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# Reaction chemistry at joined interfaces between silicon nitride and aluminium

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Joined interfaces of HIPed additive-free silicon nitride ceramics/aluminium braze bonded at a low temperature of 1073 K for 18 ks or at a high temperature of 1473 K for 1.8 ks in vacuum of 1.3 mPa and of β silicon nitride powders/aluminium powders bonded at the low temperature for 1.8 ks or 18 ks in the same vacuum are identified by analytical transmission electron microscopy and X-ray diffraction method. Mullite, some small crystals and β′-sialon are detected at the interface of the ceramics/aluminium braze bonded at the low temperature and 15R AlN-polytype sialon, β′-sialon, aluminium nitride, mullite and silica-alumina noncrystalline are detected at that bonded at the high temperature. At the interface of the two kinds of powders, aluminium nitride and silicon are also detected besides β′-sialon and silica-alumina noncrystalline even though the bonding was conducted at the low temperature. The interfacial reactions of the joints are influenced not only by bonding temperature but also by the oxide formed at the interface before bonded.

## 1. Introduction

In order to achieve reliable brazing of silicon nitride ceramics using aluminium braze, many workers have investigated the optimum brazing conditions. Suganuma *et al.* [1] showed that high bond strength could be obtained at brazing temperatures higher than 1050 K at a constant brazing time of 0.6 ks. This result indicates that, even though the wettability of aluminium liquid to silicon nitride ceramics is not good yet at temperatures below 1200 K [2], silicon nitride ceramics can be brazed using aluminium with ease even at a temperature as low as 1050 K. To elucidate the bonding mechanism of aluminium to silicon nitride ceramics, the present authors have studied the interface between aluminium and silicon nitride ceramics by means of analytical transmission electron microscopy. The aluminium brazing of silicon nitride ceramics, which were HIPed additive-free ceramics and a kind of pressureless–sintered ceramics, was conducted at 1073 K for 1.8 or 0.9 ks in vacuum of 1.3 mPa. Regardless of the kind of the silicon nitride ceramics, two reaction layers were observed, one was a thick silica-alumina non-crystalline layer facing aluminium and the other was a thin layer to be considered as β′-sialon, facing silicon nitride [3–5]. This result implies that oxygen seems to play an important role in the interfacial reaction.

Naka *et al.* [6] found by an X-ray diffraction (XRD) method and transmission electron microscopy (TEM) that two reaction phases were formed at the interface between pressureless-sintered silicon nitride ceramic and liquid aluminium on holding at 1473 K for 3.6 ks in vacuum below 1.3 mPa. The phases were 15R AlN-polytype sialon and an amorphous phase of alumina, differing with those obtained by the present authors. Recently Milberg *et al.* [7] analysed the brazed interfaces between aluminium and each of hot-pressed and reaction bonded silicon nitride ceramics using XRD and TEM. The brazing was conducted at 1823 K for 3.6 ks under a nitrogen atmosphere. They reported that the reaction products were β′-sialon and alumina for hot-pressed silicon nitride ceramics and 15R AlN-polytype sialon, aluminium nitride, silicon and the X-phase for reaction bonded silicon nitride ceramics. Ikuhara *et al.* [8] brazed reaction bonded silicon nitride ceramics using aluminium braze at 1470 to 1970 K for 1.8 ks in nitrogen gas and also observed the 15R AlN-polytype sialon using a high resolution electron microscope.

The mixture of silicon nitride powders and aluminium powders was also examined by XRD after heating at 1273 K in vacuum [9] or at 1823 K in an argon atmosphere [7]. Only aluminium nitride and silicon are detected but not sialon and oxide. It must be pointed out that the silicon nitride powders used in the experiments were composed of mainly an α phase although there was a little in silicon nitride ceramics.

It is clear from the above mentioned work that silicon nitride is bonded with aluminium by means of interfacial reaction. But there are a few discrepancies among the authors' results on the reaction products of silicon nitride and aluminium. Such discrepancies

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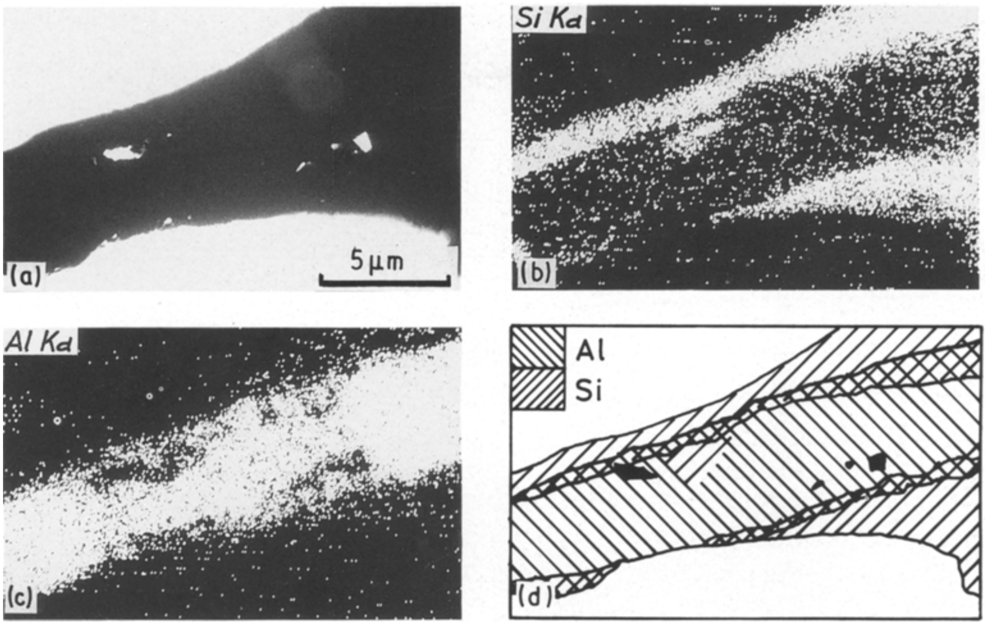


*Figure 1* Images of (a) STEM and of (b and c) $AlK_\alpha$ and $SiK_\alpha$ X-rays at the same interfacial area in the LT joint, and (d) a sketch showing the layers containing both aluminium and silicon.

would come from differences of the kind of silicon nitride ceramics and brazing conditions, such as temperature, time, and atmosphere. In general, brazing at high temperatures brought 15R AlN-polytype sialon and that at low temperatures β′-sialon and an amorphous phase. In order to clarify the reason for the discrepancies and to elucidate the chemistry at the interface, the present authors have examined the effects of a high brazing temperature and a long brazing time on the reaction products, and the reaction of a mixture of β silicon nitride powders and aluminium powders.

## 2. Experimental procedure

An aluminium plate, 0.6 mm thick, was sandwiched between two HIPed additive-free silicon nitride ceramic workpieces, which were of the same kind as those used in the previous work [3, 5]. The sandwiched ones were heated on each condition of 1073 K for 18 ks and 1473 K for 1.8 ks under a small pressure of about 1 MPa in vacuum below 1.3 mPa for the fabrication of aluminium brazed joints of silicon nitride ceramics. In the present work, the joints brazed on the former condition (lower temperature and longer duration) are called LT joints and those on the latter condition (higher temperature and shorter duration) HT joints. To prepare specimens for analytical transmission electron microscopy, thin plates were cut off from the joints normal to the brazed interfaces between silicon nitride ceramics and aluminium, ground to be thinner than 0.1 mm in thickness, and then were thinned down by argon ion bombardment, in which the accelerating voltage of the ion gun was 3 kV. To prepare the mixture of two kinds of powders, aluminium powders and silicon nitride powders were mixed in a volume ratio of about 1 : 1. The mixture was pressed into tablet shape of 12 mm diameter and 4 mm thick using a cold isostatic press under a pressure of 200 MPa. The tablets were heated to 1073 K in vacuum of 1.3 mPa for 1.8 ks or 18 ks, and then were studied by XRD and TEM. The preparation of TEM specimens was the same as that mentioned above.

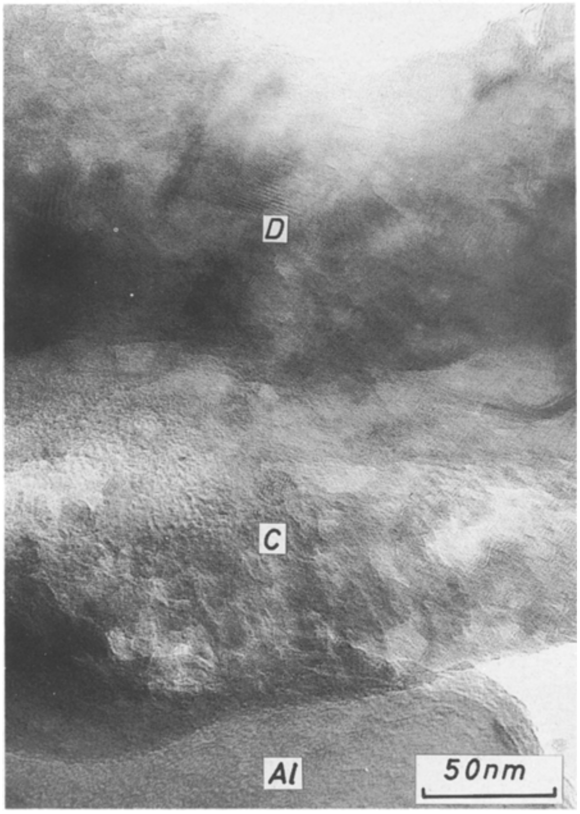
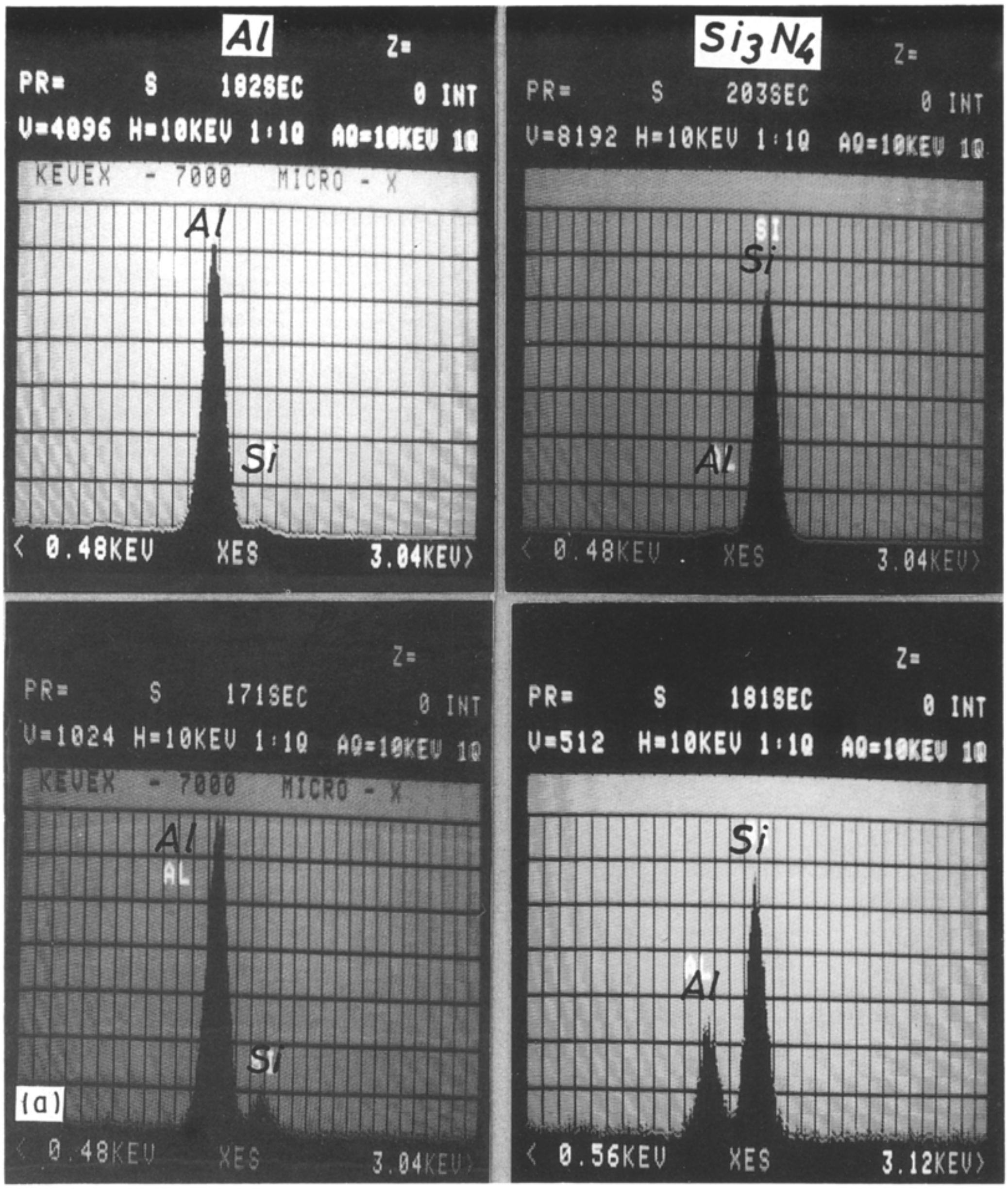


*Figure 2* TEM image showing interfacial reaction layers of the LT joint.

## 3. Results

### 3.1. LT joint

Fig. 1 shows the images of scanning transmission



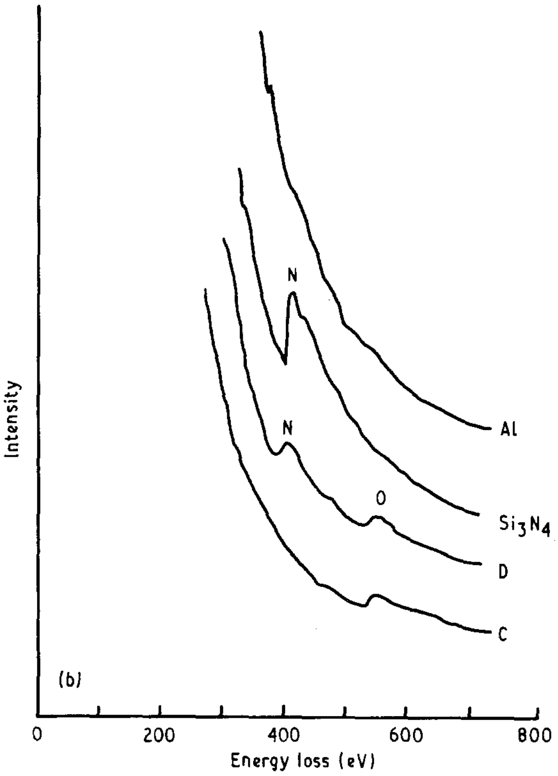


*Figure 3* (a) EDX spectra of the areas C (bottom left) and D (bottom right) in Fig. 2 and of silicon nitride and aluminium of the same joint, (b) EELS spectra.

electron microscopy (STEM) and of $AlK_\alpha$ and $SiK_\alpha$ X-rays at the same area in the LT joint. There exists a reaction zone about 500 nm thick between silicon nitride and aluminium. This zone consists of two reaction layers C and D as shown in Fig. 2. On the basis of the results of energy dispersive X-ray spectrometry (EDX) and electron energy loss spectroscopy (EELS) in Fig. 3a and b, the layers C and D contain Al, Si, O, and Al, Si, O, N, respectively, similar to the results obtained so far [3–5]. On the other hand, the electron diffraction (ED) patterns shown in Fig. 4a and b indicate that, though the layer D is constituted of β′-sialon, the layer C is composed of some mullite crystals and some small crystals instead of a silica-alumina noncrystalline phase observed in the joints brazed at a duration shorter than 1.8 ks. This evidence means that brazing of longer duration has a tendency to crystallize the amorphous layer facing aluminium.

β′-sialon is known to have the same crystal structure as silicon nitride, only some $Si^{4+}$ and $N^{3-}$ ions

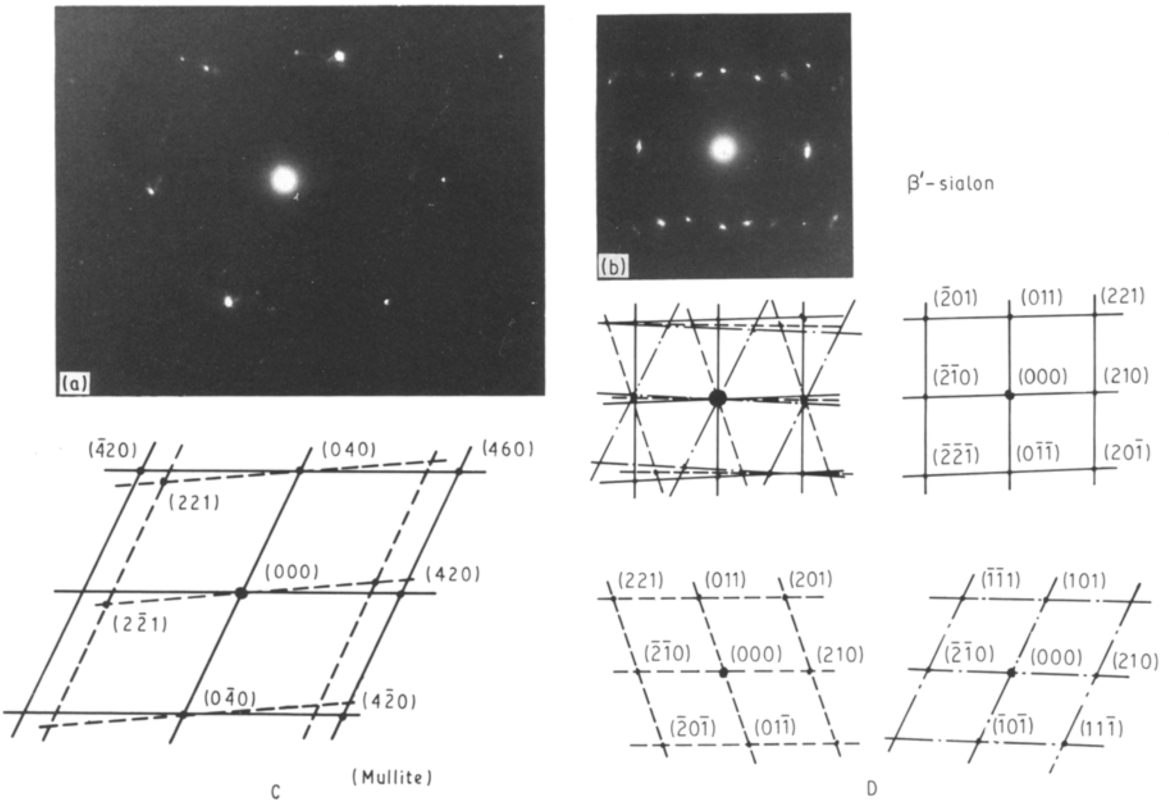


*Figure 4* ED patterns of the areas C and D.

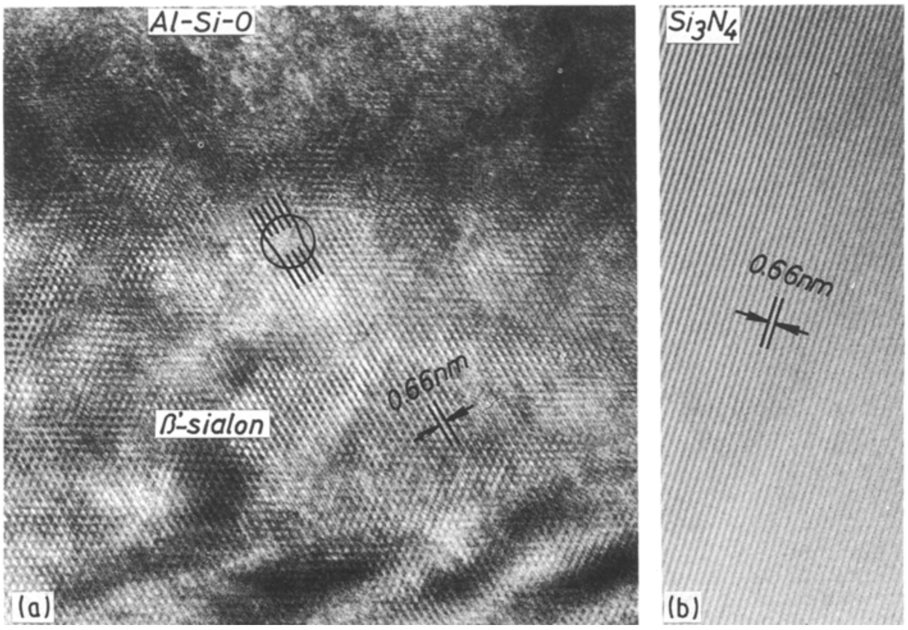


*Figure 5* Lattice image of β'-sialon formed at the interface of the LT joint, showing strained lattice planes and some dislocations.

are replaced by $Al^{3+}$ and $O^{2-}$ ions, respectively [10]. Fig. 5a shows a lattice image of the β'-sialon which forms at the interface of the joint. Comparing it with the lattice image of the silicon nitride (Fig. 5b) taken from the same specimen, it is clear that the (1 0 0) lattice planes of the β'-sialon are strained at a lot of places and some dislocations can be found in the image. This may be due to the random substitution of aluminium and oxygen ions for silicon and nitrogen ions.

## 3.2. HT joint

The images of STEM and of $AlK_\alpha$ and $SiK_\alpha$ X-rays for the HT joint are shown in Fig. 6. The zone containing both aluminium and silicon is considerably thicker as compared with that in the LT joint. The diffusion of the elements is accelerated owing to high brazing temperature. Fig. 7 shows a TEM image taken from the HT joint. From the analyses of EDX, EELS and ED, the areas A and B consist of β'-sialon and 15R AlN-polytype sialon, respectively, both containing Al,

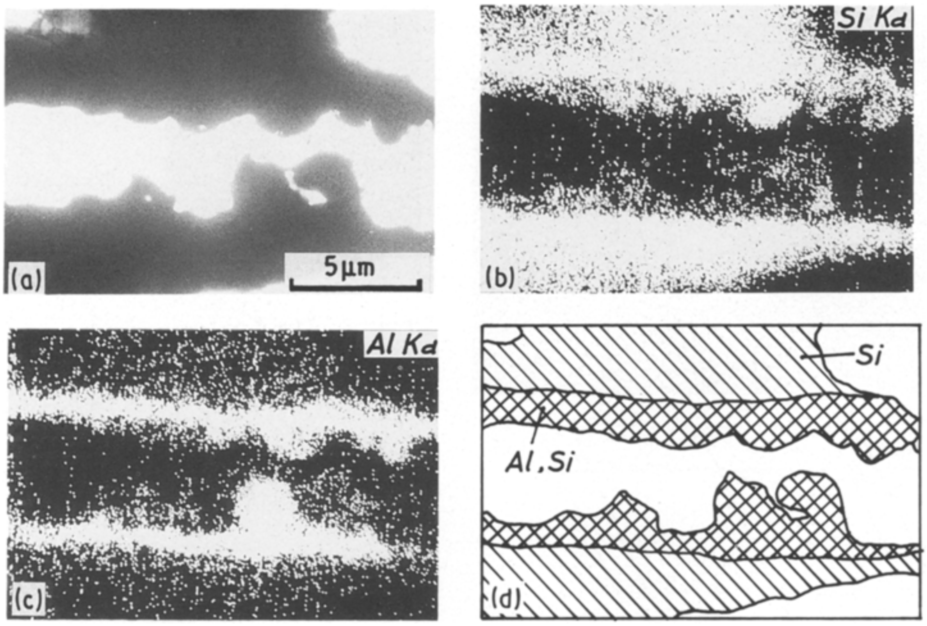


*Figure 6* Images of (a) STEM and of (b and c) $AlK_\alpha$ and $SiK_\alpha$ X-rays at the same area in the HT joint, and (d) a sketch showing the layers containing both aluminium and silicon.

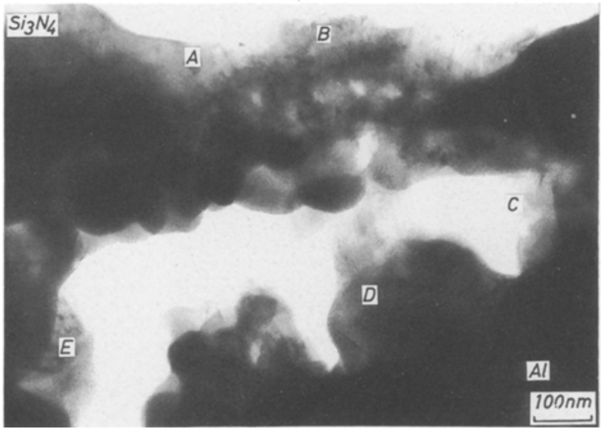
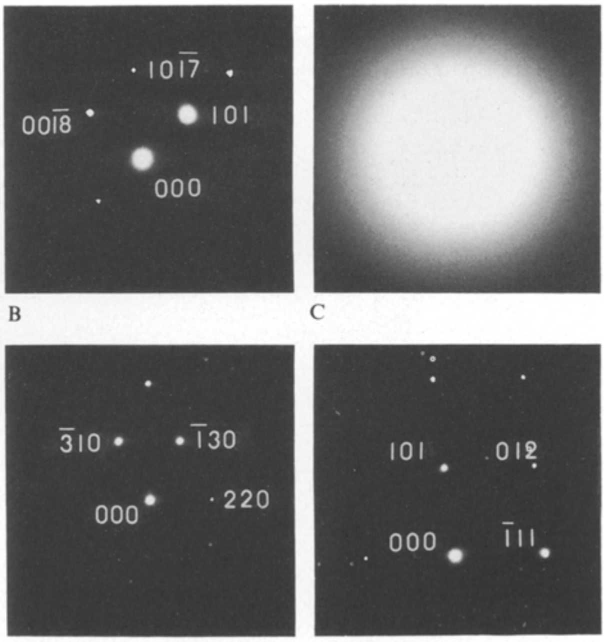


*Figure 7* TEM image taken from the HT joint.



B C

D E

*Figure 8* ED patterns of the areas B, C, D and E. (B) 15R AlN-polytype sialon, (C) silica-alumina noncrystalline, (D) mullite, (E) aluminium nitride.

Si, N and O. There is still silica-alumina noncrystalline (C) between the 15R AlN-polytype sialon and aluminium, but mullite (D) and AlN (E) are also detected in this region. The ED patterns of the areas B, C, D, and E are shown in Fig. 8.

## 3.3. Mixture of silicon nitride powders and aluminium powders

The XRD spectra of the mixture are shown in Fig. 9. Besides the peaks of silicon nitride (β) and aluminium of the original powders, there are also the peaks of silicon and aluminium nitride in the mixture after heating at 1073 K for 1.8 ks or 18 ks. The height of the peaks of silicon increases twice as the heating time is prolonged to ten times. It is obvious that the reaction

$$Si_3N_4 + 4\,Al = 4\,AlN + 3\,Si \qquad (1)$$

occurs in the mixture during heating and that the reaction progresses fast at the early stage of heating. This is different from the case of joints where sialons and silica-alumina noncrystalline are usually formed at the interface although some aluminium nitride and silicon are also detected when joining was conducted at higher temperatures. In order to make the reason for the discrepancy clear, the process of the formation of aluminium nitride and silicon in the mixture must be studied.

Figure 10a shows a TEM image of the mixture heated at the same temperature for 18 ks. An ED pattern and an EDX spectrum of the crystal A are shown in Fig. 10b. The crystal formed on a concave surface of silicon nitride is aluminium nitride containing some silicon. A silicon crystal (S) forms at the

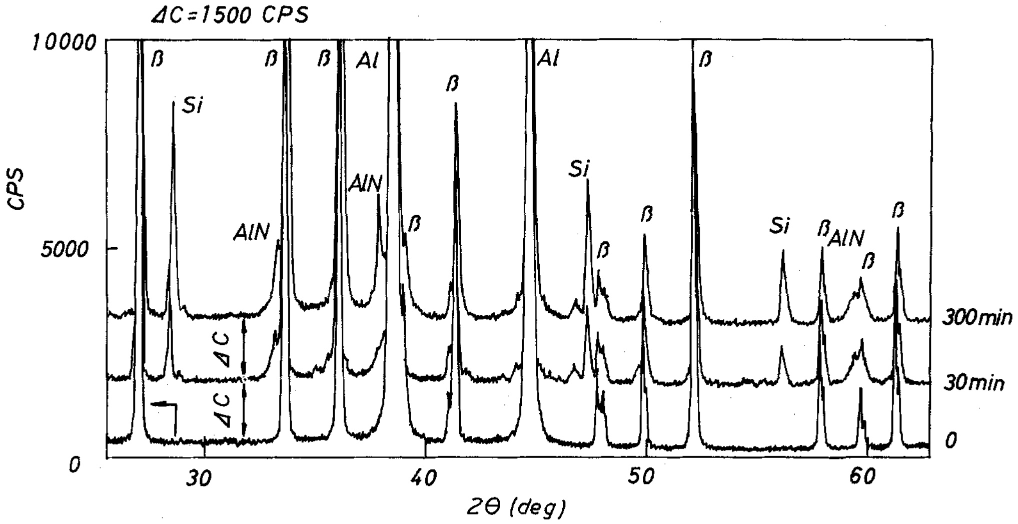


*Figure 9* XRD spectra of the mixture of silicon nitride powders and aluminium powders. (β) β-$Si_3N_4$.

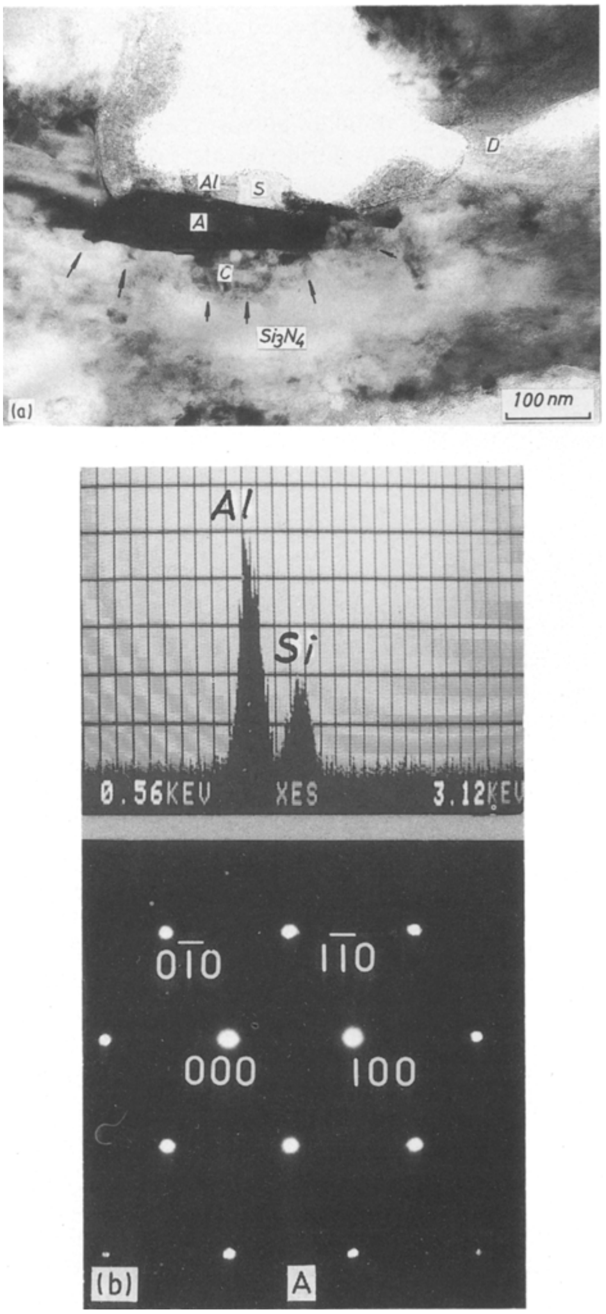


*Figure 10* (a) TEM image of the mixture heated at 1073 K for 18 ks in a vacuum of 1.3 mPa and (b) EDX spectrum and ED pattern of the area A.

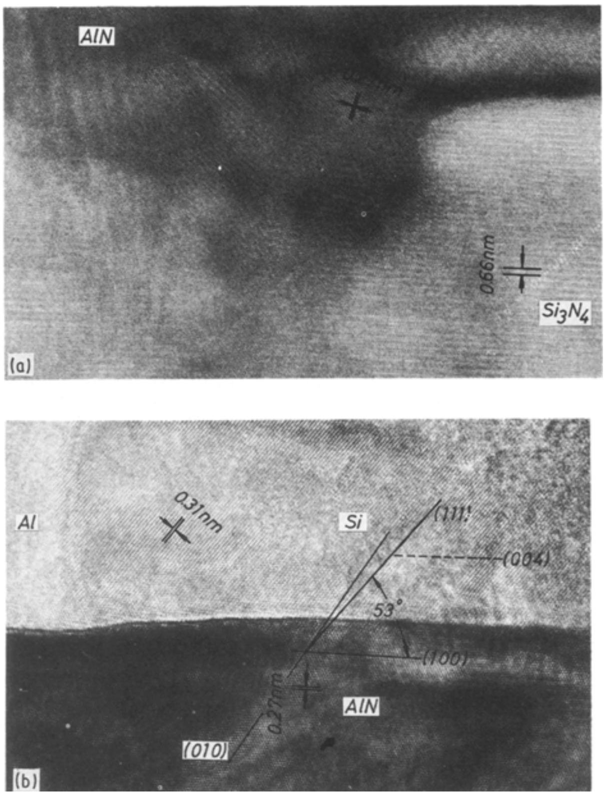


*Figure 11* Lattice image of (a) the area C in Fig. 10a, and (b) at the interfacial area of aluminium nitride crystal (A) and silicon crystal (S) in Fig. 10a.

surface of the aluminium nitride crystal and grows inside aluminium. There are also some egg-like areas in silicon nitride (marked by black arrows), which are attached to the aluminium nitride crystal. In Fig. 11a showing a lattice image of the area C in Fig. 10a, there are the image of (1 0 0) planes of silicon nitride and that of the {1 0 0} planes of aluminium nitride. Fig. 11b shows a lattice image at the interfacial area of the aluminium nitride and the silicon crystals. The silicon crystal grows in parallel to a (1 0 0) plane of aluminium nitride. The angle between the $(1\,1\,1)_{Si}$ and the $(1\,0\,0)_{AlN}$ planes is about 53°, which is nearly equal to that between the $(1\,1\,1)_{Si}$ and the $(0\,0\,4)_{Si}$ (54.7°). Since the $(0\,0\,4)_{Si}$ plane is vertical to the photograph,

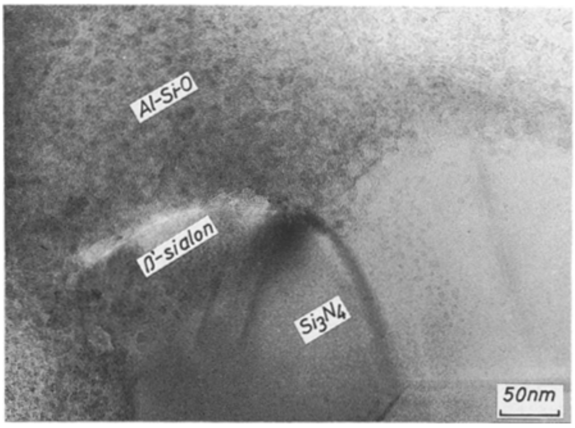


*Figure 12* TEM image at another place in the same specimen as that for Fig. 10 (a). $\beta'$-sialon and silica-alumina noncrystalline (Al-Si-O) formed at the interface between silicon nitride and aluminium.

which is confirmed by ED analysis, the silicon crystal can grow in parallel to the $(1\,0\,0)_{\mathrm{AlN}}$ plane with the crystallographic relationship of $(0\,0\,4)_{\mathrm{Si}}//(1\,0\,0)_{\mathrm{AlN}}$ and $[1\,\bar{1}\,0]_{\mathrm{Si}}//[0\,0\,1]_{\mathrm{AlN}}$.

The above mentioned results show that an aluminium nitride crystal is first formed at the interface between aluminium and silicon nitride and then grows into silicon nitride. Because the solubility of silicon in aluminium is about 30 at % at 1073 K and it decreases to 0.05 at % at 573 K, silicon decomposed from silicon nitride can dissolve in aluminium at first and then precipitates epitaxially on the surface of the aluminium nitride crystal during cooling.

It is also clear from Fig. 10a that aluminium nitride crystal does not form homogeneously on all the surface of silicon nitride. There are some parts of the surface covered by silica-alumina noncrystalline, as found at the area D. Fig. 12 shows another TEM image for the same specimen, both silica-alumina noncrystalline and $\beta'$-sialon are detected at the interface of silicon nitride and aluminium. It is considered that aluminium nitride and silicon form at the interface where aluminium directly contacts with silicon nitride and that $\beta'$-sialon and silica-alumina noncrystalline form at the interface where oxide, such as aluminium oxide, exists between aluminium and silicon nitride before bonded.

## 4. Discussion

In reviewing the work of the present authors and that of the other groups [6–9], it is obvious that $\beta'$-sialon and silica-alumina oxides are usually formed at the interface of the joint brazed at a lower temperature, while $\beta'$-sialon, 15R AlN-polytype sialon, aluminium nitride, silicon and the silica-alumina oxides are formed on the brazing at a higher temperature. However in the case of the mixture of both powders of silicon nitride and aluminium, aluminium nitride and silicon are formed generally even at a low temperature.

These phenomena can be explained as follows. Since $\beta'$-sialon is the same as silicon nitride in crystal structure, it can form only by the diffusion of aluminium and oxygen into silicon nitride, without a change in crystal structure. This may be the reason that it forms easily even at a low temperature. The formation of aluminium nitride and silicon is thermodynamically possible at all the brazing temperatures, but for the formation, aluminium liquid has to be in direct contact with silicon nitride without any oxides and the nucleation of aluminium nitride has to occur. 15R AlN-polytype sialon, which has the same wurtzite structure as aluminium nitride, also needs the nucleation for the formation. As a brazing temperature is raised, it becomes easier that aluminium oxide on the surface of liquid aluminium decomposes in vacuum [11]. The diffusion of aluminium and silicon and the nucleation of aluminium nitride and 15R AlN-polytype sialon are also made easier, hence these compounds and silicon are expected to form easily at high brazing temperatures. In the case of the mixture of silicon nitride powders and aluminium powders, the surface oxide of aluminium powders can be scratched and broken by silicon nitride powders during mixing and pressing, thus some aluminium powders can contact tightly with silicon nitride powders. As a result, the formation of aluminium nitride occurs easily.

Most of the reaction products contain oxygen even when the heating was conducted in vacuum or in inert gases. The oxygen comes from oxides in silicon nitride ceramics and on faying surfaces of the ceramics and aluminium braze, and from the atmosphere during brazing [1, 4, 5].

## 5. Conclusions

Mullite, some small crystals and $\beta'$-sialon are detected at the interface of the joint brazed at 1073 K for 18 ks in vacuum of 1.3 mPa. Such a long duration tends to crystallize the silica-alumina noncrystalline, which is formed as an interfacial product in the joint brazed at a short time of 1.8 ks. When the mixture of silicon nitride powders and aluminium powders was heated under the same condition as this, aluminium nitride and silicon are also produced quickly besides $\beta'$-sialon and silica-alumina noncrystalline. At a higher temperature of 1473 K, since the diffusion of aluminium and silicon in silicon nitride is accelerated, 15R AlN-polytype sialon, $\beta'$-sialon, aluminium nitride, mullite and silica-alumina noncrystalline can be formed at a brazing period of 1.8 ks. The brazing temperature and the amount of oxygen supplied to the interface influence the interfacial reaction.

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