

# *In-situ* high temperature X-ray diffraction study of Co/SiC interface reactions

T. FUJIMURA\*, S.-I. TANAKA

Tanaka Solid Junction Project, ERATO, Japan Science and Technology Corporation,  
1-1-1 Fukuura, Kanazawa-ku, Yokohama 236-0004, Japan  
E-mail: to-fujimura@kawasaki-steel.co.jp

*In situ* experiments on the Co/SiC interface reaction were carried out with a high temperature X-ray diffractometer capable of measuring the X-ray diffraction pattern in 1–4s using an imaging plate. The kinetic formation processes of the interface reaction layer were measured in short-period exposure experiments with the apparatus. The time-temperature phase diagram of Co/SiC in N<sub>2</sub> was determined. Co<sub>2</sub>Si and CoSi were formed at the Co/SiC interface between 921 and 1573 K in N<sub>2</sub>. The formation of CoSi obeyed the parabolic rate law. The value of the activation energy was 95 kJ/mol. The results of thermal expansion coefficient measurements suggest that when a sample is cooled to room temperature, compressive strain caused by CoSi occurs on SiC. © 1999 Kluwer Academic Publishers

## 1. Introduction

SiC has been interested in the electronic device at high temperature and in severe environments [1]. Therefore, it is important that the elementary processes of metal/SiC interface reactions are investigated. In this work, we focused our attention on interface reactions of Co and SiC, because Co silicide has been widely used in VLSI technology for contacts and/or interconnects in silicon-based devices [1]. The interface reactions of Co/SiC have been investigated by several researchers [1–7]. All of them concentrated on carrying out measurements after the reaction, but *in situ* experiments are necessary to reveal the elementary reaction processes in detail. In these experiments, X-ray diffraction methods have an advantage for observation of crystal structure changes during the interface reaction.

In this paper, we describe *in situ* experiments on the Co/SiC interface reaction, which were carried out with a high temperature X-ray diffractometer [8, 9], capable of measuring the X-ray diffraction pattern in 1–4s using an imaging plate to elucidate the elementary formation processes of the reaction layer, the relationship between time and temperature in the phase transformation, the activation energy of the reaction layer, and the thermal strain relationship between the reaction layer and the substrate (SiC).

## 2. Experimental procedure

Polycrystalline  $\alpha$ -SiC (6H) [sintering additives; B, C: Toshiba Corporation] was cut into pieces measuring 20 mm  $\times$  10 mm  $\times$  0.5 mm. These were polished with a diamond whetstone and cleaned in acetone for use as substrates. A Co [purity 99.99%] thin film was de-

posited on the substrate by means of vacuum deposition at  $1 \times 10^{-3}$  Pa. The thickness of the thin film was 0.5  $\mu$ m.

Fig. 1 shows a schematic of the high temperature X-ray diffractometer [8, 9] which consists of a Seemann-Bohlin camera [10] and an imaging plate (IP) [11]. Because the Seemann-Bohlin camera is a parafocusing camera which produces high intensity diffraction lines and the two-dimensional IP has good X-ray sensitivity, this high temperature system can record complete diffraction patterns in 1–4s. Using Cu X-rays at 54 kV and 260 mA filtered by a Ni filter, a peak intensity of approximately 8000 counts is obtained from the (1 1 0) reflection of  $\alpha$ -Fe using a 2s exposure [8, 9].

The samples were heated from room temperature to between 871 and 1573 K at a rate of 60 K/min, held there for 1 h, and cooled to room temperature. This temperature process was performed in N<sub>2</sub>. The *in situ* measurements were carried out with repeated exposures (exposure time: 2s) during the heating process.

## 3. Results and discussion

### 3.1. Formation of reaction layer

Hexagonal type Co changed to cubic type Co (high temperature phase) during heating in N<sub>2</sub> and only cubic type Co existed at 871 K. Fig. 2 shows the change of the X-ray diffraction patterns of Co/SiC held at 921 K in N<sub>2</sub>. There are dead angles at the center of the diffraction patterns, because the apparatus uses two sheets of IP. Co<sub>2</sub>Si was found, and the intensity of the Co<sub>2</sub>Si diffraction peaks increased with time. There was a diffraction peak of C obtained by the dissolution of SiC. There were diffraction peaks of the polymorph of SiC. This

\* Present address: Analysis & Material Science Laboratory, Technical Research Laboratories, Kawasaki Steel Corporation, 1, Kawasaki-cho, Chuo-ku, Chiba 260-0835, Japan.

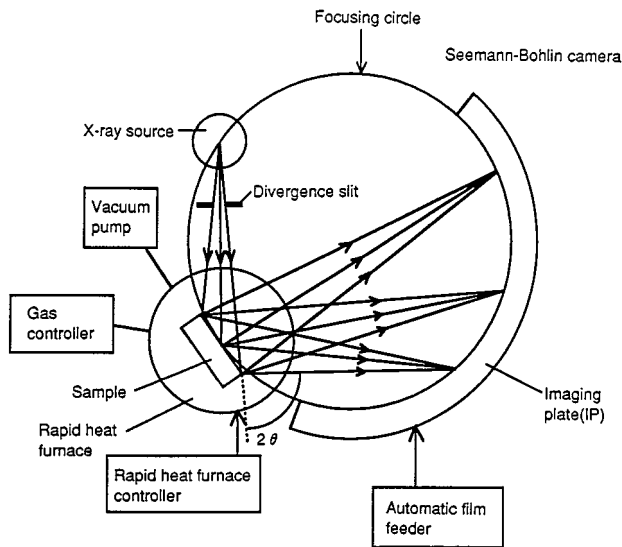


Figure 1 Schematic of the high temperature X-ray diffractometer [8, 9].

existed from the beginning and was not formed during the heating process. Fig. 3 shows the change of the X-ray diffraction patterns of Co/SiC held at 1173 K in  $N_2$ . The intensity of the  $Co_2Si$  diffraction peaks decreased with time, and the  $Co_2Si$  diffraction peaks disappeared at about 30 min. The CoSi diffraction peaks appeared at about 15 min, and the intensity of the CoSi diffraction peaks increased with time. Note that Co coexisted at this temperature. Fig. 4 shows the change of the X-ray diffraction patterns of Co/SiC held at 1573 K in  $N_2$ . The intensity of the Co diffraction peak disappeared with time, and all Co changed to CoSi after about 23 min. Fig. 5 shows a time-temperature phase diagram of Co/SiC in  $N_2$ . Note that these results were obtained under the experimental conditions in this work. According to the experiments conducted by Porter *et al.* [6], Co silicide and C coexist. Therefore it is thought that the same phenomenon, i.e., the coexistence of Co silicide and C, occurred in this work.

The above observations suggest that the reaction formulas are  $2Co + SiC \rightarrow Co_2Si + C$ ,  $Co_2Si + SiC \rightarrow 2CoSi + C$  and  $Co + SiC \rightarrow CoSi + C$ , where  $Co_2Si$  was formed a little. A model of these reactions is shown in Fig. 6. The diffusion path between SiC and Co is thought to be  $SiC \rightarrow Co_2Si + C \rightarrow Co$ , but  $Co_2Si$  changes to CoSi at high temperature. Because the diffusion path between SiC and Ni of  $\delta-Ni_2Si$  and  $\theta-Ni_2Si$  (high temperature phase of  $\delta-Ni_2Si$ ) growth in the experiments of Ni/SiC conducted by Fujimura and Tanaka [12] was  $SiC \rightarrow \delta-Ni_2Si + C \rightarrow Ni$ , but  $\delta-Ni_2Si$  changed to  $\theta-Ni_2Si$  at high temperature.

### 3.2. Activation energy of CoSi growth

In order to determine the growth rate of the CoSi layer at 1370, 1472 and 1573 K from the time history of the integrated intensity of (2 1 1) reflection of CoSi, the time history of the thickness of the CoSi layer at each temperature was calculated. It was assumed that the thickness of the CoSi layer formed from all of the deposited Co corresponds to the integrated intensity of (2 1 1) reflection in CoSi when the reaction layer of CoSi was completely formed. However, in this calculation, the effects of thermal expansion were ignored, since the values were compared with those obtained in thermal treatment experiments performed by other researchers. The relationship between the square of the thickness ( $x$ ) of CoSi layers at each temperature and time ( $t$ ) is shown in Fig. 7. It is apparent that the parabolic rate law ( $x^2 = Kt$ ;  $K$ : rate constant) [13] is upheld.

Since  $K$  is proportional to the diffusion coefficient,

$$\log K = 0.4343(-Q/RT) + A,$$

where 0.4343 is the conversion constant from natural logarithms to common logarithms,  $Q$  is the activation energy,  $R$  is the gas constant,  $T$  is the temperature and  $A$  is a constant.  $Q$  is obtained from the gradient of  $\log K$  and  $1/T$ . Fig. 8 shows the relationship between  $\log K$

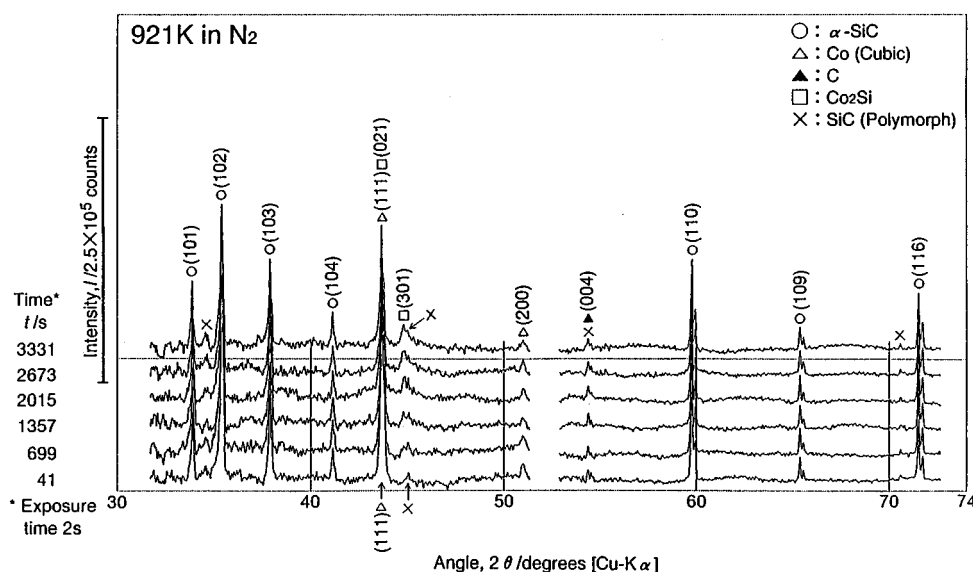


Figure 2 Change of the X-ray diffraction patterns of Co/SiC held at 921 K in  $N_2$ .  $Co_2Si$  was found, and the intensity of the  $Co_2Si$  diffraction peaks increased with time.

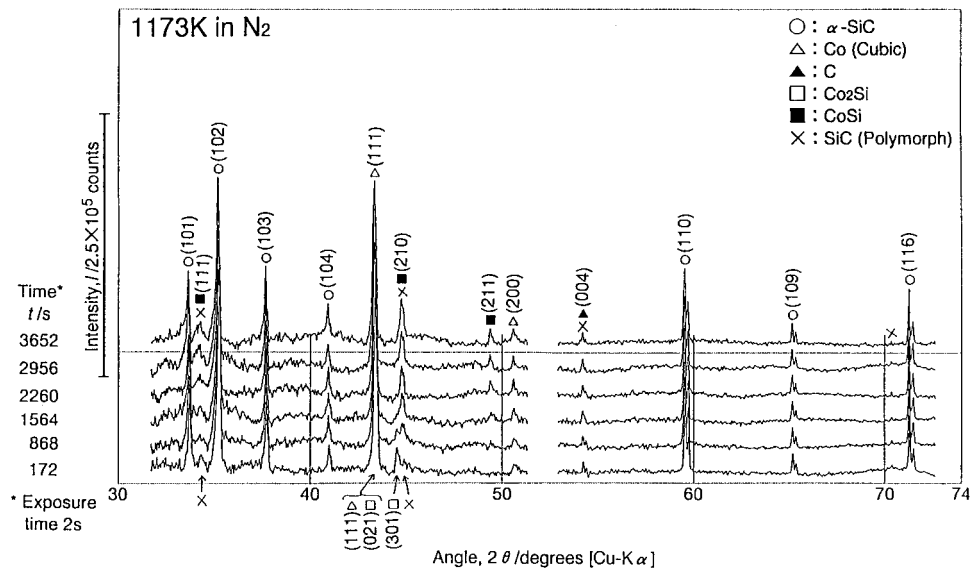


Figure 3 Change of the X-ray diffraction patterns of Co/SiC held at 1173 K in N<sub>2</sub>. The Co<sub>2</sub>Si diffraction peaks disappeared at about 30 min. The CoSi diffraction peaks appeared at about 15 min. Note that Co coexisted at this temperature.

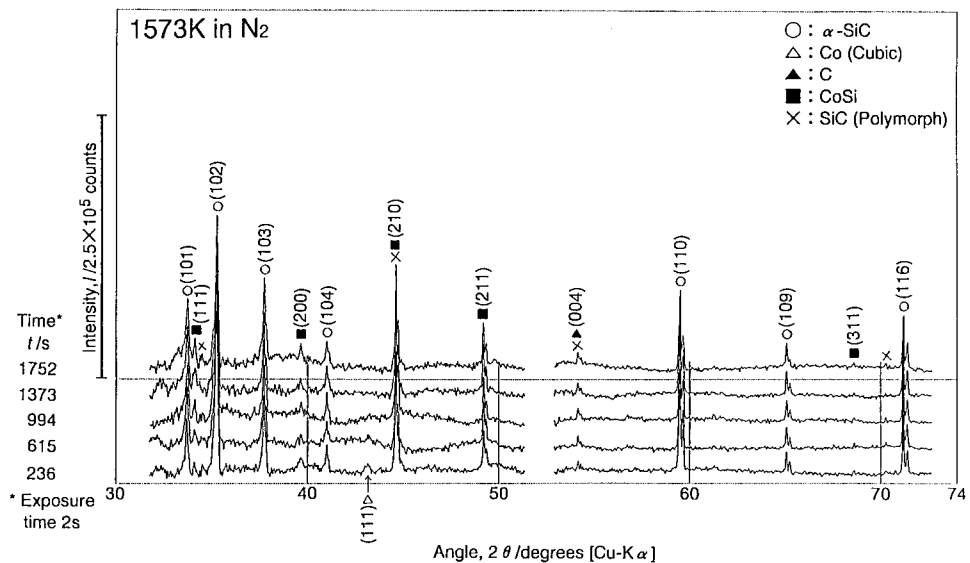


Figure 4 Change of the X-ray diffraction patterns of Co/SiC held at 1573 K in N<sub>2</sub>. All Co changed to CoSi after about 23 min.

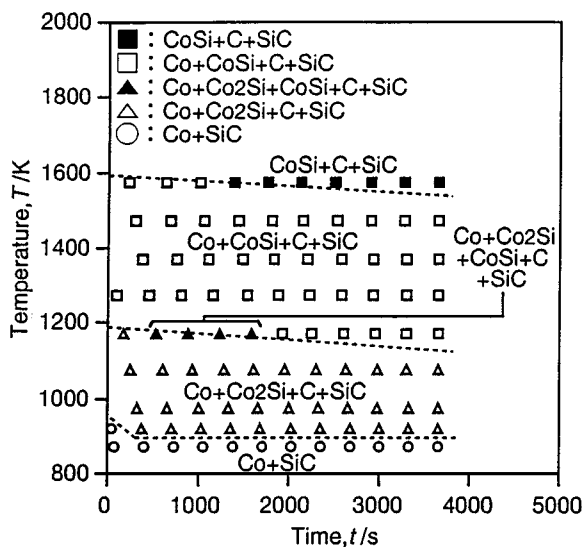


Figure 5 Time-temperature phase diagram of Co/SiC in N<sub>2</sub>.

and  $1/T$  for the growth of CoSi in our experiments. The value of  $Q$  was 95 kJ/mol.  $Q$  value for Co<sub>2</sub>Si<sub>3</sub> layer growth in the experiments of Co/SiC (1173–1423 K) in Ar conducted by Nogi *et al.* [2] was 106 kJ/mol, which is close to our value. Their reaction layer differs from our that, because our work was performed in N<sub>2</sub>.

TABLE I Thermal expansion coefficients evaluated from the lattice constants of SiC, Co and CoSi, which were calculated from the X-ray diffraction patterns at different temperatures. Reference values [14–16] are shown for comparison

Material (System)	Thermal expansion coefficient ( $\times 10^{-4}/\text{K}$ )		
	$a$	$c$	Reference
$\alpha$ -SiC (Hexagonal)	0.07	0.06	0.05 [14]
Co (Cubic)	0.16	—	0.16 [15]
CoSi (Cubic)	0.15	—	0.15 [16]

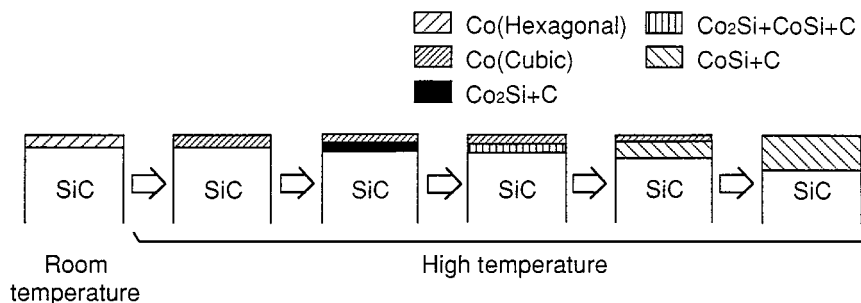


Figure 6 Formation model of the reaction layer at Co/SiC interface in  $N_2$ .

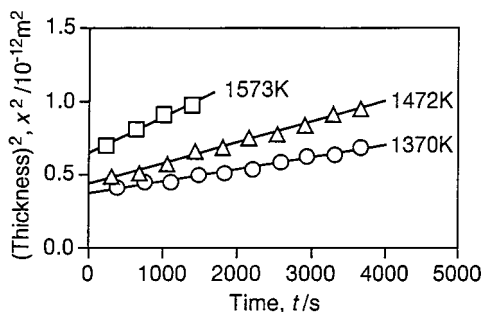


Figure 7 Relationship between the square of thickness ( $x$ ) of CoSi layers at each temperature and time ( $t$ ). The parabolic rate law is upheld.

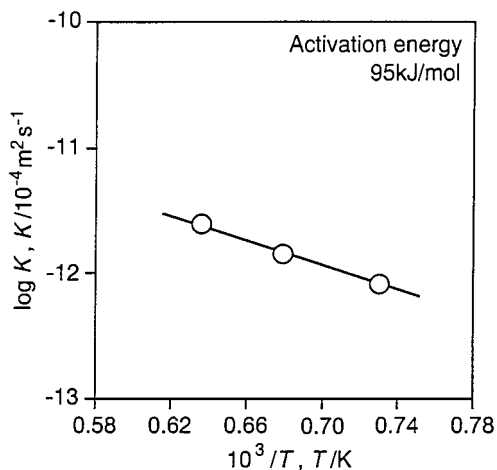


Figure 8 Relationship between  $\log K$  and  $1/T$  for the growth of CoSi. Activation energy was estimated as 95 kJ/mol.

### 3.3. Strain at interfaces

The average strains around the interfaces were verified, taking into account the reported values of the thermal expansion coefficients. Table I shows the thermal expansion coefficients evaluated from the lattice constants of SiC, Co and CoSi, which were calculated from the X-ray diffraction angles at different temperatures. The reference values [14–16] are shown for comparison. The value for CoSi is close to that for Co and is larger than that for SiC. It is thought that as a sample cools to room temperature, compressive strain caused by CoSi occurs on SiC.

### 4. Conclusions

*In situ* high temperature X-ray diffraction experiments were carried out on the Co/SiC interface reaction. The following conclusions were reached.

(1) The kinetic formation processes of the interface reaction layer were measured by short-period exposure experiments with a high temperature X-ray diffractometer.

(2) The time-temperature phase diagram of Co/SiC in  $N_2$  was determined.  $Co_2Si$  and CoSi were formed at the Co/SiC interface between 921 and 1573 K in  $N_2$ . The elementary reaction processes were  $2Co + SiC \rightarrow Co_2Si + C$ ,  $Co_2Si + SiC \rightarrow 2CoSi + C$  and  $Co + SiC \rightarrow CoSi + C$ , where  $Co_2Si$  was formed a little. Note that these results were obtained under the experimental conditions in this work.

(3) The formation of CoSi obeyed the parabolic rate law. The activation energy was 95 kJ/mol. This value is close to the value of Nogi *et al.* [2], but their reaction layer was  $Co_2Si_3$ . It is thought that the mismatch is caused by the difference of experimental atmosphere.

(4) The results of thermal expansion coefficient measurements suggest that when a sample is cooled to room temperature, SiC is compressed by CoSi at the interface.

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