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Kinetics of Growth of Reaction Phases at Ceramic/Metal Interfaces†

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Abstract

Reaction Phases are formed at interfaces between dissimilar materials such as ceramic and metals. The growth of reaction phases are dominated by elemental diffusion at the interface between dissimilar materials, and the growth rates of total reaction phases are expressed by $x^2 = kt$, and the cases of SiC/Metal (M: Ti, Cr, Nb, Ta) are presented.

KEY WORDS: (Solid State Reaction) (Multiple Phase Growth) (Diffusion Path) (Interface Structure) (Activation Energy)

1. Introduction

The combination of dissimilar materials effectively improves characteristics of structural components. A knowledge of the interface structure is necessary to give the dissimilar materials components high reliability. In the interface between dissimilar materials such as ceramic and metals joints, a variety of reaction phases are formed[1-3]. This work describes the fundamentals of interfacial reactions and diffusion between ceramic and metal, and growth rates of reaction phases at the interfaces.

2. Formation of reaction Phases at the interface between dissimilar materials

2.1 Phase Stability and Diffusion Path
During bonding at high temperatures, metals react with ceramics, and form reaction phases at ceramic/metal interfaces. In evaluating the reactivity of metals with ceramics, it is useful to consider the phase stability in a corresponding ternary model A-B-C system such as that in shown in **Fig.1**. In this system, three binary compounds of AB, BC and AC co-exist in the ternary system. In the AC ceramic- B metal system, A and C are constituent elements of the ceramic, and B is the element of the metal.

In bonding AC ceramic to B metal, B first reacts with AC, and forms AB and BC compounds as indicated below;

$$B + AC \rightarrow AB + BC \qquad (1)$$

The change in free energy of reaction (1) is given as,

$$\Delta G = \Delta G°_{AB} + \Delta G°_{BC} - \Delta G°_{AC} - \Delta G°_B$$
$$+ RT\ln\{(a_{AB}{}^+a_{BC})/(a_B{}^\bullet{}^a{}_{AC})\} \qquad (2)$$

,where $\Delta G°$ is the standard Gibbs energy of formation of the phase. The interface reaction between the ceramic and metal is caused by the lowering of the Gibbs energy due to formation of new phases. If the Gibbs energy change is negative, $(\Delta G \langle 0)$, the interfacial reaction (1) will continue until the metal component is completely consumed.

The thermodynamic calculation tell us what will happen when equilibrium conditions are achieved, but does not tell us what combinations of phases may form under actual conditions. In the A-B-C system given in **Fig.1**, we can only propose the formation of compounds of AB and BC when AC compound is in contact with B, metal, but we can't say what phases will form between AC and B. In the example of the binary system of A and B, the only possible path is A/AB/C, but that is not the only one for the ternary AC compound/B metal couple. When B metal is in contact with AC compound, several phases such as AB and BC may appear, and there are two possible paths of AC/AB/BC/B and AC/BC/AB/B as given in **Figs.1**(a), (b), and (c). According to Kirkaldy and Brown [5], in a given specific ternary couple there is only one diffusion path. Although it is possible in principle to calculate the diffusion path, it is
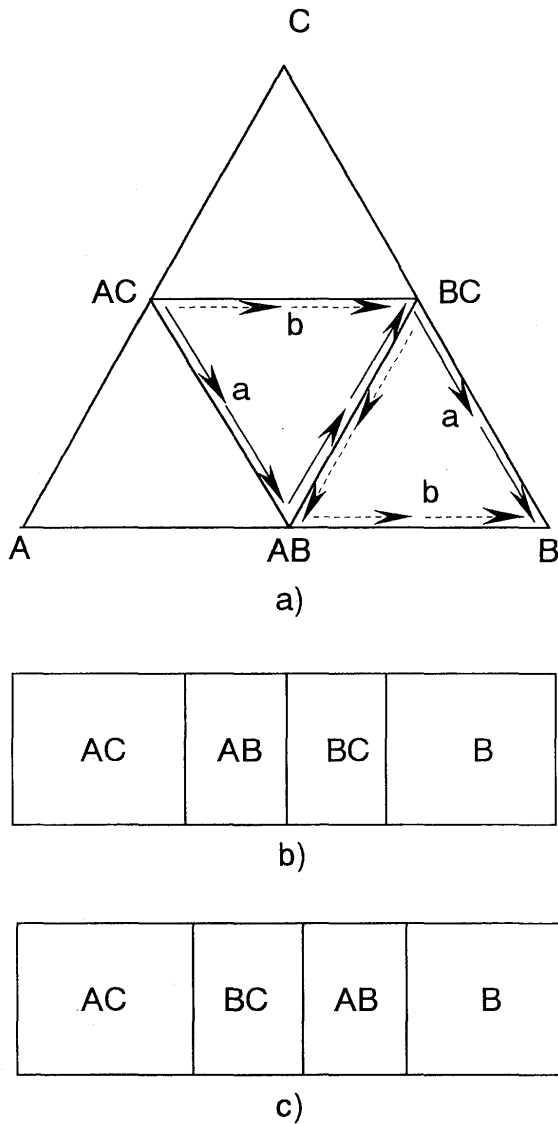
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a)

b)

c)

Fig. 1 (a)A-B-C ternary model diagram and hypothetical diffusion paths of a and b.

(b)A possible diffusion path for a couple of AC compound/M metal.

(c)Another possible diffusion path for a couple of AC compound/M metal.

difficult to calculate it under the current state of the present knowledge of the ternary Si-M-C system. We must depend on experiments to determine the diffusion paths of SiC/M couples.

The microstructure of the SiC/Ti/SiC interface bonded at 1473 K for 0.9 ks represented in **Fig. 2**. $Ti_5Si_3C_x$ containing TiC and granular TiC appear next to SiC and Ti, respectively. The interface reaction between SiC and Ti continues with further bonding time.

Fig. 3 shows the schematic change of reaction phases at SiC/Ti/SiC interface with bonding time at 1473 K [4].
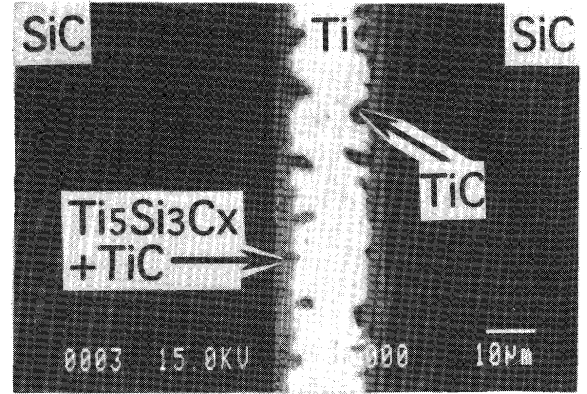

Fig. 2 Microphotograph of SiC/Ti/SiC joint at 1473 K for 0.9 ks.
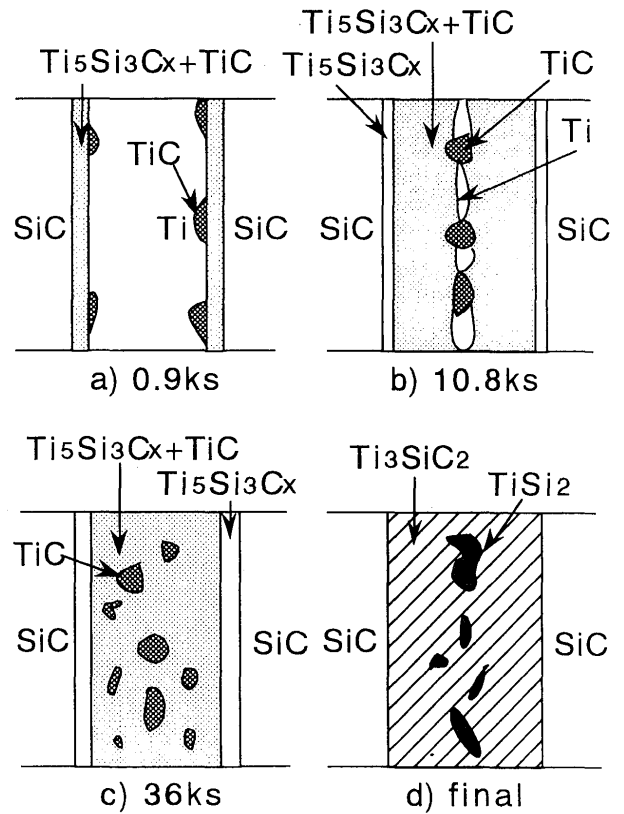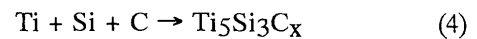

Fig. 3 Change in reaction phases in SiC/Ti couples with bonding time at 1473 K.

Ti first reacts with SiC. TiC next to Ti and $Ti_5Si_3C_x$ containing TiC next to SiC in **Fig. 3**(a) are formed at 0.9 ks as,
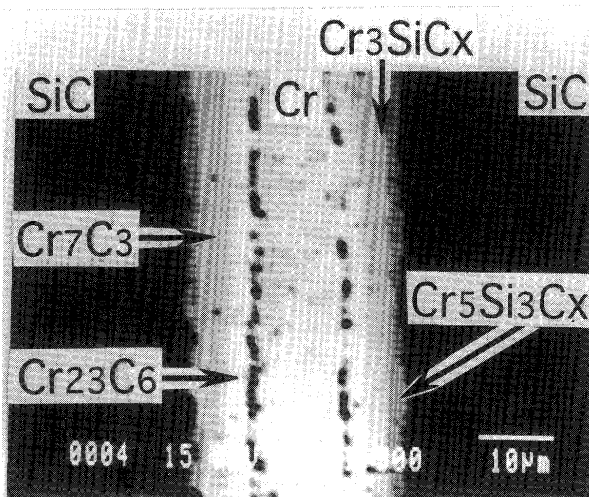
$$Ti + C \rightarrow TiC \qquad (3)$$

$$Ti + Si + C \rightarrow Ti_5Si_3C_x \qquad (4)$$

Fig. 4 Microphotograph of SiC/Cr/SiC joint at 1573 K for 1.8 ks.

Table 1 Diffusion coefficients in phases for the SiC/Ti system at 1473 K.

$$D_C(\beta\text{-Ti}) = 8\times10^{-6}\,cm^2/s$$
$$D_{Si}(\beta\text{-Ti}) = 1\times10^{-8}\,cm^2/s$$
$$\tilde{D}(\text{formation of TiC}) = D_C(\text{TiC})$$
$$= 10^{-10} \sim 10^{-12}\,cm^2/s$$
$$D_{Ti}(\text{TiC}) = 10^{-20}\,cm^2/s$$
$$\tilde{D}(\text{TiSi}_2) = 9\times10^{-10}\,cm^2/s$$
$$\tilde{D}(\text{TiSi}) = 3\times10^{-10}\,cm^2/s$$
$$\tilde{D}(\text{Ti}_5\text{Si}_3) = 3\times10^{-10}\,cm^2/s$$
$$\tilde{D}(\text{Ti}_3\text{Si}) = 4\times10^{-11}\,cm^2/s$$

During bonding the diffusion of Si and C from SiC cause the saturation of Si and C and the precipitation of TiC in $Ti_5Si_3C_x$. When the $Ti_5Si_3C_x$ zone grows thicker at the region adjacent to SiC, no more excess titanium reaches it from Ti. Thus no TiC precipitates there and the $Ti_5Si_3C_x$ single phase zone develops as shown in **Fig.** 3(b). This leads to a pile-up of excess carbon at the $SiC/Ti_5Si_3C_x$ interface until the saturation limit for Ti3SiC2 is reached and a zone of Ti_3SiC_2 forms as,

$$\text{Ti} + \text{Si} + \text{C} \rightarrow \text{Ti}_3\text{SiC}_2 \qquad (5)$$

At this bonding time between 10.8 ks and 36 ks the complete diffusion path between SiC and Ti is established. The interface at this step is $SiC/Ti_3SiC_2 / Ti_5Si_3C_x/Ti_5Si_3C_x+TiC/TiC/Ti$ as the complete diffusion path between SiC and Ti.

At the bonding time of 36 ks, the central part of Ti is completely consumed by the reactions. The continuous diffusions of Si and C from SiC move the structures to the equilibrium, and form the additional phase of $TiSi_2$.
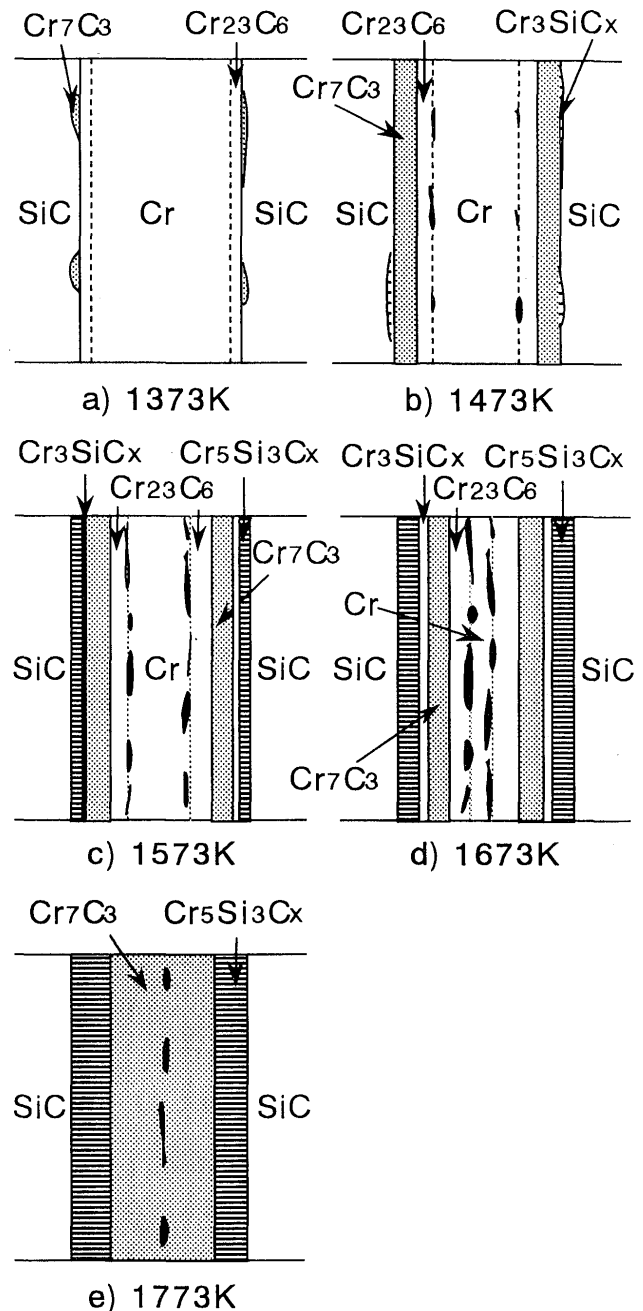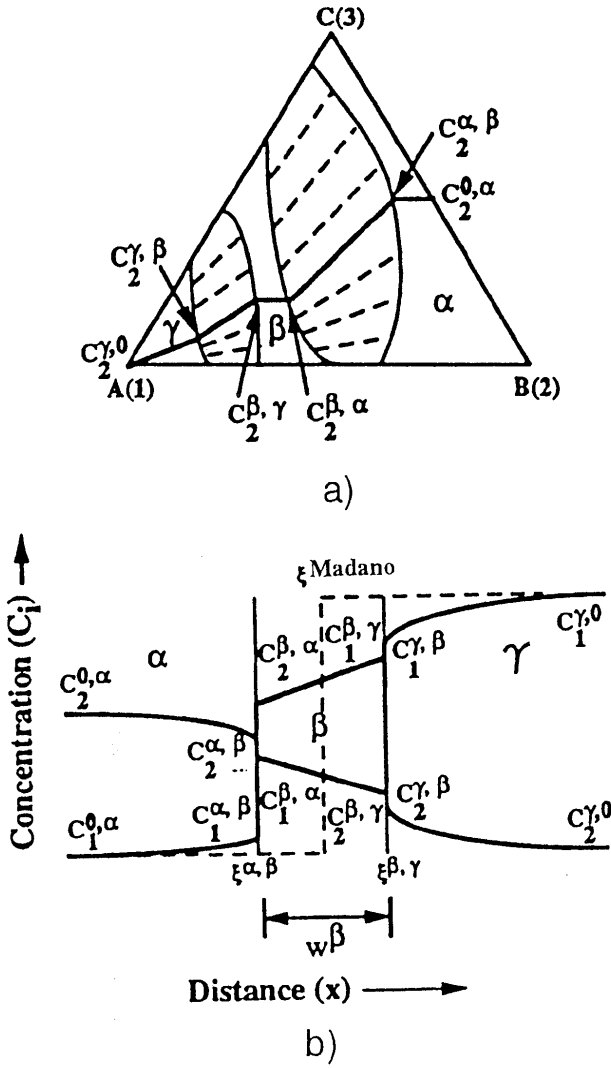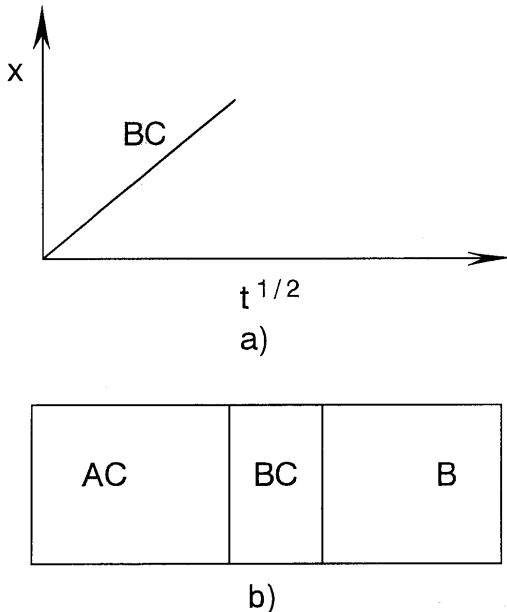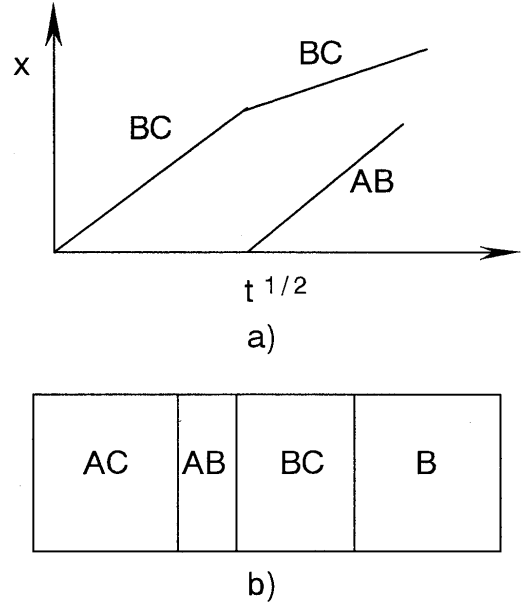

Fig. 5 Change schematic of reaction phases in SiC/Cr/SiC couples with bonding temperature for 0.9 ks.

In **Fig. 4**, the SiC/Cr interface bonded at 1573 K for 1.8 ks, $Cr_{23}C_6$ and Cr_7C_3 next to Cr and $Cr_5Si_3C_x$ +Cr_3SiC_x next to SiC appear. **Fig. 5** illustrates the schematic change of interface structure with bonding temperature. At the SiC/Cr interface, reaction (6) and (7) take place by supplying Cr from the Cr side and C from the SiC side. The Cr_7C_3 granular and $Cr_{23}C_6$ layer phases are formed and the interface structures becomes $SiC/Cr_7C_3/Cr_{23}C_6$ as indicated in **Fig.5** (a).

a)

b)

Fig. 6 Elemental distributions in β between α and γ.

Fig. 7 Change in thickness of AB with $t^{1/2}$.

a)

b)

Fig. 8 Change in thickness of AB with $t^{1/2}$ when BC appears.

$$Cr + C \rightarrow Cr_{23}C_6 \qquad (6)$$

$$Cr + C \rightarrow Cr_7C_3 \qquad (7)$$

At the higher temperature of 1473 K, the Cr_7C_3 becomes a layer zone and the Cr_3SiC_x is newly formed according to reaction (8)
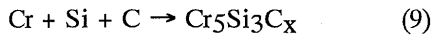
$$Cr + Si + C \rightarrow Cr_3SiC_x \qquad (8)$$

The structure of the SiC/Cr interface becomes $SiC/Cr_3SiC_x/Cr_7C_3/Cr_{23}C_6/Cr$ (Fig.5(b)). Thus, the phases are formed along the tie-lines $Cr_{23}C_6$-Cr_7C_3-Cr_3SiC_x in accordance with the Cr-Si-C phase diagram. During bonding, reactions (6) and (7) continue on the Cr side and reaction (8) on the SiC side proceeds to supply C and Si.

The elements in reaction (6),(7), and (8) are supplied by the following diffusion processes. In the first process SiC decomposes into Si and C at the beginning of bonding, and the Si and C diffuse as Cr_3SiC_x. Further carbon diffuses through Cr_7C_3 and $Cr_{23}C_6$ layer phases to the Cr side. In the second process Cr diffuses through the reaction phases to the SiC side. The C in reaction (6) is supplied by the first process. The Cr in reaction (8) is supplied by the second process. The elements of reaction (7) are supplied by the two process (1) and (2).

At the higher bonding temperature of 1573 K the amount of the elements arriving by these diffusion processes is that necessary to form the three phases Cr_3SiC_x, Cr_7C_3 and $Cr_{23}C_6$. Then $Cr_5Si_3C_x$ newly

forms at the interface between SiC and Cr_3SiC_x by reaction (9).

$$Cr + Si + C \rightarrow Cr_5Si_3C_x \qquad (9)$$

The formation of the reaction phase $Cr_5Si_3C_x$, which is connected by tie-line to SiC as well as Cr_3SiC_x in the Cr-Si-C phase diagram, completes the diffusion path between SiC and Cr. This diffusion path, which is formed during bonding, is $SiC/Cr_5Si_3C_x/Cr_3SiC_x/Cr_7C_3/Cr_{23}C_6/Cr$. The Si and C diffuse from SiC to Cr though the compounds along the lie-lines, and Cr diffuses transversely along the tie-line from Cr to SiC.

At the bonding temperature 1673 K, the four reaction phases increase in thickness, and the chromium foil reduces its thickness significantly. At the higher bonding temperature of 1773 K, Si and C continue to diffuse from the SiC side to Cr_3SiC_x and $Cr_{23}C_6$, though the Cr in the central part is completely consumed by the phase reaction. Consequently, the phases Cr_3SiC_x and $Cr_{23}C_6$ disappear due to continuing elemental diffusion, and the interface structure changes to $SiC/Cr_5Si_3C_x/Cr_7C_3/Cr_5Si_3C_x/SiC$ (Fig.5(e)).

2.2 Kinetics of Phase Formation and Growth

The basic quantitative formulation for the growth of phases formed in a bulk diffusion path is discussed in terms of ternary diffusion theory. Kirkaldy [5] and
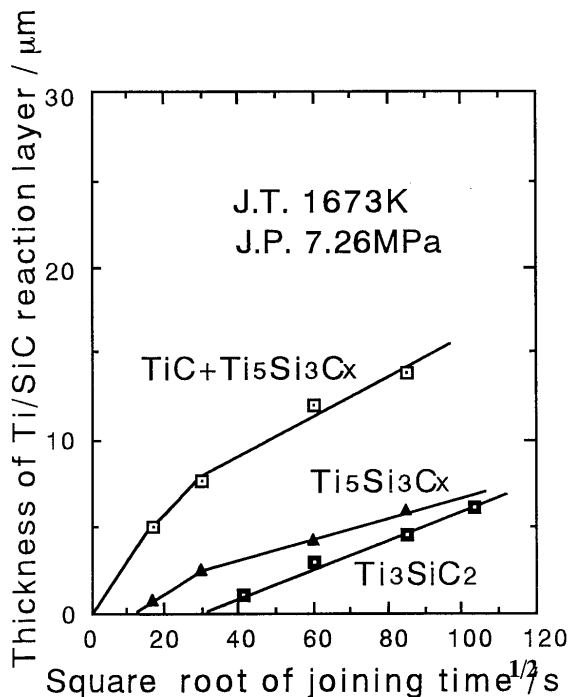
Chang [6] have applied their solution to the growth of multi-phase ternary systems. **Figure 6** represents the formation of β and the composition at distribution between α and β. The shift of $x^{\alpha,\beta}$ at the interface between α and β in a two-phase ternary diffusion couple is given as,

$$x^{\alpha,\beta} = \kappa\sqrt{t} \qquad (10)$$

, where k is a complex factor including diffusion factors. This concept can be also applied to the growth of β from a ternary α/γ diffusion couple as given in **Fig. 6** [6]. The growth of the β-phase layer as a function of time is,

$$x^{\beta} = [\kappa^{\beta,\gamma} - \kappa^{\alpha,\beta}]\sqrt{t} = \kappa^{\alpha,\beta,\gamma}\sqrt{t} \qquad (11)$$

The intermediate phase grows as the square root of bonding time, t , where the factors of $\kappa^{\alpha,\beta,\gamma}$ include the diffusions at the interface between β and γ or α and β. Similar relations are also thought to occur in the growth of a intermediate phase separated by other interfaces.

In actual formations of several reaction phases at the diffusion path AC/AB/BC/B, the phases will appear after a incubation time after the appearance of the first reaction phase. The reaction phase AB first grows with a slope against $t^{1/2}$ as shown in **Fig. 7**(a), where the interface structure is given in **Fig. 7**(b). The AB phase growth adopts another slope after the formation of BC, as shown in **Figs. 8**(a) and (b).

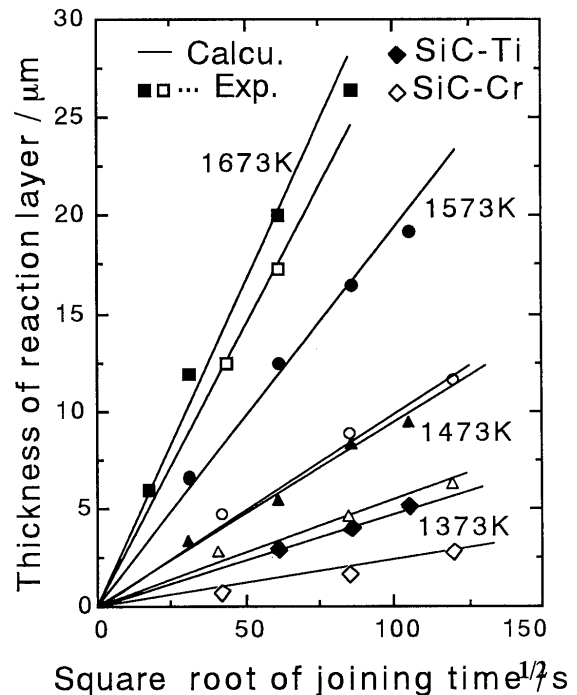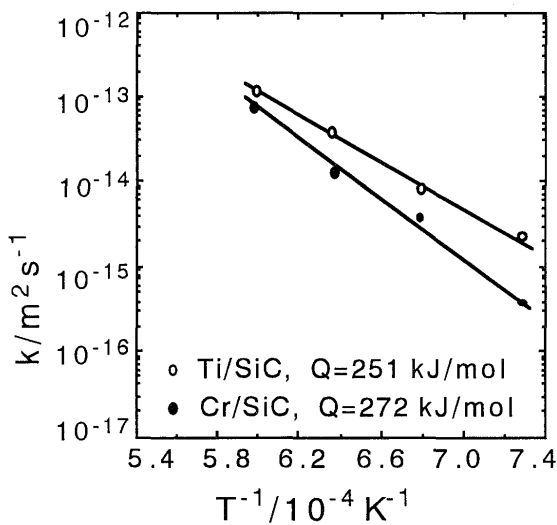Fig. 9 Change in thickness of reaction phases in SiC/Ti.

Fig. 10 Change in total thickness of reaction phases in SiC/Ti or SiC/Cr with $t^{1/2}$.

Table 2 Activation energies of Q and reaction constants of ko for SiC/Metal.

Composite	Q(kJ /mol)	ko(m²/s)	Ref.
SiC/Ti	251	1.38×10^{-5}	Present work
SiC/Ti	250	1.84×10^{-5}	K.Kurokawa [8]
SiC/Ti	274	4.58×10^{-4}	P.Martineau [9]
Cr/SiC	272	1.95×10^{-5}	Present work
Cr/SiC	220	- - -	K.Kurokawa [8]
SiC/Nb	359	1.48×10^{-5}	Present work
SiC/Ta	266	1.82×10^{-5}	Present work

Fig. 11 Temperature dependence of k for SiC/Ti and SiC/Cr.

Before the interface reaction the complete diffusion path between SiC and Ti, $Ti_5Si_3C_x$ contacting TiC appears at 1473 K for 0.9 ks as shown **Fig. 3**(a). Backhause-Ricoult discussed the growth kinetic of the reaction zone 1). He estimated the diffusion coefficients for 1473 K, which are listed in **Table 1**. The estimated diffusion constant of Ti_5Si_3 is in agreement with our experimental observation of $k=9.6 \times 10^{-15} m^2/s$ at 1473 K.

At the interface of the SiC/Ti couple [4], the reaction layers of $Ti_5Si_3C_x$ including TiC, $Ti_5Si_3C_x$ and Ti_3SiC_2 phases are in sequence formed at SiC/Ti interface, and the ternary compound of Ti_3SiC_2 appears at the final stage at 1673 K as shown in **Fig. 9**. This late appearance of Ti_3SiC_2 is explained by the slow formation of Ti_3SiC_2 at the interface between SiC fiber and Ti matrix in SiC fiber reinforced Ti-base composites.

Experimental data [7] indicate that the total thickness, including all reaction phases, grows as the square root of bonding time at a bonding temperature, and the reaction constant k is given as,

$$x^2 = k \cdot t \qquad (12)$$

$$k = k_0 \cdot \exp(-Q/RT) \qquad (13)$$

where ko and Q are the rate constant and activation energy for reaction phase, regarding the reaction phases as a single layer. **Fig. 10** represents the change in total thickness of reaction phases for SiC/Ti and SiC/Cr with $t^{1/2}$. The rate constant of SiC/Ti and SiC/Cr are also plotted against T^{-1} as shown in **Fig. 11**. The data of Q and ko for SiC/Metal systems are summarized at **Table 2**. From the values in **Table 2** we can calculate the growth rates of reaction phases at the SiC/Metal interface, which are given by the lines in **Fig. 9**.

3. Conclusions

Reaction mechanisms at interface between dissimilar materials are discussed in this article. The phase stabilities of reaction phases are discussed using a change in free energy of interfacial reactions between dissimilar materials such as ceramic/metal systems. The sequence of reaction phases at the interface is dominated by a diffusion path between ceramic and metal, expressed on the corresponding ternary phase diagram.

The case of SiC/Ti is presented. The growth rates of reaction phases are discussed, and the change in total thickness of reaction phases are expressed with $t^{1/2}$ and the cases of SiC/Metal presented. By using the activation energies and rate constants we can calculate the growth rate of the reaction zone at the SiC/Metal interface.

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