Materials Science Research International, Vol.7, No.3 pp.194-199 (2001)

General paper

Evaluation of Cu-AlN Joint Brazed with In-Based Active Brazing Filler Metals —Brazing Temperature and Heat Resistance—

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Abstract: The In-Ti active fillers were examined for joining metallic copper (Cu) to aluminum nitride (AlN) ceramics. Brazing was carried out with In-Ti active brazing filler metals with various compositions, and the microscopic structure and mechanical strength of the Cu-filler-AlN-filler-Cu joint at various temperatures were investigated. When brazed with an In-rich filler of In-1wt%Ti, most of In atoms in the filler were diffused into the Cu plate leaving a Ti-rich reaction layer of 2-4μm thick at the Cu-AlN joint interface. The 4-point bending strength at 500℃ increases linearly with the brazing temperature, whereas the strength at room temperature saturates at 40 MPa. The specimen brazed at 820℃ has the strength of 58 MPa and 33 MPa at 500℃ and 600℃, respectively. On the other hand, when using Ti-rich fillers, e.g., In-7.7wt%Ti, In-15wt%Ti and In-23.8wt%Ti (the same as Ti_3In_4 composition), granular Ti-rich phases were formed at the interface, and the microcracks were observed in the AlN.

Key words: *AlN, Cu, Indium-based active brazing filler metal, Four-point bending strength, Titanium-rich layer*

1. INTRODUCTION

Aluminum nitride (AlN) possesses high thermal conductivity, thermal expansion matching to silicon, high electrical resistivity and heat-resistance up to 1000℃. These excellent characteristics are desirable for electric packaging applications of highly integrated electronic devices. Also, AlN ceramics are expected to be used as an electric insulator of thermoelectric (TE) power generators utilizing the Seebeck effect of thermoelectric semiconductors. Generally, a TE module is composed of thermocouples, each of which is terminated by metal electrodes, and insulators for electrically isolating the power generation circuit from the heat source and sink (see Fig.1). The insulators used for the TE module need a high electrical resistivity and a high thermal conductivity. As long as TE modules are used for retrieving the electricity from a low-temperature heat source (<200℃), one may be able to use a polymer film as the insulators. However, if one attempts to use the TE modules in high-temperature waste heat systems (400-500℃), such as an exhaust system of motor vehicles, one must employ a ceramic plate. A thin plate of AlN ceramics with a high degree of electrical resistivity and thermal conductivity is, thus, a promising candidate as an insulation component of the TE module used for high-temperature waste heat systems.

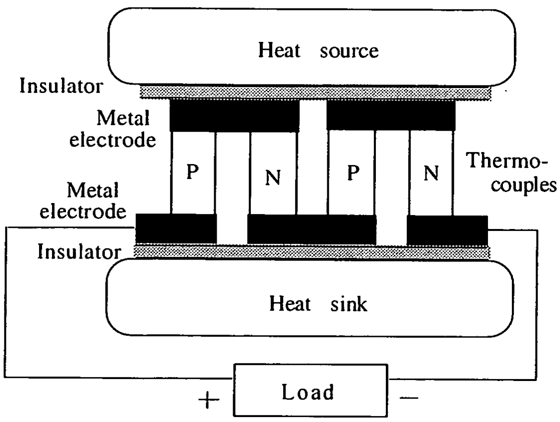

Fig.1. A schematic diagram of a thermoelectric module.

For constructing the TE module with an AlN ceramic insulator, it is required to develop a technique of bonding the metal electrodes to the ceramic plate. A high bonding strength at least being comparable to the strength of AlN ceramics is needed at high temperatures, and lowering the bonding temperature is important for preventing the degradation of TE semiconductors during bonding processes.

Recently, an active metal brazing using In-Ti binary filler alloys has been reported to bond a metal to nitride ceramics at 700℃ [1], which is about 100℃ lower than that of the most generally used Ag-Cu-Ti filler. However, no systematic data on the bonding strength at high temperature. Hence, in this work, we have focused our attention onto the technique of directly brazing Cu to AlN with In-Ti active fillers. We have also attempted to lower the bonding temperature by changing the composition of In-Ti alloys and to increase the bonding strength at high temperatures as well as at room temperature. This paper describes the microscopic structure of the joint part of Cu-AlN the results of four-point bending tests, and discusses the origin of high bonding strength of the Cu-AlN joint with In-Ti active fillers.

2. EXPERIMENTAL

Active fillers of In-Ti with various compositions, In-1wt%Ti, In-7.7wt%Ti, In-15wt%Ti and In-23.8wt%Ti, were prepared by alloying In (99.9wt%) and Ti (99.9 wt%) powder with an arc furnace in argon atmosphere.

Received December 14, 2000
Accepted July 27, 2001

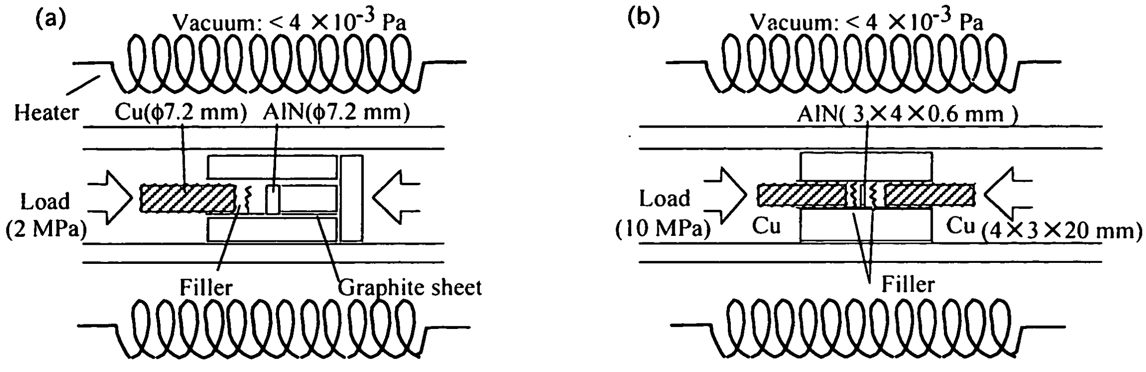

Fig.2. Configurations AlN and Cu and assembly diagrams for brazing. (a) Brazing for microscopic observation. An AlN disc and a Cu column were brazed under the load of 3 MPa in vacuum. (b) Joining for 4-point bend tests. An AlN plate was inserted between Cu square bars with filler. The brazing was performed under the load of 10 MPa in vacuum.

The alloy In-23.8wt%Ti corresponds to Ti_3In_4 in chemical formula [2]. The fillers were examined by X-ray diffractometry (XRD) using Cu-Kα radiation and the polished surfaces were observed with an optical microscope.

Two types of test specimens were prepared by brazing Cu to AlN (see Fig.2). One is for microscopic observation of the joint portion. The joint was completed using a Cu column (7 mm in diameter) and an AlN disc (7.2 mm in diameter) with 20 mg filler as shown in Fig.2(a). Prior to brazing the AlN discs were mechanically polished (roughness: <15 μm) and then cleaned in acetone using ultrasonic vibration. Brazing was performed at 820℃ for 30 min in vacuum (<4 mPa). A compressing load of 2 MPa was applied to the specimens while brazing. After brazing, for a certain interval the specimens were furnace-cooled. The microstruture was analyzed by scanning electron microscopy (SEM) and electron-probe microanalysis (EPMA) with a JEOL JXA-8621MX machine.

The other type (see Fig.2(b)) is for investigation of the lowest brazing temperature and 4-point bending tests. The shape of the AlN plate is 3×4 square with 0.64 mm thickness (SH-15 from TOKUYAMA Co.). The surface roughness is less than 0.6 μm (Ra value). The AlN plate was inserted between Cu square bars (3×4×20 mm) with about 20mg of filler in the jig internally covered by a graphite sheet. The compressing load during brazing was 10 MPa. The 4-point bending tests were performed by INSTRON 8562 at room temperature (RT), 500℃ and 600℃ in inert gas of argon. The displacement rate was set to be 0.5 mm/min in conformity with JIS-R1604.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis and the Lowest Brazing Temperatures

Figure 3 shows the XRD patterns of In-Ti fillers. The XRD peaks from crystalline Ti_3In_4 (filled circles), and metallic In (filled triangles), arise intensely, but the peaks of metallic Ti are absent in all fillers. Several unidentified peaks, open squares in the XRD pattern are tentatively ascribed to unstable phases of In or Ti_3In_4 formed by rapid cooling. Since the intensities were much smaller than those of In or Ti_3In_4, most Ti atoms in the fillers seem to be incorporated into Ti_3In_4.

Brazing of Cu to AlN was attempted at various temperatures. After brazing, the test specimen was loaded by shear stress until it was fractured. If the test specimen was fractured at the portion of AlN ceramics, we have judged it as "well bonded". If fractured at the Cu-AlN joint part, we have judged it as "weakly bonded". Thus, we have determined "the lowest bonding temperature" from the "well bonded" specimens. Figure 4 shows the lowest bonding temperature as a function of Ti/In ratio of the filler. It should be noted that the lowest bonding temperatures for In-1wt%Ti and In-7.7wt%Ti are lower than the melting point of Ti_3In_4, 796℃.

According to Ohashi et al. [3], the melting point of a fine particle, T_m, in the different matrix material is expressed as

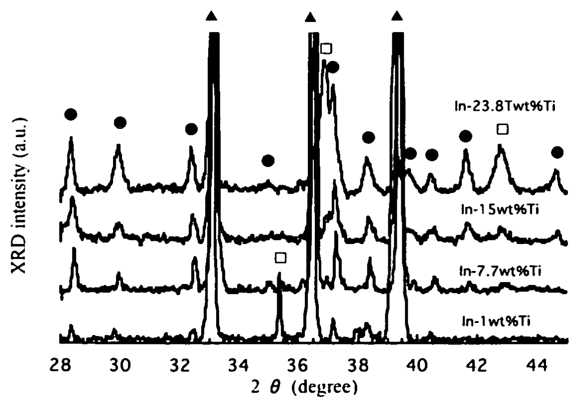

Fig.3. XRD patterns of In-1wt%Ti, In-7.7wt%Ti, In-15wt%Ti and In-23.8wt%Ti. The marks ● and ▲ indicate Ti_3In_4 peaks and metallic In, respectively. The mark, □ shows unidentified peak.

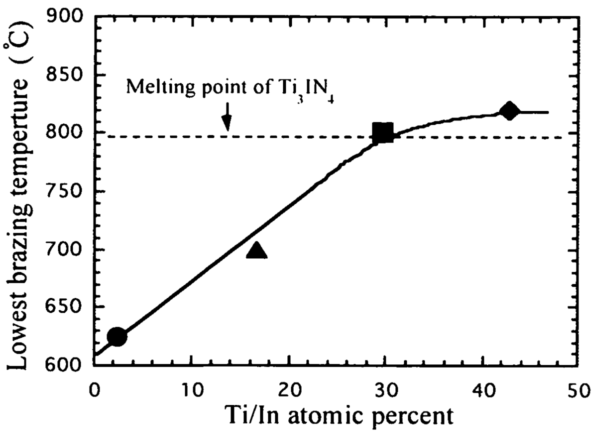

Fig.4. The lowest brazing temperature for the fillers of In-1wt%Ti(●), In-7.7wt%Ti(▲), In-15wt%Ti(■) and In-23.8wt%Ti(◆). The In/Ti ratio of In-23.8wt%Ti corresponds to that of Ti_3In_4, the melting point of which is 796℃.

$$T_m / T_0 = 1 - 2\,(\gamma_{sm} - \gamma_{lm}) / rL_0, \qquad (1)$$

where T_0 is the melting point of the same bulk material as the particle, γ_{sm} , γ_{lm} are the interface energies between the matrix material surface and the solid phase and between the matrix material surface and liquid phase of the particle, respectively. The variable r is the radius of the particle, and L_0 is latent heat at melting of the particle. It is assumed that the interface energy between solid Ti_3In_4 and AlN matrix, γ_{sm} is larger than that between liquid Ti_3In_4 and AlN, γ_{lm}. Thus, Eq.(1) suggests that the small particles of Ti_3In_4 might melt even below the melting point of bulk Ti_3In_4. Such a mechanism of melting point decrease may contribute to the decrease of the lowest bonding temperature of In-1wt%Ti and In-7.7wt%Ti fillers.

Figure 5 shows the optical micrographs of the polished surface of the fillers. The glossy and dark areas would be identified as Ti_3In_4 and metallic In, respectively, judging from comparison of the ratio of glossy and dark areas and the chemical compositions. The reason why metallic In was observed to be dark is that the soft surface was hard to be made flat by mechanical polishing. The grain size of Ti_3In_4 in In-1wt%Ti and In-7.7wt%Ti fillers are 10-20 μm and 50-150 μm, respectively. This result is agreement with above speculation.

3.2. Microscopic Observations

Figure 6 shows EPMA images of Ti near the joint part of test specimens brazed with different fillers at 820℃ for 30 min. At this brazing temperature, all test specimens were "well bonded" (see Fig.4). However, one can recognize an apparent difference in the test specimens brazed with In-1wt%Ti and with the others. In the specimens brazed with In-7.7wt%Ti, In-15wt%Ti and In-23.8wt%Ti, the granular or thick-layered Ti-rich phases

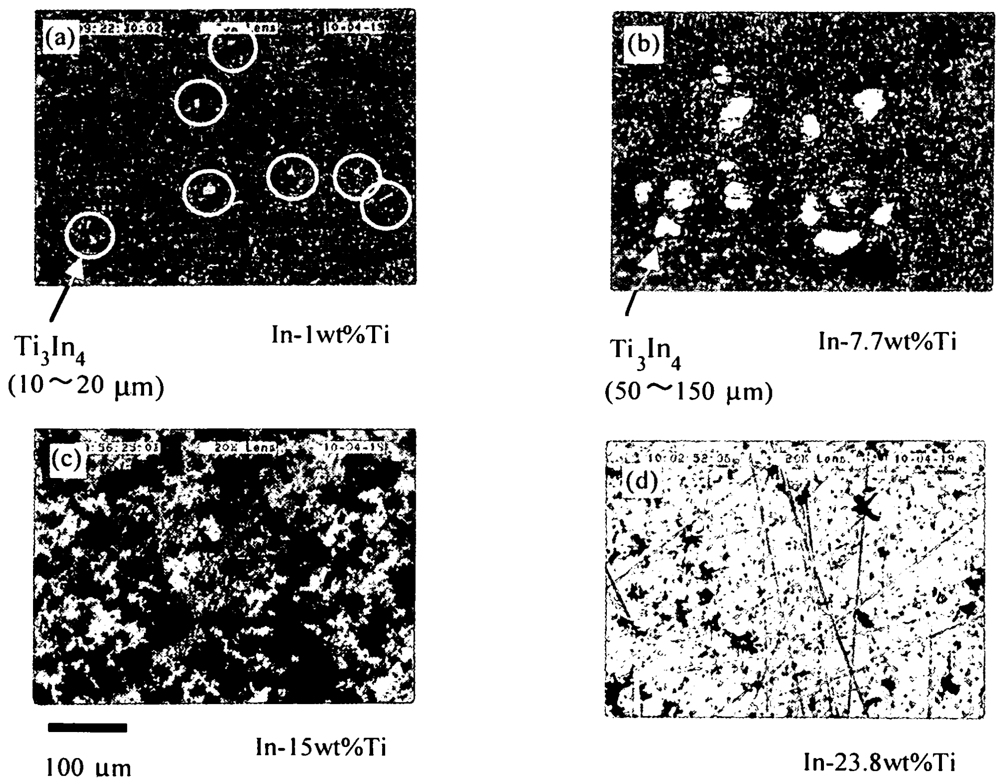

Fig.5. Optical micrographs of the polished surfaces of In-Ti fillers. (a) In-1wtTi, (b) In-7.7wt%Ti, (c) In-15wt%Ti and (d) In-23.8wt%Ti. The white circles in Photo (a) enclose the small glossy areas.

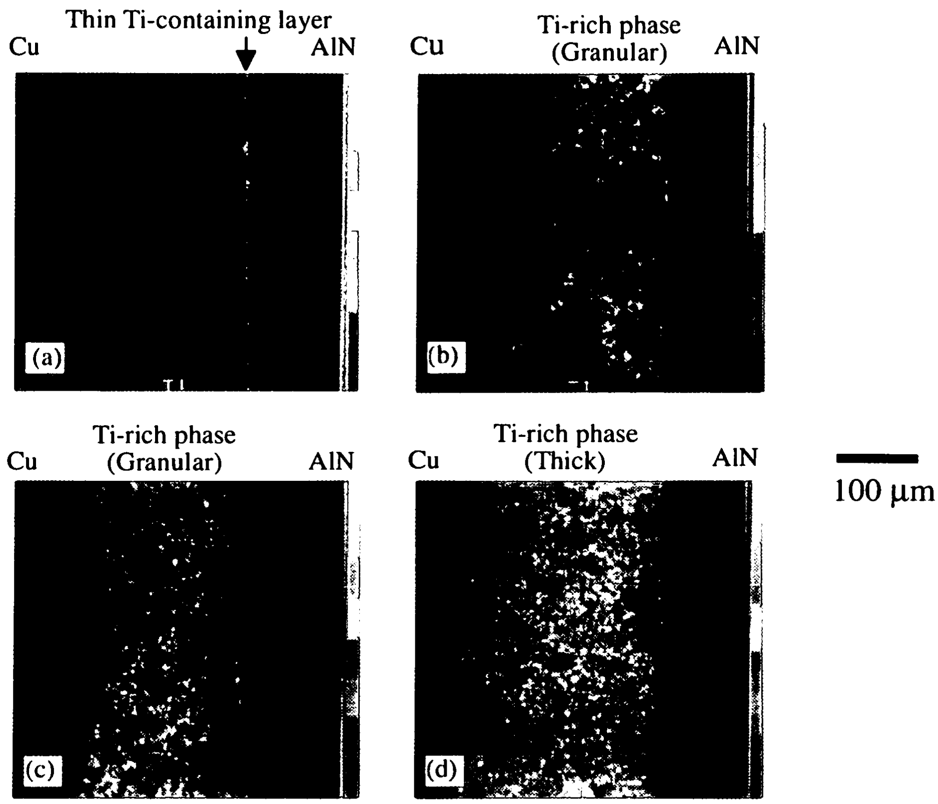

Fig.6. EPMA images of Ti-Kα. Images (a), (b), (c) and (d) show the joints of specimens brazed with In-1wt%Ti, In-7.7wt%Ti, In-15wt%Ti and In-23.8wt%Ti, respectively. The colors in the higher position of the right-side bar indicate the higher Ti-content.

exist in the Cu side of the interface (see Figs.6(b), (c) and (d)). These granular or thick-layered phases might be associated with unmelted Ti_3In_4 particles with relatively large sizes. On the other hand, the joint with filler In-1wt%Ti has no such granular or thick-layered Ti-rich phase but only the thin Ti containing layer in the interface (see Fig.6(a)).

Figure 7 shows the EPMA images of Al, In and Cu in the case of In-1wt%Ti. The In atoms in the filler were found not to segregate as metallic In but to diffuse into Cu leaving Ti atoms at the joint interface region of AlN and Cu. The Ti atoms form a thin layer of 2-4 μm thick. The Ti-rich layer contains In and Cu atoms (see Figs.7(c) and (d)) but hardly overlaps with the distribution of Al atoms (see Fig.7(b)). This type of structure around the joint interface has never reported in literature concerning brazing of In-Ti active fillers, but this structure seems to be essentially important as the origin of strong bonding. In the brazing process, the Ti-rich layer may be reactive with nitrogen of AlN. Judging from the analogy of brazing Cu to nitride ceramics with Ag-Cu-Ti alloy [4-6], it is likely to form TiN containing impurities of In and Cu atoms. If such a TiN-like thin layer is actually formed, it may have a strong bonding force to AlN.

On the other hand, at the Cu side, diffused In into Cu may cause a strong bonding force. Also, alloying In and Cu may soften the Cu near the thin and rigid Ti-rich layer. Such softening may play an important role in the relaxation of thermal stress on the Ti-rich layer and AlN. The Ti-rich reaction layer formed may block the diffusion of In and Cu into AlN and that of Al into Cu. The reason why there is no layer of pure metallic In is that compressive stress in the brazing pushed out the surplus metallic In from the interface between the Ti-rich layer and Cu.

According to Kuzumaki et al.[5] or ElSaway et al.[6] the thickness of the reaction layer for the maximum shear strength ranges from 2-4 μm and the mechanical properties of the bonding zone are generally degraded by thickening the reaction layer because of the introduction of voids and/or cracks. Therefore, it is considered from our experimental results that the In-1wt%Ti filler is the most promising one.

The granular or thick-layered Ti-rich phase of joints with filler In-7.7wt%Ti, In-15wt%Ti and In-23.8wt%Ti may be due to recrystalized Ti_3In_4. If the filler originally involves much Ti, some Ti atoms may not be able to react with nitrogen supplied from AlN. Then, an excess Ti may form Ti_3In_4 in the interface region.

Furthermore, we have obtained another important data. Any structural damages, such as microcracks and voids were not detected by SEM observation of the test specimen brazed with In-1wt%Ti, but tiny cracks were detected in the AlN part of the interface region when brazed with In-7.7wt%Ti or In-15wt%Ti. In case of In-

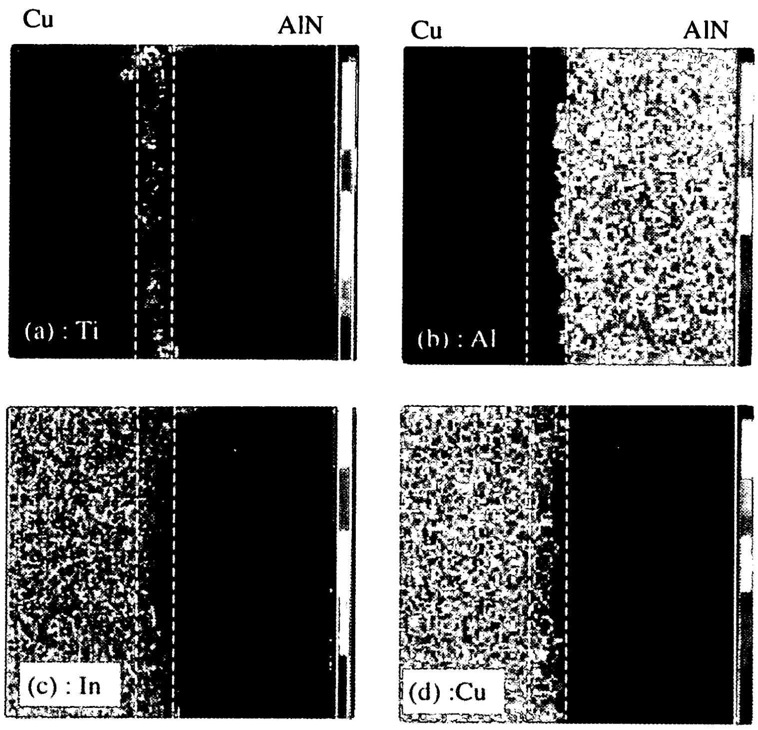

Fig.7. Detailed EPMA images of Ti-Kα, Al-Kα, In-Lα and Cu-Kα at the joint of the specimen brazed with In-1wt%Ti. The regions between the white dash lines correspond to the same location.

23.8wt%Ti filler, cracks were observed not only in AlN part but also in the thick layered Ti-rich phase of Cu side. From the results described above, we have concluded that the best In-Ti filler is about In-1wt%Ti.

3.3. Four-Point Bending Strength

We have carried out the 4-point bending tests to investigate the bonding strength of test specimens brazed with In-1wt%Ti. The 4-point bend strength is defined by

$$\sigma = \frac{3P(L-l)}{2wt^2}, \qquad (2)$$

where P is the maximum load at fracture of the specimen, L and l are the external and internal span of 4-point bending tests, w and t are the width and thickness of specimens.

Figure 8 shows the bond strength determined by the 4-point bending tests performed at room temperature and 500℃ as a function of brazing temperature. The strength at room temperature increases as the brazing temperature rises up to 675℃, but saturates above this temperature. The specimens brazed below 675℃ were partially broken at the joint part, but those brazed above 675℃ were broken out at the AlN portion. On the other hand, the strength at 500℃ proportionally increases with the brazing temperature. In this case, the fracture occurred at the interfaces. Huh et al. reported that the 4-point bending strength of the Cu-AlN joint brazed with In-1%Ti at 700℃ for 30 min was about 24 MPa (this value was calculated with their data in the literature [3] using Eq.(2)). The strength of our joint brazed at 700℃ for 30 min is larger than that by Huh et al. This is probably due to the formation of Ti-rich reaction layers at the interface region.

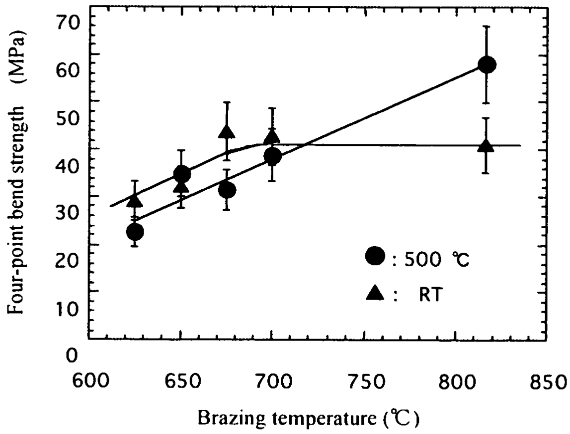

Fig.8. Effect of brazing temperature on the 4-point bending strength of test specimens brazed with In-1wt%Ti. The strength was measured at room temperature and 500℃.

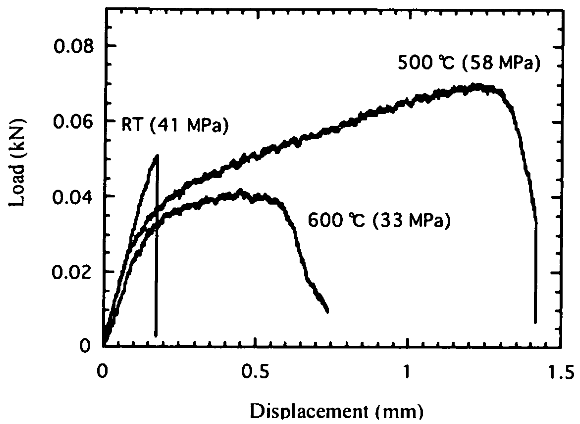

Fig.9. Load-Displacement curves of 4-point bend tests at room temperature, 500℃ and 600℃ for In-1wt%Ti. The displacement rate was 0.5mm/min.

Figure 9 shows the load-displacement curve of the 4-point bend tests at room temperature, 500℃ and 600℃. The specimens were brazed with In-1wt%Ti at 820℃ for 30 min. The strength at 500℃ was larger than that at room temperature, but the strength at 600℃ was smaller than that at room temperature. The nonlinearity of load-displacement can be explained by the increase of plasticity of metals near the interface by In diffusion into Cu as shown in Figs.7(c) and (d). The degradation of the strength at 600℃ would be ascribed to limitation of heat resist-ance in the highest In concentration part close to joint, judging from the breaking at the interface at high temperature.

The results described above imply that the joints withstand against at least 500℃ which is much higher than melting point of metallic In. Brazing with In-1wt%Ti is applicable to joining an AlN insulator and a Cu electrode for constructing TE modules which work in high temperature waste heat systems (400–500℃).

4. CONCLUSIONS

The Cu-AlN bonds by active metal brazing using In-Ti filler alloys were investigated with SEM and EPMA analyses. The formation of a Ti-rich reaction layer of about 2-4 μm thick was observed when brazed with the In-1wt%Ti filler. Most of In atoms were verified to diffuse into Cu, leaving Ti atoms at the interface between AlN and In-diffusing Cu. The specimens brazed with the Ti-richer fillers, e.g., In-7.7wt%Ti, In-15wt%Ti and In-23.8wt%Ti include the microcracks in the AlN and surplus Ti-rich phase in the joint of the interface.

A high bonding strength was obtained by brazing with the In-1wt%Ti filler at 625℃ which is 75℃ lower than that reported by Huh et al. The 4-point bend strength of the joint brazed at 820℃ was as high as 40 MPa at room temperature and 58 MPa at 500℃. The formation of Ti-rich reaction layer and the diffusion of In into Cu may cause the high bonding strength. Thus, the In-Ti active filler may be used for constructing the thermoelectric modules operating at high temperatures.

Acknowledgement — We would like to thank Dr. A. Kai and Dr. K. Matsubara for stimulating discussion. We acknowledge Mr. N. Narimatsu for laboratory contributions. We are also indebted to Mr. Harita, TOKUYAMA Co. for supplying AlN ceramic plates. This work was partly supported by a Grant from NEDO (New Energy and Industrial Technology Development Organization) and Scientific Research from the Ministry of Education, Science, Sports and Culture.

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