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Electric field-assisted and field-depressed segregation of reactive metals to the bonding interface in braze alloy joining

T. MINEGISHI, T. SAKURAI, S. MOROZUMI
Chiba Institute of Technology, Narashino 275, Japan

Segregation of reactive metals at the bonding interface has been observed in various ceramic and/or metal joints bonded with reactive metal-bearing braze alloys. When a d.c. of 20 mA cm^{-2} is applied to the ceramic/braze/ceramic system at a brazing temperature of, say, 1373 K, the electric field assists the segregation at the braze–ceramic interface on the cathode side and suppresses the segregation at the interface on the anode side. This may imply that reactive metal atoms in the braze can migrate as a cation. E.m.f. measurement on the ceramic (AlN or ZrB_2)–metal foil systems with increasing temperature shows that a negative e.m.f. to the ceramic pole appears from about 900 K for AlN and from 500 K for ZrB_2, as does the thermally stimulated current in polymers. These temperatures coincide well with those where the electrical conductivity of AlN and ZrB_2, respectively, begins to increase with increasing temperature. Therefore, it is considered that the polarization of the ceramics may take place and assist the migration, and consequently segregation, of reactive metals in braze alloys to the braze–ceramic interface during brazing.

1. Introduction

It is well known that reactive metal bearing (such as titanium) braze alloys are very useful for joining metals and/or ceramics, and that, simultaneously, the metal segregates at the bonding interface [1–3]. The mechanism of the segregation, however, is not well understood. For example [2], when zirconium diboride (ZrB_2) ceramic was joined to itself with copper (Cu) braze alloys containing titanium (Ti), zirconium (Zr), and hafnium (Hf) at the same atomic per cent, respectively, the degree of segregation of the reactive metals, estimated by the thickness of the metal-segregated layer at the interface, was not inversely proportional to the standard free energy of formation of the borides: the thickest layer was formed in the Ti-bearing braze alloy, though the free energy of formation of titanium diboride (TiB_2) is the highest of the three. Similar phenomenon was also observed in the joining of aluminium nitride (AlN). Thus, the segregation behaviour of Ti in Cu braze alloys was investigated by varying the joining temperature and the time for joining of AlN. The result showed that the thickness of the Ti-segregated layer at the bonding interface increased linearly with temperature and time, as illustrated in Fig. 1. This might apparently suggest that Ti atoms migrated to the interface, as if they were forming an ion current in the molten braze alloy during brazing treatment.

Therefore, the present paper deals with the effect of electric field on the segregation of Ti in a Cu–Ti braze alloy to the braze–ceramic interface in the joining of AlN and ZrB_2 ceramics. As the segregation of Ti at the bonding interface was also observed in molybdenum (Mo) joints [4], a similar effect was expected in the metal joining systems. The molybdenum (Mo)–Tungsten (W) system was also investigated, as a

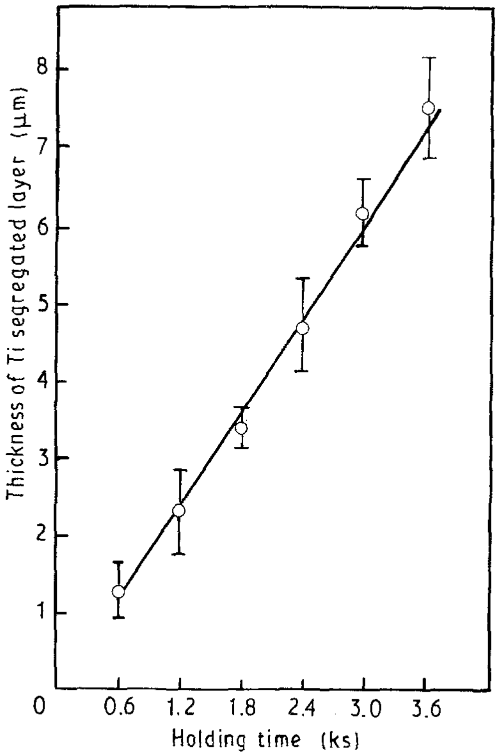

Figure 1 Variation of thickness with holding time at 1273 K of the Ti-segregated layer at the braze–ceramic interface in an AlN joint bonded with Cu–Ti braze alloy.

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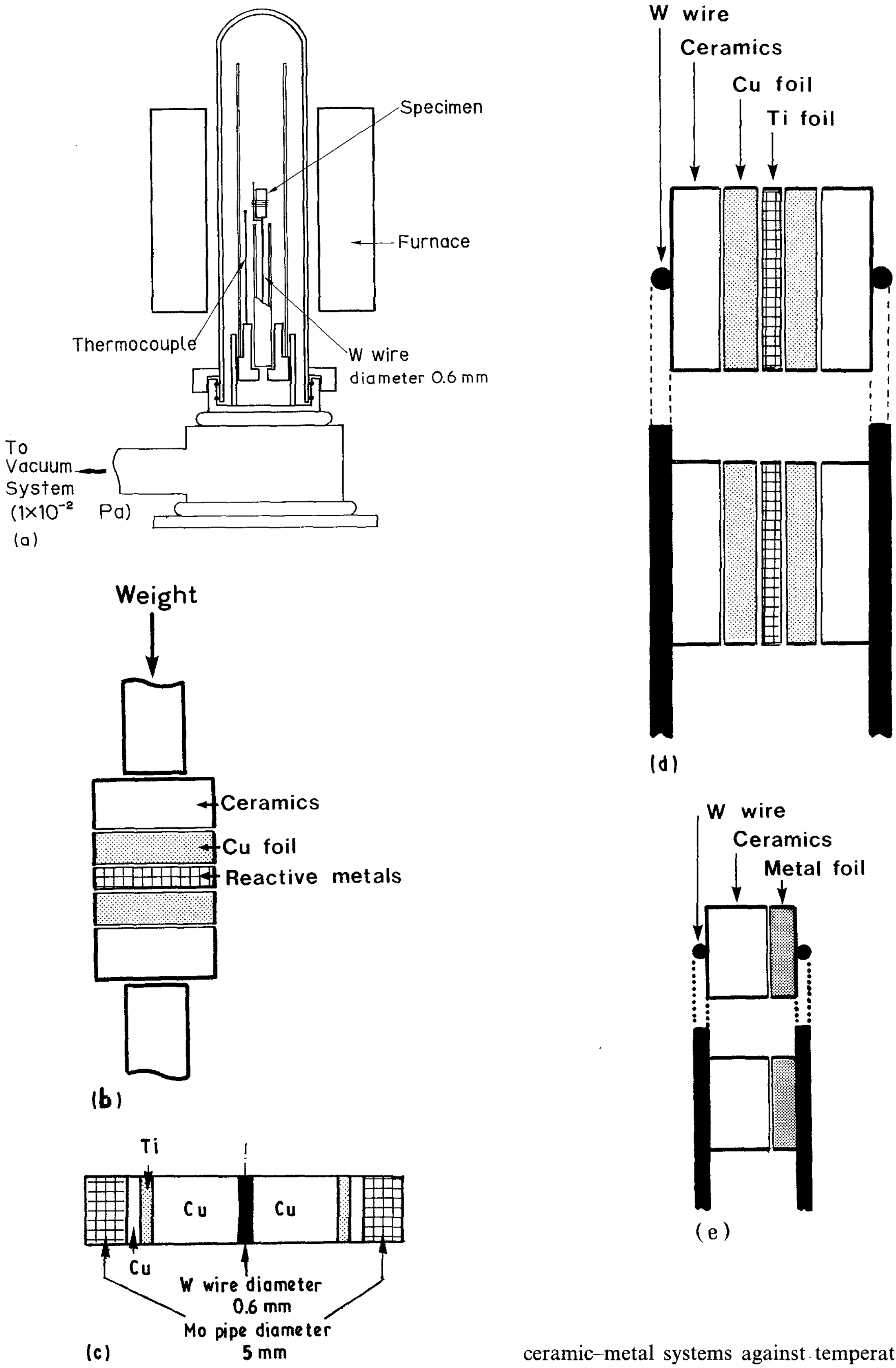

Figure 2 (a) Heating apparatus, and specimen arrangements of (b) ceramic/Cu/reactive metal/Cu/ceramic system for brazing, (c) Mo/Cu/Ti/Cu/W system for electric-field effects, (d) ceramic/Cu/Ti/Cu/ceramic system for electric-field effects, and (e) ceramic/metal system for e.m.f. measurement.

reference. In addition, as it was inferred that the ceramics themselves may contribute to the segregation behaviour of reactive metals by any ionic processes, electromotive force (e.m.f.) was measured on the ceramic–metal systems against temperature. Finally, the results were considered from the thermally stimulated current (TSC) point of view.

2. Experimental details

2.1. Materials and specimen arrangements

Fig. 2 shows vertical sections of (a) the heating apparatus, and specimen arrangements of (b) ceramic/Cu/reactive metal (Ti, Zr, or Hf)/Cu/ceramic system for brazing, (c) Mo (tube wall)/Cu/Ti/Cu/W (wire) system

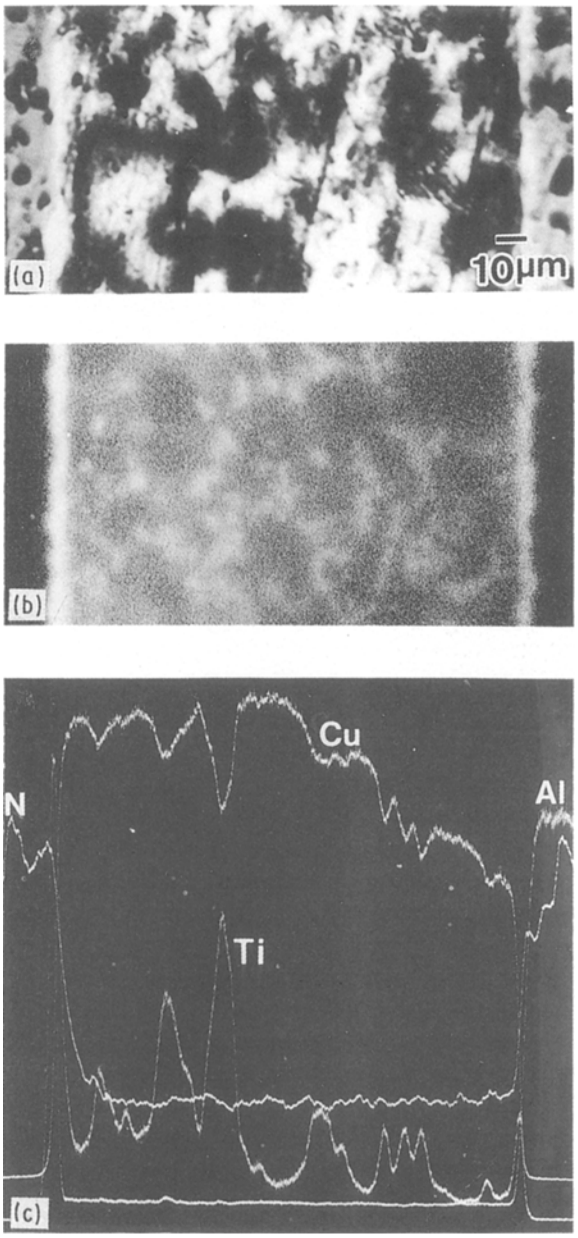

Figure 3 (a) Microstructure, (b) TiK_α X-ray image, and (c) line profiles of the AlN joint bonded with Cu–Ti braze alloy at 1273 K for 1200 s.

for electric-field effects, (d) ceramic/Cu/Ti/Cu/ceramic system for electric-field effects, and (e) ceramic/metal system for e.m.f. measurement. The ceramic materials used in the present work were sintered AlN and ZrB_2, and cut to a size of 5 mm square and 3 mm thick. The thickness of the metal foils was approximately 20 µm for Ti, Zr and Hf, and 50 µm for Cu, in order to obtain Cu–20 at % reactive metal braze alloys, respectively, at the brazing temperature.

2.2. Procedure

Brazing of ceramics was performed under a weight of 300 g in a vacuum of 10^{-2} Pa for 1.200 s at a given temperature between 1.273 and 1.473 K.

Experiments on electric-field effects were performed by heating the specimen arrangements shown in Fig. 2c and d at 1373 K for 600 s: Fig. 2c is for the Mo/Cu–Ti/W system, where the Cu-4 at % Ti alloy with a 0.6 mm diameter W wire at the centre is located in an Mo tube of 5 mm o.d. and 4 mm i.d.; a direct current (d.c.) of 5 mA was applied between the W wire and Mo tube wall. Fig. 2d is for the ceramic/Cu–Ti/ceramic system, where the Cu/Ti/Cu three foil layer is sandwiched between two pieces of the ceramic; a d.c. of 5 mA, i.e. a current density of 20 mA cm^{-2}, was applied to the ceramic by the W lead wire attached to the ceramic.

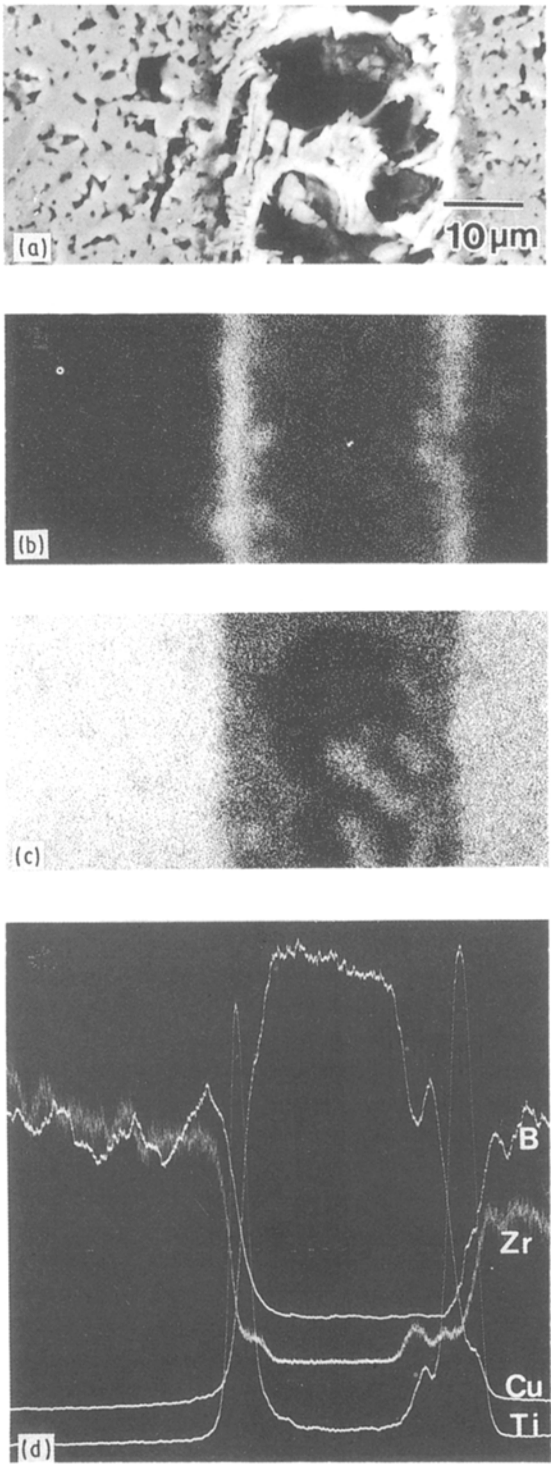

Figure 4 (a) Microstructure, (b) TiK_α X-ray image, (c) ZrL_α X-ray image, and (d) line profiles of the ZrB_2 joint bonded with Cu–Ti braze alloy at 1273 K for 1200 s.

E.m.f. was measured up to 1.373 K at a heating rate of about 1 K s^{-1}, and at 1.373 K for 300 s on several

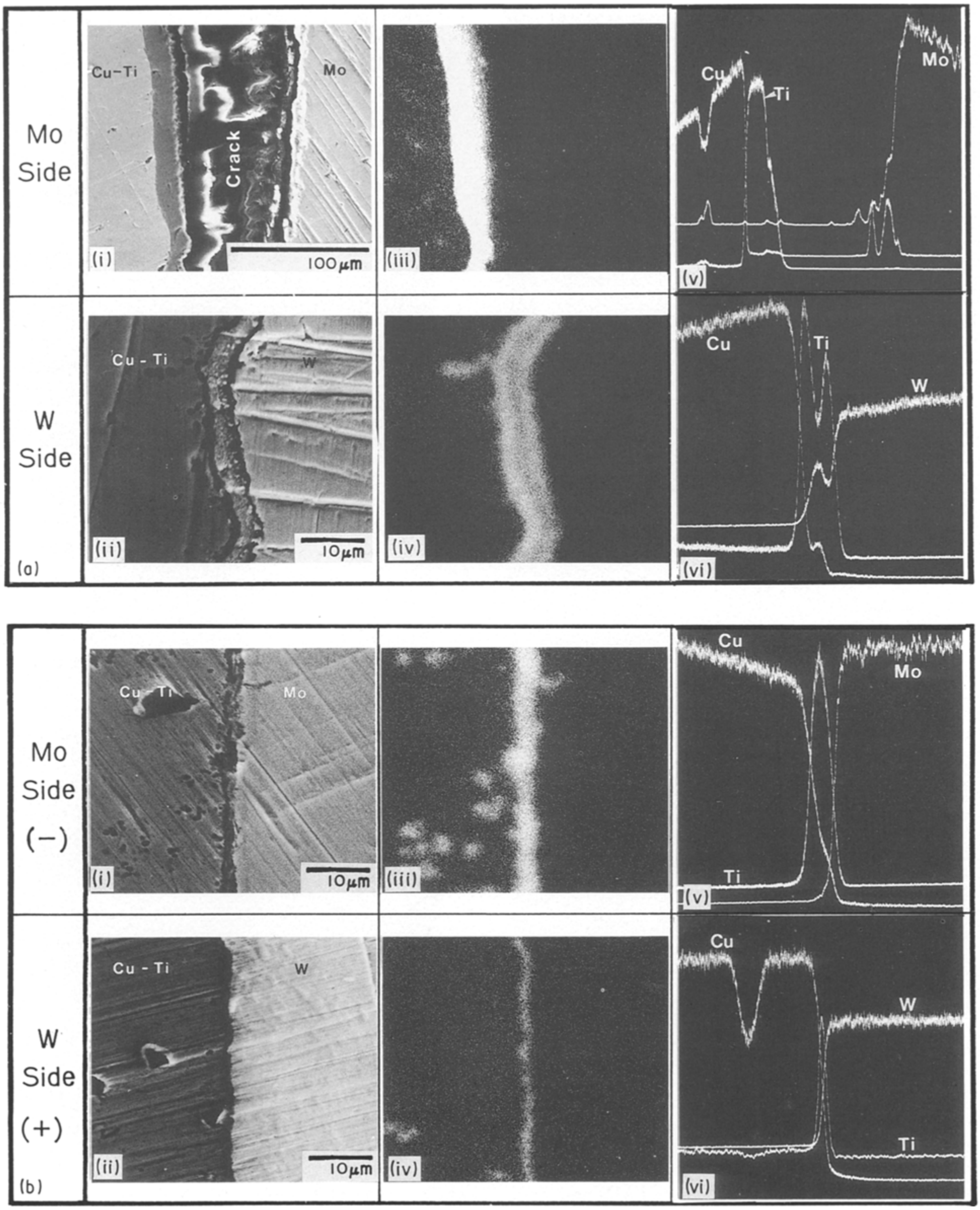

Figure 5 Aspect of segregation of Ti at the braze–metal interface in the Mo/Cu–Ti/W system heat treated at 1373 K for 600 s, (a) without applied d.c., (b) with a d.c. applied from the W side to the Mo side, (c) with an inverse d.c. (i, ii) Secondary electron images, (iii, iv) TiK_α X-ray images, iv, vi line profiles (ordinate intensity in a.b. units).

combined sets of AlN or ZrB_2 and various metal foils in the specimen arrangement of Fig. 2e, where each metal foil was inserted between the W lead wire and AlN or ZrB_2.

In conjunction with the measurement of e.m.f., temperature dependence of electric conductivity of AlN and ZrB_2 was also measured on the specimen arranged as in Fig. 2e without metal foil.

3. Results

3.1. Brazing

Figs 3 and 4 illustrate microstructures, electron probe microanalysis (EPMA) X-ray images and line profiles at the section of AlN and ZrB_2 joints, respectively, after brazing treatment with the Cu–Ti braze alloy for 1200 s at 1273 K, which show segregation of Ti at the bonding interface. The thickness of the Ti-segregated

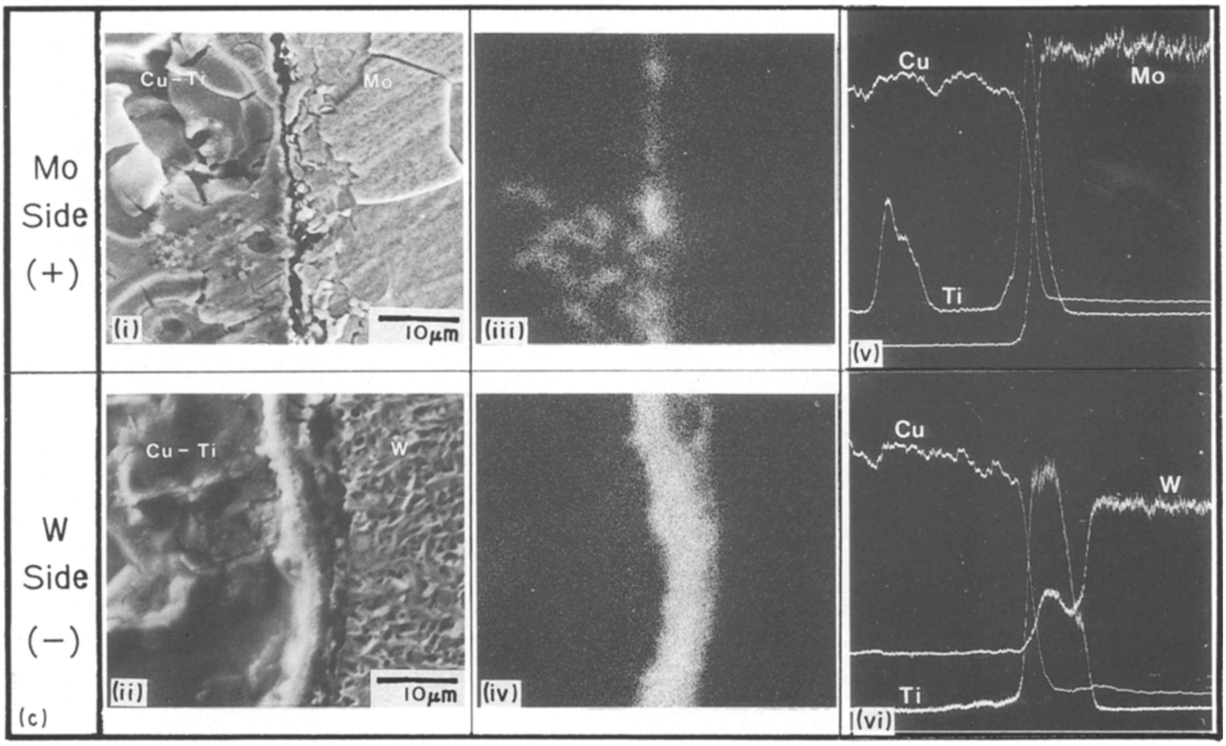

Figure 5 Continued

layer increased with increasing temperature, as mentioned above. Similar segregation of Zr and Hf at the interface was also observed in the Cu–Zr and Cu–Hf braze alloys, respectively.

3.2. Mo/Cu–Ti/W system for electric-field effects

As mentioned above, when Mo was joined to itself with a Cu–Ti braze alloy, segregation of Ti was seen at the bonding interface. In the Mo/Cu–Ti/W system shown in Fig. 2c, segregation of Ti to both the Mo and W sides was seen, as shown in Fig. 5a. However, application of a d.c. to the system during brazing assisted the segregation of Ti at the Mo cathode side and depressed it at the W anode side, as shown in Fig. 5b. An inverse d.c. induced the opposite segregation behaviour, as shown in Fig. 5c. This may imply that in the braze alloy, Ti atoms can migrate as cations by the electrotransport mechanism.

3.3. Ceramic/Cu–Ti/ceramic system for electric-field effects

Similar results to the segregation of Ti in Mo/Cu–Ti/W system were obtained in the ceramic/Cu–Ti/ceramic systems, as shown in Fig. 6 for the AlN/Cu–Ti/AlN system, and Fig. 7 for the ZrB_2/Cu–Ti/ZrB_2 system, which were heat treated under a d.c. in the specimen arrangement shown in Fig. 2d. Ti atoms migrated to the cathode and were segregated at the braze alloy–ceramic cathode interface by the d.c.

3.4. E.m.f. measurement

Variations of e.m.f. with increasing the temperature to 1373 K, and then with holding time at 1373 K, are shown in Fig. 8a and b for AlN–metal systems and in Fig. 9 for ZrB_2–metal systems.

In the AlN–metal systems, negative e.m.f. to the AlN pole against metal pole appears from about 900 K. After steep peaks, the e.m.f. turns to positive for all metal foils except Al and Cu–3 wt % Ti alloy foils. Then, the e.m.f. turns again to negative for Ti, Zr, Hf and Cu foils at near brazing temperature, say 1373 K, where the negative e.m.f. is kept for a while with holding time.

Meanwhile, variations of e.m.f. in ZrB_2–metal systems show a gradual increase of negative e.m.f. to ZrB_2 pole against metal pole from about 500 K. The absolute value of the negative e.m.f. however, is not as high as that in AlN–metal systems.

The aspect of the e.m.f. curves of both AlN–metal and ZrB_2–metal systems is not the same as the normal thermal e.m.f. curves, where e.m.f. increases approximately linearly with temperature.

The temperature dependence of electrical conductivity of AlN and ZrB_2 is shown in Fig. 10 where the conductivity is represented as an inverse ratio (R/R_t) of resistance, R_t, at elevated temperatures to that, R, at room temperature. It is very evident that the conductivity of AlN increases steeply from about 900 K with temperature, while that of ZrB_2 increases from 500 K, and that the degree of the increase in conductivity of ZrB_2 is less than that of AlN, although the conductivity of the former is much higher than that of the latter. The increase in the conductivity of ceramics at high temperature can be attributed to the property as an intrinsic semiconductor and/or increase in ionic conductivity.

4. Discussion

When ceramics and metals were joined with reactive metal-bearing braze alloys, the reactive metal could

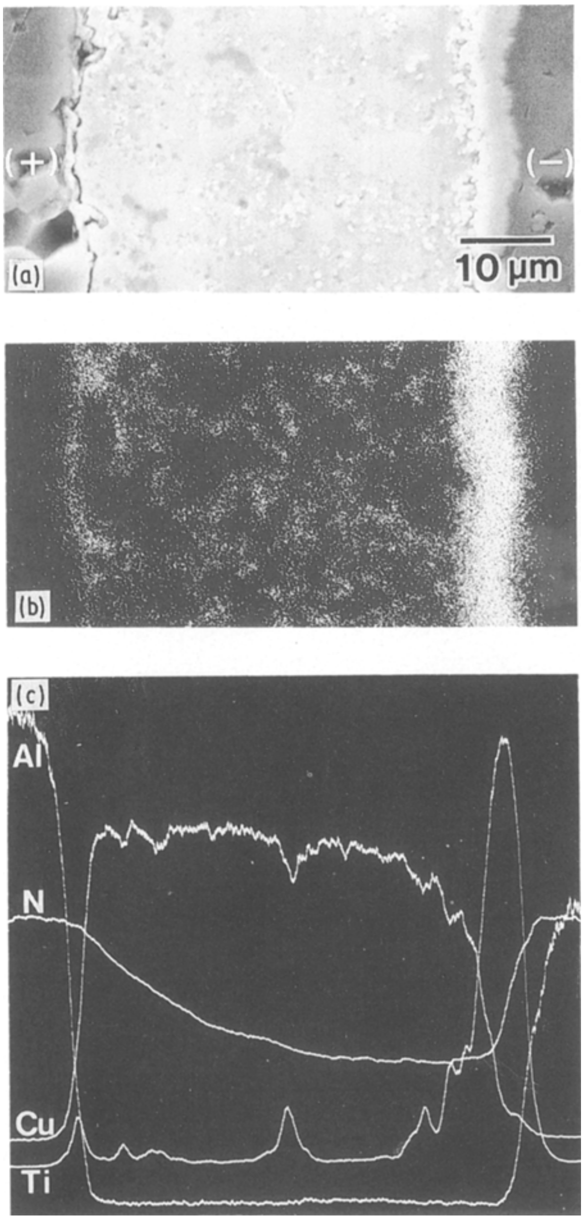

Figure 6 Aspect of segregation of Ti at the braze-ceramic interface in the AlN/Cu–Ti/AlN system heat treated at 1.373 K for 600 s under applied d.c. and examined by EPMA: (a) secondary electron image; (b) TiK_α X-ray image, (c) line profiles.

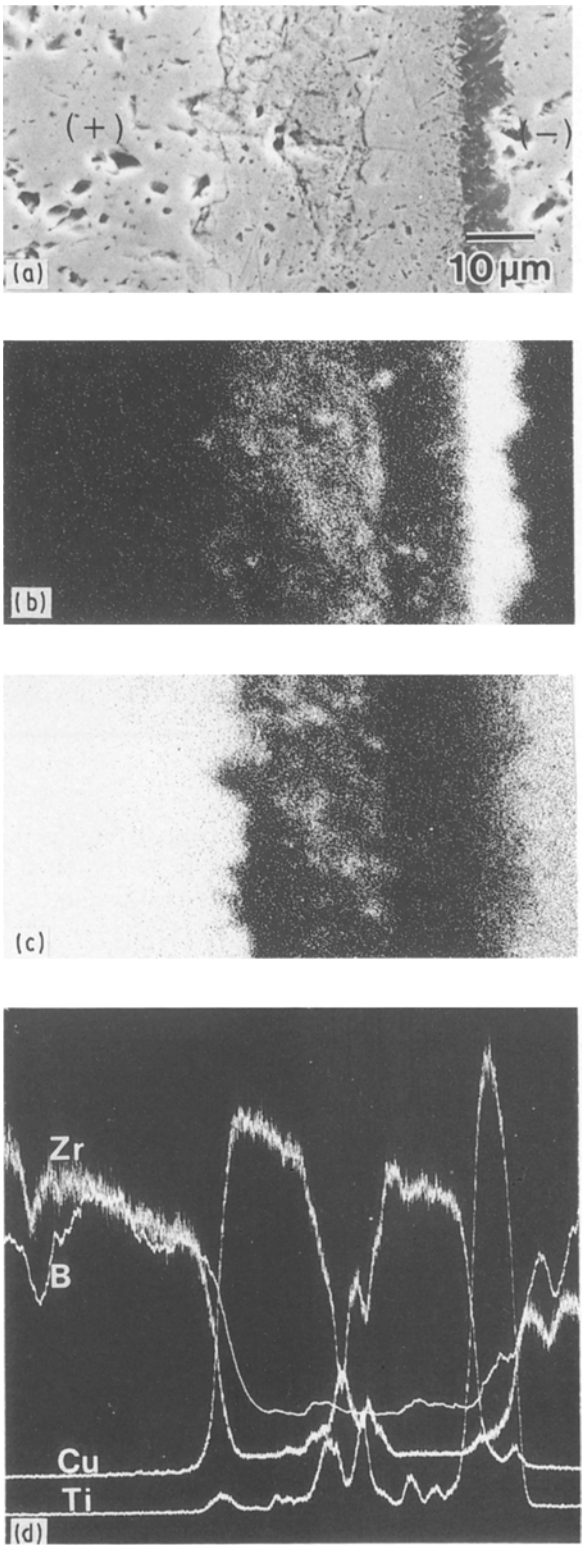

Figure 7 Aspect of segregation of Ti at the braze–ceramic interface in the ZrB_2/Cu–Ti/ZrB_2 system heat treated at 1373 K for 600 s under applied d.c. and examined by EPMA: (a) secondary electron image; (b) TiK_α X-ray image, (c) ZrL_α X-ray image, and (d) line profiles.

migrate and segregate at the bonding interface, and the application of a d.c. to the joining systems assisted the segregation at the cathode-side interface and depressed it at the anode side in both metal/metal and ceramic/ceramic joints, as illustrated in Figs 3–6. This may imply that a reactive metal, say Ti, can migrate probably by the electrotransport mechanism as a cation with one valence in the molten braze alloy. If so, the quantity of electricity can be calculated using the Faraday law, with appropriate electrochemical values. Then, the quantity of electricity needed to segregate Ti was obtained as 5.4 C. That is, only 5.4 C was necessary for migration of almost all of the Ti atoms in the braze to segregate them at the bonding interface. Similarly, the quantity of electricity for Zr and Hf was obtained as 2.4 and 1.4 C, respectively. The lower quantity of electricity for Zr and Hf may be associated with higher valence numbers of more than one for Zr and Hf atoms, which may result in a smaller amount of segregation of Zr and Hf at the interface.

The aspect of the e.m.f. curves shown in Figs 7 and 8 is similar to the well-known thermally stimulated current curves of polymer insulators, etc. The point of initiation of the generation of negative e.m.f. to the ceramic pole is about 900 K for AlN and 500 K for ZrB_2, as shown in Figs 7 and 8, which coincides well

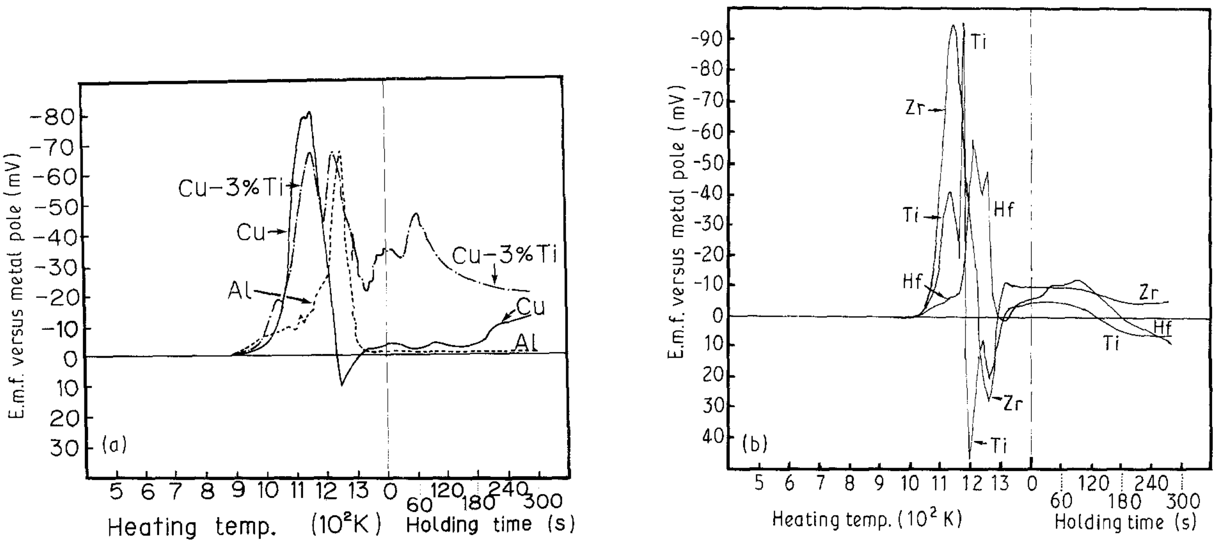

Figure 8 (a) and (b) variations of EMF with temperature and with time at 1373 K in AlN/metal systems.

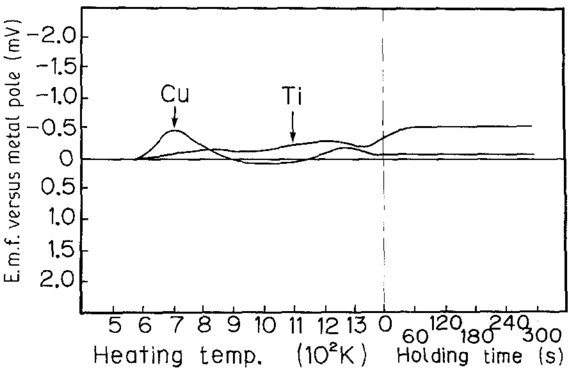

Figure 9 Variations of e.m.f. with temperature and with time at 1373 K in ZrB_2/metal systems.

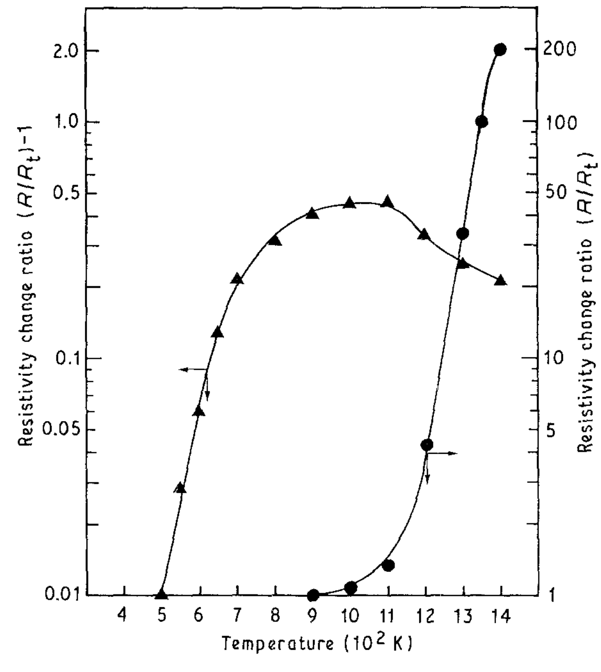

Figure 10 Temperature dependence of the electrical conductivity of (●) AlN and (▲) ZrB_2: the conductivity is represented by an inverse ratio (R/R_t) of electrical resistance, R, at elevated temperatures to that, R_t, at room temperature.

with the temperature point where the electrical conductivity begins to increase with temperature. These two points may have an important relation to each other. That is, generation of negative e.m.f. to the ceramic pole above the initiation temperature may be attributed to the polarization of the ceramic. Therefore, it can be deduced that if an electric circuit is constructed in the ceramic/reactive metal-bearing braze/ceramic system, the ceramic can be polarized and behaves as a cathode against the braze, and then, the reactive metal can migrate in the braze as a cation and segregate at the metal/ceramic interface. In contrast, in the metal/reactive metal-bearing braze/metal system, a flow of free electrons from the braze to the metal, probably arising by expansion and melting of the braze alloy, can take place, and this flow may induce the migration of reactive metal atoms to the interface.

5. Conclusions

Segregation of reactive metals (Ti, Zr and Hf) at the braze–ceramic interface was investigated in ceramic (AlN and ZrB_2) joints bonded with reactive metal-bearing Cu braze alloys. The following results were obtained.

1. Segregation of reactive metals at the braze alloy–ceramic interface was observed in the ceramic joints, as well as metal joints as a reference.
2. Application of a d.c. to the joining systems during brazing assisted the segregation at the cathode-side interface and depressed it at the anode-side interface.
3. A negative e.m.f. to the ceramic pole was generated in the ceramic–metal foil systems above a specific temperature: about 900 K for AlN and 500 K for ZrB_2. This temperature coincided with the temperature at which the electrical conductivity of the ceramics began to increase with increasing temperature.
4. Finally, it was considered that the polarization of the ceramics might take place and assist the migration, and consequently segregation, of reactive metals in

braze alloys to the braze–ceramic interface during brazing.

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