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Chemical Instability of Silicon Carbide in the Presence of Transition Metals

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SiC has been proved chemically unstable at temperatures >1073 K (800°C) in the presence of cobalt, nickel, or iron. The instability results from reactions of cobalt, nickel, or iron with SiC to produce silicides and free carbon. A method of calculation is proposed for thermodynamic analyses of these reactions. The results show that the silicides of cobalt, nickel, and iron are thermodynamically more stable than SiC. The metal–silicon eutectic may provide kinetic condition to the reactions. Calculations also are performed for reactions of SiC with other transition metals. Instabilities of SiC in the presence of those metals are predicted.

I. Introduction

The increasing demand of ceramics as structural components has highlighted the utility of materials containing SiC (silicon carbide). In dealing with SiC ceramics and SiC-related composites, an important fact that is ignored in many cases is that SiC is relatively unstable from a thermodynamic point of view. Using solid silicon as the standard, the heat of formation (ΔH) of SiC is 62.8 kJ/mol (at 298 K (25°C)), which is one order of magnitude lower than that of Si_3N_4 (silicon nitride) ($\Delta H = 738$ kJ/mol at 298 K) and most oxide ceramics (e.g., for Al_2O_3, $\Delta H = 1674$ kJ/mol at 298 K).[1] In many cases, little attention has been given to the chemical instability of SiC, because normally a silica protective layer is present. The protective layer of silica usually can be formed at the surface of SiC if the oxygen partial pressure is 1 mm Hg (~133 Pa) or higher.[2] The formation of the layer is initially rapid but will decrease as the thickness of the layer increases. This layer prevents SiC from further oxidation at temperatures <1200°C. Above this temperature, slight oxidation occurs. SiC is, for most applications, kinetically stable.[3] A typical example is using SiC as heating elements in an unprotected environment.

In a reducing atmosphere, the thermodynamic instability of SiC becomes dominant. In a reducing atmosphere or at low oxygen partial pressure, oxygen reacts with the SiO_2 layer to produce SiO, which evaporates, and the unprotected SiC becomes unstable. The oxygen present in the reducing atmosphere then continuously reacts with SiC to form SiO and CO gases. This sometimes is called "active oxidation" of SiC, in comparison to "passive oxidation," which occurs when higher oxygen partial pressures (>1 mm Hg (~133 Pa)) are involved.[2] In the case of a vacuum, SiC reacts with the SiO_2 layer, and more-extensive consumption of SiC occurs.[4] SiC also can react, at relatively high temperatures, with Al_2O_3 in a reducing atmosphere to produce gaseous phases of SiO, CO, and Al_2O, also making SiC unstable.[5]

In the presence of metals, SiC becomes unstable. In the search for metallic additives to SiC as sintering aids, Negita[6] noted that metal additives, the carbides of which are thermodynamically more stable than SiC, make SiC unstable. According to Negita,[6] the metallic additives react with SiC to form metal carbides, leaving free silicon. Thermodynamic predictions for metals including beryllium, calcium, chromium, molybdenum, niobium, tantalum, titanium, tungsten, and zirconium indicate that they are carbonized at high temperature by the carbon in SiC, and free silicon is precipitated. Negita[6] also predicted that SiC will be stable in the presence of iron, cobalt, and nickel, because their carbides are less stable than SiC, and they will not be carbonized by the carbon in SiC. Using this information, SiC can be considered as a possible candidate for use in structural parts in contact with these metals, their melts, and vapors. These metals also may be possible additives for use as sintering aids for SiC ceramics or composites.[6]

In this paper, the chemical instability of SiC also can be observed when a metal, of which the silicide instead of the carbide is thermodynamically more stable than SiC, is coexisting with SiC. SiC hereupon is considered to be a silicide of carbon. The instability of SiC in this situation results from possible reactions of SiC with metals to produce metal silicides and free carbon. In considering the situation of SiC contacting with metals and in searching for metallic sintering aids for SiC ceramics, attention must be given to the stability comparisons between metal silicides and SiC, as well as between metal carbides and SiC; the former will be the main topic of this paper, and the latter has been discussed by Negita.[6] To explain these results, a calculation method is proposed to estimate the free-energy changes of the reactions between SiC and metal. This method works well in the explanations of the experimental results of the reactions of SiC with cobalt, nickel, and iron studied in this paper and, consequently, is used to predict the instabilities of SiC in the presence of some other transition metals.

II. Experimental Procedure

The α-SiC powder used in this study (H. C. Starck, Inc., New York) had an average particle size of 0.55 μm and a specific surface area of 15.70 m^2/g. Reduced cobalt, nickel, and iron powders (Merck, Darmstadt, Germany) were analytical grade; their average particle size was <3 μm.

The mixing of SiC with various compositions of cobalt, nickel, or iron powders was accomplished by conventional methods. Green samples 10 mm in diameter by 5–10 mm thick and 20 mm in diameter by 10–15 mm thick were compressed under a uniaxial pressure of 100 MPa and then heated at 10°–15°C/min to the temperature of interest and kept under either an argon or nitrogen gas atmosphere for 30 min. Differential thermal analysis (DTA) experiments were performed using heating and cooling rates of 10°C/min under an argon gas atmosphere. The DTA samples contained equimolar amounts of SiC and

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cobalt, nickel, and iron each. Two Chromel–Alumel™ (Hoskins Manufacturing Co., Detroit, MI) thermocouples were inserted into the sample (20 mm in diameter by 15 mm) and the Al_2O_3 reference. Both the sample and reference were situated in a parallel manner in a BN (boron nitride) crucible. The thermocouple tip was protected carefully. The system was checked, so that no unrelated reaction except that between SiC and cobalt, nickel, or iron could occur. Heating and cooling temperatures and the temperature difference were recorded on a sensitive two-channel recorder. The final DTA thermograms were drawn accordingly. X-ray diffractometry (XRD) (Model Geigerflex, Rigaku Co., Tokyo, Japan) was used for phase analyses of the final products of all reactions.

III. Results

The DTA thermograms obtained from the reactions of SiC with cobalt, nickel, and iron, in which the molar ratio of the components in each system is 1:1, under an argon gas atmosphere, are shown in Fig. 1. The temperature ranges of the endothermic peaks during heating and the exothermic peaks during cooling are marked. These temperature ranges are far below the melting points of pure cobalt, nickel, and iron and also are lower than all eutectic temperatures of the systems composed of these metals and silicon. An equimolar-ratio mixture of SiC and cobalt was kept at 1223 K (950°C) under an argon gas atmosphere for 2 h. Small alloy balls, identified as Co_2Si and CoSi by XRD, were found after cooling. One plausible explanation for these facts is that cobalt, nickel, and iron may form eutectic liquids with the silicon in SiC during heating, and the eutectic reactions could start at temperatures lower than the corresponding eutectic temperature of the pure metal and silicon systems. Eutectic reactions between metals and the silicon in SiC and Si_3N_4 also have been found in eutectic joining of ceramics and metals.[7] The depression of the eutectic temperature also was observed and was attributed to the existence of carbon.[7]

The final products of the reactions of SiC with cobalt, nickel, and iron under a wide range of temperatures and compositions were examined by XRD. The XRD phase identification results are listed in Table I, along with the reaction conditions. Some of these conditions (temperature and composition) covered a range instead of a certain point, meaning that, within these ranges, the results were the same. Representative XRD plots obtained from the reaction products of SiC with cobalt, nickel, and iron are shown in Figs. 2, 3, and 4, respectively. The reaction conditions of these representative plots are indicated in the figure captions.

Table I and Figs. 2, 3, and 4 all show that metal silicides and free carbon were formed in all reactions of SiC with cobalt, nickel, and iron. Carbon precipitation easily was observed (samples turned dark or black). No pure metals remained, and no metal carbides were found, which is in agreement with the prediction of Negita.[6] SiC was not consumed completely. A considerable amount of β-Si_3N_4 always was found after reaction of SiC and cobalt under nitrogen gas atmosphere at temperatures >1573 K (1300°C). However, the other two systems, where nickel or iron was used instead of cobalt, showed no β-Si_3N_4 formation. SiC can be concluded to be unstable in the presence of cobalt, nickel, or iron, and the instability of SiC

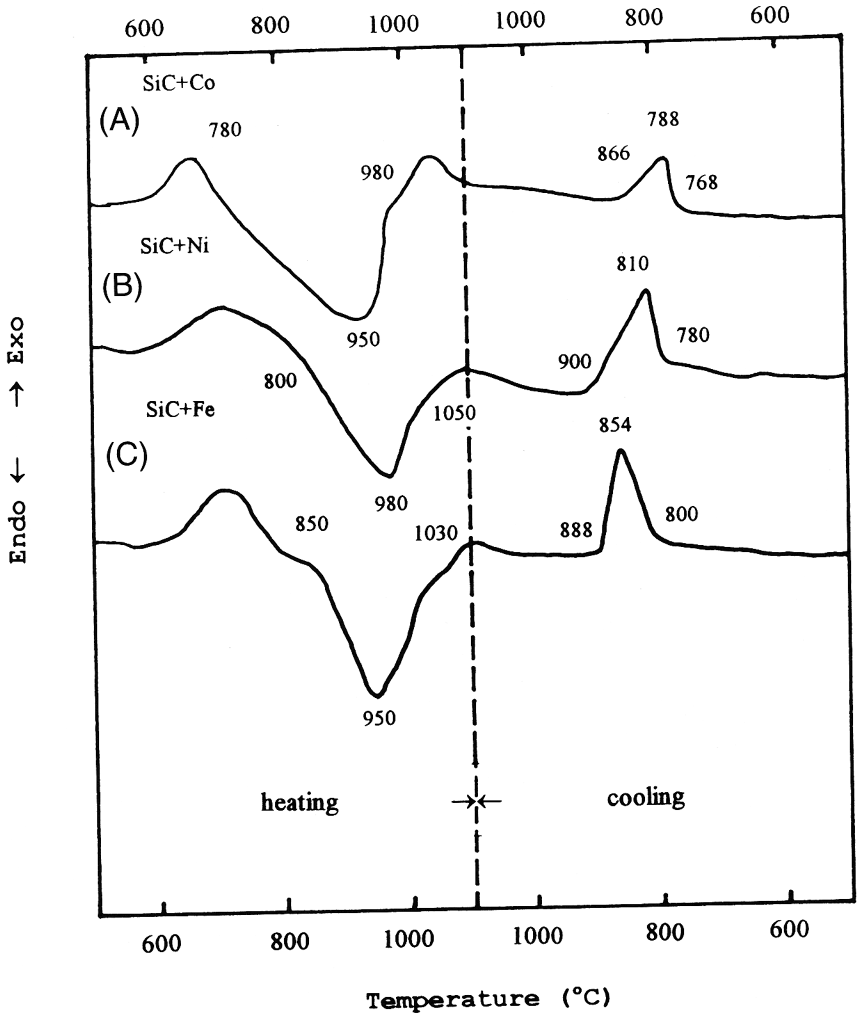

Fig. 1. Reaction thermograms of SiC–M reaction (where M is cobalt, nickel, or iron) ((A) SiC + cobalt, (B) SiC + nickel, and (C) SiC + iron).

Table I. XRD Phase Analyses of Products of SiC–M Reactions

M*	Reaction condition	Products
Cobalt	850°–1600°C, argon, 1 h	SiC, Co_2Si, CoSi, carbon
Cobalt	1300°–1600°C, N_2, 1 h	SiC, Co_2Si, CoSi, carbon, Si_3N_4
Nickel	850°–1600°C, argon, 1 h	SiC, $\delta(Ni_2Si)$, $\gamma(Ni_{0.74}Si_{0.26})$, carbon
Nickel	850°–1600°C, N_2, 1 h	SiC, $\delta(Ni_2Si)$, $\gamma(Ni_{0.74}Si_{0.26})$, carbon
Iron	900°–1600°C, argon, 1 h	SiC, Fe_3Si, carbon
Iron	850°–1600°C, N_2, 1 h	SiC, Fe_3Si, carbon

*The amount of each M was 10–50 mol%.

results from the formation of the metal silicide instead of carbide. In the presence of metals, SiC stability must be judged either by the possibility of metal silicide formation or by the possibility of metal carbide formation. Because metal–silicon eutectic reactions have been presumed to promote the reaction of SiC with metals, more attention may need to be given to the SiC instability caused by metal silicide formations.

In Table II, final silicide phases for each SiC–M reaction system were always in the composition range of 10–50 mol% metal and the temperature range of 1123–1873 K (850°–1600°C). It may be suggested that the final phases after the three reactions are independent of relative proportions of added metals. Co_2Si and CoSi always were found in the reaction of SiC with cobalt; however, much cobalt was added. $\gamma(Ni_{0.74}Si_{0.26})$ and $\delta(Ni_2Si)$ in SiC–Ni reactions and Fe_3Si in SiC–Fe reactions also were produced in a wide range of metal compositions. These results are analyzed in the following section.

IV. Thermodynamic Analyses and Discussion

SiC has been shown experimentally to react under either argon or nitrogen gas atmosphere with cobalt, nickel, and iron to form metal silicides and free carbon. SiC is definitely unstable in the presence of cobalt, nickel, or iron. The overall reaction of SiC with each of the metals may be written as

$$(1-x)\mathrm{M} + x\mathrm{SiC} \rightleftarrows \mathrm{M}_{1-x}\mathrm{Si}_x + x\mathrm{C} \qquad (0)$$

in which M is a metal and x the atomic percentage of silicon in $M_{1-x}Si_x$.

A thermodynamic analysis was performed to find the free-energy change of reaction (0) in the temperature range 1400–2000 K (1127°–1727°C), which is the temperature range conventionally concerned. The explanation of the experimental results obtained for cobalt, nickel, and iron was attempted, along with the prediction of SiC stability in the presence of

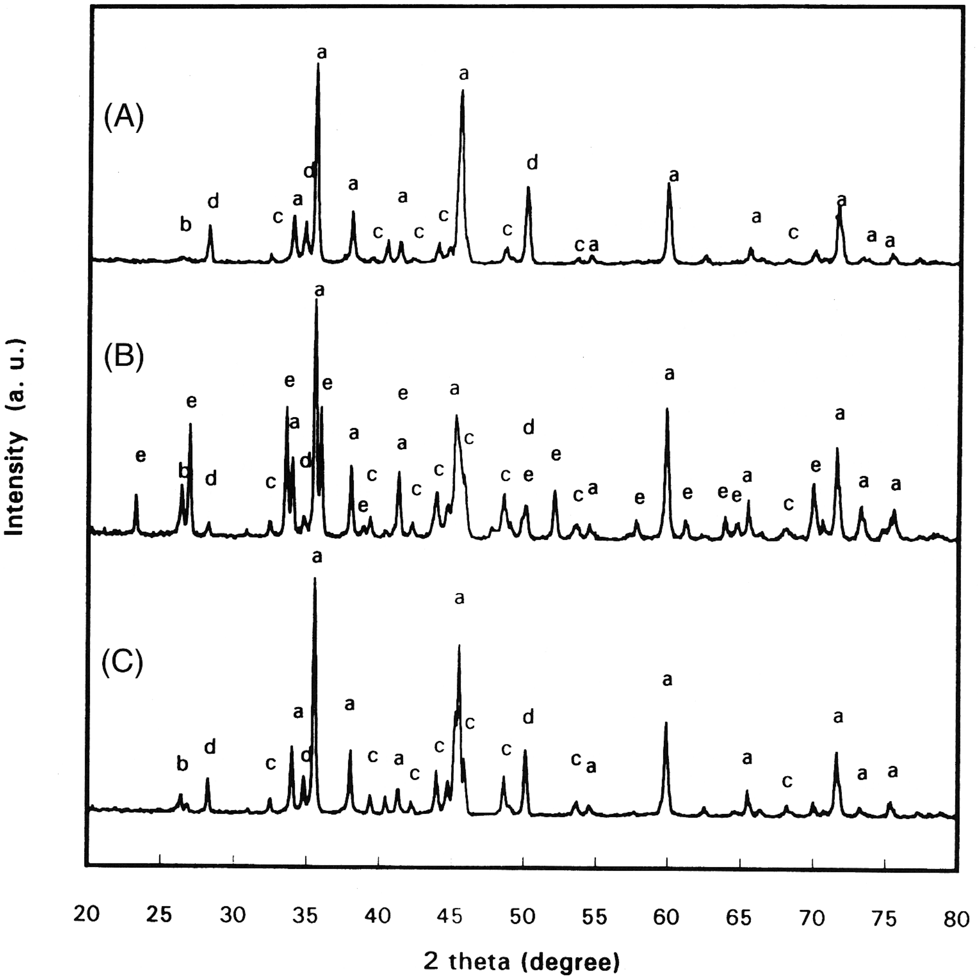

Fig. 2. XRD phase analysis after reaction between SiC and cobalt: (A) SiC–9 mol% cobalt under argon gas atmosphere at 1200°C for 1 h, (B) SiC–30 mol% cobalt under nitrogen gas atmosphere at 1300°C for 1 h, and (C) SiC–30 mol% cobalt under argon atmosphere at 1200°C for 1 h. ("a" is SiC; "b", carbon; "c", Co_2Si; "d", CoSi; and "e", Si_3N_4.)

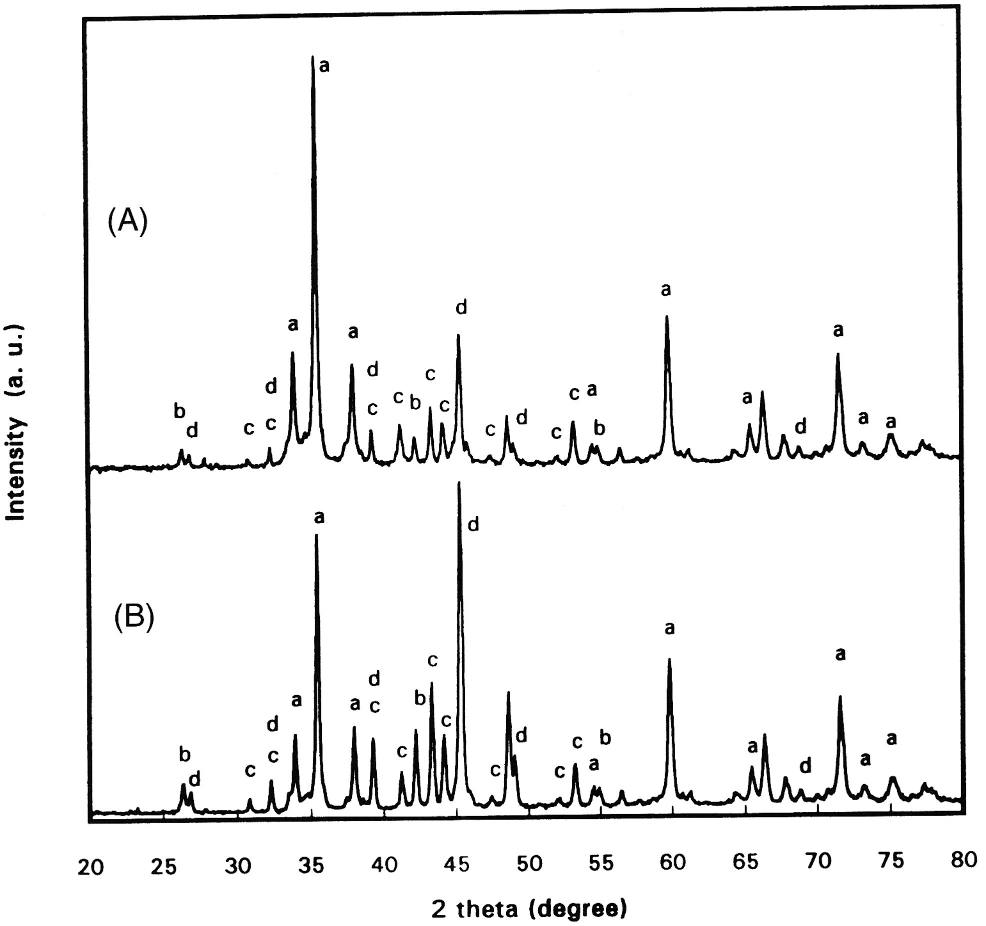

Fig. 3. XRD phase analysis after reaction between SiC and nickel: (A) SiC–9 mol% nickel and (B) SiC–30 mol% nickel, both under argon gas atmosphere at 1200°C for 1 h. ("a" is SiC; "b", carbon; "c", $\gamma(\mathrm{Ni}_{0.74}\mathrm{Si}_{0.26})$; and "d", $\delta(\mathrm{Ni_2Si})$.)

some other transition metals. Thus far, the reported thermodynamic data for many of the silicides are limited, and some of the data are for particular temperatures; therefore, a method to calculate the free-energy change of reaction (0) is proposed. This method is based on the basic thermodynamic properties of the materials involved and on metal–silicon phase diagrams and can be used for all silicides found in metal–silicon phase diagrams and for a wide range of temperatures. Whenever possible, the results obtained by this method are compared with data obtained by different authors.

For the analysis, reaction (0) may be decomposed into the following steps:

$$(1-x)\mathrm{M}(s) \rightleftarrows (1-x)\mathrm{M}(l) \tag{1}$$

$$x\mathrm{SiC} \rightleftarrows x\mathrm{Si}(l) + x\mathrm{C}(s) \tag{2}$$

$$(1-x)\mathrm{M}(l) + x\mathrm{Si}(l) \rightleftarrows \mathrm{M}_{1-x}\mathrm{Si}_x(l) \tag{3}$$

$$\mathrm{M}_{1-x}\mathrm{Si}_x(l) \rightleftarrows \mathrm{M}_{1-x}\mathrm{Si}_x(s) \tag{4}$$

where s and l represent solid and liquid, respectively.

Assuming the enthalpy and entropy changes of reaction (1) are independent of temperature and are equal to the values at the melting point of M, the free-energy change of reaction (1), ΔG_1, is

$$\Delta G_1 = (1-x)\left(L_\mathrm{M} - \frac{L_\mathrm{M}}{T_\mathrm{M}}T\right) \tag{1a}$$

where L_M is the latent heat of the metal M, T_M the melting point of the metal M, and T the temperature. Both T and T_M are in Kelvin. L_M and T_M for the metals were found in Refs. 8 and 9.

The standard heat and entropy of formation for SiC, with respect to liquid silicon and solid carbon, are 122470 J/mol and 37 J/(mol·K), respectively, in the temperature range 1685–2273 K (1412°–2000°C).[1] Because no gas is involved, the free-energy change of reaction (2), ΔG_2, thus can be calculated using

$$\Delta G_2 = 122470x - 37xT \tag{2a}$$

Reaction (3) is a solution-forming process from two liquids. The free-energy change of reaction (3), ΔG_3, can be computed on the basis of μ_Si and ΔH_Si (the partial molar free energies of silicon and the partial molar heats of silicon, respectively) at the reference temperature T_0 in M–Si liquid solutions. The values of μ_Si and ΔH_Si for various silicon compositions in liquid M–Si systems (where M is cobalt, nickel, and iron) at T_0 = 1873 K (1600°C) can be found in the Metals Reference Book.[10] The calculation of ΔG_3 may be performed through the following steps:

$$\Delta G_3 = \Delta G_{T_0} - (T - T_0)\Delta S_{T_0} \tag{3a}$$

where $\Delta G_{T_0} = x\mu_\mathrm{Si} + (1-x)\mu_\mathrm{M}$ and enthalpy and entropy changes also are assumed to be independent of temperature in the temperature range concerned. The value of μ_M, the partial molar free energy of M in the M–Si liquid system at T_0, can be estimated from μ_Si by performing numerical integration of the Gibbs–Duhem equation:[11]

$$\mu_\mathrm{M} = \int_{X_\mathrm{M}}^{1} \frac{(1-X_\mathrm{M})}{X_\mathrm{M}}\, \mathrm{d}\ln \mu_\mathrm{Si} \tag{3b}$$

X_M, equal to $1-x$, is the molar fraction of metal in the M–Si liquid solution. ΔS_{T_0} is the entropy change of the M–Si liquid solution at T_0, which can be calculated from μ_Si and ΔH_Si by using basic thermodynamic equations based on similar assumptions made earlier.

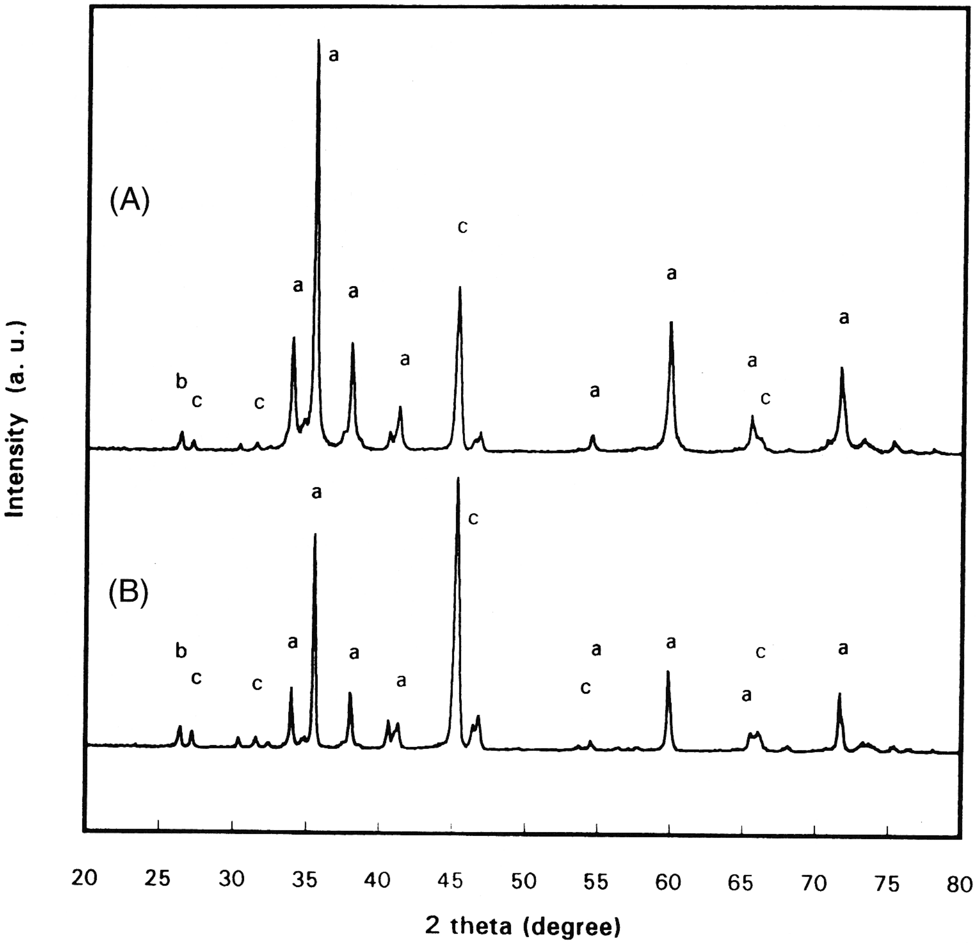

Fig. 4. XRD phase analysis after reaction between SiC and iron: (A) SiC–8.5 mol% iron and (B) SiC–30 mol% iron, both under argon gas atmosphere at 1200°C for 1 h. ("a" is SiC; "b", carbon; and "c", Fe_3Si.)

Reaction (4) is the process in which the liquid solution is solidified. The free-energy change of reaction (4), ΔG_4, is

$$\Delta G_4 = \Delta H_A - \frac{\Delta H_A}{T_A} T \qquad (4a)$$

where T_A is the melting point of the compound $M_{1-x}Si_x$ and $-\Delta H_A$ the heat of fusion per mole of this compound. Equation (4*a*) ignores the heat-capacity difference between liquid and solid $M_{1-x}Si_x$. ΔH_A can be evaluated via M–Si phase diagrams by using the following equation:[12]

$$\frac{\partial \ln X_A}{\partial T} = \frac{-\Delta H_A}{RT^2} \qquad (5)$$

where $X_A = X_A(T)$ and is the liquidus in molar fraction of the solvent of $M_{1-x}Si_x$ in the M–Si phase diagrams. Equation (5) is valid only if $M_{1-x}Si_x$ is a solvent of a dilute solution of silicon or M in $M_{1-x}Si_x$. Equation (5) can be integrated and arranged to give

$$\Delta H_A = \frac{RTT'(\ln X_A - \ln X'_A)}{T' - T} \qquad (6)$$

Table II. Free-Energy-Change Calculations of Silicide Formations through Reactions of SiC with Cobalt, Nickel, and Iron

Silicides in reaction (0)	Free-energy change (J)		Free-energy change (J/mol)		Free-energy change, ΔG_0 (J)
	ΔG_1	ΔG_2	ΔG_3	ΔG_4	
$Co_{2/3}Si_{1/3}$	$10333 - 5.85T$	$40823 - 12.33T$	$-38363 + 1.20T$	$-45937 + 28.59T$	$-33144 + 11.88T$
$Co_{1/2}Si_{1/2}$	$7750 - 4.39T$	$61235 - 18.50T$	$-43938 + 4.51T$	$-33800 + 20.70T$	$-8753 + 2.32T$
$Co_{1/3}Si_{2/3}$	$5167 - 2.93T$	$81646 - 24.67T$	$-40518 + 4.90T$	$-104419 + 70.30T$	$-58124 + 47.60T$
$Ni_{0.74}Si_{0.26}$ (γ)	$12893 - 7.46T$	$33312 - 10.06T$	$-29503 + 0.76T$	$-48709 + 31.34T$	$-32008 + 14.57T$
$Ni_{2/3}Si_{1/3}$ (δ)	$11689 - 6.77T$	$41640 - 12.58T$	$-35787 + 1.63T$	$-47184 + 29.64T$	$-29643 + 11.92T$
$Ni_{1/2}Si_{1/2}$ (η)	$8855 - 5.13T$	$61235 - 18.50T$	$-46609 + 4.51T$	$-48950 + 38.70T$	$-25469 + 19.58T$
$Ni_{1/3}Si_{2/3}$ (ζ)	$5844 - 3.42T$	$81646 - 24.67T$	$-40621 + 4.06T$	$-33040 + 26.10T$	$14238 + 1.95T$
$Fe_{3/4}Si_{1/4}$	$11400 - 6.30T$	$30618 - 9.25T$	$-23479 + 0.95T$ $-24463 + 0.98T$*	$-25736 + 16.89T$	$-7197 + 2.29T$
$Fe_{2/3}Si_{1/3}$	$10138 - 5.60T$	$40823 - 12.33T$	$-31134 + 4.50T$ $-36566 + 2.78T$*	$-83668 + 56.34T$	$-63841 + 42.91T$
$Fe_{1/2}Si_{1/2}$	$7600 - 4.20T$	$61235 - 18.50T$	$-36898 + 4.05T$ $-39050 + 3.21T$*	$-39810 + 22.01T$	$-7873 + 3.36T$
$Fe_{1/3}Si_{2/3}$	$5068 - 2.80T$	$81646 - 24.67T$	$-28479 + 3.21T$ $-31413 + 2.27T$*	$-131700 + 88.21T$	$-73467 + 63.95T$

*ΔG_3 calculated based on the data of Zaitsev *et al.*[15]

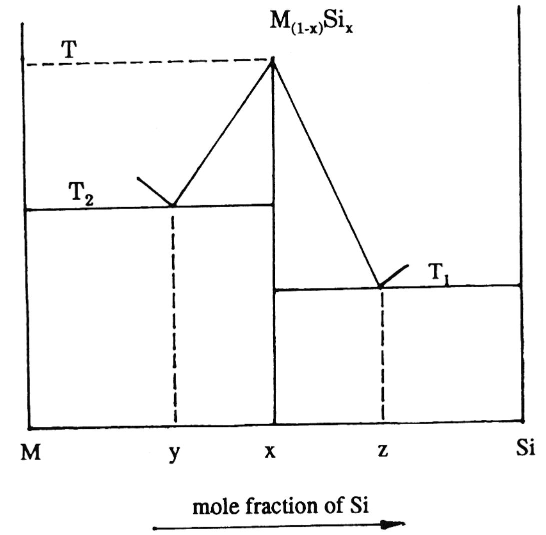

Fig. 5. Typical phase diagram of $M_{1-x}Si_x$ in M–Si system.

(X_A, T) and (X'_A, T') are two points on the liquidus of $M_{1-x}Si_x$ most convenient for calculations in the phase diagram. In these calculations, (X_A, T) corresponds to the pure $M_{1-x}Si_x$ and its melting point, and (X'_A, T') is the eutectic point in either the silicon or M side of $M_{1-x}Si_x$ on the phase diagram; choosing either the silicon or the M side depends on which side makes the solution more dilute. R is the gas constant. The calculation of ΔH_A is displayed schematically in Fig. 5, according to which

$$\Delta H_A = \frac{RTT_1[\ln(1-x) - \ln(1-z)]}{T_1 - T} \tag{7}$$

and

$$\Delta H_A = \frac{RTT_2(\ln x - \ln y)}{T_2 - T} \tag{8}$$

for the silicon side and the M side of $M_{1-x}Si_x$, respectively. The M–Si phase diagrams were taken from Ref. 13. All possible silicides of cobalt, nickel, and iron and some silicides of other metals of interest have been considered in the free-energy-change calculations. Eutectic reactions between two $M_{1-x}Si_x$ usually are found, and the eutectic temperatures are within the temperature range concerned. The calculation of thermodynamic functions on the basis of phase diagrams can be traced to Wagner.[14] He proposed a method based on extrapolated eutectic temperatures on a phase diagram to calculate the free energy of

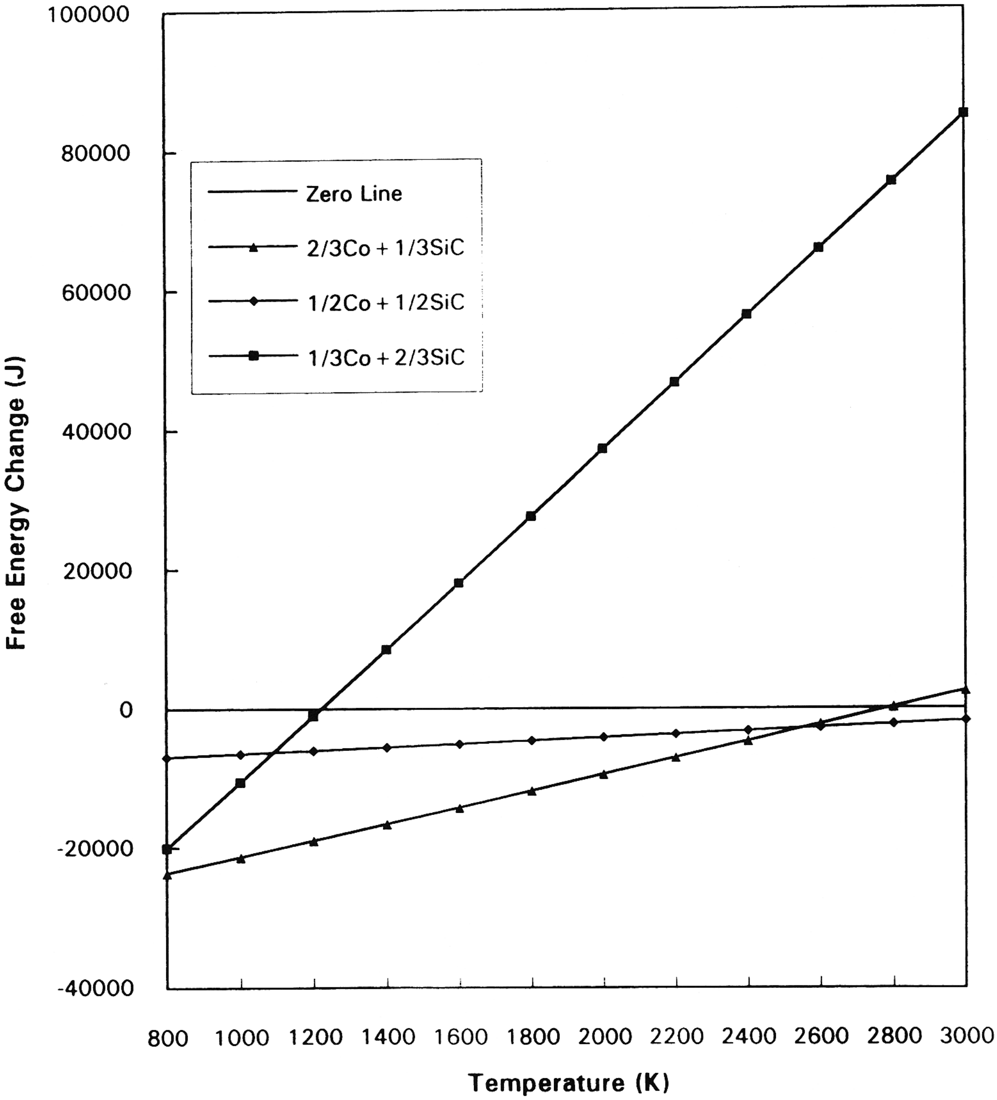

Fig. 6. Free-energy change of reaction of SiC and cobalt.

formation of a compound from its molar heat of fusion. The calculated value was for the extrapolated eutectic temperature. Some equations are quite similar to those in this paper.

Thus, the free-energy change of reaction (0) is

$$\Delta G_0 = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 \qquad (0a)$$

The results from the calculation for ΔG_1, ΔG_2, ΔG_3, ΔG_4, and ΔG_0 for all possible reactions of SiC with cobalt, nickel, and iron to form their silicides shown in the phase diagrams[13] are listed in Table II. The reliability of some of these calculations can be checked by comparison between our calculations and some reported data. A liquid Fe–Si system has been studied by Zaitsev *et al.*[15] The molar thermodynamic functions of formation of $[(1 - x)\text{Si} + x\text{Fe}](l)$ at 1700 K (1427°C) were calculated on the basis of vapor pressures of iron and silicon over the liquid Fe–Si system obtained through a Knudsen effusion method with a mass-spectrometry analysis. The results also can be used to calculate the ΔG_3 value in this paper. The results, marked with an asterisk (*), also are in Table II; ΔG_3 values calculated on the basis of Zaitsev *et al.*[15] are 3–5 kJ/mol lower than the results of this paper. The values of ΔG_3 calculated from the data of Hultgren *et al.*,[16] not listed in Table II, are even lower than the results of this paper but are comparable.

The calculated ΔG_0 value for all of the possible reactions of SiC with M (where M is cobalt, nickel, and iron) are plotted in Figs. 6, 7, and 8, respectively. In the temperature range of 1400–2000 K (1127°–1727°C), free-energy changes of reaction (0) for forming Co_2Si and CoSi in the SiC–Co system and $\gamma(Ni_{0.74}Si_{0.26})$ and $\delta(Ni_2Si)$ in the SiC–Ni system are negative, and free-energy change of reaction (0) for forming $Fe_{3/4}Si_{1/4}$ in the SiC–Fe system is the most negative. This supports the fact that Co_2Si and CoSi, $\gamma(Ni_{0.74}Si_{0.26})$ and $\delta(Ni_2Si)$, and Fe_3Si always were found in the reactions of SiC with cobalt, nickel, and iron, respectively; however, much cobalt, nickel, or iron was added.

The temperature dependence of the molar Gibbs energies of Fe_2Si, FeSi, and $FeSi_2$, with respect to solid silicon and iron, also have been studied by Zaitsev *et al.*[17] These values can be used to calculate the value of ΔG_0 for $Fe_{2/3}Si_{1/3}$, $Fe_{1/2}Si_{1/2}$, and $Fe_{1/3}Si_{2/3}$ in this study. Relatively large differences were found, but, as far as the instability of SiC is concerned, they are similar. For SiC–Ni and SiC–Co systems, the value of ΔG_0 also was estimated from the molar enthalpies of formations of nickel silicides and cobalt silicides listed in Ref. 10. The estimated value of ΔG_0 not only is different from the value of ΔG_0 in this study, but also indicates that SiC is stable in the presence of nickel and cobalt, which is in contradiction with the experimental results. The contradiction may be caused by rough estimations of the heat capacities.

According to the DTA results, the real reaction routes of reaction (0) for cobalt, nickel, and iron are presumably through the eutectic reactions of cobalt, nickel, and iron with the silicon

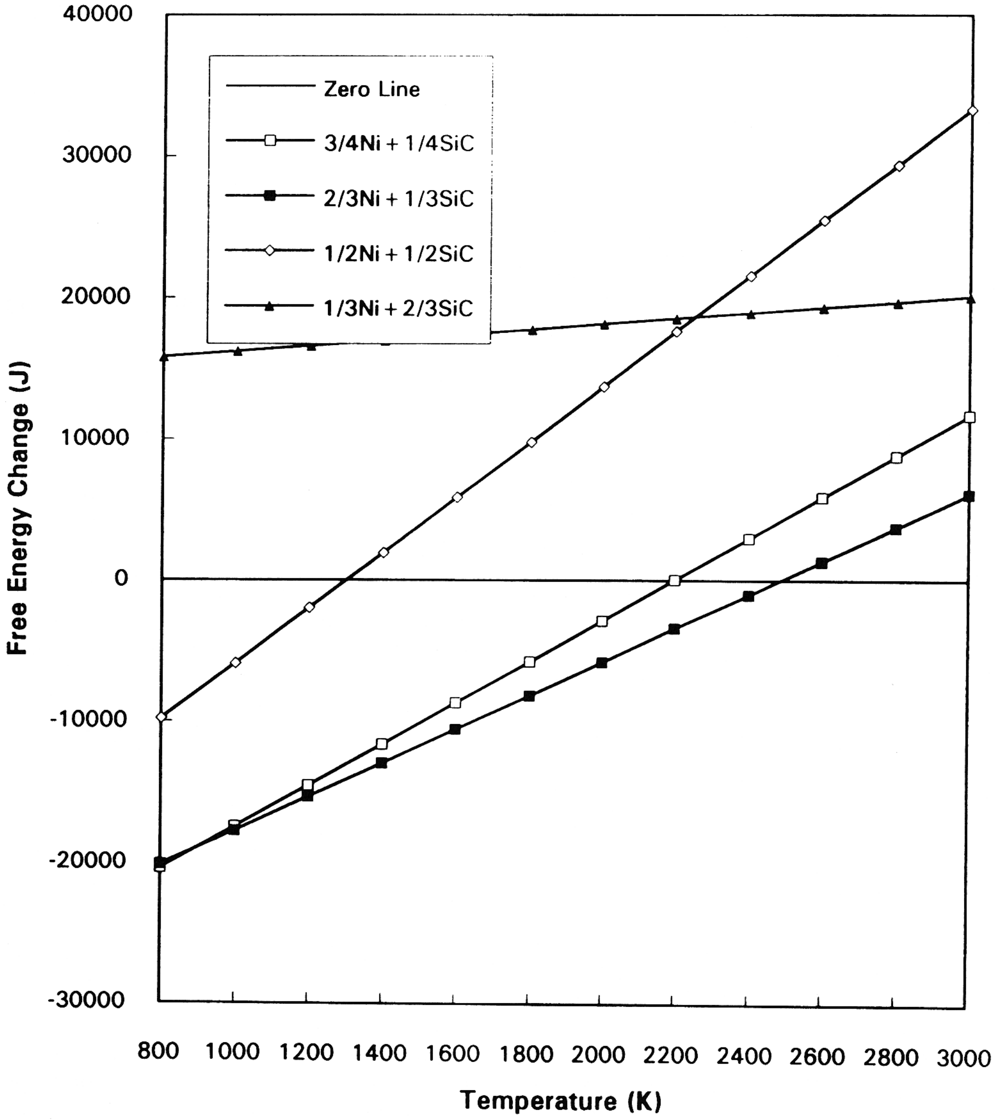

Fig. 7. Free-energy change of reaction of SiC and nickel.

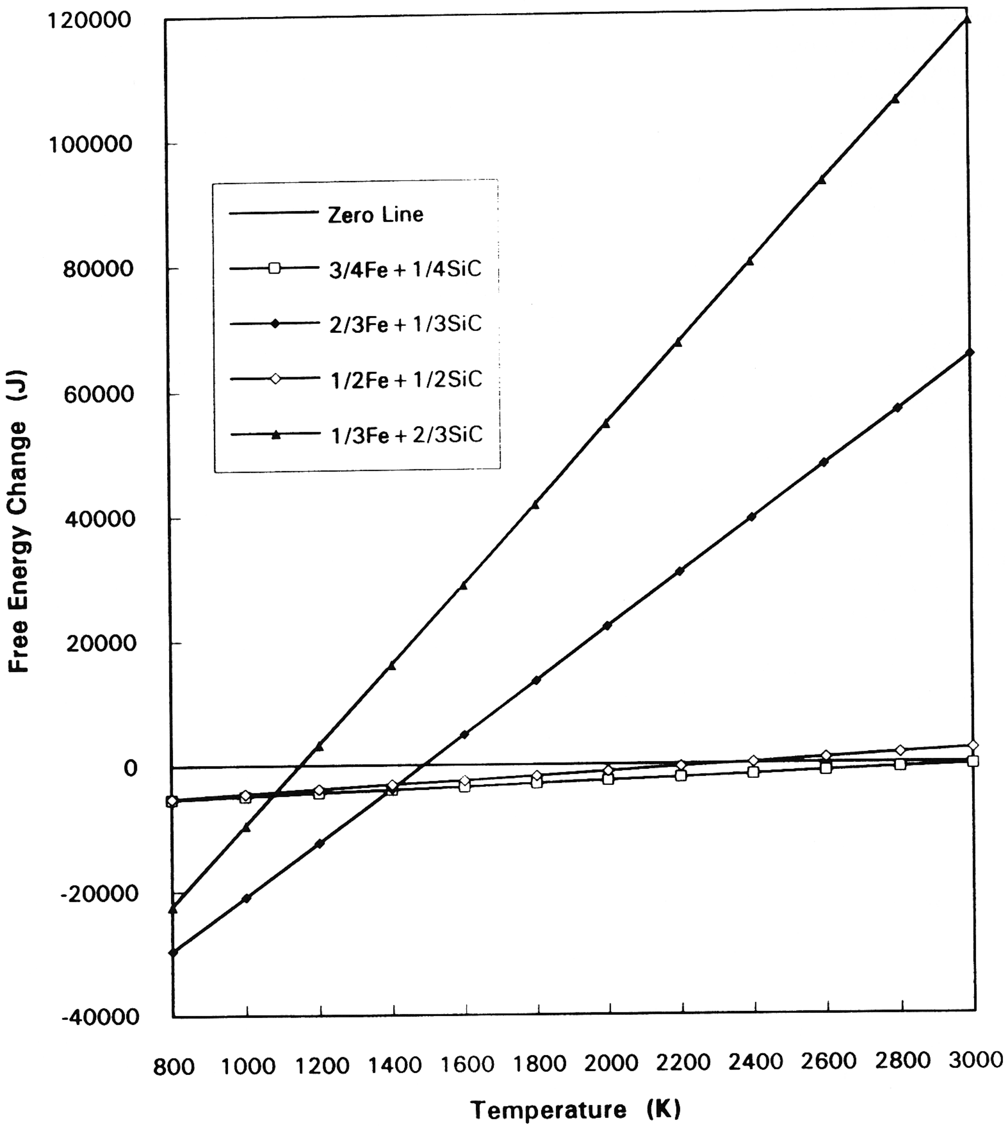

Fig. 8. Free-energy change of reaction of SiC and iron.

in SiC. Using SiC–Co as an example, the eutectic melting, Co + SiC $\rightarrow$ (Co,Si)(l) + C, occurred at ~1053 K (780°C) and terminated at 1253 K (980°C) (Fig. 1). The eutectic solidifying during cooling, (Co,Si)(l) + C $\rightarrow$ Co_2Si + CoSi + C, occurred at 1139–1041 K (866°–768°C) (Fig. 1). Apparently, these reactions occurred within temperature ranges rather than at definite temperatures. Examination of the phase diagrams of the Si–Co system[13] shows that the temperature of the eutectic point between Co_2Si and CoSi is 1559 K (1286°C), which is much higher than the presumed eutectic temperature range measured in the reaction of SiC and cobalt. These results could be attributed to the existence of the carbon in SiC, because one more component creates another degree of freedom, according to the phase rule, and lowers the eutectic temperature.[7] Cobalt also can act as a catalyst, which could be responsible for the decomposition of SiC. The same argument also is applicable to the SiC–Ni system. The liquification–solidification eutectic reactions involved in the SiC–Ni system may be Ni + SiC $\rightarrow$ (Ni,Si)(l) + C (973–1323 K (700°–1050°C)) and (Ni,Si)(l) + C $\rightarrow$ $\gamma(Ni_{0.74}Si_{0.26})$ + $\delta(Ni_2Si)$ + C (1173–1053 K (900°–780°C)). However, according to the phase diagram,[13] the eutectic reaction, (Ni,Si)(l) $\leftrightarrow$ $\gamma(Ni_{0.74}Si_{0.26})$ + $\delta(Ni_2Si)$ should occur at 1554 K (1281°C).[13] The SiC–Fe system seems to be different, and only Fe_3Si was found. The identification of endothermic and exothermic peaks (Fig. 1) for this system is not as certain as it is for the other systems. However, the reaction of SiC with iron still can be assumed to take the route of the eutectic reaction. Fe_3Si finally was formed probably because of some solid-state reaction.

The negative free-energy change generally may provide the driving force, and low-temperature liquid formation through eutectic reaction may offer kinetic convenience to the SiC–M reactions (where M is cobalt, nickel, and iron). These thermodynamic and kinetic conditions make SiC completely unstable. Even though Negita[6] suggested that cobalt, nickel, and iron might act as sintering aids for SiC ceramics after comparing the stabilities of their carbides with SiC, these metals cannot be used as sintering aids for SiC ceramics, because they react with SiC to form silicides instead of carbides and leave free carbon instead of free silicon.

Because eutectic liquid formation often is involved in the reactions of SiC and metals, the chemical instability of SiC in the presence of metals defined by the stability comparison of silicides may be relatively important. The eutectic reaction, including its low reaction temperature and liquid phase formation, provides kinetic convenience to the SiC and metal reaction. This type of kinetic condition does not exist when carbide formation is dominant.

The calculation method proposed for thermodynamic analysis also may be applied to the stability predictions of SiC coexisting with some transition metals at elevated temperature. Similarly, ΔG_1 and ΔG_2 can be evaluated by simple computation based on Refs. 1, 8, and 9, and ΔG_4 can be obtained by

Table III. Free-Energy-Change Calculations of Silicide Formations through Reactions of SiC with Transition Metals

Silicides in reaction (0)	Free-energy change (J)		Free-energy change (J/mol)		Free-energy change, ΔG_0 (J)
	ΔG_1	ΔG_2	ΔG_3	ΔG_4	
$Cr_{1/2}Si_{1/2}$	$10450 - 4.90T$	$61235 - 18.50T$	$-42482 + 4.51T$	$-106785 + 63.47T$	$-77582 + 44.45T$
$Cr_{1/3}Si_{2/3}$	$6967 - 3.27T$	$81647 - 24.67T$	$-37424 + 4.49T$	$-48170 + 27.29T$	$3020 + 3.84T$
$Hf_{1/3}Si_{2/3}$	$8023 - 3.21T$	$81647 - 24.67T$	$-37424 + 4.49T$	$-140529 + 77.38T$	$-88283 + 53.99T$
$Mo_{1/3}Si_{2/3}$	$8872 - 3.06T$*	$81647 - 24.67T$	$-37424 + 4.49T$	$-302911 + 132.10T$	$-249816 + 108.86T$
$Nb_{1/3}Si_{2/3}$	$7715 - 2.06T$*	$81647 - 24.67T$	$-37424 + 4.49T$	$-161564 + 73.01T$	$-110186 + 50.23T$
$Ta_{1/3}Si_{2/3}$	$8233 - 2.53T$	$81647 - 24.67T$	$-37424 + 4.49T$	$-37610 + 16.26T$	$14846 - 6.45T$
$Ti_{5/8}Si_{3/8}$	$3524 - 1.80T$	$42929 - 13.88T$	$-39910 + 4.50T$	$-36680 + 15.26T$	$-30138 + 4.08T$
$Ti_{1/3}Si_{2/3}$	$6297 - 3.23T$	$81647 - 24.67T$	$-37424 + 4.49T$	$-117402 + 66.97T$	$-66882 + 43.56T$
$V_{3/4}Si_{1/4}$	$97380 - 44.61T$*	$30618 - 9.25T$	$-29080 + 0.70T$	$-169213 + 77.01T$	$-70344 + 23.91T$
$V_{1/3}Si_{2/3}$	$43280 - 19.83T$*	$81647 - 24.67T$	$-37424 + 4.49T$	$-89905 + 46.11T$	$-2402 + 6.1T$
$Zr_{1/3}Si_{2/3}$	$6700 - 3.15T$	$81647 - 24.67T$	$-37424 + 4.49T$	$-101927 + 54.42T$	$-51004 + 31.09T$

*L_M values in the calculation of ΔG_1 were calculated from phase diagrams using Eq. (5).

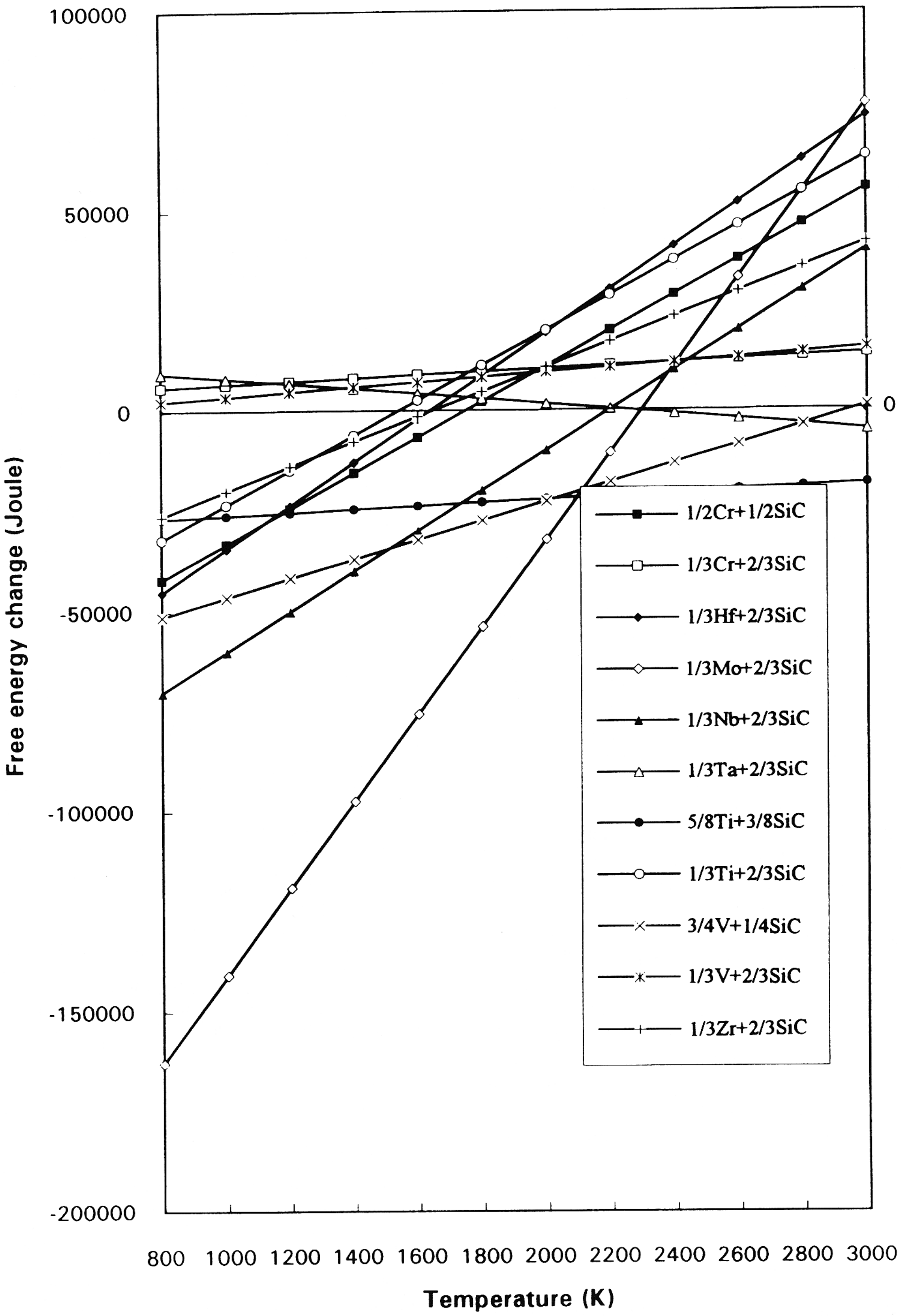

Fig. 9. Free-energy change of reaction of SiC and various metals.

using the M–Si phase diagrams[13] as was done earlier. Because only phase diagrams of M–Si (where M is chromium, hafnium, molybdenum, niobium, tantalum, titanium, vanadium, and zirconium) are available in Ref. 13, the predictions, therefore, are limited to the systems of SiC with these transition metals. L_M values for molybdenum, niobium, and vanadium have not been reported; therefore, ΔG_1 values for these transition metals are evaluated using Eq. (5), in which $M_{1-x}Si_x$ is replaced by pure M and L_M is replaced by $-\Delta H_A$ of pure M.

The value of ΔG_3 must be estimated less accurately because μ_{Si} and ΔH_{Si} of liquid solutions of M–Si (where M is chromium, hafnium, molybdenum, niobium, tantalum, titanium, vanadium, and zirconium) cannot be found. The value of ΔG_3 was determined as an average of ΔG_3 values of liquid solutions of cobalt, nickel, and iron in silicon. The reason for this is that transition metals have almost equal electronegativities and similar chemical affinities to silicon. According to Kleppa,[18] most liquid solutions can be treated as regular solutions, and the interacting parameter L is only a function of the electronegativity coefficients of the two components. The values of ΔG_3 in the cobalt, nickel, and iron cases are only slightly different, and the entropy change in ΔG_3 is almost ideal mixing. Taking an average of ΔG_3 values of SiC–M (where M is cobalt, nickel, and iron) as ΔG_3 for some other transition metals is a reasonable approximation. The calculation results of the silicides of the predicted systems are listed in Table III and plotted in Fig. 9. Table III and Fig. 9 contain only the silicide-forming reactions of SiC with these metals, involving low-temperature eutectics and having the lowest ΔG_0 values among all possible silicide-forming reactions of each system. For example, in the SiC–Mo system, only $Mo_{1/3}Si_{2/3}$ is listed and plotted; others, such as $Mo_{3/4}Si_{1/4}$ and $Mo_{5/8}Si_{3/8}$, are not because of their involvement in high-temperature eutectics and large positive ΔG_0 values.

The thermodynamic properties of the V–Si system were reported by Storms and Myers.[19] The standard free energies of formations at 1650 K (1377°C) for $V_{3/4}Si_{1/4}$ and $V_{1/3}Si_{2/3}$ are −36581.6 and −35334.5 J/mol, respectively. By combining the free-energy change of reaction (2), the values of ΔG_0 at 1650 K (1377°C) for the reactions forming the aforementioned compounds also were calculated from these values and were −21226.1 and 5606 J/mol, respectively. These values are different from our values (−30892.5 and 7663 J/mol) but give the same relative stability of SiC in the presence of vanadium. The liquid Cr–Si system was studied by Riegert *et al.*[20] ΔG_3 and its entropic parts for $Cr_{1/2}Si_{1/2}$ and $Cr_{1/3}Si_{2/3}$ at 1900 K (1627°C) can be obtained by using the free-energy changes of liquid Cr–Si solutions given by Riegert *et al.*;[20] these values were −33913 and −28893 J/mol, and 5.76 and 5.054 J/(mol·K), which are quite similar to the ΔG_3 values from this study.

Using the temperature range of 1400–2000 K (1127°–1727°C) as that of interest, a comparison of free-energy changes plotted in Fig. 9 indicates that metals, such as molybdenum, niobium, titanium, and vanadium, react with SiC to produce $Mo_{1/3}Si_{2/3}$, $Nb_{1/3}Si_{2/3}$, $Ti_{5/8}Si_{3/8}$, and $V_{3/4}Si_{1/4}$, respectively, giving the most-negative free-energy changes. ($Ti_{5/8}Si_{3/8}$ may never be formed because TiC formation is dominating.) Chromium and tantalum, giving positive free-energy changes, will not react with SiC in this temperature range. Other metals, such as hafnium and zirconium, are critical because their value of ΔG_0 runs over the zero line of free-energy change. From the silicide point of view, molybdenum, niobium, titanium, and vanadium may be predicted to make SiC unstable at elevated temperatures, and chromium and tantalum do not. Hafnium, titanium, and zirconium may or may not cause decomposition of SiC, depending on other conditions, such as eutectic temperatures of metals and silicon, impurities, and other kinetic conditions.

V. Conclusions

(1) SiC is not stable in the presence of cobalt, nickel, and iron in the temperature range 1400–2000 K (1127°–1727°C). The instability is caused by the reaction of SiC with metals to produce metal silicides instead of carbides, leaving free carbon precipitated. Low-temperature eutectic reactions of metals and the silicon in SiC provide kinetic convenience to the overall reaction.

(2) The instability of SiC in the presence of cobalt, nickel, or iron can be explained by thermodynamic analysis of the reactions of SiC with metals. A calculation method for the estimation of the free-energy change of the reactions has been proposed based on basic thermodynamic properties and phase diagrams of the materials involved. Results from experiments and thermodynamic analyses generally agree.

(3) Applying the proposed method to calculate the free-energy changes of the reactions of SiC with some other transition metals indicates that SiC may not be stable in the presence of molybdenum, niobium, titanium, and vanadium but may be stable with chromium and tantalum. Stability is critical with hafnium and zirconium.

(4) In defining the instability of SiC in the presence of metals, the comparison of the stabilities of metal silicides and the comparison of the stabilities of metal carbides, with respect to SiC, are of equal importance thermodynamically. Kinetically, however, silicide formation is more favorable than carbonization, and the instability of SiC caused by silicide formation is of greater importance and, as such, may need to be considered carefully when studying the interaction of metals with SiC.

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