JOURNAL OF MATERIALS SCIENCE **32** (1997) 2715–2721

Interfacial structure and reaction mechanism of AlN/Ti joints

M. H. EL-SAYED
Osaka University, Japan

MASAAKI NAKA
Welding Research Institute, Osaka University, Japan

J. C. SCHUSTER
Institute of Physical Chemistry, University of Vienna, Austria

Bonding of AlN to Ti was performed at high temperatures in vacuum. The bonding temperature ranged from 1323 to 1473 K, while the bonding time varied from 7.2 up to 72 ks. The reaction products were examined using elemental analysis and X-ray diffraction. TiN, Ti_3AlN (τ_1), and Ti_3Al were observed at the AlN/Ti interface, having various thickness at different bonding conditions. The thickness of TiN and Ti_3AlN layers grew slowly with bonding time. On the other hand, growth of the Ti_3Al layer followed Fick's law. The activation energy of its growth was found to be 146 kJ mol^{-1}. When thinner Ti foil (20 μm) was joined to AlN at 1473 K for a long time (39.6 ks), the Ti central layer has completely consumed and another ternary compound Ti_2AlN(τ_2) started to form. A maximum bond strength was achieved for an AlN/Ti (20 μm) joint made at 1473 K for 28.8 ks, after which the bond strength of the joint deteriorated severely.

1. Introduction

Many modern engineering applications are employing ceramic parts. In most cases it is required to join these ceramics to metals with sufficient bond strength as metals can compensate for the poor workability and brittleness of ceramics. To obtain sound joints a detailed understanding of interfacial phenomena of ceramic joints is necessary. Many investigators [1–3] reported that Ti metal can easily react with ceramics. Martineau *et al.* [1] observed TiC and Ti_5Si_3 in Ti/SiC composites. Naka *et al.* [2] studied the phase reaction and diffusion path of the SiC/Ti couples in the range 1373 to 1773 K. They have shown that TiC, $Ti_5Si_3C_x$ and Ti_3SiC_2 were formed at the Ti/SiC interface. Barbour *et al.* [4] studied the degradation process and the phases formed for the Ti/Si_3N_4 system in the range 773 to 1073 K and have shown the formation of TiN and Ti_5Si_3 phases at the interface. AlN is another important ceramic due to its high thermal conductivity [5]. Therefore, the aim of this work is to investigate compounds formed by phase reactions at the interface between AlN and Ti, and to study the growth kinetics of the compounds formed in the temperature range 1323 to 1473 K.

2. Experimental procedure

Solid cylinders 5 mm in diameter and 6 mm in length of AlN ceramic containing Y_2O_3-based sintering additives (from Tokuyama Soda Corp., Japan) were used. They were joined using either 50 or 20 μm Ti foil. Joining was performed in vacuum under a bonding pressure of 7.26 MPa using a high frequency source (400 KHz, 6 kW) with a graphite heating element. The bonding temperature ranged from 1323 to 1473 K while the bonding time varied from 7.2 up to 72 ks.

The reaction products formed at the interface region were investigated by observing the microstructure using scanning electron microscopy (SEM), analysing the elemental distribution using electron probe microanalysis (EPMA), and identifying the product phases using X-ray diffraction analysis (XRD). Furthermore, to check the bonding ability and the soundness of the joint, bond strengths of the AlN–20 μm Ti–AlN couples were measured using a fracture shear test (Fig. 1) with 1.67×10^{-2} mm s^{-1} crosshead speed.

3. Results and discussion

3.1. Phase reactions and diffusion path

Evidence of a reaction between AlN ceramic and Ti metal appeared at the initial bonding condition of 1323 K for 7.2 ks (used in this research work), but the bond exhibited low strength. When using 50 μm Ti foil, a 4 μm reaction zone layer was formed at the interface between AlN and Ti joined at 1323 K for 21.6 ks as shown in Fig. 2. The EPMA elemental analysis for this joint is presented in Fig. 3. The reaction layer formed shows an average composition of

0022–2461

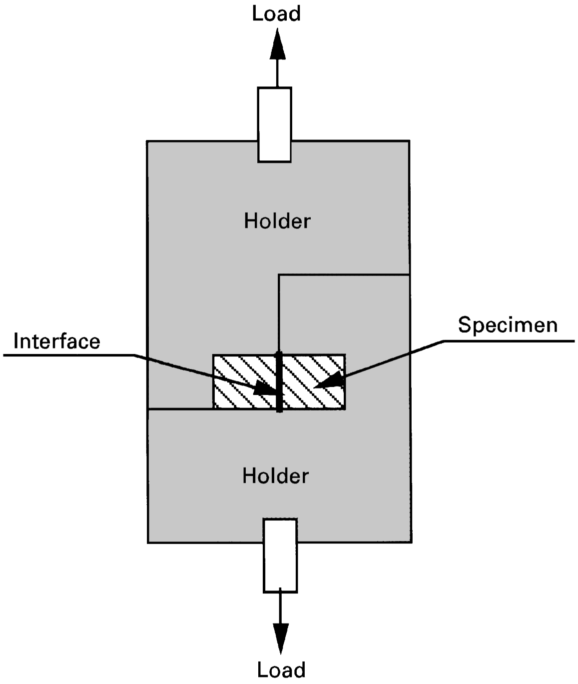

Figure 1 A schematic of the shear testing rig.

23.6 at % Al, 73.7 at % Ti and 2.7 at % N which might represent Ti_3Al as the dominant phase beside a trace of TiN.

Several reaction product zones can be distinguished from the microphotographs and line analyses across the reaction zones of AlN joined by using 50 μm Ti foil at 1473 K for 7.2, 14.4 and 21.6 ks respectively (Figs 4 to 8). The zone most dominant (beside the Ti central zone) consists of Ti–(20 to 24) at % Al and grew from 4.5 to 11.5 μm (with a standard deviation of 1 μm) when increasing the bonding time from 7.2 to 21.6 ks at 1473 K.

The X-ray analyses (Fig. 9) performed against the fracture surface of the AlN/Ti joint made at 1473 K for 21.6 ks, revealed that the Ti–24 at % Al zone corresponds to the hexagonal intermetallic compound Ti_3Al (either α-Ti (solid solution of 25 at % Al) or ordered intermetallic phase Ti_3Al). The calculation performed indicated that the lattice parameters of the detected Ti_3Al has an *a*-value of 0.578 nm and a *c*-value of 0.464 nm, which fit closely to the literature values [6]. The elemental line analysis for the joints indicated a minimum in aluminium content within the transition zone towards AlN. This minimum in the Al content is attributed to the formation of TiN, which

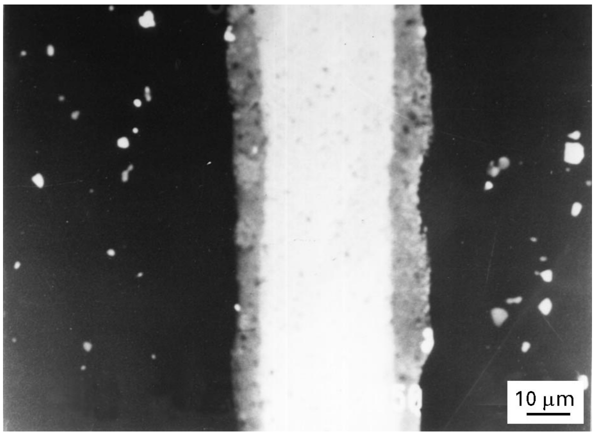

Figure 2 SEM microphotograph for a joint made at 1323 K for 21.6 ks.

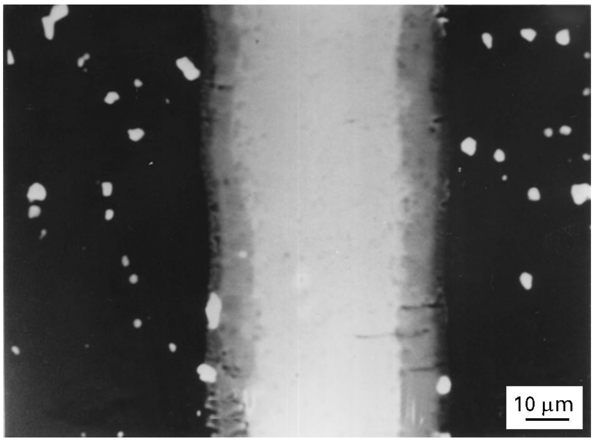

Figure 4 SEM microphotograph for a joint made at 1473 K for 7.2 ks.

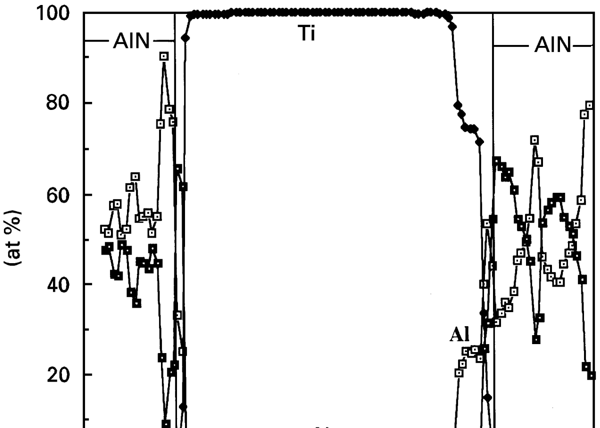

Figure 3 EPMA line analysis for a joint bonded at 1323 K for 21.6 ks.

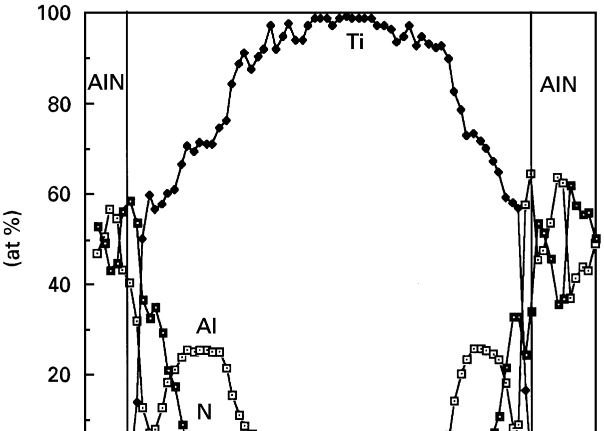

Figure 5 EPMA line analysis for a joint bonded at 1473 K for 7.2 ks.

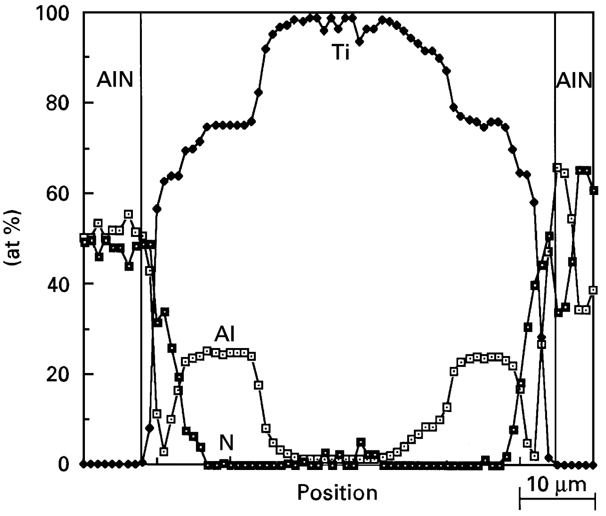

Figure 6 EPMA line analysis for a joint bonded at 1473 K for 14.4 ks.

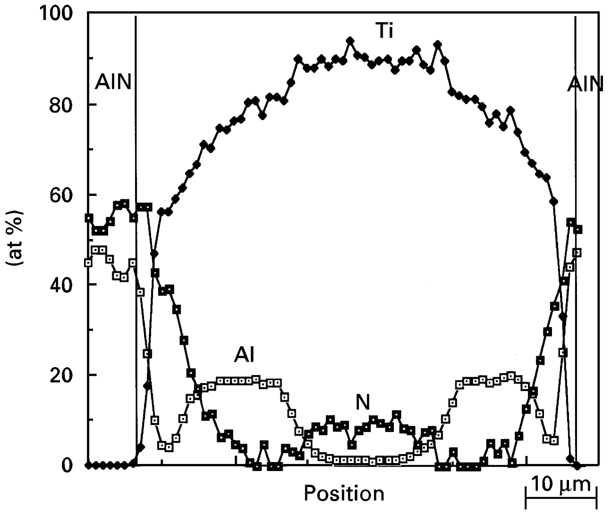

Figure 8 EPMA line analysis for a joint bonded at 1473 K for 21.6 ks.

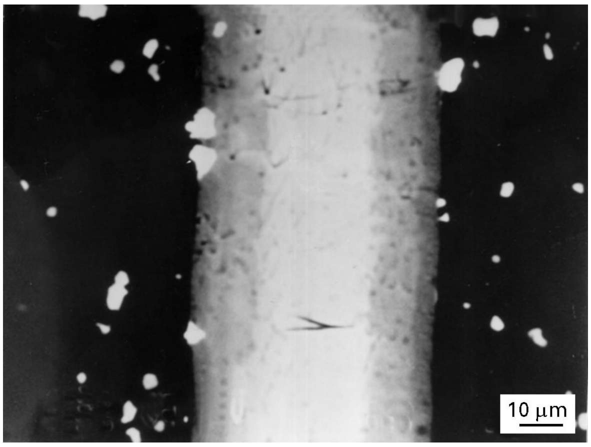

Figure 7 SEM microphotograph for a joint made at 1473 K for 21.6 ks.

contains 40% N as shown in Figs 4 and 6. XRD performed on the fracture surface of a joint bonded at 1473 K for 21.6 ks supports the existence of TiN (f c c; $a = 0.424$ nm). The gradual increase in Al content towards Ti_3Al corresponds to the ternary phase τ_1-Ti_3AlN (cubic, perovskite-type, $a = 0.411$ nm). From the results of SEM observations, elemental line analyses and X-ray diffraction analyses the structure of the joints are estimated. A schematic diagram showing the different reaction layers formed at the AlN–Ti interface when using 50 μm Ti foil is given in Fig. 10 for different bonding conditions. Thus, across the reaction zone the layer sequence AlN/TiN/τ_1-Ti_3AlN/Ti_3Al/Ti occurs at a bonding time of 7.2 ks or more at 1473 K. This sequence represents a complete diffusion path across the system isotherm (Fig. 11) [7], where local equilibrium is established between all adjacent product layers.

Using titanium foil of only 20 μm thickness resulted, at 1473 K after 39.6 ks, in the complete consumption of Ti. As the interface reactions approached equilibrium, a thick τ_2-Ti_2AlN layer is formed between TiN and the τ_1-Ti_3AlN + Ti_3Al central zone (Fig. 12). XRD of the fractured surface of this sample yielded AlN, τ_2-Ti_2AlN, TiN, and τ_1-Ti_3AlN (Fig. 13).

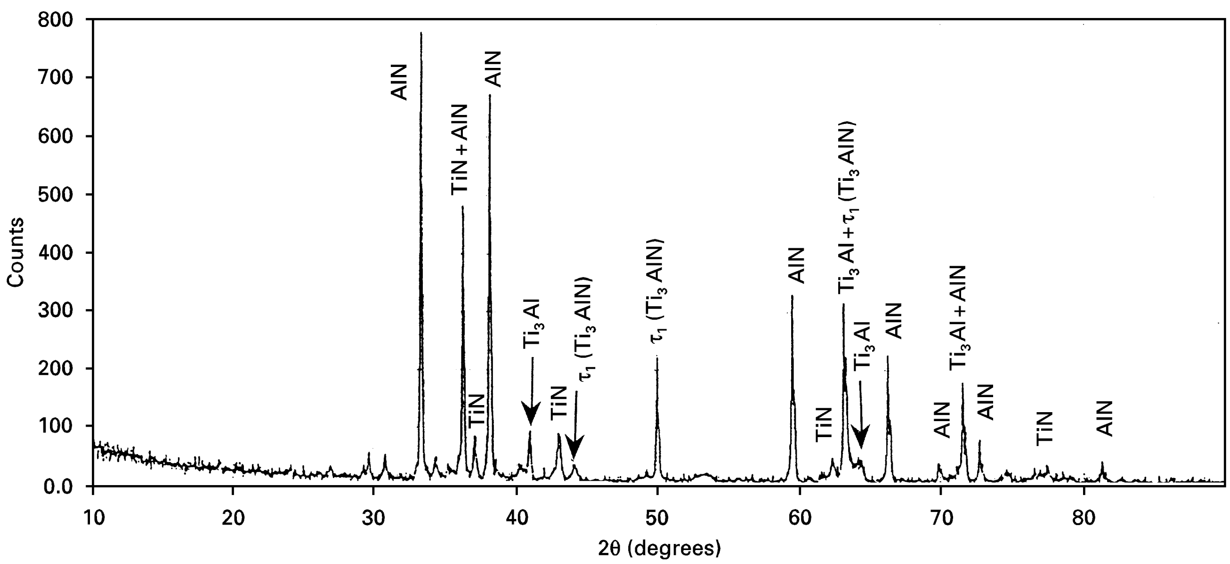

Figure 9 XRD performed on the fracture surface of a joint bonded at 1473 K for 21.6 ks.

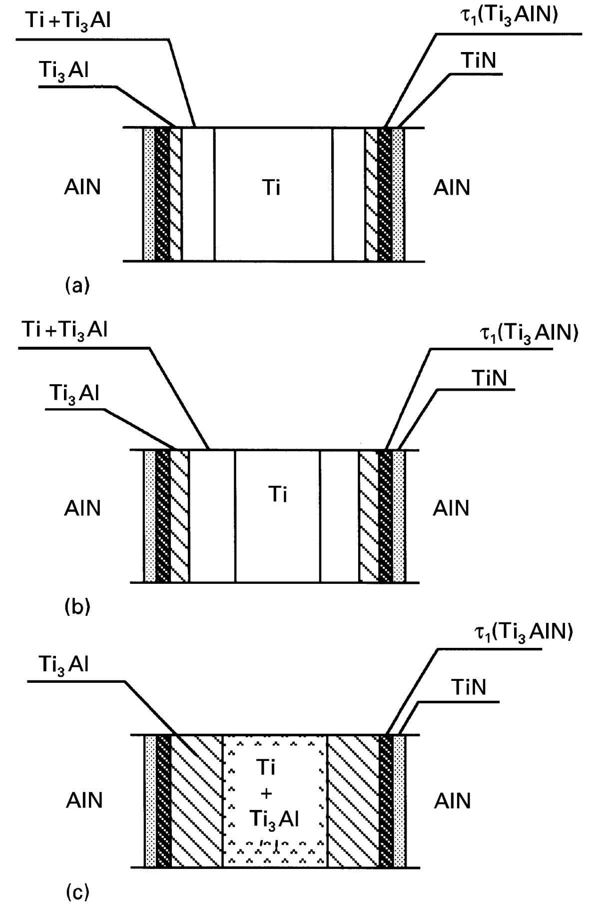

Figure 10 Schematic diagram showing the different reaction layers produced at the AlN/Ti interface when using 50 μm Ti foil: (a) 1473 K and 7.2 ks, (b) 1473 K and 21.6 ks and (c) 1473 K and 39.6 ks.

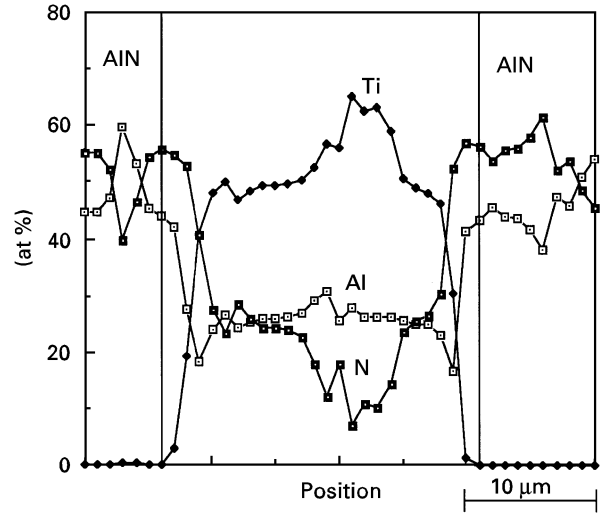

Figure 12 EPMA line analysis for a joint bonded at 1473 K for 39.6 ks.

A schematic diagram of the AlN/Ti interface bonded at 1473 K for different bonding times using 20 μm Ti foil is given in Fig. 14. The fracture feature of the joint indicated later also shows that the reaction phase zones are composed of TiN, τ_1-Ti_3AlN and Ti_3Al.

Since the overall sample composition can be located on the isothermal section of the Ti–Al–N system (Fig. 11) on a line connecting Ti with AlN close to AlN, the coexistence of τ_2-Ti_2AlN and TiN with AlN corresponds to the equilibrium state. Finally, a comparison between the observed values for the lattice

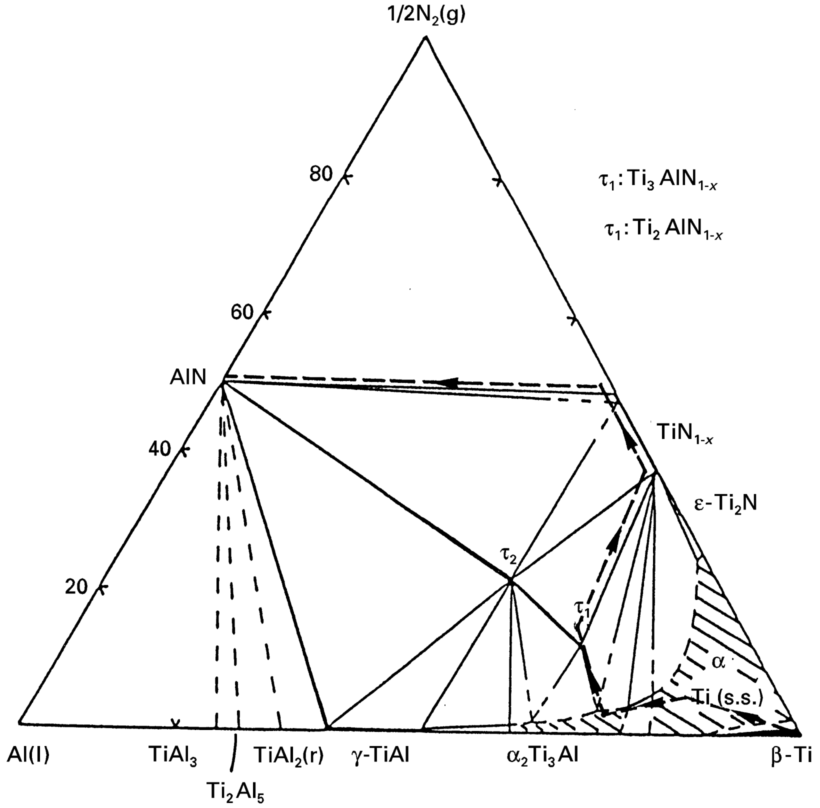

Figure 11 Diffusion path observed across the Ti–Al–N system (isotherm at 1273 K from [7]).

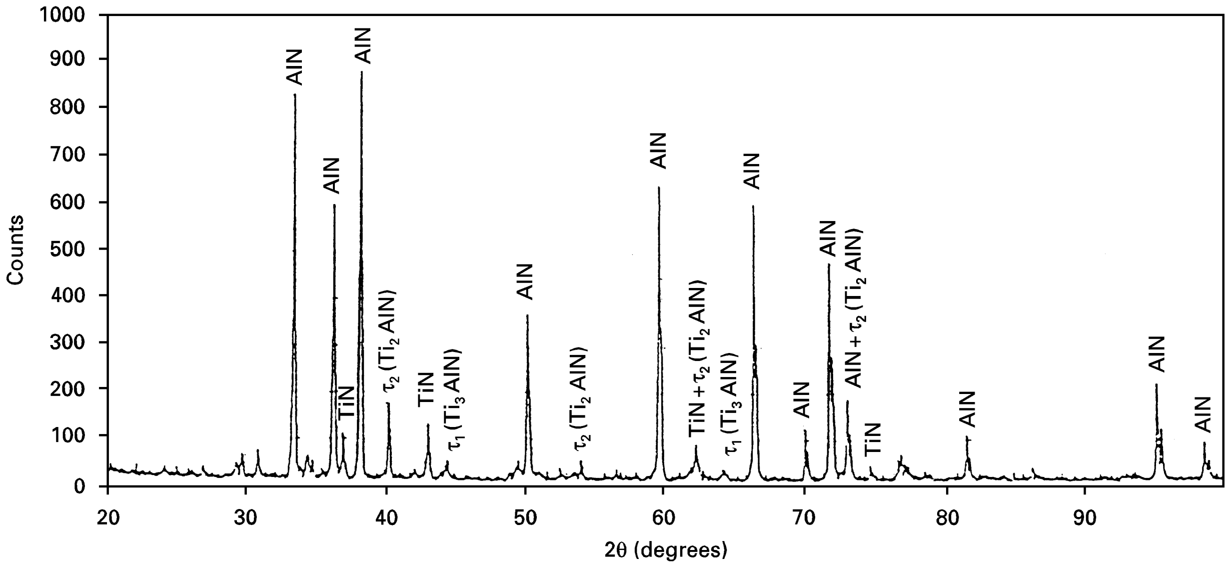

Figure 13 XRD (CuK_{α_1}-radiation) performed on the fracture surface of a joint bonded at 1473 K for 39.6 ks.

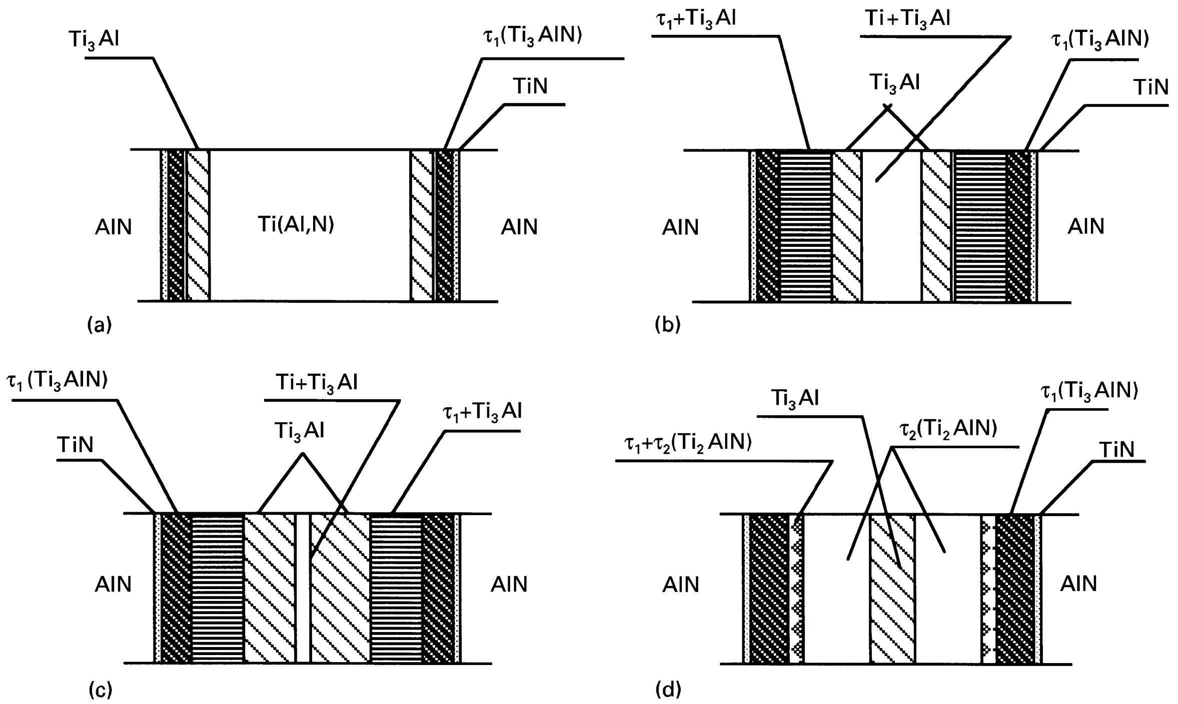

Figure 14 Schematic diagram showing the different reaction layers produced at the AlN/Ti interface when using 20 μm Ti foil: (a) 1473 K and 7.2 ks, (b) 1473 K and 21.6 ks, (c) 1473 K and 28.8 ks and (d) 1473 K and 39.6 ks.

parameters of different compounds at the AlN/Ti interface and the reported values for these compounds is given in Table I.

TABLE I Comparison between the observed and reported values of the lattice parameters *a* and *c*

Phase	Crystal state	*a*, *b*, *c* [6] (nm)	*a*, *b*, *c* (obs.) (nm)
Ti_3Al	Hexagonal	$a = 0.578$ $c = 0.464$	$a = 0.578$ c = 0.464
TiN	Cubic	$a = 0.424$	$a = 0.424$
Ti_3AlN	Cubic	$a = 0.411$	$a = 0.411$
Ti_2AlN	Hexagonal	$a = 0.298$ $c = 1.357$	$a = 0.298$ $a = 1.356$

3.2. Reaction mechanism and growth of the reaction layers

At the beginning of bonding at 1473 K, Ti reacts with AlN forming a Ti solid solution containing elemental Al and N as described by Equation 1.

$$\mathrm{Ti} + \mathrm{AlN} \rightarrow \mathrm{Ti(Al, N)} \qquad (1)$$

Sequentially, at the interface between AlN and Ti, TiN and Ti_3AlN (τ_1) nitrides are formed adjacent to AlN, as described by Equations 2 and 3.

$$\mathrm{Ti} + \mathrm{N} \rightarrow \mathrm{TiN} \qquad (2)$$

$$\mathrm{Ti} + \mathrm{Al} + \mathrm{N} \rightarrow \mathrm{Ti_3AlN}, \qquad (3)$$

Further, Al diffuses through TiN and Ti_3AlN to Ti to form Ti_3Al intermetallic compound adjacent to Ti. Ti nitrides ($TiN + Ti_3AlN$) grow slowly; the nitride thickness changed only a few microns upon increasing the temperature from 1323 to 1473 K at 21.6 ks bonding time, or by changing bonding time from 7.2 to 21.6 ks at constant bonding temperature. On the other hand, a noticeable increase in thickness by increasing bonding time and/or temperature occurs for the Ti_3Al layer which grew from 6.1 μm after 7.2 ks to 12.4 μm after 72 ks at 1473 K. After consuming the 20 μm Ti foil, Ti_2AlN (τ_2) started to form according to equation 4.

$$Ti + Al + N \rightarrow Ti_2AlN \tag{4}$$

The growth of compounds formed at the interface of dissimilar materials is often expressed by Equations 5 and 6:

$$x^2 = kt \tag{5}$$

$$k = k_0 \exp(-Q/RT) \tag{6}$$

where x and t are the thickness of the compound and the bonding time, respectively, while, k, k_0 and Q are rate constants and activation energy for growth of the compound formed [8]. R is the gas constant and T is absolute temperature. The growth of Ti_3Al layer in AlN/Ti couples at a bonding time of 21.6 ks are plotted against $1/T$ in Fig. 15. The activation energy for growth is found to be 146 ($\pm$ 30) kJ mol^{-1}.

The activation energy for the Ti_3Al growth (146 kJ mol^{-1}) is comparable to the activation energy for Ti diffusion (169 kJ mol^{-1}) and that of Al diffusion (115 kJ mol^{-1}) in titanium. However, the k_0 factor (3.8×10^{-10} m^2 s^{-1}) for the Ti_3Al growth in the AlN/Ti joint is lower than that of Ti in Ti (6.6×10^{-9} m^2 s^{-1}), or that of Al in Ti (9.75×10^{-9} m^2 s^{-1}) [9]. This could be attributed to the presence of a diffusion barrier consisting of Ti nitrides (TiN and Ti_3AlN) at the interface between AlN and Ti. This nitride barrier retards Al diffusion into the Ti central layer of the Ti/AlN joint.

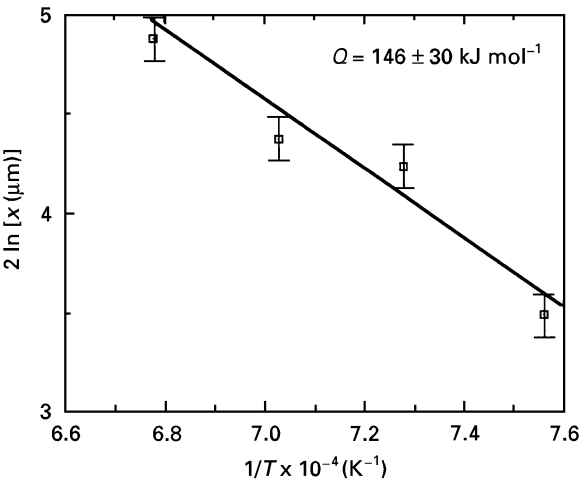

Figure 15 The (2 ln$x$) plotted versus ($1/T$) (joining time 21.6 ks).

3.3. Bond strength

The bondability between AlN and Ti was evaluated by measuring fracture shear strength of the AlN/Ti (20 μm)/AlN joints. Fig. 16 shows a plot of the fractured shear stress against bonding time for the joints made at 1473 K. The strength of the joints increases with increasing formation of reaction products until a maximum bond strength is obtained after 28.8 ks. All joints show the same type of fracture mode as shown in Fig. 17. The fracture originated and mainly propagated along the AlN/TiN interface and passed through the joining layer to the other side of TiN/AlN interface. The main part of the fracture surface was on the TiN side of the AlN/TiN interface. The fractography also shows that the reaction phases are composed of TiN, τ_1-Ti_3AlN and Ti_3Al. The consumption of the soft Ti metal foil and the formation of a brittle τ_2-Ti_2AlN cause the bonding strength to decrease with further heat treatment. When bonding conditions of 1473 K for 72 ks were applied, AlN ceramics decomposed severely and many void and cracks appeared in the joint. As a result, the bond strength was adversely affected.

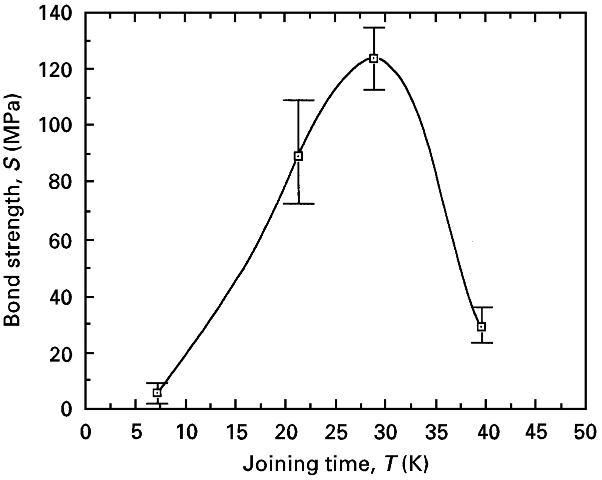

Figure 16 Fracture shear stress dependence on bonding time at 1473 K.

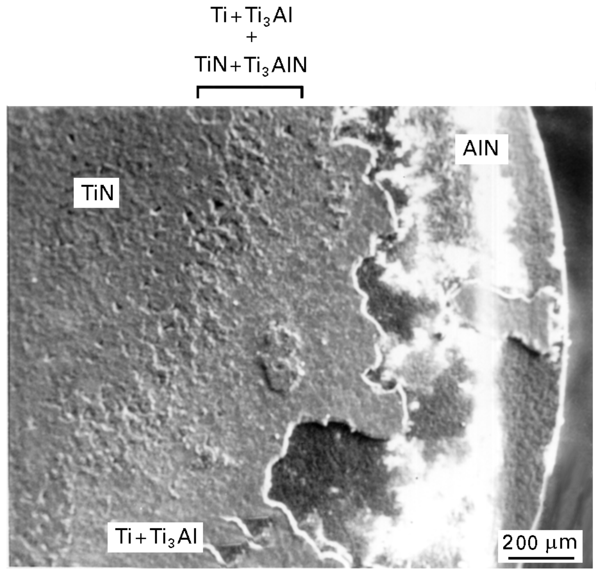

Figure 17 Results of spot analyses on the fracture surface of an AlN/Ti specimen bonded at 1473 K for 39.6 ks.

4. Conclusions

Titanium of 50 μm thickness reacted with AlN and formed TiN and Ti_3AlN adjacent to AlN, as well as Ti_3Al adjacent to Ti at a bonding time of 7.2 ks at 1473 K. The thickness of the nitrides has slowly increased with increasing bonding time. Growth of Ti_3Al follows Fick's law with an activation energy of $146\,kJ\,mol^{-1}$. The complete diffusion path established between AlN and Ti after a bonding time of 7.2 ks at 1473 K is AlN/TiN/$Ti_3AlN(\tau_1)$/Ti_3Al/Ti. This path can be explained by the Ti–Al–N ternary phase diagram. In the joint of AlN using 20 μm Ti foil, Ti was completely consumed after a bonding time of 39.6 ks. Ti_2AlN (τ_2) appeared since the interfacial reaction approaches equilibrium.

A maximum bond strength of AlN/Ti joints was established after a bonding time of 28.8 ks at 1473 K, just before the appearance of Ti_2AlN (τ_2) ternary compound.

References

1. P. MARTINEAU, R. PAILLER, M. LAHAYE and R. NASLAIN, *J. Mater. Sci.* **19** (1984) 2749.
2. J. C. FENG, M. NAKA and J. C. SCHUSTER, *J. Japan Inst. Metals* **59** (1995) 978.
3. W. J. WHATLEY and F. E. WAWNER, *J. Mater. Sci. Let.* **4** (1985) 173.
4. J. C. BARBOUR, A. E. T. KUIPER, M. F. C. WILLSEMEN and A. H. READER, *Appl. Phys. Lett.* **51** (1987) 953.
5. T. FUNABASHI and K. ISOMURA, *Ceram. Jpn.* **26** (1991) 749
6. P. VILLARS and L. D. CALVERT "Pearsons Handbook of Crystallographic Data for Intermetallic Phases", 2nd Edn (American Society for Materials, Materials Park, Ohio, USA, 1991).
7. M. PIETZKA, Thesis, University of Vienna, Vienna, Austria (1992).
8. Y. A. CHANG, R. KIESCHKE, J. DEKOCK and X. ZANG in "Control of Interfaces in Metal Ceramics Composites", edited by R. Y. Lin and S. C. Fishman (The Material Society, Warrendale, Pa., USA, 1993) pp. 3–25.
9. E. A. BRANDERS and G. B. BROOK "Smithells Metals Reference Book" (Butterworth, Heinemann, Oxford, UK 1992) pp. 13–15.

Received 30 August 1995
and accepted 23 October 1996