between titanium coating and alumina.

in crack initiation and propagation. Crack initiation was commonly associated with surface defects and subsurface pores near the surface. The cracks extended by linking voids along the grain-boundary phase.

Similar observations were made for 95% alumina, as shown in Fig. 6b. However, the fracture surface of the titanium-coated 95% alumina differed in morphology from that of uncoated 95% alumina. The cracks in the titanium-coated 95% alumina propagated in the faceted form through the grain-boundary glassy phase, as shown in Fig. 6b, in contrast to the cracks in the uncoated case which moved randomly through the grain-boundary phase. Also, it was clear that the adhesion between the coating and the alumina was strong enough to avoid separation of the coating from the surface of the bar. Occasionally, fracture surfaces associated with, presumably, the basal plane of α-Al_2O_3 were found. The 99.5% alumina had better resistance to crack initiation than 95% alumina based on a 15% strength decrease compared to a 25% strength decrease. The strength difference between the 99.5% and 95% alumina was statistically significant.

3.3.2. *Single-crystal alumina*

A typical fracture surface of uncoated sapphire is shown in Fig. 7(a) in which the initiation site, the beginning stage of propagation (slow and smooth), the second stage of propagation (fast and rough), and the final failure in the compressed region during bend test, can be seen. Most cracks in uncoated sapphire were initiated from the chamfered edges that had been damaged during the machining process.

The titanium-coated sapphire failed differently from the uncoated case. As shown in Fig. 7b, the fracture surface was smooth, without any indication of a tortuous path of crack propagation. Several flaws were found on the tensile surface of the MOR bars (see arrows). In most samples one initiation site was seen; however, in many titanium-coated sapphire samples, two or three flaws which could be initiation sites were seen on the fracture surfaces. Further, the final failure in the compressed region during bend test was not distinct.

3.4. Microstructure

Fig. 8 is a transmission electron micrograph taken in cross-section from the titanium-coated 95% alumina. Reaction between titanium and Al_2O_3 grains at 980 °C for 10 min resulted in a Ti_3Al-type second phase at the interface, and Ti_5Si_3 between the titanium and silicate glass-boundary phase. The strain field (arrow 1) that formed between the Ti/Ti_5Si_3 indicated that the interface was semicoherent or coherent. In many cases, the Ti_3Al-type phase formed a columnar structure. It was also evident that another second phase started forming in the glassy phase at the interface, arrow 2 in Fig. 8. Energy dispersive X-ray analysis (EDXA) showed that this phase was depleted of calcium, otherwise it had a similar composition as the glassy phase.

Titanium coated 99.5% alumina showed the presence of spherical precipitates (10–20 nm diameters), indicated by arrows in the grain-boundary region (Fig. 9). This is significantly different in morphology from the 95% alumina. The titanium-coating layer on top of the alumina was removed during ion-milling and is not shown in the figure. The precipitates are new phases due to either the reactions of titanium with the glassy phase or crystallization of the glassy phase. The small volume fraction of grain-boundary glass phase in the 99.5% alumina and the size of the precipitates hindered a more detailed investigation of the reaction products.

Interaction between the titanium coating and sapphire resulted in a Ti_3Al-type phase which was similar to that seen in polycrystalline alumina (see Fig. 10). The titanium-coating layer on the top of the Ti_3Al-type phase was removed during sample preparation. The results of Rutherford backscattering revealed that the Ti_3Al phase and titanium layer contained a significant amount of oxygen [9]. This was also supported by energy dispersive X-ray analysis [10]. In the case of

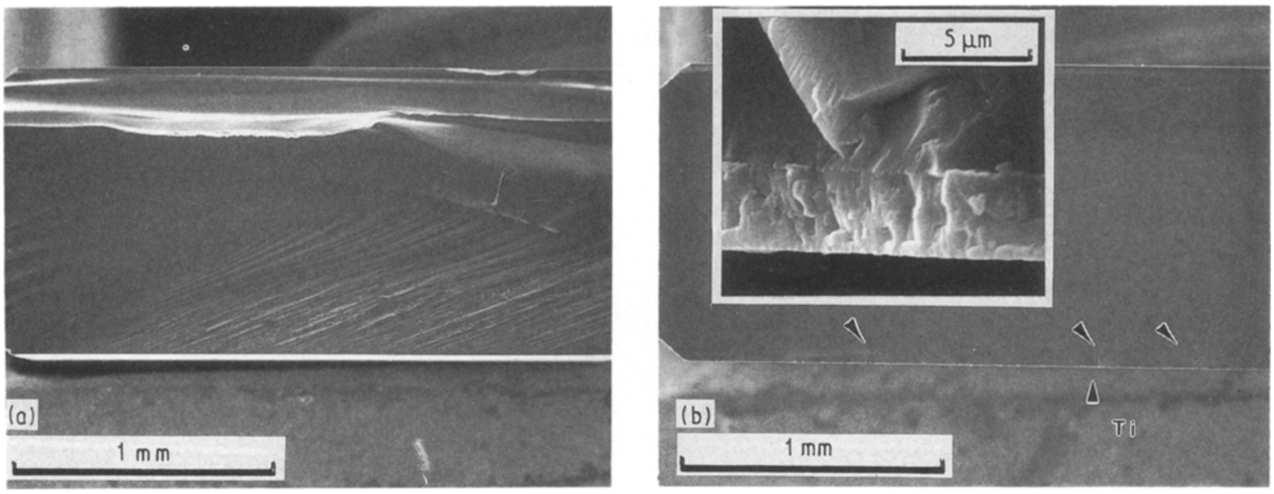

Figure 7 Typical fracture surfaces of sapphire, (a) uncoated and (b) titanium-coated. Cracking was initiated at a chamfered corner of uncoated sapphire, whereas more than one potential flaw for crack initiation was observed (see arrows) from the titanium-coated sapphire.

Figure 8 Interface microstructure of titanium/95% polycrystalline alumina. Reactions at the interfaces of titanium/alumina and titanium/-grain-boundary glassy phase resulted in an Ti_3Al-type phase and Ti_5Si_3, respectively. Arrow 1 shows the strain contour in the vicinity of Ti_5Si_3. Another second phase, depleted of calcium from the glass composition, formed at the interface, arrow 2.

sapphire, the Ti_3Al-type phase did not form columnar morphology.

4. Discussion

4.1. Wetting

The braze alloys studied did not wet uncoated alumina (> 90°). The use of reactive coating materials such as titanium, zirconium, hafnium and tantalum was justified in promoting the wetting of braze metal on the alumina ceramic. The beneficial role of these reactive coating materials was attributed either to their readiness to form a second phase(s) in the presence of liquid metal and/or to lower surface energies of the liquid metals with one of these elements [11, 12]. With most reactive metal coatings, the effect of free energy associated with the chemical reactions occurring at the ceramic–coating interfaces is believed to be predominant over the gas/liquid, liquid/solid, and gas/solid surfaces energies involved.

The second phases formed at the interface during high-temperature processing do not necessarily facilitate the wetting of the molten metals. Rather, the ongoing interface reactions themselves are presumed to promote the wetting. For example, Ag–Cu or Au–Ni alloys do not wet the TiN or titanium silicide phases which were obtained from the titanium/silicon nitride reactions. It is likely that the titanium in the coating dissolves back into the liquid metal and then titanium becomes surface active in the liquid metal to

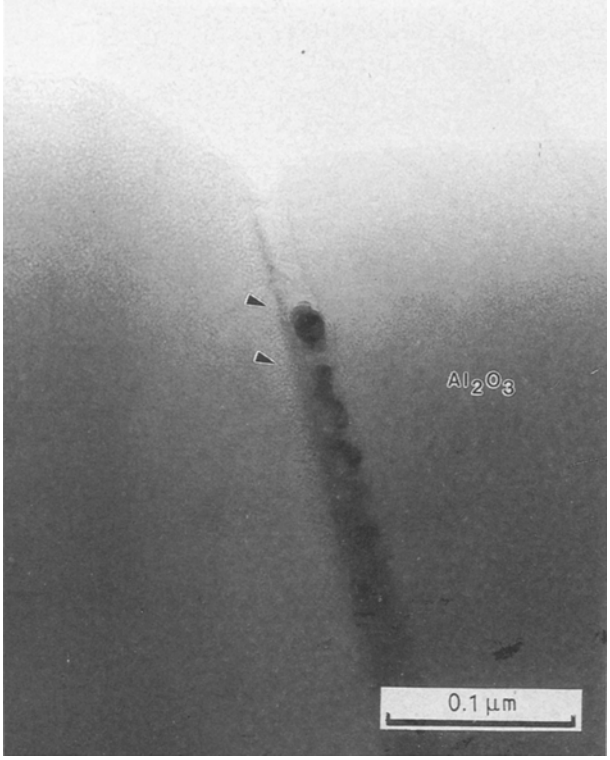

Figure 9 Interface microstructure of titanium/grain-boundary glass phase of 99.5% polycrystalline alumina. Reaction between titanium and 99.5% alumina resulted in spherical phases of 0.01–0.02 μm diameter. The titanium-coating layer which was on the top of the grain boundary was removed during the ion-milling process.

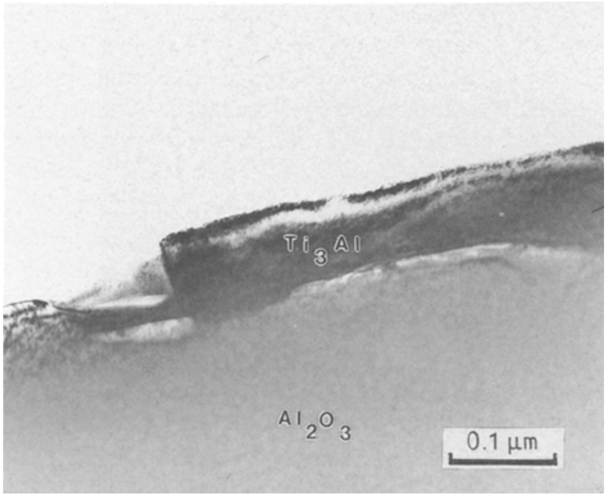

Figure 10 Interface microstructure of titanium/sapphire. Titanium reacted with sapphire and formed a Ti_3Al-type phase. The titanium-coating layer on the top of a Ti_3Al-type phase was removed during sample preparation.

react with substrate ceramics, depending on the alloy compositions [3, 12]. The titanium dissolution helps liquid metal spread over the coated surface effectively.

4.2. Polycrystalline alumina

Scanning electron microscopy (Fig. 5) showed that the microstructure and its resulting properties were controlled by the amount of amorphous phase present at the grain boundaries. The presence of a silicate grain-boundary phase enhanced the mechanical strength of the ceramics at low temperatures. This was largely due to a low concentration of defects (voids), as in the 95% alumina. 95% alumina also has relatively small grains (10–15 μm in size). However, high-temperature properties of ceramics change adversely as the content of the glassy phase increases.

Our previous study [4] of reactive metal coatings on silicon nitride found that the degradation in mechanical strength was caused by interactions between the reactive coating and amorphous grain-boundary phase. The titanium coating had the same effects on the mechanical properties of alumina as on silicon nitrides. For 99.5% and 95% alumina, the MOR strengths of the titanium-coated alumina were 15% and 25% less than that of the uncoated aluminas, respectively. The extent of degradation increases with the content of the grain-boundary phase. As observed from silicon nitrides, this is attributed to the fact that higher content of glassy grain-boundary phase simply has more chance to react with the coating.

Titanium coatings exhibited behaviour like that of TiO_2 and ZrO_2, which have been effectively used as nucleating agents to improve high-temperature properties of some silicon nitride ceramics [13]. As shown in Figs 8 and 9, crystallization of the glass phase or precipitation of a crystalline phase at the grain boundaries induces strain between the crystalline phase and the surroundings [14]. The formation of a crystalline phase in the glassy grain-boundary phase would cause a reduction in volume [15, 16]. This reduction in volume would induce tensile forces in the glassy phase and result in the glassy phase becoming susceptible to cracking. Tensile forces would be induced in the glassy grain-boundary region when a portion of the amorphous grain-boundary phase was replaced by a crystalline phase of a higher density.

4.3. Single-crystal alumina

It was clear that the reduction in MOR strength of 99.5% and 95% alumina ceramics was due primarily to the interactions between the coating material and the amorphous phase at the grain boundaries. It was expected that the single-crystal alumina would be immune to the strength reduction resulting from the coating/grain-boundary phase reaction. The unexpected and significant reduction in the MOR strength of sapphire due to the titanium coating implies that there is another mechanism responsible for the observed phenomenon in sapphire.

When sapphire was coated with titanium, the Weibull modulus of coated sapphire doubled. This showed that the titanium coating reduced the influence of the major factor for the low Weibull modulus of the uncoated bars. This suggested that the effect of surface damage, which was the cause of low Weibull modulus of this material, was surpassed by that of the titanium/sapphire interactions, resulting in better consistency in the MOR strength. The scanning electron micrograph in Fig. 7 illustrated the shift in failure modes from a single critical flaw of uncoated bars to multiple flaws of titanium-coated bars. In addition to the number of critical flaws, the locations of the flaws were moved from the chamfered corner of the uncoated bars to the face of the titanium-coated bars.

Transmission electron microscopy performed on 95% alumina and sapphire showed the formation of the Ti_3Al-type phase. Because Al_2O_3 is a very stable oxide thermodynamically, it is not feasible to form TiO_2 and Ti_3Al from titanium and Al_2O_3. In an earlier study [9], carried out in a vacuum range of 10^{-10}–10^{-8} torr, (1 torr = 133.322 Pa) it was proposed and supported by Rutherford backscattering spectroscopy that the following reaction would take place

$$8Ti + Al_2O_3 = 3Ti_{0.67}[O_{0.33}] + 2Ti_3Al[O] \quad (1)$$

$$\Delta G^{\circ}_{rxn} = -431800 + 3.98\,T\ln T - 87.64T \quad (2)$$

According to this reaction, the formation of oxygen solid solution in titanium and Ti_3Al made the reaction at 1000 °C extremely feasible. The growth kinetics of the $Ti_3Al[O]$ was found to be controlled by grain-boundary diffusion [9].

It was expected that the titanium layer in the vicinity of Al_2O_3 converted to Ti[O] and $Ti_3Al[O]$. The formation of the TiO_2 layer was very likely at the outer surface due to the vacuum condition during heat treatment. Auger analysis with titanium-coated silicon nitride showed evidence of TiO_2 on the surface of the titanium-coating after heat treatment at 980 °C for 10 min [4].

The observed reduction in the MOR strength of sapphire was attributed to strain due to the thermal expansion mismatch of these materials and the brittle nature of $Ti_3Al[O]$ and TiO_2. The thermal expansion coefficients of Ti_3Al and α-Al_2O_3 are 9.6–14.4×10^{-6} and 5.5–$7.9 \times 10^{-6}\,°C^{-1}$ in the temperature range 25–1000 °C, respectively. Assuming that the change in the thermal expansion coefficient due to the formation of $Ti_3Al[O]$ solid solution is minor compared to that of Ti_3Al, the stress developed in the $Ti_3Al[O]$ due to the difference in thermal expansion coefficients of $Ti_3Al[O]$ and α-Al_2O_3 would be in the range of 650 MPa, according to Equation 3

$$\sigma = E\Delta T(\alpha_{Al_2O_3} - \alpha_{Ti_3Al}) \quad (3)$$

where α is the average thermal expansion coefficient, ΔT is the change in temperature (975 °C), and E is Young's modulus of Ti_3Al, 120 GPa [17]. The room-temperature ultimate tensile strength of Ti_3Al is 130–200 MPa [18]. The $Ti_3Al[O]$ layer should be cracked at room temperature. The stresses in the sapphire are slightly compressive but essentially zero, due to the much greater thickness of the sapphire compared to the $Ti_3Al[O]$ layer. The low fracture toughness of TiO_2, $Ti_3Al[O]$ and sapphire coupled with strong adhesion at the interface will allow for the easy propagation of the cracks in the $Ti_3Al[O]$ phase into the sapphire substrate. The above can explain the presence of multiple flaws in sapphire. A significant reduction in the MOR strength of the sapphire appeared to be caused by the residual stresses in the titanium-containing layer(s).

4. Conclusions

In joining, the primary purpose of coating is to achieve better bond strength by promoting wetting of the ceramic substrate by the braze alloy. Reactive coating materials such as titanium, zirconium hafnium and tantalum were found to be effective in promoting wetting of braze metal on alumina ceramic. However, strong reactions between reactive coatings and ceramic substrates reduced the MOR strength of the polycrystalline alumina by 15%–25%. The level of degradation in the MOR strength of the alumina increased as the volume fraction of the grain-boundary glassy phase increased.

Of various coatings, titanium caused the most significant degradation on the properties after heat treatment at 980 °C. This was attributed to the relative activeness of the titanium coating compared to other coatings in forming second phases at the interface in this temperature range. Some of the coatings, such as zirconium and tantalum, become more active at temperatures higher than 980 °C (> 1300 °C). The most significant reduction in MOR strength was observed when the titanium coating interacted with sapphire. The reactions between the titanium coating and sapphire reduced the MOR strength by 65%.

Among the factors responsible for the degradation, the reactions between titanium and the grain-boundary glassy phase were the major cause for polycrystalline alumina. Titanium interacted with the grain-boundary phase, forming Ti_5Si_3 and other microcrystalline phases at the interface region. The presence of interface strains showed that the formation of crystalline phases near the interface made the grain-boundary region highly susceptible to cracking. This cracking was due to the volume change that accompanied the reactions.

In the case of sapphire, the degradation in the mechanical properties was ascribed to residual stresses in the $Ti_3Al[O]$ layer and the brittle nature of the $Ti_3Al[O]$ layer which formed at the interface between the titanium coating and the sapphire. The formation of TiO_2 was also presumed to be responsible for low resistance to cracking. The effect of Ti/α-Al_2O_3 interactions, which resulted in a cleavage failure of the sapphire, was not responsible for the weakening of the polycrystalline alumina due to the size of the grains and their random orientations.

Despite the advantages of reactive metal coatings in various application areas of alumina, this investigation revealed some drawbacks of reactive metal coatings. Processing of coated alumina at high temperatures always entails reactions at the coating/ceramic substrate interface and increases the probability of ceramic failure. Therefore, depending on the applications, it is necessary to predetermine the processing and application temperatures when the titanium coating is the only choice for a specific application. Where the coated ceramic undergoes thermal cycles with dynamic loading, extra caution is needed to avoid catastrophic failure. It is also suggested to use other coating materials such as zirconium, hafnium or tantalum in place of titanium if high-temperature processing of applications are unavoidable.

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