TECHNICAL NOTE

Intermediary Layer of Titanium Oxide in Al_2O_3/Cu Joint Using Amorphous Cu-Ti Filler Metals†

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In the joining of metals and ceramics, the reactions occurring at the interface greatly affect the quality of the joint. Knowledge of the reactions involved is necessary to control the process conditions.

In joining alumina to steel using copper filler metal in a slightly oxidizing atmosphere[1], an intermediary layer compound $FeAl_2O_4$ is formed at the bonding interface between alumina and steel. In the joining of ceramics to metals using Mo metallizing, an oxide is added to the metal powder; and in the liquid state this oxide wets both the metal and the ceramic[2),3)]. In solid-state bonding of metals to ceramics, a direct interaction of the materials takes place[4),5)]. The present paper describes the presence of intermediate phases at the bonding interface between alumina and copper using amorphous Cu-Ti filler metal.

The materials used were high purity commercial alumina (99.5%) and tough pitch copper (0.03%O). The

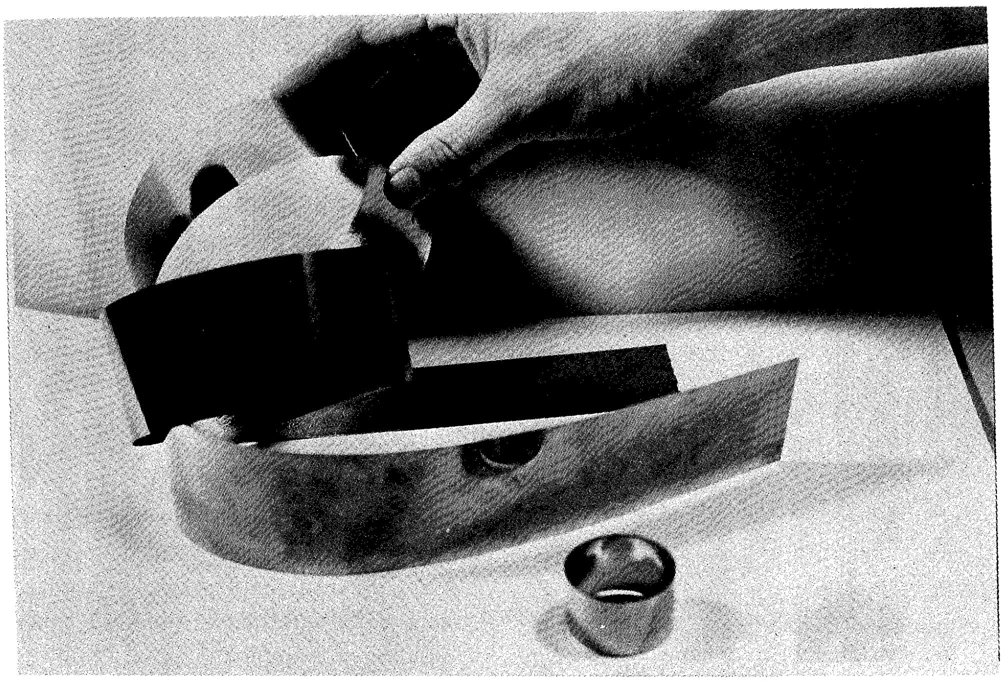

Fig. 1 Appearance of amorphous $Cu_{50}Ti_{50}$ filler metal. This foil possesses an excellent flexibility as shown in the figure.

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amorphous Cu-Ti filler metals were ejected on a rotating wheel though a quartz orifice. The filler metals were 5 cm in width and 50 μm in thickness. The amorphous structure of filler metal was confirmed by X-ray diffractometry. The composition range of Cu-Ti filler metal was 30 to 65 atomic percent titanium. **Figure 1** shows the appearance of filler metals. The joining was conducted in 5×10^{-5} torr at 1025°C for 30 min. The liquid filler metal wetted both alumina and copper during joining and hence a strong bond was formed after cooling down. Various types of joints were produced using amorphous $Cu_{50}Ti_{50}$ filler metal. A butt joint of alumina rod with copper rod and a butt joint of alumina cylinder with copper cylinder are shown in **Fig. 2**.

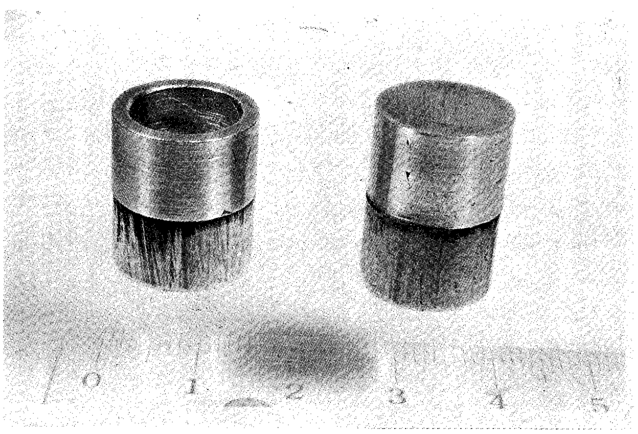

Fig. 2 Butt joint of Al_2O_3 rod with copper rod (right), and butt joint of Al_2O_3 cylinder with copper cylinder (left). The upper and lower parts in the specimens are copper and Al_2O_3, respectively.

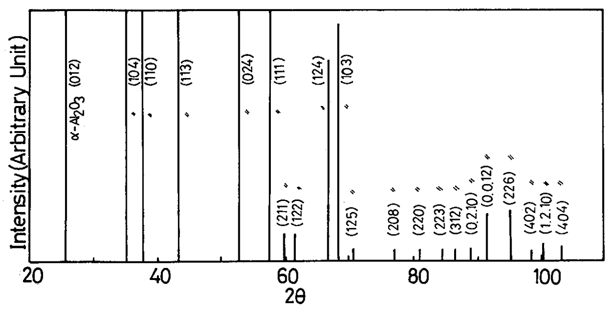

Fig. 3 X-ray diffraction pattern of the revealed surface on Al_2O_3 with $Cu \cdot K_\alpha$, after dissolution of copper and filler metal from a Al_2O_3/copper joint.

In order to characterize the intermediary layer of joint, copper and filler metals were dissolved from the alumina/copper joint in concentrated hot HC1, and X-ray diffraction analysis with $Cu \cdot K_\alpha$ radiation and X-ray photoelectron spectroscopic examination with $Mg \cdot K_\alpha$ excitation were conducted to identify the intermediary compound. X-ray diffraction analysis indicated only the alumina, and did not identify the intermediary compound as shown in **Fig. 3**. The revealed surface of alumina was, therefore, analysed by X-ray photo-electron spectrometry. The Cls spectrum from the contaminant carbon was used for the calibration of binding energy of electrons. The $Ti2p_{3/2}$, $Ti2p_{1/2}$, Al2p and Ols electron spectra are given in **Figs. 4** to **6**, respectively. The binding energies of the $Ti2p_{3/2}$, $Ti2p_{1/2}$ are taken as 458.50 and 464.30 eV, respectively. The spectra of Ti2p are attributed to TiO_2. The thermodynamic calculation suggests the presence of titanium oxide containing lower oxygen content than that of TiO_2. The free energies ($\Delta F°$) of the following reactions are considered at 1025°C[6].

$$2Ti(l) + O_2(g) = 2TiO(s) \quad \Delta F° = -194.5 \text{ Kcal/mol} \tag{1}$$

$$4/3Ti(l) + O_2(g) = 2/3Ti_2O_3(s) \quad \Delta F° = -187.0 \text{ Kcal/mol} \tag{2}$$

$$6/5Ti(l) + O_2(g) = 2/5Ti_3O_5(s) \quad \Delta F° = -181.6 \text{ Kcal/mol} \tag{3}$$

$$Ti(l) + O_2(g) = TiO_2(s) \quad \Delta F° = -170.9 \text{ Kcal/mol} \tag{4}$$

where the symbols of s, l and g denote the state of solid, liquid and gas, respectively. The comparison of $\Delta F°$ of Eqs. (1) – (4) indicates that the instabilities of titanium oxides increase in the sequence of TiO, Ti_2O_3, Ti_3O_5 and TiO_2.

The binding energy of the Al2p electron (74.65 eV) measured is very close to that of Al_2O_3 (74.70 eV). The spectra of Ols are separated into Ols in Al_2O_3 (531.25 eV) and Ols in TiO_2 (529.20 eV). The binding energy of Ols in Al_2O_3 observed is different from that of Al_2O_3 (531.55 eV). This fact indicates that titanium dissolves into alumina and forms $(Al, Ti)_2O_3$ solid solution at the interface of the joint. Further, the isothermal solidification process during joining took place between copper metal and filler metal. During joining, first copper dissolves into liquid filler metal. Copper containing titanium, then, precipitates from the liquid filler metal. These results give the structure at the interface of joint of Al_2O_3 with copper using Cu-Ti filler metal as shown in **Fig. 7**.

It can be concluded that the intermediary compounds of titanium oxide TiO_x and $(Al, Ti)_2O_3$ are formed during joining using amorphous Cu-Ti filler metals.

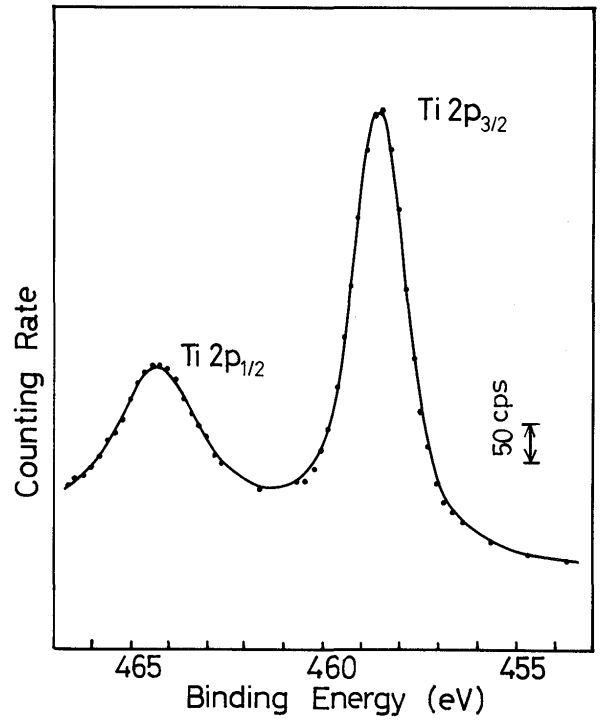

Fig. 4 Ti2p specrum of the revealed surface on Al_2O_3, after dissolution of copper and filler metal from a Al_2O_3/copper joint.

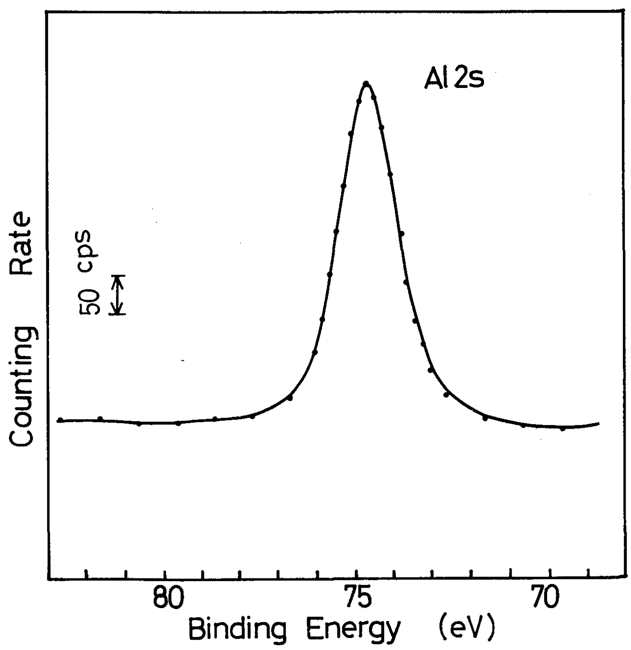

Fig. 5 Al2p spectrum of the revealed surface on Al_2O_3, after dissolution of copper and filler metal from a Al_2O_3/copper joint.

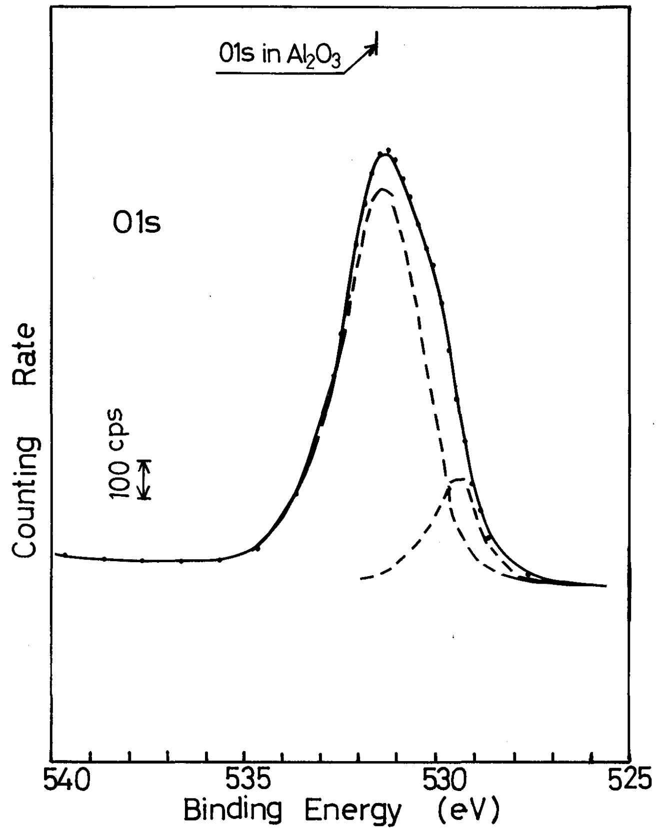

Fig. 6 Ols spectrum of the revealed surface on Al_2O_3, after dissolution of copper and filler metal from a Al_2O_3/copper joint.

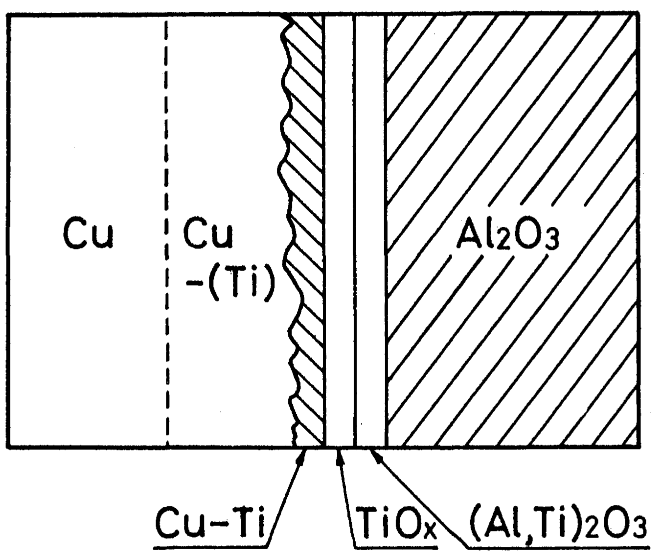

Fig. 7 Structure at the interface of Al_2O_3/copper joint using Cu-Ti filler metal.

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