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High Temperature Reactions of Ti with SiC†

Masaaki NAKA*, Jicai FENG** and Julius C. SCHUSTER***

Abstract

Bonding of SiC to SiC was conducted using Ti foil at bonding temperatures from 1373 K to 1773 K in vacuum. The total diffusion path between SiC and Ti was investigated in detail at 1673 K using Ti foil with a thickness of 50 μm. At a bonding time of 0.3 ks, TiC at the Ti side and a mixture of $Ti_5Si_3C_x$ and TiC at the SiC side were formed, yielding the structure sequence of β-Ti/TiC/$Ti_5Si_3C_x$+TiC/SiC. Furthermore, at the bonding time of 0.9 ks, a Ti_5Si_3Cx layer phase appeared between SiC and the mixture of $Ti_5Si_3C_x$ and TiC. Upon the formation of Ti_3SiC_2 (T phase) after the bonding time of 3.6 ks, the complete diffusion path was observed as follows: β-Ti/TiC/$Ti_5Si_3C_x$+TiC/$Ti_5Si_3C_x$/Ti_3SiC_2/SiC. The activation energies for growth of TiC, $Ti_5Si_3C_x$ and Ti_3SiC_2 were 194, 242 and 358 kJ/mol, respectively.

KEY WORDS: (Ceramics/Metal Interface) (Solid State Bonding) (Diffusion Path) (Silicon Carbide) (Interface Structure) (Titanium Silicide) (Growth Kinetics)

1. Introduction

An understanding of phase reactions between ceramics and metals is required for the fabrication of ceramic-metal joints and ceramic reinforced metal composites. The knowledge of compounds formed and of the diffusion path across the ceramic/metal interface is necessary to control the interface structures, which essentially control the mechanical properties. SiC, which possesses superior high temperature mechanical properties, is a candidate for structural applications. The formation of Ti_5Si_3, TiC and Ti_3SiC_2 has been reported in SiC fiber reinforced Ti composites[1,2] and SiC/Ti joints[3,4]. While these results give partial information on the reactions occurring between SiC and Ti, they do not permit elucidation of the entire sequence of phase reactions occurring at those interfaces. It is the aim of the present paper, to describe in detail the interfacial phenomena, including the diffusion path, in the SiC/Ti system, and to relate them to the Ti-Si-C phase diagram.

2. Experimental procedure

The materials used were cylindrical SiC rods of 6 mm diameter and 4 mm thickness, containing a few percent of alumina as a sintering aid, and Ti foil of 50 μm thickness. The bonding was done in vacuum below 1.33 mPa, using a high frequency heater equipped with a graphite tube. The bonding conditions were, bonding temperatures from 1373 K to 1773 K, and bonding times from 0.3 to 144 ks under a bonding pressure of 7.26 MPa. The microstructures and phases at interfaces were investigated by x-ray diffraction (CuKα radiation) and electron probe microanalysis.

3. Results and discussion

The reaction layers, which form at the SiC and Ti interface upon bonding at 1673 K for times of 0.3 ks or longer, were analyzed. **Figs. 1** and **2** show the evolution with time from 3.6 ks to 36 ks at 1673K of interface microstructures and of quantitative elemental compositions respectively. Initially, granular TiC phase is formed adjacent to Ti, and (TiC+$Ti_5Si_3C_X$) duplex phase is formed adjacent to SiC. After a bonding time of 3.6 ks two additional reaction zones appeared between the (TiC+$Ti_5Si_3C_X$) and the SiC. A single phase $Ti_5Si_3C_X$ zone adjacent to (TiC+$Ti_5Si_3C_X$), and a Ti_3SiC_2 zone next to the SiC. $Ti_5Si_3C_X$ is a solid solution of carbon in binary Ti_5Si_3. It has a hexagonal Nowotny-phase type crystal structure. Ti_3SiC_2, a true ternary phase denominated T-phase, has a complex hexagonal crystal structure [5]. **Fig. 3** shows the x-ray diffraction patterns of interfaces revealed by successive polishing. The analysis yielded the lattice parameters of a= 0.7456nm,

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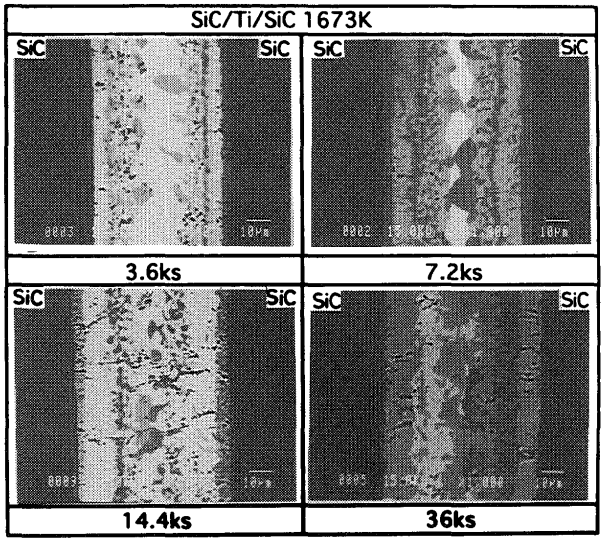

Fig.1 Microstructures of SiC/Ti/SiC

c= 0.5170nm for the Nowotny phase, and a= 0.3069nm, c= 1.767nm for the T-phase. These lattice parameters for the Nowotny phase are characteristic of material having a composition at the Ti rich homogeneity limit and high carbon content (c=1). The lattice parameter found for TiC is a= 0.4316nm. For purely binary TiC such a lattice parameter corresponds to 37at% carbon [6]. However it should be noted, that in the initial pattern (Fig.3A) TiC with two significantly different lattice parameters is present. One, assumed to belong to the granular TiC, is rather small (a= 0.4286nm) indicating a very low carbon content. The other lattice parameter, assumed to belong to TiC in the duplex $Ti_5Si_3C_x$+TiC zone, is rather large (a= 0.4353nm) indicating a very high carbon content. Unreacted titanium is still observed at the central part of the SiC/Ti/SiC couple at this bonding time. As will discussed below, the sequence of phases observed at these bonding conditions shows the complete diffusion path between SiC and Ti.

After longer bonding times no more unreacted Ti remains. Upon bonding for 14.4 ks the central part of the couple is a TiC+$Ti_5Si_3C_x$ zone, and the thickness of

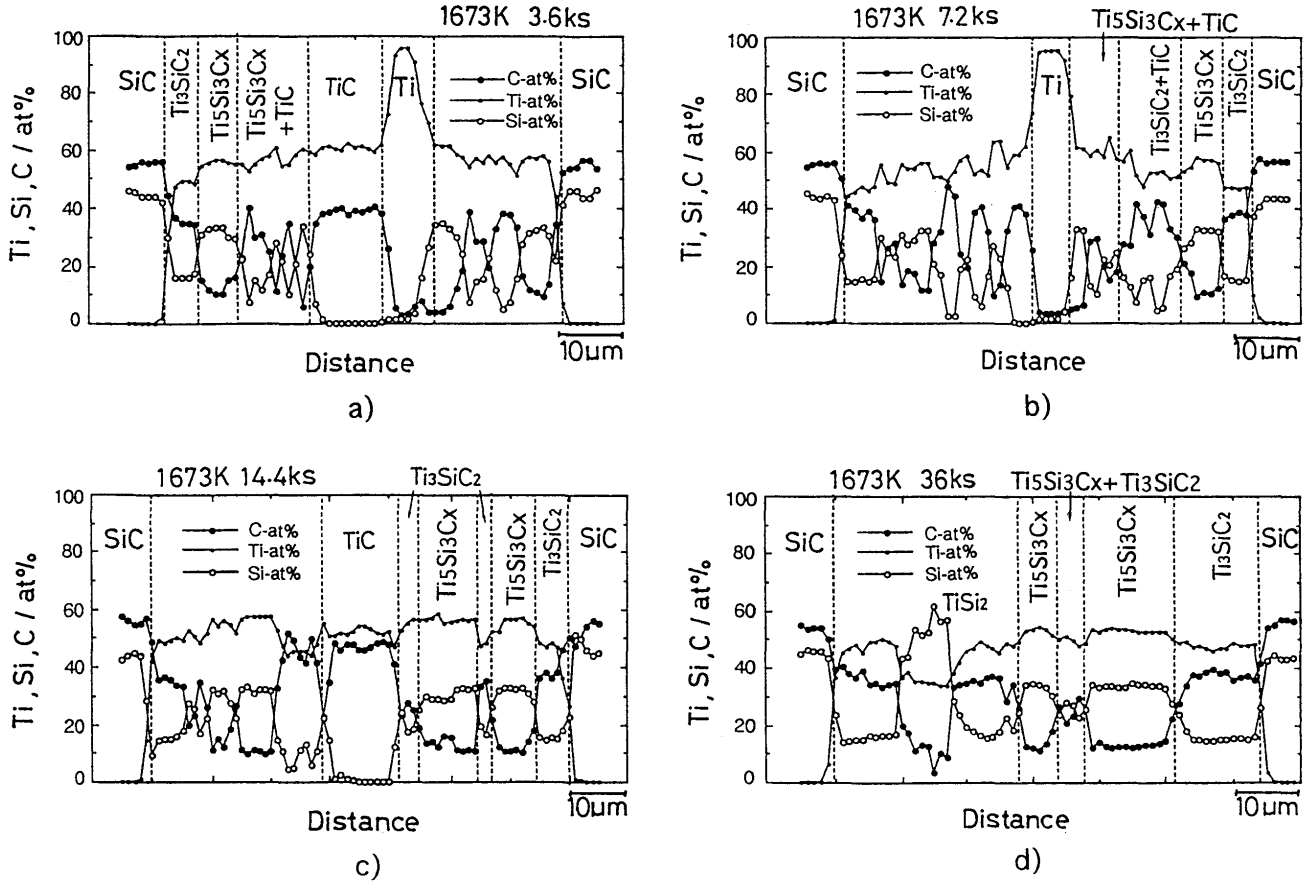

Fig.2 Line analyses of Ti, Si, and C in SiC/Ti/SiC joints at 1673 K. (a)3.6 ks, (b)7.2 ks, (c)14.4 ks, (d)36 ks.

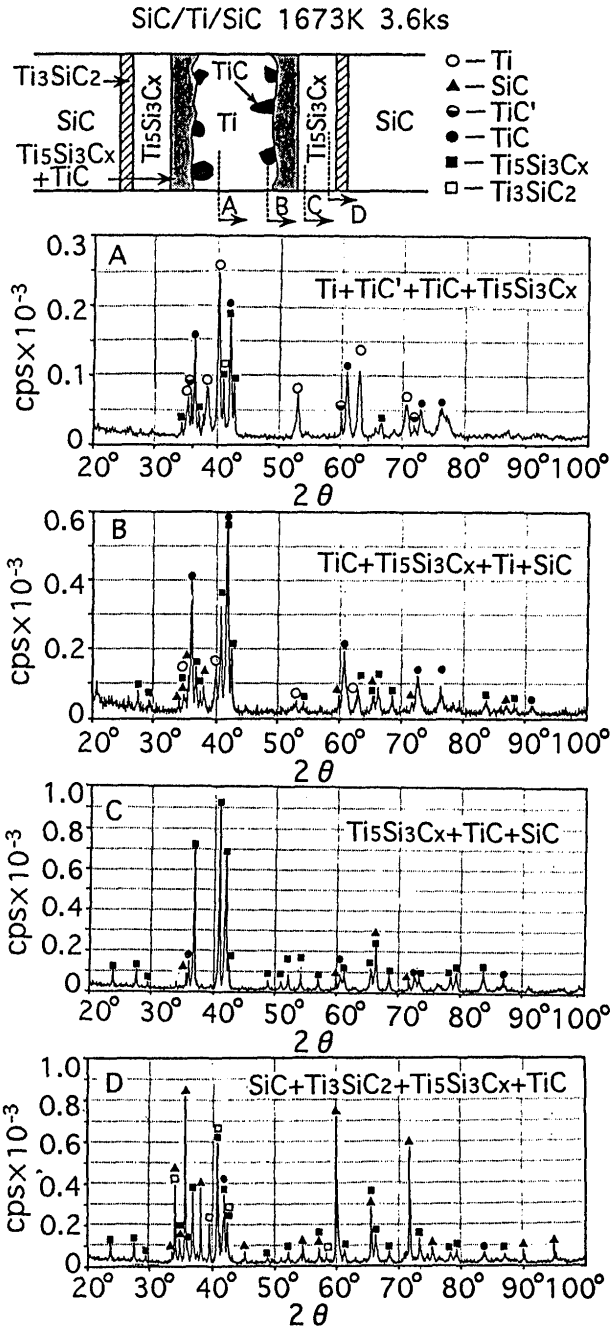

Fig.3 X-ray diffraction patterns of revealed interfaces for SiC/Ti/SiC joint bonded at 1673 K for 3.6 ks.

Ti_3SiC_2 layer increases significantly. Microprobe analysis shows the chemical composition for $Ti_5Si_3C_x$ and Ti_3SiC_2 to be Ti(bal.), Si 28.9-31.5 at%, C 12.8-16.6 at%, and Ti(bal.), Si 14.7-16.5at%, C 35.2-38.1at% respectively. Microprobe analysis of the granular TiC yields 34.7-39 1at% carbon and about 1at% silicon. These results match very well with the XRD data.

At the bonding time of 36 ks, the additional

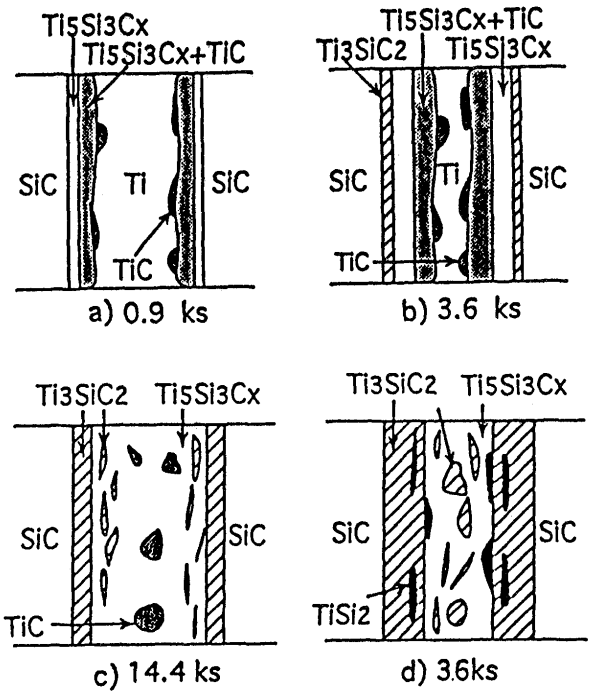

Fig.4 Change in microstructure of interface for SiC/Ti/SiC joint with bonding time at 1673 K.

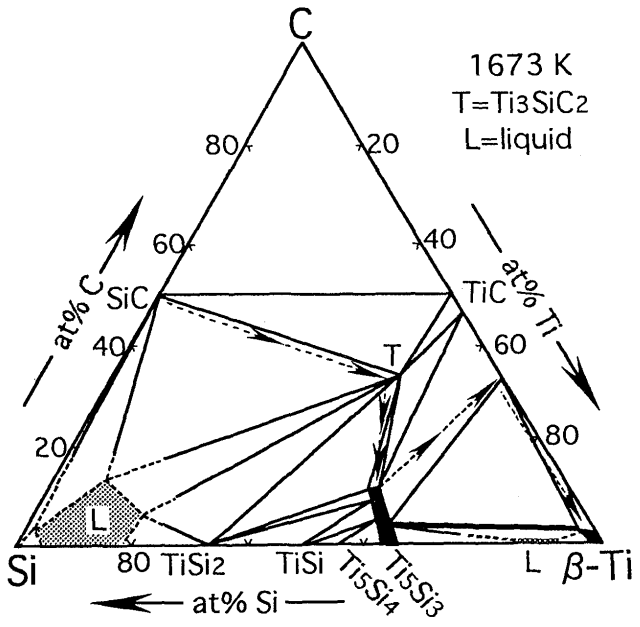

Fig.5 Diffusion path between Ti and SiC superimposed on proposed Ti-Si-C phase diagram at 1673 K.

formation of $TiSi_2$ in the interface zone is observed. Microstructural features, such as shape of the grains as well as intergrowth with the T-phase, indicate, that $TiSi_2$ has been formed from a liquid phase rather than by a solid

state reaction. The evolution of the interfacial microstructures as described above is shown in **Fig.4**.

Fig.5 shows an isothermal section of the system Ti-Si-C proposed for 1673 K. It is based on the assumptions, that all tie lines observed for 1373 K [7] and 1473 K [6] are stable at 1673 K, except that the silicon rich liquid phase, which dissolves considerable amounts of carbon, coexists with Ti_3SiC_2. The dotted line superimposed on this isothermal section indicates the diffusion path as deduced from the phase sequence observed after bonding SiC with Ti at 1673 K for 3.6 ks. At these conditions local equilibrium across all

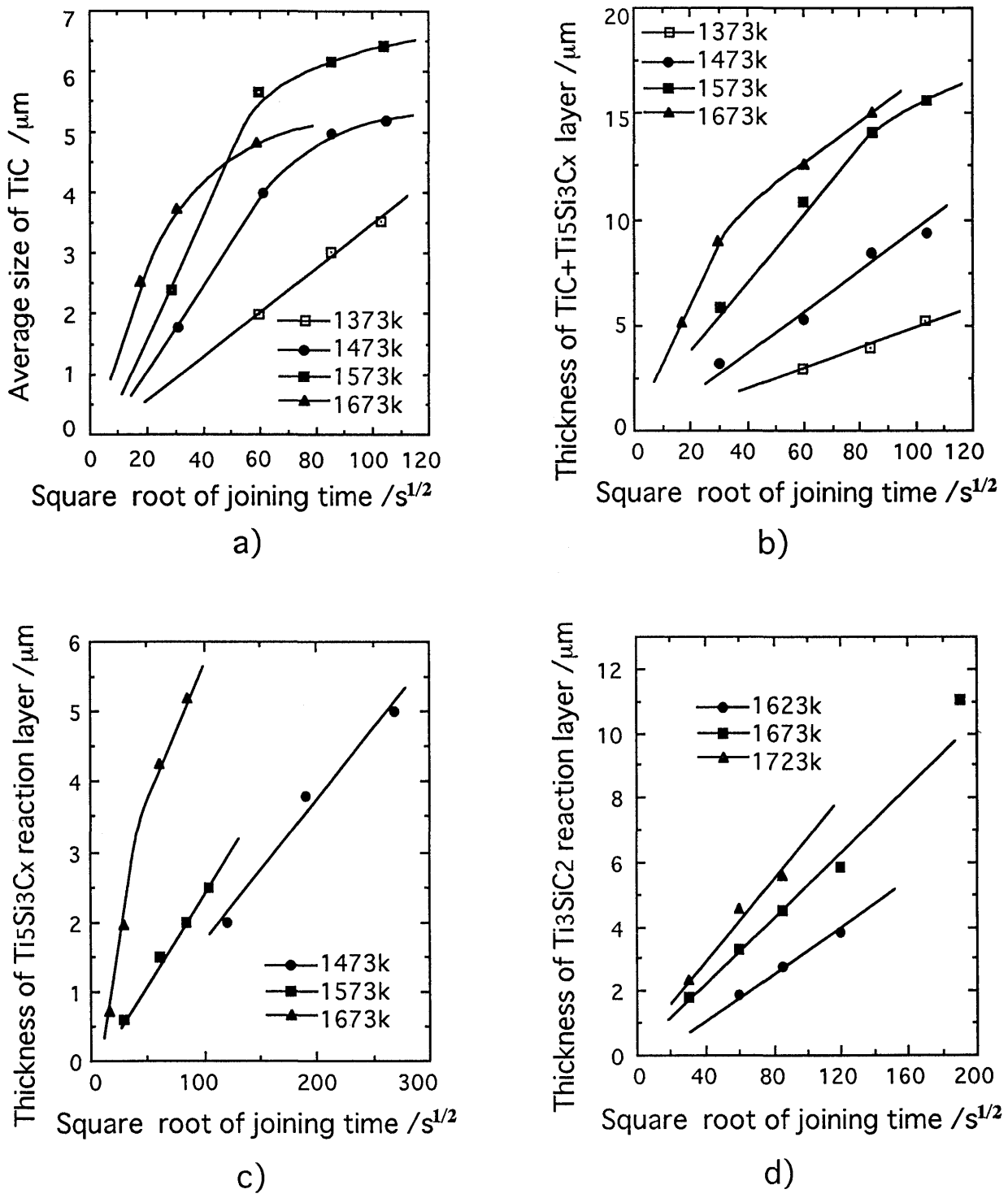

Fig.6 Reaction layer thickness SiC/Ti plotted in times of $t^{1/2}$.
(a)TiC, (b)TiC+$Ti_5Si_3C_x$, (c)$Ti_5Si_3C_x$, (d)Ti_3SiC_2.

interfaces is established and neither of the end members of the diffusion couple SiC/Ti are entirely consumed. Thus, the complete diffusion path found from the data of the present investigation is: Ti/TiC/TiC+$Ti_5Si_3C_x$/ $Ti_5Si_3C_x$/Ti_3SiC_2/SiC, which clarifies issues unresolved in a recent compilation of SiC/metal [7].

With the overall composition of the interface zone being close to SiC on the composition line connecting SiC to Ti, from Fig.5 the occurrence of (SiC+Ti_3SiC_2+liquid) is expected at equilibrium. During cooling, the liquid phase must react with T-phase to form SiC+$TiSi_2$, in order to yield the (SiC+$TiSi_2$+T-phase) phase field observed for the Ti-Si-C system for 1473 K orbelow[6,7]. Thus, the assumption of a tieline between T-phase and the liquid phase at 1673 K explains the morphology of the microstructure observed at room temperature after relatively slow cooling from bonding for 36 ks at 1673 K, and the microstructure of that specimen can be taken to represent the final equilibrium stage of the interfacial reaction.

The growth of compounds at an interface between materials is often expressed as,

$$x^2 = kt \quad (1)$$

$$k = k_0 \exp(-Q/RT) \quad (2)$$

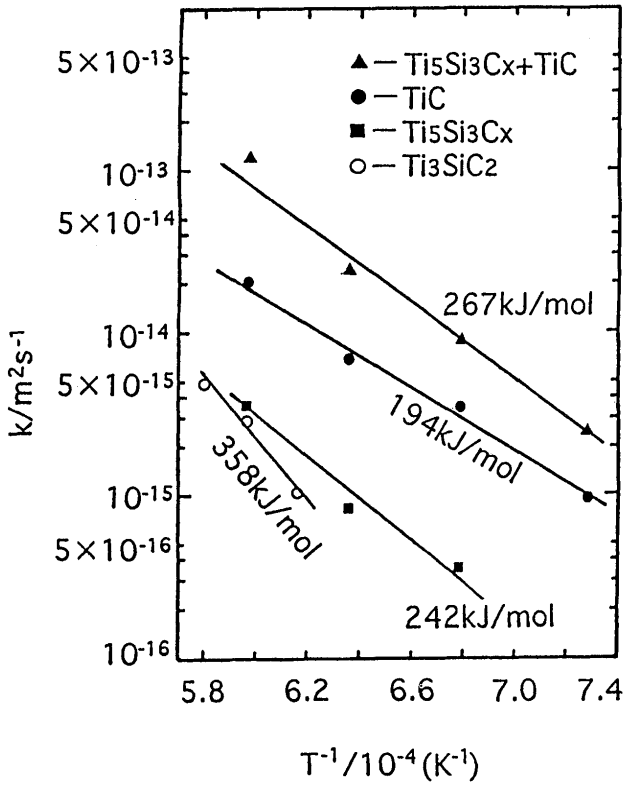

Fig.7 Rate constants for growth of compounds in SiC/Ti system plotted with time.

Table.1 Values of Q and k_0 for reaction products of SiC/Ti system.

Composite	Q(kJ/mol)	$K_0(m^2/s)$	Refs.
Ti5Si3Cx +TiC	267	2.83×10^{-5}	Present work
TiC	194	2.17×10^{-8}	Present work
Ti5Si3Cx	242	1.07×10^{-7}	Present work
Ti3SiC2	358	3.85×10^{-4}	Present work
SiC/Ti	250	1.84×10^{-5}	K.Kurokawa et al.
SiC/Ti	274	4.58×10^{-4}	P.Martineau et al.

[8],where x is the thickness of compounds formed, and k and k_0 are rate constants for the growth, and Q is the activation energy for growth of compound. The growth rates of compounds formed at the interface between SiC and Ti are shown in **Fig.6**. Since it has irregular shape, the diameter of the TiC granular phase is estimated from the average value of two diameters. The slope for the growth of TiC is changed due to the formation of $Ti_5Si_3C_x$ at 1473 K and 1573 K, and due to $Ti_5Si_3C_x$ and Ti_3SiC_2 at 1673 K (Fig. 6(a)). The slope of (TiC+$Ti_5Si_3C_x$) duplex zone growth also changes due to the formation of Ti_3SiC_2 at the interface at 1573 and 1673 K as shown in Fig. 6(b). The growth of $Ti_5Si_3C_x$ and Ti_3SiC_2 are shown in Figs. 6(c) and (d).

The rate constants for growth of compounds expressed by eq.(2) are plotted in **Fig.7**. The activation energies for growth rates of compounds are 194, 267, 242 and 358 kJ/mol for TiC,$Ti_5Si_3C_x$+TiC, $Ti_5Si_3C_x$ and Ti_3SiC_2, respectively. Since these values increase with increasing complexity of the crystallographic environment of carbon in each phase, carbon may control the growth of TiC, $Ti_5Si_3C_x$ and Ti_3SiC_2 layers. Carbon may diffuse more easily in the phase which has a more simple crystal structure. The growth of the mixed zone of $Ti_5Si_3C_x$+TiC may have a different mechanism. In **table1**, the values found in the present investigation are compared with values reported in the literature for the total reaction zone growth in SiC/Ti couples [1,4] The kinetic constants for growth found for Ti_3SiC_2 explain why it is difficult to observe this phase at 1273 K, the experimental condition commonly used for SiC/Ti composite fabrication.

4. Conclusions

The compounds formed at the interface between SiC and Ti were investigated at bonding temperatures from 1373 to 1773 K in vacuum. At the bonding temperature

of 1673 K, TiC next to Ti and a mixture of the $Ti_5Si_3C_x$+TiC phases next to SiC are formed at the beginning of bonding. $Ti_5Si_3C_x$ single phase has appeared at a bonding time of 0.9 ks. At a bonding time of 3.6 ks, the complete diffusion path between SiC and Ti at 1673 K could be observed as, β-Ti/TiC/$Ti_5Si_3C_x$+TiC/$Ti_5Si_3C_x$/Ti_3SiC_2/SiC. This path is consistant with the Ti-Si-C ternary phase diagram, confirming the local equilibrium at the interfaces between the compounds formed at the SiC/Ti couples. The activation energies for growth of compounds formed at 1673 K were 194, 242, and 358 kJ/mol for TiC, $Ti_5Si_3C_x$ and Ti_3SiC_2, respectively. The value for a mixed zone of $Ti_5Si_3C_x$ +TiC was 267 kJ/mol. After further bonding time, Ti was consumed and the structure of the interface proceeded towards the equilibrium state. A liquid phase occured, which formed $TiSi_2$ upon cooling.

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