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Effect of oxide additive in silicon nitride on interfacial structure and strength of silicon nitride joints brazed with aluminium

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Silicon nitride ceramics with Y_2O_3 and Al_2O_3 as sintering additives were brazed with aluminium, and the brazed strength and the interfacial structure of the joints were compared with those of the joints made of additive-free silicon nitride ceramics. It is concluded that the additives in silicon nitride ceramics take part in the interfacial reaction, make the reaction layer thicker, and hence increase the brazed strength greatly.

1. Introduction

Densification of silicon nitride is difficult without additives in a conventional sintering technique. Usually some oxide additives are added for densifying silicon nitride ceramics with ease. The present authors found that the bond strength of additive-free silicon nitride ceramics brazed with aluminium was increased by oxidation of the faying surface of the silicon nitride ceramics prior to the brazing, and that oxygen played an important role in the brazing [1]. Thus oxide additives in silicon nitride may also contribute to an increase in the joint strength.

In the present work, two kinds of silicon nitride ceramic were used. One was additive-free silicon nitride ceramic densified by hot isostatic pressing (HIPing), and the other was pressureless-sintered silicon nitride ceramic with added yttria and alumina as additives. The latter is called additive-added ceramics in this paper. The two kinds of ceramic were brazed with aluminium. The bending strength of the brazed joints was measured and the fracture surface was examined by scanning electron microscopy (SEM) and analysed by X-ray photoelectron spectroscopy (XPS). The interfacial structure was analysed by means of analytical transmission electron microscopy (AEM) including energy-dispersive spectrometry (EDS) and electron energy-loss spectroscopy (EELS) to elucidate the effect of the oxide additives in silicon nitride ceramics on the interfacial structure and strength of the brazed joints.

2. Experimental procedure

The process for the fabrication of additive-free silicon nitride ceramics was the same as that described in the previous work [1] except for the following treatment to minimize the oxygen content of the ceramics. After the compacted blocks of silicon nitride powders were lined with BN powders, they were held at 473 K in a vacuum of 10^{-1} Pa for 1.8 ksec to remove moisture in the BN powder before encapsulation into glass tubes. Additive-added silicon nitride ceramics with 8% (Y_2O_3 + Al_2O_3) as sintering additives were supplied by Toshiba Ceramics Co. Ltd, Tokyo. The size was 13 mm square and 20 mm long. The bending strength of the silicon nitride ceramics was about 600 MPa at room temperature. The method for brazing silicon nitride ceramics with aluminium was described in detail in the previous work [1], but in the present work the brazing time was shortened to 0.9 ksec and the aluminium plate for brazing was varied to 0.2 mm thick. Such changes have no appreciable effect on the bending strength and the interfacial structure of joints.

3. Results and discussion

3.1. Constituents of silicon nitride ceramics

X-ray diffraction patterns of the two kinds of silicon

TABLE I Intensity ratio of IO1s/IN1s and Si2p binding energy of faying surfaces of silicon nitride ceramics as-ground and heat-treated in a vacuum

Treatment	Sample			
	Additive-free		Additive-added	
	Si2p (eV)	IO1s/IN1s	Si2p (eV)	IO1s/IN1s
As-ground	101.9	2.3 ± 0.2	101.9	5.0
Heat-treated (1.8 ksec)	102.2	2.0	102.7	4.8
Heat-treated (10.8 ksec)	102.6	2.1	–	–

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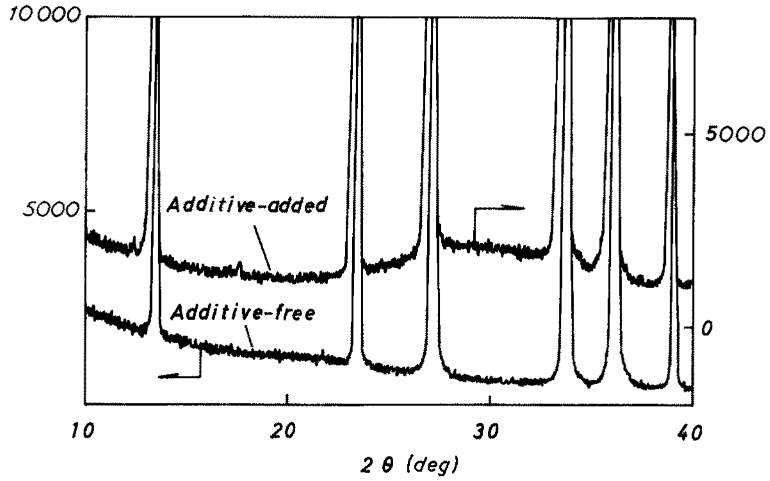

Figure 1 X-ray diffraction patterns of the two kinds of silicon nitride ceramic used for brazing.

nitride ceramics used in the present work are shown in Fig. 1. The pattern of additive-free silicon nitride ceramics consists only of the diffraction peaks of β-silicon nitride, differing largely from that in the previous work [1]. Additive-added silicon nitride ceramics show a pattern composed of a low and diffuse peak occurring from an amorphous phase around $2\theta = 30°$, many peaks coming from β-silicon nitride and some unknown minor peaks. The amorphous phase proved by AEM analysis to be an Si–Y–Al oxide which exists on grain boundaries, in particular at triple points. The EDS spectrum and the electron diffraction (ED) pattern of the phase existing at a triple point are shown in Fig. 2 together with the TEM image. From the results mentioned above, a major difference as to structural constituents between the two kinds of silicon nitride ceramic is that the additive-added silicon nitride ceramics contain an Si–Y–Al oxide amorphous phase on the grain boundaries and at the triple points.

The XPS spectra of the faying surfaces of the two kinds of silicon nitride ceramic are shown in Fig. 3. In the case of additive-free silicon nitride ceramics, it is noted that the O1s peak which appears at about 532 eV is observed with strong intensity together with silicon and nitrogen peaks. In the case of additive-added ones, the Y3d peak is also observed at about 160 eV. The intensity ratio IO1s/IN1s of the O1s peak to the N1s peak and the Si2p binding energy are summarized in Table I. Generally, the oxidation of silicon nitride should increase the Si2p binding energy [2]. Comparing additive-added silicon nitride ceramics with additive-free ones, the value of the IO1s/IN1s ratio of the former is larger than that of the latter, as expected, but the Si2p binding energy of both the ceramics is just the same (101.9 eV). In other words, although the additive-added silicon nitride ceramics contain more oxygen than the other ones, the degree of oxidation does not differ between the two.

3.2. Bending strength of brazed joints

Fig. 4 shows the Weibull plots of the four-point bending strengths of the two kinds of silicon nitride joint. The mean strength and the Weibull modulus of additive-added silicon nitride joints are considerably higher than those of additive-free ones.

3.3. Fractography

Fractographs of an additive-added silicon nitride joint are shown in Figs 5a and b. The fracture of the joint occurred in silicon nitride and in aluminium, but not in close vicinity to the brazed interfaces. This indicates that the brazed interfaces could be strongly bonded. Fig. 5c shows the fractograph of an additive-free silicon nitride joint. The grinding marks on the faying surface of silicon nitride ceramic are observed on the

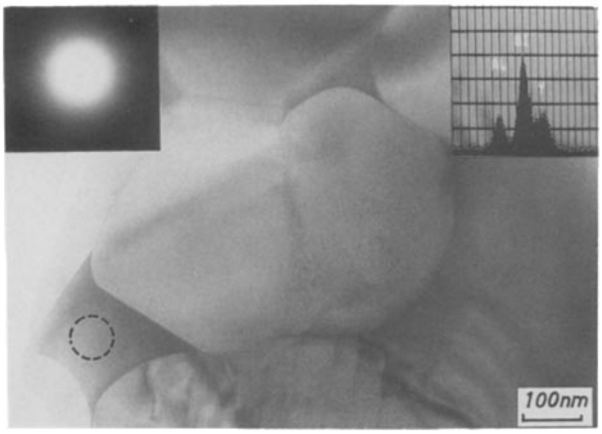

Figure 2 TEM image of additive-added silicon nitride ceramic and an electron diffraction pattern and an EDS spectrum taken from a triple point in it.

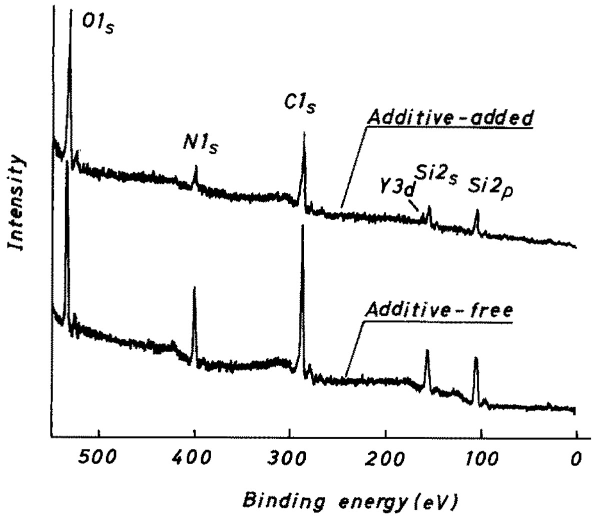

Figure 3 XPS spectra of the faying surfaces of silicon nitride ceramics.

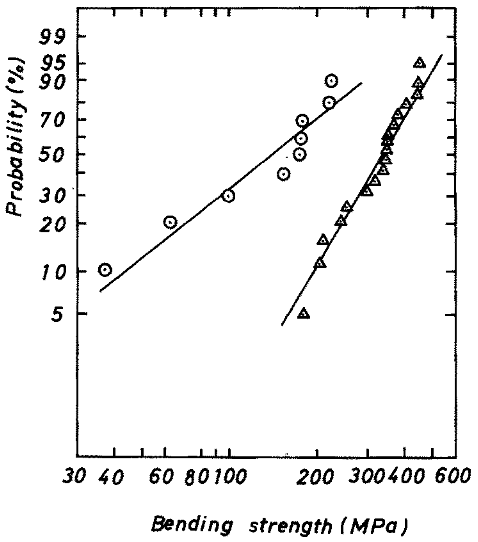

Figure 4 Weibull distribution of four point-bending strengths of the two kinds of joint. (⊙) Additive-free: mean = 148 MPa, m = 1.6. (△) Additive-added: mean = 332 MPa, m = 3.3.

fracture surface. The XPS spectrum of the fracture surface is shown in Fig. 6, where the peaks of aluminium, oxygen, silver and gold appear, but no peak of silicon or nitrogen is found. Gold and silver came from the electrically conductive coating given to the fracture surface to protect the sample from charging up during SEM observation. Oxygen is considered to be partly absorbed on the sample surface and partly in the surface oxide of aluminium which would be formed with ease even in a vacuum [3]. After the same fracture surface was etched by argon ions for 3.6 ksec in a vacuum of 10^{-4} Pa in the XPS equipment, the peaks of silicon appear but the peak of nitrogen does not. It is concluded that, since the Si2p binding energy is 102.1 eV, which corresponds with that of silicate [4], and aluminium silicate has been detected as one of the reaction products on the brazed interface of the same kind of joint by AEM analysis in previous work [5], the peaks of silicon come from silicate, but not from silicon nitride. From the results mentioned above, the fracture path in additive-free silicon nitride joints runs in aluminium very close to the brazed interfaces, as sketched in Fig. 5d.

TABLE II Thickness of silica–alumina non-crystalline reaction layer

Sample	Thickness (nm)
Additive-free	450, 350
Additive-added	1200, 800, 1000

TABLE III Properties of materials

Material	α (K^{-1})	E (MPa)
Aluminium	23×10^{-6}	0.7×10^5
Silicon nitride	2×10^{-6}	3×10^5
Mullite	5×10^{-6}	1×10^5

3.4. Interfacial structure

Fig. 7 shows the TEM image, the EDS and EELS spectra and the ED patterns of the brazed interface in an additive-added silicon nitride joint. As in the interfacial reaction layer in additive-free silicon nitride joints, which some of the present authors have examined in previous work [5], the constituents in Areas C and D between silicon nitride and aluminium are non-crystalline silica–alumina and β'-sialon, respectively. Table II lists the thickness of the silica–alumina non-crystalline layer measured from different specimens. The reaction layer in additive-added silicon nitride joints is much thicker than that of additive-free silicon nitride joints.

3.5. Behaviour of oxide additives in brazing

When the silicon nitride ceramics were heat-treated at a temperature of 1073 K for 1.8 and 10.8 ksec in vacuum less than 1.3×10^{-3} Pa, the Si2p binding energy increases and the value of the IO1s/IN1s ratio decreases, as shown in Table I. The increase in the Si2p binding energy after heat-treatment is larger in the additive-added silicon nitride ceramics than in the additive-free ones. This fact means that oxygen existing on the grain boundaries in additive-added silicon nitride ceramics can take part in the surface oxidation of silicon nitride, and thus in the interfacial reaction during brazing [1], because the temperature and the degree of vacuum in the heat-treatment were the same as those in the brazing in the present work. As a result,

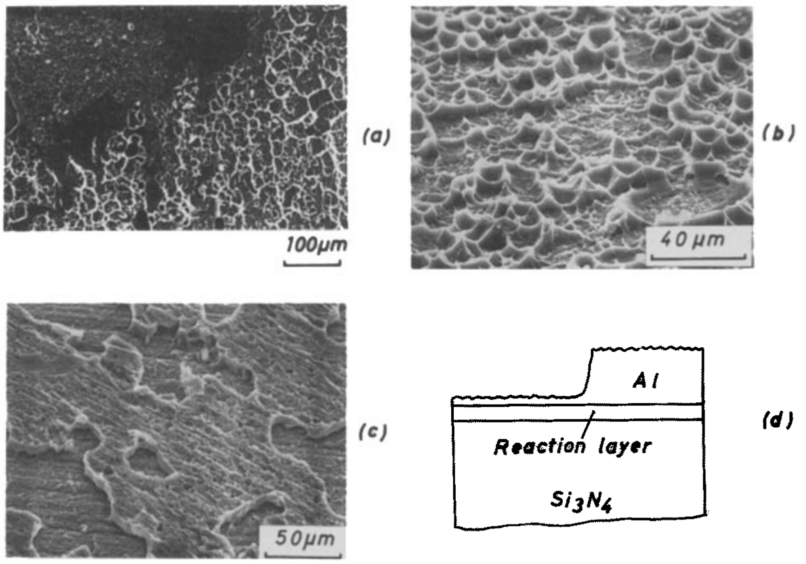

Figure 5 Fractographs (a, and b) of a joint of additive-added silicon nitride ceramics and (c) of a joint of additive-free silicon nitride ceramics; (d) a sketch map showing the fracture path in the joint of additive-free silicon nitride ceramics.

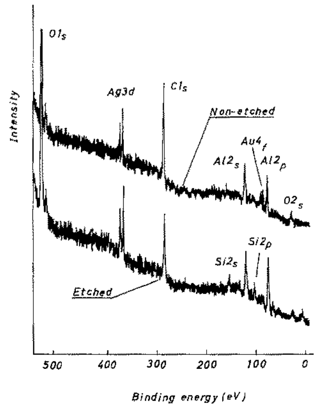

Figure 6 XPS spectra of fracture surface of a joint of additive-free silicon nitride ceramics.

a thicker silica–alumina non-crystalline layer formed at the interface of the joint of additive-added silicon nitride than in the case of the additive-free one. On the other hand, the decrease in the value of the $I\mathrm{O1s}/I\mathrm{N1s}$ ratio is considered to result from removal of absorbed moisture from the surface of silicon nitride by the heat-treatment.

3.6. Relaxation of thermal stress due to the reaction layer

From the results obtained in the present work and the previous work [1], the higher brazing strength of the joint seems to relate to a thicker silica–alumina non-crystalline layer which may relax thermal stress at the interface to a smaller value.

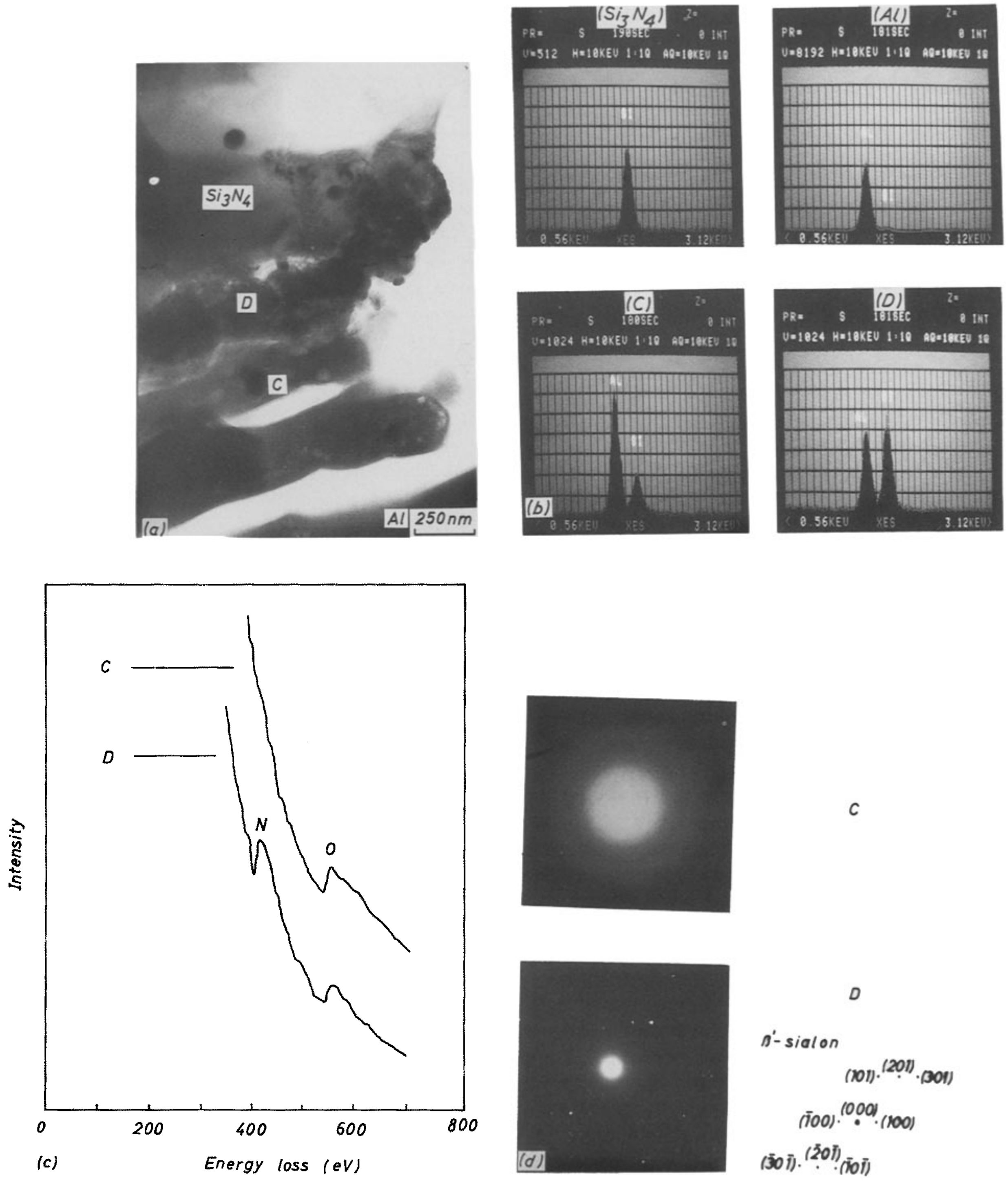

Figure 7 (a) TEM image, (b) EDS spectra, (c) EELS spectra and (d) electron diffraction patterns of the interfacial region in a joint of additive-added silicon nitride ceramics.

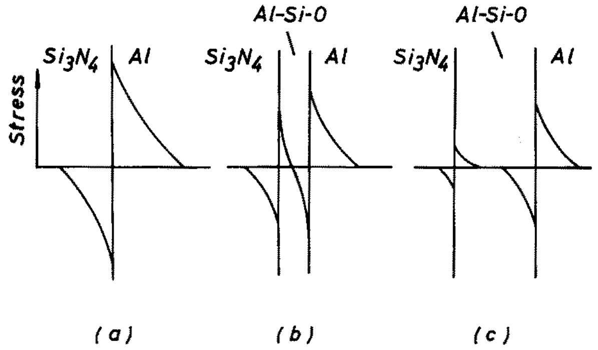

Figure 8 Schematic drawing showing the distribution of thermal stress in some brazed joints: (a) without interlayer, (b) with a thin interlayer, (c) with a thick interlayer.

When a joint is cooled down from the brazing temperature, thermal stress develops in the joint due to the thermal expansion mismatch between two different materials, as shown in Fig. 8. If the materials can deform only elastically with the stress and the stresses developing on the both sides of the reaction layer do not interfere with each other in this layer (Fig. 8c), the stress in the close vicinity of the interface between two adjacent materials i and j is expressed roughly as follows:

$$\sigma_i = -\sigma_j = \frac{E_i E_j}{E_i + E_j}(\alpha_i - \alpha_j)\Delta T$$

where E is Young's modulus, α is the thermal expansion coefficient and ΔT is the temperature change. The thermal stress cannot be calculated, due to lack of the values of α and E for non-crystalline silica–alumina. Assuming that non-crystalline silica–alumina is identified as mullite (Table III), the calculated thermal stresses at the interfaces Si_3N_4/Al (Fig. 8a), Si_3N_4/mullite and mullite/Al (Fig. 8c) are 476, 114 and 296 MPa, respectively. Reflecting the difference between the thermal expansion coefficients of the two adjacent materials, the thermal stress at the interface becomes smaller in the order of Si_3N_4/Al, mullite/Al and Si_3N_4/mullite and the existence of mullite or non-crystalline silica–alumina makes the thermal stress considerably smaller.

If the non-crystalline layer is not thick enough, the stresses on both sides of the layer will interfere with each other and the thermal stress will increase (Fig. 8b). As a result, the thinner the layer, the higher the thermal stress and hence the lower the brazing strength of the joint.

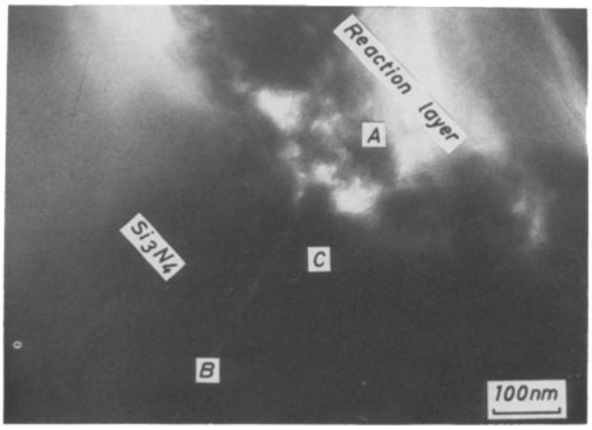

Figure 9 TEM image from a grain boundary in contact with the reaction layer in additive-added silicon nitride ceramic joint.

3.7. Behaviour of grain boundary of silicon nitride in brazing

Fig. 9 shows the TEM image of the grain boundary in an additive-added silicon nitride ceramic in contact with the reaction layer. The EDS spectra of Points A, B and C are shown in Fig. 10. Points A, B and C are in the interfacial reaction layer, on the grain boundary, and in a silicon nitride grain, respectively. Point B has a higher aluminium content than Point C and also than the grain boundary of the silicon nitride (Fig. 2). This indicates that aluminium diffuses much faster on the grain boundary than in the silicon nitride grain.

4. Conclusion

Silicon nitride ceramics with yttria and alumina as additives were brazed at 1073 K under a vacuum of 10^{-3} Pa using aluminium. The additive increased the brazed strength of the joints remarkably. The fracture of the joints of additive-free silicon nitride ceramics occurred in aluminium in close vicinity to the brazed interface, but the joints made of additive-added ones fractured in aluminium and in the silicon nitride ceramics. A silica–alumina non-crystalline layer and a β'-sialon layer were formed successively from the aluminium side during the brazing. The former became thicker due to the additive, as compared with the additive-free case. The thicker layer is considered to relax more the thermal stress occurring from the thermal expansion mismatch between silicon nitride ceramics and aluminium.

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Figure 10 EDS spectra of Points A, B, C in Fig. 9.

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