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The nature of sialon joints between silicon nitride based bodies

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Quite strong joints between silicon nitride based bodies have been made by incorporating a layer of aluminium and oxides between the bodies and heating in a nitriding atmosphere. The joints are resistant to thermal shock and maintain their strength at 1200° C. Microscopic, DTA and X-ray diffraction studies indicated that sialon phases are present in the joints, and that the bonding reaction involves the reduction of Si_3N_4 by aluminium and the subsequent renitriding of the resultant silicon, as well as the simultaneous nitriding of a portion of the aluminium. Transmission electron microscopy of a joint between hot pressed and reaction bonded silicon nitrides showed that 15R aluminium nitride polytype sialon was present on the reaction bonded side of the joint and β'-sialon on the hot pressed side.

1. Introduction

When a monolithic body of required shape cannot be fashioned from a silicon nitride based ceramic, perhaps because prohibitively expensive machining is necessary or because completely enclosed voids are involved, it is often desirable to join two or more separate bodies. A prime example of such a situation is the duo-density silicon nitride gas turbine rotor [1], wherein a reaction bonded silicon nitride blade ring is joined to a hot pressed silicon nitride hub. A number of joining methods have been reported, including some rather complex hot pressing procedures [1, 2], a technique [3] which uses ZrO_2 as a binder, another [4] which makes use of a transient liquid phase, and a process [5] which converts mating surfaces of silicon nitride based bodies to sialon phases. If it could be accomplished at a reasonable temperature, a reaction between the surface regions of two silicon nitride bodies and an intervening layer of, say Al_2O_3 and AlN, might be expected to form some sort of sialon phase which might join the bodies. Of course, little or no such reaction occurs with solid Si_3N_4 bodies. However, if a layer of metallic aluminium, along with SiO_2 or Al_2O_3, is placed between mating surfaces of Si_3N_4 or sialon bodies and the assembly is heated in a nitriding atmosphere to about 1400° C or higher for a time which depends on the temperature, a reaction occurs and a bond is formed. In the course of the study reported herein, joints were made between all combinations of hot pressed Si_3N_4, reaction bonded Si_3N_4 and pressureless sintered sialon, but most of the work was done on joints between hot pressed and reaction bonded Si_3N_4, referred to hereafter as HPSN and RBSN, respectively. This report is concerned with a description of the nature and microstructure of the aforementioned sialon joints.

2. Experimental procedure

In order to prepare joints for study, the required layer of aluminium, along with Al_2O_3 or SiO_2, was applied in a number of ways, including the sandwiching of an 18 μm (0.7 mil) aluminium foil between the specimens with Al_2O_3 and SiO_2 supplied by the passive oxide layers on the aluminium and Si_3N_4; the vacuum evaporation of layers of aluminium ranging in thickness from 13 to 220 nm on the mating surfaces of either or both surfaces; the evaporation of alternating layers of aluminium and Al_2O_3 on either or both of the faces to be joined; and the deposition of mixed Al–Al_2O_3 powders between these faces. The HPSN was Norton HS-130, while the RBSN was produced at the Ford Motor Company [6], as was the sialon [7]. Joints were usually made by heating in a nitriding atmosphere for 1 h at 1550° C, although temperatures as low as 1400° C and as high as 1950° C were used. At the lowest temperature the bonding reaction was slow, while at the highest temperature extensive decomposition of the Si_3N_4 occurred. The assemblies to be joined were heated under vacuum to above the melting point of aluminium, then either under nitrogen for the remainder of the treatment, or under argon to some temperature between the aluminium melting point and 1300° C followed by nitrogen for the remainder of the treatment.

In order to get some idea of the strengths of the bonds formed by this technique, stacks of test bars 3.0 × 0.5 × 0.3 cm were bonded together, then cut transverse to the joints to make MOR test bars with several joints per bar. These were ground and polished to a 15 μm finish in preparation for testing. Fig. 1 shows a stack of joined bars and a test bar with eight joints. These composite bars were first tested in three-point bending at room temperature. A portion of the fragments remaining from the first break was then re-tested at room temperature, while another portion was tested at 1200° C. Some of the fragments from the second room temperature test, along with some from the initial 1200° C test, were then re-tested at 1200° C. Bonded specimens were tested for resistance to thermal shock by being subjected to 520

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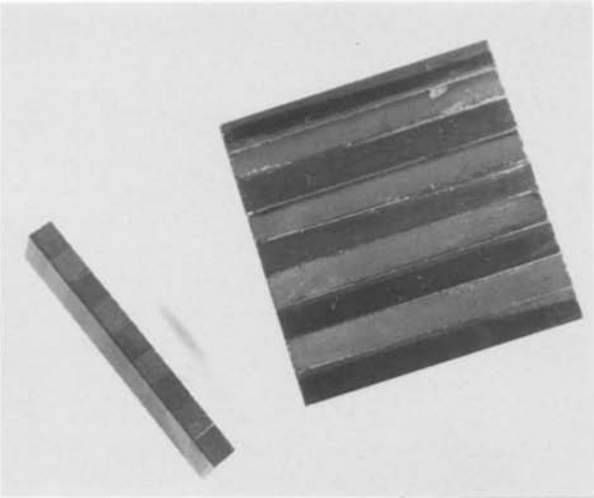

Figure 1 Stack of joined bars and test bar with eight joints.

cycles of heating to 1000° C, holding for 1 min, and quenching to room temperature in 10 sec.

The joint regions were examined by X-ray diffraction, optical microscopy and scanning electron microscopy (SEM), as well as, in the case of one joint between HPSN and RBSN formed with an 18 μm aluminium foil, transmission electron microscopy (TEM). The SEM examination included silicon and aluminium analysis. For X-ray diffraction, joints were split apart. For TEM a 3 mm disc was cut ultrasonically from the bonded Si_3N_4 body, with the interface between the hot pressed and reaction bonded materials along a diameter of the disc. This disc was mechanically polished to a thickness of $\sim 75\,\mu$m and finally thinned to electron transparency using a 6 KeV argon ion beam inclined at 15° to the surface. Fig. 2 shows the TEM specimen prepared in this manner. Both Si_3N_4 bodies thinned much faster than did the area of the joint. The foil was examined with a Siemens 102EM equipped with a high angle double tilting stage and with a Philips 400T at Case Western Reserve University. All TEM results reported herein were obtained from the specimen shown in Fig. 2.

Additional information about the bonding reaction was obtained from differential thermal analysis (DTA) experiments on mixtures of Si_3N_4 and aluminium powders and of SiO_2 and aluminium powders under argon and nitrogen atmospheres, combined with X-ray diffraction analysis of the resulting mixtures.

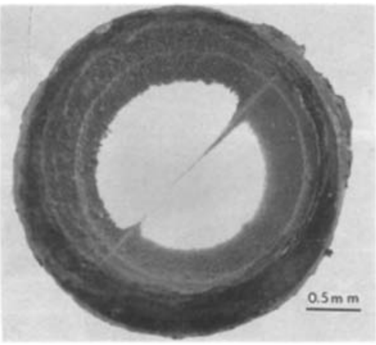

Figure 2 Ion-milled foil of hot pressed silicon nitride bonded to reaction bonded silicon nitride. The interface between the two silicon nitride bodies is where the two "needles" protrude into the centre of the hole.

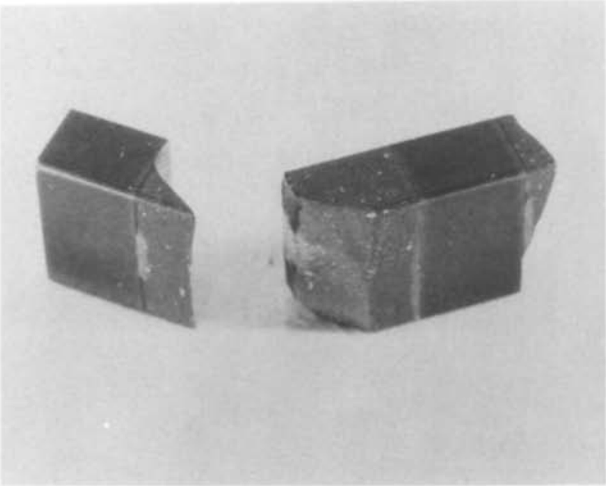

Figure 3 Example of fracture running partly through joint and partly through silicon nitride bar.

3. Results

From the collection of MOR tests described above, it could be estimated that, at room temperature, the

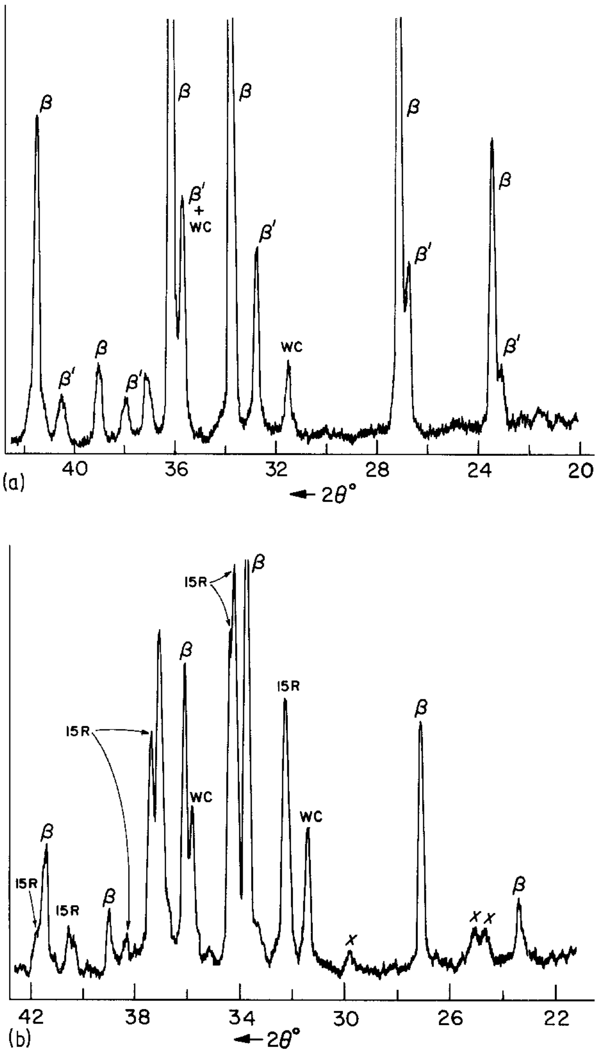

Figure 4 Cu*Kα* X-ray diffraction patterns of split joint showing the presence of (a) β'-sialon and (b) 15R AlN polytype sialon. ×200.

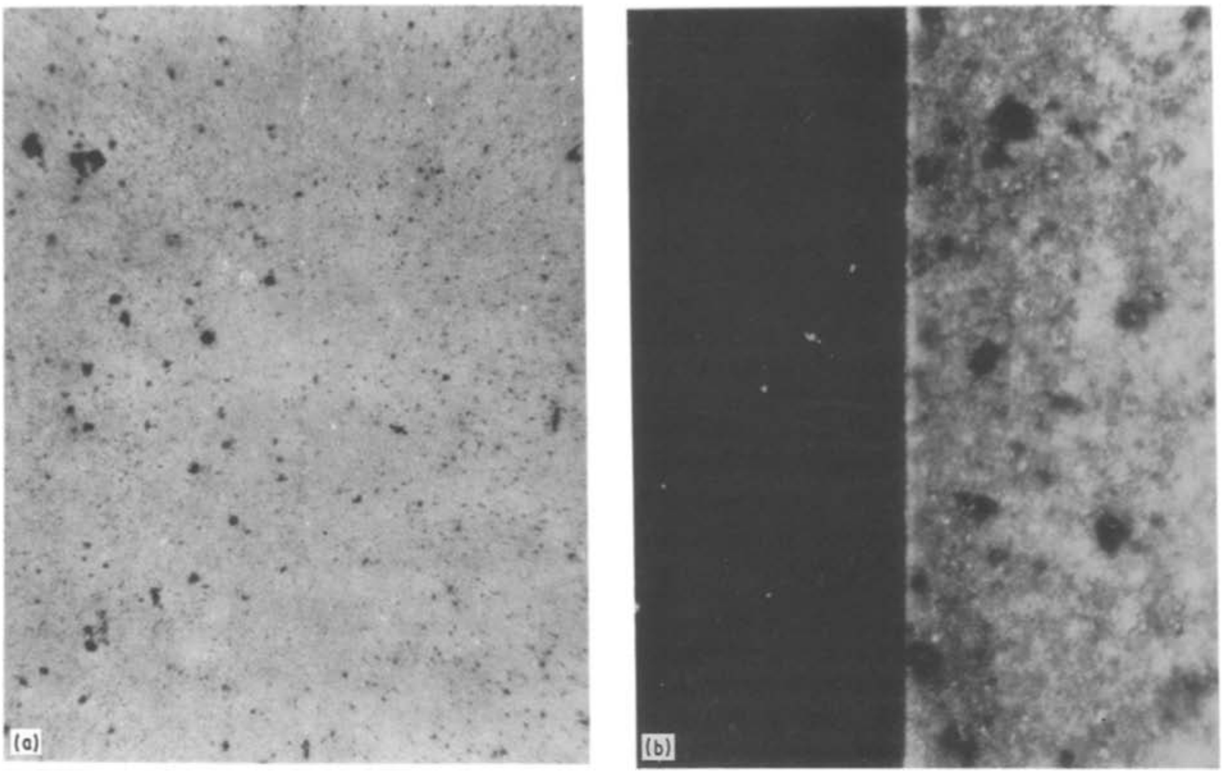

Figure 5 Optical micrographs of a "good" joint in (a) unpolarized and (b) polarized light.

joint strengths ranged from 35 to 210 MPa, with 90% exceeding 55 MPa. It could also be concluded that the joints were as strong at 1200° C as they were at room temperature. The fracture in the strongest joints generally ran partly through the joint and partly through the RBSN or HPSN, while in the weaker joints it ran only through the joint. Fracture in a strong joint is illustrated in Fig. 3. Specimens withstood the described thermal shock test with no apparent damage.

Fig. 4 shows X-ray diffraction patterns obtained from split joints. In Fig. 4a peaks associated with β' sialon are identified along with those of β-Si_3N_4 and tungsten carbide (presumably from original milling media), while in Fig. 4b those of 15R AlN polytype sialon and X-phase [8] are identified. Clearly, sialon phases are present in the joints.

Fig. 5a shows an optical micrograph of a "good" joint between HPSN and RBSN taken in unpolarized light. The joint is vertical through the centre of the field with the hot pressed material on the left, and is virtually invisible. Fig. 5b shows the same joint in

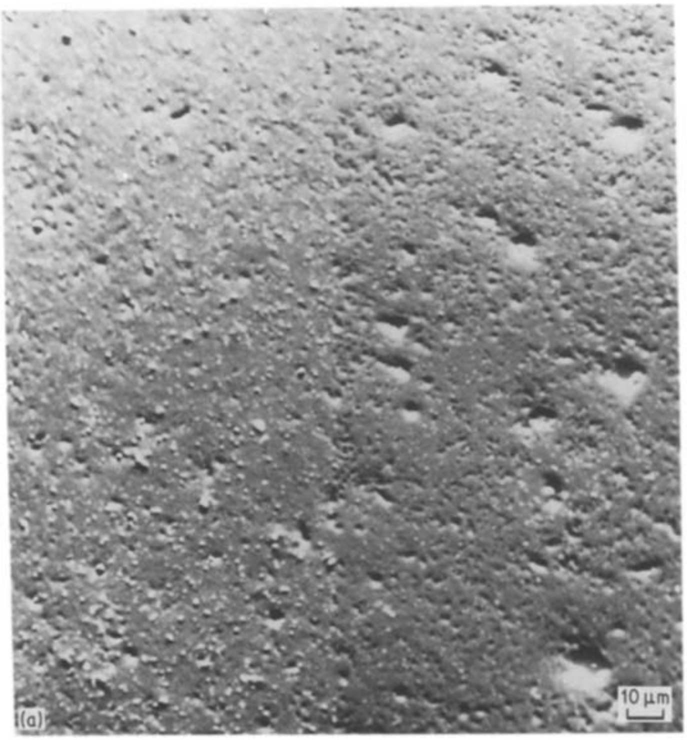

Figure 6 Scanning electron micrographs of the joint shown in Fig. 5. (a) Secondary electron image, (b) Si*Kα* and (c) Al*Kα* X-ray maps, of the same area as (a).

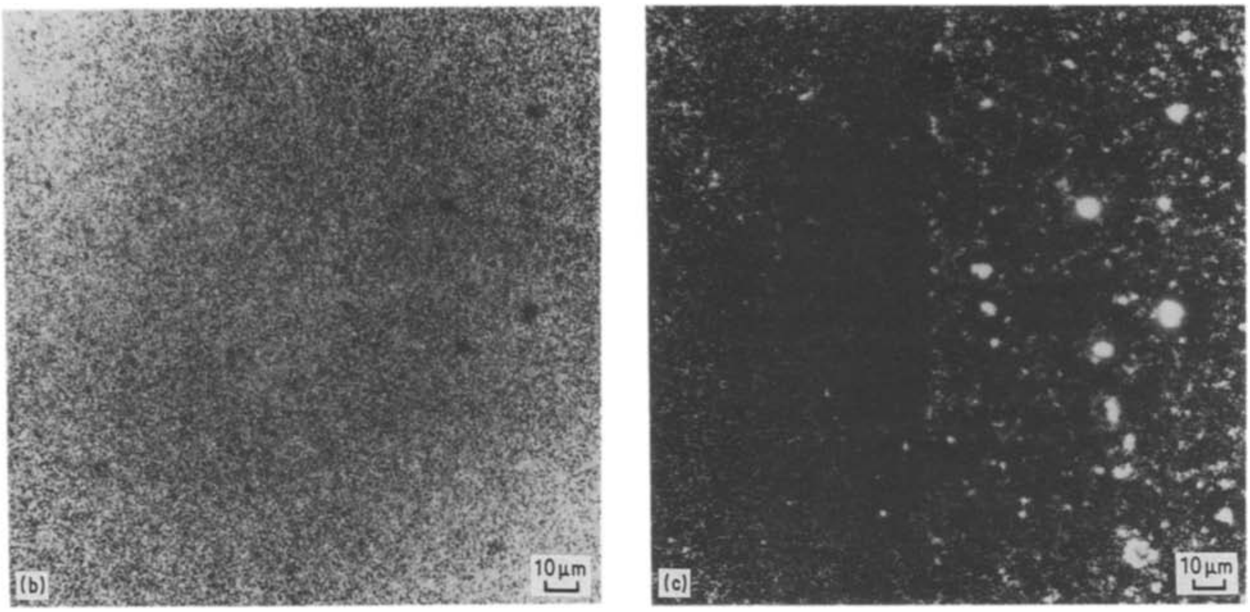

Figure 6 Continued.

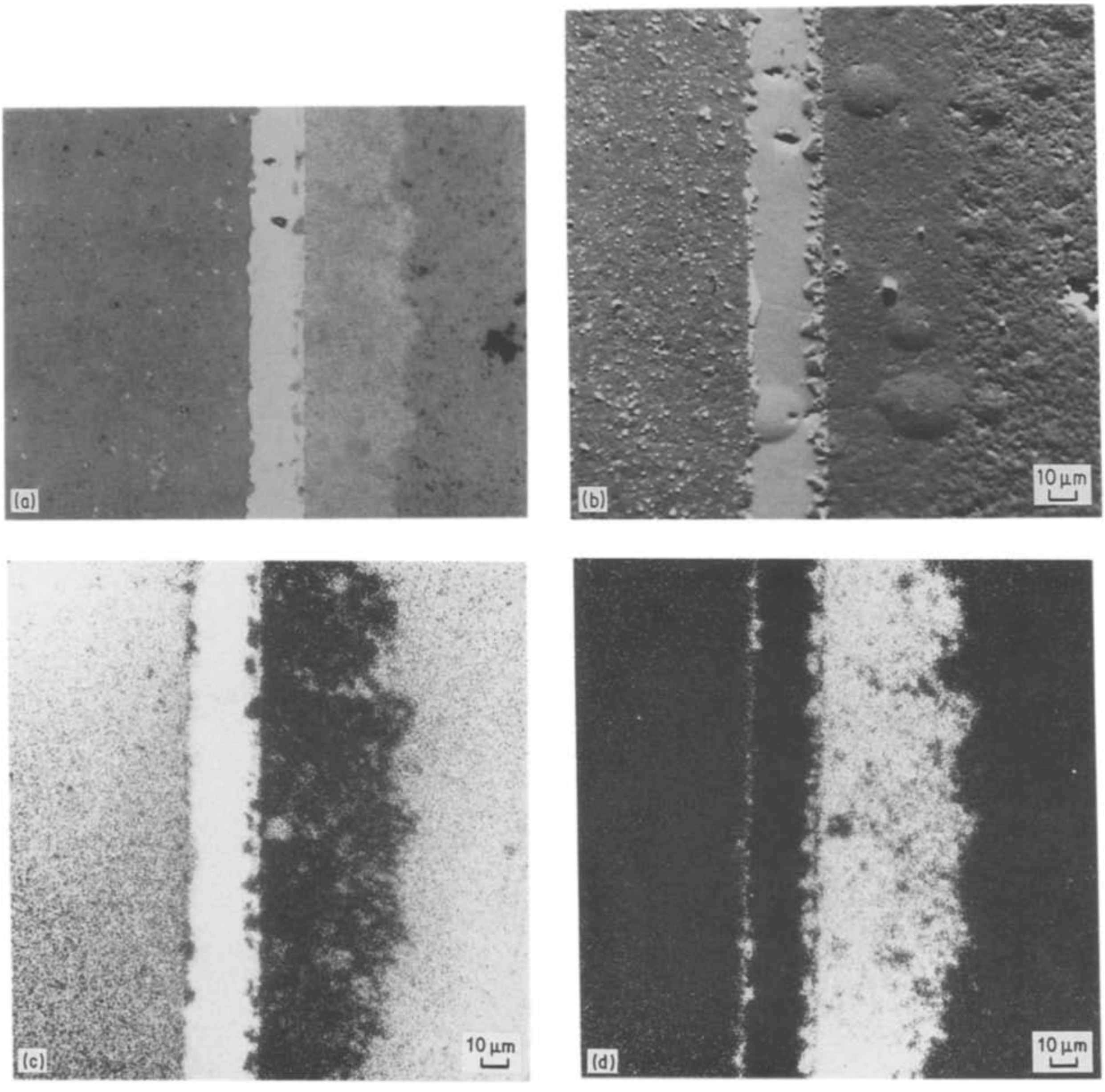

Figure 7 Micrographs of a poor joint, made with a considerable excess of aluminium and oxide. (a) Optical micrograph, ×200; (b) SEM, (c) Si$K\alpha$ and (d) Al$K\alpha$ X-ray maps.

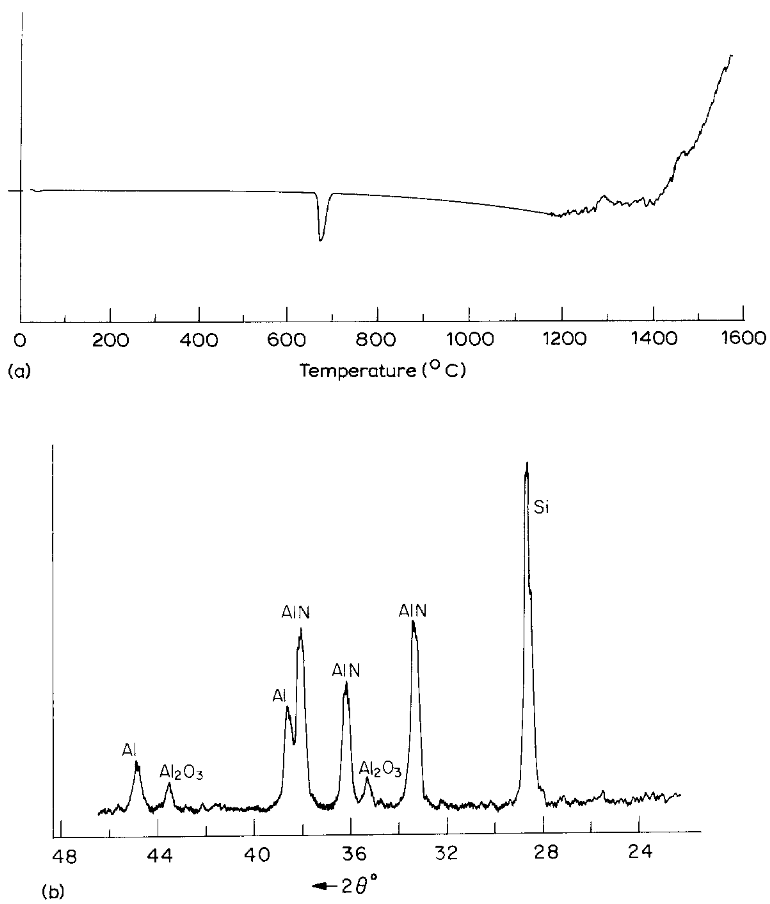

Figure 8 (a) DTA trace of Si_3N_4 and aluminium powder mixture heated under argon to 1550° C, (b) Cu$K\alpha$ X-ray diffraction pattern of resulting material.

polarized light; clearly, the two materials now reflect differently, but this is the only evidence of the joint. Fig. 6 shows scanning electron micrographs of the same joint. Fig. 6a is a secondary electron image: here the joint is just visible. Figs 6b and c show Si$K\alpha$ and Al$K\alpha$ X-ray maps of the same area. Note that there seems to be no change in silicon concentration at the joint, but that there appears to be a slight deficiency of aluminium in the immediate vicinity of the joint and an excess in the RBSN. Fig. 7a is an optical micrograph of a poor joint, one made with a considerable excess of aluminium and oxide. Note that there is a thick metallic layer separating the Si_3N_4 specimens. Fig. 7b is a scanning electron micrograph of the same area demonstrating that there is a substantial region of diminished porosity in the RBSN, which is on the right. Si$K\alpha$ and Al$K\alpha$ maps of the same joint are shown in Figs 7c and d. Note that the metallic layer is silicon, not aluminium, that there is a deficiency of silicon for quite a depth into the RBSN and a slight deficiency at the surface of the HPSN, and that aluminium has replaced silicon in the Si_3N_4 specimens. These last micrographs suggest that the first step in the bonding reaction is the replacement of silicon in the silicon nitride specimens by aluminium, with the silicon migrating to the interface.

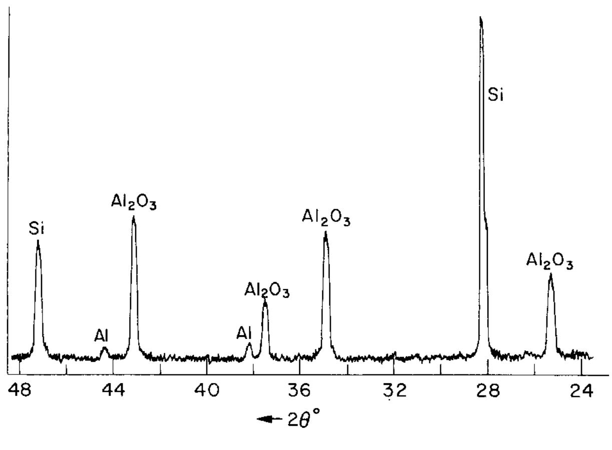

Figure 9 Cu$K\alpha$ X-ray diffraction pattern of SiO_2 and aluminium powder mixture after heating to 1550° C in argon.

Fig. 8 shows a DTA trace obtained as a mixture of Si_3N_4 and aluminium powders were heated in purified argon at 1550° C, along with an X-ray diffraction pattern of the resulting material. The features of note on the DTA trace are the endotherm corresponding to the melting of aluminium and the broad exotherm starting at about 1400° C. The X-ray diffraction pattern shows that the material has been transformed into silicon and AlN, which suggests that the exotherm corresponds to the reaction of aluminium with Si_3N_4, and agrees with the X-ray maps of the joint shown in Fig. 7. The remaining peaks in the X-ray diffraction pattern are due to aluminium, which was present in excess, a trace of remaining Si_3N_4, and Al_2O_3. It is believed that the Al_2O_3 resulted from the reaction of aluminium with SiO_2 present in the Si_3N_4. That this is possible is shown by Fig. 9, which is the X-ray diffraction pattern of a stoichiometric mixture of SiO_2 and aluminium heated to 1550° C under argon in the DTA apparatus. Virtually all the aluminium has been converted to Al_2O_3 and all the SiO_2 to silicon. To check on the identification of the DTA exotherm with the reaction of aluminium and Si_3N_4, a mixture of these materials was heated to only 1060° C in argon. In this case the X-ray diffraction pattern in Fig. 10

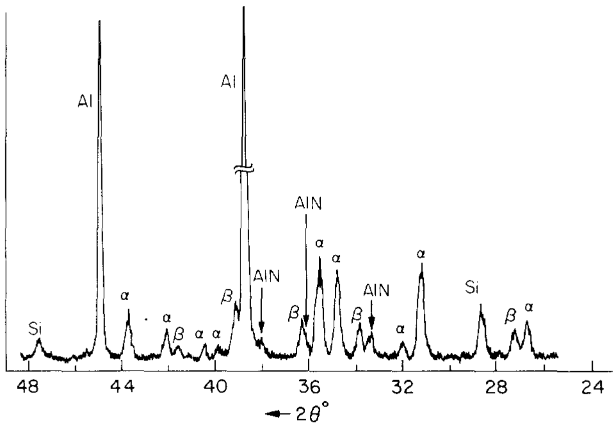

Figure 10 Cu$K\alpha$ diffraction pattern of Si_3N_4 and aluminium powder mixture heated under argon to 1060° C. α, β: Si_3N_4.

shows that very little reaction occurred. The fact that there was any reaction at all, however, indicates that aluminium can reduce Si_3N_4 slowly even at this low a temperature. The DTA trace obtained when a mixture of aluminium and Si_3N_4 was heated to 1550° C in N_2, along with the X-ray diffraction pattern of the resulting material, is shown in Fig. 11. The only significant difference from the DTA trace obtained in argon (Fig. 8) is the exotherm at about 900° C, which is believed to correspond to the nitriding of aluminium. In this case the X-ray diffraction pattern shows less silicon and considerably more Si_3N_4 than in the argon case, suggesting either that less aluminium was available to react with the Si_3N_4, some of it having already been nitrided, or that some of the silicon formed was renitrided.

As mentioned above, the area of the sialon joint was more resistant to ion milling than either the hot pressed or reaction bonded silicon nitrides. A low magnification electron micrograph of this area is shown in Fig. 12. At the centre of the joint is a large single crystalline region which is more electron transparent than the surrounding material. The top and left side of the joint are comprised of very small grains (~ 0.1 μm), while the area on the right hand side has broken off and cannot be analysed. The HPSN and RBSN are seen in the lower right and left corners of the micrograph, respectively.

The microstructures of the HPSN and RBSN along both sides of the joint were very similar to those far away from the joint. Fig. 13a shows a typical area on the hot pressed side of the joint approximately 20 μm from the tip and 5 μm from its centre. Many grains in this area were analysed by electron diffraction, and all were found to have diffraction patterns consistent β-Si_3N_4. However, since β-Si_3N_4 and β′-sialon exhibit identical electron diffraction patterns except for a small difference in the d-spacings, it is extremely difficult to distinguish between them using electron diffraction. Energy dispersive spectroscopy (EDS) on grains of various sizes in this same area revealed that a few of these contained a small amount of aluminium and, therefore, were actually β′-sialon. The largest observed Al/Si atomic ratio within a single grain was about 0.1 (Fig. 13b). However, closer to the centre of

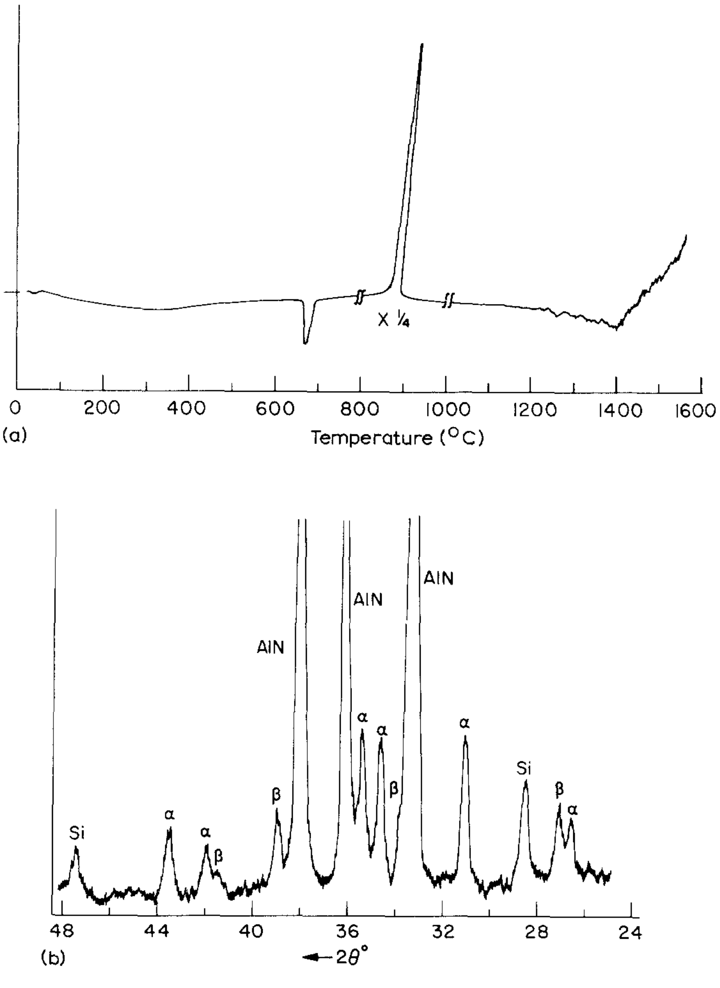

Figure 11 (a) DTA trace of Si_3N_4 and aluminium powder mixture heated under N_2 to 1550° C, (b) Cu$K\alpha$ X-ray diffraction pattern of resulting material. α, β: Si_3N_4.

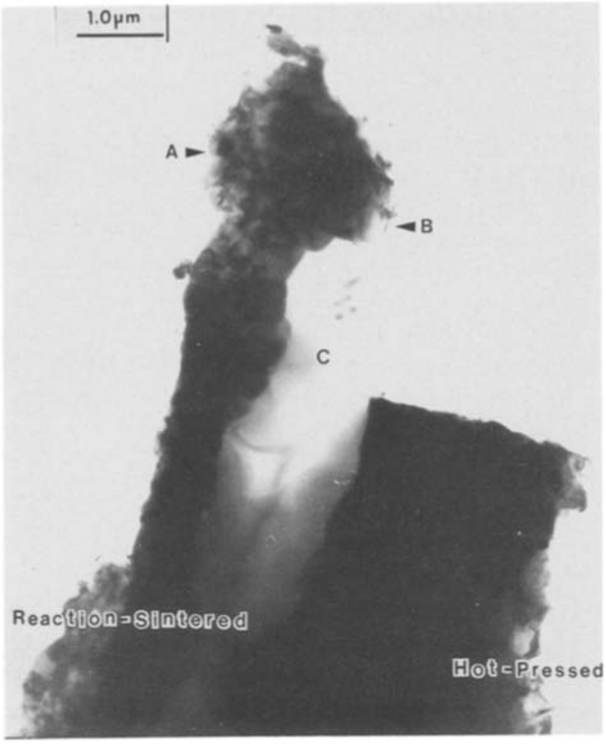

Figure 12 Low magnification transmission electron micrograph of sialon joint.

the joint, the aluminium concentration was probably higher.

A similar area on the reaction bonded side of the joint was also analysed. Because of the small grain size in this region, electron diffraction patterns from individual grains could be obtained in only a very limited number of cases. The interplanar spacings of two different grains matched those of β-Si_3N_4, while the diffraction pattern of one other grain, shown in Fig. 14, corresponded to that of metallic aluminium. EDS analysis on the small grains in this area was also difficult, since many of them tended to overlap. On average, however, this area contained more aluminium than did a comparable area on the hot pressed side of the joint. Generally, EDS analysis on this side of the joint was performed with a beam several tenths of a micrometer in diameter in order to obtain an aluminium to silicon ratio averaged over several grains. Iron was also detected in several of the spectra obtained in this region.

In analysing for heavy elements by EDS proceeding along the reaction bonded side of the joint to the tip, it was found that the Al/Si atomic ratio went from 0.26 away from the tip to nearly unity at the tip itself (Fig. 15). Since most grains near the tip were less than 0.1 μm across, useful diffraction patterns were difficult to obtain. However, many interplanar spacings from grains located in this area matched those of 15R AlN polytype sialon although some others were found to match AlN, as shown in Fig. 16. It must also be noted that, while the largest d-spacings in Fig. 16 can easily distinguish 15R from other sialon phases, aluminium whose d-spacings are smaller and many times overlap those of 15R, cannot easily be distinguished. Thus, this area might possibly contain residual unreacted aluminium as well as 15R AlN polytype sialon and AlN. Electron energy loss spectroscopy performed on this same area showed only the presence of carbon and nitrogen, the former presumably due to carbon deposited on the sample to prevent charge buildup and, possibly, to contamination in the microscope. The lack of any detectable oxygen edge demonstrates that the fine grained material is not an oxide.

In the same area several grains were large enough to be identified unambiguously by electron diffraction. One grain (A in Fig. 12) was close to the tip of the reaction bonded side and was identified, using three prominent zone axes, as $FeSi_2$. This grain is probably a remnant of the original RBSN. A second large grain (B in Fig. 12) on the opposite side of the tip was identified as α-Al_2O_3. It might have resulted from the passive oxide layer originally on the aluminium foil. Finally, EDS spectra from the large crystalline region at the centre of the joint (C in Fig. 12) showed only the presence of silicon. Electron diffraction unambiguously identified this region as elemental silicon and not a Si–O–N compound.

4. Discussion

The transmission electron microscope work suggests that the sialon joint between reaction bonded and hot pressed silicon nitride can be characterized by a region, adjacent to the RBSN, which is composed

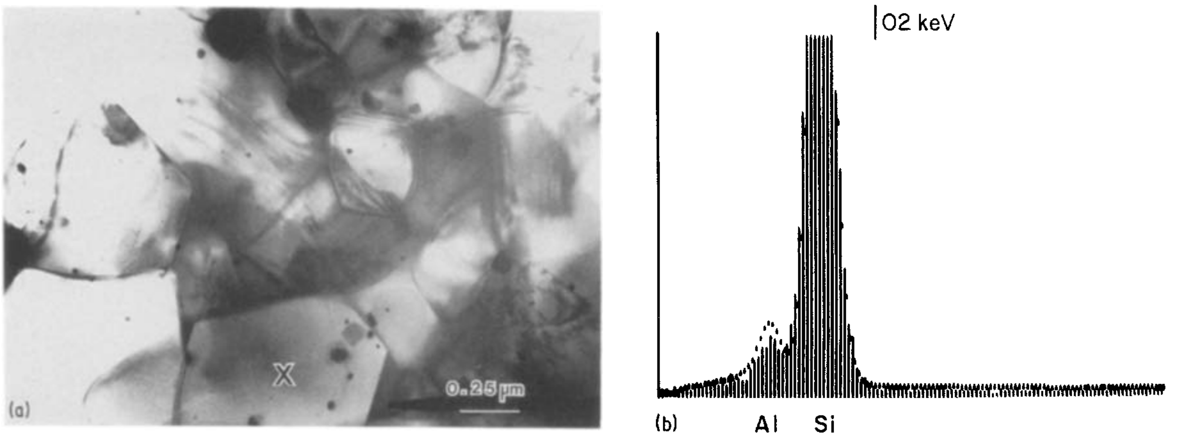

Figure 13 (a) TEM showing grain morphology on the HPSN side of the joint. The EDS spectrum (b) was taken from the grain marked x and shows the presence of a small amount of aluminium indicating that the grain is β'-sialon. Aluminium, 8.68 at %; silicon, 91.32 at %.

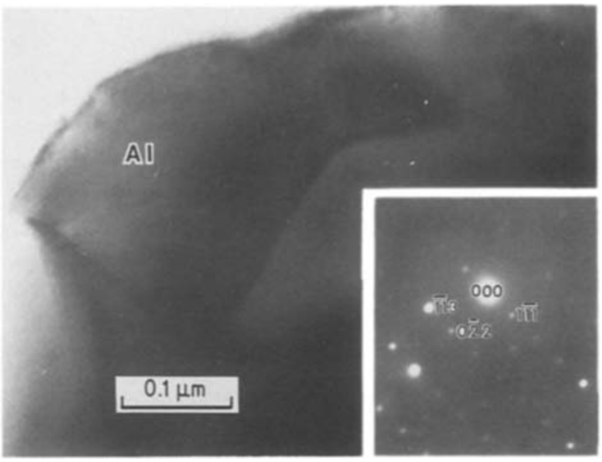

Figure 14 TEM showing grain of metallic aluminium found on RBSN side of joint. The electron diffraction pattern shows the [2 1 1] zone axis of aluminium.

primarily of 15R AlN polytype sialon, and a less extensive β'-sialon region adjacent to the HPSN. Near the centre of the joint, where these two regions meet, there may be pockets of elemental silicon as well as some excess aluminium and aluminium nitride.

The DTA and X-ray diffraction studies show that, when aluminium and Si_3N_4 are heated to sufficiently high temperature in a N_2 atmosphere, the aluminium reacts with both the N_2 and the Si_3N_4, and that the silicon resulting from the latter reaction tends to be renitrided. In addition, they show the presence of β' sialon and 15R AlN polytype sialon in the joint region.

The optical and scanning electron microscopy show there is substantial penetration of aluminium into the RBSN, a lesser penetration into the HPSN, and a migration of silicon to the interface.

Taken together these studies suggest that aluminium at the interface penetrates and reacts with contacting silicon nitride bodies, the penetration being much greater into the more porous RBSN than into the fully dense HPSN. The silicon, which is one of the initial products of the reaction of aluminium with Si_3N_4 bodies, migrates to the interface, there to be renitrided to form Si_3N_4 and, possibly in combination with aluminium and oxygen, sialons. The aluminium which has penetrated the RBSN reacts to form AlN and, with oxygen which may have originated in the passive layer on Si_3N_4, 15R AlN polytype sialon. That which has penetrated the HPSN, and is in lower concentration than in the reaction bonded material, reacts to form β'-sialon. Where reaction is incomplete reactants remain, e.g. silicon in the centre of the joint and aluminium on the reaction bonded side of the centre.

5. Conclusions

Sialon joints between silicon nitride based bodies appear to consist chiefly of sialon phases which result from the reaction of aluminium and oxides with the silicon nitride. The oxides may have been added along with the aluminium used to prepare the joints or may have had their origin in the passive oxide layers always present. The reactions forming the sialons involve penetration of aluminium into the Si_3N_4 bodies, migration of silicon out of these bodies to the interface,

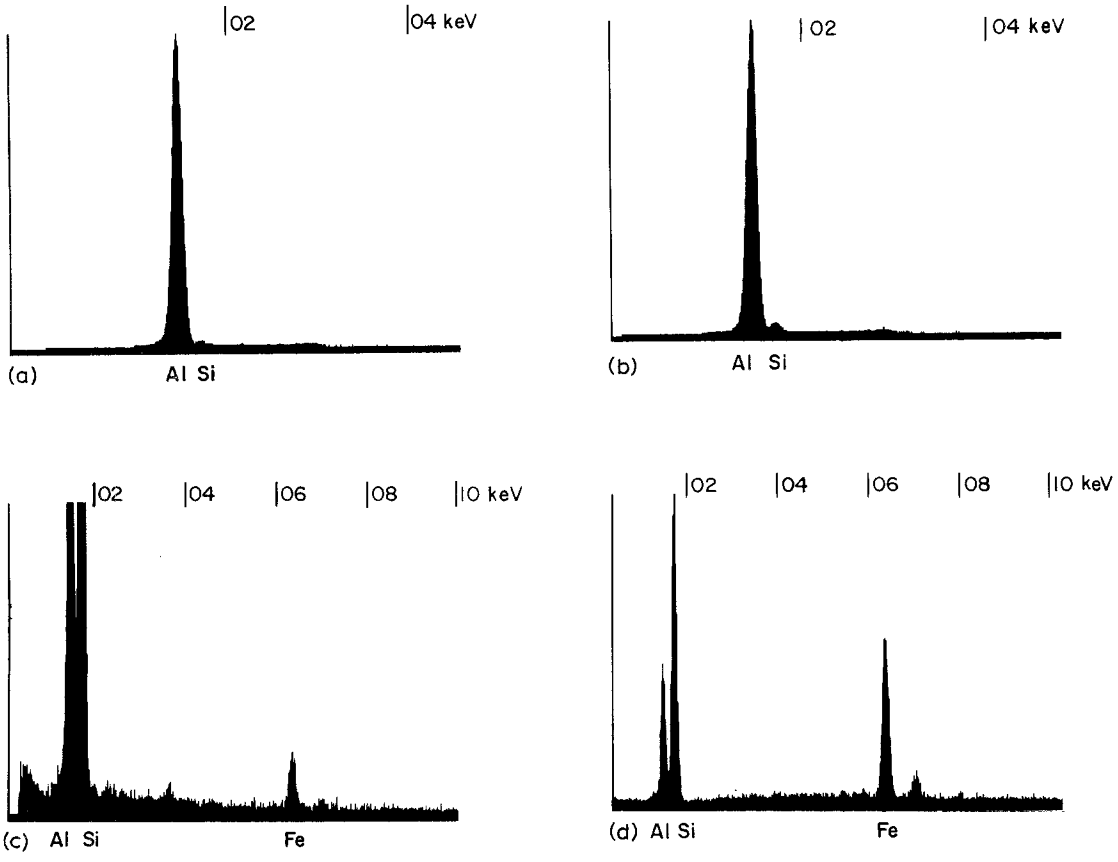

Figure 15 EDS spectra of material on the RBSN side of the sialon joint. Spectra (a) and (b) were taken near the tip of the joint shown in Fig. 12, while spectra (c) and (d) were taken approximately 10 and 20 μm away from the tip, respectively.

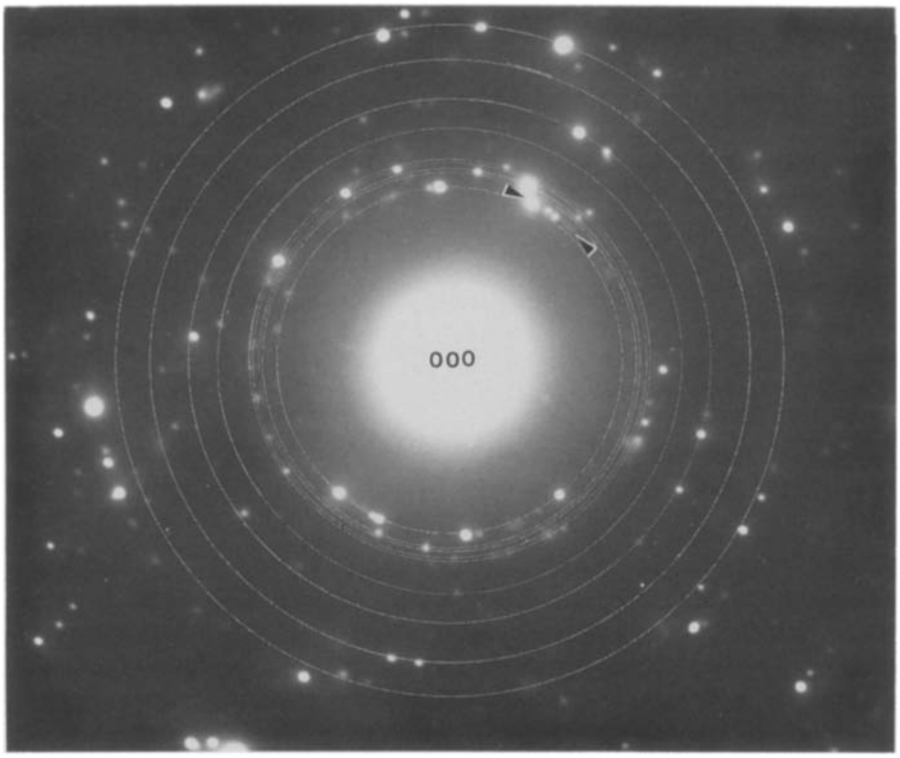

Figure 16 Electron diffraction pattern taken near the tip of the joint. The concentric circles correspond to d-spacings for 15R AlN polytype sialon. The arrows indicate the largest d-spacing for AlN.

renitriding of the silicon, nitriding of aluminium and reactions among silicon and aluminium nitrides and oxides. Because reaction bonded silicon nitride is more porous than the hot pressed variety, it permits greater penetration of aluminium and N_2, which probably accounts for the fact that 15R AlN polytype sialon is found on the reaction bonded side and β'-sialon on the hot pressed side of a joint.

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