

Role of Ti diffusion on the formation of phases in the Al_2O_3 – Al_2O_3 brazed interface

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Abstract Diffusivities of Ti, Cu, Al and Ag in the interface of Al_2O_3 – Al_2O_3 braze joints using Ag–Cu–Ti active filler alloy, have been calculated by Matano–Boltzman method. The Matano plane has been identified for each elemental diffusion at various brazing temperatures. The diffusivities of Ag, Cu and Al are almost insignificant on formation of interface during brazing, whereas the diffusivity of Ti changes significantly with the brazing temperature and controls the formation of different reaction product in the interface. Presence of TiO and $\text{Ti}_3\text{Cu}_3\text{O}$ phases in the interface has been confirmed by transmission electron microscopy (TEM).

Introduction

The application of ceramics in structural components, has received extensive attention in recent decades due to their excellent high temperature strength and resistance to corrosion and wear. Ceramics are more refractory and less dense than metals and can be stronger than metals, therefore it has enormous scope of application in electronics, aerospace, nuclear and automotive industries [1, 2]. The ceramics are now being used in batteries, integrated

circuits, cutting tools and also as biomaterials. However, because of their brittle nature, joining of ceramics to ceramics/metals is frequently required. The ability to produce a reliable ceramic–ceramic/metal and composite joint is a key enabling technology for many productions, prototype and advanced developmental items and assemblies. Joining of two materials, whether homogeneous or heterogeneous almost always causes changes in the microstructure and mechanical properties in the vicinity of joint. A better understanding of the microstructure and mechanical property relationships of the braze joints will give valuable feed back to the materials developmental activities both in conventional and new material areas [3]. One of the basic problems in brazing of ceramics lies in their poor wetting by the conventional brazing alloys. The wetting behaviour of the ceramic surfaces by the liquid metals has long been the subject of study. It is well known that in many systems the wetting process depends on the chemical reactions occurring at the solid/liquid interface. Normally, the active filler alloys used for direct joining contain reactive additive elements such as Ti, Zr, Ta etc. These elements enable the surface of the ceramic to be wetted during brazing and thus provide a good joint [4]. The purpose of adding active element is to improve the wetting properties of the ceramics. At elevated temperatures (1073 K and above), the active element reacts with the non-metallic materials to form a complex interfacial layer that is wettable by the silver–copper brazing alloy.

The systematic characterization of the interface of ceramic braze joint is most important to understand the quality of the joint [5]. Presence of different reaction products in the interface determine the nature/quality of the joint. As the amounts of the reaction products in the interface of alumina braze joint are low and there are more than one phases, it is difficult to identify the phases.

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Therefore, there is a need for confirmation of the phases present in the interface. In this paper an attempt has been made to confirm different phases formed during brazing. It has been felt that the analysis of the nature of diffusivity of different elements across the brazed interface will help understand the brazing quality. In this paper an attempt has also been made to determine the diffusivities of Ti, Cu, Al and Ag across the interface of alumina braze joint system.

Experimental

Ag and Cu of 99.9 wt% pure were used to prepare silver based eutectic alloy and 99.5 wt% pure Ti was incorporated into the alloy by melting technique to prepare 97(Ag28Cu)3Ti active filler alloy [6]. The alloy was prepared in an electrical resistance-heating furnace under argon flowing atmosphere. The weight of the active filler alloy ingot was ~100 gm. Conventional chemical analysis of the active filler alloy confirms the composition as 70.3 wt% Ag, 26.8 wt% Cu and 2.9 wt% Ti. The active filler alloy was cold rolled down to 0.5 mm thick strip. The alloy foil was further thinned down to 0.2 mm mechanically by grinding on emery paper.

A16SG alumina powder (Alcoa, USA) was compacted and sintered at about 1873 K for 30 min in air at the rate of 10 K/min with 0.5 wt% MgO as sintering aid. The sintered Al_2O_3 was cut into 7 mm length \times 7 mm breadth \times 4 mm thickness by a precision cut-off machine using diamond wafer blade (MECATOME P 100, Presi, France). The surfaces of the Al_2O_3 pieces were polished with 0.5 μm diamond paste. The polished Al_2O_3 pieces were then ultrasonically cleaned with ethyl alcohol and petroleum ether to remove the dirt, and grease. A thin foil of active filler alloy were cut into 6 mm length \times 6 mm breadth \times 0.2 mm thick size and was placed between two Al_2O_3 pieces. A constant load of ~1 Kg was placed over the assembly to keep the filler alloy in contact with the substrates [7–11] and kept in a graphite resistance furnace (ASTRO, Thermal Inc., USA). The joining processes were carried out under vacuum at 1073, 1173, 1273, 1373, and 1473 K and soaked for 15 min. at the highest temperatures. Before heating, the furnace was purged with argon gas (IOLAR I) three times to minimise the oxygen partial pressure. At room temperature the vacuum level was ~30 millitorr, whereas at the brazing temperatures it was ~50 millitorr. The brazed samples were cut by precision cut off machine with diamond wafer blade and then characterized by SEM, EPMA and TEM. The carbon coated samples were used for Scanning Electron Microscopy (Jeol 840A, Japan) and Electron Probe Micro Analysis (EPMA) (JXA-8600 M, Jeol, Japan). The quantitative compositional analyses of the samples were carried out at an equal

interval of 2 μm along a line across the interface by EPMA.

The interface was systematically characterized by TEM [12]. The samples for TEM analyses were prepared by dimple grinding [3] and ultrasonically cleaned with acetone. A number of samples were analyzed by Transmission Electron Microscope (CM 200 Philips, Netherlands, fitted with EDAX-DX 4) for identification of the phases present in the interface.

Quantitative EPMA results were taken into consideration for calculating the diffusivity of Ti, Al, Cu & Ag by graphical integration. A software program was developed [13] to find out the Matano plane, from the concentration vs. distance plot (obtained from EPMA) and then the diffusivity of the individual elements were calculated by the Matano–Boltzman method using the Eq. ii.

Results and discussion

Scanning electron micrograph of Al_2O_3 – Al_2O_3 brazed at 1273 K shows that well-defined interfaces have been formed adjacent to both the alumina substrates. The widths of the interfaces are ~10 μm (Fig. 1). A representative electron probe microanalysis (EPMA) of the Al_2O_3 – Al_2O_3 brazed at 1273 K is shown in Fig. 2. It is observed that the joining process is due to the inter diffusion 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 layers of different reaction products. The interface characterized by XRD may not always conclusive, particularly when there are multiple phases present within a very small (~10–15 μm) area. Thus the reaction products formed in the interface are analysed and confirmed by TEM.

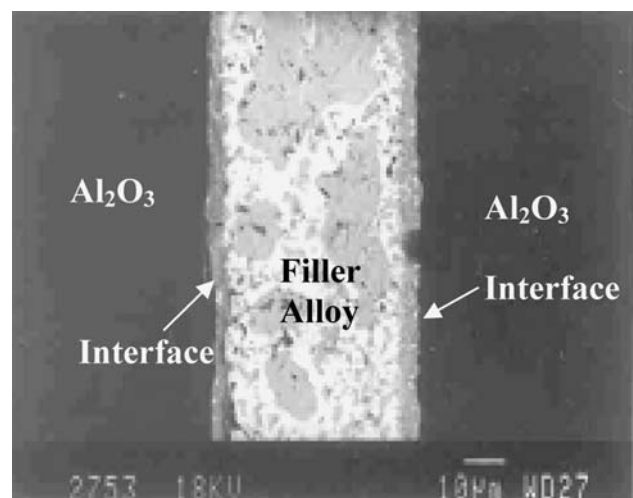


Fig. 1 Scanning electron micrograph of Al_2O_3 – Al_2O_3 brazed sample

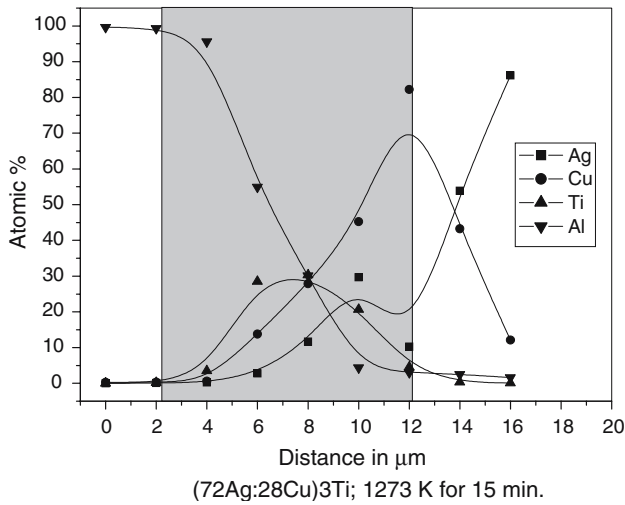


Fig. 2 EPMA analysis of Ag, Cu, Ti and Al across the Al_2O_3 – Al_2O_3 brazed joint

Selected area diffraction patterns (SADP) obtained from the grains at the interface are shown in Figs. 3 and 4. Analyzing the diffraction pattern and EDX in Fig. 3 confirms the presence of TiO . Whereas, Fig. 4 confirms the $\text{Ti}_3\text{Cu}_3\text{O}$ phase. The corresponding indexing are depicted in the inset of the respective figures. EPMA analysis (Fig. 2) shows that the Ti-rich layer formed adjacent to the Al_2O_3 surface. Therefore, considering EPMA and TEM results, the presence of cubic TiO phase has been concluded at the Al_2O_3 surface. Presence of TiO and $\text{Ti}_3\text{Cu}_3\text{O}$ phases are equally important to attribute the bond strength between Al_2O_3 and the Ag–Cu–Ti filler alloy [14]. The TiO and $\text{Ti}_3\text{Cu}_3\text{O}$ phases provide a gradual transition in physical properties and help minimize the effect of local stresses that develop from the mismatch between the coefficient of thermal expansions of Al_2O_3 and residual filler alloy (containing mostly Ag and Cu).

EPMA analysis of braze joint was used to determine the diffusivity of different elements. The diffusivity was

calculated by the Matano–Boltzman method. The position of Matano interface for each of the elemental diffusion was determined by graphical integration using a computer programme specially developed for this purpose [13]. For each individual case (i.e. elemental diffusion) separate programs have been written. With the help of Fick's second law, the diffusivity \tilde{D} has been calculated, using the Eq. ii. Then according to the Fick's second law, i.e.

$$\frac{\partial n_i}{\partial t} = \frac{\partial}{\partial x} \left(\tilde{D}_i \frac{\partial n_i}{\partial x} \right) \quad (\text{i})$$

where n_i is concentration of the i th species. x is the direction in which diffusion occurs and t is the time.

Matano [15] has shown that, when \tilde{D}_i depends on x through n_i [16] and is expressed as

$$\tilde{D}_i(n_i) = -\frac{1}{2t} \frac{\int_0^{n_i} x \partial n_i}{(\partial n_i / \partial x)} \quad (\text{ii})$$

where the origin x axis must be chosen so that

$$\int_0^{n_i, \max} x \partial n_i = 0 \quad (\text{iii})$$

This origin defines the Matano plane. At Matano plane, the diffusion is in equilibrium state. Two typical examples, one for Ti and other for Al are shown in (Figs. 5 and 6). The nature of the curves for Cu and Ag are very much similar but follow a trend opposite to that in curve for Al, which resembles the usual diffusion pattern.

From Fig. 7 and Table 1 it is observed that within the temperature range of 1073–1473 K the diffusivities of Ag, Cu, and Al are almost parallel to the X axis. Whereas, the diffusivity of Ti gradually increases with temperature up to ~1350 K, and remains almost parallel to X-axis till

Fig. 3 TEM micrograph, SAD pattern and EDX analyses of Al_2O_3 braze joint confirm the presence of TiO at the interface

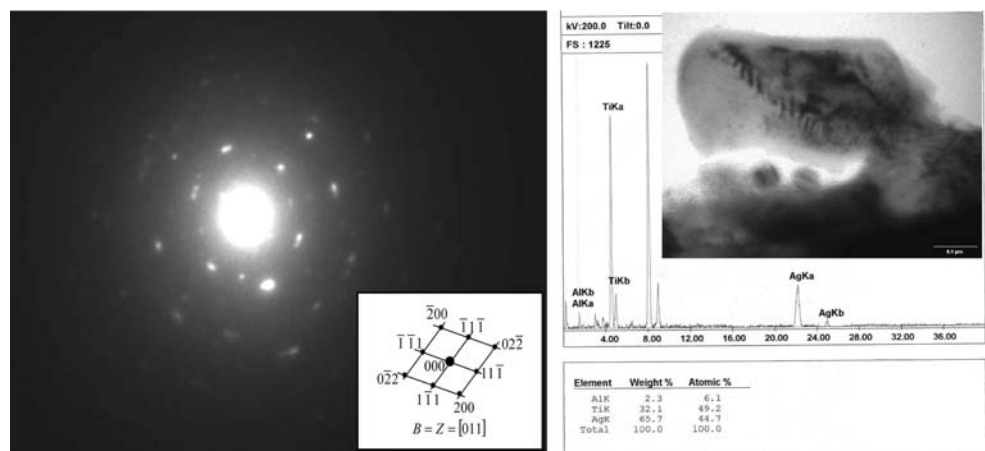


Fig. 4 TEM micrograph, SAD pattern and EDX analyses of Al₂O₃ braze joint confirm the presence of Ti₃Cu₃O at the interface

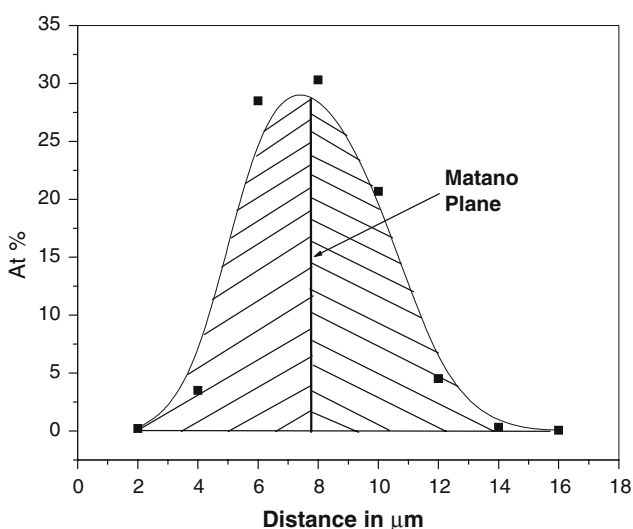
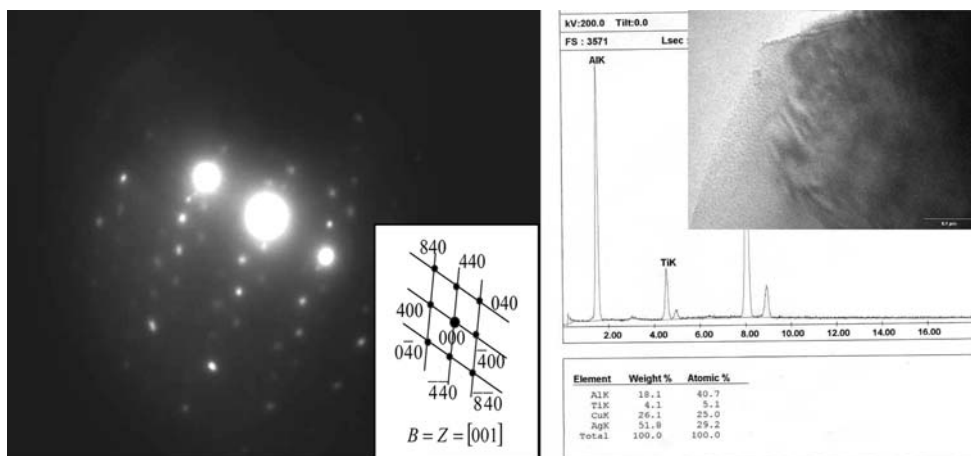


Fig. 5 EPMA analysis of Ti across the interface of Al₂O₃–Al₂O₃ brazed at 1273 K with 97(Ag28Cu)3Ti filler alloy

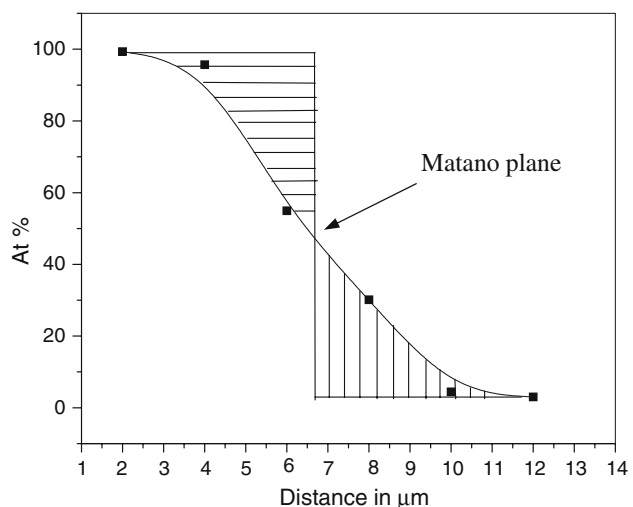


Fig. 6 EPMA analysis of Al across the interface of Al₂O₃–Al₂O₃ brazed at 1273 K with 97(Ag28Cu)3Ti filler alloy

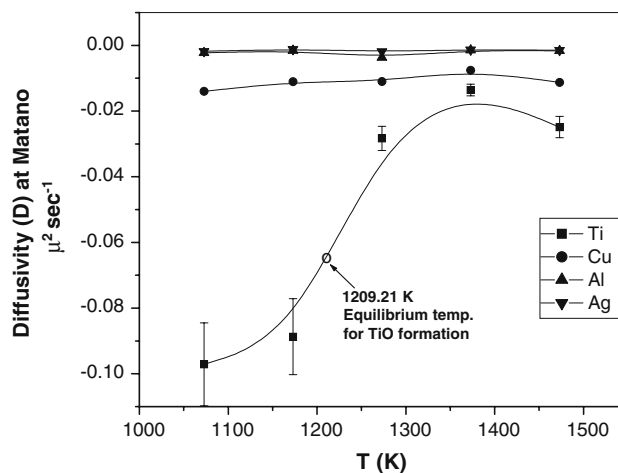
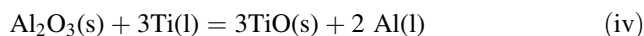


Fig. 7 Diffusivity of Ti, Cu, Al and Ag measured in liquid braze filler metal

1396 K, then it starts decreasing. This clearly shows that the influence of Cu, Ag or Al diffusion is negligible for alumina brazing with Ag–Cu–Ti active filler alloy. This is because the reduction potential of Ag and Cu is not sufficient to reduce Al₂O₃ to Al. Therefore, these have very little effect on the over all reactions. The diffusion of Ti plays the most significant role on the alumina brazing.

The thermodynamic feasibility of any reaction at a particular temperature can be determined by calculating the free energy change for the reaction at that particular temperature. In the present study the reaction between the active element of Ag–Cu–Ti filler alloy, i.e. Ti, and the ceramic substrate, promotes the brazing successfully as follows,



Under the brazing atmosphere the pressure is kept constant, thus the feasibility of the above reaction at dif-

Table 1 Variation of diffusivity of different elements with temperature

Temp. (K)	Diffusivity, \tilde{D} ($\mu\text{m}^2 \text{s}^{-1}$)			
	Al	Cu	Ti	Ag
1073	-0.00226	-0.0077	-0.0971	-0.0018
1173	-0.00159	-0.0111	-0.0887	-0.0012
1273	-0.00368	-0.011	-0.02833	-0.00183
1373	-0.00145	-0.0076	-0.0136	-0.00129
1473	-0.00164	-0.0113	-0.0249	-0.00144

Table 2 Thermodynamic data for the reaction $\text{Al}_2\text{O}_3(\text{s}) + 3\text{Ti}(\text{l}) = 3\text{TiO}(\text{s}) + 2\text{Al}(\text{l})$

T (K)	ΔH (J mol^{-1})	ΔG (J mol^{-1})	ΔS (J K^{-1})	K_{eqm}
1073	41980	4971	34	0.572
1173	45291	1374	37	0.886
1209.20	46546	0.1	35	0.9999
1209.21	46546	0.0	35	1.0000
1209.22	46547	-0.6	35	1.0001
1273	48826	-2514	40	1.2682
1373	52562	-6689	43	1.7967
1473	55862	-11140	45	2.483
1573	55416	-15671	45	3.3143

ferent brazing temperature can be calculated using Gibb's—Helmholtz equation, i.e.

$$\Delta G_T = \Delta H_T - T\Delta S \quad (\text{v})$$

The relevant thermodynamic data for the formation of TiO during brazing have been tabulated in Table 2 [17–19]. The experimental result shows that although the diffusion of Ti is observed even at 1073 K but it sharply increases after 1173 K, which is in good agreement with the thermodynamic feasibility of the formation of TiO(s). Similar type of diffusivities have also been observed when alumina was brazed with 97(Ag40Cu)3Ti filler alloy [20]. From Fig. 7 and Table 2 it is observed that the equilibrium temperature for the formation of TiO(s) is 1209.21 K. and the reaction is thermodynamically feasible after this temperature. In the present study the sample prepared within the temperature range of 1173–1373 K, TiO and $\text{Cu}_3\text{Ti}_3\text{O}$ phases have been confirmed by TEM analyses (Figs. 3 and 4). Presence of TiO and $\text{Cu}_3\text{Ti}_3\text{O}$ in the interface indicates that the Ti concentration in the liquid filler metal was high enough to reduce the alumina surface hence the brazing takes place.

Conclusion

The nature of elemental diffusion during active metal brazing can be determined by Matano–Boltzman method. The rate of Ti diffusion in the liquid filler metal controls

the formation of different oxide phases in the interface, hence facilitates the brazing process. In case of alumina-{97(Ag28Cu)3Ti}-alumina system, substantial amount Ti diffusion is observed within 1173–1373 K, which is desirable for the formation of the different reaction products such as TiO, $\text{Cu}_3\text{Ti}_3\text{O}$. Diffusivities of Ag, Cu and Al are almost independent with the brazing temperatures.

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