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AEM characterization of interfacial reactions between Ti-coating and 95% Al_2O_3–5% silicate ceramics

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Characterization of the interface reaction region of Ti–95% Al_2O_3 upon exposure to heat treatment at 980 °C has been carried out to investigate changes in microstructure and chemistry of interfacial phases by using energy dispersive X-ray spectroscopy and convergent beam electron diffraction methods. Reactions of titanium-coating with an amorphous grain boundary phase and Al_2O_3 substrate form silicide layers and columnar Ti_3Al grains at the interface respectively.

1. Introduction

Ceramic–metal-braze joints need optimized coatings on ceramics to obtain good wetting and adhesion. There has been a considerable interest in reactive metallic coatings such as Ti, Zr, and Ta on structural ceramics. For the optimization of ceramic–metal-braze joints the understanding of microstructural interactions between the metal coating and the ceramics is critical. A number of studies have shown that Ti-containing alloys react rapidly with various ceramic substrates, such as Si_3N_4 and Al_2O_3 to form intermediate or transitional phases at the interface. However, the reaction between titanium-containing alloys and ceramics are often complex and hence very detailed information is needed to characterize their effects on wetting behaviour.

Peddada *et al.* reported no reaction products at the Ti–sapphire interface at 700 °C. They showed an epitaxial growth feature despite the large lattice mismatch between the Al_2O_3 substrate and the Ti growth but felt that this interaction required further study [1]. On the other hand, it has been reported that titanium can dissolve considerable quantities of oxygen at 1127 °C and forms a family of oxides ranging from TiO and TiO_2 [2]. Ohuchi used an X-ray photoluminescence spectroscopy (XPS) technique to investigate the interfacial reactions at Ti–Al_2O_3 [3]. In his experiment, an intermetallic Al–Ti alloy was found to form at temperatures less than 1200 °C. Ito *et al.* reported that the titanium concentration showed a slight increase at the interface between the intermediate layer and alumina based on results of scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) observations on a Ti–Al_2O_3 joined part [4]. Previous studies of interfacial reactions at Ti–Al_2O_3 system is summarized in Table I. In all of this work, the clear identification of reaction products on a submicrometre scale has not been reported in terms of crystal chemistry and structure.

This paper presents some results of recent investigations of the ceramic–metal interface to better understand the chemical reactions taking place between a Ti coating and 95% Al_2O_3 substrate. Analytical electron microscopy (AEM) analysis on several reaction products of the 95% alumina–5% silicate with Ti is described in terms of both the microstructure and chemistry of the interface. By virtue of its fine spatial resolution and the ability to elicit crystallographic information from small areas, energy dispersive X-ray spectroscopy (EDXS) and convergent beam electron diffraction (CBED) analysis reveal detailed information relating to the microstructural morphology and microchemistry which are not apparent by other techniques. The use of cross-sectional TEM imaging also allows for clear observation of morphological features at the interface.

2. Experimental procedure

Titanium metal was deposited onto a ceramic substrate which contained 95% Al_2O_3 and 5% silicate by electron beam evaporation at 300 °C in a 10^{-3} Pa vacuum. This process produced samples having a titanium layer 3 μm. To simulate a typical brazing cycle with a Au–18%Ni braze alloy the material was then annealed in vacuum at 980 °C for 10 min. Cross-sectional TEM samples were prepared by cutting 0.5 mm thick perpendicular sections, which were then joined using epoxy and core-drilled to obtain 3 mm discs. The discs were then mechanically polished and dimpled down to a total thickness of 10 μm followed by ion milling to perforation with 4–5 keV Ar^+ ions at an incidence angle of 12 °. The preparation of thin foils sometimes presented difficulties due to preferential thinning of some phases along the interface. However, specimens of good quality permitted observation and identification of interfacial phases. Analytical TEM

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TABLE I Previous studies of interfacial reactions at Ti–Al_2O_3

System	Reaction products	Analytical techniques
Ti-containing braze alloy/commercial alumina	TiO_2, glassy CaO SiO_2 phase	SEM/EPMA [6]
Ti–sapphire (825 °C)	Ti_3Al	XPS, RBS, TEM [3, 7]
Ti–sapphire (700 °C)	Little reaction	TEM [1]
Cusil ABA–Al_2O_3 (900 °C)	Ti–Al–O, Cu–Ti alloys	EPMA [2]
TA6V–Al_2O_3 (870 °C)	No TiO, $Cu_2(Ti, Al)_4O$	EPMA [5]

analysis was carried out in a Philips EM400T operating at 120 keV with a spot size of approximately 60 nm.

3. Results and discussion

3.1. Interactions between Ti-coating and α-Al_2O_3

Previous microstructural studies of the Ti–Al_2O_3 system have been in disagreement about the nature of the reaction at the interface as mentioned in a previous section. In the Ti–Al_2O_3 system the primary concern is the formation of Ti-contained phases as a result of diffusion of Al and O from the substrate. Most literature suggests that Ti reacts with the Al_2O_3 ceramic surface to form compounds such as TiO. These compounds would act as a transition layer between the ceramic and braze components. After brazing for 30 min at 900 °C, Peytour *et al.* detected a TiO reaction zone (1–2 µm thick). They claimed that bonding of the alumina matrix to the titanium-containing braze is promoted by the reaction of Ti with the oxygen from alumina to form titanium oxides [5]. Although a direct reduction of alumina by Ti according to

$$3Ti + Al_2O_3 \rightarrow 3TiO + 2Al \qquad (1)$$

is thermodynamically not possible at 980 °C, the tendency of oxygen to dissolve in Ti rather than in alumina is known to be the cause for the formation of a strong bond between the Ti-based braze alumina. These data show that the kinetics of the reactions leading to TiO formation are difficult to control, and that the nature of the reaction products depends on the heat treatments and the initial composition of the braze alloy.

In the present work, the TiO compound was not detected within the experimental limit at the Ti–Al_2O_3 interface. Instead, Ti_3Al phase was found and seemed to act as a transition layer between the titanium metal and the alumina substrate. This was evident in cross-sectional TEM studies using EDXS and CBED for the detection and measurement of the composition and crystal structures at the interface. The morphology of the layer closest to the alumina substrate is shown in the TEM micrograph of Fig. 1. The alumina substrate is at the bottom left as confirmed by EDXS and electron diffraction. CBED studies show that the crystal lattice has a rhombohedral structure based upon both whole pattern and bright-field pattern showing "3m" symmetry and that it is identified as α-Al_2O_3 as expected (Fig. 2). Lattice parameters ($a = 0.476$ nm, $c = 1.299$ nm) of this phase was confirmed by comparing experimental high-order Laue zone (HOLZ) lines with those of computer-simulated patterns on the [0 0 0 1] zone axis. There was no appreciable changes of lattice parameters due to oxygen content changes in α-Al_2O_3. Adjacent to the alumina substrate is a darker layer of fine-grained Ti_3Al whose composition and crystal structure were confirmed by EDXS and CBED. The grains in this diffusion zone are somewhat columnar in shape and are typically of the order of 0.3 µm wide. In all cases the Ti_3Al layer appeared to be continuous along the interface.

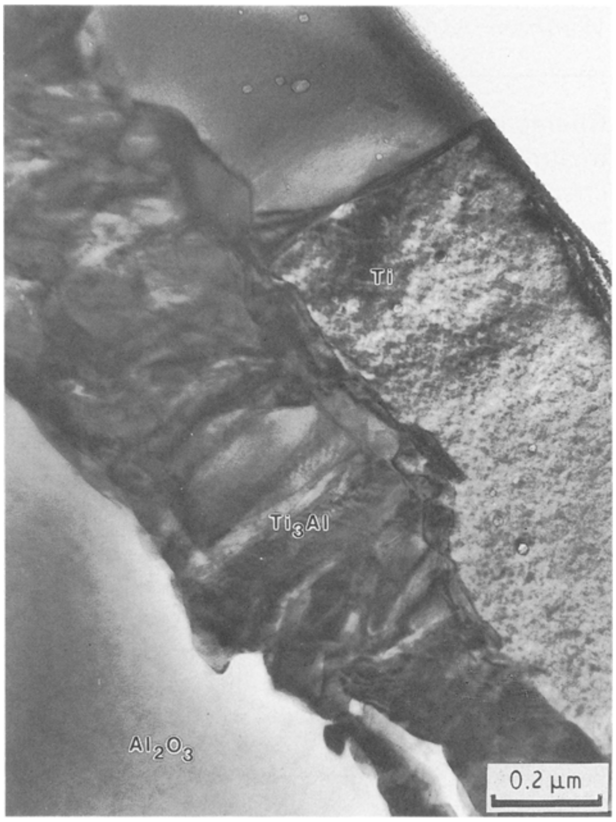


Figure 1 A cross-sectional TEM micrograph of Ti-coating, alumina substrate, and reaction product Ti_3Al phase.

Initially, dissolution of the alumina in contact with the metallic titanium seems to take place to form Ti_3Al phase by solid state reaction. Selverian *et al.* suggested that a Ti–Al intermetallic compound was formed due to a reduction of sapphire to Al by Ti followed by Al desorption [7]. They suggested the reaction between Ti and sapphire as follows:

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

$$\Delta G^\circ = -431\,800 + 3.98T\ln T - 87.64T \qquad (3)$$

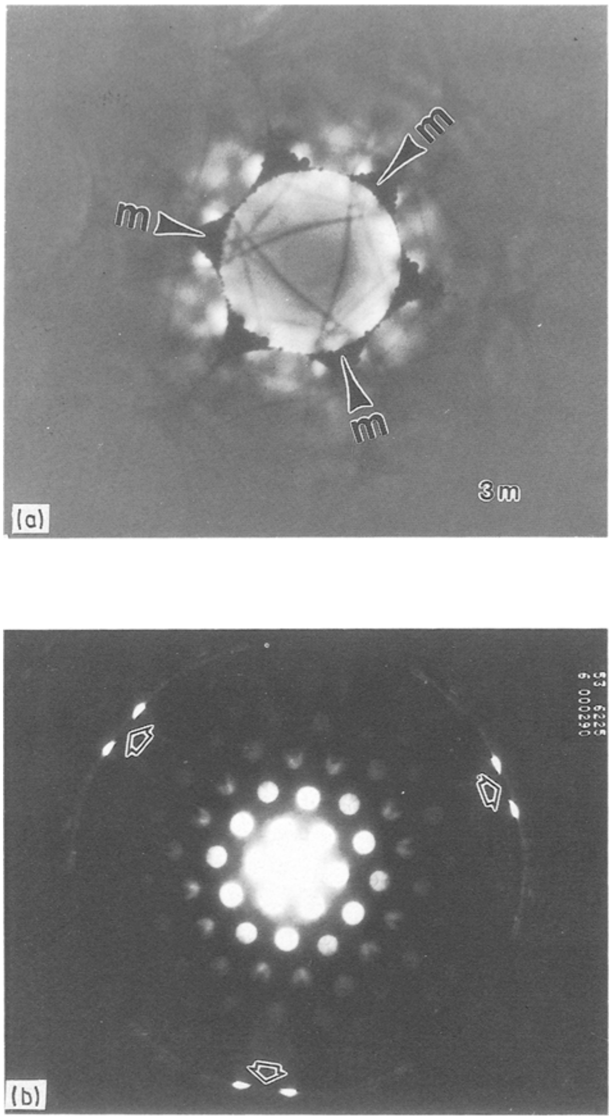


Figure 2 (a) High-order Laue zone lines and (b) whole CBED pattern of the [0001] zone axis obtained from α-Al_2O_3 (space group $R\bar{3}C$) showing "3m" symmetry.

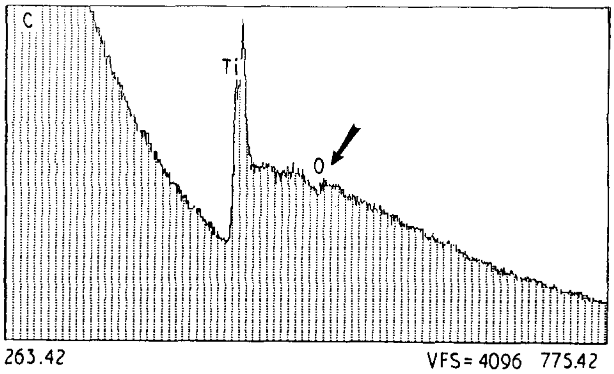


Figure 3 Electron energy loss spectrum was collected from the Ti_3Al phase showing small content of oxygen.

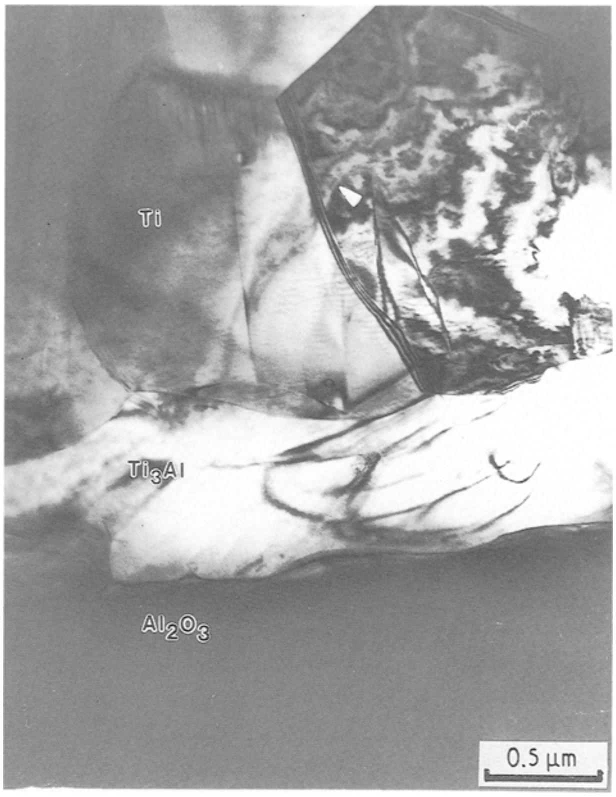


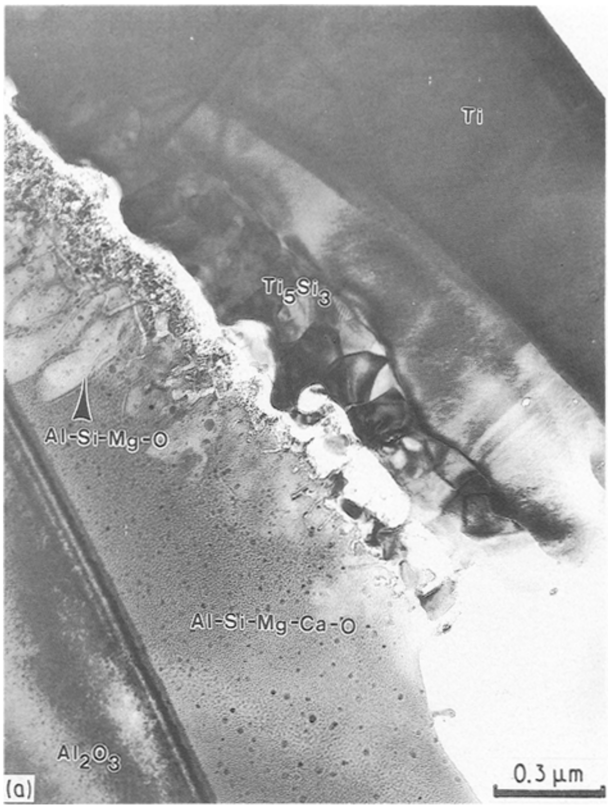
Figure 4 Both Ti-coating and interfacial grains of Ti_3Al phase exhibit high density of dislocations.

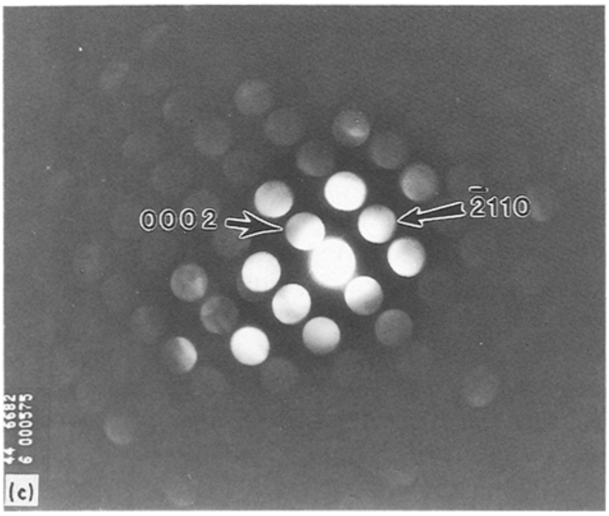
where $Ti_3Al[O]$ refers to Ti_3Al with oxygen in solid solution and $Ti_{0.67}[O_{0.33}]$ refers to Ti with oxygen in solid solution. The reaction is thermodynamically favourable at all temperatures studied in their experiments. The same phase product, Ti_3Al, between Ti and commercial alumina was observed in our experiment. The presence of oxygen in this phase is of interest. Oxygen was not easily detected by use of an ultra-thin window EDXS detector due to peak overlap and sample thickness problems between titanium and oxygen. Electron energy loss spectroscopy (EELS) was therefore used to investigate the presence of oxygen within the Ti_3Al phase (Fig. 3). A very small amount of oxygen was detected in both the titanium and Ti_3Al phases. This may imply that oxygen diffused out of these phases during processing.

Although few defects were found in the alumina substrate, interfacial grains of the Ti_3Al phase often contained a considerable number of dislocations. An example is shown in Fig. 4. A weak beam dark field image was obtained by tilting the specimen 10° out of the [1 2 0] zone axis and used to confirm the presence of these dislocations. An array of dislocations are clearly visible. These dislocations can be interpreted as primary misfit dislocations accommodating strains due to thermal expansion mismatch between the metal and ceramic. It is suggested that the near-interface defects are a result of thermal expansion mismatch between the alumina substrate and Ti_3Al reaction products during cooling. Although dislocations were present in the Ti_3Al layer, no intergranular or transgranular cracks were observed in neither Ti_3Al phase nor alumina substrate.

3.2. Formation of new phases due to amorphous grain boundary phase

Titanium-coatings are used to join commercial alumina similar to the 95% Al_2O_3 of this study. Commercial alumina often contains SiO_2, CaO, MgO, Cr_2O_3, etc., as impurities. From present observations there





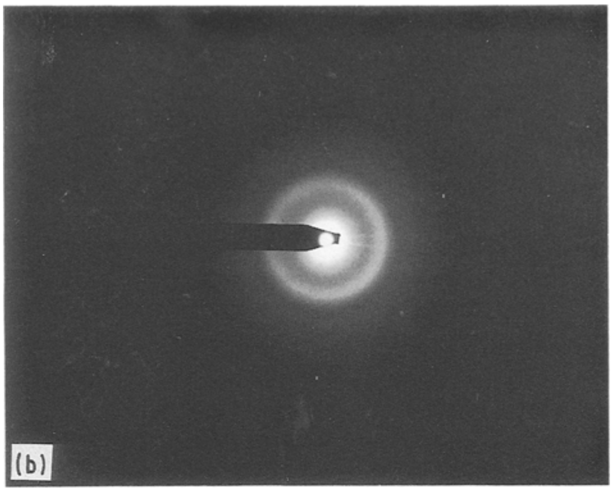


Figure 5 (a) Bright-field TEM micrograph shows several distinct and continuous reaction layers like Ti_5Si_3, Ti_3Al, and Al–Si–Mg oxide as well as Al–Si–Mg–Ca oxide grain boundary phase; (b) electron diffraction pattern obtained from Al–Si–Mg–Ca oxide phase showing amorphous nature; (c) microdiffraction pattern obtained from Ti_5Si_3 phase which was indexed as hexagonal structure ($a = 0.7429$, $c = 0.5139$ nm)

appeared to be an incorporation of the amorphous grain boundary phase into the interfacial reaction. Cassidy *et al.* studied fracture behaviour of brazed commercial alumina and suggested that fracture was occurring in the $CaO \cdot SiO_2$ glassy phase of the alumina near the braze layer [6]. However, detailed mechanism and microstructures at the interface were not clarified due to the limited spatial resolution of electron microprobe analysis on bulk materials.

An example of the type of microstructure found at the interface near the grain boundary phase in this study is illustrated in the bright-field TEM micrograph (Fig. 5a). Several distinct and continuous reaction layers, the result of reaction with the amorphous grain boundary phase were found between the original Al_2O_3 substrate and the metallic Ti coating. The use of EDXS analysis at the interface showed the amorphous grain boundary phase to be present after reaction with the titanium coating layer:

1. a glassy phase of Al–Si–Mg–Ca–O shown by microdiffraction pattern (Fig. 5b);
2. a crystalline phase of Al–Si–Mg–O which did not contain any Ca;
3. a thin reaction layer of Ti–Si with a thickness of 0.1 to 0.2 µm observed to form directly above these two phases along the original Ti-coating interface.

The crystalline Al–Si–Mg–O phase is comprised of finger-like grains with typical diameters of 0.6 µm between the glassy grain boundary phase and Ti–Si grains (Fig. 5a). The Ti–Si phase was confirmed by a CBED pattern from one of these silicide grains, indexed in a manner consistent with the hexagonal structure of Ti_5Si_3, lattice parameters $a = 0.7429$ nm, $c = 0.5139$ nm (Fig. 5c). The measured Ti:Si peak ratio for individual silicide particles varied in the range of 1.5 to 1.7. The formation of titanium silicide at the Ti–Al–Si–Mg–O interface can be explained by the reaction suggested by Bhansali *et al.* [8]. Probably, the Si further diffuses into the Ti-coating layer forming a stable silicide. As is often the case for phenomena controlled by diffusion, the reaction zone phases are in metastable equilibrium with SiO_2. This was also illustrated by the Ti–Si–O ternary phase diagrams presented by Hillel *et al.* [9]. The ternary phase diagram at 1000 °C show that for decreasing SiO_2 content in the initial mixtures, the following phases are successively observed to coexist: SiO_2, Ti_2O_3, Ti_5Si_3, etc.

The reaction layer of Ti_5Si_3 would contribute to the chemical bonding. However, the presence of metallic phases and the reaction layer at the interface can also cause additional interfacial stresses when these joints are subjected to thermal cycling. The changes in chemistry and morphology which occur as a result of interfacial reaction may play an important role in

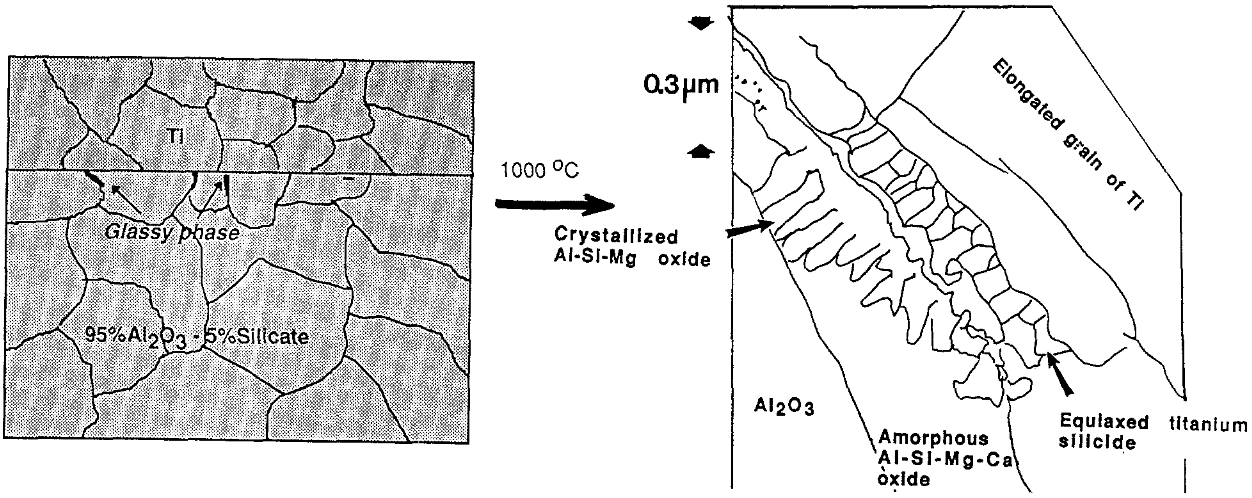


Figure 6 Drawing taken from TEM cross-section of interface before and after annealing.

determining the precise position where fracture occurs within the interface and will affect the overall performance of the brazed materials at high temperatures. In this case, fracturing appeared to occur intergranularly within the reaction products of the glassy grain boundary phase, e.g. between Al–Si–Mg–O and Ti–Si phases. Mechanical properties of Ti-coated 95% and 99% alumina showed that the 95% alumina had a greater reduction in MOR strength (e.g. 25% reduction) compared to that of the 99% alumina (e.g. 15%) which contained less silicate grain boundary phase [10]. The present work serves to show that the reaction layers of titanium on a commercial ceramic substrate should be controlled to ensure strong bonding between the braze and the ceramics in practical applications.

4. Conclusion

The current study has explored the interface region between Ti-coating and commercial alumina substrate. It appeared that the titanium reduced the alumina substrate to produce columnar grains of Ti_3Al in which a small amount of oxygen was in solid solution. The Ti_3Al grains at the interface often display arrays of dislocations, presumably arising from a thermal expansion mismatch. The formation of silicide compounds such as Al–Si–Mg–O and Ti_5Si_3 due to the presence of amorphous grain boundary phases (i.e. Al–Si–Mg–Ca–O) has not been previously reported. These phases suggest that grain boundary phases and impurities may play a significant role in adhesion and the development of stresses at ceramic–metal interfaces.

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