Effect of composition of titanium in silver–copper–titanium braze alloy on dissimilar laser brazing of binder-less cubic boron nitride and tungsten carbide

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Abstract. Laser brazing with Ti as an active element in silver–copper alloy braze metal has been carried out for binder-less cubic boron nitride and tungsten carbide, using silver–copper–titanium braze alloys with titanium content that varied between 0.28 mass% and 1.68 mass%. Observations of the interface using electron probe microanalysis and scanning acoustic microscopy show that efficient interface adhesion between binder-less cubic boron nitride and the silver–copper–titanium braze alloy was achieved for the braze with a titanium content of 0.28 mass%.

1. Introduction
The brazing process is used in many industrial fields for developing engineering structures and electronic devices [1-13]. This process has several advantages, making it suitable for use in joining dissimilar materials and materials that are difficult to connect precisely; furthermore, this process can be efficiently applied to the mass production of these structures and devices. It is also required applying to ceramic materials, which are frequently bonded to metals. Moreover, the development of high-functionality products in recent years has led to the demand for a new joining process for different materials.

Boron nitride ceramics is one of the products with various functional characteristics. In particular, cubic boron nitride (c-BN) has high hardness, thermal conductivity, and thermal and chemical stability that is second to that of diamond [14]; c-BN is suitable as a material for cutting tools, especially those for cutting hardened steel. Conventional sintered c-BN is manufactured commercially in a liquid-phase sintering process using binder material such as Al, and the volume fraction of the binder phase varies from 10 to 50%. Because the binder phase exists between c-BN crystal grains, it is difficult to produce effects expected from the ceramics’ original excellent properties. Therefore, specifications of tools are partly determined by the types and amount of binder phase in the material.

To solve this problem, high-purity and binder-less c-BN was developed [14]. This binder-less, polycrystalline c-BN consists of fine particles with good wear resistivity owing to the direct contact of crystal grains in the absence of a binder [14]. Thus, this binder-less c-BN is expected to be applied in high-performance cutting tools. Binder-less c-BN is very expensive, however, and it is difficult to
shape monolithically fabricated cutting tools made of binder-less c-BN because of its hardness. Therefore, dissimilar joining between binder-less c-BN and metals is necessary to bring out and utilize the former’s outstanding properties. Certain problems can arise, however, while meeting these requirements, such as the formation of joint defects resulting from thermal stress in the joint field and material deterioration resulting from heating in the brazing process.

In general, the thermal expansion coefficient of 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 [15]. The tungsten carbide–cobalt (WC–Co) alloy made by powder metallurgy has a low thermal expansion coefficient and high rigidity, which makes it a good complementary structural material to ceramics. However, only a few studies have focused on the joining of boron nitride and tungsten carbide alloy or other metals [5,8,10] by brazing in a furnace, which requires a long heating time.

Among brazing processes [16], laser brazing [10,11,13,17-30] has good characteristics for dissimilar joining: when compared with conventional furnace brazing, short heating time can be used only a small heating area is required, and damage to base materials is suppressed in the absence of a furnace. Recently, laser brazing with the addition of Ti as an active element in the Ag–Cu alloy as braze metal has been successfully applied to dissimilar joining of hexagonal BN (h-BN), single crystal diamond, and WC–Co alloy, after evacuation of the atmosphere to a vacuum of the order of 10⁻¹ Pa followed by Ar (99.999% purity) substitution to avoid oxidation of the active element Ti [12,31].

This study examines the effect of titanium content in the silver–copper–titanium braze alloy on dissimilar laser brazing of binder-less c-BN and WC–Co. In order to investigate the characteristics of the dissimilar joint, cross-sectional observation as well as elemental and structural analyses of the joint interface were performed.

2. Experimental procedure
This study used commercially available WC–Co alloy (ISO K10 grade; WC: 94 mass%, Co: 6 mass%) and binder-less polycrystalline cubic boron nitride (binder-less c-BN; c-BN > 99.9 mass%) made by the direct-conversion sintering method without sintering additives. Binder-less c-BN disks were divided into quarters, and blocks of the quadrisections were used. A braze sheet of the Ag–Cu alloy was used; it had a eutectic composition that includes Ti as the major active ingredient for direct ceramic brazing and it had a thickness of 0.1 mm. The nominal composition of the alloy is summarized in Table 1. Before brazing, the binder-less c-BN block, braze alloy, and WC–Co plate were degreased by ultrasonic agitation for 10 min in acetone and dried in air.

The sample has the shape of a top hat. A braze alloy sheet was sandwiched with a binder-less c-BN block from the top and a WC–Co plate from the bottom in a vacuum chamber. A low pressure of 2.4 MPa was applied to prevent the workpiece from moving when the braze alloy sheet was melted, and no gap adjustments for the joint were performed. A chamber with a diameter of 100 mm and inner volume of 145 mL was used in the brazing experiments. To avoid the oxidation of Ti, this chamber was evacuated to less than 10⁻¹ Pa after the samples were loaded; it was then filled with Ar gas after the evacuation. The purity of Ar gas was 99.999%. These evacuation and substitution cycles were carried out at least three times before brazing. During brazing, Ar gas continued to flow at a rate of about 5 L/min.

The laser brazing setup is shown in a perspective illustration in figure 1(a) and a cross-sectional schematic illustration in figure 1(b). The sample was located in a small vacuum chamber. The topside of the specimen was covered with a transparent quartz glass plate, which also served to fix the specimen in place. The generated YAG and LD laser beams were transferred with an optical fiber to the laser head unit and radiated through the transparent quartz glass plate to the topside of the WC–Co plate, with a radiation angle of 85°. Laser scanning of the WC–Co substrate was performed around the binder-less c-BN block. The laser brazing condition is summarized in table 2. The scanning speed of the laser was 0.6 mm/s during the first run and 1.0 mm/s during the second to fourth runs in order to
heat the specimen efficiently in a circular manner. The temperature during laser brazing was monitored at the bottom of the WC–Co plate using a thermocouple.

![Diagram](image)

(a) Perspective illustration  
(b) Cross-sectional illustration

**Figure 1.** Schematic diagram of laser brazing.

**Table 1.** Chemical composition of Ag–Cu–Ti braze alloy.

| No. | Elements (mass%) |
|-----|-----------------|
| 1   | Ag 71.49        |
| 2   | Cu bal.         |
| 3   | Ti 0.28         |
| 4   | Ag 71.34        |
| 5   | Cu bal.         |
| 6   | Ti 0.63         |
| 7   | Ag 71.21        |
| 8   | Cu bal.         |
| 9   | Ti 0.85         |
| 10  | Ag 70.90        |
| 11  | Cu bal.         |
| 12  | Ti 1.28         |
| 13  | Ag 70.26        |
| 14  | Cu bal.         |
| 15  | Ti 1.68         |

**Table 2.** Laser heating condition.

| Description                          | Value |
|--------------------------------------|-------|
| Pulsed YAG Average Output (kW)       | 0.134 |
| Pulsed YAG wave length (nm)          | 1064  |
| CW LD Output (kW)                    | 0.02  |
| CW LD wave length (nm)               | 808   |
| Pulse frequency (Hz)                 | 100   |
| Scanning speed (mm/s)                |       |
| (1\textsuperscript{st} run)          | 0.6   |
| (2\textsuperscript{nd} run)          | 1.0   |
| (3\textsuperscript{rd} run)          | 1.0   |
| (4\textsuperscript{th} run)          | 1.0   |
| Laser beam diameter (mm)             | 0.5   |

Some of the samples were subsequently cross-sectioned by a diamond saw with water cooling. The cross-sectioned specimen was then mounted by epoxy resin, cured at room temperature for about 8–10 h, ground using SiC paper with grit size #120–#1200, and polished by 3 μm and 1 μm polycrystalline diamond to provide microstructural information. Cross-sectional observations and elemental analysis of the interface were performed using an electron probe micro-analyzer (JXA-8230, JEOL Co. Ltd.) and an X-ray diffractometer (D8, Bruker AXS Co. Ltd.) with Co $K_{\alpha}$ as the radiation source. A collimator with a diameter of 50 μm was used to determine the crystallographic phase of the micro-
region. Interfacial observations and estimation of the interface area were performed using a scanning acoustic microscope (HSAM220, Hitachi Kenki FineTech Co., Ltd.) that can observe interfacial structures using ultrasonic echoes radiated from the probe in a water tank.

3. Results

In order to investigate the effect of titanium content of the silver–copper–titanium braze alloy on dissimilar laser brazing of binder-less c-BN and WC–Co, we performed cross-sectional observations, elemental and structural analyses, and adhesion evaluation of joint interfaces using several kinds of brazes containing Ti in concentrations varying from 0.28 mass% to 1.68 mass%.

Figure 2 shows the dependence of the brazing behavior on Ti composition in Ag–Cu–Ti braze alloy. The critical Ti content was determined by the shape of the braze fillet and whether the contact angle between the braze and binder-less c-BN was an acute angle. The addition of Ti seemed to be sufficient to induce good wettability between binder-less c-BN and WC–Co, even when the Ti content was just over 0.28 mass%, which is lower than that in h-BN [32].

![Figure 2](image)

**Figure 2.** Dependence of brazing behavior on Ti content of braze alloy.

![Figure 3](image)

**Figure 3.** Elemental mapping analyses of the binder-less c-BN/Ag–Cu–0.28% Ti braze alloy/WC–Co interfaces.
Figure 3 shows the results of elemental mapping analysis of the interface between binder-less c-BN and the 0.28 mass% Ti braze. Figure 3(a) shows the enlargement of the interface between binder-less c-BN and the Ag–Cu–0.28 mass% Ti braze alloy. Figures 3(b)–(h) show the distributions of B, N, Ag, Cu, Ti, O, and C, respectively, near the interface in the same area of (a). From these distributions of the elements, an accumulation and continuous layer of Ti near the interface between binder-less c-BN and the Ag–Cu–0.28 mass% Ti braze alloy were observed. Besides, O was not detected at the interface. Moreover, an accumulation and continuous layer of Ti near the interface between the Ag–Cu–0.28 mass% Ti braze alloy and WC–Co were also observed.

![Figure 3. Elemental mapping analysis of the interface between binder-less c-BN and the 0.28 mass% Ti braze alloy.](image)

**Figure 3.** Elemental mapping analysis of the interface between binder-less c-BN and the 0.28 mass% Ti braze alloy. Figures 3(b)–(h) show the distributions of B, N, Ag, Cu, Ti, O, and C, respectively, near the interface in the same area of (a).

Figure 4 shows the dependence of XRD profiles of binder-less c-BN/Ag–Cu–Ti braze alloy/WC–Co interfaces on the composition of Ti in the Ag–Cu–Ti braze alloy. All of the measurements were focused on the interface between the binder-less c-BN and the Ag–Cu–Ti braze alloy, but because the thickness of the Ag–Cu–Ti braze alloy was thinner than the diameter of the collimator (50 μm), diffraction data from the interface between the Ag–Cu–Ti braze alloy and WC–Co were also recorded simultaneously. In the XRD pattern of interfaces of the braze with 1.68 mass% of Ti, which produced a reaction layer, a peak from TiN was observed, suggesting that the reaction phase included TiN.

![Figure 4. XRD profiles of binder-less c-BN/Ag–Cu–Ti braze alloy/WC–Co interfaces.](image)

**Figure 4.** Dependence of XRD profiles of binder-less c-BN/Ag–Cu–Ti braze alloy/WC–Co interfaces on the composition of Ti in the Ag–Cu–Ti braze alloy. Owing to the thickness of the Ag–Cu–Ti braze alloy, which was lower than the diameter of the collimator (50 μm), diffraction data from the interface between the Ag–Cu–Ti braze alloy and WC–Co were also recorded simultaneously.

Figure 4 shows the dependence of XRD profiles of binder-less c-BN/Ag–Cu–Ti braze alloy/WC–Co interfaces on the composition of Ti in the Ag–Cu–Ti braze alloy. All of the measurements were focused on the interface between the binder-less c-BN and the Ag–Cu–Ti braze alloy, but because the thickness of the Ag–Cu–Ti braze alloy was thinner than the 50 μm diameter of the collimator, as shown in figure 3(a), diffraction data from the interface between the Ag–Cu–Ti braze alloy and WC–Co were also recorded simultaneously. In the XRD pattern of interfaces of the braze with 1.68 mass% of Ti, which produced a reaction layer, a peak from TiN was observed, suggesting that the reaction phase included TiN.

Figures 5(a) and (b) show the appearance of the specimen and the scanning acoustic microscopy images at the interfaces of binder-less c-BN/Ag–Cu–1.28 mass% Ti braze alloy/WC–Co, respectively. Figures 5(c) and (d) show the specimen containing the Ag–Cu–0.28 mass% Ti braze alloy. The braze alloy filled the interface between binder-less c-BN and WC–Co. Besides, a fillet existed around the binder-less c-BN block. As shown in the left side of Figure 5(a), there was a Ag–Cu–Ti braze alloy...
lump, which occasionally flowed out from the interface between binder-less c-BN and WC–Co, and its color maintained a metallic luster, which showed that there was not a large amount of titanium oxide at the surface of the braze alloy. There were no big voids where melted braze existed at the interface. Therefore, the wettability between the Ag–Cu–Ti braze alloy and binder-less c-BN, and that between the braze alloy and WC–Co appeared to be good even in the specimen containing only 0.28 mass% Ti in the braze alloy. As shown in the left center area of figure 5(d), there was a dense contrast region. To investigate this area, cross-sectional observations were performed. As seen in figure 3(a), significant gaps at the interface between binder-less c-BN and the Ag–Cu–0.28 mass%Ti braze were not observed, so the dense contrast region was presumed to be a ghost reflection.

4. Discussion
As shown in figure 2, the wettability between binder-less c-BN and WC–Co was relatively satisfactory compared to that between h-BN and WC–Co, even with a small Ti content of 0.28 mass% in the braze alloy. Similar to the case of h-BN [32], the contact angle between c-BN and the Ag–Cu braze alloy without Ti was presumed to indicate non-wetting [6]. Judging from the fact that the addition of as little as 0.28 mass% Ti appeared to be sufficient to induce good wettability between binder-less c-BN and WC–Co, the critical Ti content must exist between 0 and 0.28 mass%.

Figure 3 shows that the distribution of N was decreased sharply at the interface. Meanwhile, an accumulation of Ti near the interface was observed for the specimen containing the braze alloy with a small Ti content of 0.28 mass%. As shown in figures 3(f) and (g), the distribution of oxygen at the interface was lower than the detection limit of the electron probe micro-analyzer. Thus, it is concluded that oxidation of Ti at the interface was not observed at least mesoscopically despite the easily oxidizable property of Ti [33]. Also, at the interface between the braze alloy and WC–Co, accumulations of Ti and C near the interface were observed, as shown in figures 3(f) and (h). Therefore, it is believed that Ti reacted with C in WC–Co [34], and a continuous reaction layer was formed at the interface between the braze alloy and WC–Co. These results agree with a similar
tendency shown in an earlier study [12]. These results suggest the formation of a reacted layer such as that of Ti-N [6,12] or Ti-C [34] even in the case when the braze contained 0.28 mass% Ti. In the fabrication process of the Ag–Cu–Ti braze alloy, an intermetallic compound phase such as Cu₅Ti [35] is produced during melting of the raw materials, and it increases the hardness of the braze with increasing Ti content. From the point of view of cutting and forming of sheet-type braze alloys, it is preferable that the Ti content remains small because this intermetallic phase is hard. The results of this study show our capability to reduce Ti content below 0.3 mass% in Ag–Cu–Ti for brazing c-BN.

Compared to the case using h-BN [12], the configuration of the interface between binder-less c-BN and WC–Co was flat and its thickness was uniform, as shown in figure 3. These differences appeared to originate from the crystal grain shape and the sinterability. In case of c-BN, its grains are fine and granular, and it has a dense body [14]. On the contrary, the grains of h-BN are plate-like and the relative density of h-BN is low because of its low sinterability. The wettability of the Ag–Cu–Ti braze alloy against ceramics was good and it could fill up open pores at the surface, even in the case of h-BN [12,35]. Therefore, when binder-less c-BN was used, which has a low specific surface area, the amount of material in the reaction layer could be reduced compared to the case of h-BN [12].

From figure 4, a peak from TiN [2,6,10] was observed only for the specimen containing 1.68 mass% of Ti in the braze. This XRD peak is believed to have originated from the reacted phase at the interface. Besides, the standard free energies of the formation of nitrides [33], namely TiN and BN at 1173 K, are about -220 and -150 kJ/g mol N₂, respectively, which suggest that TiN is more stable than BN in all temperature ranges. In our study, TiN was observed only in the specimen containing 1.68 mass% of Ti in the braze because the amount of TiN was relatively small owing to the decrease in Ti content in the braze containing 1.28 mass% of Ti. Meanwhile, the formation of the Ti–N reaction layer was observed, as shown in figure 3(f), even in the specimen using the braze containing 0.28 mass% Ti. Therefore, a small Ti–N layer, which did not show metallic compound peaks in the XRD profile, could improve the wettability between binder-less c-BN and WC–Co in the Ag–Cu braze.

In both figure 5(b) and (d), there were no big voids at the interface, which indicate that the wettabilities between the Ag–Cu–Ti braze alloy containing 0.28 mass% Ti and binder-less c-BN, and also between the braze alloy and WC–Co were the same as the wettability shown by the braze alloy containing 0.28 mass% Ti. Furthermore, the configuration of the fillet in figure 5(d) indicates good wettability.

5. Conclusions

Dissimilar laser brazing of binder-less cubic boron nitride and tungsten carbide was accomplished. The dependence of the brazing behavior on the composition of Ti in the braze alloy can be summarized as follows:

1) At the interface between binder-less c-BN and the Ag–Cu–Ti braze alloy, an accumulation of Ti near the 1 μm wide interface was observed for the braze containing 0.28 mass% Ti. A distribution of N was also observed in the same area. It was presumed that the reacted phase existed near the interface between binder-less c-BN and the braze.

2) The wettability of these brazes by binder-less c-BN was also considered to be good. No large voids or cracks in the braze area were detected in non-destructive observation of the interface using scanning acoustic microscopy, even when the Ti content in the braze was 0.28 mass%.

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