Laser Brazing of a Hexagonal Boron Nitride Block to a Cemented Carbide Plate with Silver–Copper–Titanium Alloy Filler in Argon Atmosphere Including Different Oxygen Contents

by Yoshihisa Sechi **, Kimiaki Nagatsuka***, Takahiro Fujimoto****, Masahiro Tsukamoto*** and Kazuhiro Nakata***

Relationship between oxidation of Ag–Cu–Ti braze alloy and oxygen contents was investigated in the laser brazing of a hexagonal boron nitride block to cemented carbide plate in Ar atmosphere. The laser brazing was conducted in Ar-flow atmosphere in a vacuum chamber, and changing Ar-flow rate with and without pre-evacuation. No oxidation of the braze alloy was found after 3-min Ar-flow atmosphere over 5 L/min without pre-evacuation and at 5 L/min with pre-evacuation. When the Ar flow rate increased to 10 L/min without pre-evacuation, the oxygen content decreased to 3.8 ppm. In this case, the average shear strength of the brazed joint was about 8 MPa and a fracture occurred at the hexagonal, boron nitride side of the specimen, near the interface.

Key Words: Laser Brazing, Hexagonal boron nitride, Cemented carbide, Titanium, Heating atmosphere, Oxygen content

1. Introduction

The brazing process is used in many industrial fields for developing engineering structures and electronic devices1-13). This process has several advantages making it suitable for use in joining dissimilar materials precisely. Further, this process can be efficiently applied to the mass production of structures and devices. For applications involving ceramic materials, it is often required that ceramic materials be bonded to metals. Moreover, the development of high-functionality products in recent years, such as single crystal diamond tools for specular cutting lens molds for smartphones, has led to a demand for a new joining process that can join different materials. However, certain problems are encountered while meeting the above requirement. These include the formation of joint defects due to thermal stress in the joint field, and material deterioration, such as the graphitization of diamond, due to the long heating period during the conventional brazing.

Boron nitride has various functional characteristics. Hexagonal boron nitride (h–BN), especially, has a good thermal resistibility and solid-lubrication14). However, it is difficult to braze h–BN to another material because of its low wettability. Because the wettability of a material affects joining characteristics, it is speculated that brazing of h–BN ceramics, which has a difficulty to connect to braze alloys, may be suitable to demonstrate the brazing processes of dissimilar materials, such as ceramics and metals, especially in the development of laser brazing processes. 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 interface15). Cemented carbide/cobalt alloy (WC–Co) made by powder metallurgy has a low thermal expansion coefficient and high rigidity, making it suitable for use as a counter structural material. However, only a few reports have focused on the joining of h–BN and cemented carbide alloys or other metals2, 5, 8) by brazing in a furnace with a long heating time.

Among different brazing processes16), laser brazing10, 11, 13) has good characteristics for use as a dissimilar joining process in comparison with conventional furnace brazing8, 12) because of advantages such as a short heating time, small heating area, suppression of damage to the base materials, and not requiring a furnace. Therefore, we tried to develop a laser brazing process of ceramics and metals that can be carried out using simple equipment, and an easy system of controlling the atmosphere in a short heating time, without expensive equipment such as a high-vacuum system.

On the other hand, the characteristics of active elements, such as titanium, in braze materials are affected by the residual oxygen content present in the atmosphere during laser brazing of dissimilar materials. Nevertheless, only a few researchers have focused on this topic17, 18).

In this study, we describe the effect of residual oxygen content in an Ar atmosphere on laser brazing of h–BN and WC–Co using silver–copper–titanium (Ag–Cu–Ti) alloy braze alloys. In order to investigate the characteristics of dissimilar joints, structural
analyses of joint interfaces, evaluation of the adhesion, and shear strength measurements were performed.

2. Experimental procedure

Commercially available, ISO K10 grade WC–Co equivalent material, and high-purity h–BN made by the hot pressing method without using sintering additives, were used in this work as shown in Table 1. The sizes of the WC–Co material and the h–BN were 10 mm × 10 mm × 2 mm and 5 mm × 5 mm × 3.5 mm, respectively. Mass %: 70.26 Ag – 28.06 Cu – 1.68. 0.1 mm-thick Ti braze alloys, with Ti as the active component, were prepared for carrying out direct brazing of WC–Co and h–BN.

A braze sheet was sandwiched between an h–BN block from the top and a WC–Co plate below, in a vacuum chamber with a 100 mm diameter and an inner volume 145 mL, as shown in Fig. 1. The top side of the specimen was covered with a transparent quartz glass plate, which also keep the specimen in place.

Figure 2 shows the process sequence of sample making. In some case of including pre-evacuation process, the vacuum chamber was evacuated to less than 10⁻¹ Pa using a rotary pump after samples had been loaded, and substitution to the atmospheric pressure with 99.999% Ar gas completed after the pre-evacuation. These pre-evacuation and substitution cycles were carried out at least three times before brazing. In all cases, Ar gas continued to flow during brazing. For the processes in an Ar gas pre-flow atmosphere without a pre-evacuation process, different pre-flow rates of Ar were tested. The residual oxygen content in the vacuum chamber was measured by an O₂ analyzer (Yokogawa Electric Co., OX400).

The laser brazing conditions are summarized in Table 2.

![Fig. 1] Schematic diagram of laser brazing.

### Table 1. Materials used in this work.

| Material       | Nominal composition (mass %) | Density ($10^3$ kg / m³) | Relative Density (%) | Size (mm) |
|----------------|------------------------------|--------------------------|----------------------|-----------|
| Cemented Carbide | WC: 94, Co: 6               | 14.9                     | -                    | 10*10*2   |
| h-BN           | 99.99                     | 1.9                      | 82.5                 | 5*5*3.5   |

### Table 2 Laser brazing conditions.

| Condition                  | 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)         |                 |
| (1st run)                    | 0.6             |
| (2nd run)                    | 1.0             |
| (3rd run)                    | 1.0             |
| (4th run)                    | 1.0             |

![Fig. 3] Laser beam profile of pulsed YAG and CW LD hybrid laser used in this work.

![Fig. 4] Bottom temperature profiles of WC–Co plates during laser brazing.

![Fig. 5] Schematic diagram of a shear strength test.
generated YAG and LD lasers were transferred with an optical fiber to the laser head unit, and radiated through the transparent quartz glass plate to the top side of the WC–Co plate, with a radiation angle of 85°. Figure 3 shows the laser beam profile. The diameter of the defocused beam is about 1.63 mm which is suitable for heating. The laser was scanned on the WC–Co and around the h–BN block after 3 minutes of Ar pre-flow in order to reduce to the residual oxygen content. Scanning speed of the laser was determined in order to heat the specimen efficiently.

Figure 4 shows the typical profile of the bottom temperature of the WC–Co plate during laser brazing using a thermocouple. The increase of temperature continued in approximate proportion to the gradient until irradiation of the laser on the 4th run. The maximum bottom temperature of the WC-Co alloy in this case was about 70 K lower than that of the case at the Ar gas flow rate of 5 L/min with pre-evacuation because of the difference of Ar flow rate, but both temperature profiles showed a similar trend. In all cases, the braze alloys were melted on the 4th run of the scanning laser radiation12, 19).

Interfacial observation and estimation of 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. 5, and stressed to destruction in a precision universal tester (Shimadzu Cooperation Autograph, AGS-SkNB) operating at a crosshead speed of 0.5 mm/min. In order to compensate the effect of interfacial area on the shear strength test, shear strength was calculated from the maximum load divided by the interface area, estimated from scanning acoustic microscopy, and then its average shear strength was calculated using the Weibull distribution function20). In this paper, the median rank method21) was used for computing cumulative failure probability because of its good reliability despite the small number of samples. Some of the samples were subsequently cross sectioned by the ultrasonic processing machine with water cooling and mounted by epoxy resin, curing at room temperature for about 8–10 hours, grinded by diamond grinding disks, and finally polished by a 3 mm–1 mm polycrystalline diamond to provide microstructural information using an electron probe micro-analyzer (JEOL Co. Ltd. JXA-8230).

3. Result and discussion

Figure 6 shows the oxygen content in the vacuum chamber during the pre-flow of Ar. Oxygen content decreased in each condition as the pre-flow time progressed. This tendency is explained by the continuous stirred tank reactor model22).

After 3 minutes of Ar pre-flow, the oxygen content in the vacuum chamber varied from 33 ppm to 1.8 ppm according to the flow rate of Ar. In this range, the oxidation behavior of braze changed due to the oxygen content. Therefore, this pre-flow time was used to examine the influence of oxidation behavior of braze...
in this study. When the Ar flow rate was 1 – 3 L/min without pre-evacuation, tendencies of oxygen content were similar in spite of the initial variation in oxygen content that originated from discrepancies in manual bulb operation. On the contrary, for 4 – 10 L/min Ar flow rates, the oxygen content reduced according to the flow rate of Ar. This result shows that there is a threshold of the pre-flow rate of Ar for decreasing residual oxygen content. This tendency might originate from the low relative density of h–BN, which has many open pores and a relatively large surface area. Therefore, it is considered that adsorbed oxygen on the surface of h–BN could not be removed effectively during a low Ar flow rate.

At an Ar flow rate of 1 L/min without pre-evacuation, the oxygen content was 33 ppm after 3 minutes of the onset of laser brazing. This residual oxygen level is higher than the upper limit of the Nocolok flux brazing condition, which is 20 ppm for Aluminum using a conventional furnace. At 5 L/min of Ar flow without pre-evacuation, the oxygen content was 10 ppm after 3 minutes of the onset of laser brazing. On the contrary, with pre-evacuation process, oxygen content was 1.8 ppm, which was 5 times lower than that without pre-evacuation. For the increased Ar flow rate of 10 L/min without pre-evacuation, oxygen content decreased to 3.8 ppm, which was closer to that observed during 5 L/min of Ar flow with pre-evacuation.

According to appearances of the specimens in Fig. 7, during 1 L/min Ar flow rate without pre-evacuation, the surface of the braze lump which flowed out of the interface was oxidized. On the contrary, in cases of 10 L/min of Ar flow rate without pre-evacuation, 5 L/min of Ar flow rate without pre-evacuation and 5 L/min with pre-evacuation, surfaces of braze lumps which flowed out of the interfaces were not oxidized.

These results are related to the oxygen contents of the brazing atmosphere in Fig. 6, and the upper limit of the Nocolok flux brazing condition, which is about 20 to 25 ppm. Nocolok flux brazing is the brazing method of aluminum in N₂. In Ellingham diagrams of oxides, aluminum is more likely to be oxidized than titanium in all temperature ranges. Consequently, it is considered that the oxygen content of 3.8 ppm in Ar atmosphere was lower than that of the upper limit of the Nocolok flux brazing condition, as shown in Fig. 7 b). In the case that the oxygen content of 33 ppm in Ar atmosphere, as shown in Fig. 7 a), the surface of the braze lump which flowed out of the interface was oxidized. Although the temperatures and brazing times of this research are different from the Nocolok flux brazing conditions, these results show that laser brazing of ceramics and metals using active metal braze alloys, have similar tendencies. They are also easy to oxidize like the aluminum alloys undergoing Nocolok flux brazing, depending on the oxygen content of the brazing atmosphere.

Figure 8 shows cross-sectional SEM observations of an edge of the h–BN / Ag–Cu–Ti braze alloy interface and its map analysis using electron probe micro-analysis for 10 L/min Ar flow rate without pre-evacuation. In a), the upper left area is h–BN as indicated, the lower whitish area shows the Ag–Cu–Ti braze alloy, and the upper right area is epoxy resin, which is used to mount the specimen. The resin side of the Ag–Cu–Ti braze alloy corresponds to the surface of the melted braze alloy, which overflowed from the h–BN / WC–Co interface and was exposed to the Ar atmosphere which included residual oxygen. In b), the distribution of oxygen was limited to the epoxy resin area and was not observed in the Ag–Cu–Ti braze alloy. In c) and f), the distributions of silver and copper were the same as that of the braze alloy area. The distribution of titanium is shown in d). In e), the distribution of nitrogen is the same as that of the h–BN area. In d), most of the titanium exists at the interface between the h–BN and the Ag–Cu–Ti braze alloy, and the overlap of the distribution of nitrogen and titanium is observed, which suggests the formation of a reacted layer of intermetallic Ti–N compound and that the rest of the titanium was in the bulk of the braze alloy which overlapped with the concentration of copper shown in f). From b) and d), it can be seen that the distributions of oxygen and titanium do not overlap. This was apparently due to the existence of the space between the Ag–Cu–Ti braze alloy and the resin. This result shows that the oxidation layer was not observed at the surface of the melted braze alloy for the 10 L/min Ar flow rate without pre-evacuation.

In a former study, with oxygen content of 3 ppm in Ar atmosphere using a long time heating, there was weight gain of the braze alloy due to oxidation. In this study, the braze alloy was not oxidized as shown in Fig. 8 with oxygen content of 3.8 ppm in Ar atmosphere. This difference seems to be due to exposure to high temperatures for extended durations. During laser brazing, the exposure time at high temperatures for braze alloy sheets was limited to a few seconds, which was much shorter than that for furnace brazing.

A non-destructive test using scanning acoustic microscopy was performed to evaluate how the melted braze alloy spread at the interface between the h–BN and WC–Co plates. For the process in a 10 L/min Ar flow rate without pre-evacuation, there were no big voids in the central black areas where melted braze existed at the joint interface.

In this case, the average shear strength of the brazed joint was about 8 MPa and the fracture occurred on the h–BN side of the specimen, near the interface. For the process in a 5 L/min Ar gas flow atmosphere after the pre-evacuation processes, the average shear strength was about 6.5 MPa. The difference of the shear
strength tests are in the range of dispersion. Comparing these results, it revealed that laser brazing with Ag–Cu–Ti braze alloys could be performed even in an Ar gas flow atmosphere without pre-evacuation processes using high vacuum equipment.

4. Conclusions

(1) The oxidation of titanium as an active element in a braze alloy was observed at an oxygen content of 33 ppm in a brazing atmosphere at an Ar flow rate of 5 L/min without pre-evacuation.

(2) The oxidation of titanium as an active element in a braze alloy was not observed at an oxygen content of 10 ppm in a brazing atmosphere at an Ar flow rate of 5 L/min without pre-evacuation.

(3) On increasing the Ar pre-flow rate to 10 L/min without pre-evacuation, the oxygen content in the vacuum chamber decreased to 3.8 ppm, and in this case, the oxidation of titanium was not observed. The brazed joint was about 8 MPa and the fracture occurred on the h–BN side of the specimen, near the interface.

(4) Results of the shear strength test of the brazed joint suggest that this brazing joint has enough strength to connect h–BN and WC–Co using Ag–Cu–Ti braze alloys in an Ar gas flow atmosphere without a pre-evacuation process.

Acknowledgements

This work was supported by the Joint Research System of the Joining and Welding Research Institute, Osaka University. The authors would like to thank Tanaka Kikinzoku Kogyo K.K. for their assistance and supplying the Ag–Cu–Ti braze alloys. The authors would also like to express their gratitude to the Amada foundation for financial support.

References

1) Y. Nakao, K. Nishimoto and K. Saida: Bonding of Si₃N₄ to metals with active filler metals, Trans. JWS, 20 (1989), 66-76.
2) 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.
3) Y. Nakao, K. Nishimoto and K. Saida: Reaction layer formation in nitride ceramics to metal joints bonded with active filler metals, ISIJ Int., 30 (1990), 1142-1150.
4) M. Murakawa and S. Takeuchi: Forming of a grinding wheel using a dresser with brazed diamond film, Mater. Sci. Eng. A, 140 (1991), 759-763.
5) A. K. Chattopadhyay and H. E. Hintermann: On brazing of cubic boron nitride abrasive crystals to steel substrate with alloys containing Cr or Ti, J. Mat. Sci., 28 (1993), 5887-593.
6) S. D. Petes: Joining nitride ceramics. Ceram. Int., 22 (1996), 527-533.
7) A. J. S. Fernandes, M. J. Fonseca, F. M. Costa, R. F. Silva and M. H. Nazare: Ultramicrohardness cross-profiling of CVD diamond/steel brazed junctions, Dia. Rel. Mat., 8 (1999), 855-858.
8) J. Felba, K. P. Friedel, P. Krull, I. L. Pobol and H. Wohlfahrt: Electron beam activated brazing of cubic boron nitride to tungsten carbide cutting tools, Vac., 62 (2001), 171-180.
9) S. F. Huang, H. L. Tsai and S. T. Lin: Effects of brazing route and brazing alloy on the interfacial structure between diamond and bonding matrix, Mater. Chem. Phys., 84 (2004), 251-258.
10) Y. Sechi, A. Takezaki, T. Tsumura and K. Nakata: Dissimilar laser brazing of boron nitride and tungsten carbide, Smart Process Tech., 2 (2008), 27-30.
11) M. Rohde, I. Sündmeyer, A. Urbanek and M. Torge: Joining of alumina and steel by a laser supported brazing process, Ceram. Int., 35 (2009), 333-337.
12) Y. Sechi, T. Tsumura and K. Nakata: Dissimilar laser brazing of boron nitride and tungsten carbide, Mater. Des., 31 (2010), 2071-2077.
13) I. Sündmeyer, T. Hettesheimer and M. Rohde: On the shear strength of laser brazed SiC–steel joints: Effects of braze metal fillers and surface patterning, Ceram. Int., 36 (2010), 1083-1090.
14) R. H. Biddulph: Boride and carbide ceramics - the systems. Proceedings of the 1st European Symposium on Engineering Ceramics, Proc. 1st Euro. Symp. Eng. Ceram., (1985), 45-61.
15) W. Wlosinski: Interfaces in dissimilar materials joints, Fueg. Keram. Gla. Met., (1985), 22-36.
16) C. L. Jenney, O'Brien: A Welding Handbook Vol. I. (American Welding Society), (2001).
17) R. R. Kapoor and T. W. Eager: Oxidation behavior of silver- and copper-based brazing filler metals for silicon nitride/metal Joints, J. Am. Ceram. Soc., 72 (1989), 448-454.
18) A. J. Moorhead and H. Kim: Oxidation behaviour of titanium-containing brazing filler metals, J. Mater. Sci., 26 (1991), 4067-4075.
19) Y. Sechi, K. Nagatsuka and K. Nakata: Dissimilar laser brazing of h-BN and WC–Co alloy in Ar atmosphere without evacuation process, J. Phys. Conf. Ser., 379 (2012), 012048.
20) W. Weibull: A statistical distribution function of wide applicability, J. Appl. Mech., 18 (1951), 293-297.
21) P. Stanley, H. Fessler and A. D. Sivill: An engineer’s approach to the prediction of failure probability in brittle components, Proc. Brit. Ceram. soc., 22 (1973), 453-487.
22) N. Fukuchi and J. Suhara: The Gas Concentration during Gas Purging in Oil Tank (1st Report), J. Soc. Nav. Arch. Japan, 1978 (1978), 296-302.
23) M. Komura, T. Yoshikawa and K. Matsumoto: Decrease of oxygen concentration in Nocolok flux brazing Furnace for aluminum heat exchanger, Bull. Inst. Tech., 3 (2012), 31-37.
24) K. Kanda, K. Watanabe and Y. Yanagawa: JP Patent 5845189.
25) J. F. Elliott and M. Gleiser: Thermochemistry for Steelmaking, Vol. I (1960), Addison-Wesley.