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Interface chemistry of SiC/Co reaction

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SiC/Co 반응의 계면화학

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Abstract Reaction coulples of SiC with cobalt were annealed in an Ar/4 vol% H_2 atmosphere at temperatures between 950 and 1250℃ for various times between 4 and 100 h. At temperatures above 950℃, solid state reactions lead to the formation of various silicides with carbon precipitates. The typical reaction layer sequence was SiC/CoSi + C/Co_2Si + C/Co_2Si/Co_2Si + C/·····/Co_2Si/Co in the reaction zone. The mechanism of the periodic band structure formation with the carbon precipitation behaviour was examined and discussed in terms of reaction kinetics and thermodynamic considerations. The growth of the reaction zone has a square root of time dependence. The reaction kinetics is proposed to estimate the effective reaction constant from the parabolic gowth of the reaction zone. The mechanical properties of the reaction zones were determined by the microhardness test.

요 약 SiC/Co 반응커플을 Ar/4 vol% H_2 분위기하에서 950℃에서 1250℃ 범위에서 4시간에서 100시간까지 열처리하였다. 950℃ 이상의 온도에서의 고상반응으로 여러가지 규소화물과 탄소석출이 형성되었다. 이 반응 zone에 있어서의 전형적인 반응층의 순서는 SiC/CoSi + C/Co_2Si + C/Co_2Si/Co_2Si + C/·····/Co_2Si/Co이었다. 그리고 탄소석출거동을 동반한 주기적인 띠구조의 형성기구가 반응운동학과 열역학적인 고찰을 통하여 조사되어졌고 논하여졌다. 이 반응 zone의 성장은 시간의 함수관계를 가지며 이러한 반응운동학이 반응상수의 측정을 통하여 제시

되어진다. 또한 microhardness 측정을 통하여 반응 zone의 기계적인 물성이 조사되어졌다.

1. Introduction

Solid state reactions between ceramics and metals are of great interest in materials science because of the technological applications for devices fabricated with both ceramic and metal components. SiC is used for high temperatures applications in form of monolithic ceramic or metal matrix composites [1-3]. SiC is also potentially a useful semiconducting material for high temperatures, high frequency and high power electronic devices [4-6]. In all these applications as well as for the process of joining SiC and SiC to metal with metallic intermediates detailed knowledge about SiC/metal interactions and the thermal stability of SiC/metal interfaces is of primary importance [7-9]. The chemical, thermal and crystallographic compatibility, which is dependent on the interfacial reaction, thermal expansion mismatch and lattice mismatch, must be considered to establish the thermal stress gradients across the formed reaction zone.

The properties of SiC/metal contacts are of increasing technological interest as the result of the large band gap of single crystal SiC (2.9 eV) [5]. The large band gap allows SiC to be used in a variety of solid state devices. In the case of other more common semiconducting devices, knowledge of the reactivity, thermal stability and electronic structure of semiconductor/metal interfaces is extremely imporant for understanding the devices and controlling device performances. One area of interest is the use of the low temperatur silicide forming metals on SiC substrates in the attempt to form contacts after thermal annealing. Many metals have a strong tendency to interdiffuse at semiconductor/metal interfaces and most metals readily form carbides or silicides. A thorough characterization and understanding of SiC/metal interfaces, in terms of reactivity and thermal stability, is therefore crucial in the design of SiC devices.

Recently, a few studies of the interaction between SiC and various types of metals have been reported [10-15]. However, most of works were phenomenological in nature because of the complex chemistry of interface formations, and the mechanisms proposed by the works were somewhat obscure due to the complicated experimental conditions. Therefore, more detailed investigations of the interfacial reaction are required for the improved understanding of SiC/Co interfaces. In this paper, we investigate the interface structure and reaction kinetics of SiC/Co from a different perspective using thick metal foils. More detailed investigations are presented to provide interface formations, periodic band structure and carbon precipitation behavior, and mechanical properties of the reaction zones are proposed by the microhardness test.

2. Experimental procedure

The starting materials used for the experiments were high density sintered α-SiC from "Elektroschmelzwerk Kempten", ESK, and thick cobalt foils from Alfa Prod./Johnson Matthey Company. The polycrystalline SiC contained 1.5 wt% total impurities, such as carbon and aluminium (ESK). The cobalt foil has a purity of 99.997 % and a thickness about 0.5 to 1 mm. SiC plates were cut into small pieces with a diameter of 20 mm and a thickness of 3 mm and ground with a BN/C disk. The SiC plates were then polished with a diamond disk using diamond pastes of 30, 15, 3, 1, μm and hyprez liquids (polishing solution). The ceramic and metal samples were ultrasonically cleaned in ethanol, rinsed with water and dried. After polishing the surface of SiC showed an average roughness of 4.7 nm by the measurement of surface profilometry. The SiC surface has a typical mixed structure of globular to long/plate form, and the average grain size is about 4 μm.

Most systematic annealings were conducted in a high temperature vacuum furnace with a graphite heating element manufactured by Degussa/Germany. The ceramic and metal reaction couples were placed in a graphite crucible and loaded with a weight of 5 kg. The specimens were surrounded by titanium to remove the residual oxygen during the annealing time. After positioning the samples the furnace was evacuated to be 6×10^{-6} mbar and subsequantly filled with a gas mixure of Ar/4 vol% H_2 for the annealing time. The couples were annealed at temperatures between 950 and 1250℃ for 4 to 100 h. Thermocouples of type EL18 (PtRh30/PtRh6) were used for the temperature measurement. The heating rate was set between 20 and 30 K/min and the cooling rate between 5 and 10 K/min.

The reaction couples were cut by a diamond saw, coated with nickel by electrical deposition and then imbedded in copper resin. After mounting the reaction couples were ground on a diamond disk, polished with diamond paste of 30, 15, 6, 3 and 1 μm and finished using an with Al_2O_3 suspension. The polished cross sections were investigated using optical microscopy and scanning electron microscopy (SEM). Quantitative atomic concentration profiles of silicon, carbon and cobalt were measured using electron probe microanalysis (EPMA). The mechanical properties of the reaction zone were determined using microhardness test.

3. Results

Fig. 1 shows a cross-sectional view of the overall reaction zone of SiC/Co after annealing at 1050℃ for 64 h. The reaction consists of various kinds of distinct region. This constitution could be identified by the measurements using EPMA. Based on the EPMA, quantitative analysis over the overall reaction zones is represented in form of line scan for the element silicon, carbon and cobalt in Fig. 2, which is corresponding to the region in Fig. 1. Adjacent to the SiC (SiC reaction zone) a layer of cobalt silicide with carbon precipitates was observed in Fig. 1 (b). Concentration profiles across the SiC reaction zone, which was determined by EPMA in Fig. 2 (b), indicated the formation of CoSi + C. Neighbouring the SiC reaction zone

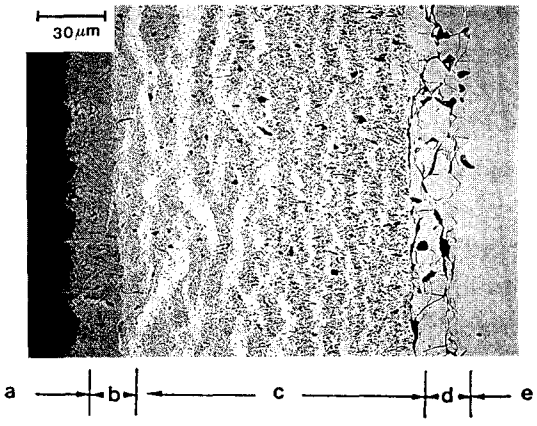


Fig. 1. Scanning electron micrograph showing a cross-sectional view of the overall reaction zone of SiC/Co after 64 h at 1050℃ ; (a) SiC, (b) SiC reaction zone of CoSi + C, (c) alternating layers of Co_2Si + C/Co_2Si/Co_2Si + C/····· (d) metal reaction zone of Co_2Si and (e) Co metal.

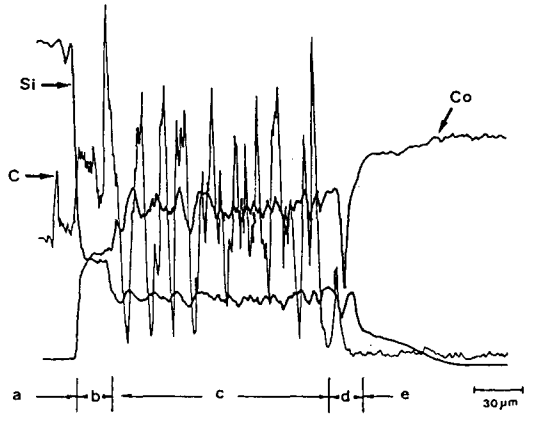


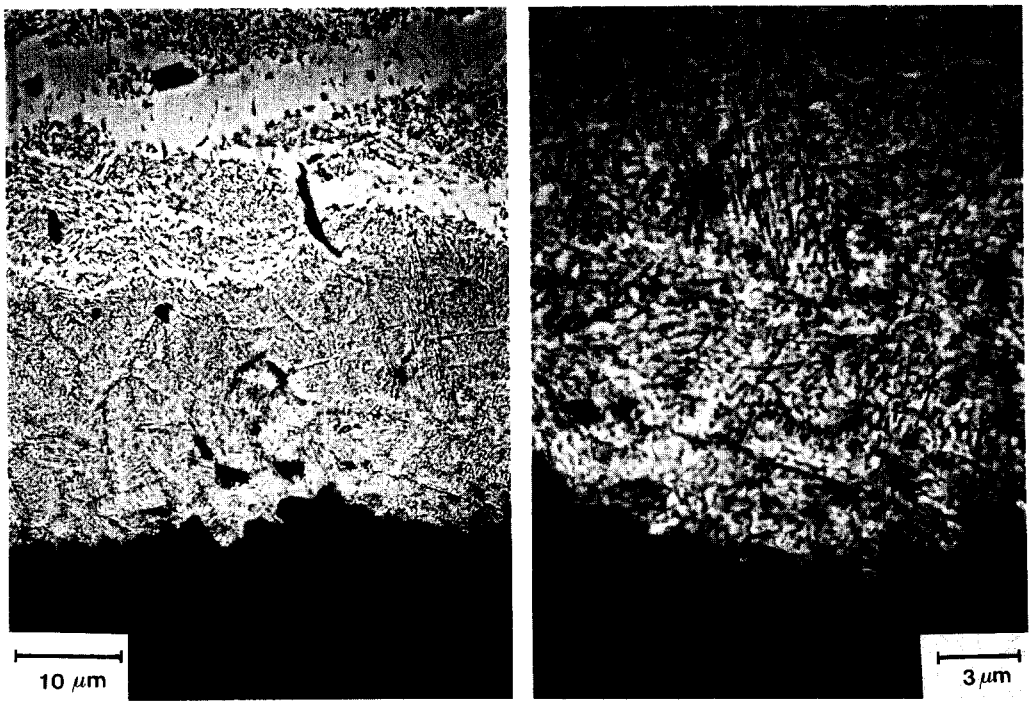
Fig. 2. EPMA line scan for silicon, carbon and cobalt over the corresponding SiC/Co reaction zone in Fig. 1 ; (a) SiC, (b) SiC reaction zone of CoSi + C, (c) alternating layers of Co_2Si + C/Co_2Si/Co_2Si + C/·····, (d) metal reaction zone of Co_2Si and (e) Co metal.

two coexisting phases are followed by resulting in the alternating layer sequence of small stripes from cobalt-rich silicide (Co_2Si) extending the carbon precipitates in the wide reaction zone in Fig. 1 (c) and Fig. 2 (c).

The micrsotructure of the carbon existed in the area adjacent to the SiC reaction zone is composed of very fine carbon precipitates by comparison with grob carbon precipitates in the areas farther removed from SiC reaction front to cobalt metal. On the other hand, adjacent to the cobalt metal (metal reaction zone) cobalt-rich silicide (Co_2Si) is formed in the absence of carbon precipitates in Fig. 1 (d), as resulted in EPMA in Fig. 2 (d). In all cases of SiC/Co samples, pores and cracks were observed in this metal reaction zone during annealing experiments between 950 and 1250℃ for various times. According to the concentration profile for cobalt, silicon and carbon by EPMA, an inward difussion of silicon into the cobalt metal was detected to a depth of 70 μm in Fig. 2 (e).

In the contact area to the SiC reaction interface a relatively wide band from CoSi with fein carbon precipitates was observed. Fig. 3 (a) and (b) show high magnifications microstructures of the SiC reaction zone of CoSi + C. In this contact area exhibited in a mixed state, very fein carbon precipitates are existed by a type of stripes along the boundary phase. The distribution of the carbon precipitates along the boundary phase is suggested to be the results of the behaviour of the typical microstructure of SiC of globular form to long/plate form.

Finer details of the carbon precipitates be-



(a) (b)

Fig. 3. High magnification scanning electron micrographs of the SiC reaction znoe showing a relatively wide band from CoSi with fein carbon precipitates.

haviour in the alternating layers are shown in the EPMA images of Fig. 4. The secondary electron image and X-ray maps with the distribution of the element silicon, carbon and cobalt could be identified that the carbons are revealed in a regular arrangement in the reaction phase of Co_2Si independing on the distribution of silicon and cobalt.

The periodic band structure with carbon precipitates was examined by quantitative analysis of the element silicon, carbon and cobalt showing the avarage concentration in Table 1. The analysis were performed over the corresponding SiC/Co reaction zone (Fig. 1) from the SiC over the SiC reaction zone with the various layers (1st dark layer, 2nd light layer, 3rd dark layer,……) to the cobalt. The avarage concentration of cobalt and silicon in 1st dark layer adjacent to SiC shows 25.6 wt% silicon, 51.6 wt% cobalt and 23.5 wt% carbon corresponding to the value of 24.3 at% silicon, 23.5 at% cobalt and 52.3 at% carbon. This atomic ratio points at the presence of CoSi and carbon corresponding to two carbon atoms against CoSi. In the adjoining light layer the reaction phase of Co_2Si with the concentraction of 20.6 wt% (32.0 at%) for silicon, 80.1 wt % (68.0 at%) for cobalt is existed without carbon. The concentration of carbon in all dark layers fluctuates between 21.52 and

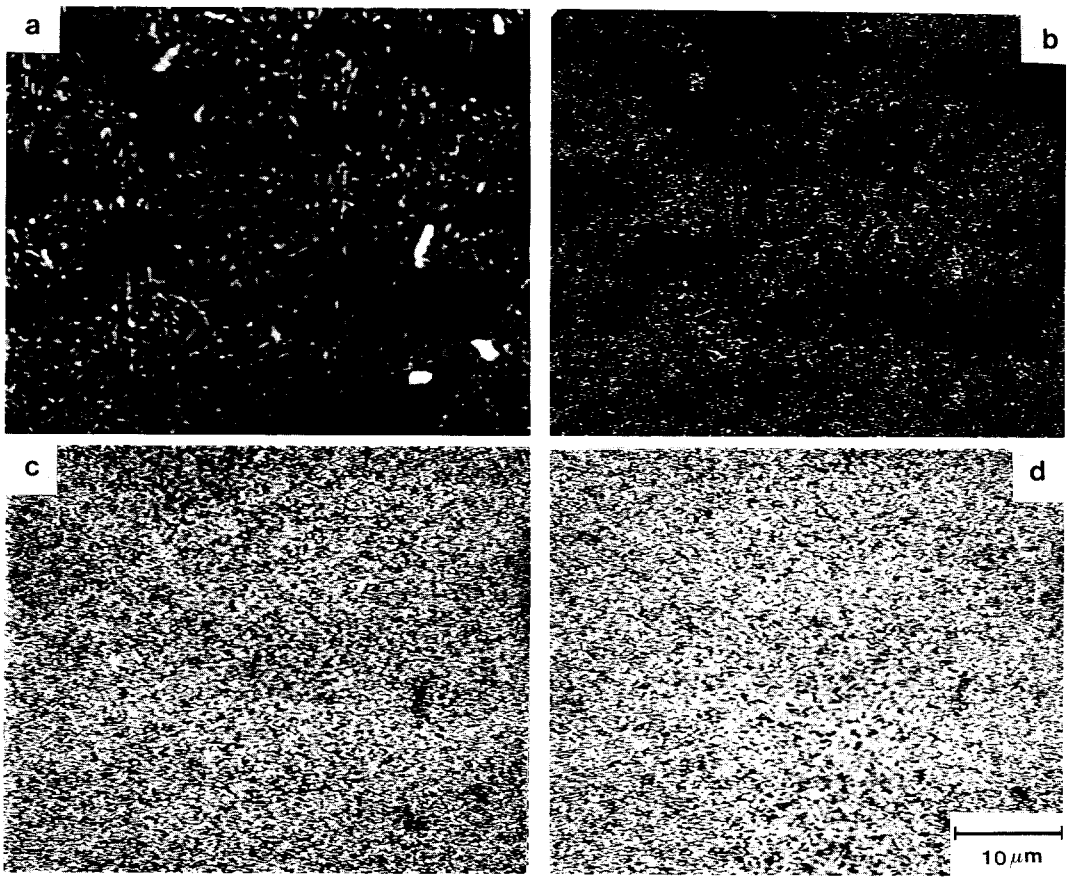


Fig. 4. EPMA images of the alternating layers : (a) secondary electron image; (b) carbon x-ray map; (c) cobalt x-ray map; (d) silicon x-ray map.

23.45 wt%. It is noted that the value of carbon has no tendency to increase and decrease. The concentration relationship of silicon/cobalt was confirmed to be also constant but independent on the presence of the carbon precipitations. This atomic relationship correspond to Co_2Si. The atomic relationship of the three elements in the dark layers yields to one Co_2Si and about three carbon atoms.

A SEM micrograph (Fig. 5) shows the distinguishable boundary between the light layer from Co_2Si and dark layer from Co_2Si +C in details. The carbon particles are distributed partially and randomly in the lihgt area in comparison with the dark area featured by the fein carbon precipitations between Co_2Si phases. The concentration of Co_2Si in the dark area is equivalent to it in the light area. The width of the bands of Co_2Si and $Co_2Si + C$ becomes smaller depending upon the location from the SiC reaction interface. Moreover the periodic carbon precipitataions are revealed by the structure change according to the location from SiC reaction interface. This structure change of

Table 1
Average concentration of silicon, cobalt and carbon in the SiC/Co reaction zone

Microstructure	wt% Si	wt% Co	wt% C
A. SiC	65	0	35
B. Reaction zone			
1st dark layer	25.6	51.6	23.5
2nd light layer	20.6	80.1	0
3rd dark layer	16.1	64.1	21.8
4th light layer	20.7	80.4	0
5th dark layer	16.4	65.0	23.5
6th light layer	20.6	79.9	0
7th dark layer	16.0	65.0	21.5
8th light layer	20.5	79.8	0
9th dark layer	16.4	65.8	22.9
10th light layer	20.6	80.2	0
11th dark layer	16.2	65.8	22.5
12th light layer	20.6	80.3	0

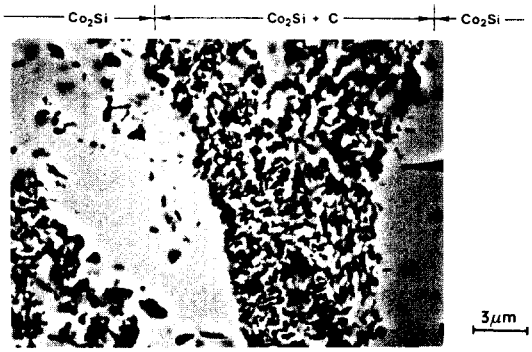


Fig. 5. Scanning electron micrograph of the distinguishable boundary between Co_2Si and $Co_2Si + C$ phase in the alternating layer.

carbon could be observed by the overall reaction zone. It is due to the different thermodynamic driving force and kinetics between the reaction at the SiC reaction interface and the reaction at the metal reaction interface. A SEM micrograph (Fig. 6) shows the metal reaction zone in the area adjacent to cobalt. As resulted in SEM/EDAX and EPMA, it is evidenced to be the carbon free Co_2Si phase. After annealing at 1050℃ for 64h the thickness of this zone indicates about 25 μm. In contrast to the periodic band structure in the center of this reaction zone, crack and pore formations were observed in all SiC/Co samples.

The generation of the cracks is caused by the various plastoelasic process of the reaction phases, SiC and metal, which is based on the various thermal expansion coefficients during cooling of the samples from annealing temperatures. It was already suggested in the works [16, 17] that during

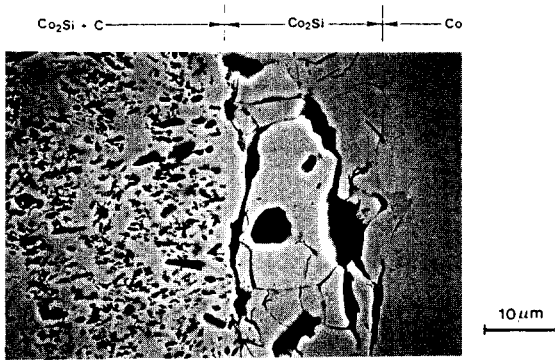


Fig. 6. Scanning electron micrograph of the metal reaction zone.

cooling process of a ceramic/metal reaction couple critical tensile stress is induced at the ceramic edge and critical compressive stress at the metal edge. In temperature ranges between 293 and 1273 K the thermal expansion coefficients show $4.0 \sim 6.0 \times 10^{-6}$/K for SiC, $6.9 \sim 16.3 \times 10^{-6}$/K for Co and 11.1×10^{-6}/K for CoSi. During SiC/Co reaction the volume reduction of the reaction products could be induced to cause the mismatch. The volume reduction of the reaction products of $Co_2Si + C$ and $CoSi + C$ cound be calculated to be $\Delta V = -1.18$ cm³/mol SiC and $\Delta V = -0.74$ cm³/mol SiC.

The mechanical properties of the periodic band structure with carbon precipitates were examined by the microhardness test. The avarage microhardness value in the SiC/Co reaction zone are listed in Table 2. The analysis was performed over the cross-sections of the reaction zone from the SiC over the SiC reaction zones with the various layers to the cobalt. As the result, the 1st SiC reaction zone ($CoSi + C$) shows substantially high microhardness value of 2691 kp/mm², in comparison to the low value of 349 kp/mm² in the metal reaction zone. The carbon precipitation zone (CPZ) of $Co_2Si + C$ as well as carbon free zone (CFZ) of Co_2Si shows 1267 to 689 kp/mm². It is assumed that the value of the microhardness has the tendency to decreases associated with the location from the SiC reaction interface.

Table 2
Average microhardness value in the SiC/Co reaction zone

Zone	Phase	Microhardness (kp/mm²)
Ceramic	SiC	3844
SiC reaction zone	$CoSi + C$	2691
CPZ	$Co_2Si + C$	1267
CFZ	Co_2Si	689
CPZ	$Co_2Si + C$	835
Metal reaction zone	Co_2Si	349
Metal	Co	232

CPZ ; Carbon precipitation zone.
CFZ ; Carbon free zone.

The kinetics of the reaction SiC and cobalt have been studied systematically at temperatures between 950 and 1250℃ for various times between 4 and 100 h. On the assumption that the reaction is diffusion controlled, the thickness of the reaction zone follows a parabolic growth law. The thicknesses of the reaction zone have been plotted at various temperatures as a function of the square root of annealing time in Fig. 7. As the reaction thickness shows linear and parabolic relationship, the reaction seems to be

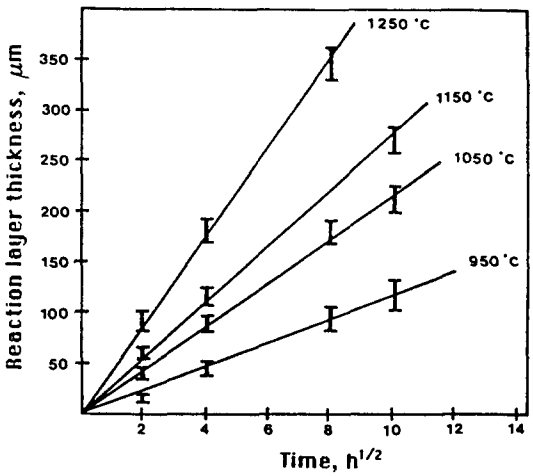


Fig. 7. Growth of the reaction thickness ir SiC/Co reaction zone vs square root of time for various times and temperatures.

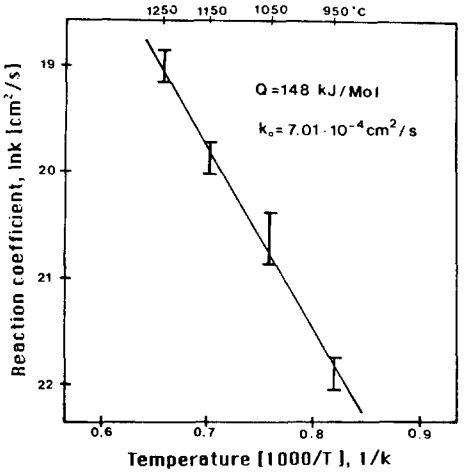


Fig. 8. Reaction coefficients in SiC/Co reaction zone vs reciprocal absolute temperature [$\ln k = f(1/T)$].

diffustion controlled. The reaction coefficient is proportional to x^2/t, so that the logarithm of the reaction coefficients vs the reciprocal of the absolute temperature has been plotted in Fig. 8. The activation energy and the frequency factor are proposed to be 148 kJ/mol and 7.01×10^{-4} cm^2/s respectively. The activation energy is similar to the values for various metal silicides formed by reactions between Si and metals at lower temperatures [18].

4. Discussion

The results could be explained in terms of interface structures and reaction kinetics, which lead to the formation of cobalt silicides and carbon precipitates in the diffustion controlled reaction zones. Considering the overall reactions between SiC and cobalt, the thermodynamics of the reactions could be described by calculating the Gibb's free energy (ΔG) [19] for various reactions within the system. Table 3 shows Gibb's free energy of the possible reactions for SiC/Co system at 1050℃. The result predicts which phases are stable at the thermo dynamic equilibrium. At temperature 1050 ℃, cobalt is known to react with silicon to form two silicides CoSi and Co_2Si, because the ΔG-values are highly negative. Less negative values are calculated for the corresponding reaction $Co + SiC = CoSi + C$ and $Co + \frac{1}{2}SiC = \frac{1}{2}Co_2Si + \frac{1}{2}C$, because of the energy needed for SiC decomposition. $CoSi_2$ and Co_2C are thermodynamically not possible at this temperature. As a result, the solid state reaction between SiC and cobalt could be prescribed by the decomposition of SiC and the formation of $CoSi + C$, $Co_2Si + C$ and Co_2Si predominantly.

The mechanism of the periodic band struc-

Table 3
Gibb's free energy of the possible reactions for the SiC/Co system at 1050℃

Possible reactions	Gibb's free energy at 1050℃ (kJ/mol)
$Co + \frac{1}{2} SiC = \frac{1}{2} Co_2C + \frac{1}{2} Si$	27.5
$Co + 2\,SiC = CoSi + 2C$	1.4
$Co + \frac{1}{2} SiC = \frac{1}{2} Co_2Si + \frac{1}{2} C$	- 33.5
$Co + SiC = CoSi + C$	- 37.4
$Co + Si + CoSi$	- 86.7
$Co + \frac{1}{2} Si = \frac{1}{2} Co_2Si$	- 48.8

ture formation in SiC/Co reaction zone could be interpreted by the following four processes in Fig. 9. As shown in Fig. 9 (a), it is clear that SiC must be decomposed into silicon and carbon because of cobalt diffusion in SiC. In this case, when the cobalt reaches SiC interface the same amount of cobalt dissolves much more SiC, yielding much more free carbon. After decomposition of SiC, two types of interfacial reactions could be occurred in Fig. 9 (b). In the case of the reaction at SiC interface, cobalt reacts decomposed silicon and produces the reaction phase of CoSi + C. Considering the Gibb's free energy based on 1 g-atom cobalt at 1050℃ in Table 3, the possible reactions at SiC interface are as follows :

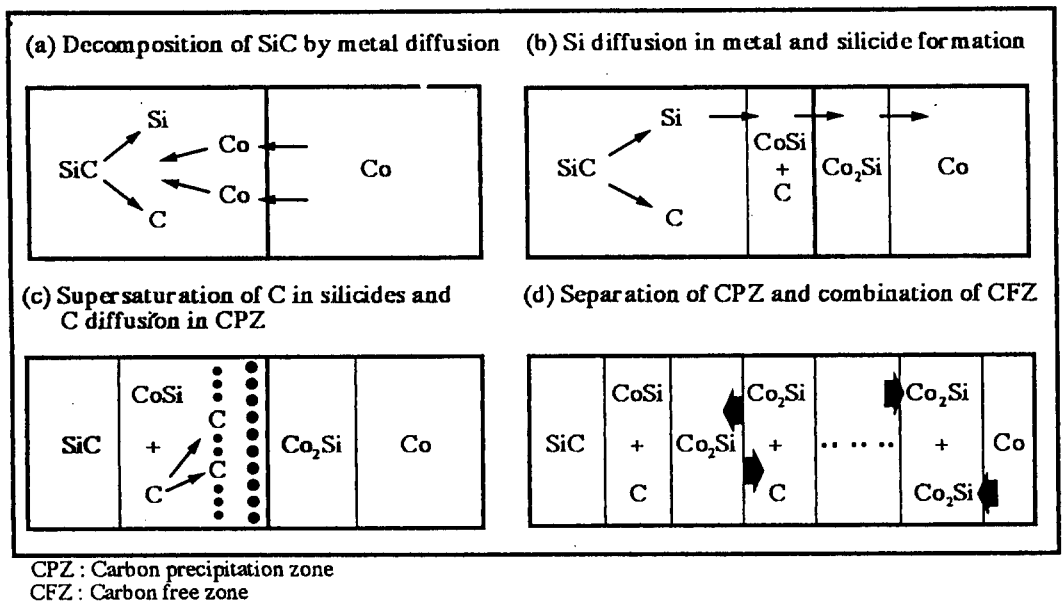


Fig. 9. Schematic representation of the mechanism of periodic band structure formation in SiC/Co reaction zone.

$$Co + SiC = CoSi + C : \Delta G = -37.4 \quad kJ/mol \quad (1)$$

$$Co + \frac{1}{2}SiC = \frac{1}{2}Co_2Si + \frac{1}{2}C : \Delta G = -33.5 kJ/mol \quad (2)$$

This thermodynamic data show the preferential formation of CoSi + C at this SiC reaction interface.

On the other hand, silicon diffused into cobalt and produces cobalt silcide at cobalt interface. At this reaction interface the Gibb's free energy based on 1 g-atom silicon at 1050℃ are as follows :

$$Si + 2Co = Co_2Si + C : \Delta G = -97.6 \ kJ/mol \quad (3)$$

$$Si + Co = CoSi : \Delta G = -86.7 \ kJ/mol \quad (4)$$

It is noted that only the reactions between silicon and cobalt by the silicon diffusion into cobalt and cobalt diffusion into cobalt silicide could be available at metal reaction interface. According to the thermodynamic data, the reaction phase of Co_2Si is formed predominantly at this metal reaction interface.

In addition, as shown in Fig. 9 (c), small carbon particles with a high density in CoSi precipitate out and diffuse along the silicide-carbon interfaces in CPZ. The pure silicide matrix band becomes broader and carbon supersaturation increases, until a new carbon precipitation occurs. Finally in Fig. 9 (d), as the reaction goes on, the CPZ at the SiC reaction zone becomes to separate into CPZ and CFZ by the carbon diffusion, and the CFZ at the cobalt reaction zone becomes to be combined by the two kinds of CFZ which were formed by the silicon diffusion into cobalt and cobalt diffustion into cobalt silicides.

Consequently, the carbon precipitations are revealed by the structure change according to the location from SiC reaction interface. This structure change of carbon could be explained by the thermodynamics and kinetics between the reaction at SiC reaction interface and the reaction from the location from the SiC reaction interface to cobalt reaction interface. According to the thermodynamic data at 1050℃, the decomposition of SiC at SiC interfacs exhibits positive Gibb's free energies, and the silicide formation at cobalt interface shows highly negative values. This difference of the Gibb's free energy provides the thermodynamic driving force to exhibit the structure change generated by the carbon precipitations and graphitizations varied as a function of the distance from the SiC reaction interface to cobalt reaction interface.

5. Conclusions

The solid state reaction between SiC and cobalt at temperatures between 950 and 1250℃ for various times between 4 and 100 h lead to the formation of various silicides with carbon precipitations extending the preiodic band structure of SiC/CoSi + C/Co_2Si + C/Co_2Si/……Co_2Si/Co in the reaction zone. The preferential reaction of Co + SiC = CoSi + C is exhibited at SiC reaction interface, and the predominant reaction of Si + 2Co = Co_2Si is available at cobalt metal

reaction interface.

The mechanism of the periodic band structure formation is SiC/Co reaction zone could be interpreted by the following four processes : (1) decomposition of SiC by cobalt diffusion, (2) silicon diffusion in cobalt and silicide formation, (3) supersaturation of carbon in silicides and carbon diffusion in CPZ and (4) separation of CPZ and combination of CFZ. The periodic band structure with carbon precipitations are revealed by the structure change according to the location from SiC reaction interface. The thermodynamic driving force caused by the difference of the Gibb's free energies for the possible reaction at SiC interface and cobalt interface provides to change the interface structure with the carbon precipitation behaviour and graphitization.

The generation of the cracks in caused by the various plastoelasic process and volume reduction on the reaction phases, SiC and metal. The avarage microhardness value has the tendency to decrease associated with the location from the SiC reaction interface. The reaction kinetics of growth in thicknesses of the reaction zone shows linear and parabolic relationship. The activation energy and the frequency factor are proposed to be 148 kJ/mol and 7.01×10^{-4} cm^2/s.

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