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Calculated influences of starting materials composition on carbothermal nitridation synthesis of silicon nitride/silicon carbide composite powders

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Equilibrium phase composition at 1 atm total pressure is quantitatively calculated as the function of starting materials composition for carbothermal nitridation synthesis of Si_3N_4/SiC composite powders. N_2 flow is simulated by the N_2 amount in the starting materials. At low starting N_2 content (molar ratio $N_2/SiO_2 \leq 100$), Si_3N_4 and SiC can not exist in equilibrium at the same temperature. At higher starting N_2 content, the Si_3N_4-SiC coexisting temperature range appears above 1760 K. The upper limit of the temperature range becomes higher with increasing starting N_2 content. Starting carbon content affects the composition in the equilibrium powder products. The calculation results are compared with experiments. © *2001 Kluwer Academic Publishers*

1. Introduction

Nanometer-sized silicon carbide (SiC) particles-reinforced silicon nitride (Si_3N_4) matrix composite (Si_3N_4/SiC nanocomposite) was found to have substantial increase in mechanical properties over the Si_3N_4 monolithic material at both room and elevated temperatures [1, 2]. A considerable amount of researches have focused on fabrication methods to make Si_3N_4/SiC nanocomposite powders. One such research involved mixing micron/submicron Si_3N_4 and nanometer-sized SiC powders through mechanical milling [3]. This approach is simple, but difficult to obtain uniformly distributed SiC particles in the Si_3N_4 matrix, thus resulting in only a small increase in mechanical properties. Another research used chemical vapor deposition to prepare amorphous Si-N-C powders, which crystallized into Si_3N_4/SiC nanocomposites during sintering [4]. This method produced a homogeneous distribution of SiC particles and, consequently, resulted in superior mechanical properties. However, this method requires expensive raw materials. Other approaches include pyrolysis of organic precursors [5], coating carbon on Si_3N_4 powders by pyrolysis of methane (SiC nanoparticles would form as a result of the reaction between the coated carbon and silica (SiO_2) located on the surface of Si_3N_4 particles) [6], and partial reduction of Si_3N_4 powders by pyrolyzed carbon [7].

Industrial SiC powders are produced extensively by carbothermal reduction of SiO_2 due to its relatively low cost in comparison to other methods [8]. The size of SiC particles is, to a great extent, determined by the size of carbon particles before reduction [9]. Carbothermal nitridation of SiO_2 used to synthesize Si_3N_4 powders is also cost-effective [10]. By synthesizing Si_3N_4 and SiC simultaneously through carbothermal reduction of SiO_2 in the presence of nitrogen, a combination of low cost and uniform distribution of SiC nanoparticles are expected. This method to synthesize Si_3N_4/SiC nanocomposite powders has been experimentally investigated and generated the expected results [11].

It is convenient to conduct carbothermal nitridation of SiO_2 in flowing N_2 at 1 atm total pressure. Thermodynamic calculation is helpful for understanding the influences of such important parameters as N_2 flow, carbon content, and temperature. Some work has been done concerning thermodynamics of Si-N-O [12, 13], Si-C-O [13], and Si-C-N-O [14, 15] systems and the phase stability regions have been plotted as the function of temperature and partial pressure of gases. However, the control of partial pressures is difficult to conduct in practice. The gas-phase compositions and the phases in equilibrium with the gases in the Si-C-N-O system were calculated by Weiss *et al.* [16], but the equilibrium phase contents which vary depending on the composition of starting materials and the temperature were not clearly demonstrated. This paper reports the thermodynamic calculation of carbothermal nitridation of SiO_2 for predicting equilibrium phase contents, with starting materials composition and temperature as variables. The Si_3N_4-SiC coexisting condition is obtained.

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2. Calculation

The calculation is performed using the ZGRG program developed by Zhu [17] for thermodynamic computations of complex systems. The modeling of this program is based on the principle that a closed system is in equilibrium only when its Gibbs free energy reaches the minimum [18]. The Gibbs free energy, G, of a closed system is formulated as

$$G = \sum_{i=1}^{N} n_i \mu_i \tag{1}$$

where n_i and μ_i are, respectively, the mole number and chemical potential of species i in the system, and N is the number of species. The value of n_i must satisfy the following two constraints:

$$n_i \geq 0 \qquad (i = 1, 2, 3, \ldots N) \tag{2}$$

$$\sum_{i=1}^{N} a_{ij} n_i = E_j \qquad (j = 1, 2, 3, \ldots M) \tag{3}$$

where a_{ij} is the atom number of element j in the chemical formula of species i, E_j the mole number of element j, and M the number of elements in the system. The equilibrium composition, namely n_i^{eq}, is therefore obtained by minimizing G with the constraints of Equations 2 and 3. This is a nonlinear optimization problem. The ZGRG program uses generalized reduced gradient method (GRG), firstly developed by Lasdon *et al.* [19], as its nonlinear optimizing algorithm.

Due to the lack of sufficient data for activity and fugacity coefficients, some approximations are made. As the temperature under consideration is higher than 1000 K and the total pressure is 1 atm, the ideal gas model is employed, i.e.

$$\mu_i = \mu_i^0 + RT \ln P y_i \tag{4}$$

where μ_i^0 is the chemical potential of gas i under standard condition and $\mu_i^0 = G_i^0$, where G_i^0 is the standard Gibbs free energy of formation for species i. R is the universal gas constant, T the temperature in Kelvins, P the total pressure, and y_i the mole fraction of gas i in the gaseous phase. No solutions are considered. As for the pure condensed phases,

$$\mu_i = \mu_i^0 = G_i^0 \tag{5}$$

The species considered in the calculation and their standard Gibbs free energies of formation are shown in Table I. Since only a few specific heat data are available, the standard Gibbs free energy is described solely as a linear function of the temperature. The reference states are graphite, liquid silicon, and gaseous N_2 and O_2. The data for C(l) and Si(s) are, respectively, from Weiss *et al.* [16] and Hultgren *et al.* [20], and that for Si_2N_2O, α-Si_3N_4 and β-Si_3N_4 are from Hendry [21, 22]. The remaining data are from JANAF tables [23]. According to [15] the chemical formula for α-Si_3N_4 is $Si_{2.85}N_{3.75}O_{0.075}$.

TABLE I Standard Gibbs free energy of formation ($G_i^0 = A + BT$) in the Si-C-N-O system

Species	A (J/mol)	B (J/mol/K)	Species	A (J/mol)	B (J/mol/K)
Gases			Gases		
C	714985.7	−156.75	CO	−119945.9	−83.05
C_2	829360.1	−188.65	CO_2	−397189.3	0.268
C_3	763506.5	−185.1	SiO	−166118.5	−45.27
Si	391083.6	−111.63	SiO_2	−362659.1	32.02
Si_2	470398.7	−113.64	NO	90476.6	−12.69
Si_3	448449.5	−90.449	Liquids		
SiC	657941.0	−154.7	C	14223.6	−27.196
Si_2C	407283.4	−114.31	Si	0.0	0.0
SiC_2	544932.9	−162.38	Solids		
N_2	0.0	0.0	C	0.0	0.0
N	480695.8	−67.01	Si	−50208.0	29.797
CN	428824.9	−97.22	β-SiC	−122110.0	36.002
C_2N_2	311324.9	−44.69	α-SiC	−120319.2	36.798
SiN	311821.8	−61.15	α-Si_3N_4	−1317924.0	683.391
Si_2N	279914.9	−47.52	β-Si_3N_4	−1086624.0	539.391
O_2	0.0	0.0	SiO_2(Cr.)	−944893.6	196.91
O	255742.5	−67.01	SiO_2(Tr.)	−946651.7	197.912
			Si_2N_2O	−758716.0	190.594

3. Results and discussion

3.1. Influence of nitrogen flow

The N_2 flow is described as the starting N_2 content (SNC) in the raw materials. With starting SiO_2 and carbon being 1 mol and 2.5 mol, respectively, and the variation of SNC from 4–4000 mol, the influence of SNC on the equilibrium composition is calculated. The species existing in the equilibrium composition are shown in Fig. 1, with the exception of N_2 and some species found in a considerable small amount such as SiN(g).

It is clear from Fig. 1 that SNC determines whether Si_3N_4/SiC composite powder would exist in the equilibrium products after carbothermal nitridation of SiO_2. High SNC is necessary to produce Si_3N_4/SiC composite powders. When SNC ≤ 100 mol, Si_3N_4 and SiC can not exist in an equilibrium at the same temperature. By increasing SNC to 200 mol, the Si_3N_4-SiC coexisting region appears at the temperature between 1670 and 1705 K. The coexisting region widens to 1670–1755 K when SNC is 400 mol, and further widens to 1670–1840 K when SNC is 4000 mol. Thermodynamically Si_3N_4/SiC composite powders can be synthesized in the Si_3N_4-SiC coexisting temperature range without other solid contaminants such as Si_2N_2O.

The appearance of Si_3N_4-SiC coexisting temperature range is the result of the widening of the Si_3N_4 and SiC existing temperature ranges. It is evident that the highest Si_3N_4 existing temperature, $T_{\mathrm{SN}}^{\mathrm{high}}$, is governed by the reaction

$$\begin{aligned} &2\alpha\text{-}Si_{2.85}N_{3.75}O_{0.075}(s) + 2.7CO(g) \\ &\quad = 2.85Si_2N_2O(s) + 2.7C(s) + 0.9N_2(g) \end{aligned} \tag{6}$$

in Fig. 1a and b, by the reaction

$$\begin{aligned} &2\beta\text{-}Si_3N_4(s) + 3CO(g) \\ &\quad = 3Si_2N_2O(s) + 3C(s) + N_2(g) \end{aligned} \tag{7}$$

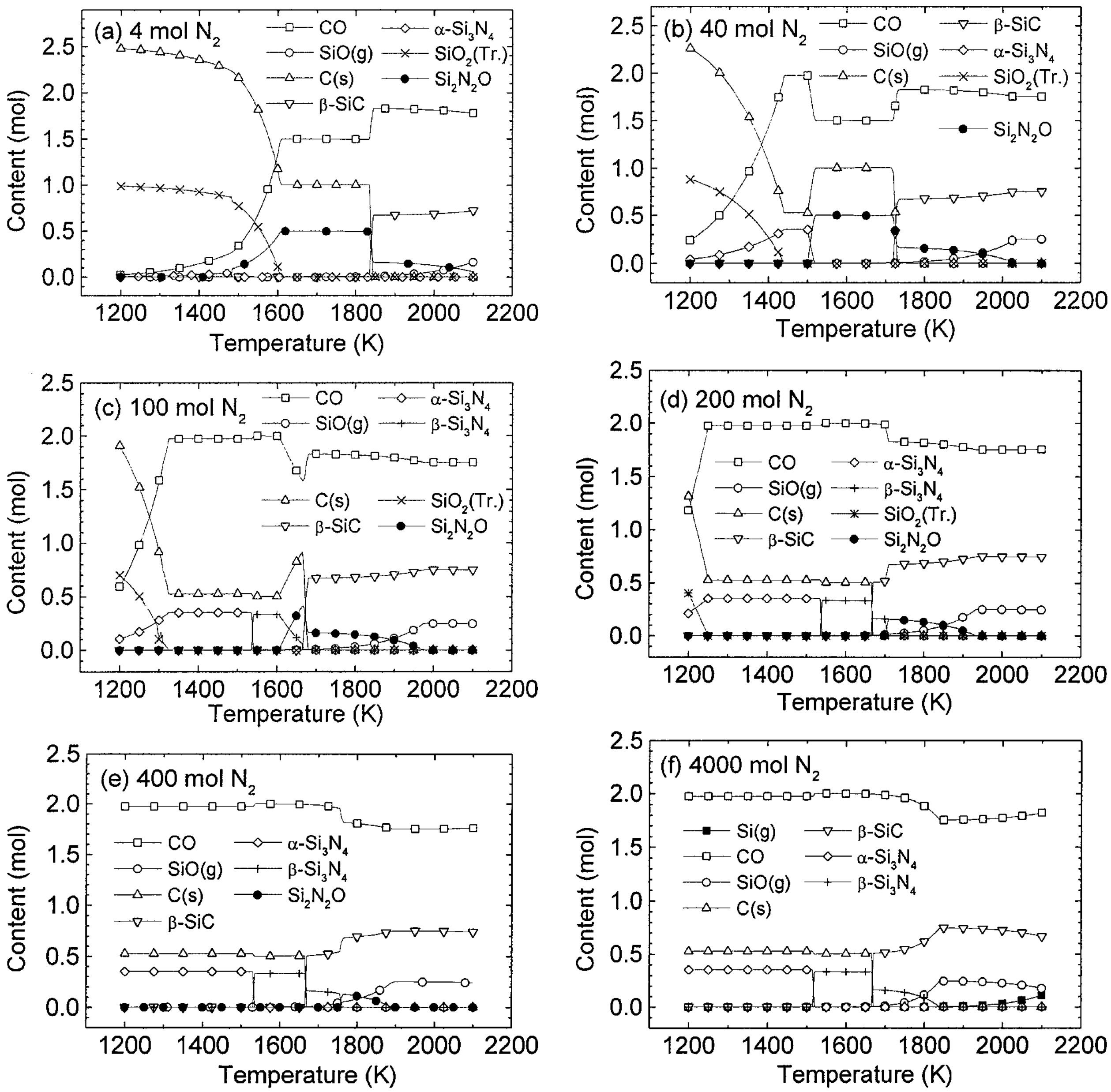

Figure 1 Calculated equilibrium composition of carbothermal nitridation of SiO_2 at 1 atm total pressure, with starting SiO_2 and carbon being 1.0 mol and 2.5 mol, respectively, and starting N_2 being (a) 4 mol, (b) 40 mol, (c) 100 mol, (d) 200 mol, (e) 400 mol, and (f) 4000 mol.

in Fig. 1c, by the reaction

$$\beta\text{-}Si_3N_4(s) + CO(g) = Si_2N_2O(s) + \beta\text{-}SiC(s) + N_2(g) \qquad (8)$$

in Fig. 1d and e, and by the reaction

$$2\beta\text{-}Si_3N_4(s) + 3CO(g) = 3\beta\text{-}SiC(s) + 3SiO(g) + 4N_2(g) \qquad (9)$$

in Fig. 1f. The lowest SiC existing temperature, T_{SC}^{low}, is governed by the reaction

$$Si_2N_2O(s) + 3C(s) = 2\beta\text{-}SiC(s) + CO(g) + N_2(g) \qquad (10)$$

in Fig. 1a–c, and by the reaction

$$\beta\text{-}Si_3N_4(s) + 3C(s) = 3\beta\text{-}SiC(s) + 2N_2(g) \qquad (11)$$

in Fig. 1d, e and f. At low SNC $T_{SN}^{high} < T_{SC}^{low}$. Since the total pressure is 1 atm and the N_2 partial pressure, p_{N_2}, is more than 0.5 atm in Fig. 1a, the increase of p_{N_2} is limited to less than 0.5 atm when further increasing SNC, while the CO and SiO partial pressures can decrease by several orders. Therefore, with the increase of SNC, Si_3N_4 will stabilize at a higher temperature according to the reaction (6)–(9), i.e. T_{SN}^{high} becomes higher, and similarly, T_{SC}^{low} becomes lower according to the reaction (10). When $T_{SN}^{high} > T_{SC}^{low}$, the Si_3N_4-SiC coexisting region appears. T_{SC}^{low} remains unchanged in Fig. 1d, e and f because at high SNC the variation of SNC has almost no influence on p_{N_2}, which determines the balance of the reaction (11).

These results are compared with reported experiments. In the experiments by Carroll *et al.* [11], the flowing N_2 consumed during the reaction is estimated at more than 100 N_2/SiO_2 molar ratio, and Si_3N_4/SiC nanocomposite powders were synthesized in the temperature range as calculated above. Because β-Si_3N_4 disappears at 1665 K and β-SiC appears at 1670 K in Fig. 1c, the Si_3N_4-SiC coexisting temperature is expected to appear at a slightly higher SNC. However, this prediction should not be considered quantitatively precise because of the approximations in the calculation and the neglect of kinetic factors. In carbothermal nitridation synthesis of Si_3N_4 powders high N_2 flow is also preferable because the wider Si_3N_4 existing temperature range is expected at higher SNC, as shown in Fig. 1. For example, Weimer *et al.* conducted the synthesis with an estimated flowing N_2/SiO_2 molar ratio of several hundreds [24].

The $\alpha \rightarrow \beta$-Si_3N_4 transformation temperature is 1540 K in Fig. 1c and d, 1535 K in Fig. 1e, and 1520 K in Fig. 1f, decreasing with the increase of SNC. This is because the transformation occurs according to the gas-involving reaction

$$\begin{aligned}&\alpha\text{-}Si_{2.85}N_{3.75}O_{0.075}(s) + 0.075C(s) + 0.075N_2(g)\\&\quad = 0.9\beta\text{-}Si_3N_4(s) + 0.075CO(g) \qquad (12)\end{aligned}$$

Jha [15] predicted that at 1 atm of N_2 pressure, the α-phase closed at ~1500 K, which is close to that predicted at high SNC in this study.

3.2. Influence of starting carbon content

In the above calculation the starting carbon content (SCC) and SiO_2 are fixed at 2.5 mol and 1.0 mol, respectively. Computation with different starting carbon content results in the same conclusion: that Si_3N_4/SiC composite powders can only be synthesized at high SNC. The composition of the equilibrium powder product prepared at high SNC varies according to the changing carbon content, which is typically illustrated in Fig. 2. At SCC < 2.0 mol, no SiC exists in the powder; at SCC > 3.0 mol, no Si_3N_4 exists. At SCC $=$ 2.0–3.0 mol, Si_3N_4/SiC composite powders are thermodynamically produced, with Si_3N_4 and SiC contents changing linearly according to the variation of SCC.

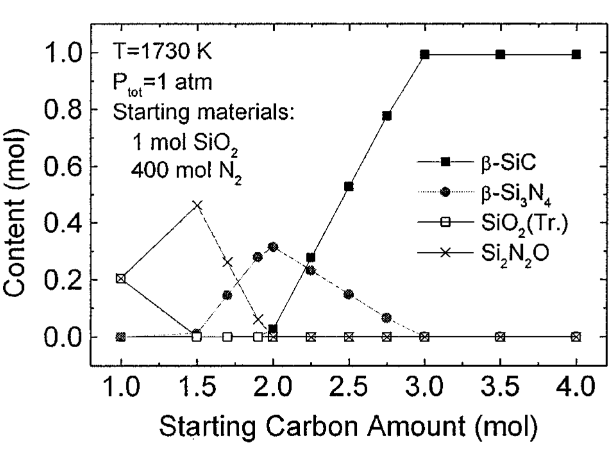

Figure 2 The composition of equilibrium composite powder product as the function of starting carbon content.

As two solid reactants, namely carbon and SiO_2, are involved in carbothermal nitridation reaction, the mixing condition of these two starting materials greatly influences the reaction kinetics. Due to the difficulty in obtaining a homogeneous mixture of the starting materials, the amount of carbon effective in the reaction is less than that contained in the mixture. Therefore, in practice, the amount of carbon should exceed the theoretical requirement in the synthesis of Si_3N_4/SiC composite powders, as in the work by Carroll *et al.* [11].

4. Conclusions

In the carbothermal nitridation of SiO_2 at 1 atm total pressure, Si_3N_4/SiC composite powders can only be synthesized at a high starting N_2 content (N_2 flow). In equilibrium there is no Si_3N_4-SiC coexisting temperature range at the molar ratio of $N_2/SiO_2 \leq 100$, while at higher N_2/SiO_2 ratio the coexisting temperature range appears. Starting carbon amount influences Si_3N_4 and SiC contents in the powder products.

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