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Interfacial strength and chemistry of additive-free silicon nitride ceramics brazed with aluminium

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Two kinds of additive-free silicon nitride ceramics were brazed with aluminium; one was with as-ground faying surfaces and the other was with faying surfaces heat-treated at 1073 K for 1.8 ksec in air. The heat-treatment of the silicon nitride ceramics formed a silicon oxynitride layer on the faying surfaces and increased the brazing strength of the joints. A silica–alumina non-crystalline layer and a β'-sialon layer were formed successively from the aluminium side at the interface of the joints. The heat-treatment which made the former layer thicker is a necessary process in making reliable, strong brazed joints.

1. Introduction

Silicon nitride ceramics have been considered as proper high-temperature materials for vehicle gas turbines and internal combustion engines. They are, however, inherently brittle and their fracture toughness is less than $10\,\mathrm{MN\,m^{-3/2}}$, which is considerably lower than that of metal. When silicon nitride ceramics are used as structural materials, in many cases they have to be joined to metals. Aluminium is recommended as one of the metals because of a good bonding ability to silicon nitride and high plasticity to relax the severe thermal stress arising from the difference of thermal expansion coefficients between the joined materials, though its melting point is low.

As for the brazing of silicon nitride ceramics with aluminium, some studies have clarified the effects of brazing conditions, alloying elements in aluminium, and faying surface conditions of silicon nitride ceramics on the joint strength [1–4]. The bonding mechanism, however, remains unclear. In previous work, three of the present authors found that two reaction layers which contained a considerable amount of oxygen were formed at the brazed interface between additive-free silicon nitride ceramics and aluminium [5]. This implies that oxygen takes part in the interfacial reaction of liquid aluminium with silicon nitride and plays an important role in the brazing of additive-free silicon nitride ceramics with aluminium.

In the present work, the joints of silicon nitride ceramics brazed with aluminium were made of two kinds of additive-free silicon nitride ceramic; one was with the as-ground faying surface and the other was with a faying surface heat-treated at 1073 K in air after grinding. The faying surfaces of the ceramics were analysed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The bending strength of the joints was measured and the fracture surfaces were observed by scanning electron microscopy (SEM). The brazed interface was analysed by means of analytical transmission electron microscopy (AEM) to elucidate the effect of heat-treatment of silicon nitride ceramics in air on the interfacial strength of the joints.

2. Experimental procedure

2.1. Fabrication of additive-free silicon nitride ceramics

Silicon nitride powder (LC12) supplied by H. C. Stark Co. Ltd was sintered to make additive-free silicon nitride ceramics using hot isostatic pressing (HIP). The chemical composition of the powder is as follows (wt %):

$$\mathrm{N:38.57,\ O:1.10,\ C:0.16,}$$
$$\mathrm{Al:0.05,\ Fe:0.02,\ Si:bal.}$$

The powder was compacted in a cylindrical form 17 mm dia. and 25 mm long with a hand press and then under a pressure of 200 MPa using a cold isostatic press. The compacted blocks were pre-heated at a temperature of 1473 K for 7.2 ksec in a vacuum of 10^{-3} Pa. Immediately after the pre-heating, each of the compacted blocks was lined with BN powder and then was encapsulated into an evacuated glass tube. The encapsulated blocks were HIPed at 2123 K for 7.2 ksec under a pressure of 200 MPa. The HIPed silicon nitride ceramics became 14 mm dia. and 20 mm long in size.

2.2. Preparation of samples

The faying surfaces of the silicon nitride ceramics were ground with a diamond wheel. A part of the as-ground ceramic was heat-treated at 1073 K for 1.8 ksec in air to oxidize the faying surface prior to brazing. Aluminium plates, 99.992% in purity, were ground to 0.6 mm thick with emery paper. The

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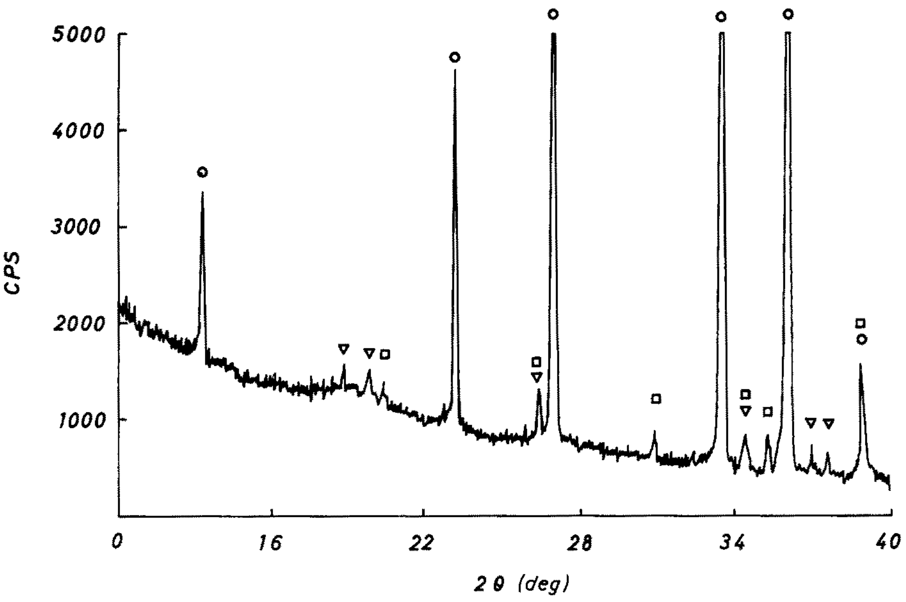

Figure 1 X-ray diffraction pattern of as-ground additive-free silicon nitride ceramics. (○) β-Si_3N_4, (▽) Si_2N_2O, (□) α-Si_3N_4.

aluminium plates and silicon nitride ceramics were cleaned ultrasonically in acetone. A thin aluminium plate was sandwiched between two silicon nitride ceramics and the sandwiched sample was heated to 1073 K in 3.6 ksec and then held at this temperature for 1.8 ksec in a vacuum of less than 1.3×10^{-3} Pa to braze the ceramics. Specimens for a bending test were cut off from the joints perpendicular to the brazed interface to be of dimensions 3 mm square and 40 mm long. To prepare AEM specimens, thin plates were also cut off from the joints normal to the brazed interface, ground to be thinner than 0.1 mm in thickness and then thinned down by argon ion bombardment, in which the accelerating voltage of the ion gun was 3 kV.

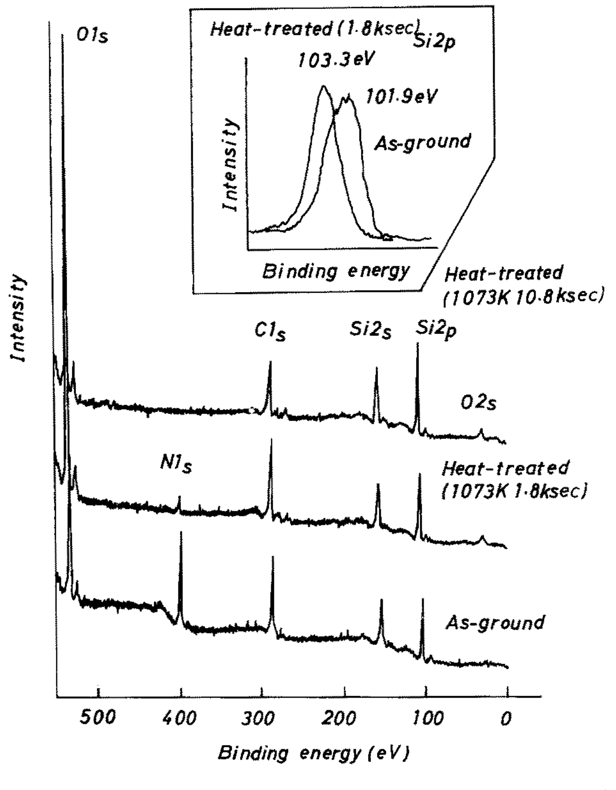

Figure 2 X-ray photoelectron spectra of the faying surfaces of as-ground and heat-treated additive-free silicon nitride ceramics.

2.3. Measurements and analyses

The four-point bending strength was measured with an upper span of 10 mm, a lower span of 30 mm and a crosshead speed of 8.3 μm sec^{-1} (0.5 mm min^{-1}). The analytical transmission electron microscope, H600FE, made by Hitachi Ltd, had an electron gun of the field-emission type and was equipped with detectors to be used for electron energy-loss spectroscopy (EELS) and energy-dispersive spectrometry (EDS), under which the focused beam diameter was less than 10 nm. An X-ray photoelectron spectroscope, ESCA650B, made by Shimadzu Seisakusho Ltd, was used to analyse the faying surface of silicon nitride ceramics under a vacuum less than 10^{-6} Pa. The scanning speeds were 1 and 0.05 eV sec^{-1}. All the data obtained were corrected for the surface charging effect, based on the Cls binding energy peak at 284.6 eV resulting from contamination. The heights of the Ols and Nls peaks were measured to calculate the intensity ratio IOls/INls.

3. Results and discussion

3.1. Constituents of silicon nitride ceramics

The XRD pattern of as-ground silicon nitride ceramics is shown in Fig. 1. The pattern consists of the diffraction peaks of β-silicon nitride and several minor peaks of α-silicon nitride and silicon oxynitride,

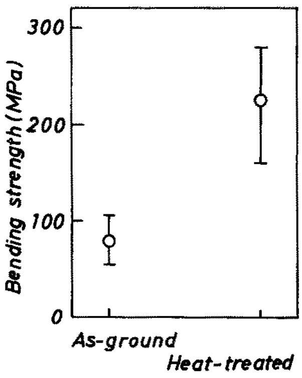

Figure 3 Four-point bending strengths of the aluminium-brazed joints of as-ground and heat-treated additive-free silicon nitride ceramics.

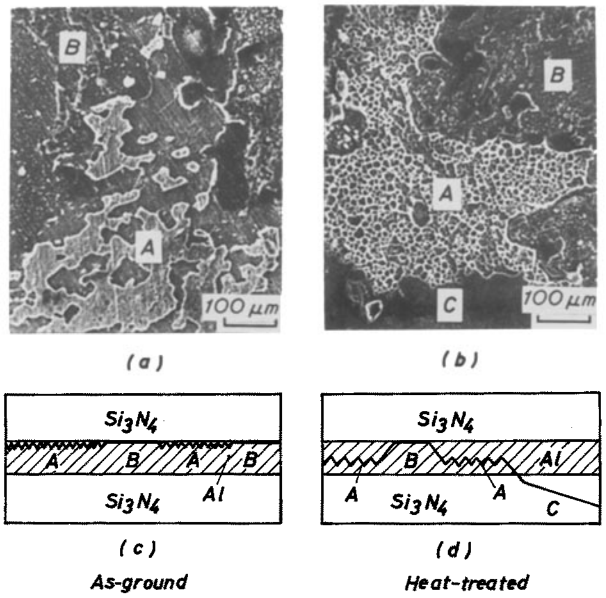

Figure 4 Fractographs of the aluminium-brazed joints of additive-free silicon nitride ceramics and sketches of their fracture paths. (a, c) As-ground silicon nitride ceramics; (b, d) heat-treated ones.

Si_2N_2O. The XPS spectra of the faying surfaces of the two kinds of silicon nitride ceramics are shown in Fig. 2. Although no oxide was added to silicon nitride ceramics, it is noted that in the as-ground state an O1s peak is observed with strong intensity together with silicon and nitrogen peaks. In the case of the heat-treated silicon nitride ceramics, the O1s peak becomes higher and the N1s peaks is very lowered. Simultaneously the Si2p binding energy increases from 101.9 to 103.3 eV after the heat-treatment for 1.8 ksec. This means that the heat-treatment in air oxidizes silicon nitride, because the Si2p binding energy of an Si–O bond is larger than that of an Si–N bond [6].

3.2. Bending strength

Fig. 3 shows the four-point bending strength of joints made of the two kinds of silicon nitride ceramic. Although the bending strength of the joints made of heat-treated silicon nitride ceramics shows a larger scatter, its mean value is twice as high as that of as-ground ones.

3.3. Fractography

The fractographs of the joints are shown in Fig. 4, where B represents the unbonded area, and A and C are the fractured areas in aluminium and silicon nitride, respectively. The fracture path of the joint of heat-treated silicon nitride ceramics is in silicon nitride and in aluminium (Fig. 4b), while that of as-ground ones is along the brazed interfaces, because grinding marks on the faying surfaces of silicon nitride ceramics are observed on the fracture surfaces (Fig. 4a). The fracture paths of the two kinds of joint are sketched in Figs 4c and d in the figure. This indicates that the brazed interfaces are strengthened by the heat-treatment of silicon nitride ceramics in air before brazing.

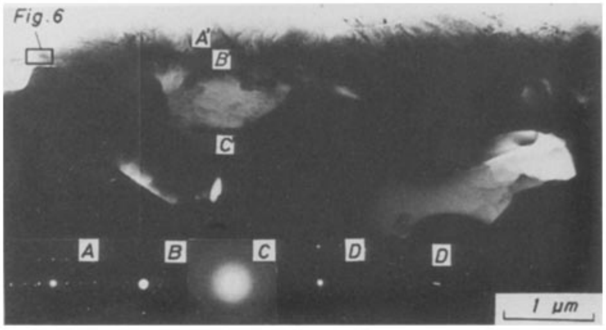

Figure 5 Transmission electron micrograph of an aluminium-brazed joint of heat-treated silicon nitride ceramics and electron diffraction patterns taken from the Areas A, B, C and D in Figs 5 and 6.

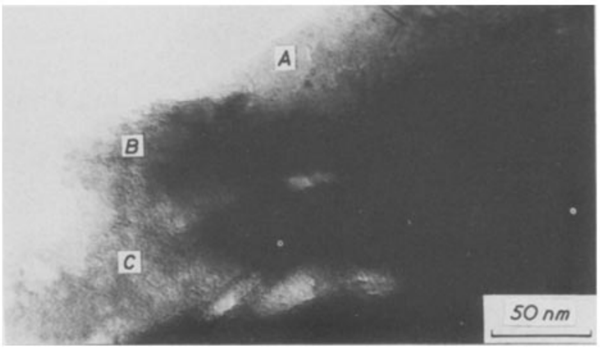

Figure 6 Highly magnified transmission electron micrograph of the region in the frame in Fig. 5.

TABLE I Thickness of the silica–alumina non-crystalline layer

Sample	Thickness (nm)
As-ground	450, 350
Heat-treated	1000

3.4. Interfacial structure

Fig. 5 shows the transmission electron micrograph of a region including the brazed interface of the joint of heat-treated silicon nitride ceramics. A highly magnified transmission electron micrograph of the region in the frame in the figure is shown in Fig. 6. The electron diffraction patterns taken from the areas A, B, C and D in Figs 5 and 6 are shown in Fig. 5. The diffraction pattern from Area C shows some rings. Figs 7 and 8 show the EELS and EDS spectra, respectively, of the same areas. From these results Areas A and D are silicon nitride and aluminium, respectively. Area B is a crystal containing silicon, aluminium,

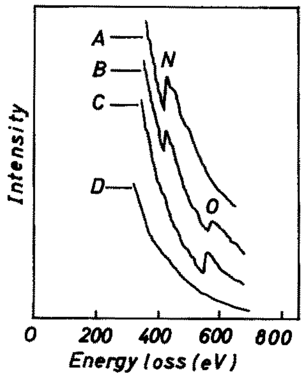

Figure 7 EELS spectra of Areas A, B, C and D in Figs 5 and 6.

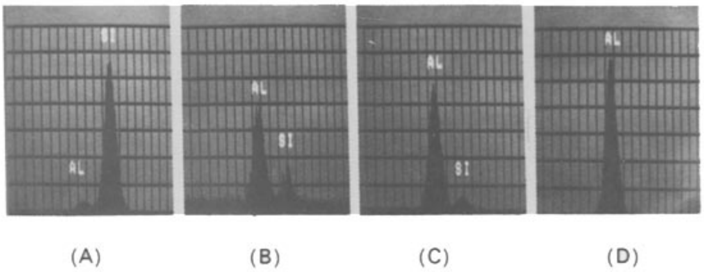

Figure 8 EDS spectra of Areas A, B, C and D in Figs 5 and 6.

nitrogen and oxygen and its electron diffraction pattern is that of β'-sialon. Area C contains aluminium, silicon and oxygen and its lattice spacings calculated from the diffraction pattern are about 0.7, 0.3 and 0.15 nm, corresponding to silica–alumina non-crystalline 15% $SiO_2 \cdot 85\% Al_2O_3$ [7]. These reaction products in the joint made of heat-treated silicon nitride ceramics are just the same as those found in the previous work [5] on joints made of as-ground silicon nitride ceramics. However, the silica–alumina non-crystalline layer becomes thicker as shown in Table I. The heat-treatment makes the non-crystalline layer grow more than twice in thickness.

3.5. Interfacial reaction

It has been reported that an oxide layer about 2 nm thick usually forms on the surface of aluminium at room temperature [8], and an oxynitride layer thinner than 3 nm on the surface of silicon nitride ceramics [6]. Since in the present work the reaction layers were about 1 μm thick, and hence contained a considerable amount of oxygen, oxygen in the silicon nitride and in the vacuum system of the brazing apparatus should obviously have participated in the reaction during brazing. In order to make the reaction clear, as-ground silicon nitride ceramics were heat-treated under the brazing conditions, i.e. at 1073 K in a vacuum lower than 1.3×10^{-3} Pa. The Si2p binding energy and the intensity ratio of IO1s/IN1s of the faying surface of silicon nitride measured by XPS are shown in Table II. The heating of silicon nitride ceramics increases the Si2p binding energy and decreases the ratio IO1s/INs. The former means that the faying surfaces of silicon nitride ceramics can be oxidized in brazing, and the latter is considered to result from the removal of absorbed moisture from the faying surface. Meanwhile, when aluminium is heated under the brazing conditions a dark surface layer is formed on the aluminium surface and it is considered to be aluminium oxides with oxygen/aluminium ratios lower than that of Al_2O_3 [9]. This means that aluminium can also be oxidized in the brazing treatment under the present conditions.

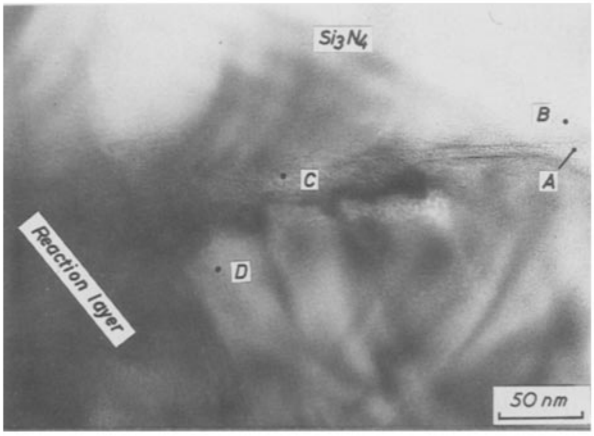

Figure 9 Transmission electron micrograph showing a grain boundary in silicon nitride ceramic in contact with the reaction layer.

On brazing, the following reactions are considered to occur at the interface between liquid aluminium and the silicon nitride:

$$\{Al\} + (O_2) \rightarrow \langle Al\text{–}O \rangle \qquad (1)$$

$$\langle Si_3N_4 \rangle + (O_2) \rightarrow \langle Si\text{–}N\text{–}O \rangle \qquad (2)$$

$$\langle Al\text{–}O \rangle + \langle Si\text{–}N\text{–}O \rangle \rightarrow \langle Al\text{–}Si\text{–}O \rangle + (N_2) \qquad (3)$$

$$\langle Al\text{–}Si\text{–}O \rangle + \langle Si_3N_4 \rangle \rightarrow \langle \beta'\text{-sialon} \rangle \qquad (4)$$

or

$$\{Al\} + (O_2) + \langle Si_3N_4 \rangle \rightarrow \langle Al\text{–}Si\text{–}O \rangle + (N_2) \qquad (5)$$

$$\{Al\} + (O_2) + \langle Si_3N_4 \rangle \rightarrow \langle \beta'\text{-sialon} \rangle \qquad (6)$$

The progress of Reactions 3 or 5 depends on the degree of surface oxidation of silicon nitride ceramics and determines the thickness of the silica–alumina non-crystalline layer. The occurrence of the reactions listed above cannot be estimated from the viewpoint of thermodynamics for lack of the necessary data. If the $\langle Al\text{–}Si\text{–}O \rangle$ non-crystalline phase in Reaction 5 is substituted by mullite, $\langle 3Al_2O_3 \cdot 2SiO_2 \rangle$, then the reaction can be written as follows:

$$\begin{aligned} &6\{Al\} + \tfrac{13}{2}(O_2) + \tfrac{2}{3}\langle Si_3N_4 \rangle \\ &= \langle 3Al_2O_3 \cdot 2SiO_2 \rangle + \tfrac{4}{3}(N_2) \qquad (7) \end{aligned}$$

The Gibbs free energy change of this reaction is -5120 kJ at 1073 K. Because mullite has already been detected in the reaction layer of a joint of which the brazing time was prolonged to 18 ksec, this result being published, Reaction 7 really can occur in the brazing process.

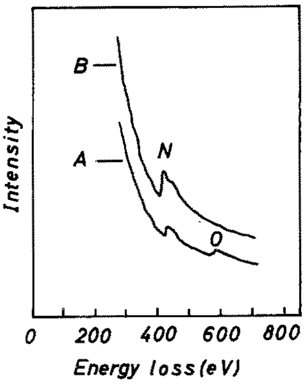

Figure 10 EELS spectra of Points A and B in Fig. 9.

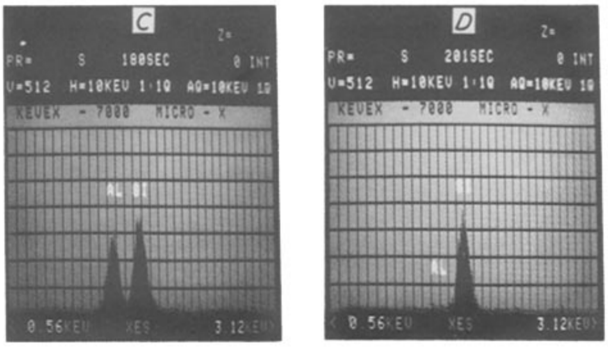

Figure 11 EDS spectra of Points C and D in Fig. 9.

3.6. Behaviour of grain boundary in brazing

In Fig. 9 is a TEM image showing a grain boundary in silicon nitride in contact with the reaction layer. The EELS spectra of Point A in the grain boundary and Point B in a silicon nitride grain are shown in Fig. 10. The grain boundary contains oxygen and nitrogen and is composed of silicon oxynitride. A reaction layer is observed to penetrate into the silicon oxynitride along the grain boundary in Fig. 9. The EDS spectra of Point C in the reaction layer and Point D in silicon nitride in contact with the reaction layer are shown in Fig. 11. The content of aluminium is much higher in the reaction layer than in the silicon nitride grain. This means that reactions proceed rapidly in the grain boundary.

4. Conclusions

The faying surfaces of HIPed additive-free silicon nitride ceramics were oxidized during heat-treatment at 1073 K for 1.8 ksec in air. This treatment formed silicon oxynitride on the surface of silicon nitride and increased the interfacial strength of the joint. A silica–alumina non-crystalline layer and a β'-sialon layer were formed successively from the aluminium side in the joints as reaction products in brazing. The former became thicker in the joint of heat-treated silicon nitride ceramics as compared with that of as-ground ones. The development of the reaction layer is necessary for making the joints strong. Therefore, since oxygen plays an important role in the formation of the layer, it is concluded that oxidation of the faying surfaces of silicon nitride ceramics is an indispensable process to produce reliable joints with high bonding strength.

TABLE II Si2p binding energy and intensity ratio IO1s/IN1s on faying surfaces of silicon nitride ceramics as-ground and heat-treated under the same conditions as in brazing

Sample	Si2p (eV)	IO1s/IN1s
As-ground	101.9	2.4
Heat-treated (1.8 ksec)	102.2	2.1
Heat-treated (18 ksec)	102.6	2.1

Acknowledgements

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