

Relationship between X-ray diffraction and unidirectional solidification at interface between diamond and brazing filler metal

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Brazing single crystal diamonds by using silver-copper eutectic filler containing reactive metal: titanium has been carried out. Unidirectional solidification brazing method was tried to obtain stable brazed strength. The diamond specimen was cooled down by contact with copper cooling mass of which temperature was controlled at a room temperature, 470 K and 670 K, respectively. The brazing temperature was 1080 K. The brazing filler was solidified from diamond brazing surface and we called this method as unidirectional solidification brazing. The brazed specimen was examined in shear strength by an original apparatus. In the case of diamond (100), the average shear strength shows more than 120 MPa and maximum shear strength is 240 MPa. These specimens are stronger than that made by usual brazing method. After the strength test, interface orientation between the diamond and the brazing filler was investigated by X-ray diffractometer. In the case of brazing diamond (100), diamond (100) – TiC (111) – Ag (111) orientation can be detected. In the case of brazing diamond (111), diamond (111) – Cu (111) orientation can be detected. Misfits for those orientations were calculated. The value for TiC (111) // diamond (100) is 0.05016, on the other hand the value for TiC (111) // diamond (111) is 0.2125. The brazed interface of diamond (111) is more delicate for thermal stress than diamond (100). © 2000 Kluwer Academic Publishers

1. Introduction

Efficient utilization of diamond requires reliable technique of brazing it to metal for tools and jewelry. Taking account of an interaction between diamond and brazing filler, it is necessary for crystallization of the filler metal to be in order with diamond surface orientation. Unidirectional solidification brazing method using silver copper eutectic filler containing titanium have been carried out. This method is how the filler metal is solidified from diamond side. As a result, silver copper eutectic columnar structure can be observed about 10 μm in length from diamond [1]. The brazed specimens were examined in shear strength by an original apparatus. The fracture morphology of the weakest phase formed at the brazed interface could be acquired. After that, the surface orientations were investigated by X-ray diffractometer.

The X-ray analyses results were discussed with planar registry introduced by Bramfitt [2] and misfit parameter of thin film growth [3]. The planar registry is a parameter of a lattice mismatch between a nucleant and a nucleus in heterogeneous nucleation.

2. Experimental procedure

Every single crystal diamond specimen was brazed in a vacuum chamber under 2.0×10^{-3} Pa. The brazing surface was each (100), (110) and (111). The brazing areas of the diamond specimens were about 6×10^{-6} m². Surface roughness was $R_{\text{max}} = 0.05$ to $0.1 \mu\text{m}$. Thin metal plate of Fe-42Ni called 42Invar alloy was brazed to the diamond for strength test. This alloy has so small coefficient of thermal expansion as glass at 670 K that thermal stress in the diamond specimen is expected to be relaxed. The plate size was about $6 \times 65 \times 0.3$ mm.

Apparatus of unidirectional solidification brazing method is shown in Fig. 1. The brazing filler is laminated foil, where titanium flakes are sandwiched between silver-copper eutectic alloy foils. The containing ratio of titanium flakes is 4.5 wt%. The thickness of the filler is 0.1 mm. The diamond specimen (number 13) and the brazing filler (number 9) were mounted on the thin plate (number 6). The plate was directly heated by electricity supplied from the copper electrodes (numbered 7) to melt the filler.

Four thermocouples were used on this processing. The thermocouple A (number 3) inserted in the copper

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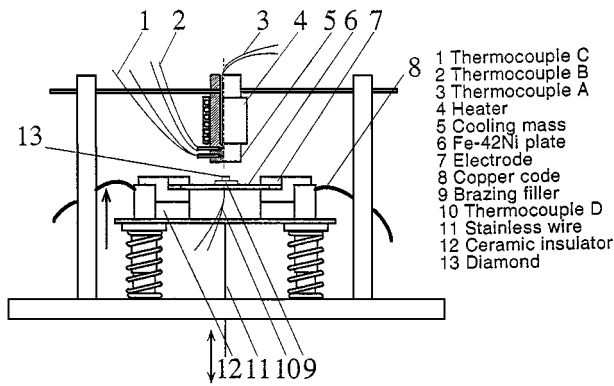


Figure 1 Unidirectional solidification brazing apparatus is composed of up and down stage, copper cooling mass and electrodes.

cooling mass (number 5) was equipped to control heating power. The cooling mass temperature was adjusted to a room temperature, 470 K and 670 K, respectively in order to change the cooling rate. The other two thermocouples of B and C (number 1 and 2) were located in the bottom of the cooling mass to measure the heat flux. The last thermocouple D (number 10) was located below the thin plate to measure the brazing temperature. The brazing temperature was 1080 K. It is 30 K above the melting point of the brazing filler. Holding time at the brazing temperature was 60 s, according to the previous study [4], where various holding time were examined and the specimens brazed for 60 s holding time showed relatively stable high bonding strength.

After the brazing filler had molten entirely, the diamond specimen was cooled down by contact with the cooling mass by going up the stage by the springs with losing the stainless wire (number 11) gradually. The brazing filler had been solidified entirely, then the thin plate was cooled down by cutting electricity.

Shear strength of the brazed interface was examined by original shear test equipment as shown in Fig. 2. Two 60 Ω strain gages were adhered to the jig on upper side and back. These gages were connected as series and connected to a bridge circuit in order to measure the fracture load with canceling the bending stress. The specimens for the strength test were manufactured by grinding as the shape shown in Fig. 2 not to measure the strength of a fillet around the diamond. The thin plate was slitted to the diamond by a grindstone of 0.3 mm in thickness. Two jigs were adhered to it as single laps.

After the strength test, the brazing filler in which the brazed interface was not separated was removed

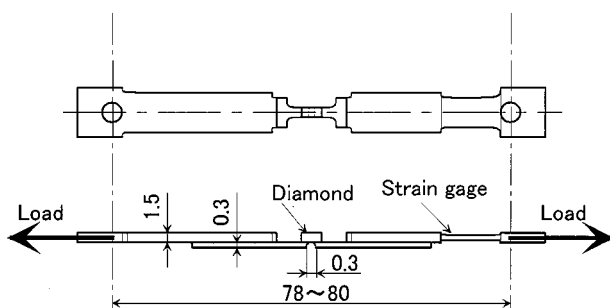


Figure 2 Original shear test jigs and specimen.

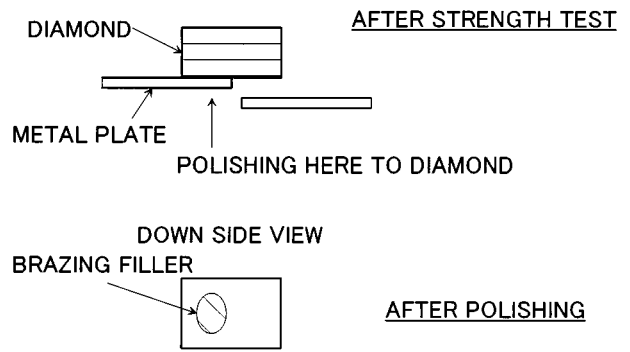


Figure 3 Process of the specimen for X-ray diffraction analysis.

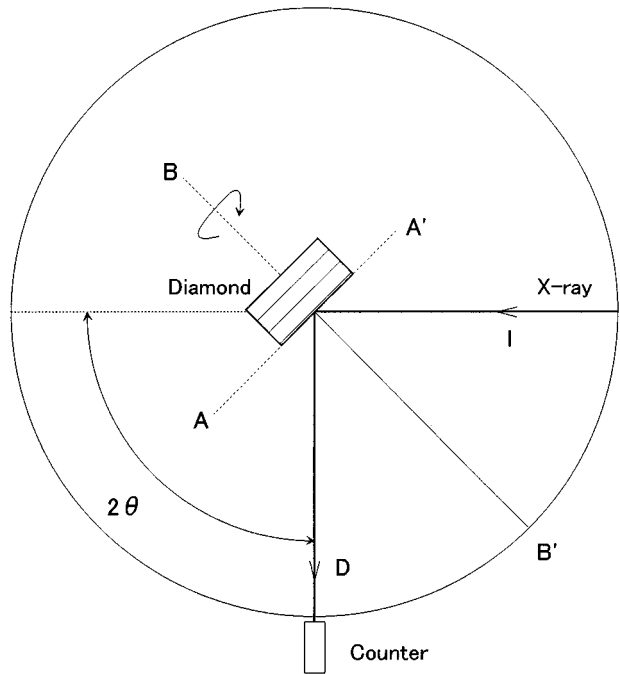


Figure 4 Schematic illustration of setting the specimen to X-ray diffractometer.

from the diamond by grinding as shown in Fig. 3. The surface of the specimen was polished parallel with the brazed interface until the reaction layer and the polished brazing filler existed on the diamond surface.

The specimen was mounted on the holder of the X-ray diffractometer on the basis of the diamond surface as shown in Fig. 4. It wasn't sent round around A-A' axis, because the cut surface of the single crystal diamond was used and fixed on the holder. It was only sent round around B-B' axis to detect the peaks for the original diamond plane. The intensity of diffracted X-ray was recorded with excluding the strong diffraction from the diamond crystal planes.

3. Results

Strength test results are presented in Table I. The marks of > in Table I mean that the bonding strength of the brazed interface is larger than the shear strength calculated from the fracture load and the brazed area. The marks of - mean that the samples are broken during producing for the strength test. The number of the data is small, because the diamond specimens are limited.

TABLE I Shear strength [MPa]

Cooling mass Temperature	Room [320 K]	470 K	670 K
Diamond (100)	>97	>140 240	130 >130 >120
Diamond (110)	79	— >160	21 140
Diamond (111)	>110	85 86 140 56	— — 120 >160

Mark of > means that bond strength is larger than shear strength. Mark of — means specimen is broken during producing.

In the case of diamond (100), average shear strength is more than 120 MPa except one datum cooled by the room temperature cooling mass. Most fracture paths were on the vertical plane in the diamond to the brazed interface. Maximum strength is 240 MPa for the sample separated at brazed interface, so the bonding strength of the brazed interface is considered to be about 240 MPa. In the case of diamond (110), the data are scattered. The strength of the most samples is under 85 MPa except two data. Fracture paths of these samples were on horizontal plane in the diamonds near the brazed interfaces. According to the two marks of — and small number of marks of >, the brazed interface is easy to crack. One sample shows more than 160 MPa. It was broken at the metal plate, so it is considered that production of the strength test specimen is not appropriate. In the case of diamond (111), one sample made by contact with the room temperature cooling mass shows more than 100 MPa. It was broken at the metal plate, so the

production of it is not good. The average data of the samples made by contact with the 470 K cooling mass show about 95 MPa. The data of the samples made by contact with the 670 K cooling mass show more than 120 MPa. The fracture paths of these samples were on horizontal plane in the diamonds near the brazed interfaces. The diamond (111) brazed interface is considered to be delicate, because the fracture path was on the horizontal plane near the interface and because the strength depends on the cooling mass temperature.

Fig. 5 shows a result of X-ray diffraction analysis and a scanning electron microscopy image of a solidified structure for a diamond (100) sample. In the case of diamond (100), the peaks of titanium carbide are only observed at the angle of TiC (111) and (222). The peak of TiC (200) was not detected for the sample, so titanium carbide crystals are formed in order. Arrows in the figure point out the peak angles of the lattice planes for standard powder specimen. Lattice space of the reaction product is the same as the standard powder specimen, because the TiC (111) peak and the TiC (222) peak are observed at the same angle of the standard specimen. Count number of the Ag (111) peak is about five times larger than the peak of Ag (200). Silver crystals are solidified in order with the TiC (111), because the standard peak of Ag (111) is about 2.5 times larger than the peak of Ag (200) for silver polycrystalline specimen. The count number of silver is much larger than that of the peaks of copper. It is suggested that the silver crystals were solidified from a lot of titanium carbide islands, and that copper crystals can not contact the diamond surface.

The scanning electron microscopy image shows the solidified structure of the brazing filler near the diamond surface. This image shows the same place XRD

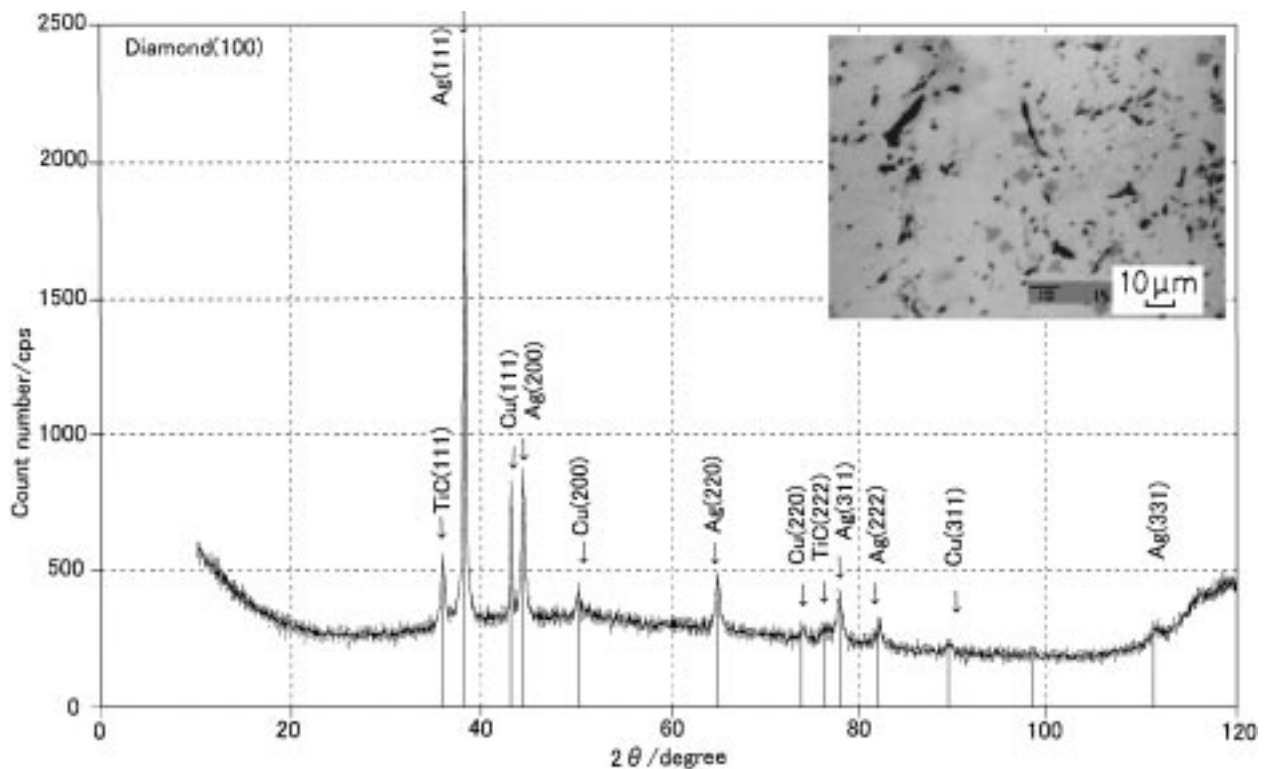


Figure 5 Result of X-ray diffraction analysis and back scattering electron image of unidirectional solidification brazed diamond (100) sample.

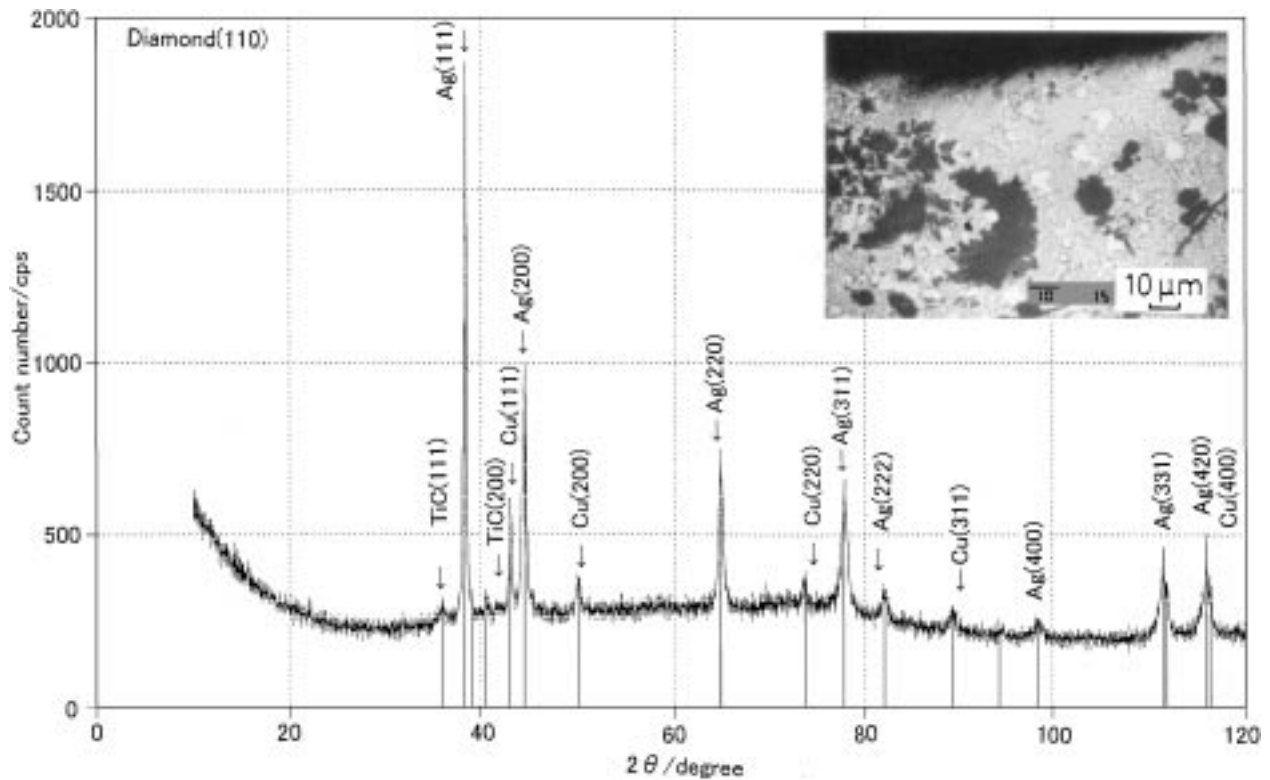


Figure 6 Result of X-ray diffraction analysis and back scattering electron image of unidirectional solidification brazed diamond (110) sample.

analyzed. Long and narrow dark parts are diamond surface. They are considered to be void of the brazing filler. Gray star like shape parts in the center of the figure are titanium carbide. White area of the background is silver. The titanium carbide stars are surrounded by silver. Eutectic structure can not to be observed. It is related to the small count number of copper by this XRD analysis.

Fig. 6 shows a result of X-ray diffraction analysis and a scanning electron image of a solidified structure for a diamond (110) specimen. In the case of diamond (110), the peaks of TiC (111) and TiC (200) are detected. Titanium carbide reaction products are formed as polycrystalline. The peaks of silver and copper are detected like polycrystalline, so the orientation at the interface cannot be observed. The scanning electron microscopy image shows the dark diamond surface upper side, a gray layer adjacent to the diamond, a lot of gray islands and fine eutectic structures. The gray layer and the gray islands are titanium carbide. A lot of titanium carbide reaction products are formed at the interface of diamond (110).

Fig. 7 shows a result of X-ray diffraction analysis and a scanning electron image of a solidified structure for a diamond (111) specimen. In the case of diamond (111), the peaks of Cu (111) is largest in the figure. This peak is six times larger than that of Cu (200). The copper crystals are solidified in order with the diamond surface. The peaks of inter-metallic compound Cu_3Ti are detected. The inter-metallic compound is formed between the titanium atoms non-reacted with the diamond and the copper atoms. A lot of copper atoms exist near the diamond (111) brazed interface. The scanning electron microscopy image shows a lot of black parts. They are considered to be void of the brazing filler. A lot of white parts are silver. Judging from the contrast

of eutectic structure in the center of figure and XRD analysis, most white gray area is copper.

4. Discussions

In the case of brazing diamond (100), titanium carbide reaction products were formed in order with the diamond surface. Misfit parameter, η is introduced to discuss the orientation of the titanium carbide reaction products. This parameter is used to explain the thin film growth morphology [3]. It is expressed in the following equation,

$$\eta = \frac{\sigma_{\text{ff}}}{\sigma_{\text{ss}}} - 1 \quad (1)$$

where σ_{ss} and σ_{ff} are the dimension less units of the atomic distances of the substrate particle and of the film particle, respectively. The atomic distances of three titanium carbide surfaces used for this calculation are shown in Fig. 8. The value of the misfit parameter for each pair is presented into the same figure. The value for TiC (111) // Diamond (100) is 0.05016. In contrast to this, the value for TiC (100) // Diamond (100) is 0.7145. The misfit of titanium carbide with diamond becomes so small in the case of the combination of TiC (111) // Diamond (100) that the titanium carbide products is considered to be formed in order with the diamond (100). This result is agreed with X-ray analysis result.

Next, we will discuss the solidification of the brazing filler from the reaction products of titanium carbide. We will introduce another parameter of a lattice mismatch to explain heterogeneous solidification of the brazing filler. The parameter, δ [%] is calculated from

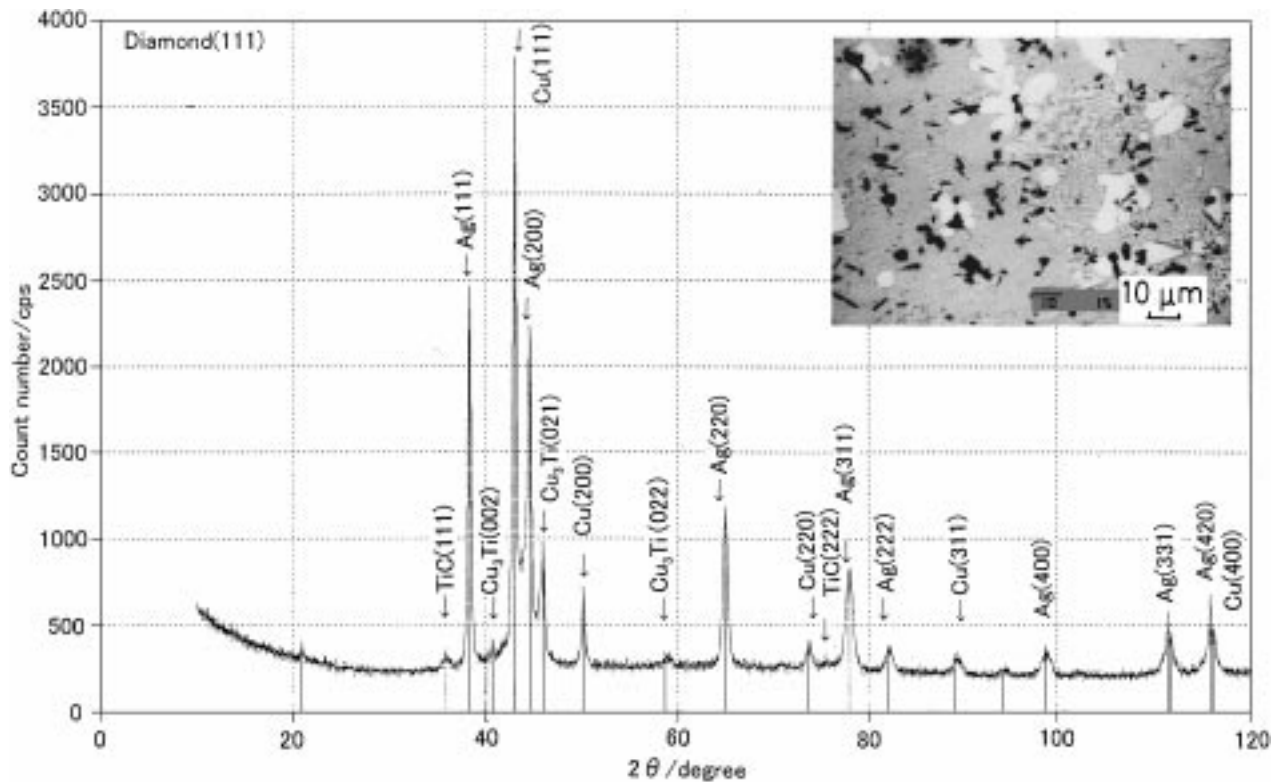


Figure 7 Result of X-ray diffraction analysis and back scattering electron image of unidirectional solidification brazed diamond (111) sample.

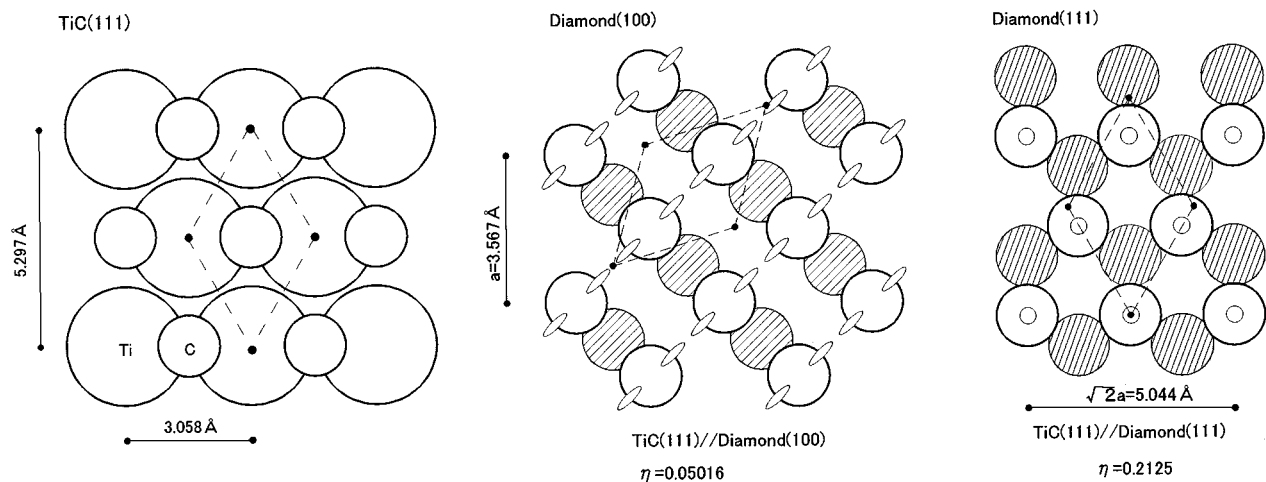


Figure 8 Lattice of stable sites on TiC (111) is shown by broken lines. Geometric combinations between this lattice and diamond (100), (111) and misfit values of each pair are shown. Shaded circles show the second layer carbon atoms. Ellipses on diamond (100) and small circles on diamond (111) mean dangling bond hands of carbon atoms.

the following equation, taking account of the lattice mismatches on the low-index planes and the gap in three directions;

$$\delta = \frac{1}{3} \sum_{i=1}^3 \frac{|d[uvw]_s^i \cos \theta - d[uvw]_c^i|}{d[uvw]_c^i} \times 100 \quad (2)$$

where $d[uvw]_c$ is the nearest-neighbor distance on the low-index plane of the nucleant, $d[uvw]_s$ is the nearest-neighbor distance on the low-index plane of the solid crystal (brazing filler element) and θ is the angle between the close-packed directions of the two substances. The Equation 2 is a little arranged from planar disregistry [2] to express the lattice mismatches on

the basis of the nucleant. About the detailed definition and the calculation procedure of the planar disregistry, please see the papers [2, 4, 5]. The value of the lattice mismatch of each combination is presented in Table II. The lattice mismatches of titanium are out of the definition of the planar disregistry, because the systems between titanium and carbon in the diamond and the titanium carbide reaction products are reactive ones. We try discussing the reaction and the segregation of titanium by using this parameter. The lattice mismatch between Ti(α) (111) // Diamond (100) is so large as 51.43%, as titanium atoms form titanium carbide with carbon atoms, then the misfit with the diamond becomes small as 0.05016. Then, the solidification of the brazing filler will occur. The value of the lattice mismatch

TABLE II Lattice mismatch altered from planar disregistry: δ

Ag/Diamond	δ [%]
(100)//(100)	14.56
(110)//(110)	14.56
(111)//(111)	14.57
Ag/TiC	δ [%]
(100)//(100)	5.516
(110)//(110)	5.518
(111)//(111)	5.516
Cu/Diamond	δ [%]
(100)//(100)	1.345
(110)//(110)	1.360
(111)//(111)	1.350
Cu/TiC	δ [%]
(100)//(100)	16.42
(110)//(110)	16.42
(111)//(111)	16.42
Ti(α)/Diamond	δ [%]
(1100)//(100)	51.43
(1100)//(110)	24.75
(0001)//(111)	17.01
Ti(α)/TiC	δ [%]
(1100)//(100)	26.58
(1100)//(110)	5.402
(0001)//(111)	3.479
(1100)//(111)	8.209

Lattice Mismatch.

between titanium carbide and silver is about 5.5. This value is smaller than that between titanium carbide and copper. The value of 5.5% indicates that heterogeneous nucleation of silver will occur. This suggests that silver crystals grow from the titanium carbide products, and that be in order with the titanium carbide products. This discussion is agreed with the result of the high peak for Ag (111) by XRD.

In the case of the brazing diamond (100), the diamond, the titanium carbide reaction products and silver crystals have a relationship of Diamond (100) – TiC (111) – Ag (111) orientations. It is agreed with the discussions above about the misfit and the lattice mismatch. Those orientations are considered to achieve the stable high bonding.

In the case of the brazing diamond (110), the reaction products of titanium carbide are formed polycrystalline, so the stable sites on diamond (110) are not shown in Fig. 8. Silver crystals are also solidified polycrystalline. It is considered that polycrystalline interface is weaker than the orientated interface. As a result, the diamond (110) brazed interface shows weak bond strength.

In the case of the brazing diamond (111), titanium carbide reaction products are formed in order with diamond (111). The misfit value for TiC (111) // Diamond (111) is 0.2125. It is larger than that for TiC (111) // Diamond (100), so the interface between TiC (111) and diamond (111) is delicate. Thus the brazed strength depends on the temperature of the copper cooling mass. The lattice mismatch for Ti(α) (0001) // Diamond (111)

is smaller than the other combinations of planes, and the value as 17.01% is smaller than the misfit between TiC (111) and Diamond (111). A lot of titanium atoms are considered to remain as non-reacted ones near the diamond. On the other hand, the lattice mismatch for Cu (111) // Diamond (111) is so small as 1.35%. A lot of copper atoms exist near the diamond surface. As a result, it is considered that the high peak for Cu (111) and the peak for Cu₃Ti reacted between titanium and copper are observed by XRD.

5. Conclusions

By cooling from the top of a diamond, unidirectional solidification brazing method has done to bond diamond to metal by using silver copper eutectic filler containing 4.5 wt% titanium flakes. In the case of diamond (100), diamond (100) – TiC (111) – Ag (111) orientation can be observed. The average shear strength of the specimens shows more than 120 MPa. It is larger than that made by usual brazing method. In the case of diamond (110), interface orientations cannot be observed. These interfaces are polycrystalline. The shear strength of these specimens shows less than 85 MPa. It is easy for the interface to crack. In the case of diamond (111), diamond (111) – Cu (111) orientation can be observed. The interfaces are in delicate thermal stress, because the misfit for diamond (111) // TiC (111) is large. The shear strength depends on the cooling rate. If the cooling mass temperature is 670 K, the shear strength shows more than 120 MPa.

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