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Interfacial Reaction between Titanium and Silicon Nitride during Solid State Diffusion Bonding[†]

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Abstract

The present work aims to bond silicon nitride using Ti foil by solid state diffusion bonding, to clarify the formation behavior of the interfacial structure and to control the structure. For each bonding experiment, a 50 μm thick Ti foil was inserted between two Si_3N_4 *pellets. The bonding temperature and time were selected from 1473 to 1673 K and from 0.2 to 32.4 ks, respectively. The interfacial structure and elemental concentration profile at the joint interfaces were estimated with SEM-EPMA and XRD. The phase sequence of the joint interfaces bonded at 1573 K is observed as* α*-Ti (N) /* Ti_5Si_3 */* $Ti_5Si_3+\alpha$*-Ti (N) /* Ti_5Si_3 */* Si_3N_4*. The strength of the joints bonded at 1573 K for 3.6 ks is as low as 3.5 MPa. Their fracture occurs always at the* Ti_5Si_3 */* Si_3N_4 *interface. In order to suppress the growth of* Ti_5Si_3*, nitrogen pre-solved Ti foil was bonded with* Si_3N_4*. The phase in contact with* Si_3N_4 *becomes* Ti_5Si_3*+TiN. The thickness of the* Ti_5Si_3 *layer is successfully suppressed.*

KEY WORDS: (Interfacial Structure) (Reaction) (Si_3N_4) (Titanium) (Solid State Diffusion Bonding)

1. Introduction

Silicon nitride (Si_3N_4) is expected to be utilized in many fields of industry as one of the key materials for high temperature structures. In most of the applications, Si_3N_4 is required to bond with Si_3N_4 together and/or with metals. For Si_3N_4 bonding, titanium is important due to its ability to enhance the adsorption and wetting between Si_3N_4 and metals. It is commonly used as an active additive of filler metals or brazes for ceramics bonding. However, an inappropriate bonding of Si_3N_4 with metals containing titanium leads to the formation of brittle phases and reduces its strength. Therefore, to control the interfacial reaction and structure in an appropriate state, in which the formation of such brittle phases are suppressed, should be one of the most important objectives for successful bonding. Some previous papers related to Ti / Si_3N_4 system have reported the interfacial diffusion and reaction in detail [1-4]. These papers also have reported that the strength of Ti / Si_3N_4 joints is very poor. Despite the importance of the system, no methods to improve the strength of Ti / Si_3N_4 joints have been presented.

The present work seeks to control the interfacial reaction during solid state diffusion bonding of Si_3N_4 using Ti foils. At first, the interfacial structure and its growth behavior are analyzed in detail. In the next step, the controlling factor of the reaction is extracted. Then finally, an example to control the reaction is presented.

2. Experimental Procedure

Si_3N_4 specimens, containing a few mass percent of alumina as the sintering aid, were shaped to diameter and length of 6.0 and 4.0 mm, respectively. Then, the surface to be bonded was polished with 3 μm diamond paste. On the other hand, 99.5 % nominally pure titanium foils with three different thickness, 20.0 μm, 50.0 μm and 150 μm, were used as the insert metal. Both of the titanium surfaces were polished with 0.3 μm alumina abrasive just before the bonding treatment in order to remove the surface scales. Two Si_3N_4 tips and a titanium foil were used for each bonding experiment. They were first washed ultrasonically with acetone. Then, the titanium foil was inserted between two Si_3N_4 tips and they were set into a induction-heating vacuum furnace. The bonding temperature and time were set at certain values between 1473 K and 1673 K and between 0.2 ks and 32.4 ks, respectively. The vacuum inside the furnace was kept

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below 1.3 × 10^{-3} Pa. Uniaxial pressure of 140 MPa was applied to the specimen, perpendicular to the bonding interface, during the bonding treatment. The interfacial structure of the obtained joints was estimated by scanning electron microscopy (SEM), wavelength-dispersive electron probe microanalysis (EPMA) and X-ray diffractometry (XRD). The joint strength was estimated by shear fracture testing at room temperature.

3. Results and Discussion

3.1 Interfacial Structure of the Joints

Interfacial structure of the Si_3N_4 / Ti joints bonded at 1473, 1573 and 1673 K were analyzed by means of SEM-EPMA and XRD. **Fig. 1** shows the interfacial microstructure of a Si_3N_4 / Ti joint bonded at 1573 K for 3.6 ks using a 50 μm thick titanium foil. **Fig. 1 (a)** is an SEM micrograph of the interface. The black region in the right side and the white region in the left side of Fig. 1 (a) correspond to Si_3N_4 and Ti, respectively. Two types of reaction products are observed in the micrograph. One is formed as a 11.5 μm thick layer between Si_3N_4 and Ti, which "L" is marked in the figure. The other is formed as grains inside the Ti foil, which "G" is marked. The layered one consists of three regions, which is marked as "L_1", "L_2" and "L_3", respectively. The regions "L_1" and "L_3" have homogeneous contrasts. This means that these regions consist of one phase. On the other hand, the region "L_2" presents two-contrast mixture, which indicates that this region consists of two phases. The granular phase "G" is observed at the grain boundaries of the titanium matrix. **Fig. 1 (b)** shows the elemental distribution profile through X to X' in Fig. 1 (a). Three points are clearly noticed from this figure. First is that the "G", "L_1" and "L_3" phases consist of only titanium and silicon. Nitrogen content in these phases is very low. The composition of these phases presents the same ratio of Ti–35 at%Si. This fact indicates that these phases are the same. Second is that the composition of the second phase in "L_2" is Ti–38 at%N. Silicon content in this phase is very low. Third is that nitrogen in titanium matrix is homogeneously distributed with a composition of Ti-21 at%N. Silicon content in the titanium matrix is very low. **Fig. 1 (c)** shows a series of X-ray diffraction patterns which correspond to the positions (1), (2) and (3) in Fig. 1 (a). The specimen were cut at one side of the Si_3N_4 vicinity of the interface and polished out about 1 μm for each XRD measurement. Each reaction product and its arrangement were identified by the position of each X-ray

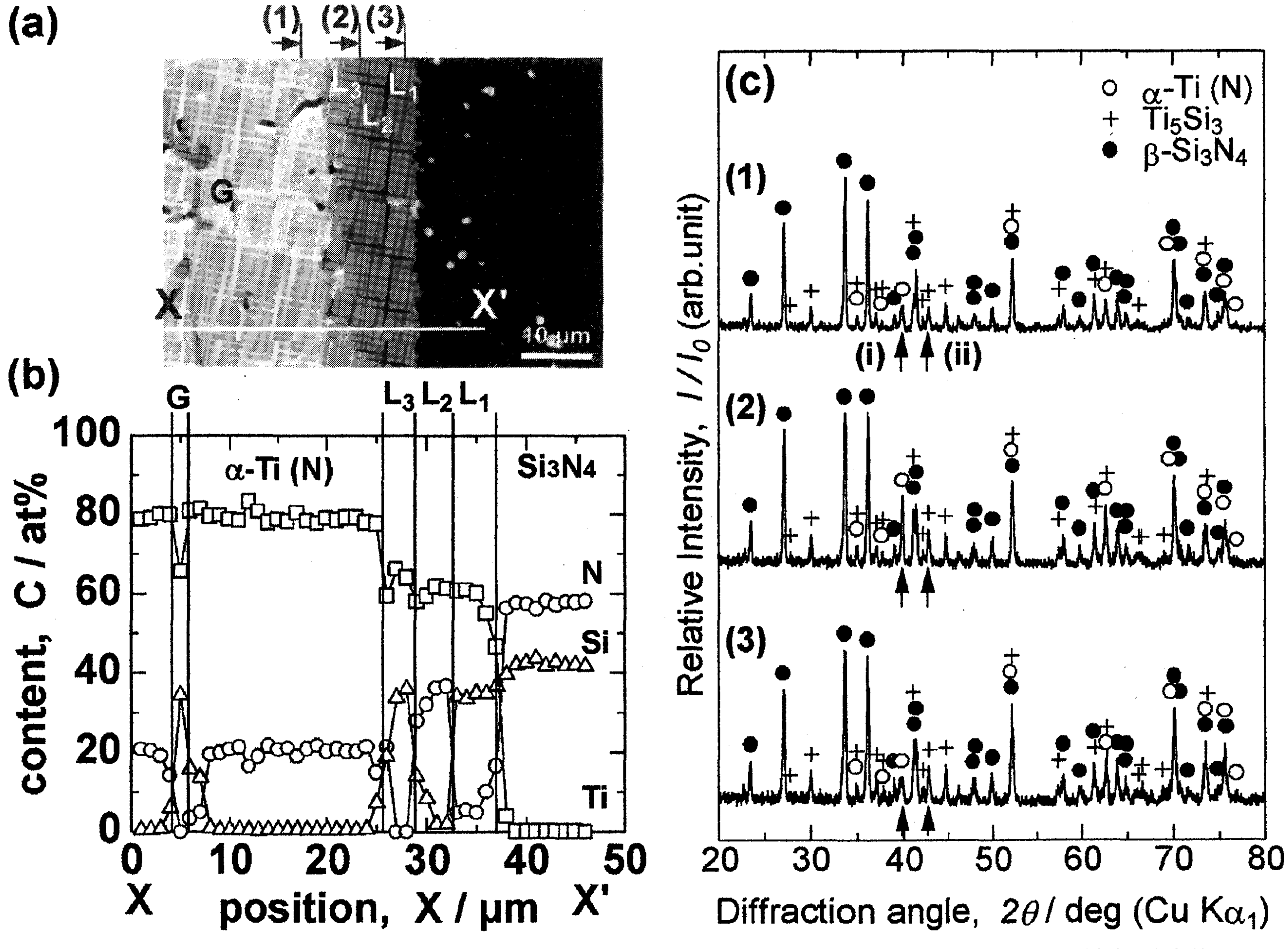

Fig. 1 Interfacial structure of a Si_3N_4 / Ti joint bonded at 1573 K for 3.6 ks using a 50 μm thick Ti foil. (a) SEM micrograph, (b) compositional distribution profile along X to X' depicted in the micrograph, (c) X-ray diffraction patterns from the positions (1), (2) and (3) depicted in the micrograph.

diffraction peak and the alteration of its relative intensity. All three patterns in Fig. 1 (c) are identified as superimposition of Si_3N_4 [5], Ti_5Si_3 [6] and α-Ti (N) [7]. The appearance of all existing phases in every step of XRD measurements is due to the difficulty of polishing flat and parallel to the interface. However, the alteration of the relative intensity appears clearly at the peaks at 39.88° and 42.82°, which are marked with arrows (i) and (ii), respectively. The peak (i) corresponds only to α-Ti (N). Comparing with pattern (1), this peak is intensified in pattern (2) and then it is shrunk in pattern (3). The peak (ii), on the other hand, corresponds only to Ti_5Si_3. This peak is intensified in pattern (2) and keeps its relative intensity in pattern (3). This result agrees well with the EPMA analysis depicted in Fig. 1 (b). These results indicate that "L_1", "L_3" and "G" are all Ti_5Si_3 single phase and that "L_2" is a mixture of Ti_5Si_3 and α-Ti (N). Therefore, the observed phase sequence can be described as Si_3N_4 / Ti_5Si_3 / Ti_5Si_3 + α-Ti (N) / Ti_5Si_3 / α-Ti (N) + Ti_5Si_3.

In the same way, the interfacial structure of the joints bonded at 1473 K and 1673 K were also analyzed. **Fig. 2** shows a SEM micrograph of a joint interface bonded at 1473 K for 3.6 ks using a 50 μm thick Ti foil with the analysis result. The phase sequence at 1473 K is described as Si_3N_4 / Ti_5Si_3 + α-Ti (N) / α-Ti (N) + Ti_5Si_3. The typical difference on the microstructures between joints bonded at 1473 K and those bonded at 1573 K is that the single phase regions of Ti_5Si_3,"L_1" and "L_3" in Fig. 1 (a), are not observed in the joints bonded at 1473 K. **Fig. 3** shows a SEM micrograph of a joint interface bonded at 1673 K for 3.6 ks using a 150 μm thick Ti foil with the analysis result. The phase sequence at 1673 K is described as α-Ti (N) + Ti_5Si_3 / Ti_5Si_3 / Ti_5Si_3 + TiN / Ti_5Si_3 / Si_3N_4. The typical difference in the microstructures between joints bonded at 1573 K and those bonded at 1673 K is that TiN appears instead of α-Ti (N) in the reaction layer of the joints bonded at 1673 K.

At first, it has to be taken into account that the analyses of the interfacial structures are carried out at room temperature. There can exist some phase transformation during cooling. In those cases, the observed microstructures may not correspond to the actual structure at the elevated temperature. There are observed two two-phase regions at the interfaces. One is the Ti_5Si_3 + α-Ti (N) or TiN mixture at the "L_2" region. The other is the α-Ti (N) + Ti_5Si_3 at the titanium matrix. For the former region, it is hard to consider that α-Ti (N) or TiN phases isolated inside Ti_5Si_3 exist stably at the elevated temperature as observed, from the thermodynamical (chemical potential gradient) point of view. They are considered to have precipitated during cooling, due to the degradation of nitrogen solubility in Ti_5Si_3. The nitrogen solubility in Ti_5Si_3 is reported as 11 at% for 1373 K [4] and 3 at% for 1273 K [8]. This means that a great solubility degradation of nitrogen in Ti_5Si_3 occurs during cooling. As a result, α-Ti (N) or TiN precipitates in the middle of the layered reaction product as the nitrogen-trapped region. Both sides of this region are considered as precipitation free zones of α-Ti (N) or TiN, in which nitrogen can escape forward to the titanium matrix or backward to the Si_3N_4. On the other hand, the latter, Ti_5Si_3 phase formed at grain boundaries of α-Ti (N) matrix is considered to be stable also at elevated temperatures. This phase is also considered as a precipitate due to the degradation of silicon solubility into titanium matrix. In this case, however, the solubility degradation is not driven by cooling. It is driven by the phase transformation of the titanium matrix from β to α, due to the composition increase of nitrogen. The silicon solubility in pure β-Ti is reported as 5 at% at 1373 K [9]. However, only 3.4 at% of nitrogen dissolution induces the phase transformation of the matrix to α-Ti [8]. In α-Ti, the silicon solubility is very low [4]. This will result in the precipitation of Ti_5Si_3 (N) during the bonding process. Therefore, the actual phase sequence at temperatures between 1473 K and 1673 K is described as α-Ti (N) + Ti_5Si_3 (N) / Ti_5Si_3 (N) / Si_3N_4. The layered

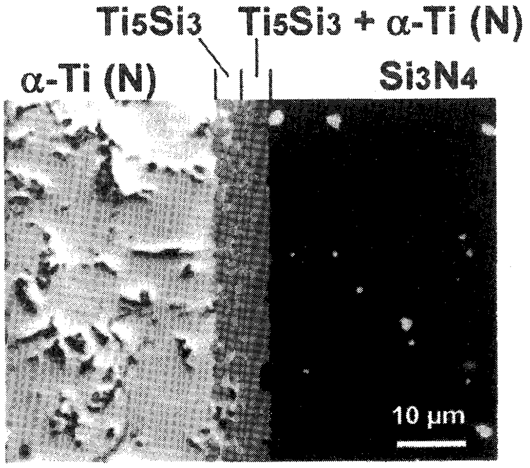

Fig. 2 Interfacial structure of a Si_3N_4 / Ti joint bonded at 1473 K for 3.6 ks using a 50 μm thick Ti foil.

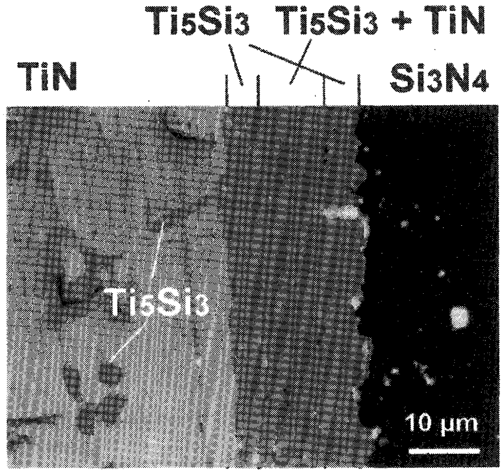

Fig. 3 Interfacial structure of a Si_3N_4 / Ti joint bonded at 1673 K for 3.6 ks using a 150 μm thick Ti foil.

reaction product is a single phase of Ti_5Si_3 (N) at these temperatures.

Although the actual phase sequence is α-Ti (N) + Ti_5Si_3 (N) / Ti_5Si_3 (N) / Si_3N_4, the diffusion path cannot be directly drawn on the available Ti-Si-N ternary phase diagrams [4, 8]. In those diagrams, tie lines from Si_3N_4 are not connected to Ti_5Si_3 (N) but to $TiSi_2$ and TiN. This is due to the fact that the temperatures of those diagrams are lower than those employed in the current study. As Ti_5Si_3 can dissolve higher amount of nitrogen at higher temperature, Ti_5Si_3 (N) will be stabilized than $TiSi_2$ at those higher temperatures. **Fig. 4** proposes a Ti-Si-N ternary chemical potential diagram at 1573 K. The diagram is drawn according to the thermodynamic data on the literature [8] with a slight modification of the Ti_5Si_3 region. In this diagram, Ti_5Si_3 can coexist with Si_3N_4. The diffusion path observed in the present work is depicted on the diagram with a dotted line.

Some previous papers have reported the formation of TiN adjacent to Si_3N_4. However, interfacial structures presented in those papers do not suggest the existence of TiN. They have proved the existence of TiN by the evidence of gold-colored phases on the fractured surfaces of the joints. The gold-colored phase is also observed in the present work. However, it is not formed at the interface but on the titanium metal corresponding to unbonded areas. This result indicates that this type of TiN is formed at areas where intimate contact of Si_3N_4 and titanium is not achieved. It is considered that this type of TiN is formed by the reaction between titanium and nitrogen gas which is generated by spontaneous decomposition of Si_3N_4. According to the thermodynamic data [8], the equilibrium nitrogen partial pressure of Si_3N_4 exceeds the total atmospheric pressure of 1×10^{-3} Pa at temperatures higher than 1225 K. As the temperatures employed in the current study are higher than this temperature, Si_3N_4 decomposes spontaneously during bonding.

3.2 Strength and Fracture Path of the Joints

The strength of the joints is very low. 3.5 MPa of shear stress is enough to fracture the joint bonded at 1573 K for 3.6 ks. **Fig. 5** shows a pair of XRD patterns which are taken from the Si_3N_4 side and from the Ti side of the fractured surface of a joint bonded at 1673 K for 3.6 ks. The XRD pattern taken from the Si_3N_4 side corresponds to Si_3N_4. On the other hand, the pattern taken from the Ti side corresponds to Ti_5Si_3 and Si_3N_4. The detection of Si_3N_4 in the pattern from the metal side is due to the exposure of the counterpart of Si_3N_4 to the surface by chipping of the Ti foil. Thus, the fracture is determined to occur at the Si_3N_4 / Ti_5Si_3 interface. In order to obtain higher strength with this system, it is required to control the interfacial reaction and its resultant structure to prevent the formation of a Ti_5Si_3 single-phase layer adjacent to Si_3N_4.

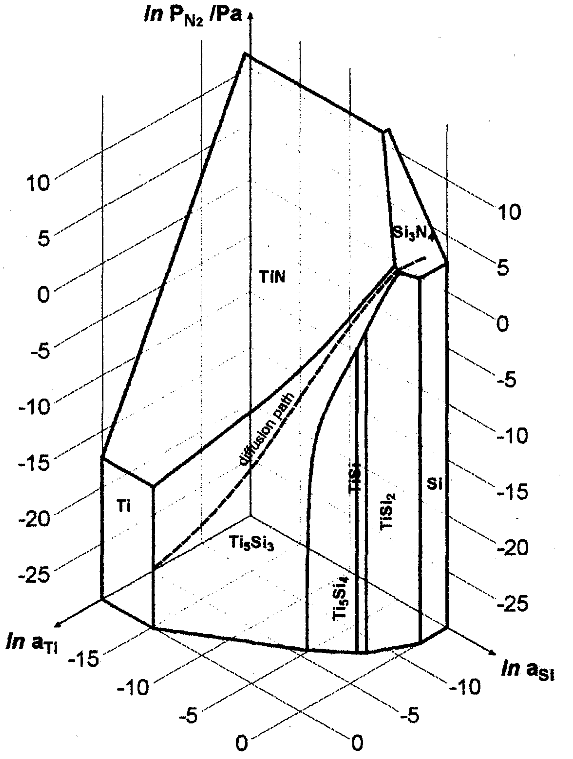

Fig. 4 Chemical potential diagram of Ti-Si-N ternary system at 1573 K. The dotted line depicts the diffusion path observed at the joint interfaces bonded at 1573 K.

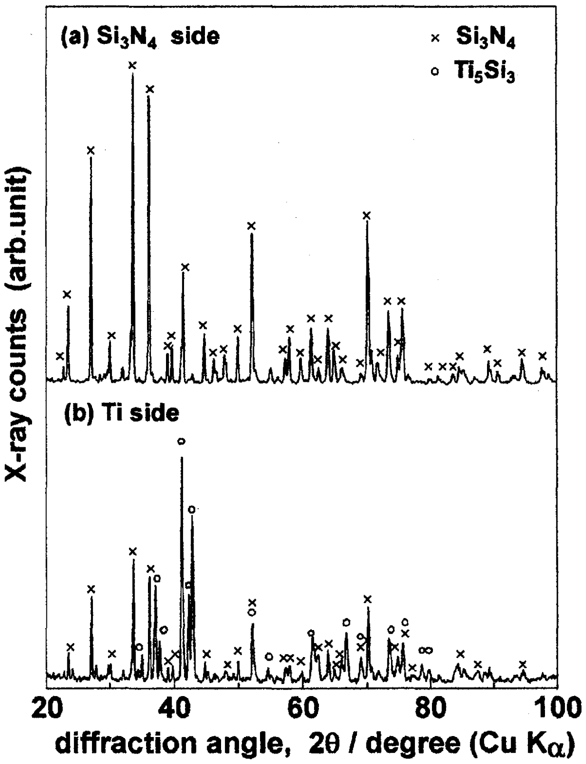

Fig. 5 A pair of XRD patterns taken from fractured surfaces of a Ti / Si_3N_4 joint bonded at 1673 K for 3.6 ks. (a) Si_3N_4 side, (b) Ti side.

Table 1 A list of thickness of the Ti_5Si_3 layer formed at Ti / Si_3N_4 interfaces during bonding at 1573 K for 3.6 ks as a function of initial thickness of Ti foils.

Initial thickness of Ti foils, th_{Ti} / μm	Thickness of the Ti_5Si_3 layer, th_{RL} / μm
20	7.0
50	11.5
150	14.0

3.3 Growth Kinetics and Control Strategy of the Ti_5Si_3(N) Reaction Layer

Table 1 shows the dependence of the thickness of the Ti_5Si_3 (N) reaction layer, th_{RL}, to the initial Ti foil thickness, th_{Ti}. All the joints listed in **Table 1** are bonded in the same condition, at 1573 K for 3.6 ks. The difference among the joints is only the initial Ti foil thickness. It appears clearly that the Ti_5Si_3 layer grows thicker when the thicker initial Ti foil is used, even if the same bonding temperature and time are applied. **Fig. 6** shows a relation between the thickness of the Ti_5Si_3 (N) reaction layer and the nitrogen content in the remaining Ti phase, C_N. One important point appears from this figure. The Ti_5Si_3 (N) layer stops its growth when the nitrogen content in Ti reaches to a certain value, C_N^*, which is determined by the bonding temperature. For example, the value of C_N^* is about 12 and 28 at% for 1573 and 1673 K, respectively. Thus, it is naturally concluded that the growth of Ti_5Si_3 layer is suppressed by nitrogen dissolved in the Ti foil.

According to this fact, the phenomenon observed in Table 1 is explained as follows. The nitrogen content in the Ti phase increases by dissolution of nitrogen decomposed from Si_3N_4. On the other hand, the other element of Si_3N_4, silicon, reacts with Ti to form Ti_5Si_3. As the mass is conserved, the amount of nitrogen atoms dissolved in Ti-phase balances with th_{RL}. As the thinner Ti foil requires smaller amounts of nitrogen to achieve C_N^*, th_{RL} is suppressed to thinner values.

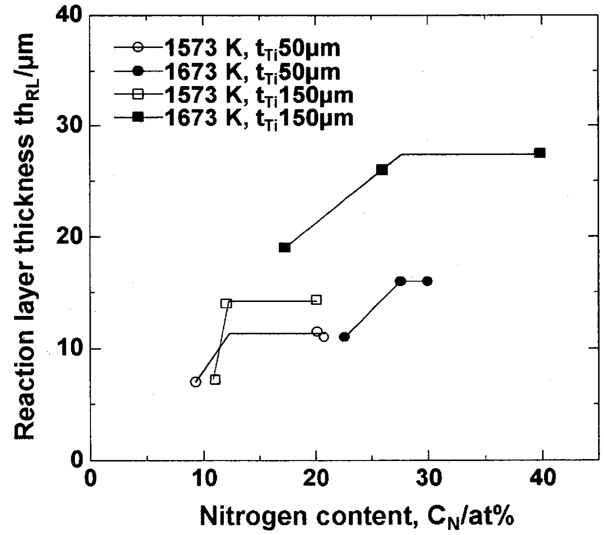

Fig. 6 A plot of the thickness of the Ti_5Si_3 layer, th_{RL}, as a function of the nitrogen content in the remaining Ti phase, C_N.

In order to prove the growth behavior described above, diffusion bonding of Si_3N_4 using nitrogen pre-solved Ti foil has been carried out. **Table 2** shows the effect of the nitrogen pre-solution to the growth of Ti_5Si_3 layer. The bonding temperature, time and initial Ti foil thickness was set to 1573 K, 3.6 ks and 50 μm, respectively. At this temperature, C_N^* is already determined as 12 at%. Two types of nitrogen pre-solved Ti foils which contain 14 and 24 at% nitrogen were prepared. The former is prepared as Ti (N) with slightly higher nitrogen content than C_N^* and the latter as that with much higher nitrogen content than C_N^*. It is obvious that the thickness of the Ti_5Si_3 layer is suppressed to thinner values with higher nitrogen pre-solved Ti foils. This fact demonstrates that the sufficient nitrogen dissolved in Ti suppresses the growth of Ti_5Si_3 layer effectively. This result agrees well with the above-mentioned growth behavior of the Ti_5Si_3 layer. **Fig. 7** shows an interfacial structure of a Ti - 24 at% N / Si_3N_4 joint bonded at 1573 K for 3.6 ks. Comparing the micrograph shown in **Fig. 7 (a)** with that in Fig. 1 (a), the

Table 2 A list of thickness of the Ti_5Si_3 layer formed at Ti (N) / Si_3N_4 interfaces during bonding at 1573 K for 3.6 ks as a function of initial nitrogen content in nitrogen pre-solved Ti foils. The initial thickness of Ti foils was set to 50 μm.

Initial nitrogen content in nitrogen pre-solved Ti foils, C_N^0 / at%N	Thickness of the Ti_5Si_3 layer, th_{RL} / μm
0 (pure-Ti)	11.5
14	7.4
24	4.0

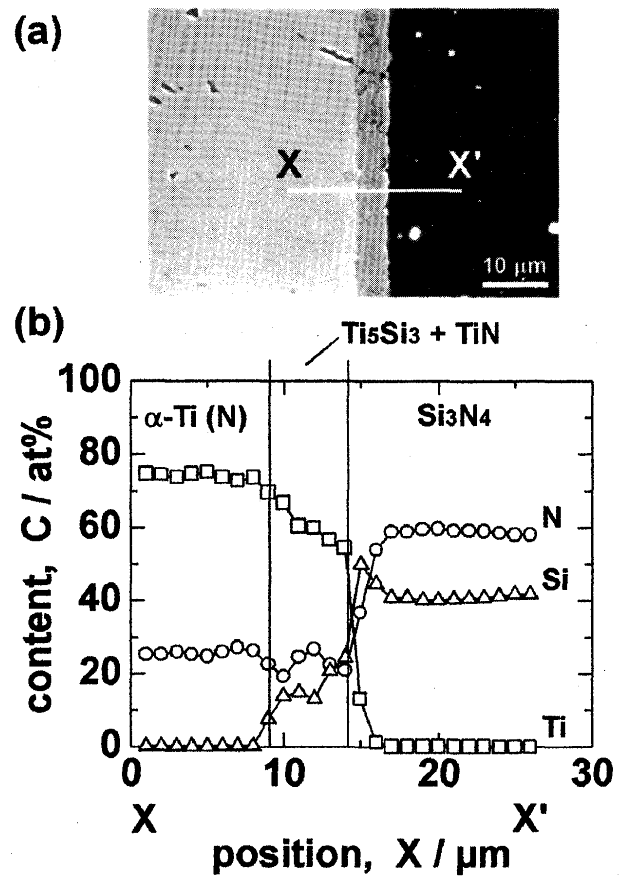

Fig. 7 Interfacial microstructure (a) and elemental distribution profile along X – X' (b) of a Ti – 24 at% N / Si_3N_4 joint bonded at 1573 K for 3.6 ks.

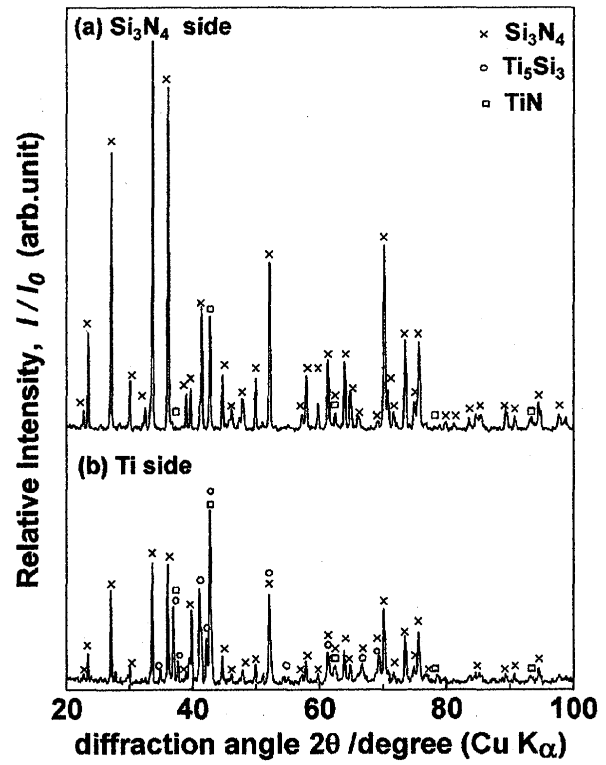

Fig. 8 A pair of XRD patterns taken from fractured surfaces of a Ti – 24 at% N / Si_3N_4 joint bonded at 1573 K for 3.6 ks. (a) Si_3N_4 side, (b) Ti side.

growth suppression of the Ti_5Si_3 layer is clearly recognized. Moreover, the formation of granular Ti_5Si_3 at the Ti grain boundaries is completely prevented when nitrogen pre-solved Ti foil is used. The phenomenon is observed even with the use of Ti-14at%N. This fact suggests that the diffusion of silicon into Ti is prevented even with the use of Ti-14at%N. **Fig. 7 (b)** shows an elemental distribution profile, which corresponds to X–X' in Fig. 7 (a). The structure of the Ti_5Si_3 layer is completely different from that shown in Fig. 1. Especially, the most important is that the single-phase region of Ti_5Si_3 is not formed adjacent to Si_3N_4. As a result, the joint of 50 µm thick Ti – 24 at% N / Si_3N_4 joints bonded at 1573 K for 3.6 ks endures 10.6 MPa of shear stress. Although the strength is still not enough for practical use, it is improved to three times higher than the joints using pure Ti. **Fig. 8** shows a pair of XRD patterns which are taken from the Si_3N_4 side and from the Ti (N) side of the fractured surface of a Ti – 24 at% N / Si_3N_4 joint. The XRD pattern taken from the Si_3N_4 side corresponds to Si_3N_4 and TiN. On the other hand, the XRD pattern taken from the Ti side corresponds to Ti_5Si_3, TiN and Si_3N_4. Thus, the fracture is determined to occur at Si_3N_4 / Ti_5Si_3 and TiN / Ti_5Si_3 interfaces. This indicates that Si_3N_4 / TiN interfaces present higher strengths than Si_3N_4 / Ti_5Si_3 and TiN / Ti_5Si_3 interfaces. Therefore, to obtain higher strength with the Ti / Si_3N_4 system, complete prevention of Ti_5Si_3 formation is required.

4. Summary

Si_3N_4 is bonded with titanium foil by solid state diffusion bonding. The interfaces of the joints were analyzed by means of SEM-EPMA and XRD. The strength of the joints was estimated by shear fraction tests. The following points are evident.

1. The interfacial phase sequence of pure-Ti / Si_3N_4 joint at each employed temperature is observed as;
   1473 K: α-Ti(N)/Ti_5Si_3/Ti_5Si_3+α-Ti(N)/Si_3N_4,
   1573 K: α-Ti(N)/Ti_5Si_3/Ti_5Si_3+α-Ti(N)/Ti_5Si_3/ Si_3N_4,
   1673 K: TiN/Ti_5Si_3/TiN+Ti_5Si_3/Ti_5Si_3/Si_3N_4.
2. The joint strength of pure-Ti / Si_3N_4 joint is as low as 3.5 MPa. The fracture occurs through the Si_3N_4 / Ti_5Si_3 interface.
3. The Ti_5Si_3 layer grows thicker when the thicker initial Ti foil is used, even if the same bonding temperature and time are applied. The layer continues growing until the nitrogen content in Ti foil reaches to a certain value, which is determined by the bonding temperature.
4. The use of nitrogen pre-solved Ti foil effectively suppresses the growth of the Ti_5Si_3 layer. The phase adjacent to Si_3N_4 becomes not a Ti_5Si_3 single phase but a Ti_5Si_3 + TiN mixed phase. The formation of granular Ti_5Si_3 at Ti grain boundaries

is completely prevented.

5. Joints of Ti - 24at% N / Si_3N_4 endures 10.6 MPa, which is three times higher than pure-Ti / Si_3N_4 joints bonded in the same condition. The fracture path is changed to Si_3N_4 + TiN / Ti_5Si_3 + TiN interface.

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