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Strength and Microstructure of Silicon Nitride/Aluminum Interface Fabricated by Squeeze Cast Brazing

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Abstract

The oxidized silicon nitride was brazed with pure aluminum by the squeeze cast method. The bending strength of the joint was above 400 MPa. The interfacial microstructure has been identified by high-resolution TEM and analytical TEM methods. Two distinct reaction layers were formed at the interface and the thickness of both layers were almost the same, about 30–40 nm. The one adjacent to silicon nitride had a nanocrystalline structure without a boundary phase. The nanocrystals were identified as β'-sialon containing silicon, aluminum, oxygen and nitrogen. Every crystal inclined slightly to the matrix grain. The other layer was the amorphous aluminum–silicon–oxygen layer. This layer had the dense structure and sometimes contained small particles composed of yttrium, calcium and iron, which were the reaction product of the boundary phase of silicon nitride and the braze.

Oxidiertes Siliziumnitrid wurde mit reinem Aluminium mittels einer Druckguß-Technik gelötet. Die Biegefestigkeit der Verbindung lag oberhalb 400 MPa. Das Gefüge des Grenzflächenbereiches wurde mit hochauflösender und analytischer Transmissionselektronenmikroskopie identifiziert. An der Grenzfläche bildeten sich zwei verschiedene Arten von Reaktionsschichten mit einer fast übereinstimmenden Dicke von etwa 30–40 nm. Die eine Schicht grenzt unmittelbar an das Siliziumnitrid an und zeigt eine nanokristalline Struktur ohne Korngrenzenphase. Die nanokristallinen Körner wurden als β'-Sialon identifiziert und enthielten Silizium, Aluminium, Sauerstoff und Stickstoff. Jedes dieser Körner war leicht relativ zum jeweiligen Matrix-Korn geneigt. Die zweite Schicht war eine amorphe Aluminium–Silizium–Sauerstoff-Schicht. Sie besaß eine dichte Struktur und enthielt stellenweise kleine Teilchen, die sich aus Yttrium, Kalzium und Eisen zusammensetzen. Diese Teilchen sind das Reaktionsprodukt der Korngrenzenphase des Siliziumnitrids mit dem Lot.

Une méthode de coulage sous pression a été utilisée pour brazer du nitrure de silicium avec de l'aluminium pur. La résistance à la flexion au niveau de la brazure est supérieure à 400 MPa. La microstructure de l'interface a été étudiée par MET et par microanalyse électronique. Deux couches distinctes de réaction ont été formées à l'interface ayant pratiquement la même épaisseur, environ 30–40 nm. L'une, adjacente au nitrure de silicium, a une structure nanocristalline sans phase frontière. Les cristaux nanoscopiques ont été identifiés comme étant du β'-sialon contenant du silicium, de l'aluminium, de l'oxygène et de l'azote. Chaque cristal est légèrement incliné vers les grains de la matrice. L'autre couche est un silico-aluminium amorphe. Cette couche présente une structure dense et parfois contient de petites particules composées d'yttrium, de calcium et de fer qui sont les produits de réaction de la phase de liaison entre le nitrure de silicium et la brazure.

1 Introduction

The technological importance of joining methods of ceramics to themselves and to metals has increased along with the expansion of the uses of ceramics in industrial fields since the beginning of the 1980s. A number of processes have been developed for joining them. The active metal brazing method represented by the silver–copper–titanium brazing has been known as one of the typical processes and has been used in the actual mass production of several kinds of ceramic parts since the middle of the 1980s, as reviewed in Ref. 1. However, most of such brazing processes are expensive batch processes. In order to expand the use of ceramic products further, it has been earnestly required to establish a certain

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economic process. From this requirement, recently, the author has developed the new joining process, which was named SQ brazing.[2] The outline of the process was reported in the previous work in detail. SQ stands for squeeze casting. This process has been widely used in production of metallic materials and metal matrix composites, and is known as one of the economic processes in metal forming. This method can be mentioned as a dynamic process while most of the conventional brazing methods are static. The SQ process has several fascinating benefits for joining ceramics. The total process is very simple and does not require any large vacuum furnace which is always needed in the active metal brazing of ceramics.

The previous report focused on the reactive system of alumina–silica ceramic and aluminum braze.[2] In this case conventional brazing could not make any sound joint because the silica binder reacted severely with aluminum melt and was reduced to silicon. In contrast, silicon nitride, which is one of the quite useful ceramics in engineering fields, is not so reactive towards aluminum melt. To make a strong interface between silicon nitride and aluminum braze by the SQ method, the pre-oxidation of the bond face of silicon nitride was effective. The oxidation treatment of silicon nitride seems to have promoted wetting between silicon nitride and aluminum melt by forming a silica layer on the bond face.[3,4] However, there was no reaction layer recognized in microscopic observation, such as optical microscopy or scanning electron microscopy/electron microprobe analysis. This might be caused by the limitation in spatial resolution in observation. The aim of the present work was, therefore, to identify the interface reaction structure of silicon nitride/aluminum formed by the SQ method, primarily with transmission electron microscopy.

2 Experimental

2.1 Materials

The silicon nitride used was a pressureless sintered sample (14 mm × 14 mm × 20 mm) supplied from Kyocera Corporation (Kagoshima, Japan) (SN-220M). It contained a small amount of sintering additives, such as yttria and alumina. The face to be bonded was 14 mm × 20 mm. The roughness of the bonding face was 0·2 μm in average surface roughness finished by grinding. The average strength of this material at room temperature was about 750 MPa measured by the four-point bending test.

Silicon nitride blocks were heated at 950°C for 1 h in air to oxidize the surface, which treatment was one of the best treatments to get good wetting between silicon nitride and aluminum reported in the previous work.[3] Pure aluminum (99·5 wt% pure, JIS1050) was used as the braze material.

2.2 SQ brazing

The set-up for the SQ brazing is illustrated in Fig. 1. Two blocks of silicon nitride were fixed in an accurate position in the mold before pouring the melting braze. The distance between two bond faces, which determined the braze layer thickness, was set to be about 200 μm. The specimens in the mold were heated to 600°C in air. Just after pouring aluminium at 800°C into the mold, the plunger came down to apply a pressure of 50 MPa to the braze surface. The pressure was held for 5 min. By this casting process aluminum melt solidifies within a minute.

2.3 TEM specimen preparation and observation

A TEM specimen was fabricated by the conventional machining–ion thinning procedure. Firstly, a thin slice was cut vertically to the joining interface with a diamond saw to be about 300 μm thick. Then it was ground to be a 100 μm thick plate. Using an ultrasonic core drill, a 2·3 mm diameter disk was cut from the thin plate and its center was dimpled to be about 30 μm thick. The disk specimen was finished with argon ion thinning at a voltage of 3 kV. Before TEM observation it was coated with a thin carbon film to prevent charging by the electron bombardment. The surface of pre-oxidized silicon nitride was also observed by TEM. Two small pieces of silicon nitride, which were oxidized under the same conditions as for the joining constituent, were stuck together with an adhesive. A TEM foil was prepared from this joint by the same method already mentioned.

High-resolution TEM observation (HRTEM) and analytical TEM observation (ATEM) were carried out separately. The transmission electron microscope for HRTEM was JEOL JEM200CX operated at 200 kV. That for ATEM was Hitachi HF2000 operated at 200 kV equipped with a cold-field emission filament. Using the latter microscope, the finest beam of about 2 nm can be used for

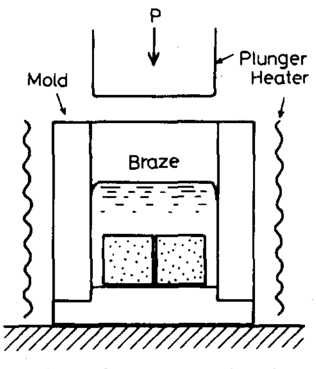

Fig. 1. Illustration of the set-up for the SQ brazing.

Table 1. Summary of three-point bending strength of the silicon nitride joints brazed by the conventional static furnace brazing in air, and in argon atmosphere,[5] in vacuum atmosphere with or without the pre-oxidation treatment of silicon nitride,[3] and by the SQ brazing method with or without the pre-oxidation treatment

Method	*Conventional brazing*[a]				*SQ brazing*[b]	
Brazing atmosphere	Air	Ar	Vacuum		Air	
Pre-treatment of Si_3N_4	—	—	—	Oxidation	—	Oxidation
Braze layer thickness	10	10	10	10	200	
Bending strength	60	420	370	420	57	404
Fracture position	I	M	M	M	I	B

[a] The average strength of silicon nitride used was 450 MPa.
[b] The average strength of silicon nitride used was 750 MPa.
I = interface fracture; M = mixed mode of interface + braze layer + silicon nitride; B = fracture in braze layer.

nanoprobe analysis without the problem of contamination during the observation in an ultra-high vacuum specimen chamber. The contamination problem during analysis sometimes results in mixing up the presence of light elements such as oxygen, nitrogen and carbon with the artifact. Elemental analysis was carried out both by energy dispersive X-ray analysis (EDX) and by energy loss spectroscopy (EELS). The spatial resolution of those analyses, which depends both on the thickness of the specimen and on the size of the electron beam to be used, was expected to be within about 5 nm. For both analysis four different points were evaluated to take the average compositional information.

3 Results and Discussion

3.1 Summary of bending strength of silicon nitride joint with aluminum braze

Table 1 summarizes the three-point bending strength of silicon nitride joint brazed with pure aluminum by several methods and in several atmospheres. The details of the bending test were reported in the previous paper.[5] By the conventional static brazing method, strength above 400 MPa was obtained only when the brazing was carried out in an inert atmosphere such as argon flow and vacuum. The air atmosphere prevented the making of a strong interface between silicon nitride and aluminum because of the formation of the thick and stable oxide layer on aluminum. In the vacuum brazing, the pre-oxidation treatment of silicon nitride increased the joint strength effectively. On the other hand, although the SQ brazing method could not achieve a strong joint with the non-treated silicon nitride, it produced a good joint from the pre-oxidation-treated one even though the brazing was carried out in air atmosphere. The joint had more than 400 MPa strength on average and did not fracture at the silicon nitride/aluminum interface. All joints with the pre-oxidized silicon nitride brazed by the SQ method fractured in the aluminum braze layer. Therefore, the interface strength is expected to be much higher than 400 MPa.

3.2 Surface of pre-oxidized silicon nitride

In order to understand the effect of the oxidizing treatment of silicon nitride before brazing, the treated surface of silicon nitride was observed by TEM. Figure 2 shows the TEM photograph of the cross-section of the oxidized silicon nitride surface. No apparent oxide layer could be observed on the silicon nitride surface. From the resolution limit of this photograph it can be concluded only that an oxide layer thicker than 10 nm was not formed on the surface after the heat treatment. This result is consistent with the fact that silicon nitride has quite excellent oxidation resistance in the temperature range up to 1000°C in general.

However, the previous report indicated the presence of a certain kind of oxide layer on the surface of the additive-free silicon nitride heat treated under similar conditions analyzed with electron spectroscopy for chemical analysis (ESCA).[4] The ESCA profile from the surface of the heat-treated silicon nitride showed the strong Si_{2p} peak at 102·6 eV, which corresponds to that of Si_{2p} in SiO_2. From this fact, in addition to the TEM observation already mentioned, this heat treatment is expected to form the silica layer on silicon nitride surface thinner than 10 nm.

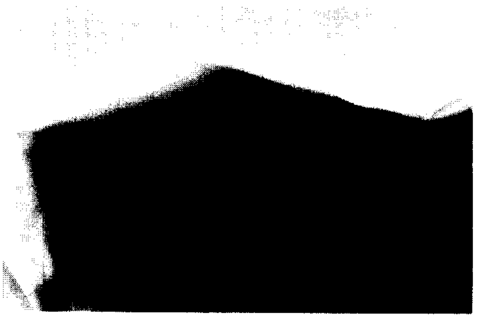

Fig. 2. TEM photograph of the cross-section of the surface of the pre-oxidized silicon nitride.

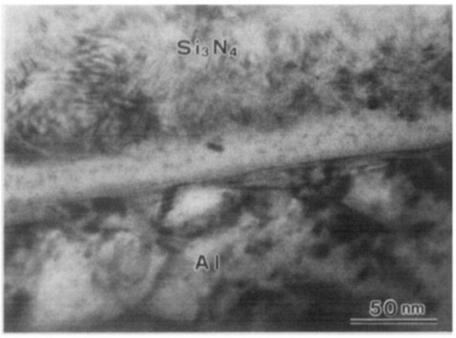

Fig. 3. TEM photograph of the silicon nitride/aluminum interface of the SQ brazed joint.

3.3 HRTEM observation of silicon nitride/aluminum interface

Figure 3 shows the TEM photograph of the interface of the joint fabricated by the SQ method with the pre-oxidized silicon nitride. In the silicon nitride, the lattice image of (100) planes is observed. A thin reaction layer is recognized at the interface. The thickness of the reaction layer is about 30–40 nm. This layer was continuously formed at every part of the interface with no voids. Inside the aluminum braze dense dislocation structure is apparent. Such dislocation structure has always been observed on the metal side at ceramic/metal interfaces because metals easily deform to accommodate thermal stress arising from thermal expansion mismatch between two constituents during cooling from joining temperature and because ceramics are hard to deform. On the other hand, the region thinner than about 50 nm into the silicon nitride grain from the interface of silicon nitride/reaction layer showed some distortion of the lattice of silicon nitride. The (100) planes bend slightly at many points and strain fringes are also observed in the region. Those appearances seem not to be caused by the dislocation structure in silicon nitride.

Figure 4 shows the HRTEM image of the microstructure of the aluminum/reaction layer interface. The electron beam was slightly apart from the ⟨110⟩ axis of aluminum and only one array of the (111) planes was observed in aluminum. No lattice image is recognized in the reaction layer as seen in the upper half. The nanodiffraction pattern taken from the reaction layer shows its amorphous structure clearly. Although it was not possible to set the interface exactly in the edge-on view because the reaction layer is amorphous, it is clear that the interface is not flat in an atomic scale but somewhat wavy.

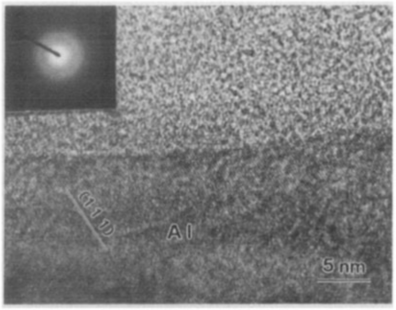

Fig. 4. HRTEM photograph of the amorphous layer/aluminum interface and the diffraction pattern from the amorphous layer. The electron incident beam is slightly inclined from the ⟨110⟩ axis of aluminum.

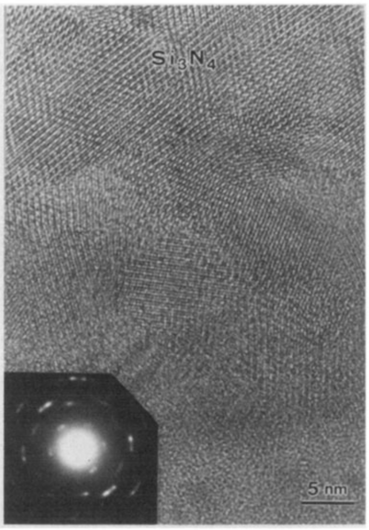

Fig. 5. HRTEM photograph of the transition region from silicon nitride to the amorphous layer. The nanocrystalline layer is observed in between them. The diffraction pattern is from the nanocrystalline layer. The incident electron beam is along the ⟨001⟩ axis of silicon nitride.

Figure 5 shows the HRTEM photograph showing the interface region from the silicon nitride grain (upper part) to the amorphous reaction layer (lower part) with the nanodiffraction pattern taken from the silicon nitride near the reaction layer. The nanocrystalline structure in the silicon nitride is clearly observed. The thickness of the nanocrystalline layer is about 30–40 nm. This thickness was equal to that observed in Fig. 3.

Figure 6 shows the HRTEM photograph taken from the thin part of the reaction layer. The

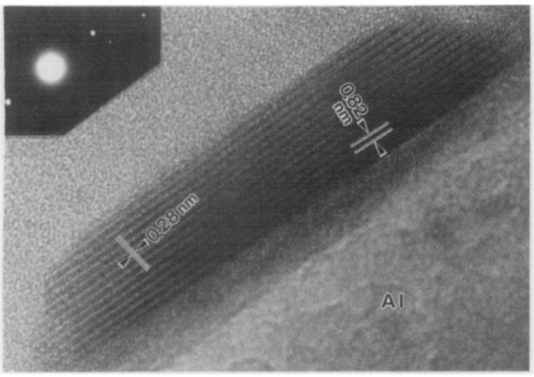

Fig. 6. HRTEM of the thin part of the nanocrystal β'-phase layer with diffraction pattern. The short lines indicate the (100) planes of β'-silicon nitride in every grain. No grain boundary phase is observed even at the triple grain boundary. The electron incident beam is along the ⟨001⟩ axis of silicon nitride.

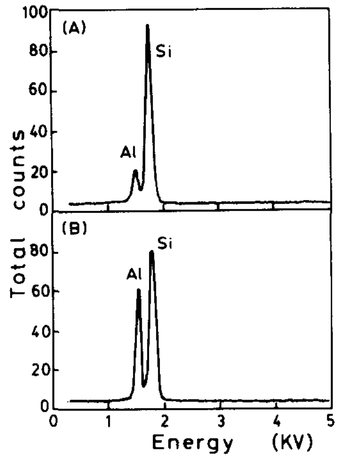

Fig. 7. EDX spectra from the reaction layers. (A) The nanocrystalline layer and (B) the amorphous layer.

photograph also shows the diffraction pattern and the (100) plane in each nanograin is denoted by the short lines. The nanocrystals slightly incline towards each other and also towards the silicon nitride matrix. The deviation angle to the silicon nitride matrix is within a few degrees. In addition, no grain boundary phase was observed even at the triple point and each nanocrystal connects to the other directly.

3.4 Compositional analysis of the interface

Figures 7 and 8 show the EDX and the EELS spectra taken from the interfacial region. From the nanocrystalline reaction layer small amounts of aluminum and oxygen were recognized, in addition to large amounts of silicon and nitrogen. From both the facts that this reaction layer showed almost the same diffraction pattern and the same lattice images seen in Figs 5 and 6 as β-phase silicon nitride and that the layer contains large amounts of oxygen and aluminum in addition to silicon and nitrogen, it is concluded that the nanocrystalline reaction product is the β'-sialon phase. In contrast, the amorphous layer which is facing towards the aluminum layer contained almost similar amounts of aluminum and silicon with a certain amount of oxygen but not nitrogen. This layer is, therefore, the aluminum–silicon–oxygen amorphous layer.

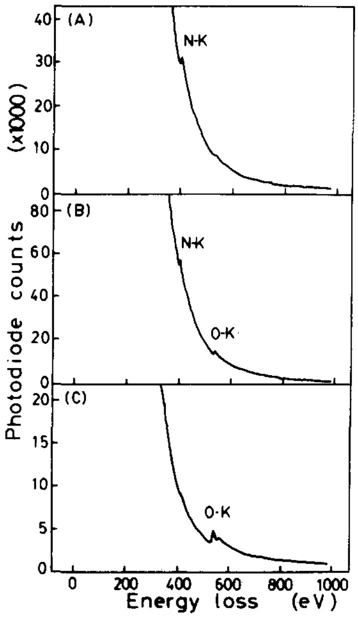

Fig. 8. EELS spectra from (A) silicon nitride, (B) the nanocrystalline layer and (C) the amorphous layer.

3.5 Reaction at the interface during squeeze casting

The results obtained in the previous sections give the interfacial morphology as illustrated in Fig. 9. The reaction at the interface takes place to form two thin reaction layers during the SQ brazing process. Into the silicon nitride grains aluminum and oxygen diffuse, and the β'-sialon nanocrystalline layer is formed. The other layer facing the aluminum braze is an amorphous layer containing aluminum–silicon–oxygen. These findings correspond primarily to previous results.[4,6] In previous work the silicon nitrides with or without sintering binder were brazed with pure aluminum in the conventional static brazing method in a vacuum furnace. The brazing temperature was 800°C, which was similar to the temperature of aluminum melt used in the present work, but the reaction time was 10 min, which was far longer. Both the β'-sialon and the amorphous reaction layers were observed at the interfaces but they were twice as thick as those observed in the present work. The longer reaction time in the previous work promoted the growth of the reaction layers. The other difference in microstructure was recognized in the amorphous layer. The static brazing method sometimes produced the porous amorphous layer at a microscopic scale and unbonded area at a macroscopic scale,[3,4,6] both of which become the defects decreasing the interfacial strength. On the other hand, the dense uniform amorphous layer in addition to no unbonded area or void was obtained in the SQ brazing method. Such

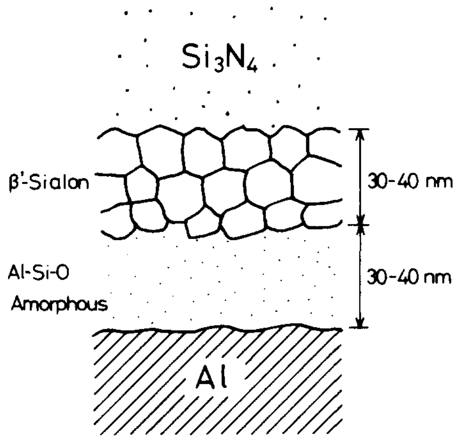

Fig. 9. Schematic illustration of the interfacial region of the SQ brazed silicon nitride joint.

dense and uniform interface structures are one of the benefits attained by this new process.

The reaction between silicon nitride and aluminum in the SQ brazing process may be expressed by the following equation:

$$Si_3N_4 + Al[O] \rightarrow \beta'\text{-sialon (Si–Al–O–N)} + \text{amorphous (Al–Si–O)} \quad (1)$$

The oxygen in the second term in the left-hand side is supplied from the reaction atmosphere. Oxygen will be also supplied from the thin Si–O oxide phase to be formed on silicon nitride by the pre-oxidation, although the presence of the oxide layer could not be identified in the present work. The silica can be reduced easily into silicon and alumina. Therefore, at the beginning, the reaction starts between Al[O] to be formed at the interface and silicon nitride as in eqn (1).

Of course, from thermodynamic considerations the following reaction can be possible under the present reaction conditions instead of the reaction expressed by eqn (1):

$$Si_3N_4 + 4Al \rightarrow 4AlN + 3Si \quad (2)$$

This reaction is expected to proceed only in an oxygen-free reaction system and it may require certain nuclei for the formation of aluminum nitride. The recent work on the reaction between β-silicon nitride whisker and aluminum alloy reported the formation of aluminum nitride layer only on the (100) surface of the whisker, which is expected to be the nucleation site under the similar casting reaction.[7] The presence of oxygen in the reaction atmosphere, however, seems to promote the reaction expressed by eqn (1) instead of that by eqn (2).

3.6 Other microstructural features

Figure 10 shows another view observed in the interfacial region, which was the precipitate having dark contrast in the amorphous layer. Such a precipitate was frequently observed only in the amorphous layer. In every case it had darker contrast compared with the amorphous matrix, with silicon nitride or with aluminum if any diffractions were excited in them. This seems to indicate the presence of a heavier element in the precipitate than silicon, aluminum, oxygen or nitrogen. EDX analysis proved this fact, as shown in Fig. 11. There are calcium, yttrium and iron recognized. Argon detected seems to be the artifact caused by the argon ion thinning process for TEM specimen preparation.

Silicon and aluminum could not be identified as one of the compositions of the precipitate because the matrix amorphous layer had these compositions and it could not be distinguished whether they were involved in the precipitate or not. Therefore, it can be said that this precipitate contains yttrium, calcium and iron at least. Yttrium and calcium are from the boundary phase which were the sintering additives of the silicon nitride used. Iron was also in the silicon nitride. However, the content was below 0·1 wt% and it is hard to assume that the iron was from the silicon nitride boundary phase in all precipitates. On the other hand, iron was also one of the elements of the aluminum braze used. The content was much higher. Therefore, it is easier to think that the iron in the aluminum braze came into the interface to react with the boundary phase of silicon nitride combined with the Al[O].

From the rough approximation of the peak height, the compound is composed of a high amount of yttrium with a small amount of calcium and with less of iron. In addition, the compound seems to be a certain oxide having a low melting temperature because it was from the boundary oxide phase in silicon nitride. Figure 12 shows the lattice image of the precipitate and its diffraction pattern. Two arrays crossing each other are observed. The spacings are 0·28 and 0·82 nm. The latter lattice spacing is that of the ordering three layers. It is quite possible that the compound contains alumina and silica also, because the boundary phase of silicon nitride contained these oxides. Therefore, it is the complex compound of these five oxides.

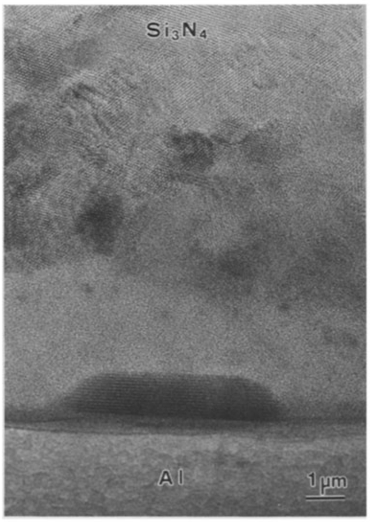

Fig. 10. HRTEM photograph of the interfacial region which shows the precipitate in the amorphous layer. The electron incident beam is along the ⟨001⟩ axis of silicon nitride.

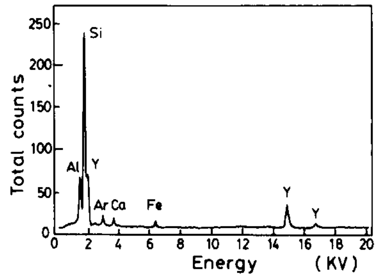

Fig. 11. EDX spectra from the precipitate in the amorphous layer.

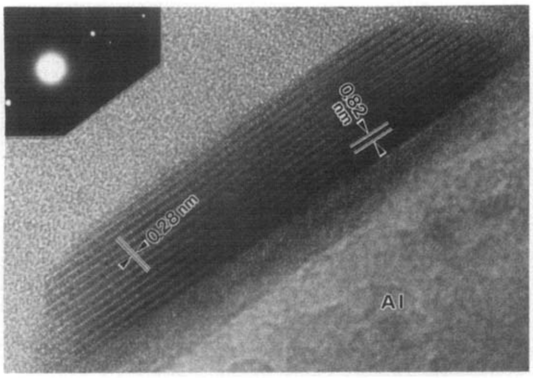

Fig. 12. Enhanced image of the precipitate in Fig. 9.

4 Conclusion

The interfacial strength of the silicon nitride joint brazed with pure aluminum by the SQ method was evaluated and its microstructure was identified by HRTEM and ATEM methods.

The strength was above 400 MPa when silicon nitride was pre-oxidized. The total layer thickness formed by the reaction was thinner than 100 nm, which could be only analyzed by TEM. The reaction layer consisted of two distinct layers. One, adjacent to silicon nitride, was 30–40 nm thick and had a nanocrystalline structure without a boundary phase. The nanocrystals were identified as β'-sialon containing silicon, aluminum, oxygen and nitrogen. Every crystal was inclined by a few degrees to the matrix grain and to each other. The other layer was the amorphous aluminum–silicon–oxygen layer, about 30–40 nm thick. This layer had a dense structure differing from a similar layer formed by conventional brazing in a vacuum furnace. This layer contained small particles composed of yttrium, calcium and iron. Those particles seemed to be the reaction product between the boundary phase of silicon nitride and the braze.

The interface structure was similar to that formed in the conventional static brazing method but was thinner and the structure was much finer and denser. Such structure is expected to give better properties to the joints. Although, unfortunately, the effect of the pre-oxidation treatment of silicon nitride has not been clear yet even by TEM work, it becomes clear that this simple treatment was effective to get such interface structure. Furthermore, the SQ method can produce a good joint of silicon nitride with the aluminum braze even in air atmosphere which had never been achieved yet. The brazing of silicon nitride to other materials such as steels and aluminum is now under examination. Successful results have been obtained in these cases, which will be reported in the future.

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