Joining of Al-plasma-sprayed Si_3N_4 ceramics

W. X. PAN*, T. OKAMOTO‡, X. S. NING¶
Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567, Japan

Aluminium was coated on silicon nitride ceramics by a low-pressure plasma spraying method, in order to form a tight bond between aluminium and the ceramics. Aluminium nitride formed as a interfacial reaction product between the aluminium coating layer and the ceramics. Two pieces of the aluminium-coated Si_3N_4 ceramics were then joined using the aluminium coating layers as filler metal in a vacuum of 1.3×10^{-3} Pa at 973 K. The average bending strength and Weibull modulus of the joint are 340 MPa and 6.3 respectively, considerably higher than the 230 MPa and 0.9 of a Si_3N_4 ceramics joint brazed with an aluminum plate under the same condition.

1. Introduction

Many studies have been carried out on the reliable joining of Si_3N_4 ceramics to aluminium, and to elucidate the bonding mechanism. Most of the interfacial reaction products between Si_3N_4 and aluminium contain oxygen, even though the joining is performed in vacuum or in an inert gas. It is found that β′-sialon and silica–alumina oxide are usually formed at temperatures lower than 1173 K[1–3], while β′-sialon, 15R AlN-polytype sialon, AlN, Si and silica–alumina oxide form at higher temperatures of 1473–1823 K[4–6]. Although the reaction forming AlN and Si is thermodynamically possible at all the brazing temperatures, it can be impeded by the existence of oxide films on the surfaces of aluminium and Si_3N_4 pieces. However, when heating a compact of Si_3N_4 and aluminium powder mixture, AlN and Si form at temperatures of 1073–1273 K[6, 7]. It was considered that the oxide film on the surface of aluminium powder was scratched and broken by Si_3N_4 powder during mixing and pressing, thus aluminium could contact with Si_3N_4 directly, which facilitated the formation of AlN and Si at the low temperature.

In the present work, aluminium was coated to Si_3N_4 ceramics by low-pressure plasma spraying. It was expected that the oxide film on the surface of melted aluminium drops could be broken when the liquid drops impacted on the solid surface of ceramics during the spraying, which would make aluminium adhere to Si_3N_4 ceramics without the effect of an oxide film, and thus make the formation of AlN possible at the low temperature of 973 K. The interfacial reaction and bond strength between the aluminium coating layer and Si_3N_4 ceramics was investigated. In addition, two pieces of aluminium-coated ceramics were joined at coated Al surfaces. The bond strength of the joint was measured and compared with that of a Si_3N_4 joint brazed with an aluminium plate.

2. Experimental procedure

2.1. Coating of Al to Si_3N_4 ceramics

Aluminium powder of average grain size 45 μm was used for plasma spraying. A schematic drawing of the spraying apparatus is shown in Fig. 1. A pressureless sintered Si_3N_4 ceramic piece of dimensions $13 \times 16 \times 20$ mm, ground with a diamond wheel, was set on a water-cooled stainless holder which could be rotated around the axis for spraying aluminium. DC plasma was generated in argon ($350\ cm^3\ s^{-1}$) as the primary, and H_2 ($20\ cm^3\ s^{-1}$) as the secondary working gases, at a chamber pressure of 1.3×10^4 Pa. Two layers of aluminium were coated on one Si_3N_4 piece. The first layer was coated to make aluminium adhere strongly to Si_3N_4 ceramics. This layer was approximately 2 μm thick, coated at a plate power of 23 kW for 35 s after the substrate had been preheated to a temperature a little higher than the melting point of aluminium. The temperature of the ceramic surface was evaluated by observing the melting of aluminium on it. Under these conditions, a coating layer thicker than 2 μm could not form because of the strong gas flow of plasma, and the fact that the substrate temperature was higher than the melting point of aluminium. The second layer was about 200 μm thick, coated at 17 kW on the first coating layer.

A cross-section fractured normal to the coating layer was observed using scanning electron microscopy (SEM). A specimen of a coating layer of only 2 μm thick on a Si_3N_4 piece was prepared and determined by X-ray diffractometry (XRD). Aluminium-coated Si_3N_4 pieces were cut to a coated area of

Present addresses: *Department of Metallurgy and Materials Science, University of Tokyo, Tokyo 113, Japan
‡Wakayama National College of Technology, Gobo, Wakayama 644, Japan
¶Central Research Laboratory, Dowa Mining Co., LTD, Hatioji, Tokyo 192, Japan

0022–2461

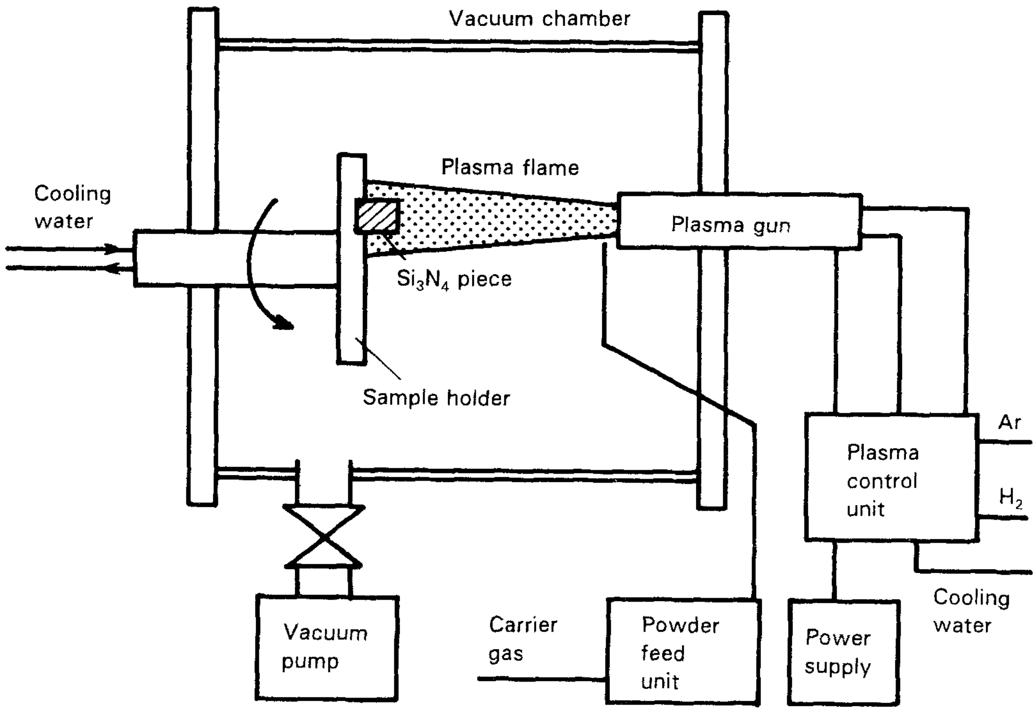

Figure 1 Schematic drawing of the plasma spraying apparatus.

3×4 mm and bonded to two metal rods of the same cross-section size with an epoxy resin, to test the bond strength between the coating layer and ceramics. The strength damage to the ceramics, which could be caused by rapid heating and cooling on spraying, was examined by coating aluminium to a 16×40 mm surface area of the ceramics, 3 mm thick, mechanically polishing the coating layer away, cutting the specimen to $3 \times 4 \times 40$ mm and bending it using the polished surface as tensile side.

2.2. Joining of Si_3N_4 piece

Aluminium surfaces of two pieces of aluminium-coated Si_3N_4 ceramics were faced to each other and were brazed with the coating layer at 973 K for 0.9 ks, under a pressure of 0.5 MPa in vacuum of 1.3×10^{-3} Pa. The joint was cooled slowly after joining. Meanwhile, two Si_3N_4 pieces without aluminium coating were brazed by using an aluminium plate of 0.3 mm thick under the same conditions as for the aluminium-coated ceramics.

Bars with dimensions $3 \times 4 \times 40$ mm were cut from each joint for a four-point bending test. The test was performed at a cross-head speed of 8.3 $\mu m\ s^{-1}$ with an upper span of 10 mm and a lower span of 30 mm. The fracture surfaces of bars after the bending test were observed by SEM. Interfacial reaction products were determined by XRD at the fracture surfaces, because the test bars fractured at or very near the interface. The microstructure at the interface was observed under a transmission electron microscope (TEM), acceleration voltage 3 MV. The foils used for TEM observation were cut off from the joints normal to the joined interface, polished mechanically, and then thinned by ion bombardment.

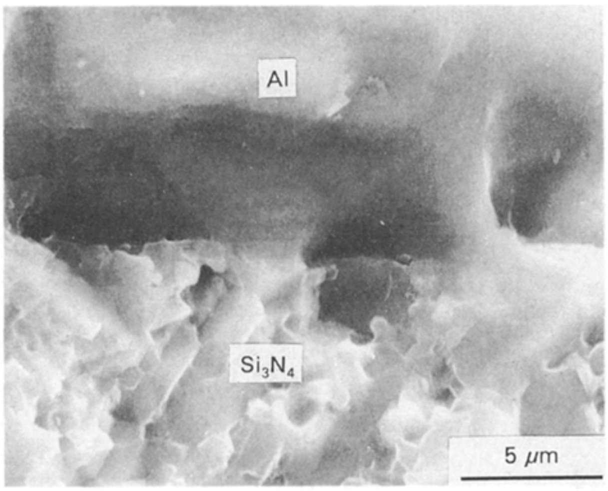

Figure 2 A SEM image of Al-coated Si_3N_4 ceramics on the fracture surface normal to the coating layer.

3. Results and discussion

3.1. Aluminium-coated Si_3N_4 ceramics

Fig. 2 shows the microstructure on the fractured cross section of an aluminium-coated Si_3N_4 piece, which reveals that the coating layer bonds tightly to ceramics with a clean and uniform interface. Table I shows the characteristics of aluminium-coated Si_3N_4 ceramics, and indicates that the strength of Si_3N_4 ceramics was

TABLE I Characteristics of Al-coated Si_3N_4 ceramics

Average strength (MPa)		$Al-Si_3N_4$ bond strength (MPa)	Interfacial reaction product (by XRD)
As-received	After spraying		
440	440	> 50	AlN, Si

not affected by plasma spraying under experimental conditions. The adhesion between the ceramics and aluminium coating layer was greater than 50 MPa according to the tensile test, in which the test bars fractured partially in the epoxy resin and partially at the interface between the resin and ceramics and/or aluminium coating layer. A small amount of AlN was detected by XRD, together with Si_3N_4 and aluminium from the specimen of the 2 μm aluminium coating layer on the Si_3N_4 piece. This suggests that the reaction

$$< Si_3N_4 > + 4\{Al\} = 4 < AlN > + 3[Si]$$

occurs at the interface between Si_3N_4 and aluminium during coating. Usually, Si_3N_4 ceramics and aluminium plate are covered with a thin layer of silicon oxide and alumina, respectively, which hinders the formation of AlN at the interface of both materials at temperatures below 1173 K[6]. The occurrence of the reaction hints that in the coating process, however, the oxide layer on Si_3N_4 ceramics surface might be partially sputtered away by the Ar + H_2 plasma during preheating, and the oxide on the surface of aluminium drops might be broken when the liquid drops impacted on the Si_3N_4 ceramics surface. This would bring aluminium into contact with Si_3N_4 ceramics directly, without the effect of their oxides. Thus AlN formed even at a temperature a little higher than the melting point of aluminium within a period of 35 s. The reaction product silicon could not be detected immediately after spraying of aluminium, but was detected after the same specimen was reheated to about 973 K and then cooled slowly. This indicates that silicon could be in aluminium in a solid solution after spraying, owing to the rapid cooling.

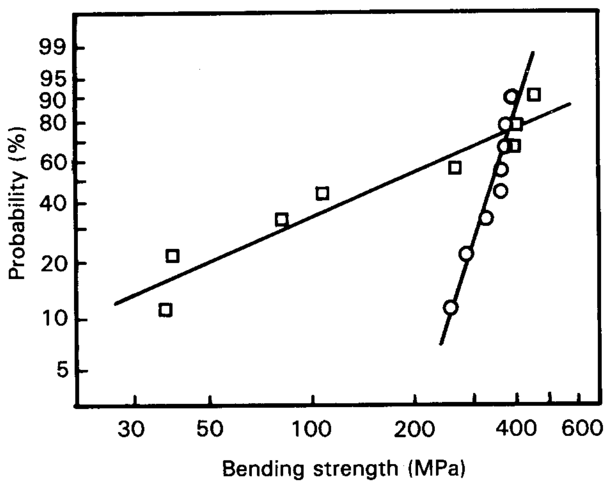

Figure 3 Weibull plots of four-point bending strength of Si_3N_4 joints, ○: joined at the coated Al surfaces and, □: brazed with the Al plate.

3.2. Si_3N_4 joints
3.2.1. Bond strength and fracture surface
Figure 3 shows the Weibull plots of test bars of Si_3N_4 ceramic joint brazed with the aluminium plate, and the joint brazed with the aluminium layers coated on the ceramics. The average bending strength of the former is 230 MPa, and that of the latter is 340 MPa. The Weibull modulus of the latter joint is 6.3, which is much higher than that of 0.9 for the former joint; this indicates that the bond state is improved by spraying aluminium to the Si_3N_4 piece before joining.

The joints fractured at or near the interface by the bending test. Fig. 4a shows a typical fracture surface of the specimen joined using aluminium coating layers. The specimen fractured almost completely in the aluminium layer, and at only a few parts in the Si_3N_4 ceramics. Fig. 4b and c shows the joint brazed using the aluminium plate. The specimen with a bending strength of about 240 MPa revealed a fracture surface as in Fig. 4b, fracturing partially in the filler metal and partially at the interface. Specimens with the lowest bending strength, as in Fig. 3, revealed the fracture surface shown in Fig. 4c: the filler metal aluminium was peeled from the ceramic surface and the ground trace of the fraying surface of Si_3N_4 piece was exposed,

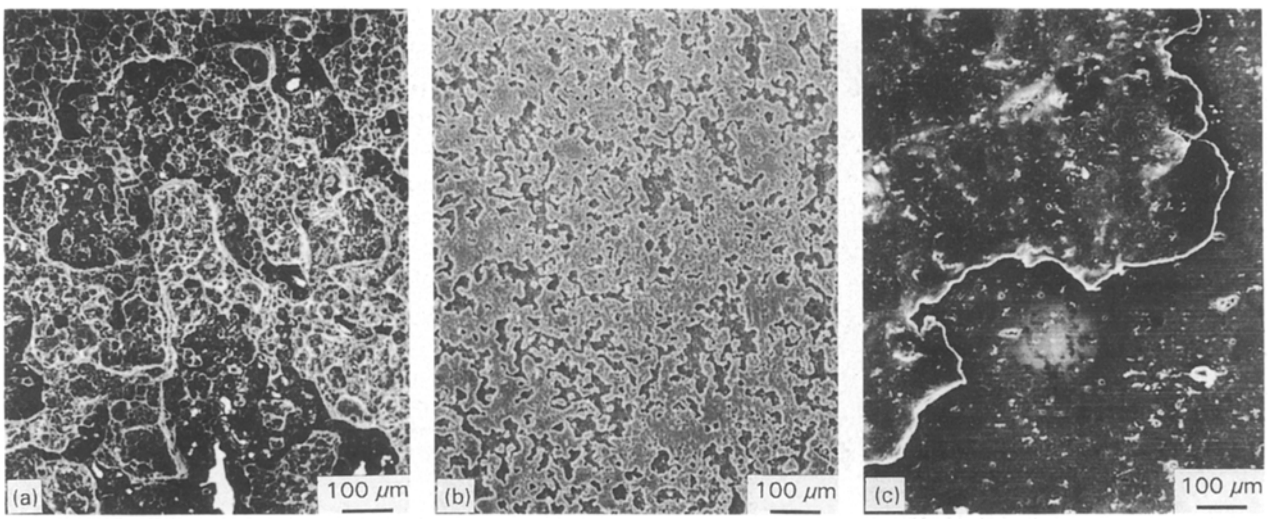

Figure 4 SEM images of fracture surfaces of the joints after the bending test. (a) joined at the coated Al surfaces and (b) and (c) brazed with the Al plate. White regions in (a) are the parts fractured in Si_3N_4 ceramics.

which suggests poor wettability of aluminium to Si_3N_4 ceramics. A reason why the bonding is not uniform (i.e. the Weibull modulus is very low) in the joint brazed with the aluminium plate could be that it is difficult to set the plate with its two surfaces in contact perfectly with the surfaces of two Si_3N_4 pieces.

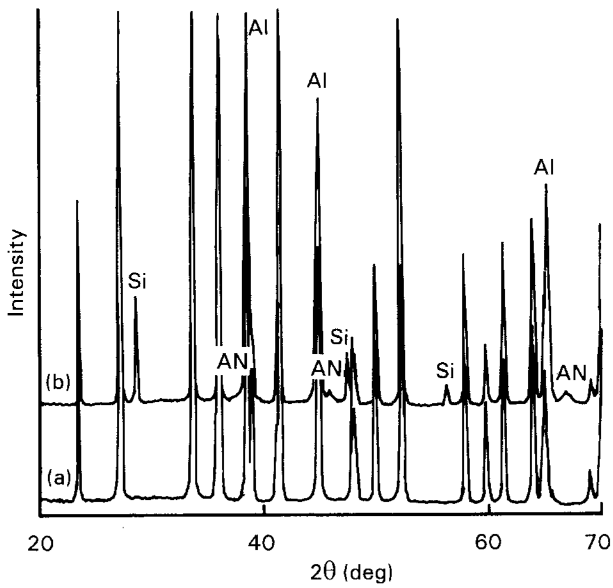

Figure 5 XRD patterns at fracture surfaces of the joints. (a) is the one brazed with the Al plate and (b) joined at Al coating layers. AN: AlN, and the peaks without any mark are those of β-Si_3N_4.

The points of the aluminium and Si_3N_4 surfaces which could not contact each other would be exposed under a weak oxidation atmosphere during heating for the joining, and thus form a weak bonding there.

3.2.2. Interfacial reaction during brazing

Fig. 5 shows XRD patterns of the joints taken at fracture surfaces after the bending test. Only Si_3N_4 and aluminium were detected on the fracture surface of the joint brazed with the aluminium plate, as shown in Fig. 5a. On the fracture surface of the joint brazed at coated aluminium surfaces, AlN and silicon were detected, adding to Si_3N_4 and aluminium (Fig. 5b). However, the intensity ratio of the peaks of AlN to Si_3N_4 or AlN to aluminium at the fracture surface of the joint apparently did not change from that of the specimen coated with 2- μm-thick aluminium. These results indicate that the interfacial reaction which produces AlN and silicon mainly occurred during coating.

The thinning rate of the interface layer by ion bombardment was very low, compared with that of Si_3N_4 ceramics and aluminium. The interface reaction layer was still too thick to be observed by a general TEM at 200 kV, even when both Si_3N_4 and aluminium were very thin. Fig. 6 shows microstructures and electron diffraction (ED) patterns at the interface of the joint from aluminium-coated Si_3N_4 ceramics, taken using the TEM at 2 MV. Fig. 6b is a high

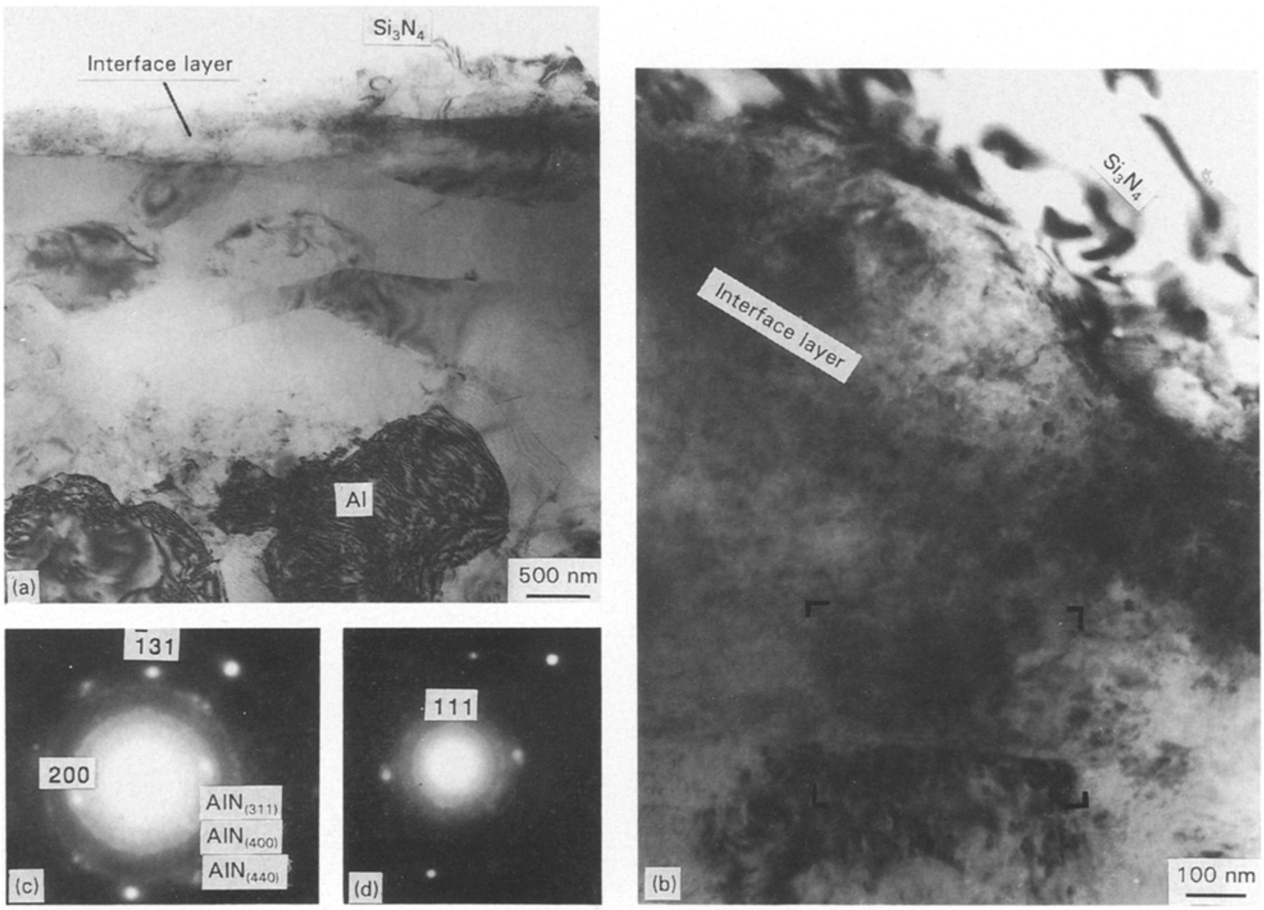

Figure 6 Microstructures and ED patterns taken by the TEM at 2 MV at the interface of the joint from Al-coated Si_3N_4 ceramics. (c) and (d) are ED pattern taken at the marked region in (b).

magnification image at the interface layer, and the ED patterns (Fig. 6c, d) are from the marked region in Fig. 6b, printed to show different brightnesses. In the pattern Fig. 6c, the signed spots indicate the diffraction of aluminium crystal. The three rings in the ED pattern may correspond to the diffractions of (3 1 1), (4 0 0) and (4 4 0) of an AlN crystal, or to those of (1 1 1), (2 0 0) and (2 2 0) of an aluminium crystal; it is difficult to determine them by measuring the diffraction pattern alone. However, in view of the fact that the joint was cooled slowly after joining, and aluminium crystals would grow to large grains which would be revealed as spots instead of rings in an ED pattern, the rings must therefore correspond to fine grains of AlN formed in aluminium. In Fig. 6d, spots corresponding to the diffraction of (1 1 1) of silicon crystals were also detected near the centre of the pattern, which confirms that silicon crystals are also formed in aluminium.

4. Conclusions

The aluminium coating layer bonds to Si_3N_4 ceramics very well, with a uniform interface. Aluminium nitride and silicon formed at the interface between Si_3N_4 and aluminium coating during plasma spraying, by eliminating the effect of a surface oxide layer of aluminium on the interfacial reaction. The Si_3N_4 joint brazed at coated aluminium surfaces fractured almost completely in the aluminium layer, while the joint brazed using the aluminium plate fractured mainly at the interface and partially in the aluminium braze. The bonding of the joint at a low joining temperature (973 K) was improved greatly by coating aluminium to Si_3N_4 ceramics before the joining.

Acknowledgement

The authors thank the members of the Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, for helping with the observation of interfacial structures.

References

1. X. S. NING, K. SUGANUMA, M. MORITA and T. OKAMOTO, *Phil. Mag. Lett.* **55** (1987) 93.
2. X. S. NING, K. SUGANUMA, T. OKAMOTO, Y. MIYAMOTO and A. KOREEDA, *J. Mater. Sci.* **24** (1989) 2865.
3. X. S. NING, T. OKAMOTO, Y. MIYAMOTO, A. KOREEDA and K. SUGANUMA, *ibid.* **24** (1989) 2879.
4. M. NAKA, H. MORI, M. KUBO, I. OKAMOTO and H. FUJITA, *J. Mater. Sci. Lett.* **5** (1986) 696.
5. M. E. MILBERG, H. D. BLAIR, W. T. DONLON and S. S. SHINOZAKI, *J. Mater. Sci.* **22** (1987) 2560.
6. X. S. NING, T. OKAMOTO, Y. MIYAMOTO, A. KOREEDA and K. SUGANUMA, *ibid.* **26** (1991) 4142.
7. Y. ARATA, A. OHMORI and S. SANO, *Trans. J. Weld. Res. Inst.* **14** (1985) 284.

Received 28 July 1992
Accepted 31 August 1993