Journal of the Ceramic Society of Japan 112 [6] 305-310 (2004)

Paper

Interfacial Microstructures and Bonding Strength between Aluminum Nitride and Silver Brazing Filler Metals Containing Various Active Elements

Yasuhiro MORIZONO, Minoru NISHIDA,* Akira CHIBA* and Takashi NAKATA**,†

Shock Wave and Condensed Matter Research Center, Kumamoto University, 2-39-1, Kurokami, Kumamoto-shi 860-8555
**Department of Mechanical Engineering and Materials Science, Faculty of Engineering, Kumamoto University, 2-39-1, Kurokami, Kumamoto-shi 860-8555*
***Graduate Student, Kumamoto University, 2-39-1, Kurokami, Kumamoto-shi 860-8555*

窒化アルミニウムと各種活性金属を含む銀ろう間の界面組織と接合強度

森園靖浩・西田 稔*・千葉 昂*・中田隆司**,†

熊本大学衝撃・極限環境研究センター，860-8555 熊本市黒髪 2-39-1
*熊本大学工学部知能生産システム工学科，860-8555 熊本市黒髪 2-39-1
**熊本大学大学院生，860-8555 熊本市黒髪 2-39-1

Effect of active element on interfacial microstructures and bonding strength of brazed AlN/AlN joints has been investigated and compared with the case of brazed Si_3N_4/Si_3N_4 joints. Brazing was carried out at 1173 to 1473 K for 3.6 ks in a vacuum using Ag–Cu filler metals containing Ti, Zr, V and Nb as an active element. The obtained joint had no defects such as un-bonded areas, regardless of active element and bonding temperature. Four kinds of active elements were divided into two groups by shear tests and microstructural observations. One was Ti and Zr, and the other was V and Nb. The bonding strength of the former was higher than that of the latter. In particular, the joint with Ti addition showed an excellent strength of about 200 MPa. Main fracture position in the joints with Ti and Zr additions was within the AlN, while most joints with V and Nb additions broke at the interface between the active filler metal and the AlN. In the former, TiN and ZrN layers consisting of fine grains were observed adjacent to the AlN. On the other hand, the joint with Nb addition had roundish grains of Nb_2N in similar locations. It was considered that the existence of fine grains contributed to the enhancement of bonding strength due to the increase of contact area and to the formation of complicated interface. These tendencies were essentially consistent with those of the brazed Si_3N_4/Si_3N_4 joints.

[Received August 11, 2003; Accepted April 27, 2004]

***Key-words :** Aluminum nitride, Active metal brazing, Bonding strength, Reaction product*

1. Introduction

Ceramic materials are generally used in combination with themselves and metals because of their poor toughness and machinability. Among bonding techniques for the ceramics, active metal brazing method has been widely utilized. Its advantages are to be a relatively simple technique and to obtain easily sound joint. Various types of active filler metals are used on the production process of ceramic/ceramic and metal/ceramic joints. Although the bonding characteristics and the interfacial microstructures of these joints have been reported, most articles deal with those of the joints brazed with the filler metal containing Ti as an active element.[1)-5)] There are few investigations for the case of the filler metal containing other elements such as Zr and V.[6)-10)] The active element in the filler metal plays an important role in the bonding. Thus, it is necessary to know a lot of information about the reaction behavior between the ceramics and the metallic elements.

The authors have reported earlier the relationship between interfacial microstructures and bonding strength in Si_3N_4/Si_3N_4 joints brazed with Ag–Cu filler metals containing various active elements.[8)] The active elements added to the Ag–Cu filler metal were Ti, Zr, V and Nb, which belong to columns 4A and 5A in periodic table and have negative standard free energy for nitride formation. These elements were divided into two groups by strength tests and microstructural observations. One was Ti and Zr, and the other was V and Nb. Consequently, it was considered that the substantial bond between the filler metal and the Si_3N_4 in the former was attributed to the formation of fine grains of nitride at the interface. In the preset study, the interfacial microstructures and the bonding strength of AlN/AlN joints brazed with Ag–Cu base filler metals are investigated and compared with those of the brazed Si_3N_4/Si_3N_4 joints. From the similarity between the brazed AlN/AlN and Si_3N_4/Si_3N_4 joints, the effectiveness of the active element on the brazing of nitride ceramics is discussed.

2. Experimental procedure

Pressureless-sintered AlN (SHAPAL, Tokuyama Corporation, Tokyo) and Si_3N_4 (TOSNITE, Toshiba Materials Co., Ltd., Kanagawa) were used in the present study. The dimensions were 7 mm × 7 mm × 5 mm in size. Their bonding surface was polished with 9 μm diamond paste. The used filler metal was an eutectic alloy of Ag–Cu binary system, which is specified by Japanese Industrial Standards Committee (JIS Z 3261). Ti, Zr, V and Nb foils were used as an active metal. The Ag–Cu sheet and the pure metal foils, which were 0.15 mm thick and 0.020 to 0.025 mm thick, respectively, were cut into square shapes of 7 mm × 7 mm. Before bonding treatment, all materials were cleaned in acetone using ultrasonic cleaner and were dried with hot air.

† Present address: Taiho Kogyo Co., Ltd., 2-47, Hosoya-cho, Toyota-shi, Aichi 471-8502
現在：大豊工業(株)，471-8502 愛知県豊田市細谷町 2-47

The bond couple whose stacking sequence was nitride ceramics, Ag–Cu sheet, pure metal foil, Ag–Cu sheet and nitride ceramics was fixed in jig composed of two Mo rods and two SUS304 austenitic stainless steel blocks. This assembly was heated at 1173 to 1473 K for 3.6 ks in a vacuum of less than 3×10^{-3} Pa, and the brazing of nitride ceramics was completed. The heating rate up to the bonding temperature was 0.17 K/s and all specimens were furnace-cooled to room temperature after holding step.

The specimens were cut perpendicular to the interface to reveal the microstructural aspects. The cross sections were ground with diamond sheets and then finished with alumina powders of about 50 nm in diameter. They were examined by optical microscopy and electron probe X-ray micro analysis (EPMA). The specimens for transmission electron microscopic (TEM) observations were prepared from slices of about 0.1 mm in thickness, which were obtained by cutting and grinding of the joint. Disks of 3 mm in diameter containing the bonding interface were made from the slices by ultrasonic cutting tool and finished with an argon ion beam milling machine. TEM observations were carried out in a JEOL JEM-2000FX microscope operated at 200 kV.

Bonding strength of the obtained joints was evaluated at room temperature by tensile shear test. A schematic illustration of jig for the test is shown in **Fig. 1**. The test was performed at a crosshead speed of 8.3×10^{-3} mm/s using tensile testing machine equipped with the jig. The bonding strength is equivalent to breaking force divided by bonding area. After the shear test, X-ray diffraction (XRD) was carried out on fracture surface of the joint.

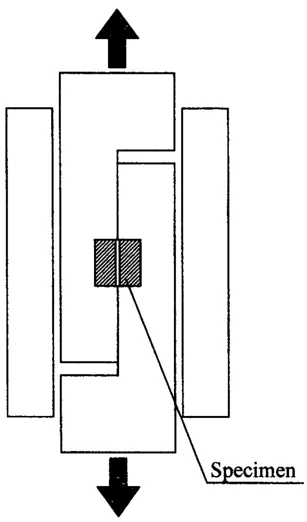

Fig. 1. Schematic illustration of jig for tensile shear test.

3. Results and discussion

3.1 External views of the brazed joints

To understand viscerally the effect of active element on bondability between Ag–Cu base filler metal and nitride ceramics, visual external examination was performed for the brazed specimens. **Figure 2**(a) shows an external view of the Si_3N_4/Si_3N_4 joint brazed at 1173 K for 3.6 ks using only Ag–Cu filler metal. Since the wetting of molten Ag and Cu on the ceramics is known to be poor,[11] the filler metal does not contribute to the bonding and becomes spherical shape. The external views of the AlN/AlN joints prepared at 1173 K for 3.6 ks using the Ag–Cu filler metals containing Ti, Zr, V and Nb are shown in Figs. 2(b) to (e), respectively. In appearance, the bonding of the AlN is accomplished in all cases. This indicates that the brazing of the AlN becomes possible by existence of the active element. The joint brazed with Ag–Cu–Ti has black areas around joint line. This is part of the filler metal, which overflows out of the interface and is discolored by oxidation. The overflowing Ag–Cu–Ti spreads over the joint surface during bonding process, while other filler metals form some agglomerates as indicated by arrows. These situations were also retained at higher bonding temperatures. As shown in Figs. 2(f) to (i), the Si_3N_4/Si_3N_4 joints brazed with the Ag–Cu base filler metals exhibit aspects similar to the AlN/AlN joints. Consequently, the brazing of AlN and Si_3N_4 is remarkably improved by addition of Ti, Zr, V and Nb. Among them, the optimal active element is Ti from the viewpoint of wetting on the joint surface.

3.2 Interfacial microstructures of the brazed AlN/AlN joints

Figure 3 shows optical micrographs of the interface in the AlN/AlN joints brazed with Ag–Cu base filler metals. There are no defects such as un-bonded areas in the bonding interface. The width of brazing zone is different because spacer to keep a certain distance was not used in the present study. Thus, these widths are reflected in the overflowing filler metal as shown in Fig. 2. Figure 3(a) is a typical structure in the joint brazed with Ag–Cu–Ti. The bonding was performed at 1273 K for 3.6 ks. Ti foil, which was set between two Ag–Cu sheets, cannot be seen, while there is a reaction layer along the Ag–Cu–Ti/AlN interface. **Figure 4** shows compositional profiles of constituent elements obtained by EPMA for this joint. Since the enrichment of Ti and N is recognized at the

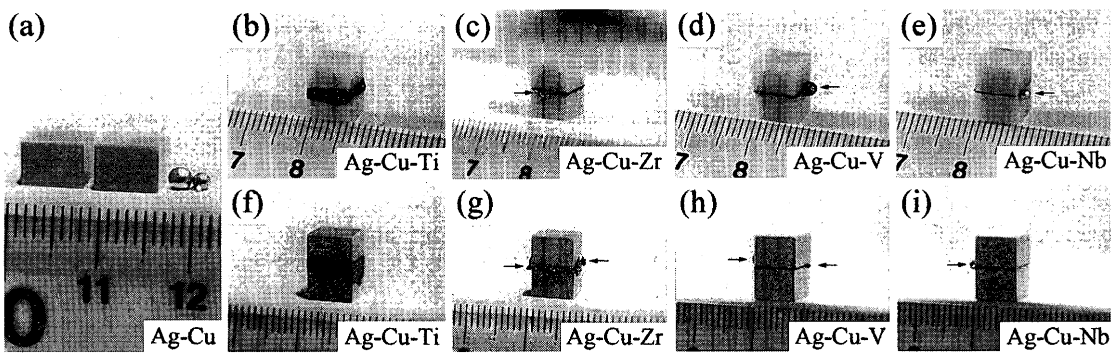

Fig. 2. External views of (a) Si_3N_4/Si_3N_4, (b)-(e) AlN/AlN and (f)-(i) Si_3N_4/Si_3N_4 joints brazed at 1173 K for 3.6 ks using various Ag–Cu base filler metals.

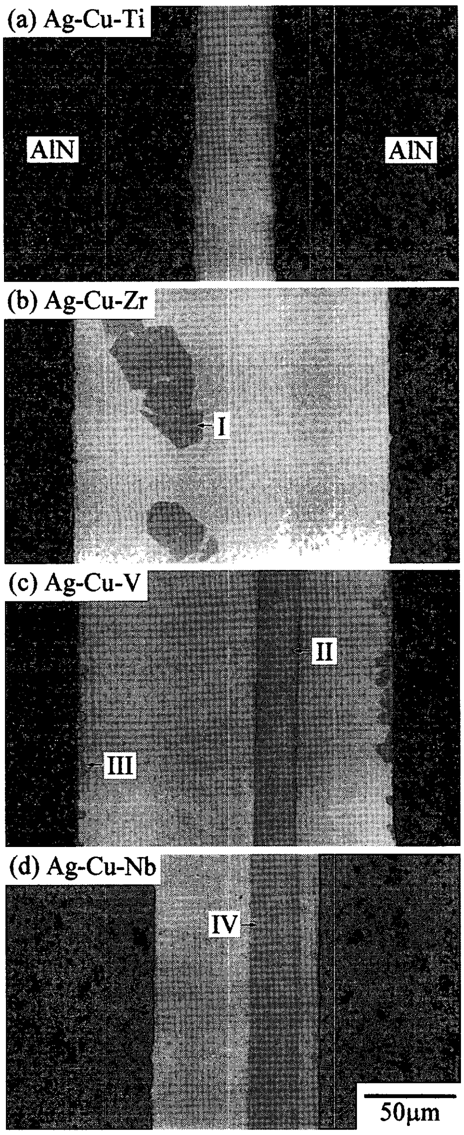

Fig. 3. Optical micrographs of the interface in AlN/AlN joints brazed with (a) Ag–Cu–Ti, (b) Ag–Cu–Zr, (c) Ag–Cu–V and (d) Ag–Cu–Nb. (a) and (b) were bonded at 1273 K for 3.6 ks. (c) and (d) were bonded at 1373 K for 3.6 ks.

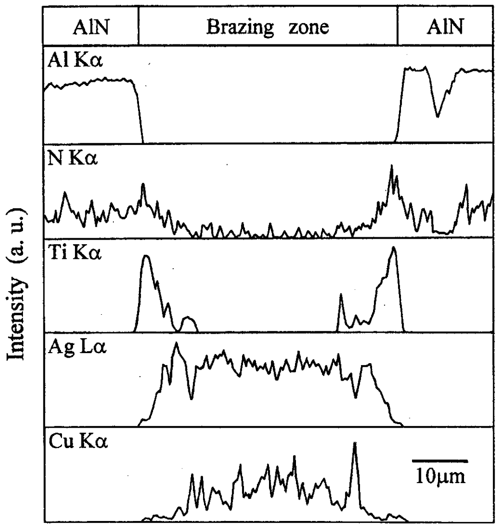

Fig. 4. Compositional profiles of the interface in AlN/AlN joint brazed at 1273 K for 3.6 ks using Ag–Cu–Ti.

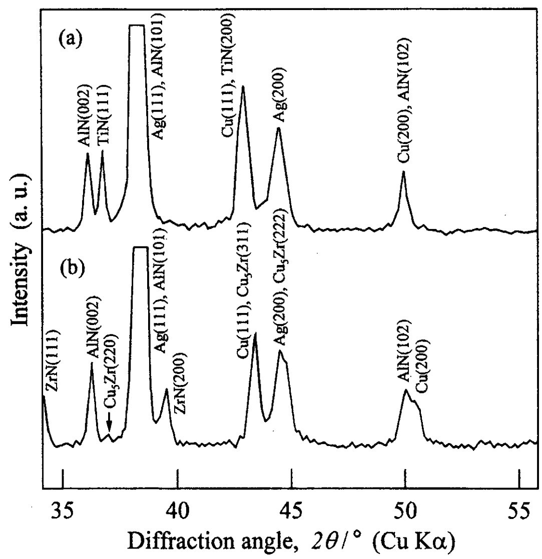

Fig. 5. X-ray diffraction patterns of fracture surface of AlN/AlN joints brazed at 1273 K for 3.6 ks using (a) Ag–Cu–Ti and (b) Ag–Cu–Zr.

position of the reaction layer, this is identified as TiN. The formation of the TiN layer also gets support from **Fig. 5**(a), which shows XRD pattern of fracture surface of the joint brazed with the Ag–Cu–Ti after shear test. It has been reported that the segregation of active element is attributed to electromotive force generated between the active filler metal and the ceramics.[6] Consequently, the TiN layer results from the segregation and the reaction of Ti at the bonding surface of the AlN.

Figure 3(b) shows the interfacial microstructure of the joint brazed at 1273 K for 3.6 ks using Ag–Cu–Zr. There are reaction products marked with I in the Ag–Cu eutectic structure. These are determined by XRD pattern in Fig. 5(b) to be Cu_5Zr, and their formation was also detected in the previous study.[8] According to Cu–Zr binary phase diagram,[12] melting point of the Cu_5Zr is in the vicinity of 1373 K. Thus, it disappeared in the joints brazed at 1373 and 1473 K. Meanwhile, although the reaction layer formed at the Ag–Cu–Zr/AlN interface is not clearly seen on an optical microscopy scale, the formation of ZrN due to the segregation of Zr is confirmed in Fig. 5(b).

The interfacial microstructure of the joint brazed at 1373 K for 3.6 ks using Ag–Cu–V is shown in Fig. 3(c). **Figure 6** presents the result of EPMA for this joint. The band-shaped product marked with II is determined as residual V foil by principal distribution of V. Many products marked with III, which take the shape of water droplet, show the same distribution as the residual V foil. Since solid solubility of V into Ag and Cu is very small,[12),13] these droplet-like products are considered to be generated by melting, migration and solidification of V foil. The amount of such products increased with increasing brazing temperature. Furthermore, it is predicted that there is a reaction layer consisting of V_2N at the interface due to the segregation of V, because the diffraction peaks of the V_2N can be seen in **Fig. 7**(a) which is a XRD pattern of fracture surface after shear test. On the other hand, the distribution in Figs. 6(e) and (f) reflects Ag–Cu eutectic structure.

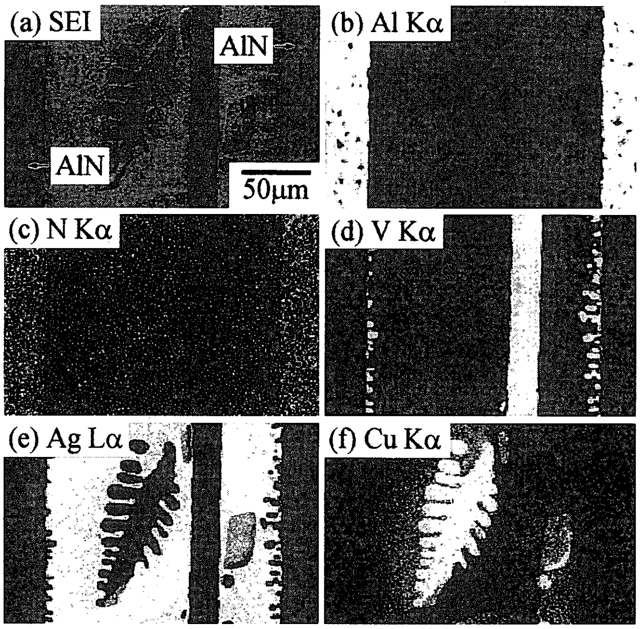

Fig. 6. (a) Secondary electron image and characteristic X-ray images of (b) Al, (c) N, (d) V, (e) Ag and (f) Cu of the interface in AlN/AlN joint brazed at 1373 K for 3.6 ks using Ag–Cu–V.

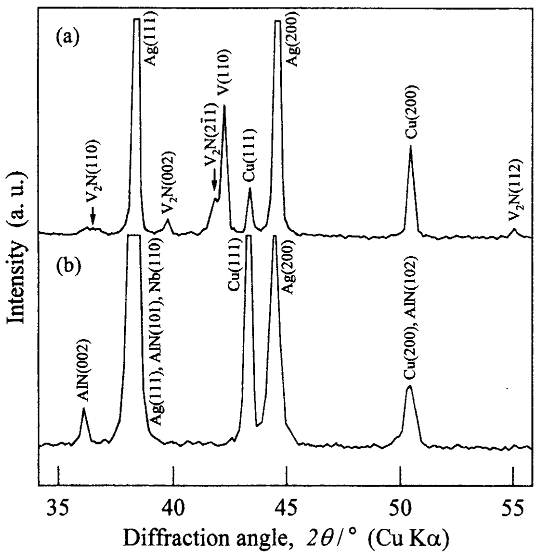

Fig. 7. X-ray diffraction patterns of fracture surface of AlN/AlN joints brazed at 1373 K for 3.6 ks using (a) Ag–Cu–V and (b) Ag–Cu–Nb.

As well as the cases of other brazed joints, Ag and Cu elements appear to have little effect on the reaction at the bonding interface.

The joint brazed with Ag–Cu–Nb has similar microstructure to that with Ag–Cu–V, as shown in Fig. 3(d). The band-shaped product marked with IV was a residual Nb foil. The reaction products due to the segregation of Nb are hardly observed even at 1373 K. In this connection, there are no peaks of the products in XRD pattern in Fig. 7(b).

Except for thickness and constitution of reaction products formed adjacent to ceramics, the microstructural aspects of the brazed AlN/AlN joints were essentially consistent with those of the brazed Si_3N_4/Si_3N_4 joints.[8] Therefore, the filler

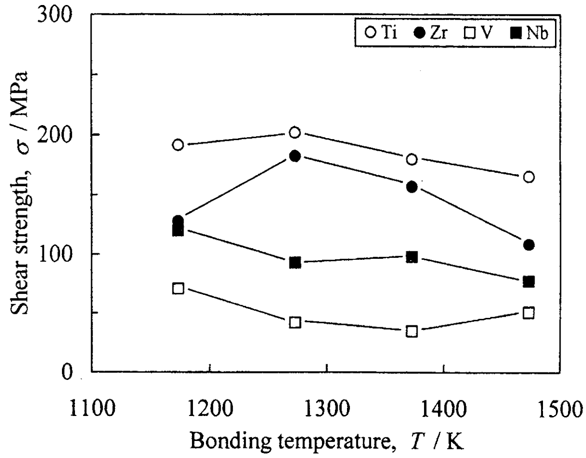

Fig. 8. Shear strength of AlN/AlN joints brazed at 1173 to 1473 K for 3.6 ks using Ag–Cu filler metals containing Ti, Zr, V and Nb.

metal containing Ti has excellent reactivity for the nitride ceramics, while the joint using Ag–Cu–Nb shows the poorest reaction at the brazing zone.

3.3 Bonding strength of the brazed AlN/AlN joints

Shear test was carried out to clarify the effect of active element on bonding characteristics of the brazed AlN/AlN joints. **Figure 8** shows the bonding strength of the AlN/AlN joints brazed at 1173 to 1473 K for 3.6 ks using various active filler metals. Before the shear test, the overflowing filler metal seen in Fig. 2 was eliminated from the joint surface. 3-times-test was conducted for each kind of joint, and the average value is plotted in the figure. The bonding strength of the joints brazed with Ag–Cu–Ti and Ag–Cu–Zr reaches about 200 MPa at 1273 K and then gradually decreases with increasing bonding temperature. However, that of the joints brazed with Ag–Cu–V and Ag–Cu–Nb is in vicinity of 50 and 100 MPa, respectively, independent of bonding temperature. It is found that Ti and Zr as an active element have more beneficial effect than V and Nb. This tendency is common to the brazed Si_3N_4/Si_3N_4 joints.[8]

The AlN/AlN joints brazed with the Ag–Cu–Ti and the Ag–Cu–Zr broke mostly within the AlN. Thus XRD patterns of fracture surface shown in Fig. 5 include many peaks of the AlN. However, main fracture position for the joints brazed with the Ag–Cu–V and the Ag–Cu–Nb was at the interface between the active filler metal and the AlN. In this case, it could be easily recognized with the naked eye that the fracture surface with metallic sheen acted in concert with its opposite surface showing the AlN substrate. Consequently, the XRD patterns obtained from the opposite side of Fig. 7 showed strongly the peaks of the AlN.

From the shear strength and the fracture position, four kinds of active elements seem to be divided into two groups, as well as the case of the Si_3N_4/Si_3N_4 joints.[8] One is Ti and Zr, and the other is V and Nb. The bonding strength of the former is superior to that of the latter. It is expected from the viewpoint of the fracture position that the former joints have substantial bond between the active filler metal and the nitride ceramics.

3.4 TEM observations of the interface between active filler metal and AlN

Bonding strength and fracture position of the brazed AlN/AlN joints varied by active element in the Ag–Cu filler metal. To examine this origin more closely, TEM observations were

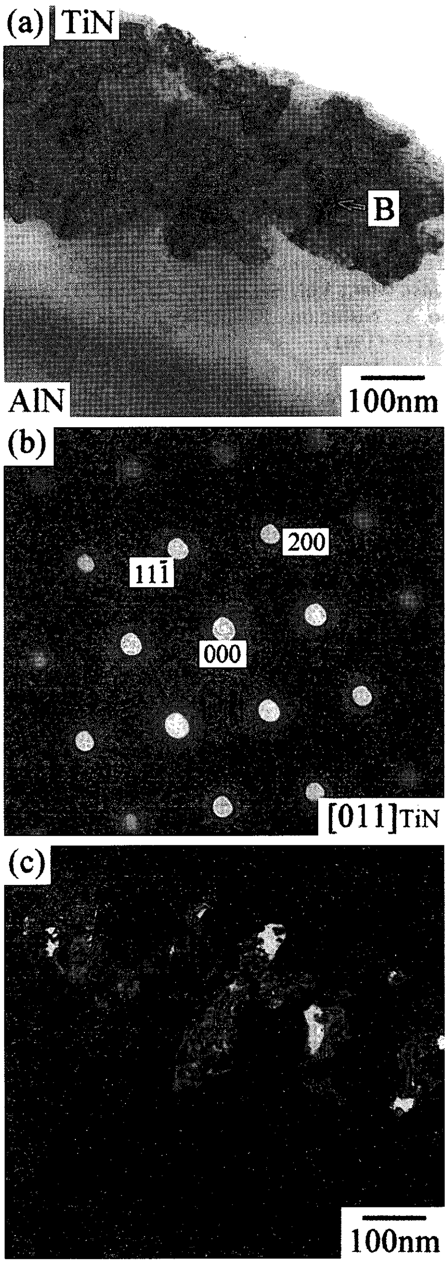

Fig. 9. (a) Bright field image of TiN layer in AlN/AlN joint brazed at 1173 K for 3.6 ks using Ag-Cu-Ti. (b) Microarea electron diffraction pattern taken from grain B in (a). (c) Dark field image taken by (200) spot in (b).

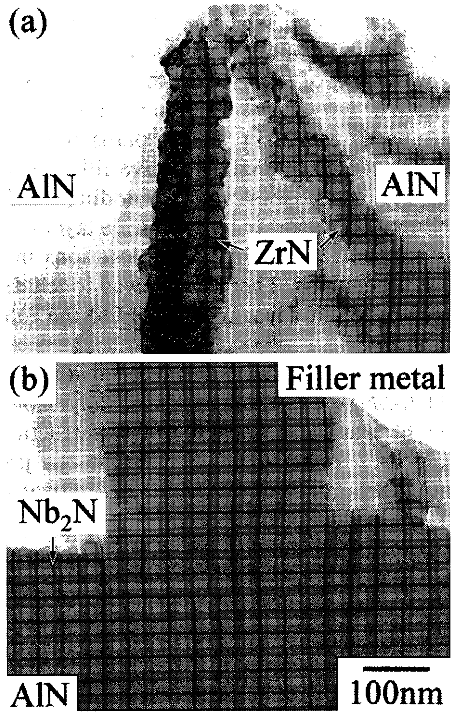

Fig. 10. TEM micrographs of reaction products in AlN/AlN joints brazed at 1373 K for 3.6 ks using (a) Ag-Cu-Zr and (b) Ag-Cu-Nb.

carried out and the effect of the active element on interfacial reaction was discussed.

Figure 9(a) shows a bright field image of the interface in the AlN/AlN joint brazed at 1173 for 3.6 ks using Ag-Cu-Ti. Reaction product gets intricately into the AlN. From Figs. 9 (b) and (c), this product is identified as TiN consisting of fine grains. Such a microstructure was also confirmed at higher bonding temperatures. **Figures 10**(a) and (b) show bright field images of the reaction products in the AlN/AlN joints brazed at 1373 K for 3.6 ks using Ag-Cu-Zr and Ag-Cu-Nb, respectively. The joint brazed with the Ag-Cu-Zr has a ZrN layer consisting of fine grains in close proximity to the AlN. The location that the ZrN grains extend into the AlN is also seen in Fig. 10(a). Although Nb_2N is formed as a reaction product in the joint brazed with the Ag-Cu-Nb, its morphology differs from those in Figs. 9 and 10(a). The Nb_2N layer seems to be an aggregation of roundish grains. Since the thickness of the Nb_2N layer is very thin, it is hardly seen in Figs. 3 (d) and 7(b). In the joint using Ag-Cu-V, the specimen for TEM observations could not be prepared because of its low bonding strength. However, it is expected from the results of previous sections that this joint has the same microstructure as shown in Fig. 10(b).

The grouping on the basis of shear test is available to TEM observation results. The AlN/AlN joint brazed with the Ag-Cu-Nb has Nb_2N grains in proximity to the AlN. Since this region becomes main fracture position on the shear test, the weak bond may be due to its morphology. Conversely, it is considered that the nitride layer consisting of fine grains leads to the substantial bond around the brazed AlN in the joints using Ag-Cu-Ti and the Ag-Cu-Zr. The fine grain layer contributes to the increase of contact area for the AlN and to the formation of complicated interface. As mentioned above, the same tendency has been recognized in the brazed Si_3N_4/Si_3N_4 joints.[8] Therefore, it is concluded that the morphology of reaction products around ceramics, as well as their lattice matching, is one of important factors to enhance bonding characteristics of the completed joint. The further investigations are required to clarify the origin and the mechanism for the formation of the fine grain layer such as TiN and ZrN.

4. Conclusions

Effect of active element on interfacial microstructures and bonding strength of brazed AlN/AlN joints was investigated. The active elements added to Ag-Cu filler metal were Ti, Zr, V and Nb. The brazing of the AlN became possible by addition of these elements. From the view point of wetting on the joint surface, the optimal element was considered to be Ti. Furthermore, these elements were divided into two groups by microstructural observations and shear tests. One was Ti and

Zr, the other was V and Nb. The former joints showed the bonding strength of about 200 MPa at a brazing temperature of 1273 K, while that of the latter ones was in vicinity of 50 to 100 MPa. Both groups also differed in fracture position on the shear test. In particular, main fracture paths in the latter joints were at the interface between the active filler metal and the AlN. In this region, the joint with Nb addition had roundish grains of Nb_2N. On the other hand, nitride layer consisting of fine grains were confirmed in similar locations in the joints wiht Ti and Zr additions. Therefore, it was concluded that the formation of fine grain layer contributed to the enhancement of bonding strength.

These results corresponded essentially with those of the brazed Si_3N_4/Si_3N_4 joints in the previous study. Consequently, it was thought that the variation of microstructural aspects and bonding strength by active elements in the preset study was common phenomena to the brazing of nitride ceramics.

Acknowledgements The authors would like to express their appreciation to Messrs. Kihachiro Imamura and Hideaki Kawasaki for their kind assistance in the conduct of the experiments.

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