Joining of Alumina to Copper Using Amorphous Cu-Ti Filler Metal†

Masaaki NAKA*, Katuhiko ASAMI*** and Ikuo OKAMOTO**

Abstract

Joining of alumina (99.62 mass% Al_2O_3) to copper was made using amorphous Cu-Ti (34–57 at%) brazing filler metals at 1173 to 1323K in 2.7×10^{-3} Pa. The amorphous filler metals, 1 cm in width and 45μm thick, were produced by liquid quenching. The superior flexibility of amorphous filler provides simplicity to joining process.

The fracture shear strength of the joints was measured at room temperature. The strength of the joints brazed at 1323 K for 1.8 ks using $Cu_{50}Ti_{50}$ filler possesses 138.27 MPa at room temperature. The strength of the joints at constant brazing time raises with an increase in brazing temperature. The strength increases slightly with an increase in titanium content in the filler. At 1298K for 1.8 ks, the strength of joints at room temperature changes from 107.8 MPa with $Cu_{66}Ti_{34}$ to 120.6 MPa with $Cu_{43}Ti_{57}$. The strength of the joints was also investigated at high temperatures up to 973K. The high temperature shear strength is almost constant up to 773K, and decreases gradually at higher temperature.

Isothermal solidification process takes place during joining, and copper dissoves into Cu-Ti filler metal, and then, copper solid solution containing Ti precipitates from Cu-Ti filler metal. On the other hand, the formation of titanium oxide TiO_x and $(Al, Ti)_2O_3$ solid solution oxide is attributable to the strong joining between alumina and Cu-Ti filler.

KEY WORDS: (Joining) (Brazing) (Ceramics) (Alumina) (Amorphous Filler) (Copper-Titanium Alloy) (Copper)

1. Introduction

Recent years have been seen dramatic developments in the application of ceramics because of their superior heat-, corrosion- and insulation- resistance. However, the inferior deformability of ceramics resulted from their brittleness and hardness in produceing large and complex parts necessiates the development of the joining method of ceramics to metals. The joining method of oxide ceramics to metal are roughly classified into (1) solid state diffusion bonding method (including gold metal method)[1], (2) active metal method,[2] (3) refractory-metal metallizing method[3] and (4) metal-oxide eutectic utilizing method[4]. The complex processes and the limited joining conditions of these methods often restrict the actual application. On the other hand, Brunner et al.[5] have reported the active metal method using ductile amorphous filler metals for joining of ceramics to metals. Although this method utilizes the flexibility and compositional uniformity of amorphous metals, the joining mechanism and actual application are not still clear. This paper also deals with the simple method to join alumina to copper by melting Cu-Ti amorphous fillers inserted between them, and makes the joining mechanism clear.

2. Experimentals

$Cu_{66}Ti_{34}$, $Cu_{50}Ti_{50}$ and $Cu_{43}Ti_{57}$ fillers are produced by rapid quenching of the liquid alloys, where the numbers attached to the fillers designated the atomic percent. The alloys (1 cm wide and 45μm thick) of desired composition which first prepared by argon arc melting were ejected onto the outer surface of a rapidly rotating wheel. The diameter and rotating speed of wheel used are 200 mm and 83.3 rps, respectively. **Fig. 1** shows the schematic apparatus. The diffraction pattern of amorphous $Cu_{50}Ti_{50}$ filler is shown in **Fig. 2** which includes that of the crystalline alloy. The ductile amorphous fillers containing high titanium content can be bent to the encounter side and punched out to the desired size.

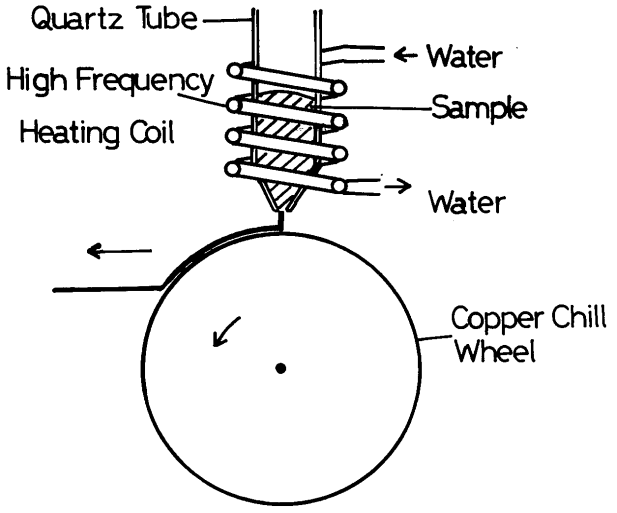

Fig. 1 Apparatus for producing amorphous filler metal.

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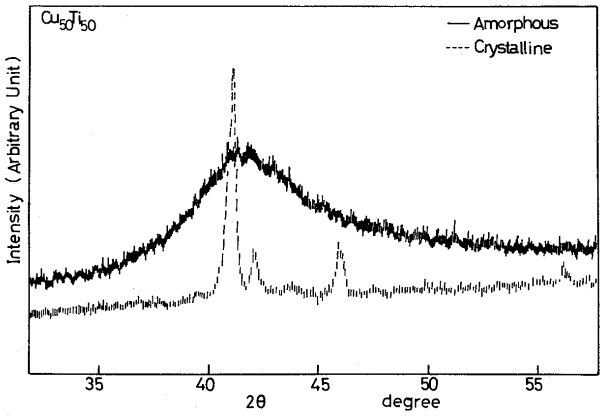

Fig. 2 X-ray diffraction pattern of amorphous $Cu_{50}Ti_{50}$ filler metal.

These add simplicity to the joining method.

The materials used are alumina (99.62 mass% Al_2O_3) and tough pitch copper in **Table 1**. Alumina of 15 mm in diameter and 3 mm in thickness, and copper of 6 mm in diameter and 3 mm in thickness were used to make a lap joint using amorphous filler metals of 6 mm diameter and 45μm thickness as shown in **Fig. 3**. The heating rate was 0.33 K/s in 2.7 mPa and the cooling rate after brazing was about 0.33 K/s down to 873 K and then 1.7×10^{-2} K/s to room temperature.

Table 1 Chemical composition of specimens used.

Material	Chemical composition (mass%)					
	Al_2O_3	MgO	Fe_2O_3	CaO	Na_2O	SiO_2
Al_2O_3	99.62	0.10	0.02	0.11	0.06	0.09
Tough pitch copper	O	Cu				
	0.03	bal.				

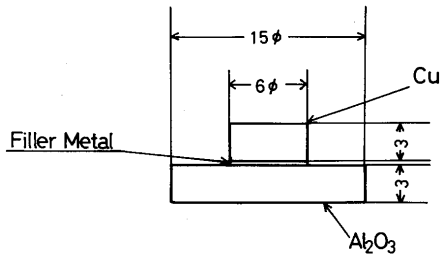

Fig. 3 Lap joint of copper and alumina.

The joining strength of the lap joint was determined by fracture shear loading using a cross head speed of 1 mm/min. The fracture at room temperature took place near the joining interface of joint. The microstructures and element distribution of joint were determined by means of scanning electron microscope and energy dispersive electron microscope (EDX) analyser.

In order to characterize the intermediary layer of joint, copper and filler metal were dissolved from the alumina/copper joint in concentrated hot HCl and X-ray photoelectron spectroscopic examination with $Mg \cdot K_\alpha$ excitation was conducted to identify the intermediate compound.

3. Results and Discussion

3.1 Joining temperature dependence and joining time dependence of joining strength

Fig. 4 shows the joining temperature dependence of joining strength of Cu/Al_2O_3 joint using $Cu_{66}Ti_{34}$ filler. At joining temperatures from 1173 to 1273 K for joining time of 0.3 ks the joining strength exhibits the same value of about 78.5 MPa, and further at joining temperatures from 1273 to 1323 K for joining time of 0.3 or 1.8 ks the joining strength increases with an increase in joining temperature. For instance, the joining strength is 132.4 MPa at joining condition of 1323 K and 1.8 ks. **Fig. 5** shows the joining temperature dependence of joining strength using $Cu_{66}Ti_{34}$, $Cu_{50}Ti_{50}$ and $Cu_{43}Ti_{57}$ fillers at joining time of 1.8 ks. At every joining temperature the

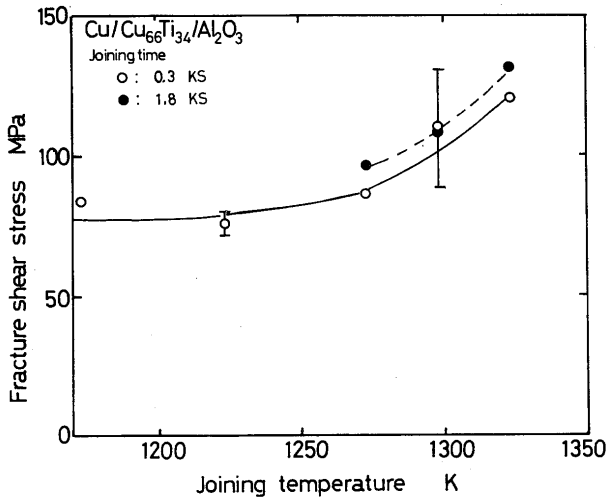

Fig. 4 Dependence of fracture shear stress of Cu/Al_2O_3 joint on joining temperature at 0.3 or 1.8 ks joining time using $Cu_{66}Ti_{34}$ filler.

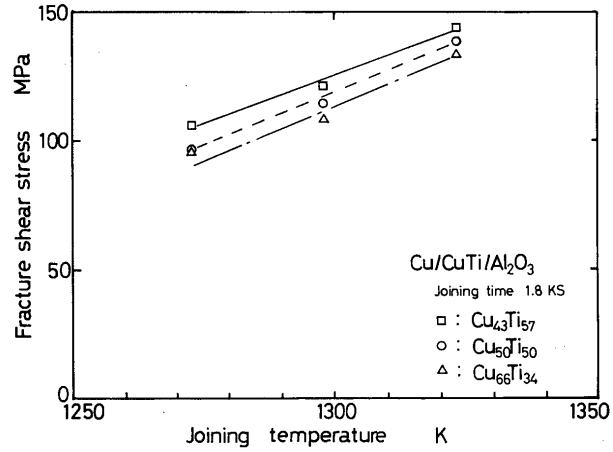

Fig. 5 Dependence of fracture shear stress of Cu/Al_2O_3 joint on joining temperature at 1.8 ks joining time using $Cu_{43}Ti_{57}$, $Cu_{50}Ti_{50}$ and $Cu_{66}Ti_{34}$ filler metals.

effect of titanium content in the filler on joining strength is not large and the joining strength using amorphous fillers increases with an increase in joining temperature. The promotion of growth of below-described TiO_x formed with Al_2O_3 is attributed to the increase in joining strength.

The change of joining strength of Cu/Al_2O_3 joint using $Cu_{50}Ti_{50}$ filler with joining time at joining temperatures of 1273, 1298 and 1323 K are shown in **Fig. 6**. At every joining temperature the strength gradually decreases through the maximum value with joining time. For instance, the maximum values are 107.9 and 120.6 MPa for joining time of 0.3 ks at joining temperatures of 1273 and 1298 K, respectively, and the maximum value at joining condition of 1323 K and 1.8 ks is 138.3 MPa. The reaction between the filler and alumina during heating up to joining temperature, and the rapid reaction between them at joining temperature lead to the short biginning time of joining at joining temperature.

The change of joining strength with time is discussed with the two similar competing effects as that are proposed by Sutton[6] in joining of alumina to nickel.

(1) The joining strength of alumina to Cu-Ti filler increases with the amount of reaction at the interface of joint (The formation of TiO_x as described below).

(2) The joining strength of the joint decreases with the degradation of alumina formed by the intermediate phase near the interface of the joint.

These two competing effects are attributable to the maximum of joining strength at joining time of 1.8 ks in Fig. 6.

3.2 Testing temperature dependence of joining strength

The joining strength of the Cu/Al_2O_3 joint brazed at 1298 K for 1.8 ks using $Cu_{50}Ti_{50}$ at testing temperatures up to 973 K is shown in **Fig. 7**. The heating rate up to testing temperature was 0.12 K/s, and the strength at testing temperature was determined by fracture shear loading using a cross head speed of 1.67×10^{-2} mm/s after holding for the time longer than 0.6 ks.

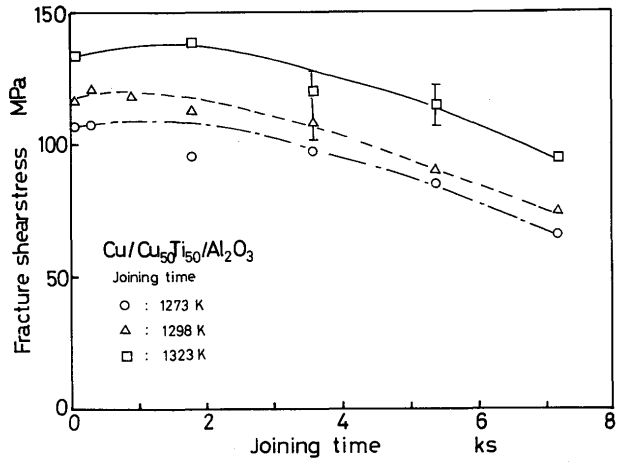

Fig. 6 Dependence of fracture shear stress of Cu/Al_2O_3 joint on joining time at 1273, 1298 and 1323 K joining temperature.

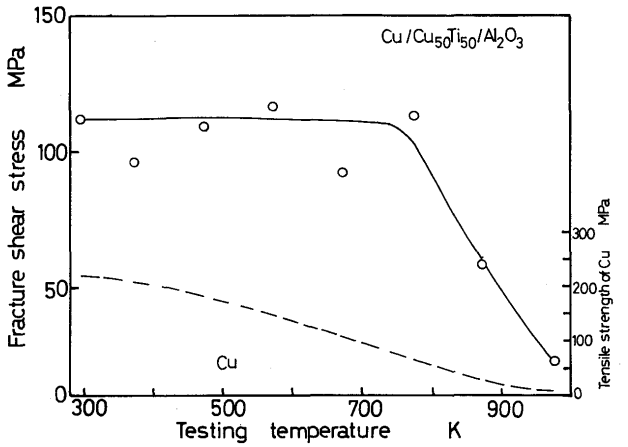

Fig. 7 High temperature fracture shear stress of Cu/Al_2O_3 joint brazed at 1298 K for 1.8 ks.

The joining strength of the joint maintains the same value of 112.8 MPa at temperatures from room temperature to 773 K, and further with increasing the strength gradually decreases down to 12.8 MPa at 973 K. The fracture of the joint takes place at the interface between the filler and alumina, or alumina near the interface at temperatures up to 873 K and the fracture takes place at copper at temperatures above 873 K. The strength of alumina doesn't change at temperatures up to around 1073 K.[7] The decrease in strength of copper with an increase in temperature[8] in Fig. 7 and the fracture structure of the joint indicate that the decrease in strength of copper with increasing temperature results in the decrease in strength of Cu/Al_2O_3 joint at temperatures above 773 K.

3.3 Thermal shock testing of joint

Knowledge of the effect of thermal stress on the degradation of strength of joint is necessary because the temperature distribution in the joint will take place and the temperature of the joint will change abruptly in the actual application.

The joints brazed at 1298 K for 1.8 ks were abruptly heated into the furnace at desired temperature and then air-cooled, oil-quenched or water-quenched after holding for 0.6 ks. **Fig. 8** shows the change of joining strength of the joint with the heat-treating temperature. The strength decreases at temperature around 723 K. The fracture of the joint takes place at the interface between the filler and alumina, or alumina near the interface at temperatures below 773 K, and alumina at temperatures above 773 K. The decrease in strength of alumina is attributable to the decrease in strength of the joint at temperature around 723 K.

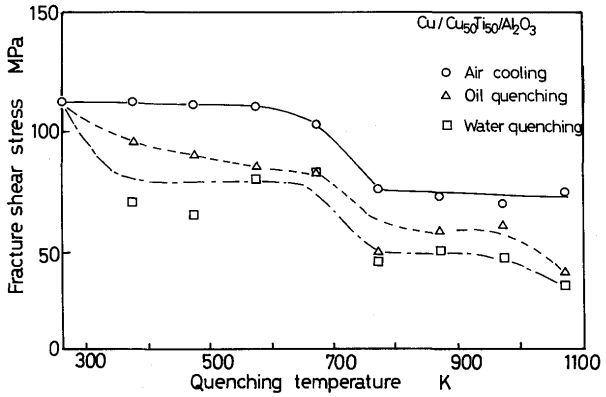

Fig. 8 Dependence of fracture shear stress on quenching temperature and quenching medium.

3.4 Structure observation of joining interface

The change in microstructure of joining interface with joining temperature and joining time was investigated.

Fig. 9 represents the compositional analysis of fine phases in the filler and the change in microstructure of the joint with joining temperature (from 1273 to 1323 K) at joining time of 1.8 ks. The amount of copper dissolved into the filler during joining increases with an increase in joining temperature as shown in Figs. 9 (a), (b) and Figs. 9 (d), (c). The EDX point analysis revealed that the fine phases are the remained $Cu_{50}Ti_{50}$ filler that possesses the initial composition of the filler. These results indicate that copper first dissolves into the filler, and then the titanium saturated solid solution precipitates from the liquid adjacent to the copper material, that is, the joining is

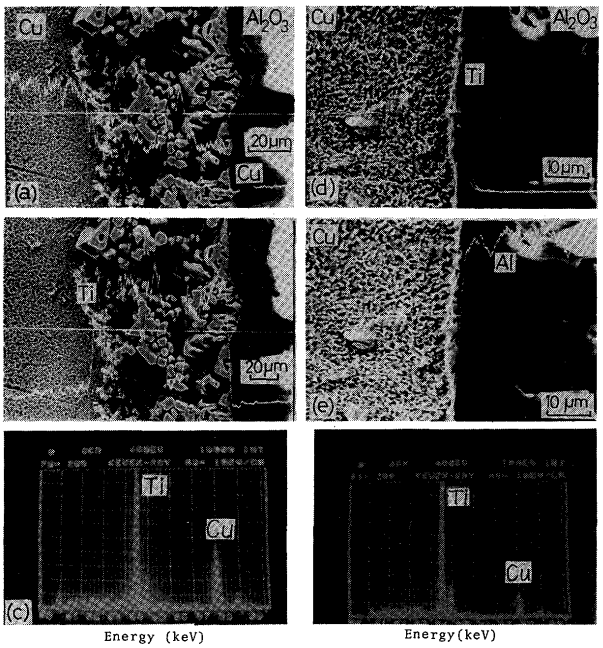

Fig. 9 Line analysis of joint interface and spot analyses of remained filler in Cu/Al_2O_3 joint made at 1273 K (a, b, c) and 1323 K (d, e, f) for 1.8 ks joining time using $Cu_{50}Ti_{50}$ filler metal.

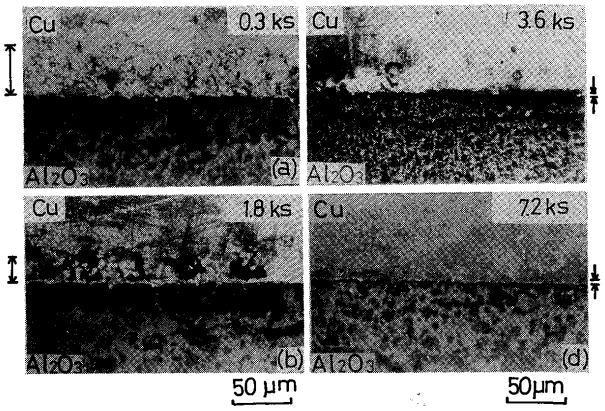

Fig. 10 Change of microstructure of Cu/Al_2O_3 joint made at 1298 K with joining time using $Cu_{50}Ti_{50}$ filler metal.

proceeded by the isothermal solidification process.

The change in structure of the joints with joining time (that is 0.3, 1.8, 3.6 and 7.2 ks) in **Fig. 10** exhibits the same change in structure with joining temperature.

3.5 Joining mechanism

The results of structure observation represent that the joining is proceeded by the isotermal solidification process and the Cu-Ti filler dissolves into the copper material and Cu-Ti filler reacts with Al_2O_3 during joining. X-ray diffraction analysis of the surface revealed by the dissolution of copper and filler metals indicated only the alumina, and did not identify the intermediary compound. The revealed surface of alumina was, therefore, analysed by X-ray photo-electron spectrometry.

The Ti2p and 01s electron spectra are given in **Figs. 11** and **12**, respectively. The spectra of $Ti2p_{3/2}$ and $Ti2P_{1/2}$ correspond to that of TiO_2.[9] The binding energy of 01s observed (531.20 eV) is a little smaller than that of Al_2O_3 (531.55 eV). The sub-peak of 01s (529.9 eV) corresponds to that of TiO_2.

This fact indicates that titanium dissolves into alumina and alumina solid solution containing titanium and formed.

The thermodynamic calculation suggests that the presence of titanium oxide containing lower oxygen content than that of TiO_2. The free energies (ΔG°) of the following reactions are considered at 1298 K.[10]

$$2Ti\,(l) + O_2\,(g) = 2TiO\,(s)$$
$$\Delta G^\circ = -1031 + 0.166T$$
$$4/3Ti\,(l) + O_2\,(g) = 2/3Ti_2O_3\,(s)$$
$$\Delta G^\circ = -1006 + 0.172T$$
$$6/5Ti\,(l) + O_2\,(g) = 2/5Ti_3O_5\,(s)$$
$$\Delta G^\circ = -982 + 0.171T$$

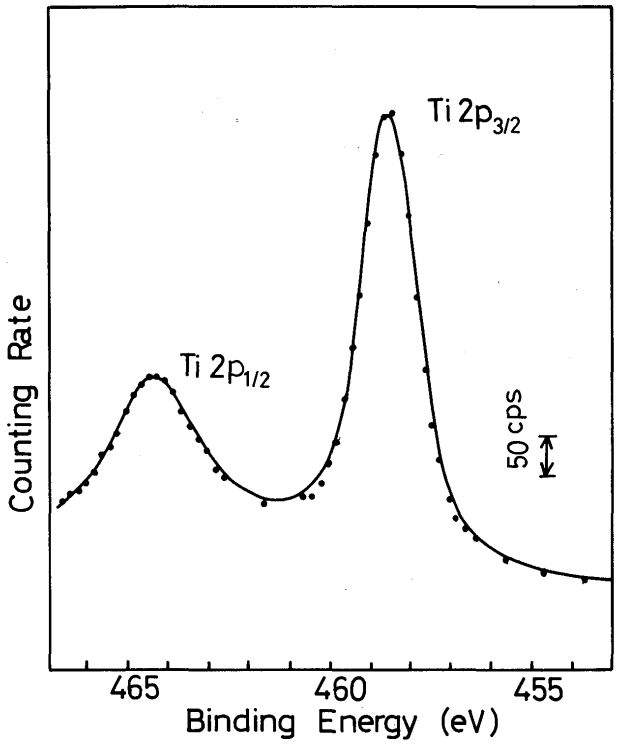

Fig. 11 Ti2p spectrum or the revealed surface on Al_2O_3, after dissolution of copper and filler metal from Cu/Al_2O_3 joint made at 1323 K for 1.8 ks using $Cu_{50}Ti_{50}$ filler metal.

$$Ti\,(1) + O_2\,(g) = TiO_2\,(s)$$
$$\Delta G^\circ = -952 + 0.182T$$

where the symbols of s, 1 and g denote the state of solid, liquid and gas, respectively.
At the joining temperature of T = 1298 K,

$$2Ti\,(l) + O_2\,(g) = 2TiO\,(s)$$
$$\Delta G^\circ = -813.8\ kJ/mol$$
$$4/3Ti\,(l) + O_2\,(g) = 2/3Ti_2O_3\,(s)$$
$$\Delta G^\circ = -782.4\ kJ/mol$$
$$6/5Ti\,(l) + O_2\,(g) = 2/5Ti_3O_5\,(s)$$
$$\Delta G^\circ = -759.8\ kJ/mol$$
$$Ti\,(l) + O_2\,(g) = TiO_2\,(s)$$
$$\Delta G^\circ = -715.0\ kJ/mol$$

The comparison of ΔG° eqs. indicates that the instabilities of titanium oxides increase in the sequence of TiO, Ti_2O_3, Ti_3O_5 and TiO_2. The intermediate oxide may be the titanium oxide TiO_x containing the smaller oxygen rather than titanium oxide of TiO_2. These results give the interface in the alumina/copper joint using Cu-Ti filler metal a structure as shown in Fig. 12. The structure of the joint is composed of (Al, Ti)$_2O_3$ solid solution containing a small amount of titanium and TiO_x oxide at the

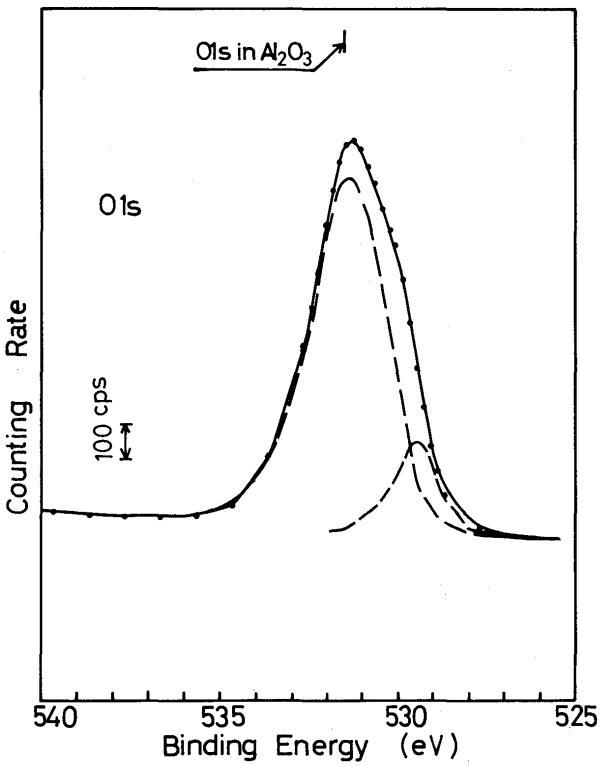

Fig. 12 O1s spectrum of the revealed surface of Al_2O_3.

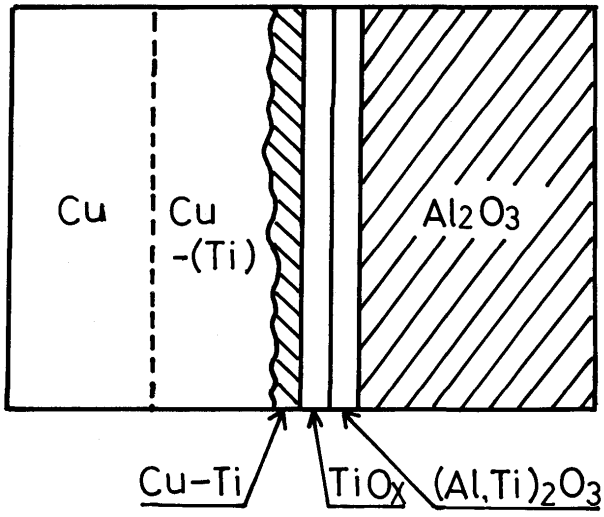

Fig. 13 Schematic diagram of the structure of the interface between alumina and copper made with $Cu_{50}Ti_{50}$ filler metal.

interface of alumina, Cu-Ti filler, copper solid solution containing titanium and copper metal in the metal side.

4. Conclusion

The amorphous Cu-Ti fillers (34 – 57 at%Ti) produced by rapid quenching of liquid alloys on the copper roller are highly flexible and add simplicity to the joining process. The present paper tried to the brazing of Cu to Al_2O_3 by inserting the fillers in vacuum. The results are summarized as follows.

(1) The fracture shear strength of the joint joined at 1323 K for 1.8 ks using $Cu_{50}Ti_{50}$ filler is 138 MPa. The increase in strength of joint with titanium content in the filler is small.
(2) The fracture shear strength of Cu/Al_2O_3 joint joined at 1298 K for 1.8 ks at testing temperatures up to 773 K is the same vale of 112.8 MPa as that at room temperature. At higher testing temperature the strength decreases with increasing testing-temperature to 9.8 MPa at 973 K.
(3) In the thermal shock testing that provides the thermal cycle of the rapid heating and rapid cooling to the joints, the degradiation of alumina is attributable to the degradiation of strength of the joint.
(4) The isothermal solidification process between copper and Cu-Ti filler takes place during joining. Copper dissolves into the filler and the solid solution containing titanium re-precipitates from the liquid filler, and then the filler dissolves into the copper. At the interface between alumina and the filler the reaction of Ti in Cu-Ti filler with Al_2O_3 takes place and the alumina solid solution containing titanium and titanium oxide are formed.

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References

1) R. V. Allen and W. E. Borbidge: J. Mater. Sci., 18 (1983), 2835.
2) W. M. Armstrong, A. C. D. Chaklader and J. F. Clark: J. Am. Ceram. Soc., 45 (1962), 115.
3) M. E. Twentyman and P. Popper: J. Mater. Sci., 10 (1975), 777.
4) J. F. Burgess, C. A. Neugebauer and G. Flanagan: J. Electrochem. Soc., 122 (1975), 688.
5) K. Brunner, M. Fisher and R. S. Perkins: Proc. Inter. Conf. Joining of Ceramics, Glass and Metal, DVS, 1980, 37.
6) W. H. Sutton: Material Science Research, 3 (1966), 577.
7) R. W. Davidge: Mechanical Behavior of Ceramics, Cambridge University Press, 1979.
8) Handbook of Metals, Maruzen, 1960, p 870.
9) C. D. Wagner: Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Co.
10) E. S. Krykov: De-oxidization, translated by Y. Gunji, Niso-Tsushin, 1975.