

Interface formation and thermodynamics between SiC and thin metal films

Chang-Sung Lim, Kwang-Bo Shim*, Dong-Woo Shin** and Keun-Ho Auh*

Dept. of Material Chemical Engineering, Chonnam National University, Kwangju 500-757, Korea

** Ceramic Materials Research Institute, Hanyang University, Seoul 133-791, Korea*

*** Dept. of Inorganic Materials Engineering, Gyeongsang National University, Chinju 660-701, Korea*

SiC와 금속박막간의 계면형성 및 열역학

임창성, 심광보*, 신동우**, 오근호*

전남대학교 물질화학공학과, 광주, 500-757

*한양대학교 세라믹소재연구소, 서울, 133-791

**경상대학교 무기재료공학과, 진주, 660-701

Abstract The interface formation and reaction-product morphology between SiC and thin metal films were studied at temperatures between 550 and 1450°C for various times. The typical reaction layer sequence was CoSi/CoSi+C/CoSi/CoSi+C/.../SiC in SiC/Co reaction at 1050 and 1250°C for 2 h, while Ni₂Si/Ni₂Si+C/Ni₂Si/Ni₂Si+C/.../SiC in SiC/Ni at 950 and 1050°C for 2 h. Carbon precipitated preferentially on the outer surface and crystallized as graphite above 1450°C for SiC/Co reaction zone and 1250°C for SiC/Ni. The mechanism of the periodic band structure formation with carbon precipitation behaviour was discussed in terms of thermodynamic considerations.

요약 SiC와 금속박막간의 계면형성 및 반응 생성물의 구조가 550°C에서 1450°C의 온도 범위에서 조사되어졌다. SiC와 코발트간의 반응에 있어서 전형적인 반응층의 순서는 1050°C에서 1250°C까지의 온도 범위에서 CoSi/CoSi+C/CoSi/CoSi+C/.../SiC이었고, SiC와 니켈간의 반응에 있어서 전형적인 반응층의 순서는 950°C에서 1050°C까지의 온도 범위에서 Ni₂Si/Ni₂Si+C/Ni₂Si/Ni₂Si+C/.../SiC이었다. 탄소의 결정화가 SiC/Co 반응에 있어서는 1450°C 이상에서

그리고 SiC/Ni 반응에 있어서는 1250°C 이상에서 바깥면으로 우선적으로 석출되었다. 또한, 탄소석출거동을 동반한 주기적인 띠구조의 형성 기구가 열역학적인 고찰을 통하여 논하여졌다.

1. Introduction

Silicon-based structural ceramics such as SiC and Si₃N₄ are under active consideration for structural use in hot machinery such as gas turbines. In these application, ceramics and metals will be in contact with each other at temperatures of at least 1000°C. Under such conditions, a chemical reaction between ceramic and metal can occur. This may lead to severe degradation of the strength of both materials. On the other hand, for ceramic/metal systems, a strong metallurgical bond between them through solid state reaction is essential in order to make ceramic matrix or metal matrix composites with good mechanical strength. In both of 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 [1-3].

Several studies have been reported to develop some basic understanding on the physical and chemical interactions at the SiC-metal interfaces [4-11]. For the reaction of SiC with various types of metals, different silicides, free carbon, metallic alloys and carbides have been observed as reaction products. Cobalt and nickel could be used to make good high-temperature contacts for utilizing the properties of SiC. They are also

of specific interest due to its silicide-forming tendency at low temperature, making a suitable material for metallization. At present a few detailed studies of the interaction of thin metal films with SiC at low temperatures have been reported [12-17].

In a previous study [18], the surface structure and critical load of thin metal films on SiC substrate. This investigation aimed at providing the surface morphology, reaction products and adhesive strength using thin metal films deposited on SiC substrates. However, more detailed information about the interfacial reaction is required for improved understanding about interfacial reaction between SiC and these thin metal films.

In this paper, the interface formation of thin sputtered metal films with 2 μm thickness deposited on SiC in order to study the prediction of all reaction products and diffusion zone, as well as the morphology of the product scale in the temperature range between 550 and 1450°C. Furthermore, a thermodynamic consideration was made for interpreting the interactions between cobalt and nickel films and SiC.

2. Experimental

The materials used for the experiments were highly dense sintered α-SiC from

"Elektroschmelzwerk Kempten", ESK, and thin sputtered cobalt and nickel films. The polycrystalline SiC contained 1.5 wt% total impurities, such as carbon and aluminium (ESK). Cobalt and nickel films were sputter-deposited on to the polished SiC substrates in a commercial sputter equipment (Laybold/Germany, type Z-400). A magnetron-type D.C. sputtering source was used to deposit the coatings. The growth rate of nickel films was calculated to be 667 nm/min under the conditions used (D.C. potential 400 V, partial pressure of Ar 7.0×10^{-2} mbar and bias voltage -150 V), and the growth rate of cobalt films was calculated to be 11.7 nm/min under the condition used (D.C. potential 500 V and partial pressure of Ar 4.0×10^{-2} mbar). The temperature of the substrate during deposition was estimated to be between 50 and 250°C. Film thicknesses were measured by the observation of film steps on reference substrates using surface profilometry. The applied film thickness was fixed at 2.0 μm for this study.

Annealings were conducted in a high-temperature vacuum furnace with a graphite heating element manufactured by Degussa/Germany. The SiC/metal samples were placed in a graphite crucible. The specimens were surrounded by titanium to remove the residual oxygen during the annealing time. After positioning the samples, the furnace was evacuated to 6×10^{-6} mbar and subsequently filled with a gas mixture of Ar /4 vol% H₂ for the annealing time.

After reaction runs, the samples were characterized in cross-section. The reaction

zone was analysed on a cross-section by optical microscopy, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). For examination of cross-sections, all samples were cut by a diamond saw, coated with gold and then embedded in copper resin. After mounting, the reaction couples were ground on a diamond disk, and polished with diamond pastes of 30, 15, 6, 3 and 1 μm . The surface was finally polished with Al₂O₃ solution.

3. Results and discussion

3.1. Interface formation of cobalt films on SiC

Annealing experiments were performed in the temperature ranges between 750 and 1450°C. In most cases, thin cobalt films were well coupled with the ceramic after annealing at temperature between 850 and 1450°C. Cross-sectional views of annealed samples treated at 850°C for 4 h were analysed by EPMA. Fig. 1 shows the line scan of the elemental cobalt, silicon and carbon across the reaction zone. The corresponding phase distribution is noted on the distinguishable boundary between Co+Co₂Si and Co₂Si+C regions. On the surface, Co+Co₂Si region was identified. In the areas adjacent to the SiC interface, a mixture of Co₂Si with carbon was formed.

A cross-sectional scanning electron micrograph (Fig. 2) shows the reaction zone after annealing at 1050°C for 0.5 h, 1 h and

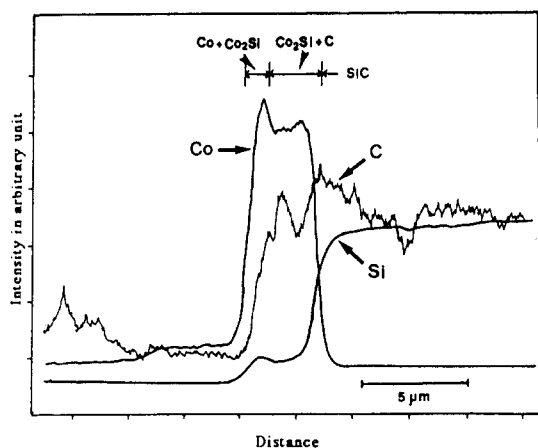


Fig. 1. EPMA line scan for cobalt, carbon and silicon over the cross-sectional SiC/Co reaction zone after 4 h at 850°C showing the distinguishable boundary between $\text{Co} + \text{Co}_2\text{Si}$ and $\text{Co}_2\text{Si} + \text{C}$ regions.

2 h. In the region neighbouring the SiC, a layer of CoSi was observed with randomly precipitated carbon. On the surface a layer was formed consisting of Co_2Si for the sample (a) and (b), and CoSi for the sample (c) without carbon. The reaction zone between cobalt thin film and SiC after annealing at 1050°C and 0.5 and 1 h in Fig. 2 (a) and Fig. 2 (b) can be described by the structure : $\text{Co}_2\text{Si}/\text{CoSi} + \text{C}/\text{CoSi}/\text{CoSi} + \text{C}/\dots/\text{SiC}$. Depending on the annealing time at this temperature, the relative quantities of CoSi increased simultaneously, while Co_2Si decreased. After 2 h at this temperature, only a CoSi+C region was observed in the reaction zone. It seemed that Co_2Si is the first reaction product between cobalt and SiC under these conditions. The migration rate of silicon in this phase is much higher than that

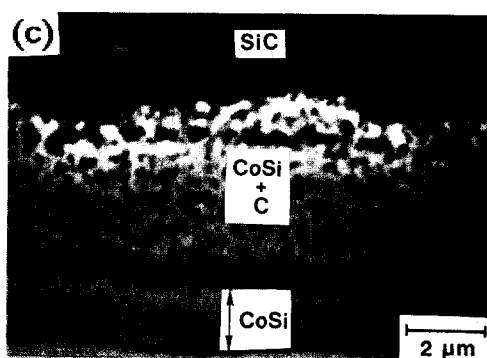
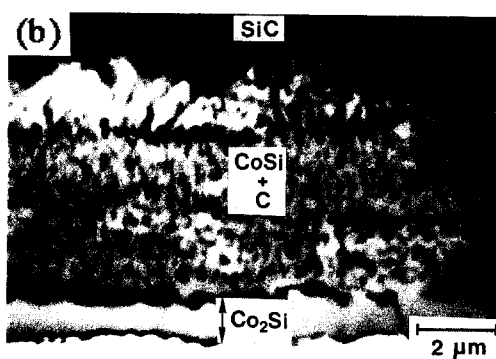
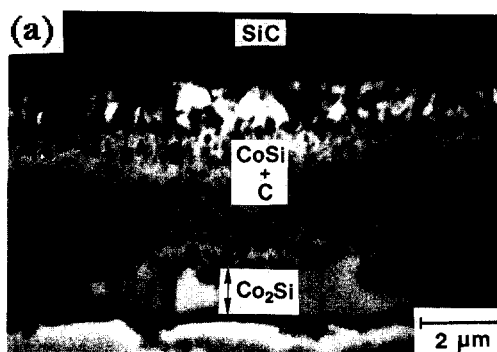


Fig. 2. Scanning electron micrographs showing the cross-sectional views of the SiC/Co reaction zone after annealing at 1050°C for (a) 0.5 h, (b) 1 h and (c) 2 h.

of carbon, and reveals the progress of the reaction up to the full consumption of metallic cobalt. The carbon remains in the neighbourhood of the SiC/Co₂Si interface. On increasing the amount of silicon Co₂Si forms CoSi, which probably dissolved carbon which, during the cooling process is deposited randomly in this phase region. At 1050°C for 2 h the amount of Co₂Si phase was fully consumed in Fig. 2 (c). This reaction zone can be described by the structure : CoSi/CoSi+C/CoSi/CoSi+C/.../SiC.

The cross-section of the sample after reaction at 1250°C for 2 h was quantitatively analysed by EPMA in Fig. 3. The line-scan shows that a periodic maximum of the cobalt intensity corresponds to the minimum of the cobalt intensity. The alternating band structure between CoSi and CoSi+C developed at 1250°C for 0.5 and 2 h could be de-

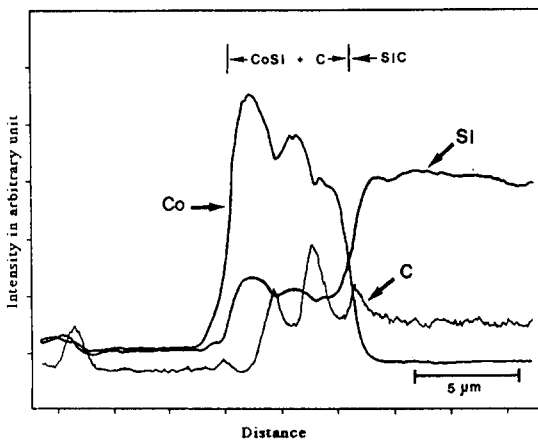


Fig. 3. EPMA line scan for cobalt, carbon and silicon over the cross-sectional SiC/Co reaction zone after 2 h at 1250°C showing the periodic intensities of carbon in the CoSi phase.

scribed as the formation of layers such as CoSi/CoSi+C/CoSi/CoSi+C/.../SiC.

Figure 4 shows a secondary electron image and X-ray maps with the distribution of the element carbon in the reaction zone after annealing at 1450°C for 2 h. The CoSi phase is distributed irregularly at the SiC boundary. Carbon was mainly deposited on the outside of the CoSi phase. At this temperature, a non-periodic structure of carbon precipitates was observed in the CoSi phase.

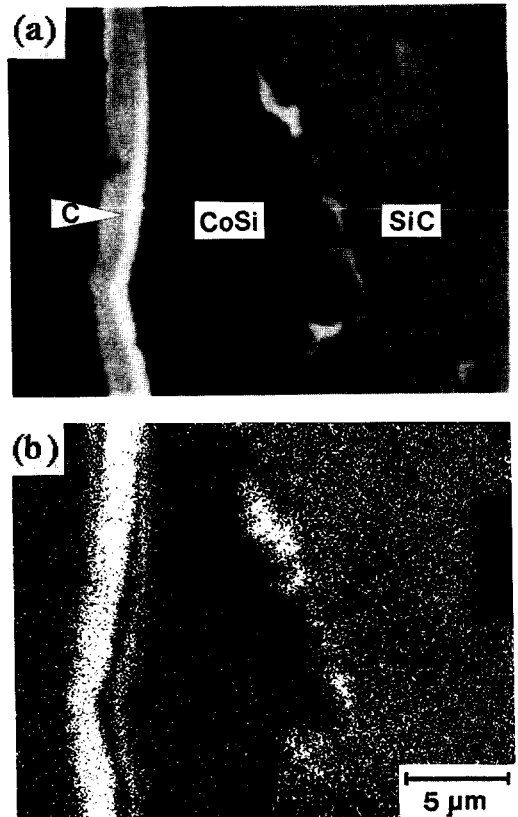


Fig. 4. EPMA images of the cross-sectional SiC/Co reaction zone after 2 h at 1450°C : (a) secondary electron image : (b) carbon X-ray map.

This structure also explains the high X-ray intensity of graphite observed for this sample. The typical phase distribution on the reaction zone from the surface to SiC after annealing at 1450°C for 2 h can be described as C/CoSi+C/C/SiC.

3.2. Interface formation of nickel films on SiC

Annealing experiments were performed in

the temperature ranges between 550 and 1250°C. In most cases, thin nickel films were well coupled with the ceramic after annealing at temperature between 650 and 1250°C. A cross-sectional scanning electron micrograph (Fig. 5) shows the reaction zone after annealing at 650, 950, 1050 and 1250°C for 2 h. In the region neighbouring the SiC, a layer of Ni₂Si was observed with randomly precipitated carbon in Fig. 5 (a) and (b). The cross-section of the annealed samples

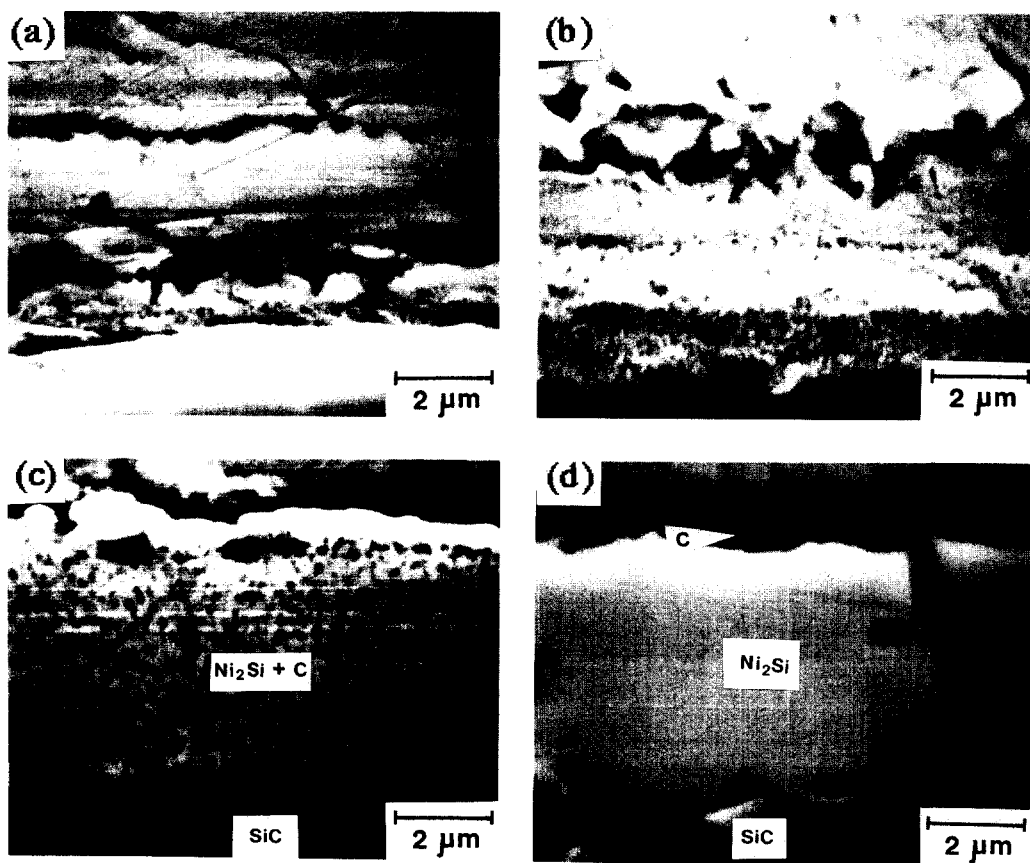


Fig. 5. Scanning electron micrographs showing the cross-sectional views of the SiC/Ni reaction zone after annealing at (a) 650°C for 2 h, (b) 950°C for 2 h, (c) 1050°C for 2 h and (d) 1250°C for 2 h.

treated at 950°C for 2 h was quantitatively analysed by EPMA.

Figure 6 shows the line scan of the elemental nickel, silicon and carbon across the reaction zone. The corresponding phase distribution is noted on this diagram. Over the interface, a mixture of Ni_2Si with carbon was identified. The line-scan shows that a periodic maximum of the carbon intensity corresponds to the minimum of the nickel intensity.

A cross-sectional scanning electron micrograph in Fig. 5 (c) shows the reaction zone after annealing at 1050°C for 2 h. In the region neighbouring the SiC, a mixture of Ni_2Si with randomly precipitated carbon was observed. On the surface of this sample a layer was formed consisting of Ni_2Si without carbon. The alternating band structure between Ni_2Si and $\text{Ni}_2\text{Si}+\text{C}$ developed at

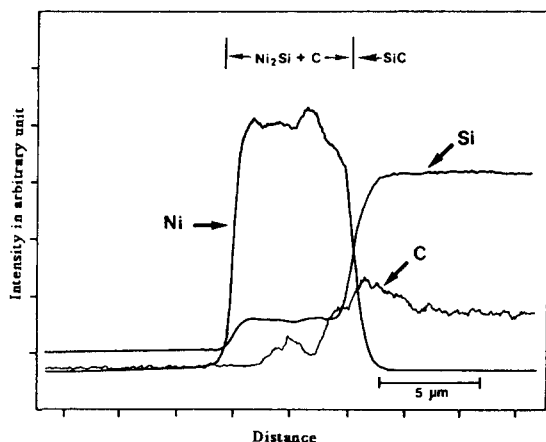


Fig. 6. EPMA line scan for cobalt, carbon and silicon over the cross-sectional SiC/Ni reaction zone after 2 h at 950°C showing the periodic intensities of carbon in the Ni_2Si phase.

950 and 1050°C for 2 h could be described as the formation of layers such as $\text{Ni}_2\text{Si}/\text{Ni}_2\text{Si}+\text{C}/\text{Ni}_2\text{Si}/\text{Ni}_2\text{Si}+\text{C}/\dots/\text{SiC}$.

A cross-sectional scanning electron micrograph in Fig. 5 (d) shows the reaction zones after annealing at 1250°C for 2 h. The Ni_2Si phase is distributed irregularly in contact to SiC. Carbon was mainly deposited on the outside of the Ni_2Si phase. At this temperature, a non-periodic structure of carbon precipitations was observed in Ni_2Si phase. This structure also explains the high X-ray intensity of graphite observed for this sample. The typical phase distribution on the reaction zone at 1250°C for 2 h can be described as is the construction of $\text{C}/\text{Ni}_2\text{Si}/\text{SiC}$.

3.3. Thermodynamics

The reaction between cobalt and nickel thin film and SiC leads to the formation of nickel silicides accompanied by carbon precipitates. Considering the thermodynamic calculating by Gibb's free energy (ΔG) for various reactions as given in the international tables [19], the reaction products between SiC and cobalt and nickel could be correlated within these systems.

In Fig. 7 the calculated values of the reactions between SiC and cobalt are plotted as a function of temperature and compared with the values of the SiC/Co system. The result predicts which phases are stable at the thermodynamic equilibrium. Cobalt is known to react with silicon and to form various silicides, Co_2Si , CoSi and CoSi_2 (Reac-

tions 5, 6 and 7 in Fig. 7), because the ΔG values are highly negative. Less negative values are calculated for the corresponding Reactions 2, 3, and 4 with SiC, because of the energy needed for SiC decomposition. Based on the present experimental results, cobalt reacts with SiC and forms various silicides at the SiC interface. In the case of reaction 2, where two moles of SiC should be decomposed per reacted nickel g-atom, ΔG indicates positive values. Therefore, CoSi_2 could not be formed in this temperature range. In addition, the formation of the car-

bide Co_2C (reaction 1) is thermodynamically impossible under these conditions. Considering the reactions between SiC and cobalt, only the formation of Co_2Si and CoSi shows a negative ΔG value and can be formed by solid stated reaction.

At 1050°C the Co_2Si layer was converted to CoSi and additional carbon precipitates were formed in the CoSi zone. According to reported diffusion data [20-23], cobalt is the dominant diffuser in the Co_2Si phase. It also diffuses through Co_2Si and CoSi and arrives at the SiC interface to react with

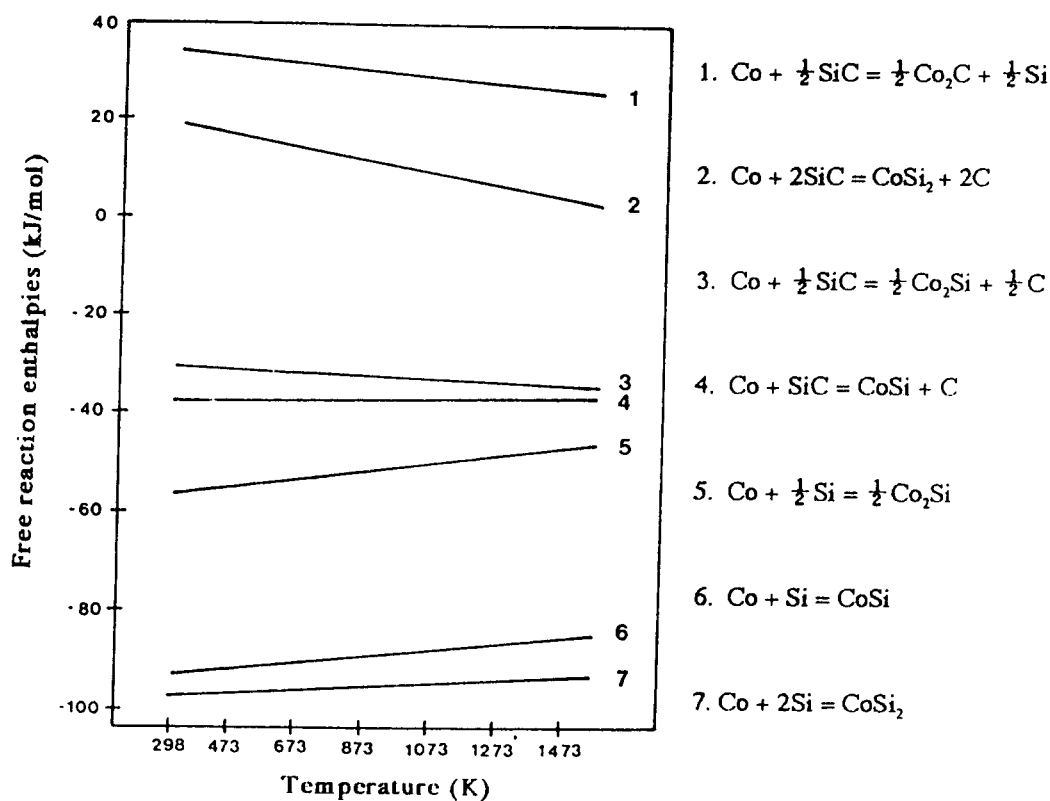


Fig. 7. Calculated free reaction enthalpies for various reactions between SiC and cobalt, as well as between cobalt and silicon as a function of temperature (based on 1 g-atom Co).

SiC. After the metallic cobalt layer is completely consumed, cobalt migration takes place from the Co_2Si , resulting in the growth of the CoSi layer. It is possible that CoSi grows at the $\text{Co}_2\text{Si}/\text{CoSi}$ and CoSi/SiC interface, resulting in the growth of CoSi with heating time and increasing temperature.

Figure 8 shows the calculated values of these reactions plotted as a function of temperature and compared with the value of the Si/Ni system. Nickel is also known to react with silicon and to form various silicides, Ni_2Si , Ni_3Si_2 , NiSi and NiSi_2 (Reaction 6, 7, 8 and 9 in Fig. 8), because the ΔG values are

highly negative. Less negative values are calculated for the corresponding reaction 2, 3, 4 and 5 with SiC, because of the energy needed for SiC decomposition. According to the present experimental results, nickel reacts with SiC and forms various silicides at the SiC interface. In the case of reaction 2, where two moles of SiC should be decomposed per reacted nickel g-atom, ΔG indicates positive values. Therefore, NiSi_2 could not be formed in this temperature range. In addition, the formation of the carbide Ni_3C (reaction 1) is thermodynamically impossible under these conditions. Considering the

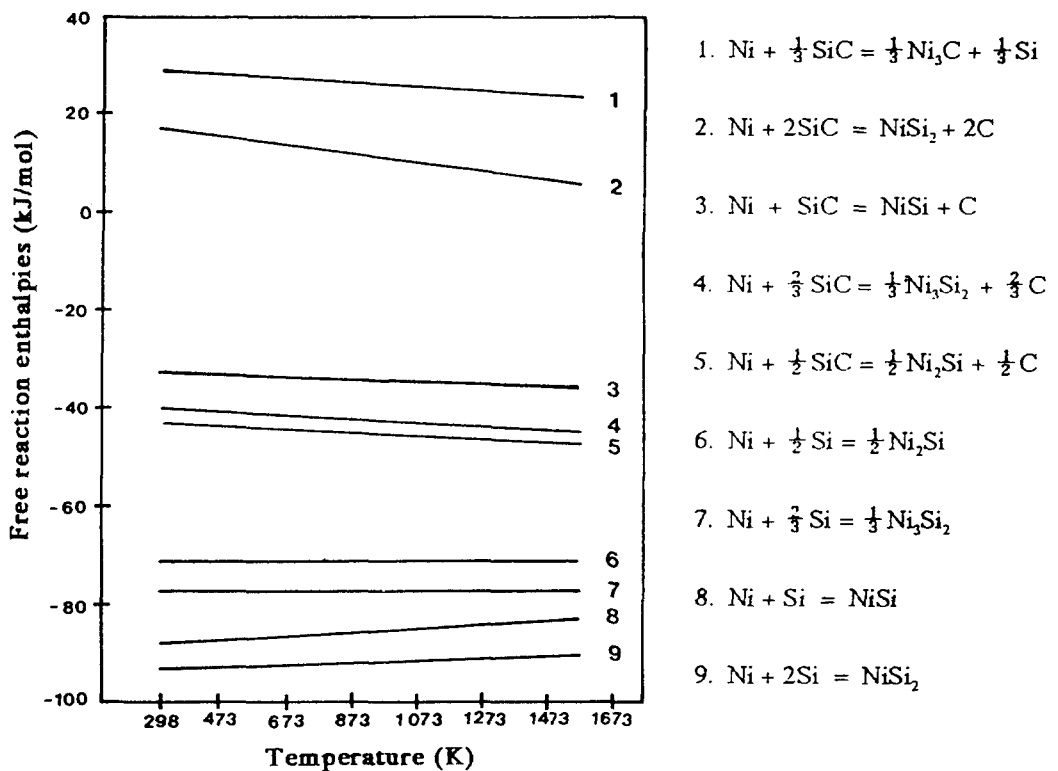


Fig. 8. Calculated free reaction enthalpies for various reactions between SiC and nickel, as well as between nickel and silicon as a function of temperature (based on 1 g-atom Ni).

reactions between SiC and nickel, only the formation of NiSi, Ni₃Si₂ and Ni₂Si shows a negative ΔG value and can be formed by solid state reaction.

Above 750°C the Ni₃Si₂ layer was converted to Ni₂Si and additional carbon precipitates were formed in the Ni₂Si. According to reported diffusion data [24-27], nickel is the dominant diffuser in the Ni₂Si phase. It also diffuses through Ni₃Si₂ and Ni₂Si and arrives at the SiC interface to react with SiC. After the metallic nickel layer is completely consumed, nickel migration takes place from the Ni₂Si, resulting in the growth of Ni₂Si at expenses of Ni₃Si₂.

Consequently, the solid state reaction between SiC and metal silicide at SiC interface could be generally described as the formation of silicide with carbon which results in the decomposition of SiC and the precipitation of carbon. On the other hand, silicon diffused into metal and produced metal reaction interface. It is noted that the predominant reaction of metal silicide without carbon is available at the metal reaction interface. Moreover, the periodic carbon precipitations are revealed at the SiC reaction interface. It is due to the different thermodynamic driving force between the reaction at the SiC reaction interface and the reaction at the metal reaction interface.

4. Conclusions

The interface formation with the reactivity and morphology of thin sputtered cobalt

and nickel films deposited on SiC were investigated in the temperature range 550 and 1450°C. The typical reaction layer sequence was CoSi/CoSi+C/CoSi/CoSi+C/.../SiC in SiC/Co reaction at 1050 and 1250°C for 2 h, while Ni₂Si/Ni₂Si+C/Ni₂Si/Ni₂Si+C/.../SiC in SiC/Ni at 950 and 1050°C for 2 h. The formation of silicide layers with carbon precipitates alternated periodically with the carbon-free layers. Carbon precipitated preferentially on the outer surface and crystallized as graphite above 1450°C for SiC/Co reaction zone and 1250°C for SiC/Ni.

The preferential formation of CoSi+C for SiC/Co reaction and Ni₂Si+C for SiC/Ni reaction is exhibited at the SiC reaction interface which results in the decomposition of SiC and the precipitation of carbon. Silicon diffused into metal and produced the formation of CoSi for SiC/Co and Ni₂Si for SiC/Ni at metal reaction interface. The formation of the periodic carbon precipitations at SiC reaction interface is due to the different thermodynamic driving force between the reaction at the SiC reaction interface and the reaction at the metal reaction interface.

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