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Author(s)	Maeda, Masakatsu; Naka, Masaaki
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Reaction and Structure at the Solid State Diffusion Bonded Ti/Si_3N_4 Interface†

Masakatsu MAEDA* and Masaaki NAKA**

Abstract

In order to clarify the interfacial structure and reaction mechanism at the interface of titanium and silicon nitride during solid state diffusion bonding, electron probe microanalysis, X-ray diffraction and transmission electron microscopy were carried out. At temperatures above 1373 K, one reaction layer consisting of TiN and $Ti_5Si_3N_X$ is formed at the joining interface. Three zones are observed in the reaction layer. First is the TiN zone adjacent to Si_3N_4. Second is the $Ti_5Si_3N_X$ zone adjacent to titanium. Third is the TiN+$Ti_5Si_3N_X$ mixed phase zone between TiN and $Ti_5Si_3N_X$ zone. As a result, the diffusion path for this system is described as Ti / $Ti_5Si_3N_X$ / $Ti_5Si_3N_X$+TiN / TiN / Si_3N_4. The growth behavior of the reaction layer was also analyzed. The initial growth rate constant and the activation energy for growth of the reaction layer are estimated as 4.9×10^{-7} m^2s^{-1} and 223 $kJmol^{-1}K^{-1}$, respectively.

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

1. Introduction

Silicon nitride (Si_3N_4), which presents high strength and resistance against corrosion and wear at high temperatures, has been attracted as high temperature structural components such as high speed rotating turbine blades. However, the mechanical brittleness and the manufacturing of it in large scale need Si_3N_4 to be bonded faithfully with metals or alloys. The major bonding technology for Si_3N_4 and metallic materials is brazing utilizing active metals, which provides reliable joints at a very low cost. However, the brazed joints possess poor reliability in temperatures higher than 800 K. For higher temperature applications, joints produced by solid state diffusion bonding technology will be more reliable, because the structure control of the bonded interface by this technology is easier than by brazing due to the lack of liquid convection. Although some studies related on the reaction between Si_3N_4 and metals have been reported[1-3], data accumulation and the understanding of the reaction between Si_3N_4 and metals are still not enough to control effectively their interfacial structures by this technology.

The present work is aimed to clarify the interfacial structure and reaction mechanism during solid state diffusion bonding between Si_3N_4 and titanium, one of the structural metals at high temperature.

2. Experimental Procedure

The specimens of Si_3N_4 were prepared to the shape of a cylindrical pellet of 6 mm diameter and 4 mm height. They contained a few mass percent of alumina as the sintering aid. The surfaces to be joined were polished with 0.25 μm diamond suspension. On the other hand, the specimens of titanium were 150 μm thickness foils of 99.5 % nominal purity. Both sides of these foils were also polished with 0.05 μm alumina suspension. In order to build joining couples, each titanium foil was sandwiched between two Si_3N_4 pellets. These couples were inserted in a high-frequency induction vacuum furnace, loading a uniaxial pressure of 60 MPa perpendicular to the joining interfaces. The vacuum inside the furnace was kept below 1.3 mPa during the joining operation. The bonding temperature and time were set at certain values between 1473 K and 1673 K and between 0.9 ks and 28.8 ks, respectively. The interfacial structure and elemental concentration profile of the joints were estimated by means of electron probe microanalysis (EPMA), X-ray diffraction (XRD) and transmission electron microscopy (TEM).

3. Results and Discussion

A series of cross sectional compositional contrast images of joint interfaces bonded at four different

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* Research Associate
** Professor

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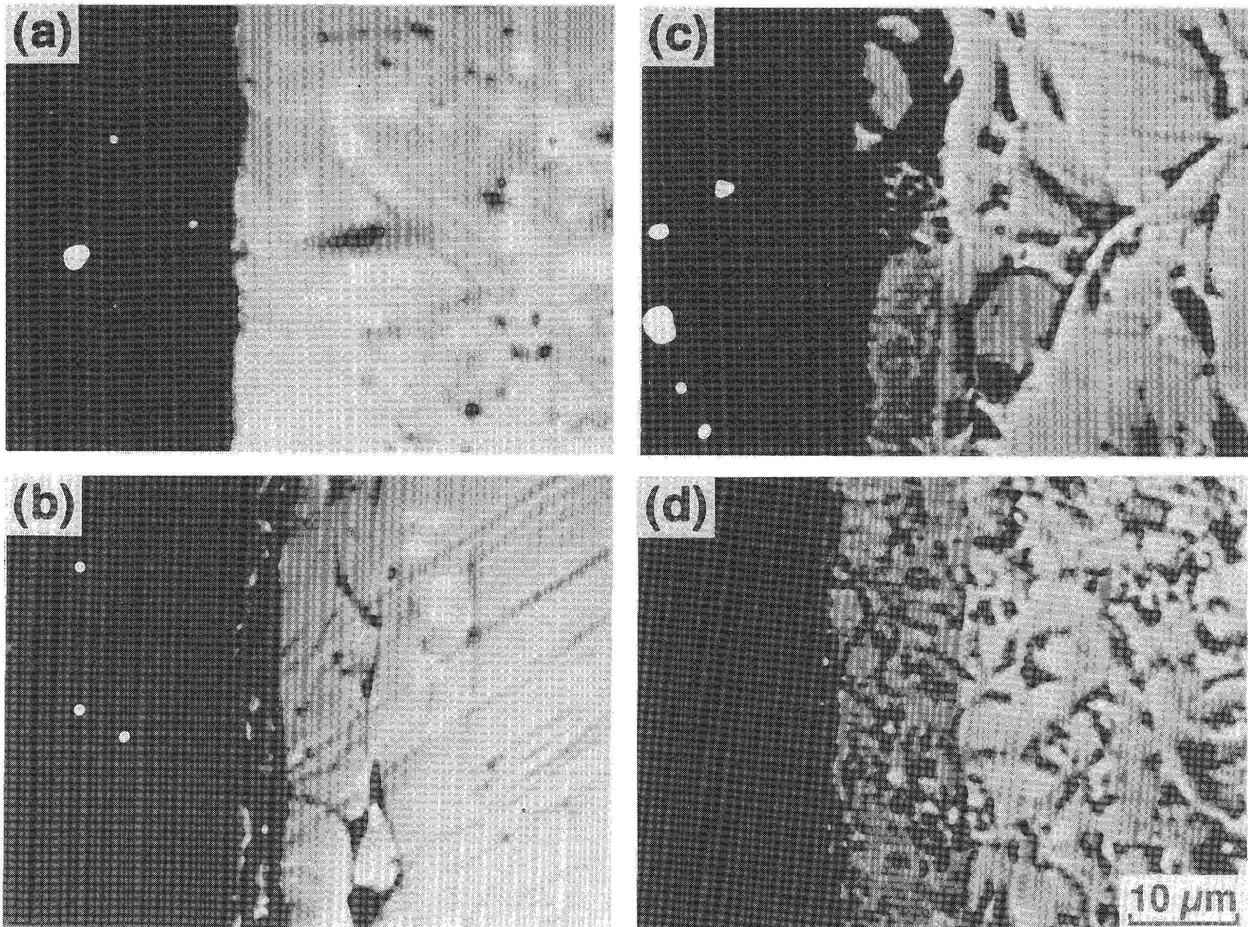


Fig. 1 SEM cross sectional micrographs of the Ti / Si_3N_4 joint interfaces bonded at four different temperatures for 3.6 ks. The bonding temperature for each joint is: a) 1373 K, b) 1473 K, c) 1573 K and d) 1673 K. The black region on the left side in each micrograph is Si_3N_4. The brighter side on the right is titanium.

temperatures for 3.6 ks is shown in **Fig. 1**. Figure 1(a) is a micrograph of a joint interface bonded at 1373 K. No phases other than titanium metal and Si_3N_4 are observed at the joint interface. Figure 1(b), (c) and (d) are micrographs of joint interfaces bonded at 1473, 1573 and 1673 K, respectively. At temperatures higher than 1373 K, a layer of reaction product appears at the interface between titanium metal and Si_3N_4. No other reaction layers appear at the interface in the temperature region from 1473 K to 1673 K, even after prolonged bonding times up to 28.8 ks. The thicknesses of this reaction layer for 1473, 1573 and 1673 K were 5.0, 7.2 and 13.1 μm, respectively. This result indicates that the growth rate of this reaction layer increases continuously with the temperature increase.

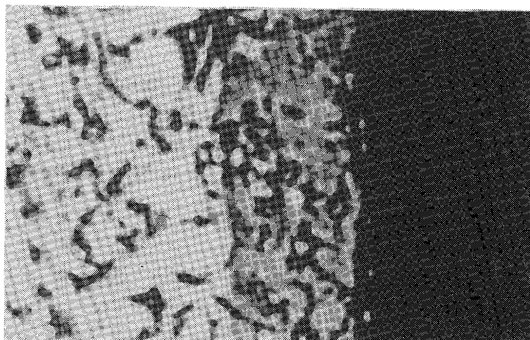
A concentration profile of titanium, silicon and nitrogen at the vicinity of a joint bonded at 1673 K for 3.6 ks is depicted in **Fig. 2**. The position of each measured point corresponds to the structure micrograph inserted at the top of Fig. 2. Two points are clear from Fig. 2. One is the oscillation of concentration curves in the reaction layer. This oscillation indicates that the reaction layer is made of two different phases, a silicon rich phase and a silicon poor phase. Moreover, the amplitude of the oscillation indicates that the silicon rich phase is concentrated at the part adjacent to titanium, while the silicon poor phase is concentrated at the part adjacent to Si_3N_4. The other is that nitrogen has already diffused into the titanium foil with a constant concentration of 20 atomic percent while titanium cannot diffuse into Si_3N_4 at all.

Fig. 3 shows a series of X-ray diffraction patterns taken from a joint bonded at 1573 K for 3.6 ks. The specimens were cut at one side of the Si_3N_4 vicinity of the interface and polished about 3 mm for each XRD measurement. Each layered reaction product and its arrangement was identified by the position of each X-ray diffraction peak and the alteration of its relative intensity. The diffraction patterns a, b and c in Fig. 3 correspond to the measurements at the positions a, b and c in the schematic figure inserted at the top of Fig. 3. Figure 3a indicates that two kinds of compounds, TiN and $Ti_5Si_3N_X$, exist at the interface besides titanium and Si_3N_4. Figure 2b is an XRD pattern taken from the same specimen after polishing the interface about 10 mm from the state of Fig. 3a. The relative intensity of the peaks from TiN and

$Ti_5Si_3N_X$ in Fig. 3b are significantly weakened comparing with Fig. 3a. Furthermore, the damping rate of the intensity for TiN is greater than that for $Ti_5Si_3N_X$. These facts indicate that the reaction layer consists of TiN and $Ti_5Si_3N_X$ and that the silicon rich and silicon poor phases correspond to $Ti_5Si_3N_X$ and TiN, respectively. The damping rate difference between $Ti_5Si_3N_X$ and TiN agrees well with the distribution of these phases in the reaction layer.

For a detailed analysis of the interface between Si_3N_4 and the reaction layer, TEM observation were carried out. **Figure 4** shows a cross sectional TEM micrograph of the interface bonded at 1573 K for 1.8 ks. The bright field image indicates that grains of Si_3N_4 are faced on TiN grains. The electron diffraction pattern is taken from the grain of TiN in the bright field image. From this observation, it was clear that almost all regions in the reaction layer adjacent to Si_3N_4 are occupied by TiN.

From these results, the structure of the Ti / Si_3N_4 joint interface are described as follows. The region of the reaction layer adjacent to Si_3N_4 is almost occupied by TiN. The amount of TiN decreases through the reaction layer towards the interface with titanium. At the interface of the reaction layer and titanium, $Ti_5Si_3N_X$ is the major compound adjacent to titanium. Therefore, the reaction



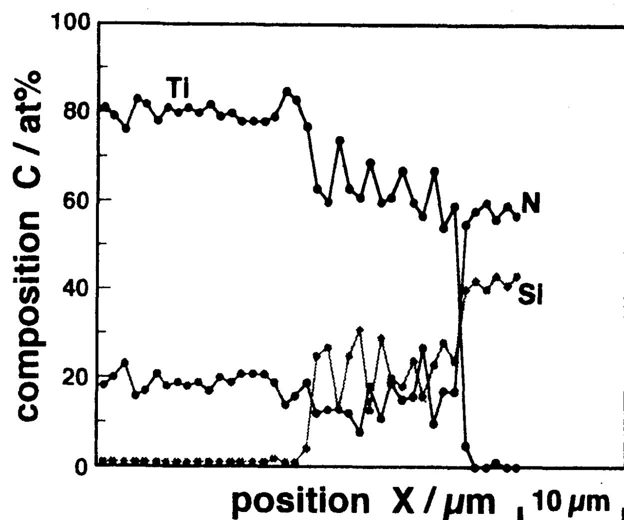


Fig. 2 Cross sectional composition profile of a Ti / Si_3N_4 joint bonded at 1673 K for 3.6 ks with the corresponding micrograph of the same magnification.

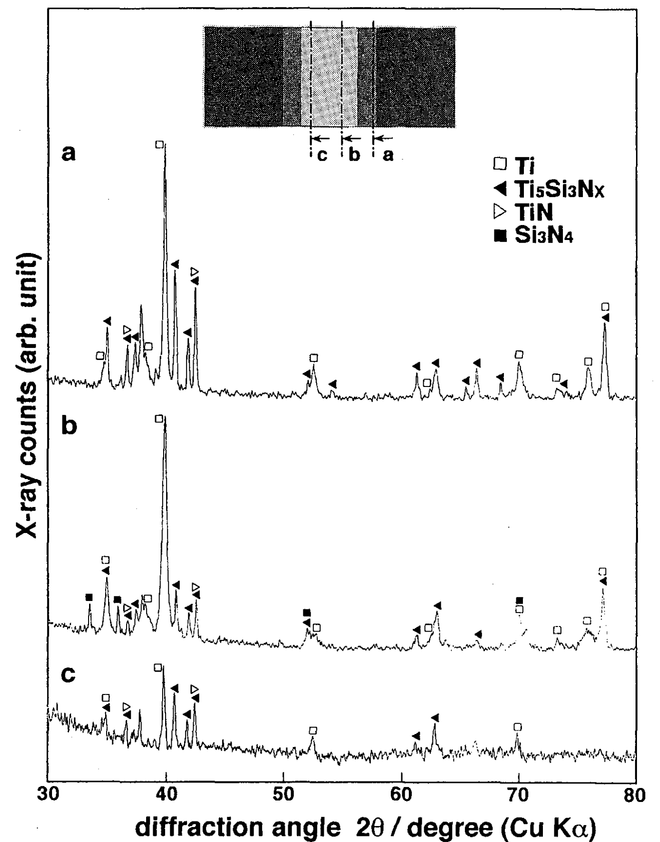


Fig. 3 A series of X-ray diffraction patterns taken from a joint bonded at 1573 K for 3.6 ks. The patterns a, b and c correspond to the measurements after polishing the interface to the positions a, b and c in the schematic figure inserted at the top of the figure.

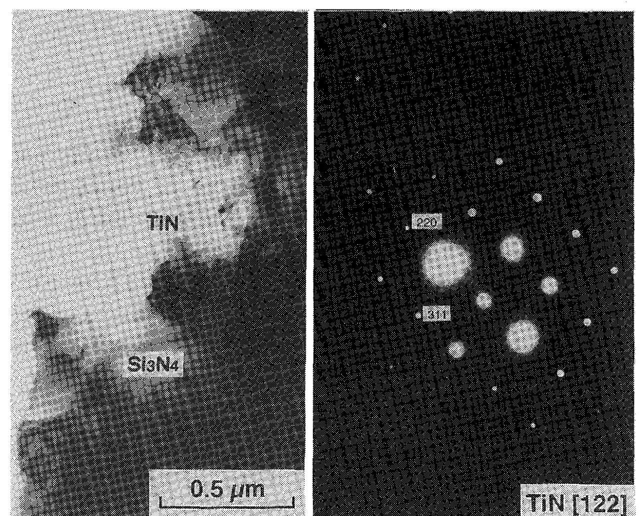


Fig. 4 TEM bright field image of an interface between Si_3N_4 and the reaction layer of a Ti / Si_3N_4 joint bonded at 1573 K for 1.8 ks with an electron diffraction pattern taken from a TiN grain adjacent to Si_3N_4.

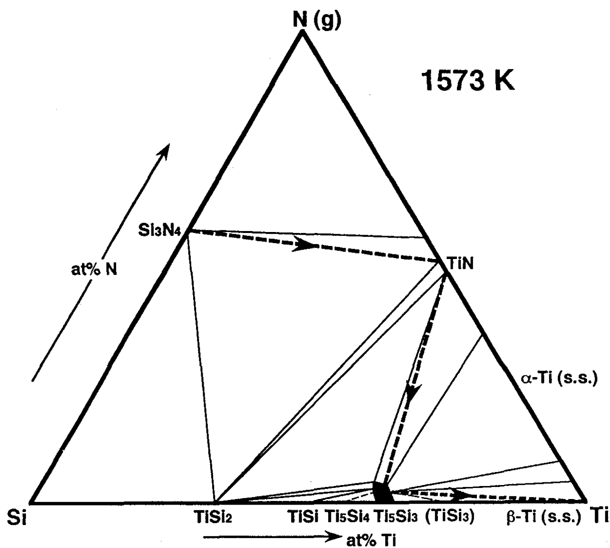


Fig. 5 Diffusion path for Ti / Si_3N_4 joints shown on the Ti-Si-N ternary phase diagram[5] with dotted lines as Ti / $Ti_5Si_3N_X$ / $Ti_5Si_3N_X$+TiN / TiN / Si_3N_4.

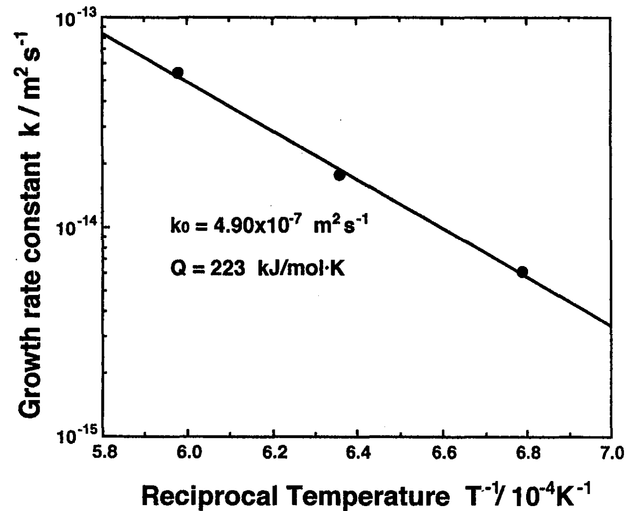


Fig. 6 Arrhenius plot of growth rate constant of the reaction layer versus temperature.

layer can divided into three zones. First is the TiN zone adjacent to Si_3N_4. Second is the $Ti_5Si_3N_X$ zone adjacent to titanium. Third is the TiN+$Ti_5Si_3N_X$ mixed phase zone between TiN and $Ti_5Si_3N_X$ zone. The diffusion path of metal-ceramic system is known to be described on the corresponding ternary phase diagram[4]. The present diffusion path of Ti / Si_3N_4 system is illustrated in **Fig. 5**, a Ti-Si-N ternary phase diagram[5], with dotted lines as Ti / $Ti_5Si_3N_X$ / $Ti_5Si_3N_X$+TiN / TiN / Si_3N_4.

The growth rate of the reaction layer increases continuously with the bonding temperature increase. **Figure 6** shows an Arrhenius plot of the growth rate constant at each temperatures. From this figure, the initial growth rate constant k_0 and the activation energy Q for growth of the reaction layer are deduced as 4.9×10^{-7} m^2s^{-1} and 223 $kJmol^{-1}K^{-1}$, respectively.

4. Summary

Solid state diffusion bonding of titanium and Si_3N_4 was carried out. Interfaces of the joints were analyzed by means of EPMA, XRD and TEM. The following points were clarified.

(1) At any bonding temperature from 1473 K to 1673 K and bonding time from 1.8 ks to 28.8 ks, one reaction layer consisting of two kinds of compounds, TiN and $Ti_5Si_3N_X$, is formed. Three zones are observed in the reaction layer. First is the TiN zone adjacent to Si_3N_4. Second is the $Ti_5Si_3N_X$ zone adjacent to titanium. Third is the TiN+$Ti_5Si_3N_X$ mixed phase zone between TiN and $Ti_5Si_3N_X$ zone. As a result, the diffusion path of Ti / Si_3N_4 system is described as Ti / $Ti_5Si_3N_X$ / $Ti_5Si_3N_X$+TiN / TiN / Si_3N_4.

(2) The initial growth rate constant k_0 and the activation energy Q for growth of the reaction layer are deduced as 4.9×10^{-7} m^2s^{-1} and 223 $kJmol^{-1}K^{-1}$, respectively.

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