Wetting properties between silver-copper-titanium braze alloy and hexagonal boron nitride

Yoshihisa Sechi*,**, Taihei Matsumoto***,**** and Kazuhiro Nakata****
* Kagoshima Prefectural Institute of Industrial Technology,
1445-1 Oda, Hayato-cho Kirishima 899-5105, Japan
** Graduate Student, Graduate School of Engineering, Osaka University,
2-1, Yamada-oka Suita 565-0871, Japan
*** Toyo Tanso Co., Ltd., Osaka 555-0011, Japan
5-7-12, Takeshima, Nishiyodogawa-ku, Osaka, Osaka 555-0011
**** Joining and Welding Research Institute, Osaka University
11-1, Mihogaoka, Ibaraki, Osaka, Japan, 567-0047

Abstract
Wetting properties between silver-copper-titanium braze alloys with different titanium contents up to 2.8 mass% and hexagonal boron nitride ceramics were investigated using sessile drop method at 1123K in Argon. The final contact angle is less than 30° when the Ti content was over 0.41 mass%. Meanwhile, the contact angle curves show different behavior. In case of using braze alloy containing 2.8 mass% of titanium, the initial contact angle is acute angle just after the melting of braze. In case of brazes containing titanium less than 2.26 mass%, the contact angle is larger than 90° at the beginning and slowly decreases to acute angle. The reaction layer of titanium nitride is observed at the interface. In addition, the reaction of Ti in the braze and N in the bulk h-BN seemed to show diffusion limited spreading.

Key Words : Silver-copper-titanium braze alloy, Hexagonal boron nitride, Contact angle, Composition dependence, Sessile drop method

1. INTRODUCTION

Bonding of ceramic to metals is a common requirement for their successful application, and the approach of a new combination on the joint is a common requirement for high functionality to the products in recent years. However, there are some problems such as the joint defect due to thermal stress in the joint field and material deterioration by heating in these dissimilar joining[1]. Among many joining methods, brazing has good characteristics for dissimilar joining process due to suppression of damage to the base materials.

Boron nitride ceramics has a various functional characteristics. Especially, hexagonal boron nitride (h-BN) has a good thermal resistibility and solid-lubrication[2], and wettability to the brazing metals is relatively low compared to the other ceramics[2, 3], so it is difficult to braze h-BN to another material. Because joining characteristics are affected by wettability, it is considered that brazing of h-BN is worthy of attention to utilize dissimilar brazing of another ceramics and metals. On the contrary, its characteristic of solid lubrication makes difficulty in brazing h-BN and the other materials because most of the molten metals show low wettability to h-BN.

Addition of titanium as an active element in Ag-Cu alloy braze makes it possible to braze h-BN and tungsten carbides directly[4].

Previously, some research works[3,5,6] were carried out about composition dependence of the brazing focusing on the reaction of Ti with h-BN, but few in case of the Ti content was under 2 mass%. In this study, the time dependence of contact angle between h-BN and Ag-Cu-Ti alloy braze is described using sessile drop method, and in order to investigate the reaction layer of the interface, cross-sectional observation and elemental analyses of interface layer were performed.

2. EXPERIMENTAL PROCEDURES

Wetting properties of h-BN with respect to molten Ag-Cu-Ti braze alloy were estimated using the sessile drop method. For this, block shaped Ag-Cu-Ti alloy and a h-BN plate were prepared and degreased as mentioned above. The surface roughness (Ra) of the h-BN plate was approximately 1.2μm because it includes many pores due to low relative density. The Ag-Cu-Ti block was placed on the h-BN plate in a vacuum chamber, and the chamber was evacuated to decrease the pressure to at least 3.7×10^{-4} Pa. The specimen was heated up to 1023K, which is higher than the melting point of the braze alloy and the brazing temperature in vacuum; then, the evacuation and Ar (99.999% purity) substitution cycle was repeated at least four times. Finally, the specimen was heated to 1123K in Ar atmosphere, and the contact angle of the molten braze alloy and the h-BN was measured under 1atm of Ar atmosphere, which was continuously flowing at a finite flow rate.

Table 1 Braze used in the experiment.

No	Elements (mass %) Ag	Cu	Ti
1	72.01	Bal.	0.00
2	71.49	bal.	0.28
3	71.53	bal.	0.41
4	71.34	bal.	0.63
5	71.21	bal.	0.85
6	70.90	bal.	1.28
7	70.15	bal.	2.26
8	69.61	bal.	2.80

Nominal compositions and properties were summarized in Table 1 and Table 2. Samples were subsequently cross-sectioned, grinded by SiC paper and polished by 3μm-1μm polycrystalline diamond to provide microstructural information. Cross-sectional observation and elemental analysis of the interface were performed using electron probe micro-analyzer and X-ray diffractometer.

3. RESULTS

Figure 1 shows the time dependence of contact angle between h-BN and Ag-Cu-Ti braze at 1123K. In case of braze without Ti, the contact angle was about 160° and time

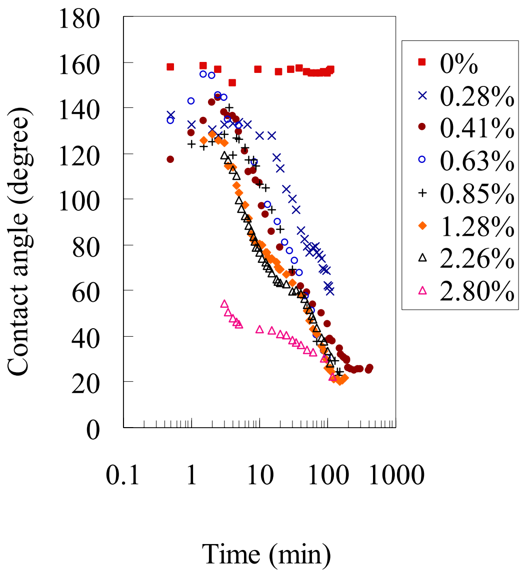

Fig. 1 Time dependence of contact angle for Ag-Cu-Ti braze alloys at 1123K.

Table 2 Boron nitride used in the experiment.

Nominal composition (mass %)	Bend strength (MPa)	Density ($\times 10^{-3}$ kg / m^3)	Relative Density (%)	Ra (μm)	Size (mm)
h-BN > 99.993	32.5	1.93	82.5	1.19	20*20*5

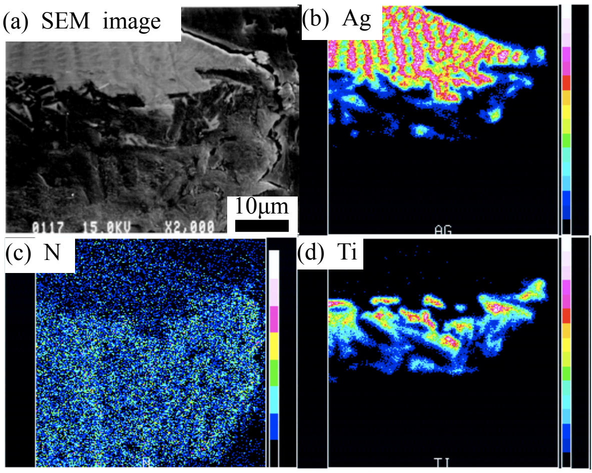

Fig. 2 Map analysis of Ag-Cu-1.28%Ti braze alloy / h-BN interface (edge).

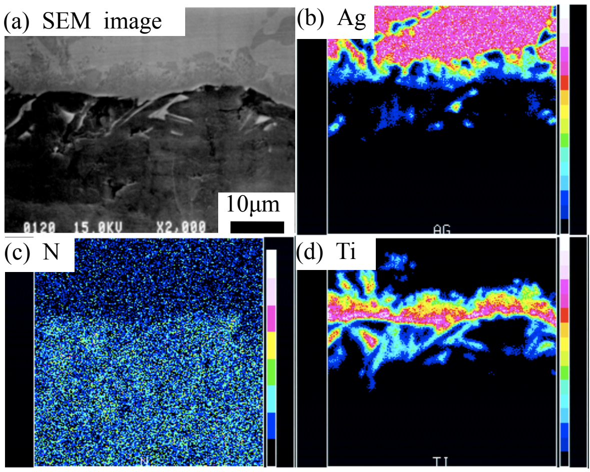

Fig. 3 Map analysis of Ag-Cu-1.28%Ti braze alloy / h-BN interface (central area).

dependence was not observed. With increasing Ti content, contact angle decreased fast and final contact angle was achieved in rather short period. In case of 2.80% Ti in braze, the contact angle was acute angle at the melting point. Small addition of Ti increased the changing rate of the contact angle, and the rates were nearly the same for Ti contents from 0.28% to 2.25%. However, when the Ti contents increased to 2.80%, the changing rate became low.

Figure 2 and 3 show map analyses of h-BN/Ag-Cu-1.28%Ti braze interface after contact angle measurement near the edge and central area. From these distributions of elements, the concentration of Ti near the interface was observed, and thickness of Ti infiltrated layer was evaluated as 2-10μm in Fig. 2. The thickness of Ti infiltrated layer at the tip of the edge was thinner than that of the inside area as shown in Fig. 2. In most cases of Ti content, the concentration of Ti at the tip of the edge was thinner than that of inside area as shown in Fig. 2. In the central area, the continuous Ti layer was observed at the braze side of the interface and also infiltrated to h-BN. In most cases, the total thickness of Ti layer was continuously or seldom increased toward the central area of the interface, so the value of center was a little larger than that of the inside area of the edge or nearly equal to it.

Figure 4 shows XRD profiles of the interface and braze after contact angle measurement specimens. Some kinds of titanium nitride existed in both interfaces using 0.63% Ti and 2.80% Ti doped in (a) and (b). While Cu_3Ti existed only in 2.80% Ti doped braze in (b).

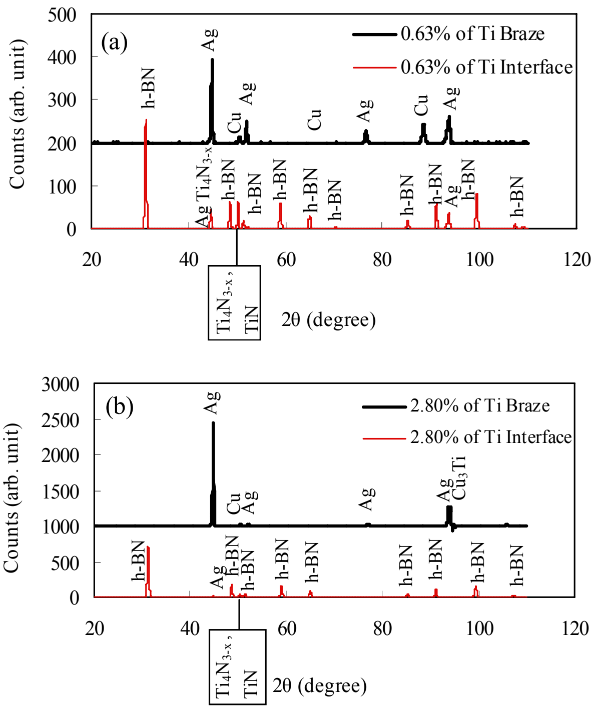

Fig. 4 XRD profiles at the interface and bulk braze.

4. DISCUSSIONS

In this study, the effect of oxidized titanium to the measurement of contact angle cannot be ignored because Ti is easily oxidized even in low partial pressure of O_2 such as the order of 10^{-23} Pa at 1123K[7], which was much lower than that of experimental atmosphere. Therefore, when Ag-Cu-Ti braze alloy was melt, titanium oxide film was thought to exist on the surface. In addition, it is difficult to remove oxide film[8] mechanically using ceramics drop tube method[9,10] because Ti reacts with most of ceramics. Therefore, block shaped metal specimen on the h-BN plate was used in this study.

From Fig. 1, most of the measurement showed dynamic behaviors such as increase of contact angle just after the specimen melt. It was caused by change of the specimen's shape from cubic to droplet. The difference of the initial contact angle between in case of 0.28% and of 2.26% seems as a deviation due to the initial shape of an Ag-Cu-Ti alloy block specimen. While in case of including 2.80% Ti, initial contact angle is an acute angle of 46˚, probably that was caused by high initial content of Ti near the solid-liquid interface adequate to make reaction between Ti and N in h-BN. It seems that only 0.28% in Ag-Cu braze can reduce contact angle on h-BN in Ar. In addition, with increasing Ti content, contact angle decreased rapidly. It seems that the difference of final contact angle between former researches[3,5,6] and this study comes from difference in atmosphere, initial braze shape and surface roughness[8,9].

At the interfacial-reaction wetting stage, its wetting rate was fast and nearly same value when Ti content of metals was 0.28% to 2.26%. This seems to show that the diffusion path of Ti to h-BN at the interface, and the main reaction mechanism are same in Ti content from 0.28% up to 2.26%. On the contrary, when Ti content of metal was 2.80%, its wetting rate was not smaller than that of 0.28% to 2.26%. This difference appears to arise from the transportation of Ti in melting drop of Ag-Cu-Ti alloy. If the liquid metal contains a low concentration of Ti, the reaction around the triple line depends on the supply of Ti in the liquid by convection and diffusion. On the other hand, in case of high concentration of Ti, the reaction around the triple line depends on the reaction velocity of Ti and h-BN because adequate amount of Ti is supplied to the triple line. In Fig. 2 (c) and (d), it is found that the larger content of Ti made thicker interfacial reaction phase, which contains TiN[3,4,11] or other titanium nitride as Ti_3N_{4-x}[12]. Figure 3 (c) and (d) showed that continuous Ti layer was formed in central area of the interface, which may be result in long heating time. On the other hand, infiltrated Ti layer in Fig. 3(d) was not so increased. These tendencies were observed around all Ti contents. It seems that thick interfacial reaction phase may interfere with the diffusion of nitrogen and further formation of reaction phase[9]. The excess amount of Ti was observed as Cu_3Ti from XRD profile as shown in Fig. 4 (b). On the contrary, most of Ti was consumed in case of 0.63% Ti braze. The reason why drastic change did not occur over 0.41% Ti seems due to excess amount of Ti that did not reacted with h-BN.

5. CONCLUSIONS

The contact angle between h-BN and Ag-Cu-Ti braze and effects of the Ti content in the braze alloy to it were investigated. Results of the study can be summarized as follow:

(1) The contact angle between h-BN and the braze decreased to less than 30˚ in the case of the braze with over 0.41 mass% of Ti, as

measured by the sessile drop method at 1123K in Ar.

(2) An excess amount of Ti, which did not react with h-BN, was found to exist in the form of Cu_3Ti in the bulk Ag-Cu-Ti braze region.

(3) The diffusion path of Ti to h-BN at the interface, and the main reaction mechanism seems to be same in Ti content from 0.28% up to 2.26% which seems to be different from 2.80% at the interfacial-reaction wetting stage and it appears to arise from the transportation of Ti.

ACKNOWLEDGEMENTS

This work was supported by Joint Research system at the Joining and Welding Research Institute, Osaka University, and Grant-in-Aid for Cooperative Research Project of Nationwide Joint-Use Research Institutes on Development Base of Joining Technology for New Metallic Glasses and Inorganic Materials from The Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES

1 W. Wlosinski : Interfaces in dissimilar materials joints Fueg. Keram. Gla. Met., (1985), 22-36

2 R. H. Biddulph : Boride and carbide ceramics- The systems, Proc. 1st Euro. Sym. on Eng. Ceram., (1985), 45-61

3 M.G. Nicholas, D.A. Mortimer, L.M. Jones and R.M. Crispin : Some observations on the wetting and bonding of nitride ceramics, J. Mat. Sci., 25 (1990), 2679-2689

4 Y. Sechi, A. Takezaki, T. Tsumura and K. Nakata : Dissimilar laser brazing of boron nitride and tungsten carbide, Smart Processing Technology 2, (2008), 27-30

5 E. Benko : Wettability studies of cubic boron nitride by silver-titanium, Ceram. Int., 21 (1995), 303-307

6 E. Benko, E. Bielanska, V.M. Perevertelio and O.B. Loginova : Formation peculiarites of the interfacial structure during cBN wetting with Ag-Ti, Ag-Zr and Ag-Hf alloys., Diam. Rel. Mat., 6 (1997), 931-934

7 L.S. Darken, R.W. Gurry : Physical Chemistry of Metals McGrow Hill, New York, 1953

8 H. Fujii, H. Nakae and K. Okada : Interfacial reaction wetting in the boron nitride/molten aluminum system, Acta metall. mater., 41 (1993), 2963-2971

9 H. Fujii and H. Nakae : Precise measurement of the wetting of ceramics by molten Aluminum, Materia Japan, 34 (1995), 1269-1275

10 N. Eustathopoulos, M.G. Ncholas, B. Drevet : Wettability at High Temperatures, Oxford: Elsevier, (1999)

11 S.D. Peteves : Joining nitride ceramics, Ceram. Int., 22 (1996), 527-533

12 W. Lengauer and P. Ettmayer : The crystal structure of a new phase in the titanium-nitrogen system, J. Less-Common Met., 120 (1986), 153-159