Characterization of the brazed joint interface between Al_2O_3 and (Ag–Cu–Ti)

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Ceramics are becoming increasingly important engineering materials in electronics, aerospace, and automotive industries because of their excellent heat resistance, high temperature strength, and corrosion resistance properties [1, 2]. With the development of new ceramic materials, including those for structural applications, there is an increasing demand for joining ceramic components to metal/ceramic structures or components [3].

The inherent brittleness associated with the ceramics limits their application as structural components when complicated geometries are needed. The joining of ceramic parts for shape fabrication can expand the utilization of such ceramics and tolerances not readily achieved otherzise [4]. The joining of ceramics is complicated due to poor wetting of ceramic surfaces by the conventional brazing alloys. Therefore, it is necessary to develop a reaction layer at the ceramic surfaces to increase their wetting behavior with the liquid filler alloy [4, 5]. One such method is the moly-manganese metallization process developed for the joining of ceramics [6]. The process is highly reliable, but requires a high degree of process control [4] and is time consuming due to the involvement of multiple steps. The process is expensive and applicable only for high temperature requirements. Another way of joining the ceramics is through the use of an active metal in the brazing alloy. The process being a single step is cost-effective and joining temperature can be between 650 and 1300 °C as required. It has been observed that the filler alloy containing an active metal like Ti or Zr can join ceramics without metallization, because these active metals react to change the chemistry of the ceramic surfaces [7].

The bond strength of the brazed joints depends on the interfacial characteristics of the ceramics and the brazing alloy. The interfacial characteristics mainly depend on the filler alloy composition, the ceramics to be joined, and the reaction conditions, such as temperature, holding time, and load applied over the braze assembly. With the same active filler alloy there are different kinds of interfacial reactions for different types of ceramics, namely oxides, carbides, and nitrides. Less attention has been given to the joining oxide ceramics, such as alumina.

The investigation of the reaction products at the interface is important in the design of the brazed joints, and it will serve as a guideline for optimizing the brazing conditions for reliable ceramic to ceramic/metal joints. In this letter the interfacial characterization of alumina and the active filler alloy, Ag–Cu–Ti, has been studied to understand the joining behavior.

Silver-based Ag28Cu eutectic alloy was prepared by melting high purity (99.9%) Ag and Cu in an electrical resistance heating furnace. 3 wt% titanium metal of 99% purity was added to the molten eutectic alloy to prepare the active filler alloy [8, 9]. Subsequently the active alloy was cold rolled to 0.5 mm thick strip. The alloy foil was further thinned down to 0.2–0.1 mm with the help of different grades of emery paper.

Cylindrical alumina pellets, made from Alcoa, USA, A16SG powder, were sintered at 1600 °C for 30 min. The sintered Al_2O_3 was cut in the form of 10 mm dia × 10 mm thick by a diamond wafer blade (precision cut off machine: MECATOME P100, Presi, France). The surfaces of the Al_2O_3 pieces were polished with 0.5 μm diamond paste on a ground glass. The polished Al_2O_3 pieces were ultrasonically cleaned with ethyl alcohol and then with petroleum ether to remove dirt and grease.

The thin foil (0.2–0.1 mm) of active filler alloy was then cut into 9 mm dia. disks, and a disk was placed between two polished Al_2O_3 disks. A dummy load of 1 kg was placed over the assembled sample which was kept in a graphite resistance furnace (ASTRO, Thermal Inc., USA). The joining process was carried out under vacuum (∼60 m Torr) at five different brazing temperatures, such as 800, 900, 1000, 1100, and 1200 °C, and in each case the holding time was 15 min.

The phases in the brazed joints were analyzed by XRD (Scifert, PTS 3003, Germany). The polished sample was carbon coated and analyzed by electron probe micro analyzer (EPMA) (JXA-8600M, Jeol, Japan) and by SEM-EDX (840A-Jeol, Japan). The EPMA dot mappings of the samples were carried out from the Al_2O_3 towards the active filler alloys for elements Ti, Al, Ag, and Cu. The analyses of the samples were performed at equal intervals of 2 μm along a line across the interface.

Silver has a low-vapor pressure and possesses adequate fluidity at high temperature. It has very good solubility in copper and also in other metals. The alloying results in the formation of solid solutions and depression of the melting point.

Titanium has a solubility of 67% at 1150 °C in copper and forms intermetallic phases, which do not have a significant role during the brazing. In the presence of silver, the tendency of titanium to associate with copper

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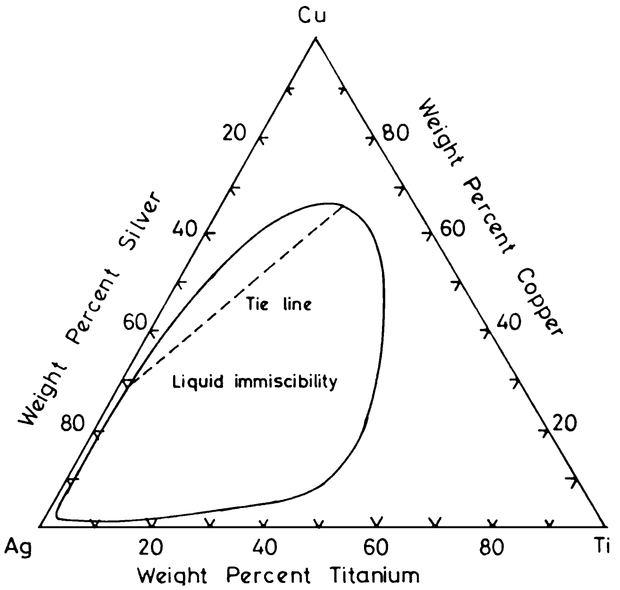

Figure 1 Ag–Cu–Ti ternary phase diagram, showing the critical tie line that links the two liquid phases of Ag-27Cu-2Ti and Ag-66Cu-22Ti.

in the alloy is reduced and the active Ti metal in the liquid is released, thereby increasing the activity of the Ag–Cu–Ti alloy [10]. According to the ternary phase diagram (Fig. 1) [11], the titanium causes the molten silver–copper alloy to separate into two fractions, one with a composition of Ag27Cu2Ti and the other with Ag66Cu22Ti. The 22 vol% titanium is more than adequately active to ensure wetting of even highly refractory ceramics such as alumina, silicon carbide, silicon nitride, or graphite.

A representative electron probe microanalysis (EPMA) of the Al_2O_3–Al_2O_3 brazed at 900 °C is shown in Fig. 2. It is observed that the joining process is due to the interdiffusion of Ti, Ag, and Cu from the brazing alloy towards Al_2O_3 and Al from Al_2O_3 towards the filler alloy, thus forming the interfacial layer. In comparison with Cu, the solubility of Ti in Ag is very low and there are two phases in the Ag–Cu–Ti filler alloys, namely Ag-rich (bright) and Cu-rich (dark) phases. Therefore, the concentrations of Ag, Cu, and Ti depend on the particular phase present in the filler alloy at that point. Thus the thickness of the interface (the shaded area in Fig. 2) has been measured on the basis of change in the aluminum concentration between the Al_2O_3 and the filer alloy. At the interface, the concentration of silver is found to be lower than the other elements (viz., Al, Cu, and Ti), but the small amount of silver is effective in increasing the activity coefficient of titanium [11, 12] for a sound joint.

From Fig. 2 it is evident that from alumina to position (a) the Ti concentration is much higher than that of Cu, whereas, around (b) position, the atomic percentage of Ti and Cu is more or less the same. Qualitative EPMA X-ray dot maps of brazed Al_2O_3 samples at different temperatures confirmed that during brazing most of the Ti is diffused towards the interfacial zone from the filler alloy. A representative dot map is shown in Fig. 3.

The X-ray diffraction analyses of the brazed joints were carried out for identification of different phases developed at the interface during the joining process. As the thickness of the interface is only 4–10 μm and there are several phases within that thin section, the following procedure was adopted to identify the phases. In each brazed sample there are altogether five layers, namely, Al_2O_3, interface, filler alloy, another interface, and Al_2O_3 as shown in Fig. 4.

To identify the phases in the interface, one of the Al_2O_3 layers was removed slowly step by step to reach the interfacial layer. After each step of removal, XRD analysis was done. Some of the XRD results are shown in the Fig. 5. Initially all the XRD peaks correspond to Al_2O_3 (Fig. 5a). After removal of a few micrometers, Ag and Cu phases were identified along with Al_2O_3 and the color of that layer looked dark (Fig. 5b). TiO and

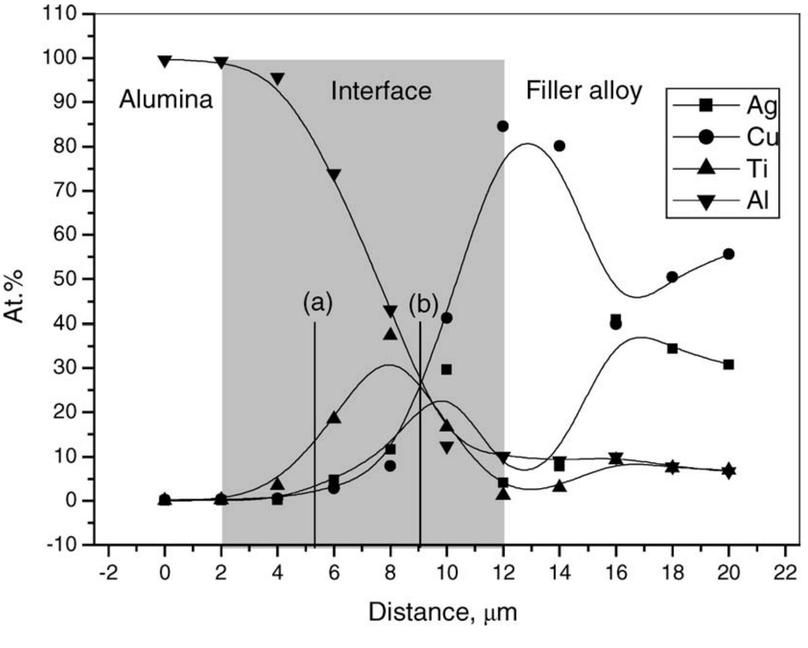

Figure 2 Electron probe microanalysis (EPMA) of transverse section of Al_2O_3 brazed with 97(Ag28Cu)3Ti at 900 °C for 15 min holding time.

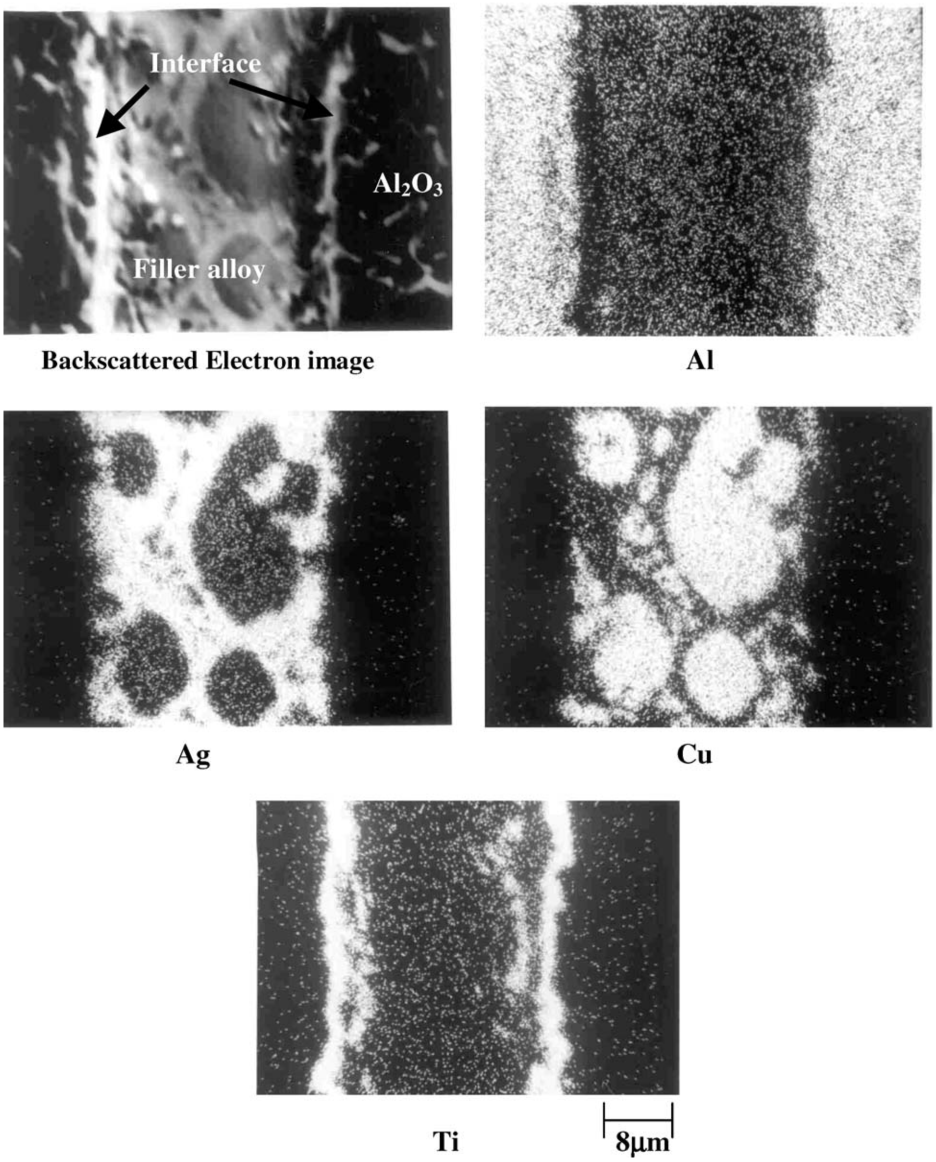

Figure 3 Backscattered electron image (BSEI) and X-ray dot maps of transverse section of Al_2O_3 brazed with 97(Ag28Cu)3Ti at 1000 °C for 15 min holding time. Magnification of all the figures is equal.

Ti_3Cu_3O phases were identified (Fig. 5c) when a few more micrometers were removed. The color of this layer appeared to be almost black. At the end, Ag, Cu, and a very small amount of Al_2O_3 were found (Fig. 5f). Both Cu_2Ti_4O and Ti_3Cu_3O are cubic in nature and have the *Fd*3*m* space group [13], therefore the major peaks of both these phases more or less coincide. However, the EPMA (Fig. 2) and SEM-EDX (Fig. 6) analyses show that adjacent to Al_2O_3 there is a very small amount of Cu and the amount of Ti is substantial, which corresponds to the TiO phase. In contrast at the middle of the interface, the atomic percentage ratio between Ti and Cu is almost 1 (Fig. 2). Therefore, the formation of the Cu_2Ti_4O phase is unlikely, and the Ti_3Cu_3O phase is favored. Both TiO and Ti_3Cu_3O phases are equally important in terms of the bond strength between Al_2O_3 and the Ag–Cu–Ti filler alloy. However, the TiO phase cannot account for the thermal expansion mismatch strains, which can affect adhesion [13–15]. The Ti_3Cu_3O phase provides a gradual transition in thermal expansion coefficient between Al_2O_3 and the filler alloy, which helps to minimize the effect of local strains developed from thermal expansion coefficient mismatches, Table I.

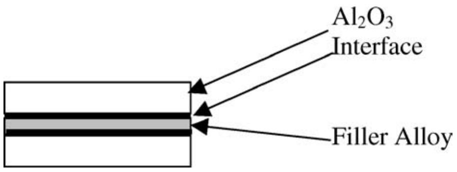

Figure 4 Schematic diagram of brazed joined sample.

TABLE I Coefficient of thermal expansion of different phases

Phase	Coefficient of thermal expansion (CTE) ($\times 10^{-6}\,°C^{-1}$)
Al_2O_3	8.5 [16]
TiO	9.2 [17]
Ti_3Cu_3O	15.1 [16]
Ag	19.2 [18]
Cu	22.0 [16]

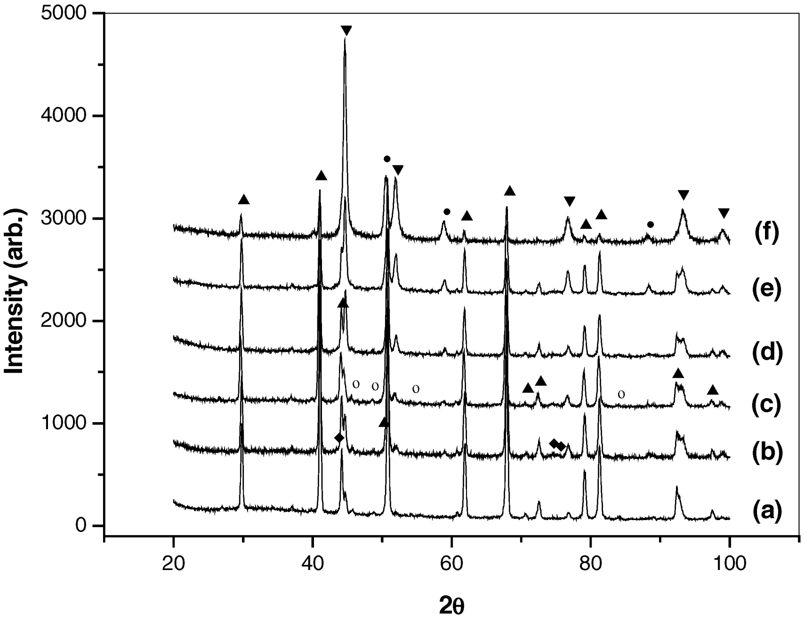

Figure 5 XRD patterns of Al_2O_3 brazed with 97(Ag28Cu)3Ti filler alloy at 1000 °C: (a) layer containing mainly Al_2O_3 and (b)–(f) gradual change of interface from Al_2O_3 to the filler alloy.

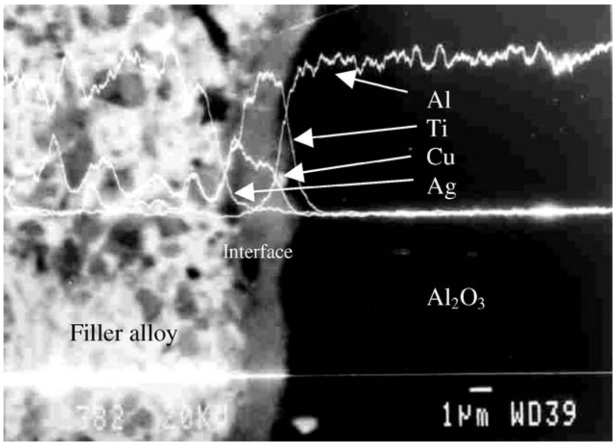

Figure 6 Line profile EDX analysis of transverse section of Al_2O_3-brazed sample at 1000 °C for 15 min holding time.

Acknowledgments

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