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Composition Dependence of Titanium in Silver-Copper-Titanium Alloy Braze on Dissimilar Laser Brazing of Boron Nitride Ceramics and Cemented Carbide

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Dissimilar laser brazing of boron nitride ceramics and cemented carbide has been investigated by using silver-copper-titanium braze alloys with different titanium contents of up to 2.80 mass%; efficient bond strength was achieved using brazes with more than 1.25 mass% of titanium. The contact angle between hexagonal boron nitride ceramics and the molten braze, which was measured by the sessile drop method at 1123 K, decreased to less than 30° when the Ti content was over 0.41 mass%. The difference in the wetting property determined by laser brazing method and that by sessile drop method is attributed to the difference in the heating process of the two methods. Structural analysis of the interface between the boron nitride ceramics and the braze was carried out by electron probe micro-analysis (EPMA).
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1. Introduction

Brazing process is used in many industrial fields for developing engineering structures and electronic devices. This process has several advantages, making it suitable for use in joining dissimilar materials and materials which are difficult to connect precisely; further, this process can be efficiently applied to the mass production of structures and devices. For the application of ceramic materials, it is frequently required that a ceramic material be bonded to metals. Moreover, the development of high functionality products in recent years has led to a demand for a new joining process that can join different materials. However, certain problems are encountered while meeting the above requirements, such as the formation of a joint defect due to thermal stress in the joint field and material deterioration due to heating in the brazing process.

Boron nitride ceramics exhibit various functional characteristics. The hexagonal boron nitride ceramics, in particular, show good thermal resistivity and can serve as a solid lubrication;[1)] further, the wettability of this ceramic to brazing metals is relatively low as compared to the other ceramics;[1,2)] as a result, it is difficult to braze hexagonal boron nitride ceramics to other materials. Because wettability of a material affects joining characteristics, it is speculated that brazing of hexagonal boron nitride ceramics may be suitable to demonstrate laser brazing of dissimilar materials such as ceramics and a metal. Cemented carbide alloys made by powder metallurgy have low thermal expansion coefficient and high rigidity suitable for fabricating structural materials. In general, the thermal expansion coefficient of a metal is higher than that of ceramics; this may result in the generation of a large thermal stress at the brazing joint, which leads to the formation of defects at the interface. In this study, laser brazing of hexagonal boron nitride (h-BN) ceramics using cemented carbides as base plates; we selected these materials because the difference between the thermal expansion coefficients of hexagonal boron nitride ceramics (4.4×10^{-6}/K) and cemented carbides (5.2×10^{-6}/K) is very small.

The laser brazing method shows characteristics suitable for joining dissimilar materials, because this process requires a short heating time and small heating area, which in turn reduces the damage to the base materials. The addition of titanium as an active element in silver-copper braze alloys enables the direct brazing of hexagonal boron nitride ceramics and cemented carbides;[3)] however, very few studies have investigated in detail the dependence of the brazing process on the titanium content of the alloy, especially in low Ti content alloys.[2,4–6)] Therefore, in this study, we investigate the effect of titanium content of silver-copper-titanium braze alloy on dissimilar laser brazing of boron nitride ceramics and cemented carbide. In order to investigate the structural characteristic at the joint, we performed cross-sectional observations and elemental and structural analysis of the ceramic/alloy interface; in addition, we performed wettability measurements.

2. Experimental Procedures

The experiments were carried out using cemented carbides, h-BN, and Ag-Cu-Ti braze. The cemented carbides were purchased from Mitsubishi Materials Corporation (Tokyo, Japan); they were classified as ISO K10 grade. The h-BN was purchased from Kojundo Chemical Laboratory Co., Ltd. (Saitama, Japan), which was prepared by hot pressing method using only high purity plate crystal. Ag-Cu-Ti alloy brazes, with Ti as the major active component, were prepared into sheets for carrying out direct ceramic brazing. The nominal compositions and properties are summarized in

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Table 1 Materials used in the experiments.

Material	Grade	Nominal composition (mass%)	Bend strength (MPa)	Density (Mg/m^3)	Relative Density (%)	Size (mm)
Tungsten Carbide	HTi 10	WC: 94, Co: 6	32000	14.9	—	$20 * 20 * 2$
h-BN	99%up	h-BN > 99.993	32.5	1.93	82.5	$5 * 5 * 3.5$

Table 2 Braze used in the experiment.

Elements (mass%)			
No	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	71.07	bal.	1.25
7	70.90	bal.	1.28
8	70.20	bal.	1.70
9	70.15	bal.	2.26
10	69.61	bal.	2.80

Table 3 Laser brazing conditions.

Pulsed YAG Average Output (kW)	0.134
CW LD Output (kW)	0.02
Pulse frequency (Hz)	100
Scanning speed (mm/s)	0.1∼1.6

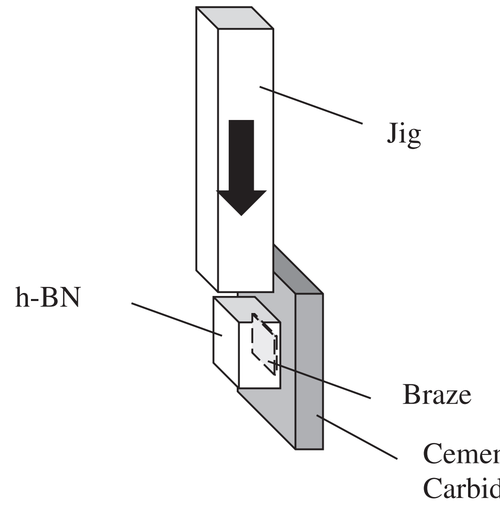

Fig. 1 Schematic diagram of experimental setup for shear strength tests.

Tables 1 and 2. The thickness of the braze sheet was 0.1 mm, and the size was determined to 80% for the joint area of h-BN to ensure that the molten braze does not flow outside the joint interface. Before brazing, the h-BN blocks, braze sheets, and cemented carbide plates were degreased by carrying out ultrasonic agitation in acetone for 10 min and drying in air. The prepared samples had a top-hat shape, in which the braze was sandwiched between the h-BN block on top and cemented carbide plate at the bottom. The samples were placed in a vacuum chamber.

A small pressure of 1.2 MPa was applied to the sandwiched sample in order to ensure that parts are joined to each other and there is no gap formation when the braze is melted. After placing the samples in the vacuum chamber, whose diameter was 100 mm, the chamber was evacuated and its pressure was reduced to less than 10^{-1} Pa; next, the atmospheric pressure was substituted with Ar gas of 99.999% purity.

This evacuation followed by substitution of air with Ar gas was performed at least three times before brazing. During brazing, Ar gas was made to continuously flow through the chamber at a flow rate of approximately 5 L/min. The laser brazing conditions are summarized in Table 3. The laser was scanned over the cemented carbide substrate encircling the h-BN block.

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 1.2 μm because its relative density was low to include many pores in it. 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 1023 K, which is lower than the melting point of the braze 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 1123 K in Ar atmosphere, and the contact angle of the molten braze and the h-BN was measured under 1 atm of Ar gas, which was continuously flowing at a finite flow rate.

To obtain microstructural information, some of the samples were cross sectioned using a low-speed diamond saw and cooled with water; the cross sections were mounted by epoxy resin and subjected to curing at room temperature for approximately 8–10 h; then, they were grinded with SiC papers of #120–1200 and polished with polycrystalline diamond which grain diameter was 3∼1 μm. Cross-sectional observation and elemental analysis of the interface were performed using an electron probe micro-analyzer (EPMA, JEOL Co., Ltd., JXA-8621MX) and an X-ray diffractometer (XRD, Bruker AXS Co., Ltd., D8; CoKα) The diameter of collimator was set to 50 μm to study the crystallographic phase in the micro region. Interfacial observation and estimation of the interface area were performed using a scanning acoustic microscope (Hitachi Kenki FineTech Co., Ltd., HSAM220). Some of the samples were placed in a shearing jig, as shown in Fig. 1, and stressed to destruction; the shear strength was calculated using the Precision universal tester (Shimadzu Co., Autograph AGS-5kNB) operated at a cross-head speed of 0.5 mm/min. The shear strength was calculated as the maximum load divided by the interface area, which was estimated from the scanning acoustic microscopy observations.

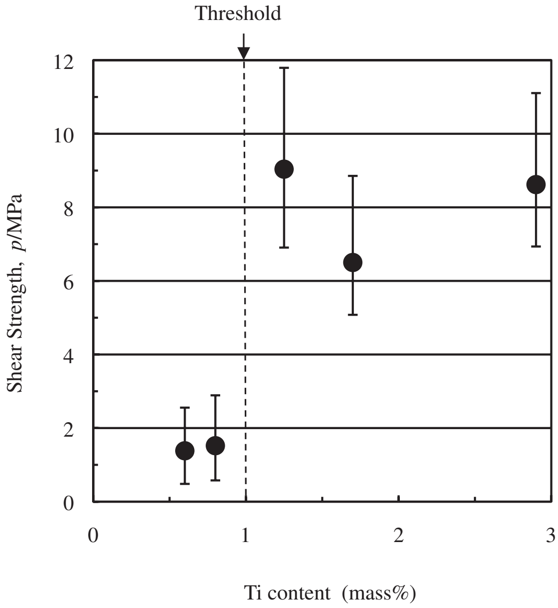

Fig. 2 Dependence of shear strength on Ti content.

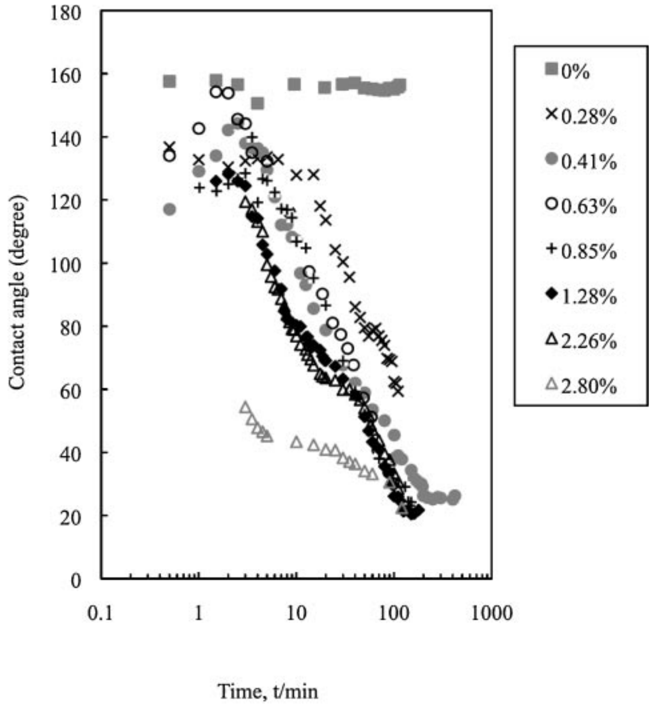

Fig. 3 Time dependence of contact angle for Ag-Cu-Ti braze alloys at 1123 K.

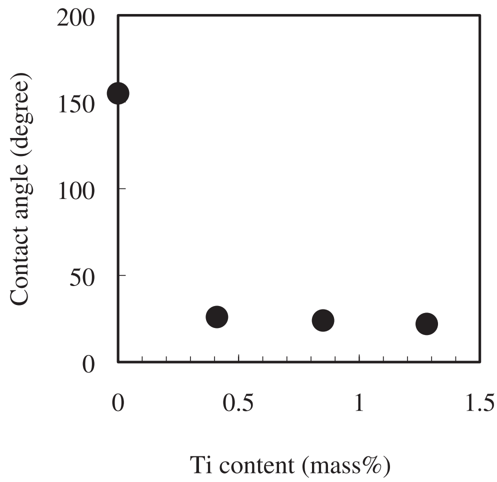

Fig. 4 Dependence of final contact angle on Ti content of Ag-Cu-Ti braze alloys at 1123 K.

3. Results

3.1 Dependence of dissimilar laser brazing behavior on titanium content

Figure 2 shows the dependence of shear strength of the braze on its Ti content. In all the samples, irrespective of the Ti content, the brazes started to melt when the highest temperature at the bottom of the cemented carbide plates increased above 873 K. The braze without Ti showed good wettability to cemented carbide, but showed no wettability to h-BN. This indicates that the dissimilar joint was not formed using this braze.

Moreover, the brazes containing 0.28% and 0.41% of Ti showed poor wettability with respect to h-BN. In the case of the braze containing 0.63% of Ti, the shear strength was calculated to be low, and some specimens broke while performing the shear strength test to form a fracture at the interface between the braze and Ti-rich layer of the h-BN surface. A high bond strength was achieved in the case of brazes with Ti content of 1.25% and higher. In the case of these samples, the fracture was formed in h-BN body near the interface.

3.2 Titanium content dependence of wettability between braze and h-BN

Figure 3 shows the time dependence of the contact angle between the Ag-Cu-Ti braze and h-BN at 1123 K. In the case of the braze without Ti, the contact angle was approximately 160°, which did not show a time dependence. With increasing Ti, the contact angle rapidly decreased and final contact angle was achieved in a short period. In the case of the braze with 2.80% of Ti, the contact angle was acute at its melting point.

Figure 4 shows Ti content dependence of the final contact angle of the samples. In the case of the braze without Ti, the contact angle was approximately 160°; however, at the Ti content of 0.41%, the contact angle decreased to approximately 30°. As the Ti content increased, the contact angle decreased and was 25° at 2.80% of Ti; though the change in the absolute value of contact angle got relatively small at 2.80% of Ti.

Figure 5 shows the map analysis of the h-BN/Ag-Cu-Ti braze interface after carrying out the contact angle measurements. In these images, the concentration of Ti near the interface is observed; the thickness of this Ti-rich region was found to be approximately 2∼10 μm. Some amount of Ti was found to overlap with the nitrogen in the h-BN. The thickness of the Ti-concentrated region at the interface observed in the case of the braze with 2.80% of Ti was more than that observed in the case of 0.63% of Ti; the Ti in the former case was observed to spread toward the braze.

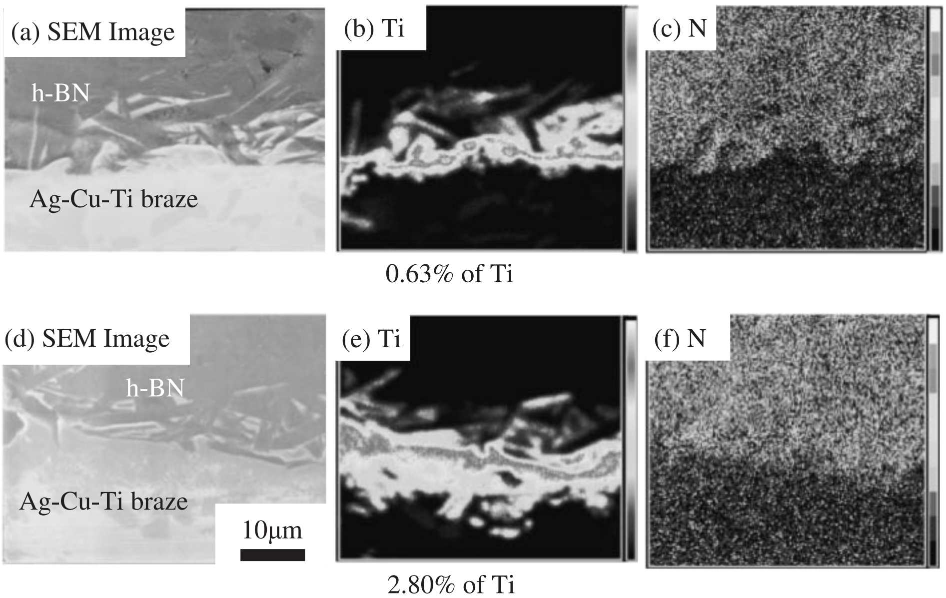

Fig. 5 Map analysis of h-BN/Ag-Cu-Ti braze interface after contact angle measurements.

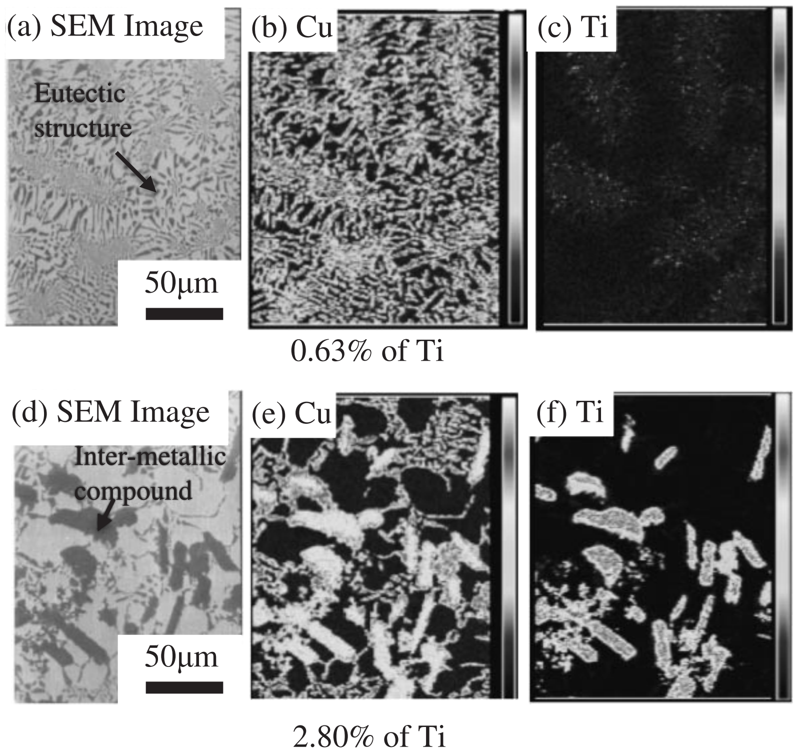

Fig. 6 Map analysis of bulk of Ag-Cu-Ti braze away from h-BN/braze interface after contact angle measurements.

Figure 6 shows the map analysis of the central region of the Ag-Cu-Ti braze, i.e., the region away from the h-BN/braze interface after the contact angle measurement. In the case of the braze with 0.63% of Ti, a eutectic structure of Ag and Cu was observed with a small amount of Ti distributed in Cu. In the case of 2.80% of Ti, a relatively large amount of Ti distribution was observed, suggesting the presence of coarse precipitates in the area containing Cu.

Figure 7 shows the XRD profiles of the samples at the interface and in the bulk of the braze after the contact angle measurements. In the case of both the samples with 0.63% of Ti and 2.80% of Ti, shown in Figs. 7(a) and 7(b), respectively, some types of titanium nitrides are found to exist at the interfaces. However, the presence of Cu_3Ti was observed only in the case of the braze with 2.80% of Ti, as shown in Fig. 7(b).

4. Discussions

From Fig. 2, it can be concluded that an effective dissimilar joint between h-BN and cemented carbide can be achieved using braze with more than 1.25% of Ti. The

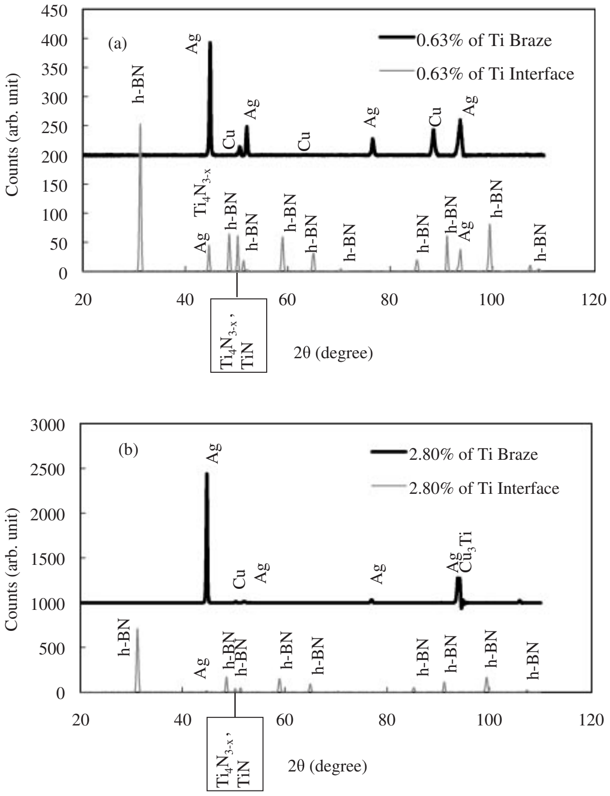

Fig. 7 XRD profile of samples at interface and bulk braze after contact angle observations.

addition of Ti as an active element to the braze seems to be an effective way of enhancing the wetting properties of h-BN,[2,4–6] which is achieved even at a low Ti content of 1.25%. In the case of brazes with more than 1.25% of Ti, the h-BN body fractures near the interface, and the average shear strengths of these samples were around 6.5 to 9.0 MPa; the difference between the highest and lowest shear strengths was 4 to 5 MPa. Since the h-BN block was prepared by hot pressing method using a high purity plate crystal, most of the grains were oriented along the direction of shear stress, and its relative density was considerably low of approximately 82.5%. This resulted in the low bulk strength of the h-BN block and the consequent grain boundary fracture. From the difference between the lowest and highest shear strength values and the low bulk strength, it appears that the average shear strength of the brazes with 1.25% of Ti to 2.80% of Ti is within the margin of variation. In contrast, in the case of the braze with 0.85% of Ti, a fracture was observed at the interface between the braze and the Ti-rich layer of h-BN surface, which resulted in the decrease in the shear strength. It is suggested that the Ti-rich layer on the h-BN surface, which is formed during the short heating period in laser brazing, was not sufficient to induce wetting between h-BN and the braze; therefore, the threshold value of Ti content exists between 0.85% and 1.25%, as shown in Fig. 2. As the Ti content of the braze increases, the thickness of Ti-rich layer also increases, as in the case of the contact angle measurements shown in Fig. 6. If the bulk strength of ceramics is high, the shear strength may attain the maximum value as the thickness of the Ti-rich layer increases above the threshold value, because the formation of a thick Ti-rich layer with Ti in excess may induce the fracture at this interface. However, the h-BN used in this study did not have a sufficiently high bulk strength to give the maximum value of shear strength. Thus, it is considered that only threshold of the shear strength was observed in this study.

From Fig. 3, it can be concluded that the addition of a small amount of Ti (0.28%) in an Ag-Cu braze can effectively reduce the contact angle between h-BN and the braze in Ar atmosphere as compared to the Ag-Cu braze without Ti. As the Ti content increased, the contact angle decreased rapidly. This suggests that the Ti in the braze reacts with N in h-BN and accelerates the interfacial wetting by the reaction at the h-BN/Ag-Cu-Ti braze interface;[7,8] further, it was speculated that the difference in the final contact angle reported in our study and those reported in previous studies[2,4–6] may be attributed to the experimental conditions such as atmosphere, initial braze shape, and the surface roughness of the h-BN block.[7,8]

From Fig. 4, it is observed that the final contact angle decreased drastically from 155°, for the braze without Ti, to 26° on the addition of 0.41% of Ti. In spite of increasing Ti content, final contact angle showed finite decrease to 22° with large additional of 2.80%. From Figs. 5(b) and 5(c), it is found that using brazes with higher Ti content resulted in the formation of a thicker interfacial reaction layer, which contains TiN[2,3,9] or other titanium nitride as Ti_3N_{4-x}.[10] However, the results of Fig. 6(f) indicate that all the Ti content does not react with N in h-BN and there exists some amount of coarse intermetallic precipitates even after a long heating time after the final contact angle is attained. It is suggested that the presence of a thick interfacial reaction layer interferes in the diffusion of nitrogen and hence hinders further formation of the reaction layer.[8] From the XRD profiles, the precipitates were identified as Cu_3Ti, as shown in Fig. 7(b). In the case of the braze with 0.63% of Ti, however, most of the Ti was consumed in the formation of titanium nitrides, as shown in Fig. 6(c). The reason why a drastic change of final contact angle was not observed in the case of brazes with more than 0.41% of Ti can be attributed to the excess amount of Ti that did not react with h-BN.

In comparison to the sessile drop method, the heating time required in the laser brazing process is rather short and within 1 min. Therefore, we can conclude that the difference in the heating cycles of the two methods is responsible for the difference in the threshold value of Ti content for efficient laser brazing (1.25% of Ti), and that for the decrease in contact angle (0.41% of Ti).

5. Concluding Remarks

The effects of the Ti content of the Ag-Cu-Ti braze alloy on the dissimilar laser brazing of h-BN and cemented carbide and on the contact angle between the Ag-Cu-Ti braze alloy and h-BN were investigated. Structural observation and analysis of the h-BN/Ag-Cu-Ti alloy interface and the shear strength tests conducted on it revealed the following results.

(1) The addition of Ti as an active element in the braze alloy is observed to efficiently enhance the bond strength between h-BN and cemented carbides even at small Ti concentrations of over 1.25 mass%.

(2) At 0.63 to 0.85 mass% of Ti, the bond strength of the brazes and h-BN was low because of the formation of an interfacial fracture.
(3) The contact angle between h-BN nitride 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 1123 K in Ar atmosphere.
(4) 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 of the contact angle measurements specimens.
(5) The difference in the wetting properties determined by laser brazing process and those determined by sessile drop method can be attributed to the difference in the heating cycles of these methods.

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