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Controlling of Ceramic–Metal Interfacial Structure Using Molten Metals†

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Abstract

This article reviews the dominating factors of wettability of ceramics by molten metals and interface strength of ceramic/metal joint. The role of titanium in copper–titanium alloys during brazing is discussed. The formation of TiN nitride or TiC, Ti_3SiC_2 carbide at the interface and the wetting of Cu–Si alloy against compounds formed during brazing are attributable to the better wettability of Cu–Ti alloy against Si_3N_4 or SiC. The Al-base alloys are also used for joining ceramics to metal. The Al rich alloys with small amount of alloying element shows the superior strength of Si_3N_4/Si_3N_4 joints. The superior wettabilities and mechanical properties of the alloys are attributable to the improvement of strength for ceramic/metal joint. The physical effect of ultrasound is also applied to joining ceramics to metals.

KEY WORDS: (Wetting) (Work of Adhesion) (Contact Angle) (Interface Structure) (Interface Strength) (Ceramic/Metal Joining) (Ultrasound)

1. Introduction

The understanding of interface phenomena is necessary for ceramic-metal joint and ceramic-fiber containing metal based composite and for brazing or bonding of the ceramic- metal joint in practical engineering application.

The wetting of alumina oxide ceramics by molten metals as interfacial phenomena between ceramics and metals have been investigated.

McDonald and Eberhart have reported that the works of adhesion of molten metals are related with the formation free energies of the metallic oxides[1]. Since the work of adhesion is defined as the formation energy to make new surface by separating molten metals from ceramics, the value of metals is used as a measure of joining ability. Apart from the formation of oxide at the interface between molten metal and Al_2O_3, the metals with easier oxidizing abilities possess better wettabilities. For instance, the work of adhesison is large for Ti which is easily oxidized. In other words, the active elements such as Ti are used as the elements in brazing fillers for oxide ceramics. The joining strength of Ni alloys with Ti and Y against Al_2O_3 is high[2]. Si_3N_4 nitride and SiC carbide composed of ionic and covalent bonding have attracted recent interests because of their superior mechanical properties at elevated temperatures.

This paper describes the dominating factors in wetting of Si_3N_4 nitride and SiC carbide by molten metals, also the intermediate phases at ceramic/metal interface and the interface strength of ceramic/metal joint.

2. The role of titanium as active element

Molten copper doesn't wet oxide and non-oxide ceramics though it, which is often used as molten filler metal, well wets metallic materials such as steels. If the wetting of ceramics is improved by alloying elements to copper, the molten copper will be used as the filler metal for joining ceramics to metals.

Figure 1 shows the titanium content dependence of equilibrium contact angle on Si_3N_4 and SiC at 1373 K in vacuum. The molten copper with contact angles below 90 degree is called to be in the wetting state, and begins to spread on the ceramics at the titanium content of 5 at % or more.

The molten metals with 20 at % titanium or more which possess the contact angle below 10 degree also well spread on the ceramics. The titanium content dependence of interface strength Si_3N_4/Si_3N_4 and SiC/SiC joints brazed with amorphous Cu–Ti fillers is shown in **Fig. 2**[3], where the strength is evaluated by fracture shearing. The interface strength of joints decreases with increasing titanium content in Cu–Ti fillers. The interface structures of Si_3N_4 and SiC joints brazed with Cu–50 at % Ti at a condition of

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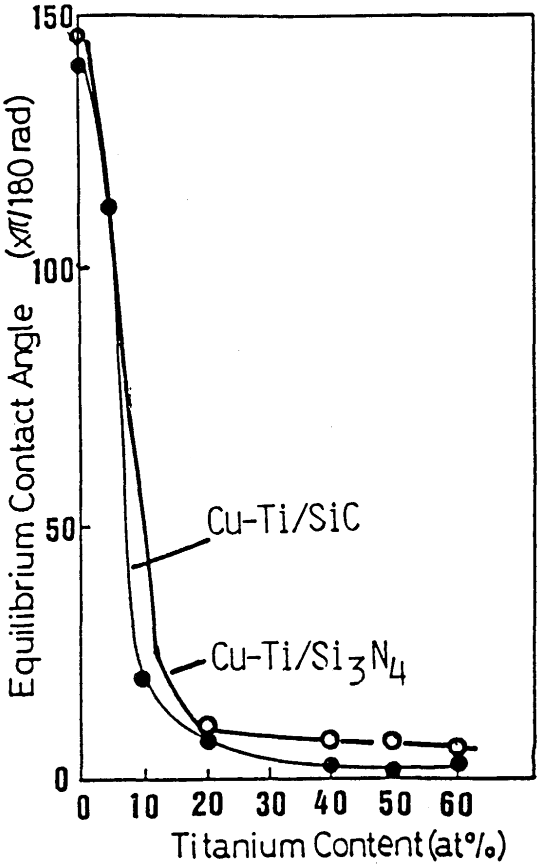

Fig. 1 Equilibrium contact angle of Cu-Ti alloys on Si_3N_4 and SiC at 1373 K.

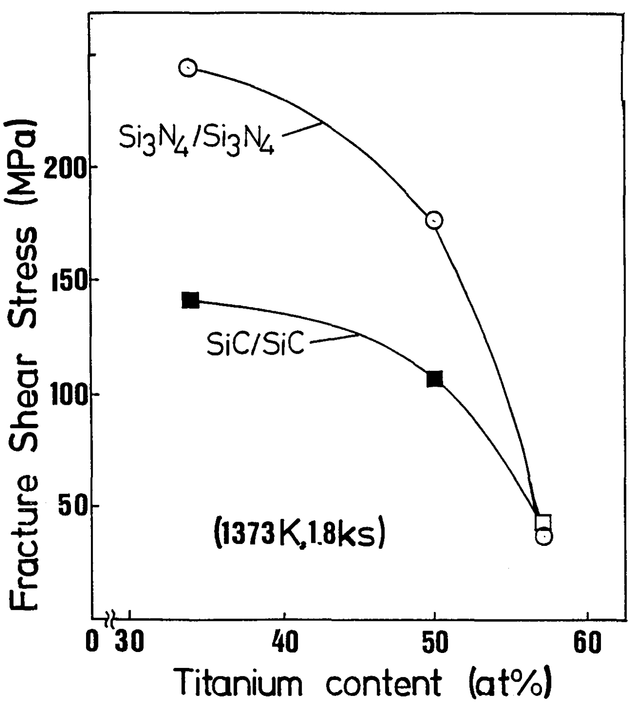

Fig. 2 Titanium content dependence of strength Si_3N_4/Si_3N_4 joint brazed with Cu-Ti alloys.

1373K and 1.8ks are shown in **Figs. 3**[4] and **4 (a), (b)**[5], respectively. The Ti rich intermediate phase at Si_3N_4 side is identified as TiN by X-ray diffraction method. Ti_5Si_3 silicide is formed in the filler which is composed of $(\gamma+\varepsilon)$ Cu-Si with 18 at% Si. The content of Si increases with increasing the brazing temperature. Ti in Cu-Ti alloy reacts with Si_3N_4 by the following equations (kJ/mol)[4],

$$Si_3N_4(s)+4Ti(\mathrm{l})=4TiN(s)+3Ti(s) \quad (1)$$
$$\triangle G=-639+0.652T$$

$$Si_3N_4(s)+9Ti(\mathrm{l})=4TiN(s)+Ti_5Si_3(s) \quad (2)$$
$$\triangle G=-130.9+0.152T$$

Ti reacts with Si_3N_4 and forms TiN nitride and Ti_5Si_3 silicide. The formed free Si also reacts with Cu. The formation of TiN at the ceamic/metal interface, and the superior wetting of molten Cu-Si alloy against Si_3N_4 and TiN are attributable to the improvement of wetting of molten copper against Si_3N_4 by the addition of titanium.

The interface structure and X-ray image analysis of element in SiC/Cu- 50 at % Ti interface indicare that TiC and Ti_3SiC_2 (Ti) carbide, Ti_5Si_3 and $TiSi_2$ silicide are formed at the interface[5]. The excess reaction of Cu-Ti alloy with SiC accounts for the lower strength of SiC joints, compared with Si_3N_4 joints.

Al_20_3 oxide, Si_3N_4 nitride and SiC carbide are wetted with Ti. The dominating factor in the wetting of Al_20_3 is the easiness of bonding of metal and oxygen. On the other hand, the factors against the wetting of Si_3N_4 and SiC are the easiness of bonding between metal and nitrogen, metal and carbon, and metal and silicon. The metal which possesses the high reactivity shows the superior wetting. In order to suppress the excess reation of titanium with Si_3N_4,

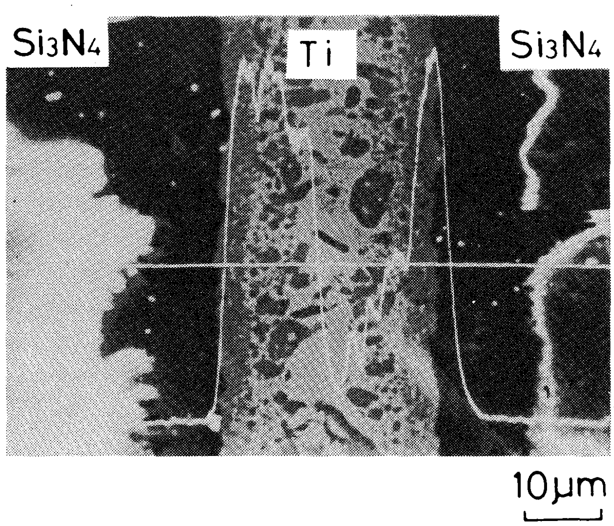

Fig. 3 Interface microsfructure of Si_3N_4/Si_3N_4 joint brazed with Cu-50 at% Ti alloy at 1373 K for 1.8 ks.

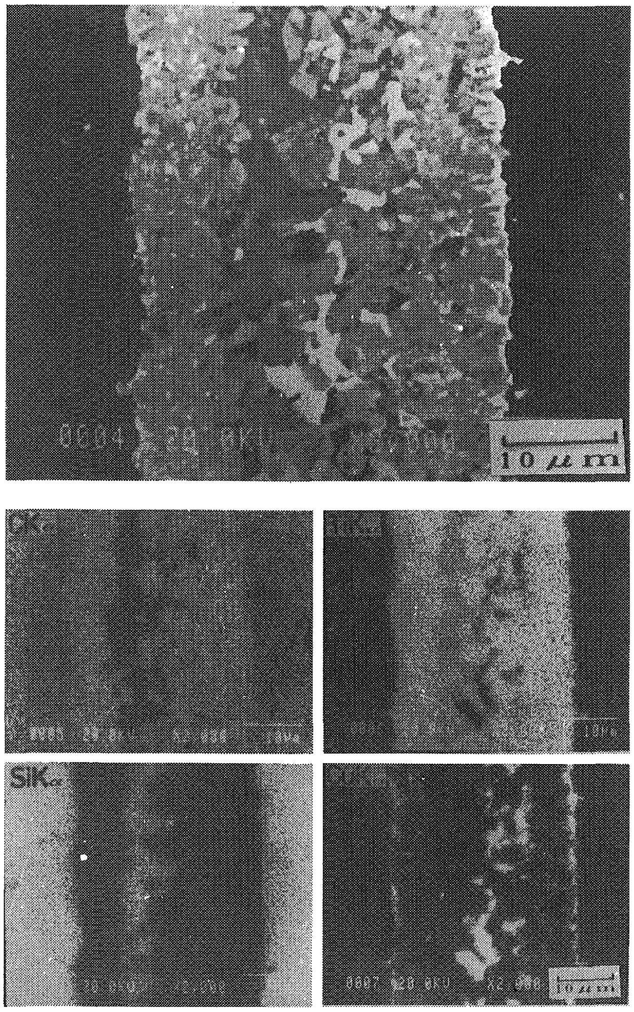

Fig. 4 Interface microsfructure of SiC/SiC joint brazed with Cu- 50 at% Ti alloy at 1373 K for 1.8 ks.

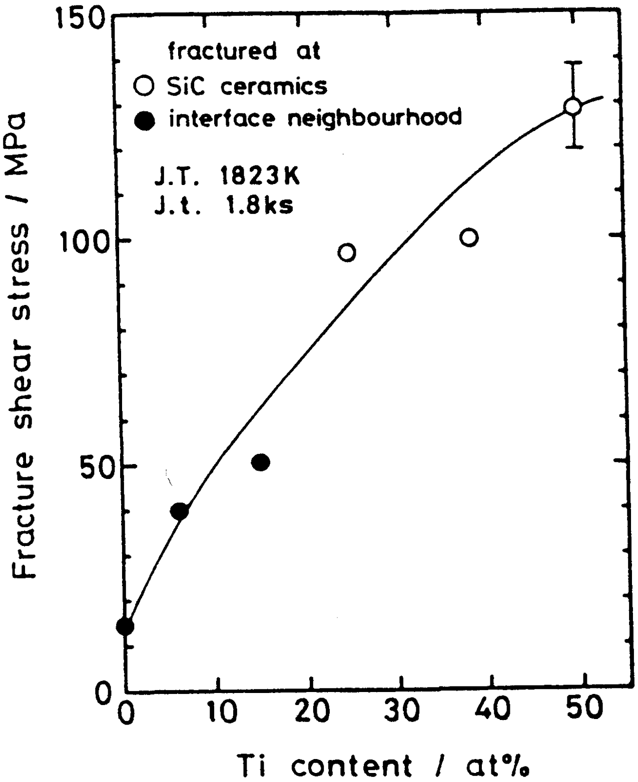

Fig. 5 Titanium content dependence of SiC/SiC joint brazed with Cu-50 at% Ti alloy at 1373 K for 1.8 ks.

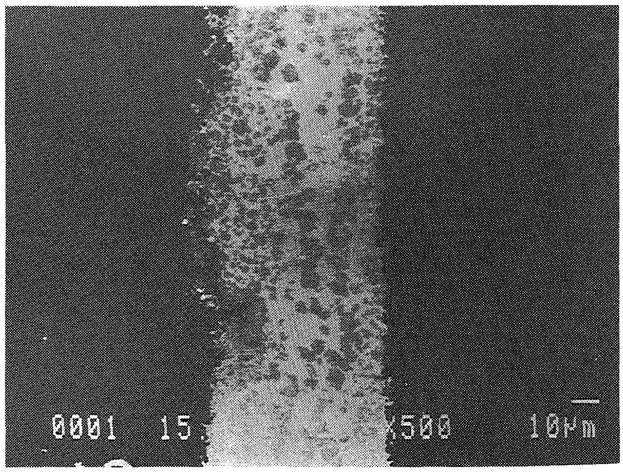

Fig. 6 Interface microsfructure of SiC/SiC joint brazed with Cu- 50 at% Ti alloy at 1373 K for 1.8 ks.

the titanium content in Ag-Cu eutectic filler with 60 at % Ag is decreased down to 4.5 at %[6], although the wetting of molten copper is improved at the titanium content of 20 at % or more. The joining mechanism of Ag-Cu-Ti alloy with Si_3N_4 is similar to that of Cu-Ti alloy, and TiN and Ti_5Si_3 are formed at the ceramic/metal interface[7].

The filler metals containing Sn and In are also reported in order to decrease the brazing temperature and titanium content. The precoating of Ti on SiC causes the Ti content down to 3.8 at % in the brazing of SiC[8]. In order to improve the heat-resistance of ceramic joint brazed, nickel instead of copper is used as a matrix element[9,10]. **Fig. 5** shows the titanium content dependence of interface strength of SiC/SiC joint brazed with Ni-Ti alloys at 1523 K for 1.8 ks. SiC joint with Ni-Ti alloy shows the different dependence of Ti content, compared with SiC joint with Cu-Ti alloy. The microstructure of SiC joint with Ni-50 at % Ti in **Fig. 6** indicates that the higher brazing temperature in SiC joint with Ni-Ti alloy causes the uniform distribution of TiC carbide in Ni matrix, compared with that in SiC joint with Cu-Ti alloy. The species and the distribution of compounds formed are important in the interface strength of ceramic/metal joint. The SiC joint with Ni-Ti filler at elevated temperature represents the superior strength as shown in **Fig. 7**.

3. The role of Al

The molten Al is used for brazing ceramics. According to McDonald and Eberhart, molten aluminum possesses the high work of adhesion[11]. The interface strength of Al/

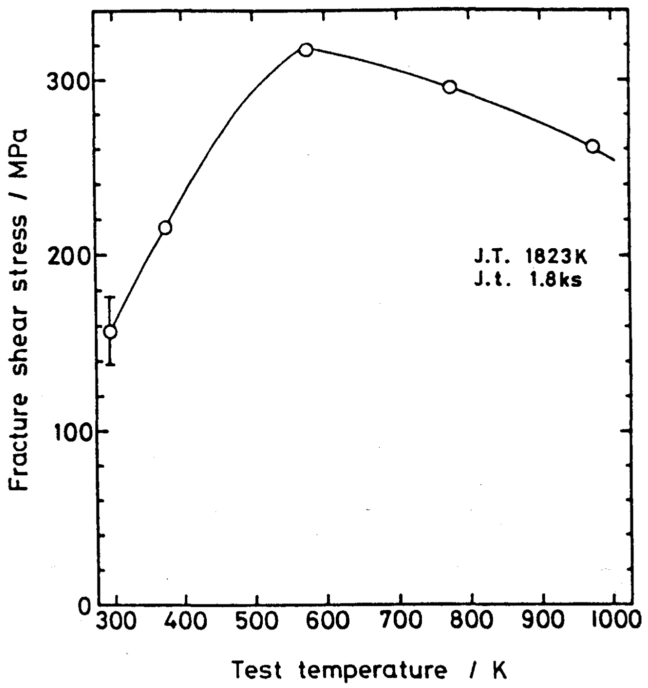

Fig. 7 Strength of SiC/SiC joint with Ni-50 mass % Ti at elevated temperatures.

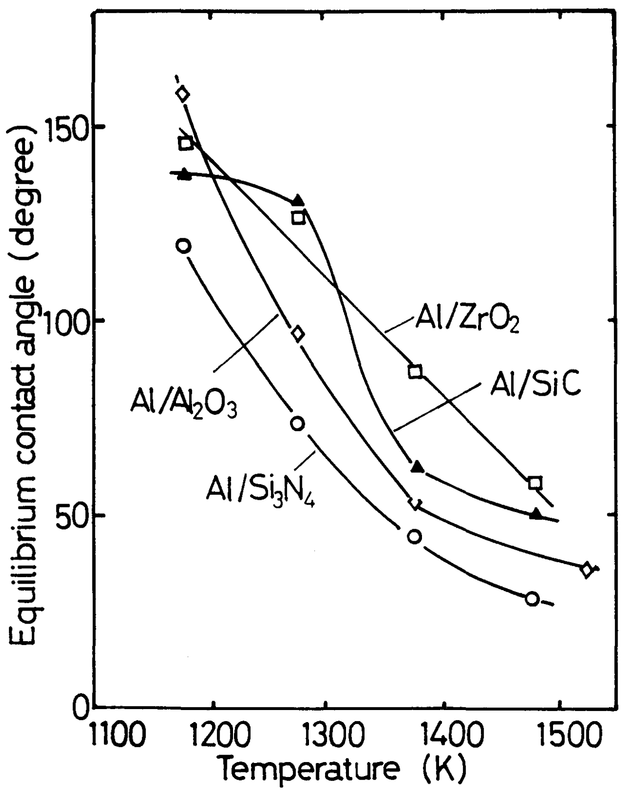

Fig. 8 Temperature dependence of Al on Al_2O_3, ZrO_2, Si_3N_4 and SiC.

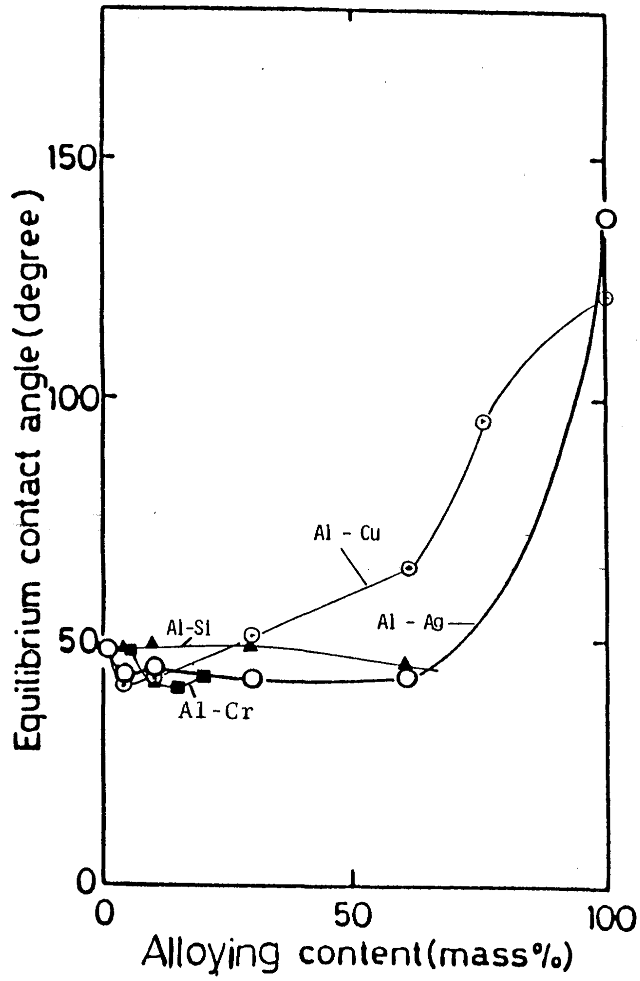

Fig. 9 Alloying content dependence of equilibrium Al base alloys on Si_3N_4.

Al_2O_3 was measured[12,13]. As shown in **Fig. 8**, the molten aluminum improves the wettability against CaO-stabilized ZrO_2, SiC and Si_3N_4 with increasing temperature[14,15]. The molten aluminum based alloys which also wet Si_3N_4 (**Fig. 9**)[17,18] are used as filler metals for joining ceramics. Al rich based alloys with small amounts of alloying elements increases the strength of Si_3N_4/Si_3N_4 joints as shown in **Fig. 10**.

In **Fig. 11** the work of adhesion of Al-Cu alloys against Si_3N_4, Al_2O_3 and ZrO_2 departs to plus values from ideal mixing one[13,16,18]. This means that the interface strength of Si_3N_4/Al will be increased by adding Cu to Al, because the work of adhesion gives a measure of interface strength. The mechanical properties of Al-Cu alloys are improved by mixing copper as shown in the microsfructure and the copper dependence of hardness of Al-Cu alloys (**Fig. 12**)[16]. The two factors of the interface strength and mechanical properties of the alloys operate in improving mechanical proparties of ceramic/metal joint. The dispersive energy rather than the fracture energy of interface works in the ceramic/metal joint from view points of the

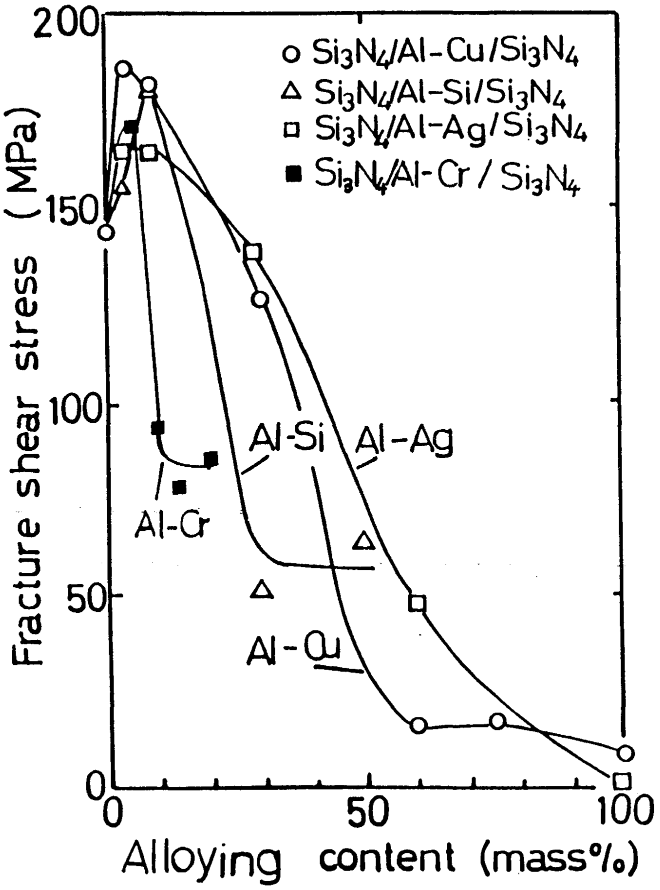

Fig. 10 Alloying contact dependence of strength of Si_3N_4/Si_3N_4 joint brazed with Al based Alloys at 1373 K for 3.6 ks.

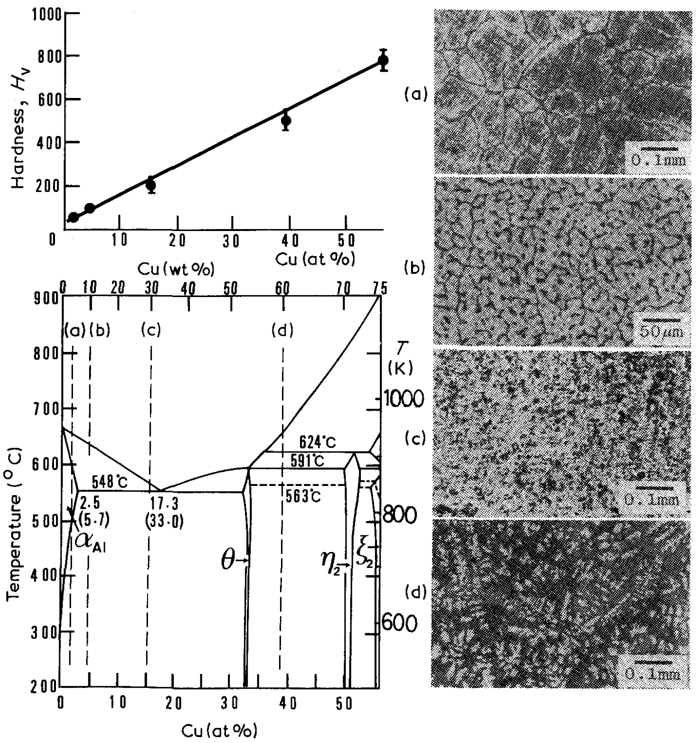

Fig. 12 Hardness and microsfructure of Al-Cu alloys.

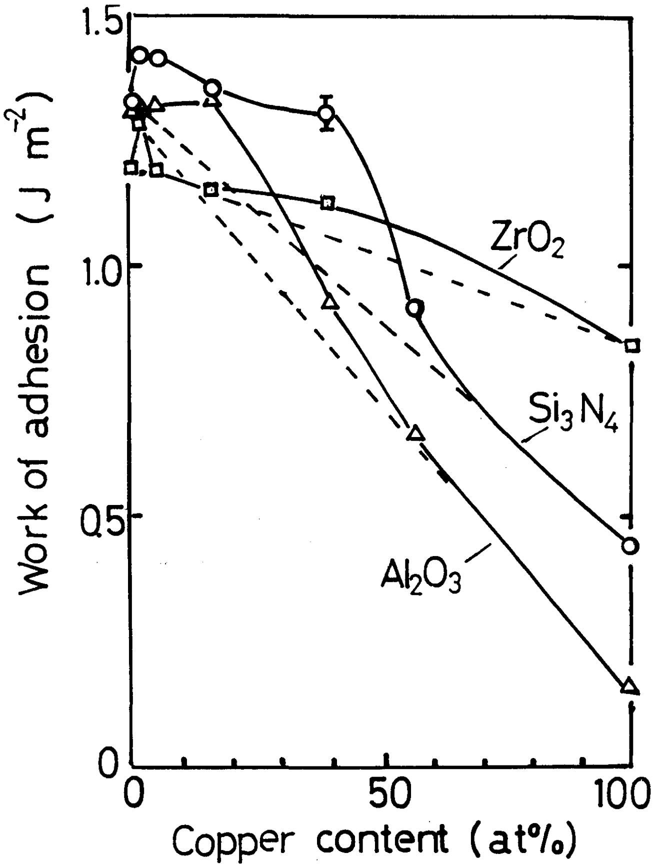

Fig. 11 Copper content dependence of work of adhesion for Al- Cu alloys on Al_2O_3, ZrO_2 and 1373 K.

fracture mechanics[19].

4. Effect of ultrasound application

The ultrasound has been applied to soldering industry fields[20,21]. The effect of ultrasound application is discassed from the new view points[22]. While the chemical effect of Ti and Al promotes the wetting of ceramics by molten metals, the energy of ultrasound also accelerates to wet ceramics. It was considered that the remove of bubbles from the surface by applying the ultrasound against ceramics. On the other hand, the another active role of ultrasound attracts new attension. The gas confined in defects near surface of ceramics were expanded and removed as bubbles by the irradiation of ultrasound. The babbles, further, continue to be expanded and compressed by the successive irradiation of ultrasound. The effect of ultrasound called as the cavitation also activates the wetting of molten metals against ceramics.

The practical process of ultrasonic brazing is shown in **Fig. 13**[23,24]. First, the alumina is metallized in molten Zn-Al alloys, and then it is joined to copper pre-metallized with the same Sn-Al alloys without loading. **Fig. 14** represents the time dependence of ultrasound application on the

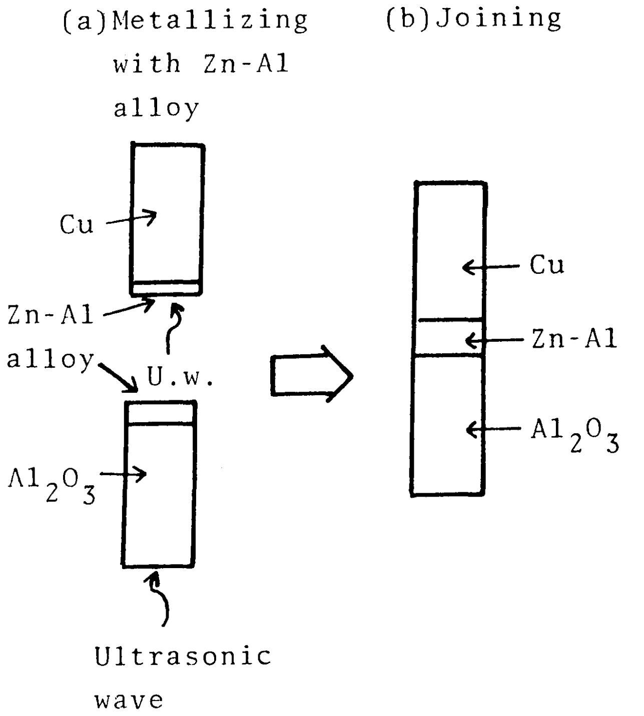

Fig. 13 Ultrasonic brazing process.

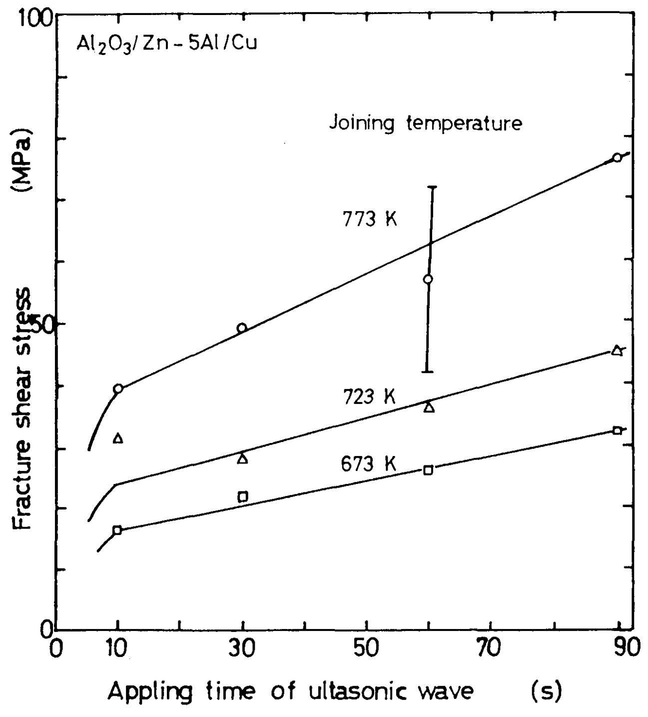

Fig. 14 Applying time dependence of strength of Al_2O_3/Cu joint with Zn-5 Al mass % Al alloy.

strength of Al_2O_3/Cu joint with Zn-5 massy Al alloy. The joining ability of the alloys against ceramics is improved by the irradiation of ultrasound while the alloys doesn't well be joined without the application of ultrasound. The effect of ultrasound operates more effectively at elevated brazing temperatures. The increase in Al content in the Zn base alloys raises the viscosity of alloys. The ultrasound doesn't be effectively appled to ceramics in the viscous alloys. The molten alloys used in the ultrasonic brazing process are Zn-Al-Cu, Sn-Pb other than Zn-Al alloys. SiC ceramics was also brazed by applying the ultrasound[25-27].

5. Summary

Joining of ceramics to metals necessiates the knowledge of wetting of molten metals against ceramics, and also the elucidation of dominating factors in interface strength of ceramic/metal joints. The molten metals wets the ceramics with or without the formation of intermediate phases. In wetting of molten metals against ceramics the intermediate phases are often formed at the ceramic/metal interfaces. The molten phases formed also wet the intermediate phases during the wetting process.

The strength or ceramic/metal joints formed is dominated by the interface strength which is evaluated from the work of adhesion of metals, and the size and diffibution state of intermediate phases formed during joining.

The those wettability of molten metals against ceramics, necessitates the the improvement of ability of metals for joining ceramic/metals. The improving methods are described as; (1) Alloying metal such as Ti to the filler, which metal possesses the easiness of bonding with nitrogen, carbon or silicon. Further, applying Al base filler metals with the superior wettability against ceramics. In order words the chemical effects of Ti and Al are used in these process. (2) The physical effects of ultrasound are used in the ultrasonic brazing process. The ultrasound accelerates to wet molten metals against ceramics.

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