# Interfacial Reaction between Cubic Boron Nitride and Ti During Active Brazing

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Thermodynamic and reaction process analyses were performed to understand the joining characteristic during high temperature brazing between cubic boron nitride (CBN) grit and a silver-base filler alloy containing Ti as an active element. Experimental information on the microstructure of the brazed joint, the composition of the interface, and the shape of the compounds formed on the surface of the grit was obtained by scanning electron microscopy, energy-dispersive x-ray, and x-ray diffraction. The results indicate that Ti in the molten filler alloy facilitated good wetting between the solid CBN crystals and braze filler alloy. The transition layer formed by the interaction of TiN and $TiB_2$ was one of the key factors in joining the CBN and steel substrate.

## 1. Introduction

In recent years, the introduction of super-abrasive materials, including cubic boron nitride (CBN) grits, in the grinding industry have resulted in improvements both in the productivity of the process and in the quality (in terms of better surface integrity and tighter tolerance) of the ground parts. Superabrasive grinding opens new fields and applications, but new problems have also arisen (Ref 1). It has been revealed that the performance of the current generation of electroplated grinding wheels with CBN grits can be strongly influenced by the joining strength between the grits and the bonding layer. Accordingly, a method to achieve the highest joining strength has been the focus of current study. In comparison to conventional electroplated tools, better grit retention, joint uniformity, and crystal exposure are the most important features of brazed CBN tools due to the joining ability between the grit, braze material, and metal substrate as a result of their chemical affinity. Thus, the performance of the brazed tools can be improved greatly, and the service life of the tools can be prolonged (Ref 2-4).

Previous research on the dependence of mechanical properties on the brazing parameters of CBN tools has been published. The mechanism of the brazing process, however, is not as clear because it is composed of complex steps: dissolution of substrate, diffusion of elements, formation of reaction products, and wetting phenomena. Furthermore, these phenomena, which occur in a very small area, are difficult to observe (Ref 5, 6). Therefore, to fully understand the brazing process of CBN grits, in the present work, the brazing behavior of CBN on steel was examined using a Ag-Cu eutectic filler alloy containing Ti as an active element. An attempt has been made to analyze the mechanism of wetting and bonding at the interface between the CBN and filler alloy during brazing, which had not been extensively investigated prior to this work.

## 2. Experimental

The CBN grits used in this investigation were CBN abrasive grains 40/50 μm in size (425/300 mesh). The base metal was commercial 45# steel, and the braze alloy was Ag-Cu-Ti powder. Prior to brazing, the surfaces of all materials to be brazed were polished mechanically and thoroughly cleaned. Then the active braze alloy powder and CBN grits were spread on top of the metallic substrate (Fig. 1). Finally, brazing was carried out in a vacuum chamber equipped with a heating system. The thermal cycle was carefully selected to ensure that the interface formed during brazing would be of an appropriate structure to secure good mechanical properties and resistance to thermal shock (Ref 6).

The specimens were cut across the interface between the CBN grits and the filler alloy, then finely polished and etched for microscopic evaluation. Scanning electron microscopy (SEM) coupled with energy dispersive x-ray spectroscopy (EDX), as well x-ray diffraction (XRD; Cu $K_\alpha$ = 0.1541 nm), were used to characterize the joints.

## 3. Results and Discussion

### 3.1 Thermodynamic Analysis of the Reaction between CBN and Filler Alloy

Difficulty in joining CBN grits to metal may arise as a result of their difference in interatomic bonding and physical properties. The low surface tension of the CBN crystal makes it unlikely that many molten metals will satisfy the wetting condition for a reaction to take place at the interface. For this reason, wetting is one of the key problems during brazing of CBN. According to the nature of attractive forces existing across the interface, wetting can be classified into two broad categories: physical wetting (nonreaction system), where the reversible physical forces such as the Van der Waals and dis-

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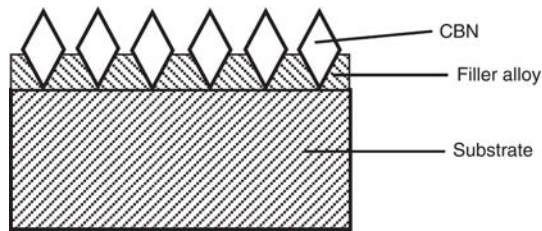
**Fig. 1** Schematic representation of the braze specimen showing CBN, filler alloy, and substrate



**Fig. 2** Changes in molar Gibbs free energy $\Delta G_T$ for reactions 1-4

persion forces provide the attractive energy required to wet the surface; and chemical wetting (reaction system), where a reaction occurs between the mating surfaces and the resulting chemical bonds are responsible for wetting (Ref 7-9). An active element, such as Ti, plays an important role in the braze filler alloy for chemical wetting behavior due to the aforementioned factors. First, the active element can reduce the surface tension between the molten braze filler alloy, CBN grits, and vapor phase. Second, the active element can react with the CBN at the interface. The current study also examines metalloid compounds that may form by chemical reactions at the interface of the CBN and Ag-Cu eutectic with Ti.

First of all, the basic cause of the occurrence of wetting is often analyzed from the viewpoint of thermodynamics. A simplistic way to model the system is by conventional thermodynamics whereby wetting is energetically possible whenever the molar Gibbs free energy change ($\Delta G_T$) for the reaction at the interface is negative (Ref 10). In the case of joining CBN to a steel substrate using Ag-Cu-Ti filler alloy, when the CBN is in contact with molten Ti, the following reactions may occur at the brazing temperature:

$$BN_{(s)} + [Ti]_{(1)} = TiN_{(s)} + [B]_{(s)} \qquad (Eq\ 1)$$

$$[Ti]_{(1)} + [B]_{(s)} = TiB_{(s)} \qquad (Eq\ 2)$$

$$3[Ti]_{(1)} + 4[B]_{(s)} = Ti_3B_{4(s)} \qquad (Eq\ 3)$$

$$[Ti]_{(1)} + 2[B]_{(s)} = TiB_{2(s)} \qquad (Eq\ 4)$$

In the literature (Ref 11, 12), the dependence of the molar Gibbs reaction energy for the four equations as a function of temperature have been reported as follows:

$$\Delta G_T(1) = -83.1 + 0.0032T \text{ (kJ/mol)}$$

$$\Delta G_T(2) = -166.5 + 0.004T \text{ (kJ/mol)}$$

$$\Delta G_T(3) = -211.7 + 0.0072T \text{ (kJ/mol)}$$

$$\Delta G_T(4) = -282.5 + 0.0153T \text{ (kJ/mol)}$$

Figure 2 shows the corresponding curves of the molar Gibbs reaction energy for the above equations from 800 to 1200 K. As can be seen for temperatures between 900 and 1200 K, the change in value of the molar Gibbs reaction energy (as the driving force for the reaction during brazing) is strongly negative. The results of thermodynamic calculations indicate that the reactive activities mentioned above are applicable. On the other hand, besides TiN, $TiB_2$ is easier, theoretically, to form
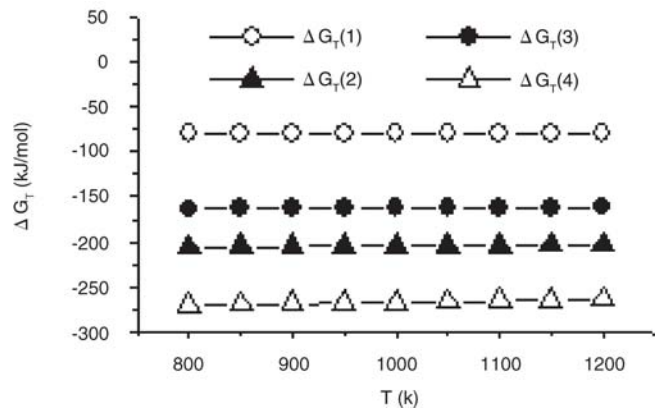
than the other Ti-boride phases, i.e., TiB and $Ti_3B_4$, because $TiB_2$ possesses the lowest $\Delta G_T$.

### 3.2 Microstructure of the Reaction Layer between CBN and Filler Alloy

Figure 3(a) is the SEM photograph of the interface between CBN and braze filler alloy. A typical linear distribution of elements in the brazed joints is also shown in Fig. 3(b). It is obvious that the composition in the interface layer is inhomogeneous. Titanium has diffused markedly from its initial position in the molten brazing alloy to the CBN/filler alloy interface. Furthermore, B and N have moved into the filler alloy layer. The diffusion distance of B is also longer than N. Meanwhile, microsegregation has occurred in the Ag-Cu eutectic microstructure though the original filler alloy is uniform. The good wetting and interfacial reaction indicates that the Ag-Cu-Ti filler can be successfully used to join the CBN/45# steel couple.

Figure 4 is the representative general SEM micrograph of the etched brazed CBN grit. Reaction products, which are composed of rodlike crystals, are found around the periphery of the grit, as shown in Fig. 5. The relevant compositions of the compounds are displayed in Table 1. XRD was also performed on the etched brazed CBN, and the results are shown in Fig. 6. Apparently, the main peaks come from the braze alloy, CBN, and reaction products (TiN and $TiB_2$). $Ti_3B_4$ and TiB were not detected in the reaction products of the CBN grits or Ag-Cu-Ti braze alloy. The characteristics of one-dimension elongated morphology of reaction products are not obvious because of the interaction of TiN and $TiB_2$ in the growth process.

X-ray photoelectron spectroscopy (XPS) of the CBN and Ag-Cu-Ti alloy interface has verified that the morphology of the reaction layer at CBN/filler alloy interface consisted of two layers. This observation is consistent with the previous research on the brazing of silicon nitride and a filler alloy containing Ti (Ref 9). The layer adjacent to the CBN (inner layer about 2 μm thick) was expected to be composed mainly of TiN. The other layer between the inner layer and filler alloy (outer layer: about 8 μm thick) was composed of TiN and $TiB_2$.

Combined with the high hardness of TiN and great toughness of $TiB_2$, a composite material layer was formed during brazing that possessed excellent physicochemical and mechanical properties (Ref 13, 14). Additionally, the filler alloy also works as a buffer layer for residual stress accommodation due
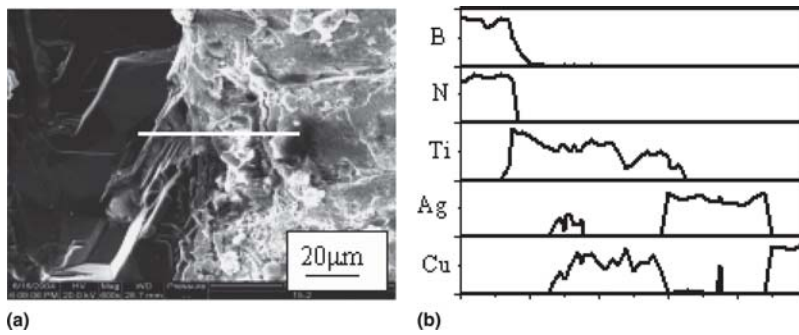
**Fig. 3** Cross section of surface of the CBN/filler alloy brazed joint: (a) SEM micrograph and (b) elemental analysis



**Fig. 4** General micrograph showing the brazed CBN crystal



**Fig. 5** SEM micrograph of compounds found in the brazed CBN crystal

**Table 1 EDX analyses of various compounds**
See Fig. 3; mole fraction, %

| Point | Chemical composition, at.% | | |
| --- | --- | --- | --- |
| | **Ti** | **B** | **N** |
| A | 75.92 | 0 | 24.08 |
| B | 60.55 | 0 | 39.45 |
| C | 87.61 | 0 | 12.39 |
| D | 45.49 | 42.74 | 11.77 |

### 3.3 Process of the Brazing Reaction between CBN and Filler Alloy

During the brazing process, the formation of a reaction layer in the wetting system was dependent on many factors: temperature, properties of the brazed parts, and the presence of Ti in the brazing powder. The presence of Ti induced the formation of a reaction layer, with the reaction layer appearing only when the critical wetting temperature was reached (Ref 9).

The results of correlative differential thermal analysis from a previous investigation have shown that two fundamental reaction stages exist during brazing of CBN using the active metal braze compound containing Ti. First, TiN, which has a face-centered cubic (fcc) crystal structure similar to pure Ti, formed gradually above 878 K. Subsequently, Ti-boride compounds with the C32 crystal structure formed above 1080 K (Ref 17). The sequence reaction events resulted, in part, from
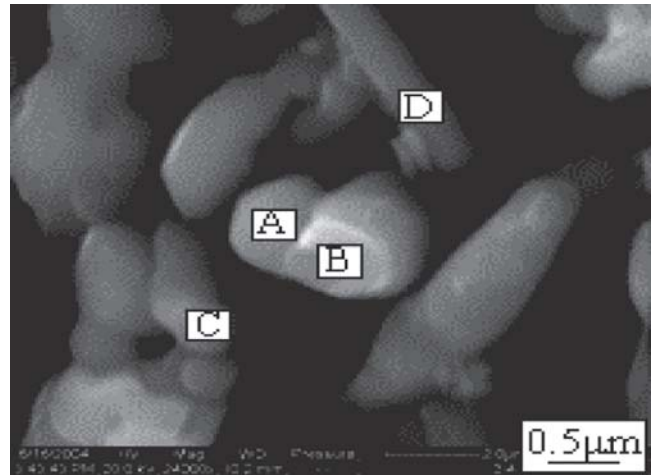
the difference in diameters of the N, B, and Ti atoms, which are 0.067, 0.097, and 0.147 nm, respectively. Diffusion and dissolution can be easily controlled at the appropriate reaction temperature to form TiN, which has a structure similar to Ti. Alternatively, B atoms diffuse into the Ti lattice, forming $TiB_2$ at 1100 K due to the larger atom radius. It is, thus, more difficult to control B atom diffusion than N atoms during brazing.

Based on the results above, the reaction process between CBN and the active element Ti in the braze alloy is illustrated in Fig. 7.

In the beginning stage, TiN is the most stable compound in all the probable chemical products in the reaction process. This was the deciding factor in the reactive system of CBN/filler alloy, and therefore, when the Ag-Cu-Ti filler began to melt, contacting the CBN crystal, Ti was dissolved in the Ag-Cu
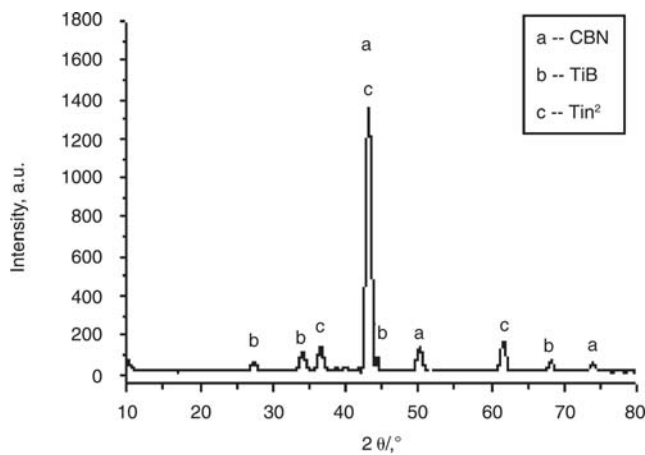
to its excellent performance (Ref 15, 16). As a result, based on the transition effect of the composite layer of TiN and $TiB_2$ with interatomic bonding characteristics compatible with both CBN and metal substrate, a good braze joint was realized and brazing residual stresses were minimized.

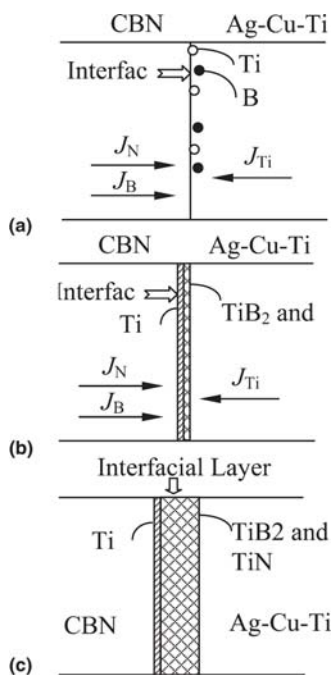**Fig. 6** XRD spectrum of the compounds on the surface of the CBN



**Fig. 7** Model of reaction process between CBN and braze filler alloy: (a) initial stage, (b) middle stage, and (c) final stage

liquid and migrated to the CBN surface. Thus, the reaction activity between Ti and N was thermodynamically preferential (Ref 17).

Because the bonding between atoms in the lacuna zone (i.e., the dislocations and growth steps in the interface) of the CBN crystal surface is not as strong as that inside the crystal, the atoms in the surface lacuna zone are in a chemically active state with high energy and can easily form new phases with the active Ti atoms. These new phases become the active center of the solid-liquid reaction between the CBN grits and the filler alloy (Ref 18, 19). The reaction at the surface of the crystal then occurs in this active center to form TiN cores, leading to the final thin Ti-nitride layer. The B atoms released from the crystal then diffuse into the filler alloy due to the concentration gradient. Moreover, because the reaction had consumed the Ti atoms at the surface, any residual active Ti atoms would try to recuperate from the decrease in activity, and hence, diffuse
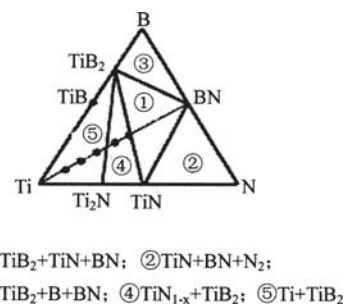


① $TiB_2 + TiN + BN$;  ② $TiN + BN + N_2$;
③ $TiB_2 + B + BN$;  ④ $TiN_{1-x} + TiB_2$;  ⑤ $Ti + TiB_2$

**Fig. 8** Ti-B-N ternary system phase diagram

quickly from the molten alloy to the requisite position in the reaction zone (Fig. 7a).

After the initial reaction, free B rejected from the CBN diffuses into the molten braze filler alloy and reacts with Ti to form Ti-borides at the interface between the TiN layer and the filler alloy according to the Eq 4 (Fig. 7b). The tie line between $TiB_2$ and TiN in the Ti-B-N phase diagram (Fig. 8) indicates that $TiB_2$ is stable in the presence of TiN, and therefore, the reaction expressed by Eq 4 was energetically possible in terms of the standard free energy change in the brazing temperature range. Accompanying the diffusion of Ti, B, and N to the requisite lattice positions, two compounds, TiN and $TiB_2$, can grow stepwise until the reaction layer is formed. The growth of the reaction layer, which obeys the parabolic growth law, was controlled by the diffusion of elements in the reaction layer (Ref 11).

Besides the reaction with Ti atoms in the region adjacent to the CBN crystal (concentration gradient effects), unreacted N atoms diffuse into the molten braze filler alloy through the layer formed in the earlier stage, producing small quantities of η Ti-rich nitride compounds (Ref 20).

When the reaction layer has enveloped the crystal, the growth of the compound layer is then controlled by the diffusion activity of the reactive atoms. The diffusion resistance force increases at this point and the activity of the Ti atoms begin to decrease to a large extent. Finally, as a result of the decrease in activity of Ti atoms due to consumption, the growth of the interfacial layer ceases. The brazing reaction is now complete, and the final reaction layer has been formed.

## 4. Conclusions

From the current study on active brazing of CBN to 45# steel using a Ag-Cu-Ti braze filler alloy, the following conclusions can be drawn.

- Thermodynamic analysis shows that besides the formation of TiN, $TiB_2$ is the most readily formed compound among the possible Ti-borides. This has been confirmed by experiment.
- A reaction model in the CBN/Ag-Cu-Ti system has been proposed. During reactive brazing, TiN and $TiB_2$ cores form as active centers on the surface of the CBN crystal. They coalesce into a continuous layer with time during brazing.
- The composite $TiB_2$-TiN layer formed during the interfacial reaction between the CBN and the braze filler metal is the key factor in achieving a good bond between CBN and steel substrate.

## Acknowledgments

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