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Microstructural characterization of interfacial reaction products between alumina and braze alloy

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The Al_2O_3/STS304, Al_2O_3/Cu and Al_2O_3/Al_2O_3 joints were brazed in vacuum with three types of Cu–Ag–Ti brazing filler metals at 1193 K for 1.2 ks. The effects of adherend metals on the microstructure and microchemistry of reaction products formed at the Al_2O_3/filler metal interface have been investigated. The reaction products of Al_2O_3/STS304 joints showed a layered structure consisting of TiO (monoclinic, $a_0 = 0.585$ nm, $b_0 = 0.934$ nm, $c_0 = 0.414$ nm), Cu_2Ti_4O (cubic, $a_0 = 1.149$ nm) and Fe_2Ti_4O (cubic, $a_0 = 1.1297$ nm). The TiO compound is a nonstoichiometric titanium monoxide with composition range of $TiO_{0.9}$ to $TiO_{1.1}$. Cu_2Ti_4O and Fe_2Ti_4O compounds can be considered as $(Cu, Fe)_2Ti_4O$ because both of them have nearly the same crystal structure and lattice constants. The reaction products of Al_2O_3/Cu and Al_2O_3/Al_2O_3 joints also showed a layered structure consisting of TiO and Cu_2Ti_4O. The TiO compound was formed by redox reaction between Al_2O_3 and segregated titanium, whereas Cu_2Ti_4O and Fe_2Ti_4O compounds formed by solid-state reaction between TiO and copper from the brazing alloy and iron from the adherend metals, respectively.

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1. Introduction

Active metal brazing or reaction-induced bonding using active metals results in the formation of reaction products at ceramic/filler metal interfaces. The mechanical, electrical and electronic properties of ceramic/metal joints depend largely on the type, morphology and thickness of the reaction products.

For alumina/alumina and alumina/Ti–6Al–4V joints brazed with Ag–Cu–Ti alloys, reaction products which have been reported are $Cu_2(Ti, Al)_4O$ [1, 2], $(Cu, Al, Sn)_3Ti_3O$ [3], Cu_2Ti_2O [4] and Cu_2Ti_4O [5], in addition to titanium oxides formed at the near-alumina interface. Several types of titanium oxides have also been reported: TiO [4], TiO_x ($1 \leq x \leq 1.5$) [6], γ-TiO [3] and TiO_x ($0.4 \leq x \leq 0.6$) [7], etc. All of these compounds result from the redox reaction between alumina and those elements segregated from brazing filler metals. The reaction products may be changed, however, when alumina is jointed to iron-based metal. According to our investigation on another system, Si_3N_4/304, this is because iron atoms from stainless steel diffuse into the filler metal then further segregate at the Si_3N_4/filler metal interface [8]. Nevertheless, it has not yet been clarified what type of iron exists at the interface, or the effect of iron on reaction product.

In this paper we discuss the effect of adherend materials, especially iron-based, on the formation of reaction products through the identification of reaction products formed at the alumina/filler metal interface for the joints brazed with three types of brazing alloys and adherend materials; 304 stainless steel, copper, and alumina.

2. Experimental procedure

Brazing alloys were produced by vacuum induction melting. Their chemical compositions are Cu–34.8 Ag–6.2Ti (BT), Cu–30.6Ag–5.5Ti–11.9Al (BA) and Cu–33.7Ag–6.1 Ti–3.0Sn (as BS) in atomic percentage. A pressureless sintered and hot-isostatically-pressed alumina (Korea Tungsten, Taegu, Korea; 99.99% Al_2O_3 powder, MgO = 1000–1500 ppm; 12.7 mm × 12.7 mm × 4.8 mm), a cold-worked 304 stainless steel, and pure copper (10 mm diameter × 5 mm thick), and brazing alloys of thin disc form (11 mm diameter × 0.12–0.15 mm thick) were used for all samples. Prior to brazing, the surface of alumina and metals was polished using 2.5 μm diamond paste and emery paper (no. 1200), respectively, then degreased in acetone with ultrasonic vibration followed

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by drying in a hot oven. Brazing was performed in quartz tube using an infrared heating vacuum furnace ($2\text{-}4 \times 10^{-5}$ torr; 1 torr = 133.322 Pa) at 1193 K for 1.2 ks. The heating and cooling times were 3.6 and 14.4 ks, respectively.

The microstructural and chemical analyses of the interfacial reaction products between alumina and filler metals were carried out using a scanning electron microscope (SEM, AKASHI ISI-DS130C) equipped with an energy-dispersive X-ray spectrometer (EDX, Philips PV 9900), a glancing X-ray diffractometer (XRD, Rigaku Rotaflex RTP300 RE, 45 kV, 150 mA) and an Auger electron microscope (AEM, VG Microtech MT500).

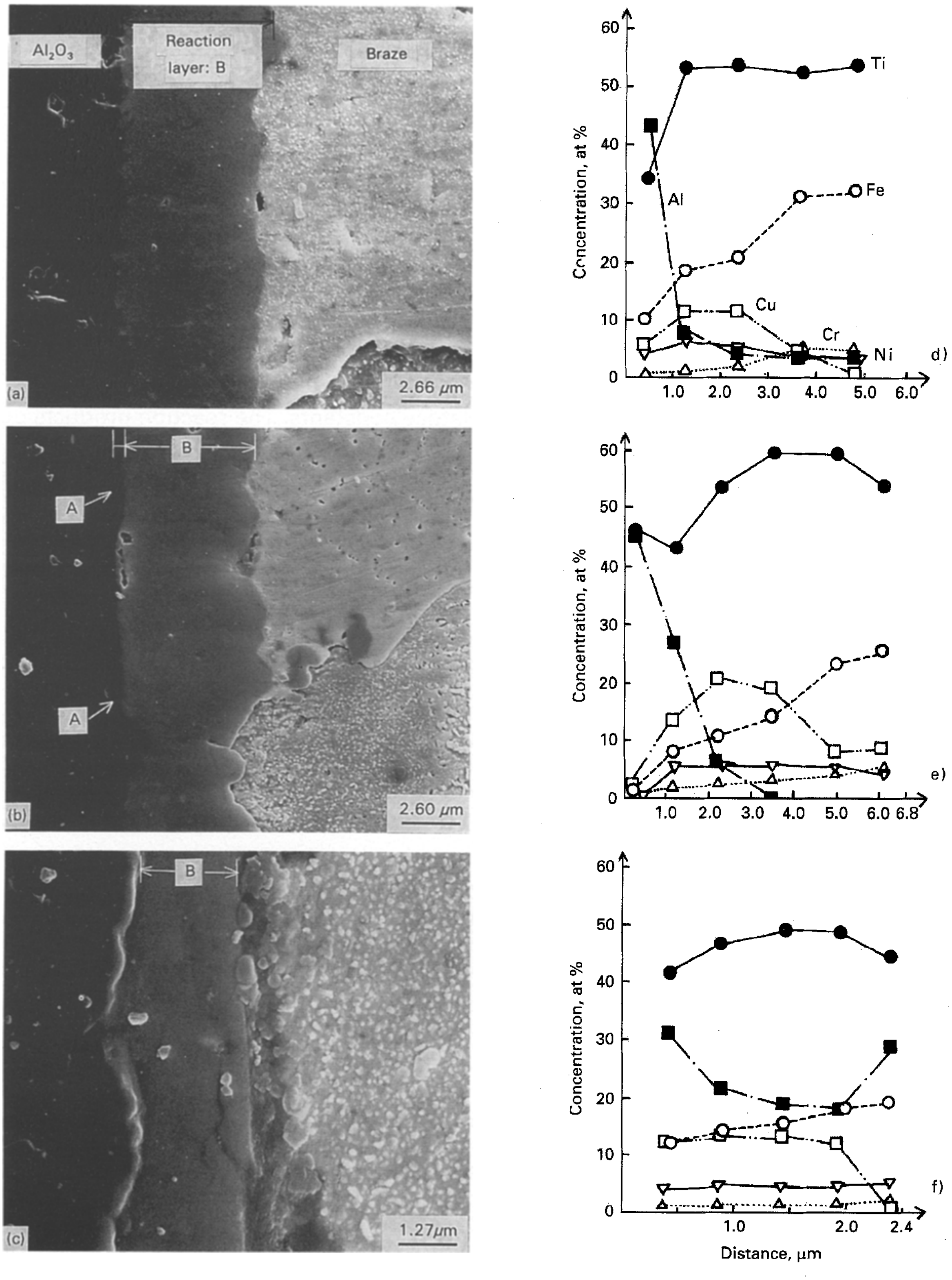

Figure 1 (a–c) SEM microstructures and (d–f) EDX composition profiles of the reaction products formed at the Al_2O_3/filler metal interface of Al_2O_3/STS304 joins brazed with (a, d) BT-, (b, e) BS-, and (c, f) BA-alloy, at 1193 K for 1.2 ks under 4×10^{-5} torr.

3. Results

3.1. Al_2O_3/304 stainless steel system

The microstructures of reaction products between Al_2O_3 and filler metals of Al_2O_3/304 joints brazed with BT, BS and BA alloys are shown in Fig. 1a–c, respectively. For joints with BT, BS and BA alloys, the reaction layers of 6.0, 6.8 and 2.4 μm thick, respectively, were formed at the Al_2O_3/filler metal interface. In addition, a new discontinuous reaction layer (A; 266–532 nm thick) appeared at the near-alumina interface with the BS filler metal. EDX composition profiles corresponding to Fig. 1a–c plotted against the distance from the Al_2O_3/reaction products interface are shown in Fig. 1d–f, respectively. Layer A contains a high concentration of titanium and aluminium. But a great part of the aluminium detected is from Al_2O_3 neighbouring the Al_2O_3/layer A interface, because a microprobe of 1 μm diameter was used. Layer B could be divided into two zones from the EDX analysis results, although the interface between the zones is not clear in the micrograph. The first zone consists of titanium, iron and copper, whereas the second zone consists of titanium and iron shown in Fig. 1d and e. With BA filler metal, a considerable amount of aluminium in addition to those elements was detected in both zones, as shown in Fig. 1f. This could be aluminium added in the filler metal as well as an aluminium decomposed from Al_2O_3. Using EDX composition profiles, Fig. 1d and e, both zones could be characterized by the distribution of copper; the higher copper concentration zone corresponds to the first zone and the lower copper concentration zone to the second zone. The distribution of iron in layer B showed a tendency to increase linearly with the distance from the alumina/reaction layer interface. This implies that iron is segregated to the Al_2O_3/filler metal interface from the braze after diffusion from stainless steel into the braze. It is believed that the segregated iron reacted with the already formed reaction products.

Fig. 2a–c show the results of XRD analysis for the reaction products formed at the Al_2O_3/filler metal interface for Al_2O_3/304 joints brazed with BT, BS and BA alloys, respectively. The alumina used in this experiment was the α-Al_2O_3 of trigonal structure with the lattice parameter of $a_0 = 0.4758$ nm and $c_0 = 1.2991$ nm. Peaks which remained after the peaks related to α-Al_2O_3 had been removed correspond to reaction products. Although it is impossible to detect oxygen by EDX analysis, with the results shown in Fig. 1b, the reaction product formed at the near-alumina interface is TiO (monoclinic, $a_0 = 0.585$ nm, $b_0 = 0.934$ nm, $c_0 = 0.414$ nm), and the products formed next to TiO are Cu_2Ti_4O (cubic, $a_0 = 1.149$ nm) and Fe_2Ti_4O (cubic, $a_0 = 1.1297$ nm). The latter two products correspond to the compounds formed in the first zone of layer B shown in Fig. 1.

3.2. The Al_2O_3/Cu system

The microstructures of reaction products between Al_2O_3 and filler metals for Al_2O_3/Cu joints with BT, BS and BA alloys are shown in Fig. 3a–c, respectively.

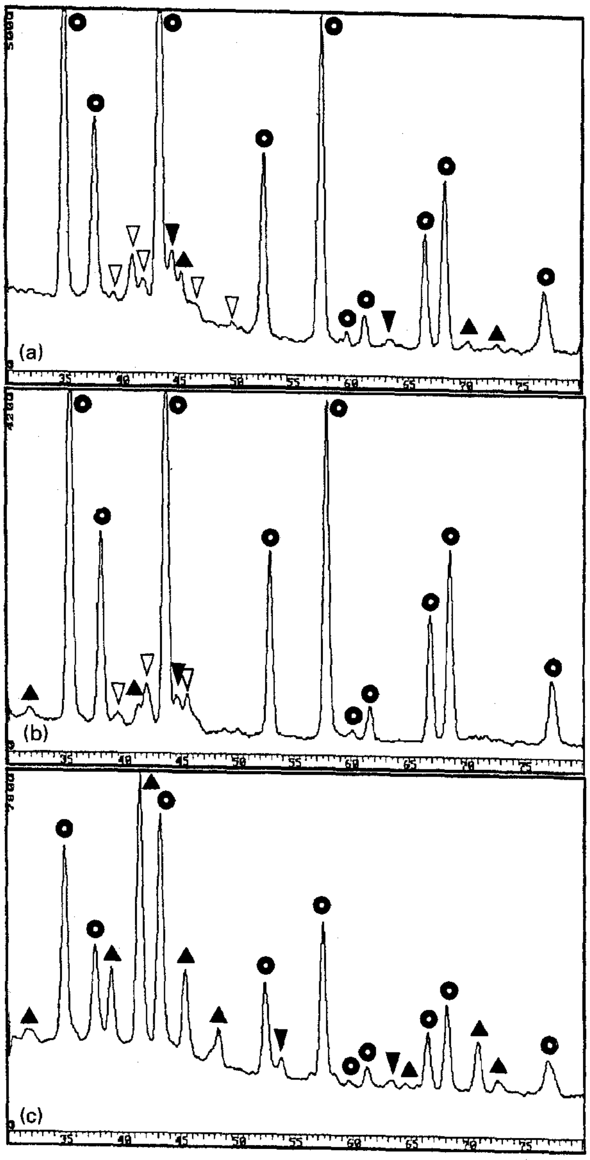

Figure 2 XRD spectra on the reaction layers formed at the Al_2O_3/filler metal interface of Al_2O_3/STS304 joints brazed with (a) BT-, (b) BS-, and (c) BA-alloy, at 1193 K for 1.2 ks and under 4×10^{-5} torr. (○) α-Al_2O_3, (▲) Cu_2Ti_4O, (▽) Fe_2Ti_4O, (▼) TiO.

EDX composition profiles corresponding to Fig. 3a–c are shown in Fig. 3d–f, respectively. The reaction layers of 8.5, 13.0 and 3.2 μm thick on average, respectively, were formed with the BT, BS and BA alloys at the Al_2O_3/filler metal interface. In addition, a new discontinuous reaction layer, indicated A in Fig. 3a, appeared at the near-alumina interface for the joint with BT filler metal. This layer can be considered to be titanium oxides similar to layer A shown in Fig. 1b. Another microstructural feature of the reaction product layer is the existence of isolated silver-rich phases C in Fig. 3a or copper-rich phases C in Fig. 3b. We can deduce that these phases were isolated between the growing grains during the growth and nucleation of reaction products. This phenomenon could be related to the excessive dissolution of adherend metal (copper) into the filler metal.

Combining the results of microstructural and EDX analysis, layer B appeared to consist of a single zone, thus differing from the case of Al_2O_3/304 joints. This is

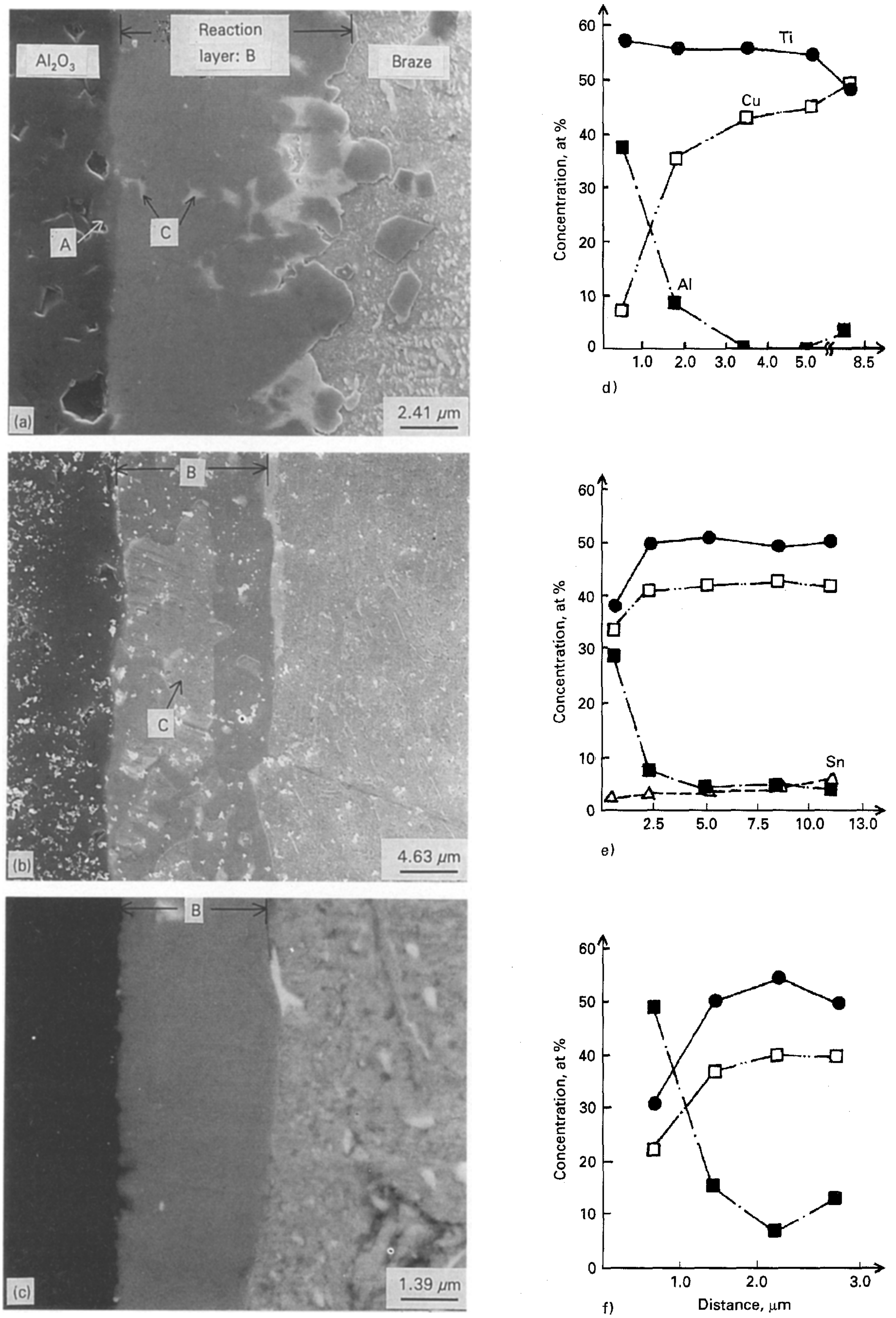

Figure 3 (a–c) SEM microstructures and (d–f) EDX composition profiles of the reaction products formed at the Al_2O_3/filler metal interface of Al_2O_3/Cu joints brazed with (a, d) BT-, (b, e) BS-, and (c, f) BA-alloy, at 1193 K for 1.2 ks under 4×10^{-5} torr.

supported by the fact that the change in copper content in the reaction layer with the distance from the interface is insignificant.

From the results of XRD analysis for the reaction products formed at the interface as shown in Fig. 4a–c for Al_2O_3/Cu joints brazed with BT, BS and BA

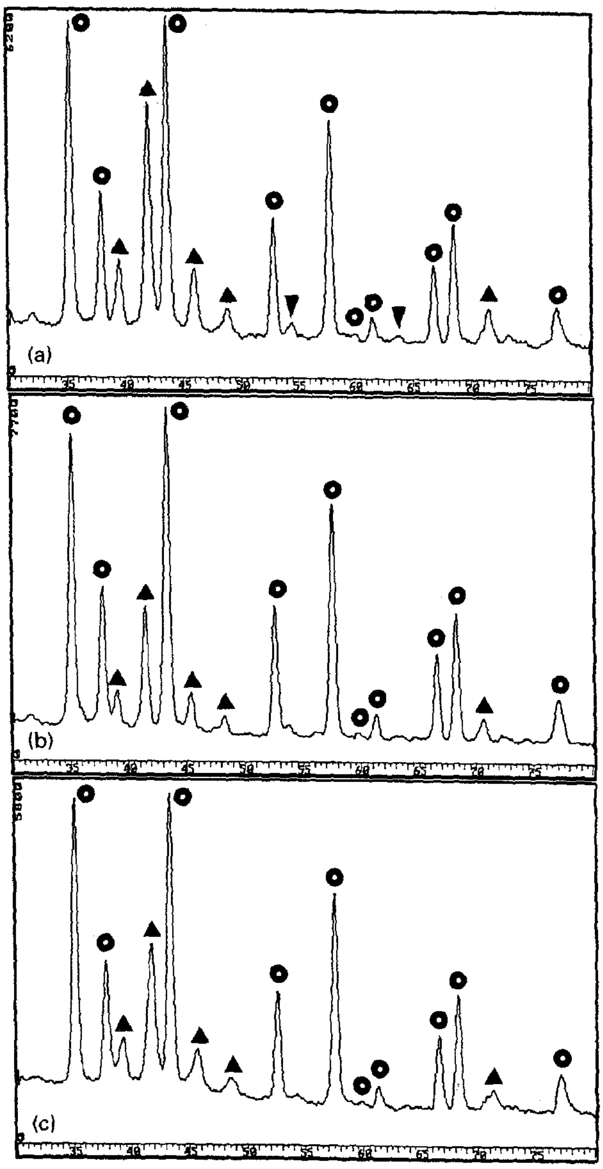

Figure 4 XRD spectra on the reaction layers formed at the Al_2O_3/filler metal interface of Al_2O_3/Cu joints brazed with (a) BT-, (b) BS-, and (c) BA-alloy, at 1193 K for 1.2 ks under 4×10^{-5} torr. (○) α-Al_2O_3, (▲) Cu_2Ti_4O, (▼) TiO.

alloys, respectively, reaction products were determined to be Cu_2Ti_4O (cubic, $a_0 = 1.149$ nm) regardless of filler metals employed.

3.3. Al_2O_3/Al_2O_3 system

The microstructures of reaction products between Al_2O_3 and filler metals for Al_2O_3/Al_2O_3 joints with BT, BS and BA alloys are shown in Fig. 5a–c respectively. EDX composition profiles corresponding Fig. 5a–c are shown in Fig. 5d–f, respectively. The reaction layers, 3.6, 3.9 and 3.2 μm thick on average, were formed at the Al_2O_3/filler metal interface with the BT, BS and BA alloys, respectively. A new continuous reaction layer, indicated A in Fig. 5a and about 1.2 μm thick, was formed at the near-alumina interface with the BT filler metal. This layer was determined to be a TiO layer from the XRD results shown in Fig. 6a.

Fig. 6a–c show the results of XRD analysis for the reaction products formed at the interface of Al_2O_3/Al_2O_3 joints brazed with BT, BS and BA alloys, respectively. From the XRD results the reaction products were found to be TiO (monoclinic, $a_0 = 0.585$ nm, $b_0 = 0.934$ nm, $c_0 = 0.414$ nm) and Cu_2Ti_4O (cubic, $a_0 = 0.1149$ nm), regardless of filler metals employed.

4. Discussion

From the analyses of the microstructure and the microchemistry of alumina/filler metal interface for joints brazed with three types of brazing alloys and adherend materials, the reaction products were determined to be TiO (monoclinic, $a_0 = 0.585$ nm, $b_0 = 0.934$ nm, $c_0 = 0.414$ nm), Cu_2Ti_4O (cubic, $a_0 =$ 0.1149 nm) and Fe_2Ti_4O (cubic, $a_0 = 0.11297$ nm). TiO is the product formed by redox reaction between Al_2O_3 and titanium, whereas Cu_2Ti_4O and Fe_2Ti_4O are the products formed by the effect of filler metal (i.e. copper) and adherend metal element (i.e. iron), respectively, which are not related to the direct chemical reaction with alumina. Nevertheless, the thickness ratio of the Cu_2Ti_4O (and Fe_2Ti_4O) layer to the total reaction layer is much larger than that of the TiO layer. Therefore, it is very important to understand the formation process of the Cu_2Ti_4O (and Fe_2Ti_4O) layer.

The formation process of these products can be better explained with Fig. 7a. Reaction products were divided into two layers. The near-alumina layer, indicated I, consists of titanium and a small amount of aluminium, as shown in Fig. 7b. Although EDX analysis was not capable of detecting oxygen, layer I was TiO, as shown in Fig. 6a. Titanium contained in filler metals is segregated to the Al_2O_3/filler metal interface causing the redox reaction with Al_2O_3, which was then decomposed into [Al] and [O]. The decomposed [O] ions were combined with the segregated titanium, resulting in the formation of TiO, which is layer I in Fig. 7a. A considerable amount of aluminium was always detected in the TiO layer, as high as 8 at % by EDX analysis. The detected aluminium appeared to be decomposed [Al] ions, but it was not clearly determined what type of aluminium existed in the TiO layer.

Once the TiO layer is formed by the redox reaction between Al_2O_3 and the segregated titanium, the filler metal element (i.e. copper) is diffused into the already formed TiO layer. This can be considered as a process model for the formation of the Cu_2Ti_4O layer by the solid-state reaction between TiO and copper. The process model could be confirmed from the microstructural features of layer II in Fig. 7a. It was also found that the copper content of phase D was lower than that of phase C from the results of EDX analysis for phases C and D as shown in Fig. 7d and e, respectively. Zone C represents the step in which Cu_2Ti_4O compound was almost formed, whereas the black zone D distributed sparsely in layer II represents the step in which the solid-state reaction between TiO and copper was in progress.

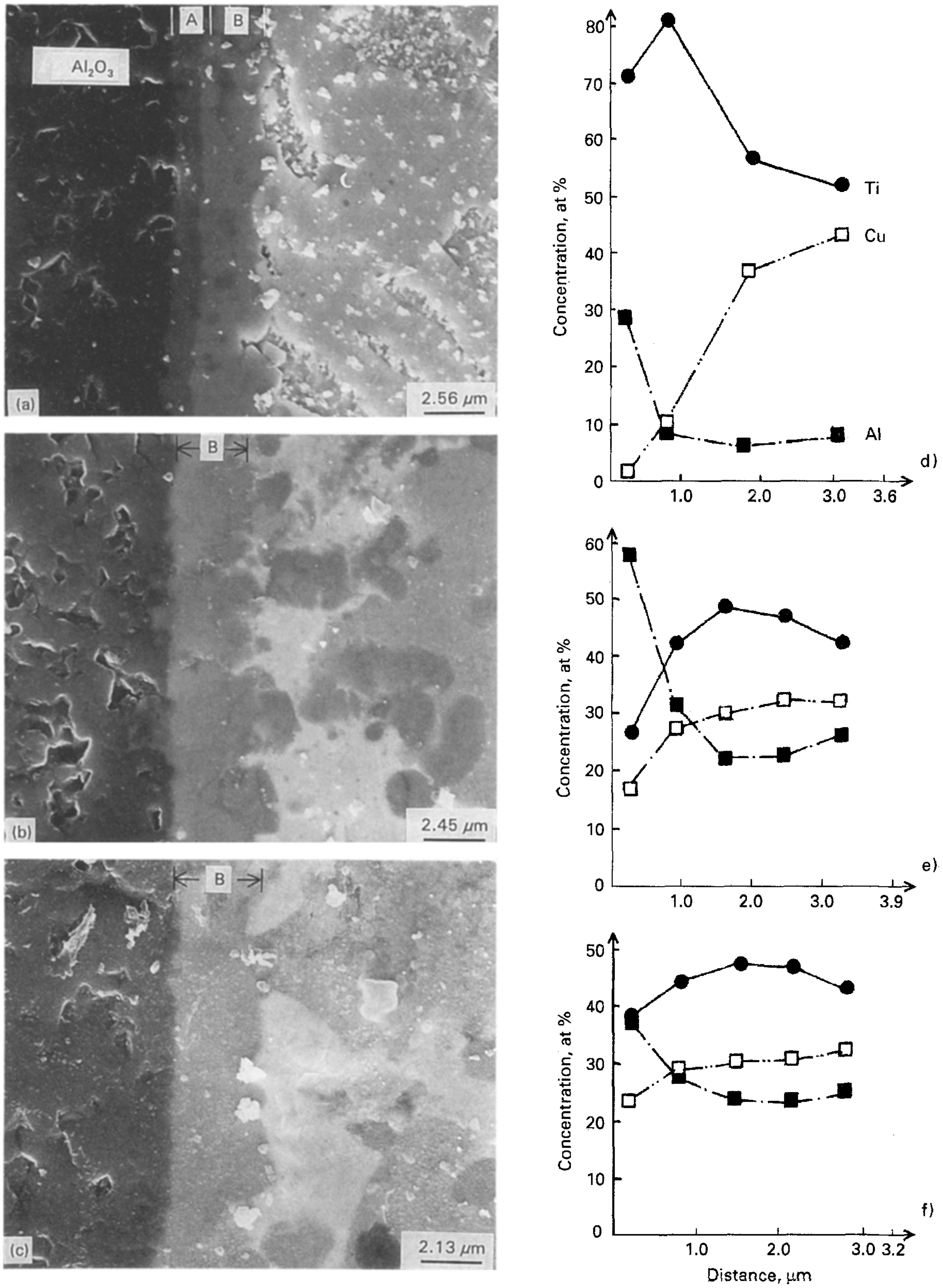

Figure 5 (a–c) SEM microstructures and (d–f) EDX composition profiles of the reaction products formed at the Al_2O_3/filler metal interface of Al_2O_3/Al_2O_3 joints brazed with (a, d) BT-, (b, e) BS-, and (c, f) BA-alloy, at 1193 K for 1.2 ks under 4×10^{-5} torr.

Aluminium was always detected in the Cu_2Ti_4O layer, as in the case of the TiO layer, but it was not determined what type of aluminium existed in the layer. It is probable that the aluminium in the TiO and Cu_2Ti_4O layers exists locally as a form of aluminium oxides. Using Auger depth profile analyses through the wide area of reaction layers as shown in Fig. 8, spectra of Auger electrons related to aluminium detected in their layers appeared intermittently or disappeared after sufficient sputtering. This question has not yet been clarified and must be further investigated using scanning transmission electron microscopy.

The solid-state reaction between TiO and copper mentioned above may possibly be deduced from the crystallographic as well as microscopic analyses results. All TiO identified by XRD analysis is

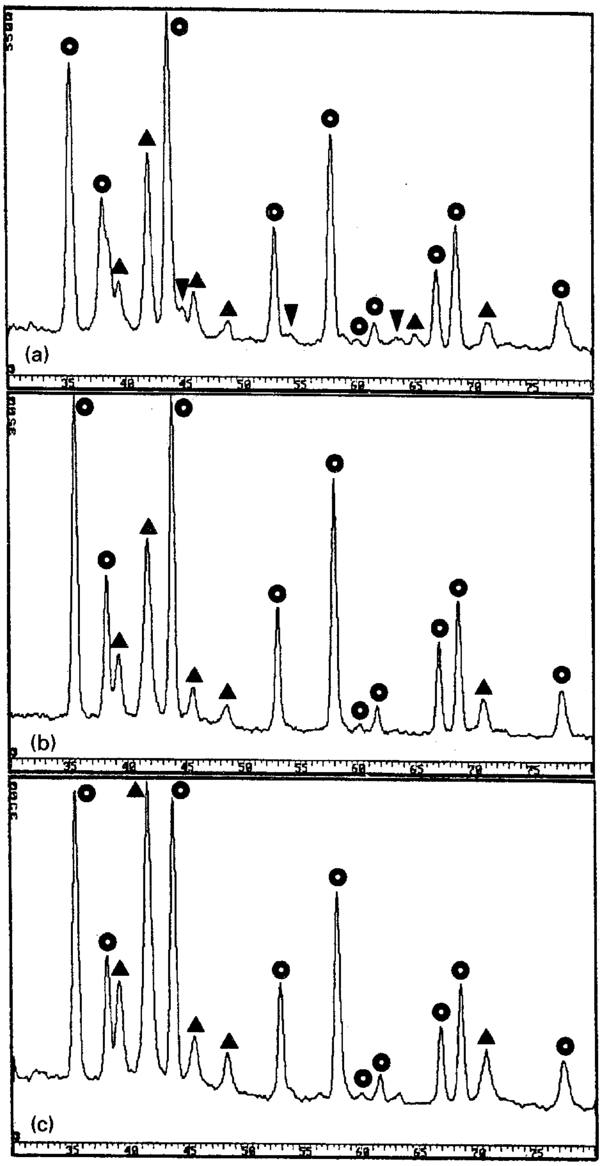

Figure 6 XRD spectra on the reaction layers formed at the Al_2O_3/filler metal interface of Al_2O_3/Al_2O_3 joints brazed with (a) BT-, (b) BS-, and (c) BA-alloy, at 1193 K for 1.2 ks under 4×10^{-5} torr. (○) α-Al_2O_3, (▲) Cu_2Ti_4O, (▼) TiO.

non-stoichiometric titanium monoxide [9] with the composition range of $TiO_{0.9}$ to $TiO_{1.1}$, which has monoclinic or a distorted NaCl-type structure composed of an ordered array of vacant lattice sites in which half of the oxygen and titanium atoms are vacant on every third (1 1 0) plane [10]. If copper atoms in contacted with the interface of the already formed titanium monoxide can diffuse into the vacant sites and the migration of these vacant sites is allowable, the Cu_2Ti_4O layer will be formed by structural rearrangement from monoclinic to cubic. The diffusion could be verified by the existence of a concentration gradient of copper and iron in the reaction layer. Therefore, the formation of the compound indicates that the diffusivity of copper and iron atoms into TiO is much faster than that of the other elements, such as silver, aluminium, tin, nickel and chromium. The total thickness of the reaction layer will be dependent on the diffusivity of metallic ions (i.e. copper) into the non-stoichiometric titanium monoxide. It is believed that the change in the total thickness of the reaction layer with the type of filler and adhered metals is also affected by the diffusivity of copper or iron into the non-stoichiometric titanium monoxide.

For Al_2O_3/304 joints, one of the main reaction products formed was the Fe_2Ti_4O compound. It is also important to understand the formation process of this product because it is probably the main reaction product whenever alumina (or other oxides) are brazed to iron-based metals. From Fig. 1, the microstructural features can be described as follows; firstly, a new discontinuous layer consisting of TiO was formed at the near-alumina interface, indicated A in Fig. 1b; secondly, the high copper concentration zone was formed at the zone adjacent to that layer; thirdly, iron was also detected with a concentration gradient in the high copper concentration zone; lastly, in the next zone, the content of copper and iron was rapidly decreased and increased with the distance from the interface, respectively. From the above results, the formation process of Fe_2Ti_4O compound can be explained as follows; firstly, by the redox reaction between Al_2O_3 and segregated titanium, a considerable amount of TiO compound is formed in a layered form; secondly, the Cu_2Ti_4O compound is formed by the diffusion of copper into the already formed TiO layer; thirdly, the Fe_2Ti_4O compound is formed by the concurrent diffusion of segregated iron and copper into the already formed TiO layer. Thus, the second and the third steps correspond to the formation process of $(Cu, Fe)_2Ti_4O$ compound. Finally, at the zone next to the $(Cu, Fe)_2Ti_4O$ layer, a Ti–Fe intermetallic compound is formed by reaction between residual titanium and segregated but undiffused iron. This process could also be verified by the microstructures shown in Fig. 9a and b, which are the top-views of reaction products. Layer A is TiO and layer B is $(Cu, Fe)_2Ti_4O$. Fig. 9b was taken from layer B and the phases were determined as a mixture of Ti–Fe compound and titanium-depleted Cu–Ag alloy. To summarize the discussion, the layered sequence of reaction products is schematically shown in Fig. 10. Although Cu_2Ti_4O and Fe_2Ti_4O compounds appeared on the X-ray spectra separately as shown in Fig. 2, they are probably in the form of $(Cu, Fe)_2Ti_4O$, because both compounds have nearly the same crystal structure and lattice constants.

5. Conclusions

Through the identification of reaction products formed at the alumina/filler metal interface for joints brazed with three types of brazing alloys and adhered

Figure 7 (a) SEM microstructure and (b–e) EDX spectra of the reaction products formed at the Al_2O_3/filler metal interface of Al_2O_3/Al_2O_3 joints brazed with BT alloy at 1193 K for 1.2 ks under 4×10^{-5} torr (EDX spectra of b–e were from A, B, C, and D, respectively).

Figure 8 Results of AEM depth analyses for the reaction products I and II indicated in Fig. 7.

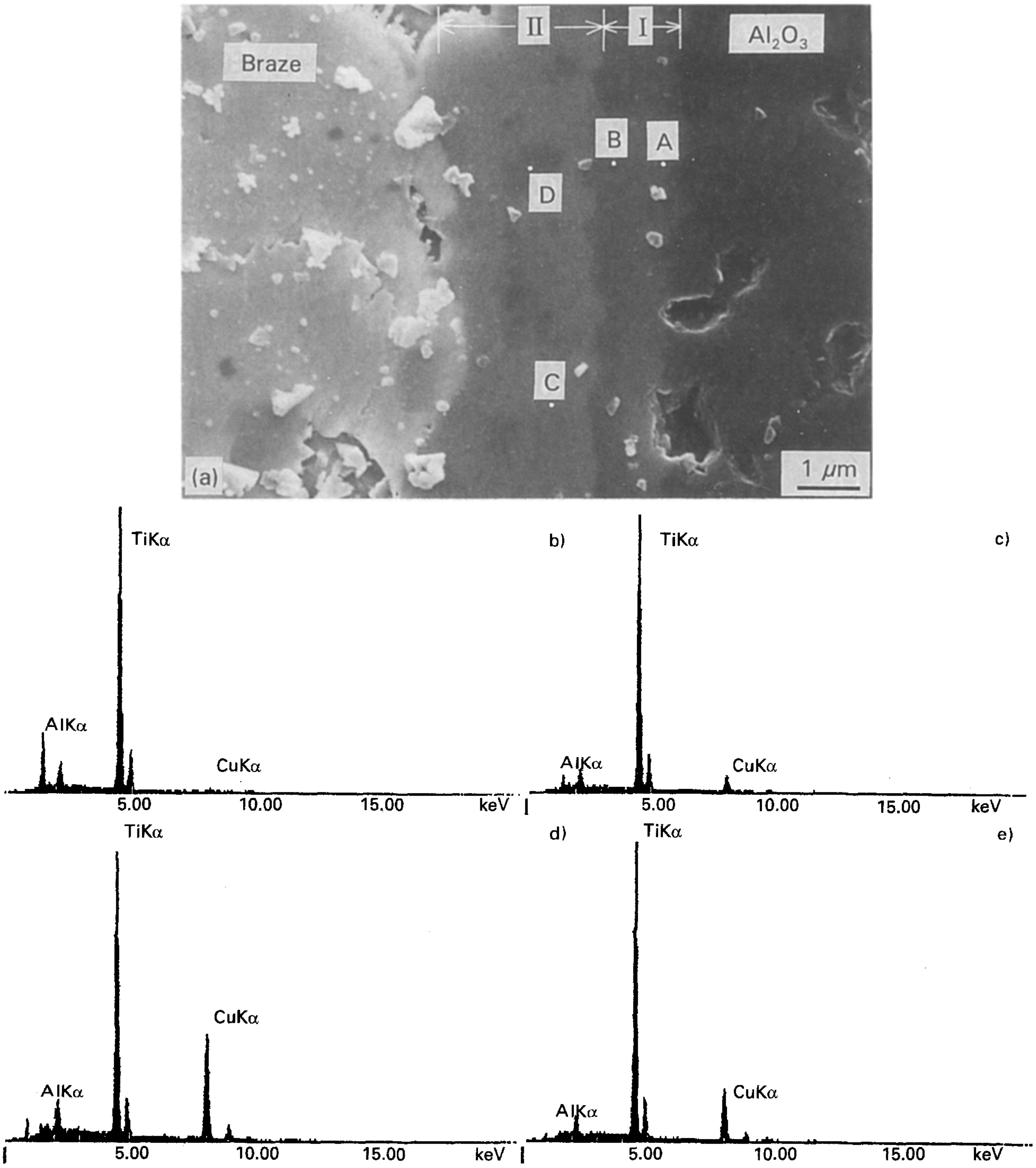

Figure 7

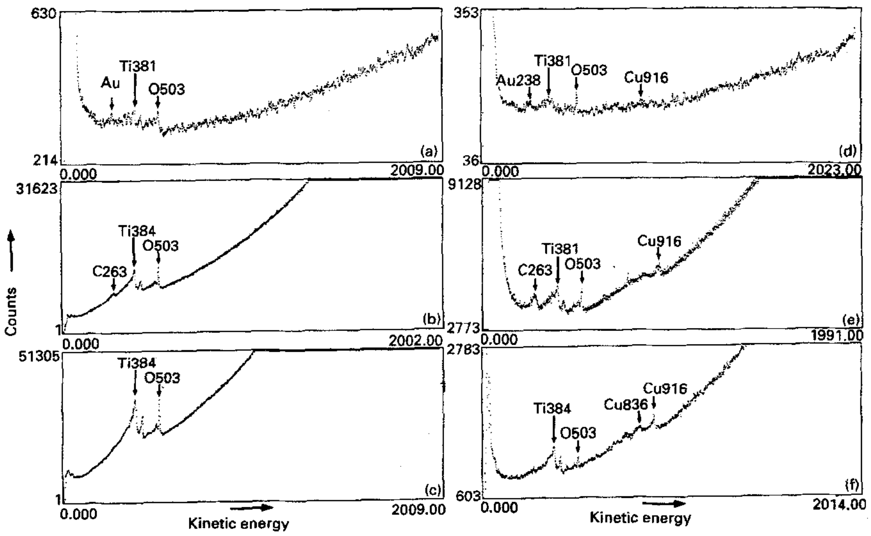

Figure 8

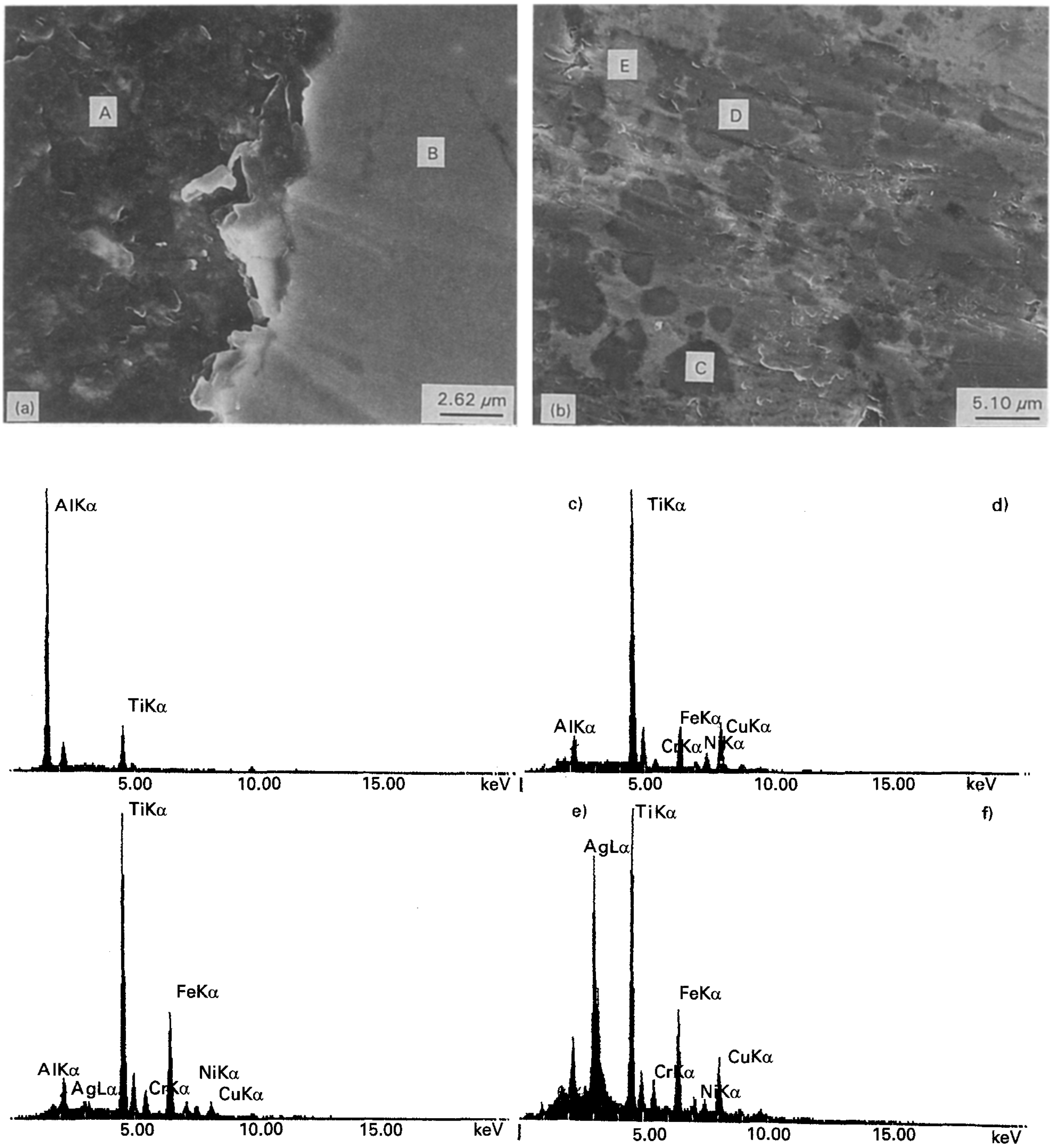

Figure 9 The top-view of (a, b) SEM microstructures and (c–f) EDX spectra on the reaction products as shown in Fig. 7 (c–f) EDX spectra of phases A, B, C and D respectively.

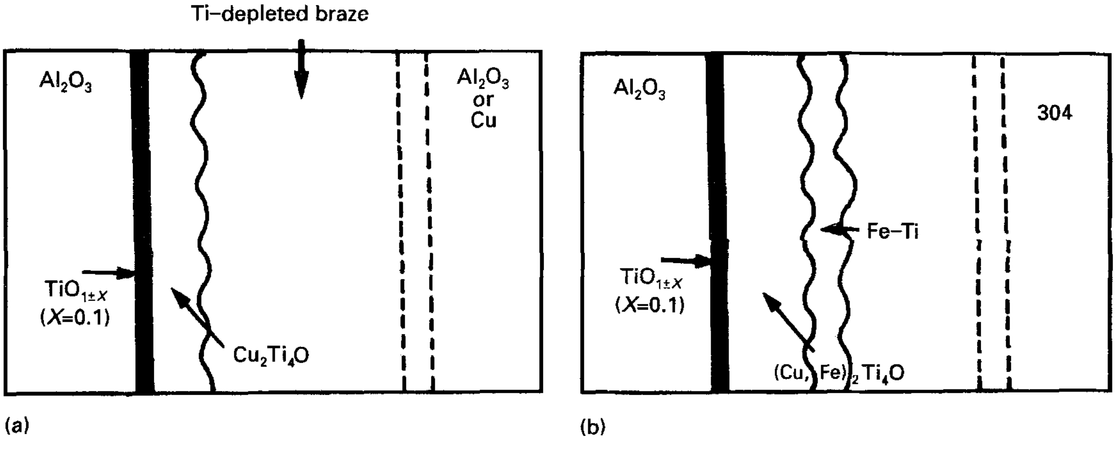

Figure 10 Schematic diagrams showing the layered structure of interfacial reaction products formed at the near-alumina interface for (a) Al_2O_3/Al_2O_3 or Al_2O_3/Cu and (b) Al_2O_3/304 joints brazed with Ag–Cu–Ti alloy.

materials, 304 stainless steel, copper, alumina, at 1193 K for 1.2 ks in vacuum, the following conclusions can be drawn.

1. The reaction products of Al_2O_3/STS304 joints showed a layered structure consisting of TiO (monoclinic, $a_0 = 0.585$ nm, $b_0 = 0.934$ nm, $c_0 = 0.414$ nm), Cu_2Ti_4O (cubic, $a_0 = 0.1149$ nm) and Fe_2Ti_4O (cubic, $a_0 = 0.11297$ nm). The TiO is a non-stoichiometric titanium monoxide with the composition range of $TiO_{0.9}$ to $TiO_{1.1}$. The Cu_2Ti_4O and Fe_2Ti_4O compounds can be considered to be in the form of $(Cu, Fe)_2Ti_4O$ because both compounds have nearly the same crystal structure and lattice constants.

2. The reaction products of the Al_2O_3/Cu and Al_2O_3/Al_2O_3 joints showed a layered structure consisting of TiO and Cu_2Ti_4O.

3. The TiO compound was formed by the redox reaction between Al_2O_3 and segregated titanium, whereas the Cu_2Ti_4O and Fe_2Ti_4O compounds were formed by solid-state reaction between TiO and copper from the brazing alloy and iron from the adherend metal.

4. The total thickness of the reaction layer depends on that of the Cu_2Ti_4O or $(Cu, Fe)_2Ti_4O$ layer. In other words, the thickness of the reaction product layer depends on the diffusivity of the filler and adherend metal elements, copper and iron, into the TiO layer.

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