

# Solid-state bonding of alumina to austenitic stainless steel

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A low temperature and low pressure bonding process for alumina and 316L austenitic stainless steel has been developed using a titanium/molybdenum laminated interlayer. The intermetallic compounds of  $Ti_3Al$  (or  $Ti_2Al$ ) and  $TiAl$  were formed at the alumina/titanium interface on bonding at above 1273 K. The activation energy of the layer growth was about  $142 \text{ kJ mol}^{-1}$ . The construction of  $Al_2O_3/Ti/Mo/steel$  gave the most stable joints. The highest tensile strength was above 60 MPa with a titanium 0.4 to 0.6 mm thick/molybdenum 0.4 to 0.5 mm thick interlayer on bonding at 1273 K for 3 h under pressure of 12 MPa.

## 1. Introduction

In the last few years great interest has been aroused in the bonding of ceramics to metals for practical applications of ceramics. There are still several problems to be solved for the perfect bonding. The thermal expansion mismatch between ceramics and metals is one of them. When the joints are bonded at elevated temperatures, thermal expansion mismatch produces a large stress concentration in the joints. This stress sometimes brings about fatal damage in the joints without any applied forces. Hence compensation for this mismatch is needed to get high strength joints.

Several methods, some using interlayers, have been developed for this purpose [1-4]. Nichols and Crispin [1] developed a soft metal method using aluminium as an interlayer for the bonding of alumina to an austenitic stainless steel. They achieved joints with a tensile strength of 70 MPa. Some of the present authors used an aluminium/Invar alloy interlayer for the bonding of silicon nitride to a ferritic steel [3]. The strength of the joint reached a bending strength of 170 MPa. Thus, it is concluded that the soft metal method is one of the successful methods. However, it has limits as to a serviceable temperature and to the strength of the joints because of using a soft metal such as aluminium.

Recently, two of the present authors developed a laminated interlayer method using hot isostatic pressing (HIP) for the bonding of alumina to a ferritic steel [4]. The bonding treatment at 1673 K for 30 min under a pressure of 100 MPa with a niobium/molybdenum interlayer produced joints with a bending strength of 500 MPa [5]. This strength was nearly equal to that of alumina. The joints also had a good resistance to thermal cycling. Because the HIP method allowed complete interfacial contact between ceramics and metals, it is one of the most recommended processes for joining. For industrial use, however, there are many needs for a low-cost bonding process. The purpose of this research was to modify the laminated

interlayer method with HIP to a low-cost bonding process using titanium instead of niobium. In this case the highest pressure and the highest temperature were about 10 MPa and 1473 K, respectively. The reason for use of titanium is that, although niobium could not be bonded to alumina below this temperature range, titanium reacts readily with alumina and can be bonded to it.

## 2. Experimental procedure

### 2.1. Materials

Alumina (Narumi China Co Ltd, A3997) used in this work was of 99.7 wt % purity and supplied as a rod 5 mm in diameter and 50 mm long. From this rod, discs 1 mm thick were cut off. Both surfaces were ground with  $10 \mu\text{m}$  diamond paste to optical flatness. The roughness of the disc surface was about  $1 \mu\text{m}$ .

Metals used were 99.86 wt % titanium, 99.9 wt % molybdenum and AISI type 316L austenitic stainless steel. These were purchased in the shape of 5 mm diameter rods. Discs were cut from the rod to appropriate thickness. Metal surfaces were also ground and polished to surface roughness of  $0.5 \mu\text{m}$ . Metal discs for a tensile test were finished precisely to have their thickness within an allowance of  $\pm 20 \mu\text{m}$ . All the discs were cleaned with acetone just before bonding.

### 2.2. Bonding treatment

Fig. 1 shows the apparatus for bonding treatments. No reaction between discs and BN discs was recognized.

The discs were first assembled as a joint specimen set in the centre of a hot pressing chamber and then it was evacuated to  $10^{-4}$  torr. Consequently, atmospheric pressure was placed on the specimen, being equivalent to a compressive stress of 3.1 MPa. Then they were heated to a bonding temperature of 1173 to 1473 K for various times. The heating rate was  $0.12 \text{ K sec}^{-1}$ . In this study, the bonding pressure was

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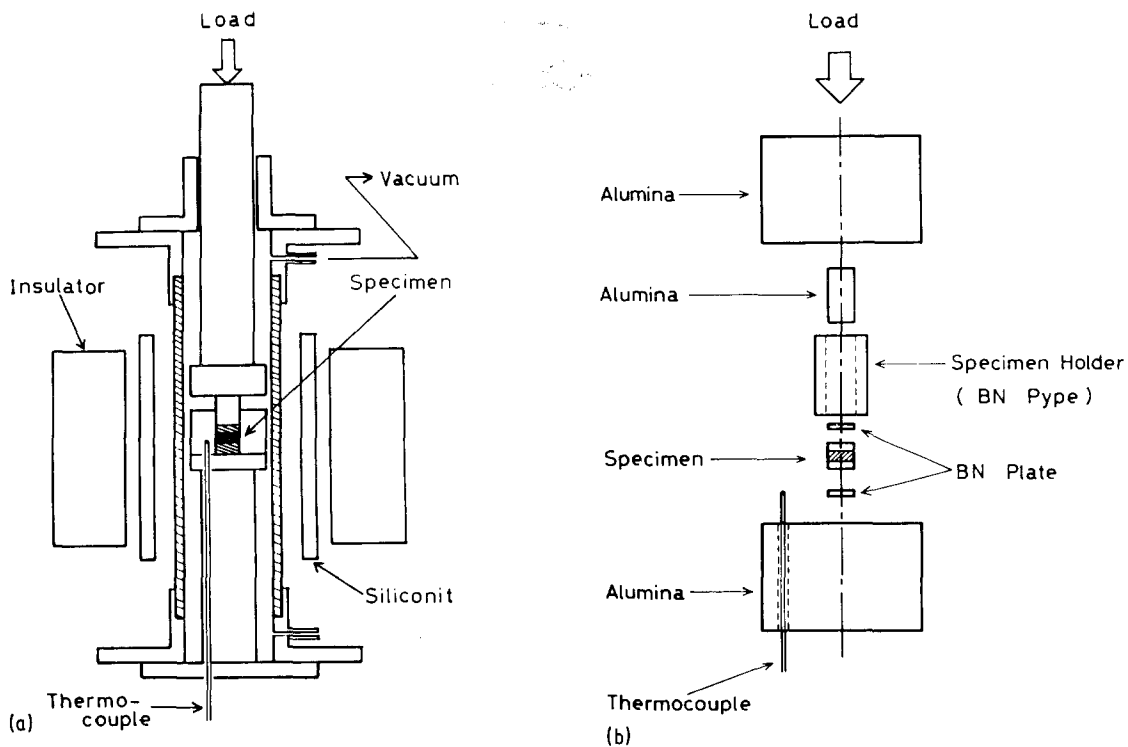


Figure 1 (a) Schematic diagram of the vacuum hot-pressing facility. (b) Joint assembly.

in the range of 3.1 to 11.9 MPa. After bonding the joints were cooled slowly to room temperature. The cooling rate was  $0.07 \text{ K sec}^{-1}$ .

The interfacial structures were observed using optical microscope (OM) and scanning electron microscopy (SEM). Elementary distribution across the interface was examined with an electron probe microanalyser (EPMA) and the reaction products were identified by an X-ray diffraction method.

The tensile strength of the joints was measured at a crosshead speed of  $0.008 \text{ mm sec}^{-1}$  using an Instron type testing machine. The two types of joints are shown in Fig. 2. An alumina disc was placed symmetrically between two metal discs. Both ends of the specimens were polished and were adhered to tensile jigs with an epoxy adhesive. The tensile strength of the epoxy adhesive was about 60 MPa.

### 3. Results

#### 3.1. Solid-state reaction between alumina and titanium

Fig. 3 shows the microstructure of the alumina/titanium interface after both materials were kept in

touch with each other at 1173 to 1473 K for 9 h under a pressure of 3.1 MPa. They were etched in a 4 ml HF–6 ml  $\text{HNO}_3$ –50 ml  $\text{H}_2\text{O}$  solution. It is clearly observed that a reaction layer is formed on the titanium side. At 1173 K, it grew up to a thickness of about  $10 \mu\text{m}$  and was observed as a single phase. It is called layer (I) in this paper. At 1273 K, in addition to further growth of the layer (I), the second layer (II) appeared in an irregular shape at the interface. This layer grew remarkably with increased reaction temperature. Especially at 1473 K, layer (II) became thick and the interface between it and layer (I) was planar. The microstructural change in alumina adjacent to the alumina/titanium interface was not observed at any temperatures.

Fig. 4 shows the elemental distribution analysed with EPMA across the interface in the joints held at 1473 K for various times. The diffusion of titanium into alumina was not detected under any conditions but aluminium diffused into titanium. The diffusion layer thickness in the specimens held for less than 4 h was too thin to distinguish a compositional difference between the two layers. In the case of the specimen held for 9 h there were two steps on the line profile which indicated the existence of two intermetallic compounds. Those steps corresponded to the microstructures shown in Fig. 3.

To determine the compositions of the two reaction layers, point analysis was conducted with EPMA on the condition of an acceleration voltage of 20 kV and a sample current of  $0.02 \mu\text{A}$ . The results are listed in Table I. The compositions were calibrated from pure aluminium and pure titanium as standards, taking calibration coefficients for penetration, absorption and fluorescence excitation of the characteristic X-ray. The results showed that layer (II) would be TiAl and that layer (I) contained 25 to 33 at % Al. Although the results might have some errors, the aluminium

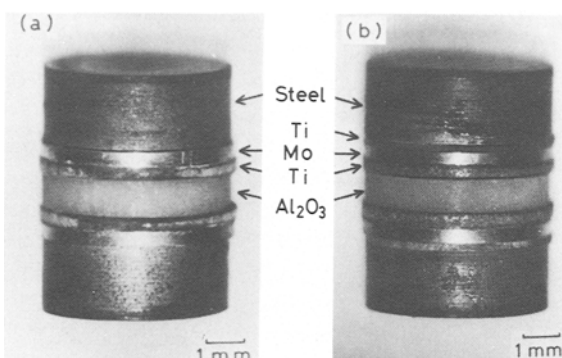


Figure 2 Alumina/316L joints. (a) with a titanium/molybdenum interlayer. (b) with a titanium/molybdenum/titanium interlayer.

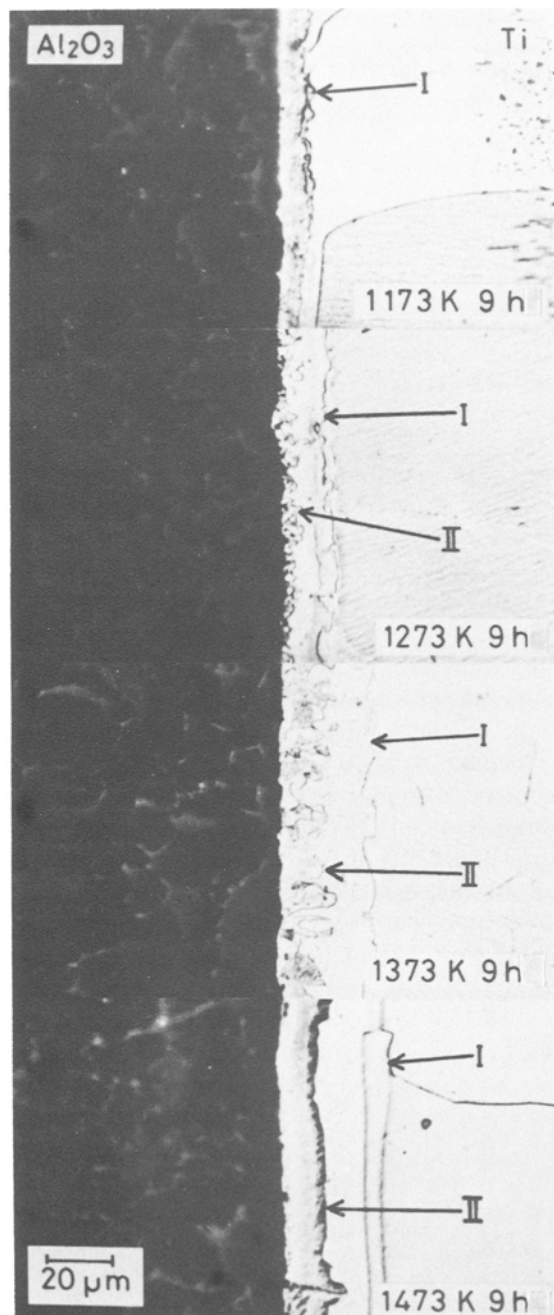


Figure 3 Reaction layers formed at the alumina/titanium interface.

concentrations in both layers tended to increase with increased holding temperature. Fig. 5 shows X-ray diffraction patterns taken at the interface of the titanium side of alumina/titanium diffusion couples which were separated at the alumina/titanium interface. When the reaction temperature was 1173 K, most of the diffraction peaks were of  $Ti_3Al$  (or  $Ti_2Al$ ), which proved the first layer (I) to be composed of  $Ti_3Al$  (or  $Ti_2Al$ ). At the reaction temperatures of 1273 and 1373 K, the layer was consisting of two phases of  $Ti_3Al$  (or  $Ti_2Al$ ) and  $TiAl$ . In the case of 1473 K, the main peak (201) of  $Ti_3Al$  disappeared and the diffraction peaks observed were only from  $TiAl$ . This means that layer (II),  $TiAl$ , grew thickly at the interface. Tressler *et al.* [6, 7] examined the reaction between fibrous alumina and titanium in the temperature range between 1050 and 1200 K. They recognized the layer formation of mainly  $Ti_3Al$  and  $TiO$ . Although the

TABLE I Compositions of intermetallic phases formed at the alumina/titanium interface

		Concentration (wt %)	
		Al	Ti
1273 K 9 h	I	$13.9 \pm 1.1$	$77.8 \pm 2.1$
	II	$24.9 \pm 2.1$	$69.6 \pm 2.1$
1373 K 9 h	I	$17.3 \pm 2.0$	$75.1 \pm 3.3$
	II	$31.7 \pm 2.8$	$63.6 \pm 3.6$
1473 K 9 h	I	$20.7 \pm 1.4$	$73.4 \pm 2.8$
	II	$34.7 \pm 1.3$	$60.9 \pm 1.6$

$TiAl$ : Ti/64.0 wt %, Al/36.0 wt %.

$Ti_2Al$ : Ti/22.0 wt %, Al/78.0 wt %.

$Ti_3Al$ : Ti/15.8 wt %, Al/84.2 wt %.

formation of  $Ti_3Al$  was the same as that in the present work, that of the  $TiO$  layer was different. The formation temperature for  $TiAl$  in the present work was about 1273 K, which was slightly higher than the related temperature in Tressler's work. The XRD (Fig. 5) and EPMA (Fig. 4) results indicate the formation of  $TiAl$ .

Fig. 6 shows the Vickers hardness in titanium as a function of distance from the alumina/titanium interface. From this figure, it is shown that a hardened region is formed beyond the aluminium diffusing layer which grew up to a thickness of  $40 \mu m$  under a reaction condition of 1373 K and 9 h. It seems that the hardened layer corresponds to the diffusion layer of oxygen from alumina because of the high diffusibility of oxygen in titanium.

Fig. 7 shows the thickness of the sum of the two layers of  $Ti_3Al$  (or  $Ti_2Al$ ) and  $TiAl$  against the square root of holding time at various temperatures. The parabolic relation is satisfied between them. This layer growth seems to be controlled by diffusion process. The rate constant for growth of the layers was plotted against the reciprocal of the absolute temperature ( $1/T$ ) in Fig. 8. The apparent activation energy for the growth of the layers was  $142 \text{ kJ mol}^{-1}$ . This value is considerably lower than that of Tressler's work,  $216 \text{ kJ mol}^{-1}$ . There seems to be several reasons for this difference. The difference in the reaction temperature seems to be one of the major reasons. Tressler's value was obtained in a temperature range below that of this work. They also pointed out that the activation energy decreased above about 1100 K. Thus, the value of  $142 \text{ kJ mol}^{-1}$  seems reasonable. However, no data are available to check the rate-controlling step for the growth of the reaction layer.

## 3.2. Mechanical properties

### 3.2.1. Alumina/titanium

Titanium discs which had the same dimension as an alumina disc were bonded onto both sides of the alumina disc under a bonding pressure of 3.1 MPa. The tensile strength of the specimens were measured at room temperature as functions of bonding temperature, bonding time and cooling rate after bonding. The results are listed in Table II. The strengths were in the range of 5 to 10 MPa. They were not influenced by the bonding variables.

The fracture of the specimens mainly occurred in

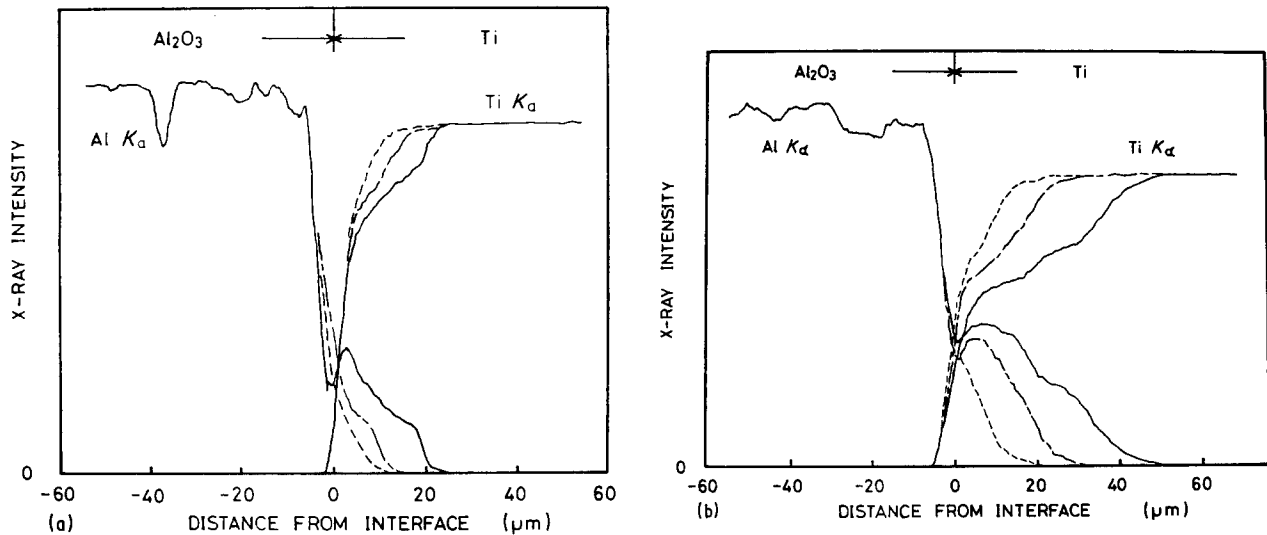


Figure 4 EPMA data for the alumina/titanium reaction couples held annealed (a) at 1273 K. (b) at 1473 K. (---) 1 h, (- · -) 4 h, (—) 9 h.

alumina regardless of bonding temperature and cooling rate. Fig. 9a shows the longitudinal section of a specimen before the tensile test. It is clearly shown that two large cracks are present in alumina, having been induced by the thermal expansion mismatch. The joints always fractured in a cap shape in alumina discs under applied tensile stress, as shown in Fig. 9b.

Alumina was bonded firmly to titanium at bonding temperatures of 1173 to 1473 K under a pressure of 3.1 MPa because pure titanium was soft enough at these temperatures to deform plastically and to get in touch with the alumina surface. This meant that the fracture of the specimens hardly occurred at the interface except for those joints that had a long bonding period. The strength of the alumina/titanium joints was low due to the thermal expansion mismatch. The isothermal heat treatment to remove the residual stress in the joints was conducted at 820 K for 2 h on cooling from the bonding temperature. The strength, however, was not more than 13 MPa and fracture also occurred in alumina. Thus, this heat treatment was not so effective. In order to increase the strength of this system, it is necessary to make a further modification of the interlayer.

### 3.2.2. Alumina/316L with titanium/molybdenum laminated interlayers

Alumina was bonded to 316L using titanium/

molybdenum interlayers as shown in Fig. 2a. Table III shows the effects of the bonding conditions on the strength of the joints. The thickness of titanium, molybdenum, and 316L was 0.2 mm or 0.3 mm, 0.4 mm and 2.0 mm, respectively. The strength of the specimens bonded at a temperature of 1173 K under a pressure of 3.1 MPa increased with increasing holding time and reached 27.3 MPa on holding for 9 h. Such a high strength was never obtained in the alumina/titanium joints. Most of the specimens fractured at the molybdenum/316L interface. From these results, it is concluded that a titanium/molybdenum interlayer is quite effective inducing little thermal stress in alumina.

TABLE II Tensile strength of alumina/titanium joints

Temperature (K)	Time (h)	Cooling rate (K min <sup>-1</sup> )	Pressure (MPa)	Strength (MPa)
1173	1	2.0	3.1	9.8
1173	1	3.4	3.1	6.5
1173	1	5.6	3.1	8.3
1173	1	6.7	3.1	6.1
1173	3	6.0	3.1	5.0
1173	4	6.7	3.1	4.6
1173	4	5.8	3.1	5.3
1373	6	4.0	3.1	4.3
1173	1	4.7	3.1	13.0
		+ 820 K 2 h		

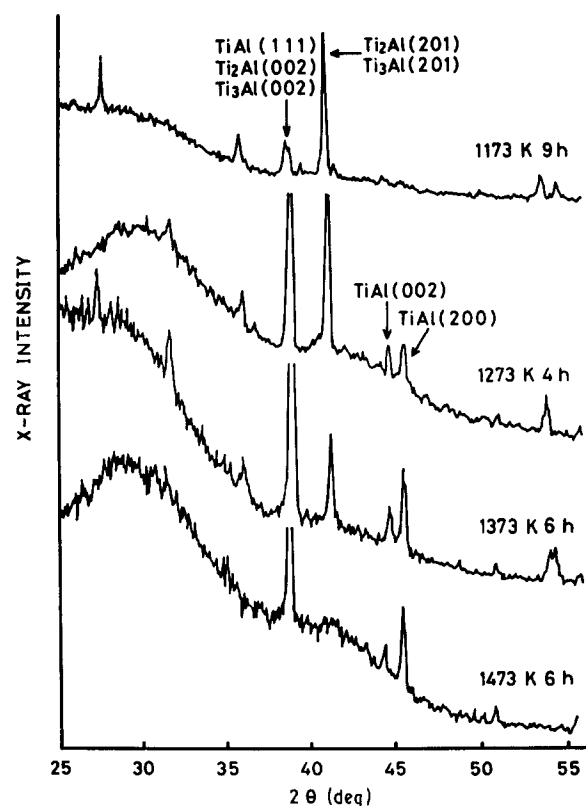


Figure 5 XRD data on the surface of titanium which reacted with alumina. CuKα, λ = 0.15405 nm.

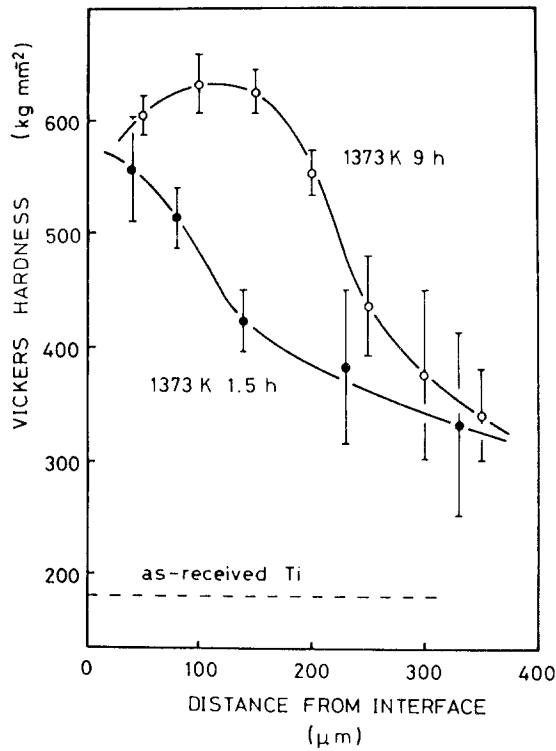


Figure 6 Vickers hardness of the titanium side, as a function of distance from the alumina/titanium interface. Load 200 g, 30 sec.

There are two means for increasing the strength at the molybdenum/316L interface; one is to elevate the bonding temperature, and the other is to increase the bonding pressure. When both temperature and pressure for bonding were raised to 1273 K and 9.4 MPa, respectively, the strength of the joints became higher than 40 MPa. Some joints fractured in alumina in close vicinity to the alumina/titanium interface and the others at the molybdenum/316L interface.

It is likely that the strength of the molybdenum/316L interface is influenced by the surface flatness of the molybdenum and 316L before bonding because these metals did not plastically deform enough to

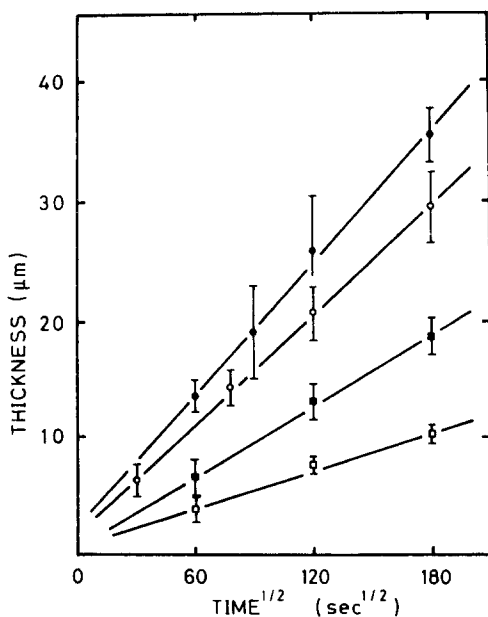


Figure 7 Growth of reaction layers as functions of holding time and temperature. (●) 1473 K, (○) 1373 K, (■) 1273 K, (□) 1173 K.

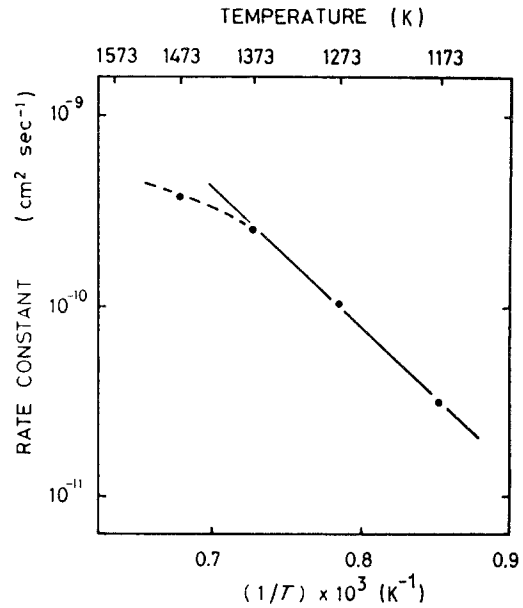


Figure 8 Parabolic rate constants against reciprocal temperature relationship for the growth of reaction layers.  $Q = 33.84 \text{ kcal mol}^{-1}$ .

bring them into contact with each other at this temperature.

It is known from Table III that the specimen which was bonded under the conditions of 1273 K, 3 h and 9.4 MPa had relatively high strength. Under this condition, the tensile strength of the alumina/Ti/Mo/316L joints was measured as a function of interlayer thickness. The results are summarized in Fig. 10. When molybdenum thickness was 0.3 mm, the strength monotonically increased with decreasing titanium thickness. In titanium thickness of 0.1 mm, the maximum strength, 25.9 MPa, was obtained and, then titanium thickness was 0.4 mm, the strength decreased

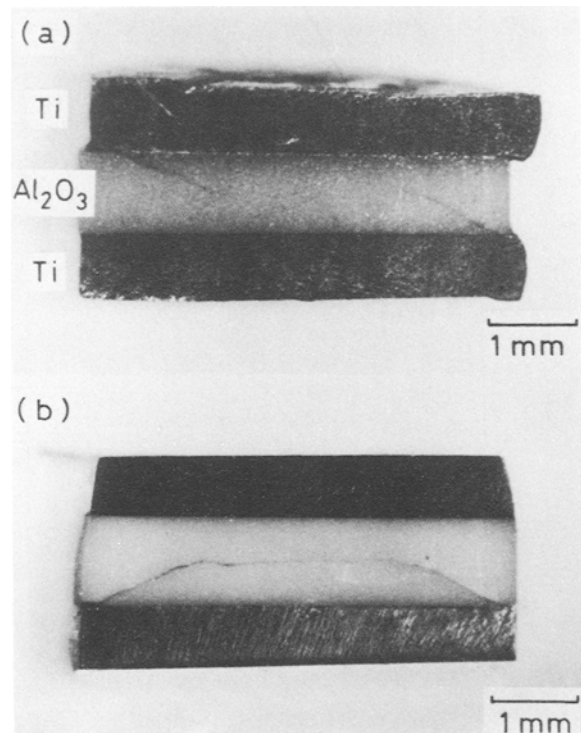


Figure 9 Cracks within joints. (a) after bonding (b) after tensile testing.

TABLE III Tensile strength of alumina/316L joints with titanium/molybdenum interlayers

Interlayer thickness (mm)		Bonding treatments			Strength (MPa)	Fracture position
Ti	Mo	Temperature (K)	Time (h)	Pressure (MPa)		
0.20	0.40	1173	2	3.1	8.5	Mo/316L
0.20	0.40	1173	4	3.1	16.8	Mo/316L
0.30	0.40	1173	8	3.1	14.0	Mo/316L
0.20	0.40	1173	8	3.1	27.3	Mo/316L
0.20	0.40	1273	4	3.1	0	Al <sub>2</sub> O <sub>3</sub> /Ti
0.30	0.40	1273	4	3.1	3.8	Al <sub>2</sub> O <sub>3</sub> /Ti
0.20	0.40	1273	3	9.4	46.5	Al <sub>2</sub> O <sub>3</sub> /Ti
0.30	0.40	1273	3	9.4	46.8	Mo/316L

to 5 to 12 MPa which was the same as that of the alumina/titanium system. The specimens fractured in a cap shape in alumina regardless of titanium thickness.

When molybdenum thickness was 0.4 or 0.5 mm, there existed three regions on the strength against titanium thickness curve as follows:

(a) In the first region, where titanium thickness was below 0.4 mm, the strength increased with increasing titanium thickness. The value was 68 MPa in titanium thickness of 0.4 mm. The fracture occurred in alumina in close vicinity of the alumina/titanium interface. Some small fragments of alumina adhered on the fracture surface of the titanium side.

(b) In the second region, where titanium thickness was from 0.4 to 0.6 mm, the strength was a maximum and exceeded 60 MPa.

(c) In the third region, where titanium thickness was more than 0.6 mm, the strength drastically

decreased with increasing titanium thickness. The joints fractured in a cap shape in alumina similar to the alumina/titanium joints. The strength was less than 26.5 MPa when the thickness of titanium was 0.8 mm.

### 3.2.3. Alumina/316L system with Ti/Mo/Ti laminated interlayers

To make the bonding quality at the molybdenum/316L interface higher, an attempt was made to insert another titanium disc between molybdenum and 316L, as shown in Fig. 2b. The result is summarized in Fig. 11. The specimens were bonded under the conditions of 1273 K, 3 h and 9.4 MPa, and the thickness of the titanium disc to be inserted between the molybdenum and 316L was 0.3 mm.

In this system, the dependence of the thickness of the titanium interlayer inserted between alumina and molybdenum on the strength was not so clear but the strength tended to slightly decrease with increasing titanium thickness. Although molybdenum thickness was altered from 0.4 to 0.6 mm, the strength was within an experimental error and never exceeded

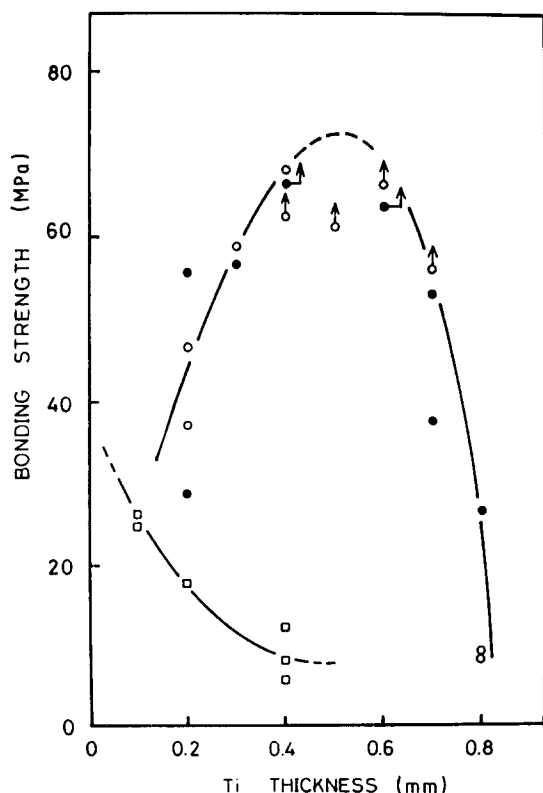


Figure 10 Effects of interlayer thickness on tensile strength of Al<sub>2</sub>O<sub>3</sub>/Ti/Mo/316L joints. (□) Mo = 0.3 mm, (○) Mo = 0.4 mm, (●) Mo = 0.5 mm.

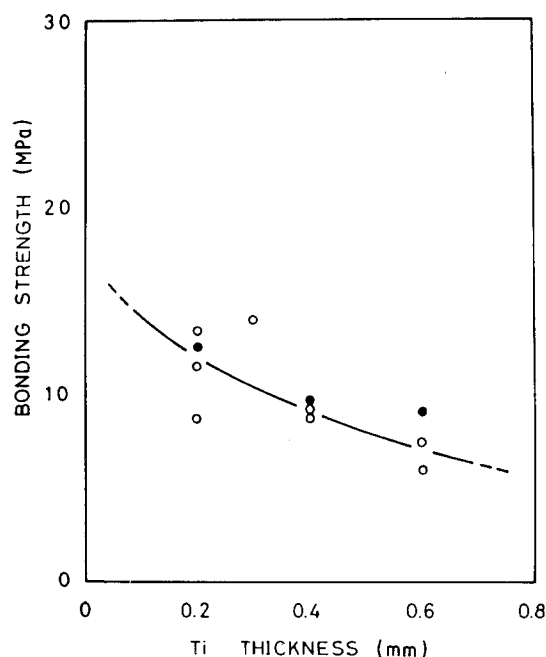


Figure 11 Effects of interlayer thickness on tensile strength of Al<sub>2</sub>O<sub>3</sub>/Ti/Mo/Ti/316L joints. The thickness of titanium represents that placed between alumina and molybdenum. (○) Mo = 0.4 mm, (●) Mo = 0.6 mm.

20 MPa. The fracture mostly occurred in alumina near the alumina/titanium interface.

#### 4. Conclusions

In the present work, the solid-state bonding of alumina/316L using laminated interlayers composed of titanium and molybdenum layers was examined to establish a low pressure and low temperature bonding process.

Metallographic observation revealed that  $Ti_3Al$  (or  $Ti_2Al$ ) was formed at the aluminium/titanium interface on the side of titanium at 1173 to 1473 K. The additional  $TiAl$  was formed above 1273 K. The activation energy of the growth of the reaction layers was about  $142 \text{ kJ mol}^{-1}$ .

Direct bonding of titanium to alumina caused a large thermal stress and the strength of the joint was very low. The joint structure of  $Al_2O_3/Ti/Mo$ /steel was the most stable. The highest strength was beyond 60 MPa when the thickness of molybdenum and of titanium was 0.4 to 0.5 mm and 0.4 to 0.6 mm, respectively. Complete the bonding at the molybdenum/316L stainless steel interface was found rather than at the aluminium/titanium interface. The bonding pressure of about 10 MPa was enough to achieve high strength

bonding at 1273 K. Thus, it is concluded that alumina and 316L stainless steel can be bonded tightly using a titanium/molybdenum laminated interlayer in the low temperature and low pressure bonding process.

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