Interfacial Reaction between Alumina and Cu-Ti Filler Metal during Reactive Metal Brazing

Accurate prediction of the properties of a brazement depends on how thoroughly we understand the kinetic and chemical reactions at the interface

BY K.-S. BANG AND S. LIU

ABSTRACT. If a chemical reaction at the interface can influence significantly the properties of a brazed joint using reactive filler metals, it is very important to understand which reaction occurs and how the reaction products grow at the interface. In this research, the interfacial reaction and the kinetics of reaction products growth in alumina brazing utilizing Cu-Ti filler metals were investigated.

Cu-Ti filler metals reduced Al_2O_3 to form TiO at the interface. Thermodynamically, reduction of Al_2O_3 is possible through the dissolution of the aluminum by the filler metal. At 1300 K, for example, interfacial reaction can proceed until the activity of aluminum reaches about 0.02 in Cu-20 at.-% Ti filler metal. With time, the TiO layer grew toward the center of the brazing filler metal following a parabolic rate law, at the cost of another complex oxide, presumably Ti_3Cu_3O, which formed next to the TiO. The activation energy of TiO growth was 208 kJ/mol (50 kcal/mol), which corresponds to the activation energy of oxygen diffusion in the TiO. Therefore, it appears likely that the growth of TiO is controlled by oxygen diffusion.

Introduction

Structural ceramics used for engineering applications are much stronger than the "traditional" ceramics because of a number of complex factors including improved processing techniques, which lead to materials having finer grain size, higher density and/or beneficial microstructural features. Advanced ceramics may also include various reinforcing additions to enhance mechanical properties. These superior properties make them very attractive for use in the automotive, nuclear, and aerospace industries. One potential application is the high-efficiency diesel engine for cars and trucks designed with a combustion chamber made of structural ceramics that eliminates the need for power-consuming cooling requirement (Ref. 1). Gas turbine engines that utilize uncooled ceramic components in the hot gas flow path allow for an increase in the turbine inlet temperature to 2500°F (1370°C) and produce significant improvements in engine efficiency and specific power (Ref. 2). Whatever the application, ceramics are often joined to other ceramics or to metals to form useful engineering components. One of the most widely used processes to join ceramics to metals is brazing. As a ceramic surface is normally not wetted by a brazing filler metal, metallization of the ceramic surface generally precedes brazing. An alternate approach, direct brazing, which is based on the knowledge that reactive metals segregate at the interface and promote complex chemical reaction with the ceramics, utilizes filler metals that contain reactive metal. Reaction products at the interface in reactive metal brazing initially enhance the metallic bond strength through the formation of chemical bonding between ceramic and a metal. However, excessive growth of the reaction products may degrade metallic bond strength because of the development of flaws at the interface (Ref. 3). Additionally, depending on the materials system and the processing conditions, multiple interface reactions can occur, in series and in parallel. Therefore, it is very important to characterize which reaction occurs at the interface and the rate at which the reaction products grow.

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KEY WORDS

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Activation Energy

Interfacial Reactions in Ceramic/Metal Joining

According to Pask (Ref. 4), two basic requirements must be satisfied to obtain a strong joint in ceramic/metal and glass/metal systems. The first requirement is the formation of an intimate interface where atomic contact exists as a result of van der Waals attractive forces (physical bond) or a continuous electronic structure (chemical bond) across the interface. In brazing, an intimate solid/liquid interface can be formed if the liquid wets the solid surface. In reactive metal brazing, a drastic decrease of interfacial tension happens, resulting in wetting, because reactions at the interface involve a much larger decrease of the free energy than simple adsorption

Table 1 — Reaction Products between Al_2O_3 and Pure Titanium or Alloys Containing Titanium

System	Temp (°C)	Load (MPa)	Time (h)	Atm (torr)	Reaction Products	Ref.
Al_2O_3/Ni-Ti	1500	—	≈0.03	5×10^{-6}	$(Ti,Al)_2O_3$, Ti_3O_5	3
Al_2O_3/Ti	1800	—	0.25	He	TiO	5
Al_2O_3/Ti	871	—	60	5×10^{-6}	O rich Ti layer, Ti_3Al	7
Al_2O_3/Ti	650–1000	—	940	1×10^{-6}	O rich Ti layer, $(Ti,Al)_2O_3$, Ti_3Al, TiO	8
Al_2O_3/Ti	1050	—	1	1×10^{-5}	Ti_2Al	9
Al_2O_3/Ti	900–1200	≈4–12	4–9	1×10^{-4}	Ti_3Al (or Ti_2Al), TiAl	10
Al_2O_3/Ti	484–566	—	0.5–9	NK[a]	unoxidized Al, O dissolved Ti	11
Al_2O_3/Cu-Ag-Ti	850–890	0.1	≈0.03–0.2	2×10^{-5}	$Cu_2(Ti,Al)_4O$	12
Al_2O_3/Cu-Ti	1150	—	2	5×10^{-5}	$(Al,Ti)_2O_3$, TiO_x	13
Al_2O_3/Sn-Ti	1150	—	≈0.3	5×10^{-6}	Ti rich product	14

(a) not known

(Ref. 5). During the first instant of interface formation, the free energy decrease is very large, but it gradually approaches its equilibrium value as the chemical potential difference decreases.

The second requirement, more critical than intimate contact, is the presence of a stable chemical thermodynamic equilibrium at the interface. In general, this requirement can be satisfied with the formation of an equilibrium reaction product at the interface, that is compatible with both its metal and the glass or ceramic. Table 1 summarizes the results of a literature survey showing the several reaction products observed between Al_2O_3 and pure Ti or alloys containing Ti. These products can be classified into four groups: 1) $(Ti,Al)_2O_3$ solid solution; 2) Ti oxide (TiO_x); 3) TiAl compounds (TiAl, Ti_2Al, Ti_3Al); and 4) complex oxide ($Cu_2(Ti,Al)_4O$). It is not surprising to see the many reaction products reported in the literature, because system parameters such as composition of the filler metal and reaction conditions (temperature, time and atmosphere) all influence the interfacial reaction.

Several reports showed that bond strength is directly related to the growth of reaction product at the interface. Scott, *et al.* (Ref. 15), investigated bond strength between copper alloyed with transition metals (Ti, Cr, V) and diamond. When a continuous carbide layer was formed at the interface, maximum bond strength was obtained. However, as the carbide layer grew in thickness, the bond strength was observed to decrease. The onset of flaw development led to the weakening of the bond (Ref. 6). The strength of the interface was attributed to two competing processes: the chemical reactions increased the bond strength as reactions proceeded, and surface roughening decreased the bond strength as reactions proceeded. Thus, maximum bond strength was obtained when chemical reactions were sufficient to ensure adequate interfacial bonding, but not so intense that the interface became weakened by excessive roughening of the ceramic surface.

Tressler and Moore (Ref. 7) investigated the kinetics of the growth of reaction product, Ti_3Al, in the titanium/sapphire system. They determined an

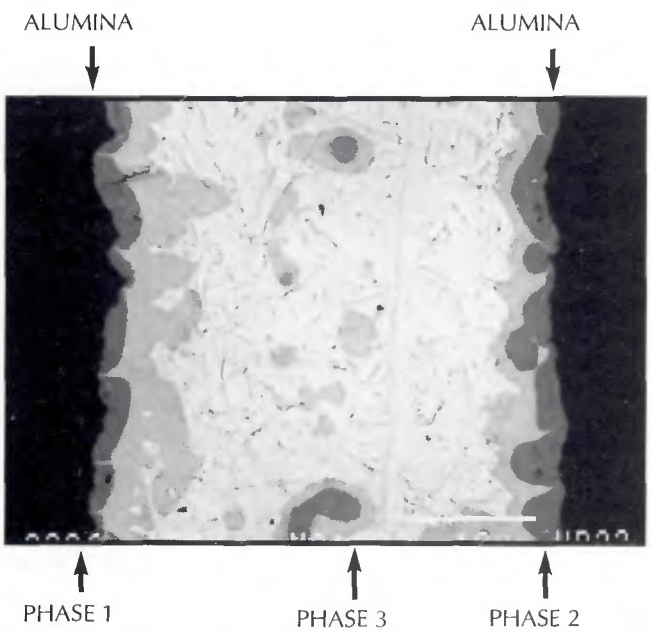

Fig. 1 — Typical SEM back-scattered image of cross-section of a Al_2O_3/Cu-Ti-Al_2O_3 brazement.

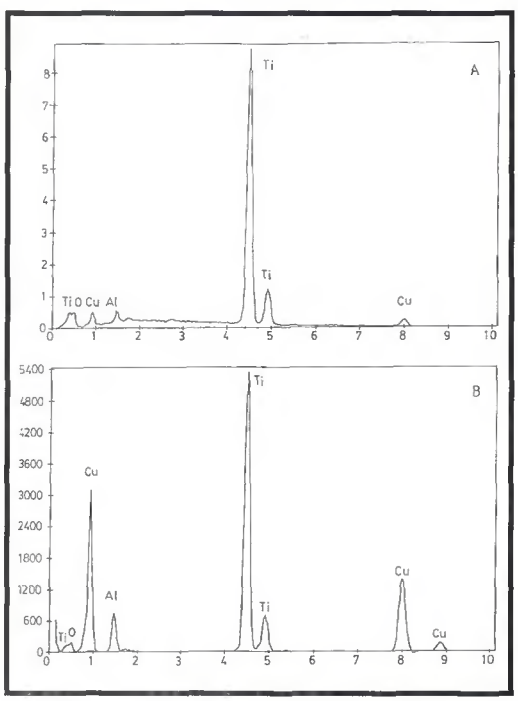

Fig. 2 — X-ray spectrum (EDS) of: A — Phase 1; B — phase 2.

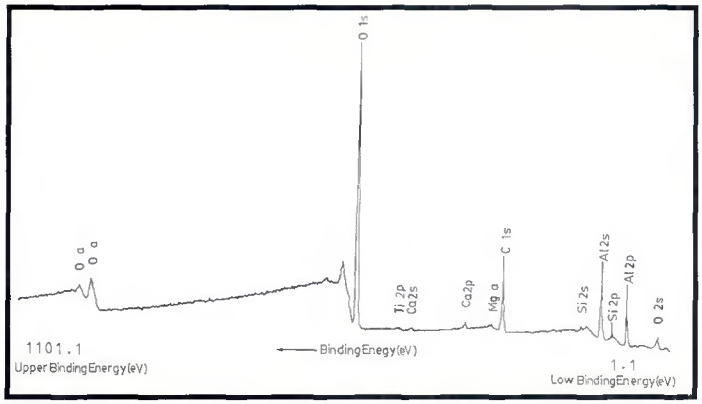

Fig. 3 — X-ray spectrum (XPS) of the fracture surface of Al_2O_3 close to the bond region.

activation energy of 209~218 kJ/mol and suggested that the rate-controlling step of the reaction was aluminum diffusion through the Ti_3Al layer. Later, Hatakeyama, *et al.* (Ref. 8), obtained an activation energy of 142 kJ/mol with the same system. He explained the discrepancy from Tressler's work resulted from the difference in temperature range used. Naka, *et al.* (Ref. 9), used Cu-Ti/Si_3N_4 system and showed the formation of TiN at the interface, which grew parabolically with an activation energy of 206.3 kJ/mol. As this value is similar to the activation energy of diffusion of nitrogen in the TiN, he suggested that diffusion of nitrogen through TiN was the rate-controlling step. Nakao, *et al.* (Ref. 10), also studied the kinetics of the growth of reaction layer with Cu-Ti/Si_3N_4 system. He confirmed the parabolic growth of TiN at the interface, but the activation energy of the growth, 318 kJ/mol, was much higher than reported by Naka. Therefore, he proposed that the rate-controlling step was the diffusion of titanium through the TiN layer.

Despite the observation of several reaction products at the interface, as shown above, few investigators reported the thermodynamics of these interfacial reactions. Tressler (Ref. 11) noticed the high solubility of oxygen in titanium (*e.g.*, up to 32 at.-% at 1100°C) and calculated the partial molar free energy of solution of oxygen in titanium with oxygen concentration. He showed that the partial molar free energy of oxygen in titanium is more negative than the standard free energy of Al_2O_3 formation, resulting in the dissolution of oxygen in titanium. Moorhead, *et al.* (Ref. 12), added the effect of dissolution of aluminum in titanium and calculated the negative free energy change of dissolution of Al_2O_3. On the other hand, Klomp (Ref. 13) proposed the free energy change of oxide ceramic/metal system with more complex interfacial reactions. In addition to the free energy changes of oxidation and reduction reaction, he also included the free energy changes of spinel formation, alloy formation and interface formation. He suggested that if the total free energy change of the overall reactions is negative, the metal would reduce the oxide ceramic even if the free energy change of redox reaction is positive.

This study investigated the interfacial reaction between alumina and Cu-Ti brazing filler metal through characterization of the reaction products. A thermodynamic interpretation was offered to explain the formation of these reaction products. Finally, the mechanism of reaction product growth was determined through kinetic studies.

Materials and Experimental Procedures

Materials

The ceramic material used is polycrystalline alumina of 99.8 wt-% purity manufactured by Coors Ceramic Co. For the brazing filler metal, a Cu-20 wt-% Ti binary alloy of approximately 950°C equilibrium liquidus temperature was chosen to simplify the interfacial reaction. In practice, however, ternary alloy systems (*e.g.*, Cu-Ag-Ti) are often preferred to further lower the melting temperature of the brazing filler metal. The brazing alloy was in the form of a paste, prepared by mixing each metal powder with glycerine. The copper powder was atomized using OFHC (oxygen-free high-conductivity) C10200-grade copper. The titanium powder is in the form of hydride (TiH_2) with the particle size of approximately 45 μm.

Experimental Procedures

Alumina substrates of 6-mm (0.24-in.) diameter and 6-mm length were used for brazing. The surfaces were polished with silicon carbide paper to grit No. 1200 and then cleaned ultrasonically in acetone. After cleaning, 0.046 g of the brazing paste was painted onto the end of one of the pieces so that the total thickness of the brazing paste was approximately 0.2 mm (0.008 in.). The alumina couple then was placed in the vacuum furnace with a dead-weight of 20 g on the top of the couple. The brazing temperatures were 1000°, 1050°, and 1100°C (1832°, 1922°, 2012°F), as compared to the equilibrium liquidus temperatures of the Cu-Ti filler metals. The samples were held at the brazing temperature for 5, 20, 40, and 60 min. The furnace was evacuated to the pressure of 5 X 10^{-5} torr before specimens were heated up to the brazing temperatures at a heating rate of 70°C/min (126°F/min). After holding at the brazing temperatures, the specimens were cooled to 50°C (122°F) at a cooling rate of 12°C/min (22°F/min) by backfilling high purity (99.9 vol-%) argon gas into the furnace.

Interfacial microstructure and reaction product growth were investigated using cross-sections of brazed joints with a JEOL JXA-840 scanning electron microscope (SEM). Samples for SEM were first polished and then carbon coated to avoid charging during observations. The composition of each phase in the brazed joints was determined by energy dispersive x-ray (EDX) analysis with a JEOL 6400-JSM SEM, which has an oxygen detector. X-ray diffraction (XRD) analyses were also performed to identify the reaction products with a Rigaku x-ray diffractometer. For several specimens, x-ray photoelectron spectroscopy (XPS) analysis was also performed to investigate the interface region more thoroughly using a Surface Science SSX-100 analyzer. The thickness of reaction products at the in-

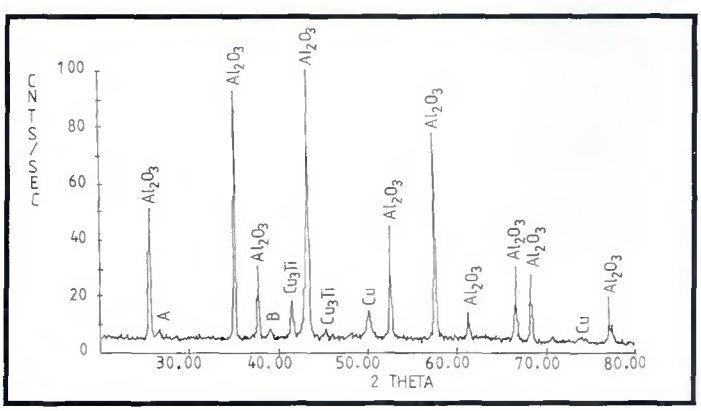

Fig. 4 — X-ray spectrum (XRD) of a Al_2O_3/Cu-Ti/Al_2O_3 brazed

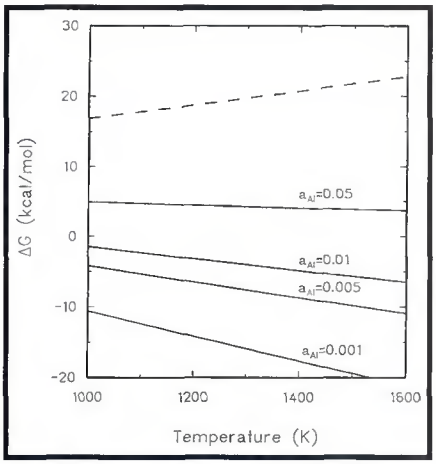

Fig. 5 — Free energy change of interfacial reaction as a function of activities of aluminum.

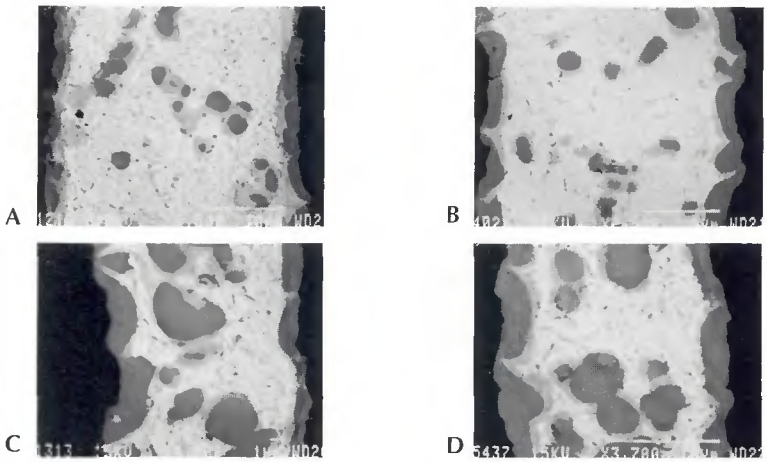

Fig. 6 — Microstructural changes of an Al_2O_3/Cu-Ti/Al_2O_3 brazed joint processed at 1100°C. A — 5 min; B — 20 min; C — 40 min; D — 60 min.

terface and area fraction of each phase were determined using a LECO Image Analysis 2001 system.

Experimental Results and Discussion

Interfacial Reaction and Thermodynamics

A typical SEM back-scattered electron image of a cross-section of a brazement is shown in Fig. 1. It is clear that the brazement has three different phases: a dark gray colored phase (hereinafter phase 1) located immediately next to the ceramic component; a light gray colored phase (hereinafter phase 2) adjacent to phase 1; and a white colored phase (hereinafter phase 3) in the middle of the brazement. In the middle of the brazement, many flake-type features and several round-shaped particles of phase 1 surrounded by phase 2 were also found. The chemical compositions of phase 1 and 2 were determined using an EDX analyzer with a thin window oxygen detector. The x-ray spectra of each phase is shown in Fig. 2. The chemical composition in at.-% corresponding to each spectrum is 4.2 Cu, 49.0 Ti, 0.8 Al, 46.0 O for phase 1, and 27.5 Cu, 28.2 Ti, 5.5 Al, 38.8 O for phase 2. From the chemical analyses, phase 1 is TiO with a small amount of copper and aluminum, and phase 2 is a complex oxide. The interfacial region was investigated more thoroughly by XPS analyses. A brazed joint was sectioned as close as possible to the interface, followed by grinding the remaining alumina until the dark gray color of TiO began to appear. This surface with the partly exposed TiO was then examined using XPS. Figure 3 shows the x-ray spectrum of the surface. The presence of carbon, calcium, magnesium, and silicon peaks may be the result of surface contamination during specimen preparation. Using data provided in the *Handbook of X-Ray Photoelectron Spectroscopy* (Ref. 14), the binding energy of the O_{1s} electrons was determined to be 530.6 eV, indicating that elements other than aluminum were present in Al_2O_3. Naka, *et al.* (Ref. 15), analyzed the surface of alumina joined with amorphous Cu-Ti filler metals by XPS and detected an Al_{2P} electron with the binding energy of 74.70 eV and two O_{1S} electrons with the binding energies of 531.25 eV and 529.20 eV, respectively. From these results, they concluded the presence of $(Al,Ti)_2O_3$ solid solution. Comparing the 530.6 eV O_{1s} electron binding energy determined in this work with the values reported by Naka, *et al.*, it is believed that some titanium was present in the alumina adjacent to the Cu-Ti/Al_2O_3 interface in the form of $(Al,Ti)_2O_3$.

The formation of complex oxides in Al_2O_3 brazing with titanium containing reactive filler metal has been reported in several researches even though the chemical compositions are not always identical. Moorhead, *et al.* (Ref. 12) observed a complex oxide with composition of 37.5 Ti, 27.6 Cu, 4.4 Sn, 0.9 Ag, and 29.6 O (in at.-%) when alumina was brazed with a Cu-44Ag-4Sn-4Ti filler metal. Barbier, *et al.* (Ref. 16), reported the presence of a $Cu_2(Ti,Al)_4O$ when brazing alumina to Ti-6Al-4V using a Cu-40Ag-5Ti brazing filler metal. Santella (Ref. 17), detected $Ti_3(Cu_{0.76}Al_{0.18}Sn_{0.06})_3O$ in the brazed joint between alumina and a Ag-Cu-Sn-Ti filler metal. The oxides reported by Barbier (Ref. 16) and Santella (Ref. 17) are in essence the same oxide with a Ti_2Ni-type crystal structure. According to Karlsson (Ref. 18), Ti_2Ni-type oxides have lower and upper phase limits for the titanium content as Ti_3Ni_3O and Ti_4Ni_2O, respectively; and nickel can be substituted by magnesium, iron, cobalt, or copper. Therefore, the oxides reported by Santella and Barbier could be considered as Ti_3Cu_3O with a Ti/Cu ratio of one, and Ti_4Cu_2O with a Ti/Cu ratio of two, respectively. Even though the oxygen concentration is high, the complex oxide identified in this experiment closely resembles Ti_3Cu_3O as the Ti/Cu ratio is one.

Phase 3 is the "matrix" of the solidified brazing filler metal. Many flake-type features could also be observed. XRD analyses were performed to determine this phase more accurately. After cutting off the alumina parts from the joint until the dark gray color of TiO was revealed, the "matrix" material was crushed and reduced to powder for diffraction analyses. Figure 4 shows the XRD pattern obtained. The Al_2O_3 peaks indicate that alumina is still present. In addition, $TiCu_3$ and copper peaks were also observed.

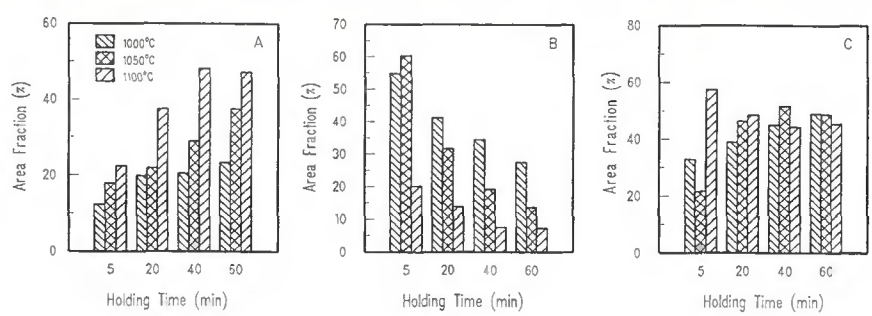

Fig. 7 — Variation of area fraction of TiO. A — Complex oxide; B — copper solid solution; C — with brazing conditions.

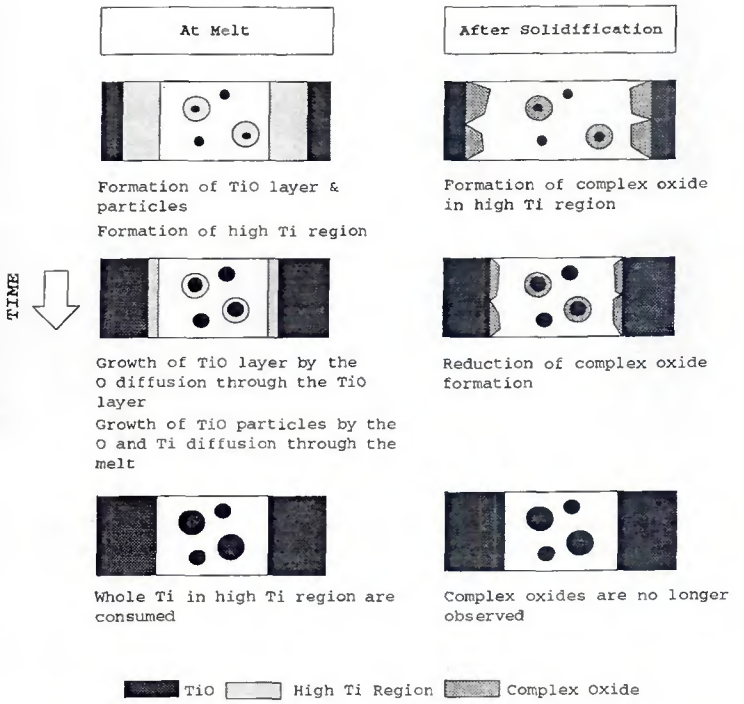

Fig. 8 — Schematic illustration of the sequence of reactions.

According to the Cu-Ti phase diagram, the "matrix" material is the copper terminal solid solution, and the flake-type features are $TiCu_3$. Furthermore, two more peaks, marked A (d = 3.34Å) and B (d = 2.30Å) were also present. Based on ASTM diffraction data, the interplanar spacings, d, for TiO are 2.07_x, 1.46_x, 3.32_8. If the higher intensity peaks, 2.07 and 1.46 overlap with 2.08 and 1.50 of the Al_2O_3 peaks, only the 3.32 peak for TiO will appear. This is a good indication that peak A (d = 3.34Å) may be originated by TiO in the interfacial region. On the other hand, peak B (d = 2.30Å) matches well with the strongest intensity peak of Ti_2Cu since the interplanar spacings for Ti_2Cu are 2.28_x, 2.084, 1.242. However, if we assume that Ti_2Cu and its ternary oxides (Ti_4Cu_2O and Ti_3Cu_3O) have identical patterns like Ti_2Fe and its ternary oxides (Ti_4Fe_2O and Ti_3Fe_3O), which was observed by Rostoker (Ref. 19), peak B may have originated by either Ti_4Cu_2O or Ti_3Cu_3O. As the chemical analysis of the complex oxide shows a Ti/Cu ratio of one, peak B indicates the presence of Ti_3Cu_3O.

It is difficult to understand how Cu-Ti filler metals could reduce alumina to form TiO at the interface, because of the greater stability of Al_2O_3 over that of TiO. However, since aluminum is detected in the solidified brazing filler metal, (*e.g.*, copper solid solution shows 94.6 Cu, 4.4 Al, and 1.2 Ti, in at.-%, in EDX analysis), the effect of dissolution of aluminum in the filler metal must be considered in the thermodynamic calculation of the interfacial reaction. Instead of a simple redox reaction, the interfacial reaction should be written as the following:

$$\langle Al_2O_3 \rangle + 3[Ti]_{Cu} = 3\langle TiO \rangle + 2[Al]_{Cu-T}$$

where < > and [ ] means solid and solute, respectively. The free energy change of this reaction can be calculated using partial reactions as:

$$\Delta G = 9066 - 13.06T + 3.75T\,logT$$
$$+3.97T\,ln\,a_{Al_{Cu-Ti}} - 5.96T\,ln\,a_{Ti_{Cu}}$$

Figure 5 shows the free energy change as a function of the activity of aluminum in the Cu-20 at.-% Ti filler metal. The activity coefficient of titanium in copper melt is assumed as unity because of the high solubility of titanium at the temperature range of interest (*e.g.*, 70 at.-% at 1100°C) (Ref. 20). It can be estimated that, at 1300 K, for example, the reaction is able to proceed until the activity of aluminum reaches about 0.02. For reference, the free energy change of the simple redox reaction is also presented in Fig. 5, the dashed line, which shows that the reaction is thermodynamically impossible.

Kinetics of Reaction Products Growth

Figure 6 shows the microstructural changes of the brazement with time at 1100°C. All microstructures showed TiO layer at the interface, TiO particles in the middle of the braze, complex oxides adjacent to the TiO and copper solid solution containing $TiCu_3$ intermetallics. However, the amount of each phase differs with different brazing conditions. Figure 7 shows the area fractions of TiO, complex oxide and copper solid solution with brazing conditions. The area fraction of TiO included both the layer at the interface and the particles in the middle of the brazing filler metal. The intermetallics in the center of the braze metal were counted as copper solid solution. Data from several duplicate samples showed that the area fraction of copper solid solution remained almost the same regardless of the brazing conditions. TiO increased and complex oxide decreased with both brazing time and brazing temperature. From these results, it is clear that the TiO layer thickened with brazing time and temperature. It grew toward the center of the brazing filler metal, consuming the complex oxide adjacent to it. The quantitative measurements of the three phases and the thickness of the different layers were made using a computerized image analysis system. Because of the large number of fields taken, over 30 for each phase, the error of measurement was estimated to be between five and ten percent. Therefore, the trends indicated are quite reliable.

At the onset of brazing, titanium in the

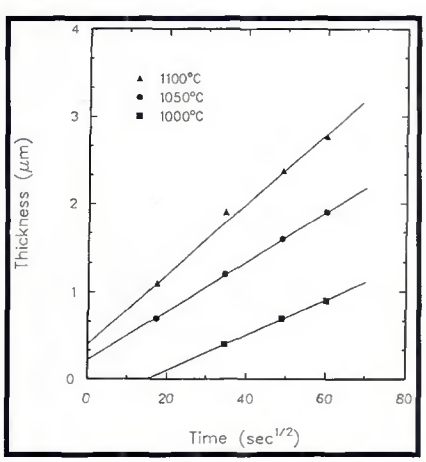

Fig. 9 — Variation of TiO layer as a function of brazing conditions.

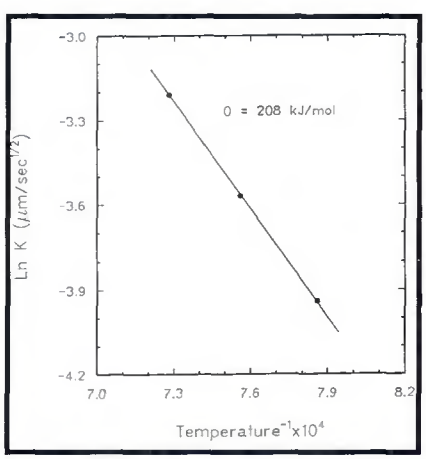

Fig. 10 — Parabolic rate constant of TiO layer as a function of reciprocal temperature.

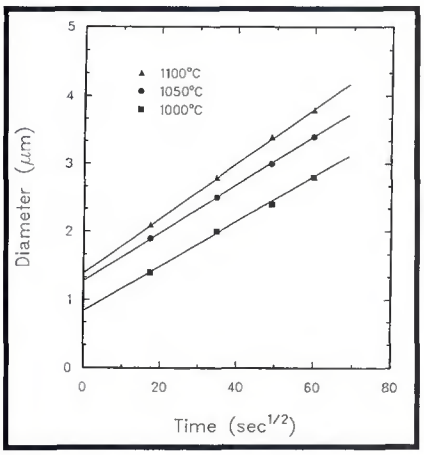

Fig. 11 — Variations of thickness of TiO particles as a function of brazing conditions.

filler metal diffuses to the interface and forms a high titanium concentration region. For short brazing times, the TiO layer formed between alumina and titanium has no chance to grow. Consequently, the wide region of molten copper with high titanium concentration transforms into the complex oxides adjacent to the TiO layer after solidification. The formation of small TiO particles in the middle of the brazing filler metal is believed to be the result of oxygen contamination. Oxygen in the melt attracts titanium to form TiO particles, each with a high titanium concentration region around it. As the brazing time increases, the TiO layer at the interface and particles in the middle of the brazing filler metal grow and consume the high titanium concentration region around it, which results in a large amount of TiO and small amount of complex oxide adjacent to TiO after solidification. Figure 8 shows the sequence of reactions schematically. Hydrogen from the hydride did not seem to have any significant effect because of the low thermal stability and low dissociation temperature. Slow heating might also have helped in the safe removal of hydrogen from the brazed joint.

The fact that the TiO layer grows toward the center of the brazing filler metal while consuming the high titanium concentration region indicates that oxygen is supplied continuously from the alumina to react with titanium at the moving interface. As long as the free energy change of the interfacial reaction is negative, alumina will dissociate, with aluminum and oxygen diffusing to the moving interface. At the interface, oxygen reacts with titanium and aluminum dissolves in the melt. Therefore, if we assume that the interfacial reactions — dissociation of alumina at the original interface, oxidation of titanium and dissolution of aluminum at the moving interface — are fast, the growth rate of the TiO layer will be controlled by the diffusion of oxygen through the TiO layer. The thickness of the TiO layer is plotted as a function of brazing conditions in Fig. 9. Notice that for 1050°C and 1100°C, the initial thicknesses of TiO layers are nonzero. This is due to the fact that the brazing temperatures were higher than the melting temperature of the filler metal. During the heating cycle, titanium already diffused and reacted with alumina to form TiO. On the other hand, it takes longer for titanium to diffuse to the interface at low temperature of 1000°C than at 1050°C and 1100°C, resulting in the delayed start of TiO formation at 1000°C. The parabolic relationship indicates that TiO growth is controlled by diffusion. The activation energy, Q, for the diffusion can be calculated from Fig. 10. The slope corresponds to $-Q/2R$, where R is the universal gas constant. The calculated activation energy is 208 kJ/mol (50 kcal/mol). As no diffusion data are reported for TiO, it is impossible to check the validity of this value. Nevertheless, from the discussion above, it is believed that the activation energy determined is for the diffusion of oxygen in TiO.

The growth of TiO particles in the middle of the brazing filler metal under different brazing conditions is shown in Fig. 11. Again, a parabolic relationship was observed. The activation energy calculated is 73 kJ/mol (17 kcal/mol). If the formation of these particles is the result of the reaction between titanium and oxygen in the molten filler metal as discussed above, the growth should be controlled by the diffusion of titanium or oxygen in the molten filler metal. Table 2 shows the literature survey of the activation energies of titanium and oxygen diffusion in molten copper. The calculated value matches well with both the activation energies for titanium diffusion and for oxygen diffusion. Therefore, it is clear that TiO particles grew as a result of the reaction between titanium and oxygen in the molten filler metal, even though it is inconclusive as to which diffusion process (oxygen or titanium) is rate-controlling.

Table 2 — Activation Energies of Titanium and Oxygen Diffusion in Molten Copper

Reaction	Activation Energy (kJ/mol)	Ref.
Oxygen diffusion in molten copper	66	27
Oxygen diffusion in molten copper	69.9	28
Oxygen diffusion in molten copper	39	29
Titanium diffusion in molten copper	69	30

Conclusions

The mechanism and kinetics of the interfacial reactions between Al_2O_3 and Cu-Ti brazing filler metals were proposed based on the characterization of reaction products and thermodynamic interpretation of the reactions. Important conclusions are:

1) Thermodynamic analyses showed that the interfacial reaction above can proceed until the activity of aluminum in the filler metal reaches 0.02 for Al_2O_3/Cu-20 at.-% Ti system at 1300 K.

2) TiO layer at the interface was observed to grow toward the center of brazing filler metal. The activation energy of TiO layer growth was 208 kJ/mol (50 kcal/mol).

3) At the center of the brazement, the TiO particles were observed to grow, consuming the complex oxide that enveloped them. The activation energy of TiO particles growth was determined to be 73 kJ/mol (17 kcal/mol).

4) Based on the growth of TiO and consumption of Ti_3Cu_3O, a model was proposed to describe the kinetics of the reactions that occur at the Cu-Ti/Al_2O_3 interface.

5) In short brazing times, a complex oxide, Ti_3Cu_3O with Ti_2Ni-type crystal structure, is formed in the high titanium region next to the TiO. However, this complex oxide decreases as the TiO increases with brazing time.

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NITROGEN IN ARC WELDING — A REVIEW

By IIW Commission II

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