

Effect of gas composition on Si₂N₂O formation in the Si–C–N–O system

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Formation of silicon oxynitride was observed during silicon nitride whisker synthesis from silica, carbon and nitrogen. The silicon oxynitride formation was limited to a bottom area of the charged powders and found both in whisker and powder. The possible reason for this localized Si₂N₂O formation is analysed, based on the effect of gas phase composition on the phase stability among β-Si₃N₄, β-SiC and Si₂N₂O. The phase stability is closely related to the $p_{\text{SiO}}/p_{\text{N}_2}$ ratio in the gas phase. To suppress Si₂N₂O formation, the $p_{\text{SiO}}/p_{\text{N}_2}$ ratio must be lower than that of the phase boundary in the Si₃N₄/Si₂N₂O equilibrium, whereas it must be higher than that of the phase boundary in the SiC/Si₂N₂O equilibrium. The formation of silicon oxynitride during silicon nitride whisker formation was caused most likely by fluctuation in the $p_{\text{SiO}}/p_{\text{N}_2}$ ratio in the gas phase surrounding the lower area.

1. Introduction

In a recent study of Si₃N₄ whisker synthesis by carbothermal reduction of silica under flowing nitrogen gas, a localized formation of silicon oxynitride, Si₂N₂O, was observed even under low oxygen partial pressures [1]. The formation of Si₂N₂O phase was limited to a lower area of the charged material [1]. This area showed a mixture of β-Si₃N₄ and Si₂N₂O, or a mixture of β'-Sialon and Si₂N₂O in both whisker and powder forms, depending on the composition of starting materials. The upper area, on the other hand, showed wool yarn-like Si₃N₄ or Sialon whiskers only. This localized formation of silicon oxynitride was attributed to a fluctuation in the $p_{\text{SiO}}/p_{\text{N}_2}$ ratio in the gas phase surrounding the lower area of charged material [1].

Formation of silicon oxynitride is one of the common problems encountered not only in whisker synthesis but also in other Si₃N₄ ceramic processings, such as composite formation, reaction bonding or sintering. Although the application of Si₃N₄ whiskers is still in its infancy, a separate formation of Si₃N₄ and Si₂N₂O is expected to be more desirable because of the probable complexity or mutually exclusive requirements for the application of these two whiskers. β-Si₃N₄ and Si₂N₂O are in thermodynamic equilibrium from 1400 to 1650 K under 0.1 MPa nitrogen pressure when the carbon activity is unity and the oxygen partial pressure is in a range of 10⁻²¹ to 10⁻²² MPa [2, 3]. β-Si₃N₄ becomes a stable phase with lower oxygen partial pressures, whereas Si₂N₂O is a stable phase with higher oxygen partial pressures [3].

There were two possible causes for Si₂N₂O formation in the lower area: (i) the flowing nitrogen gas might have had less accessibility to the lower area

than the upper area, or (ii) the SiO partial pressure was higher in the lower area compared to that in the upper area. In either case, the $p_{\text{SiO}}/p_{\text{N}_2}$ ratio might not be the same in those two areas. In this paper, the gas phase is further analysed to gain an insight into the effect of the $p_{\text{SiO}}/p_{\text{N}_2}$ ratio on phase stability. All calculations are done for 1623 K, the same temperature as in our current work [1].

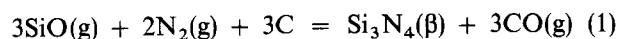
2. Thermodynamic calculation of gas phase in the Si–N–C–O system

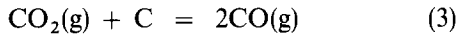
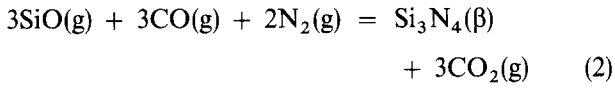
2.1. Phases in equilibrium

The phases under consideration are β-Si₃N₄, Si₂N₂O, β-SiC, carbon and a gas phase. SiO₂ is not included because it is not an equilibrium phase when β-Si₃N₄ is a stable phase [2, 3]. The main components of the gas phase are assumed to be N₂, O₂, SiO and CO/CO₂. Nitrogen gas is included because N₂ was a flowing gas in our current whisker synthesis [1]. In that study O₂ and CO/CO₂ were measured and SiO was considered as a gas species that reacted with N₂ or CO to form Si₃N₄ or SiC whiskers. The standard states of activities are pure solid components for all the solid phases, and 1 atm pure gas for all the gases.

2.2. Gas/β-Si₃N₄/Si₂N₂O equilibrium

Since the CO/CO₂ ratio has been found to be very close to its equilibrium value in the whisker synthesis process [1, 2], an overall reaction of β-Si₃N₄ formation from SiO(g) can be expressed as Equation 1 below by combining the two reactions of Equations 2 and 3:





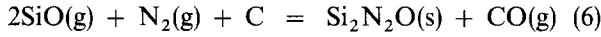
The logarithm of the equilibrium constant of Equation 1, K_1 , is expressed as

$$\begin{aligned} \log K_1 &= \log \left(\frac{a_{\text{Si}_3\text{N}_4} p_{\text{CO}}^3}{p_{\text{SiO}}^3 p_{\text{N}_2}^2 a_{\text{C}}^3} \right) \\ &= (49\,747/T) - 22.88 \end{aligned} \quad (4)$$

where p_X and a_X are the partial pressure and the activity of component X , respectively. Equation (4) is obtained from the standard free energies of formation of reactants and products in Equation 1 (3, 4, 5). When Si_3N_4 is a stable solid phase, $a_{\text{Si}_3\text{N}_4} = 1$; then p_{SiO} can be obtained from Equation 4 as

$$\begin{aligned} \log p_{\text{SiO}} &= -\frac{1}{3} \log K_1 - \frac{2}{3} \log p_{\text{N}_2} \\ &\quad + \log p_{\text{CO}} - \log a_{\text{C}} \end{aligned} \quad (5)$$

The same calculation is applied to $\text{Si}_2\text{N}_2\text{O}$ formation. The overall reaction is written as



and $\log p_{\text{SiO}}$ is expressed by the following equation at $a_{\text{Si}_2\text{N}_2\text{O}} = 1$:

$$\begin{aligned} \log p_{\text{SiO}} &= \frac{1}{2} (-\log K_6 - \log p_{\text{N}_2} \\ &\quad + \log p_{\text{CO}} - \log a_{\text{C}}) \end{aligned} \quad (7)$$

where [5]

$$\log K_6 = (29\,211/T) - 10.81 \quad (8)$$

There is a pair of p_{SiO} and p_{N_2} values with the known values of a_{C} and p_{CO} for each reaction, Equation 1 and Equation 6. Values of $\log p_{\text{SiO}}$ are calculated as a function of $\log p_{\text{N}_2}$ at 1623 K for levels of a_{C} and p_{CO} at $a_{\text{C}} = 1, 0.1, 0.01$ and 0.001 , and at $p_{\text{CO}} = 0.1, 0.01$ and

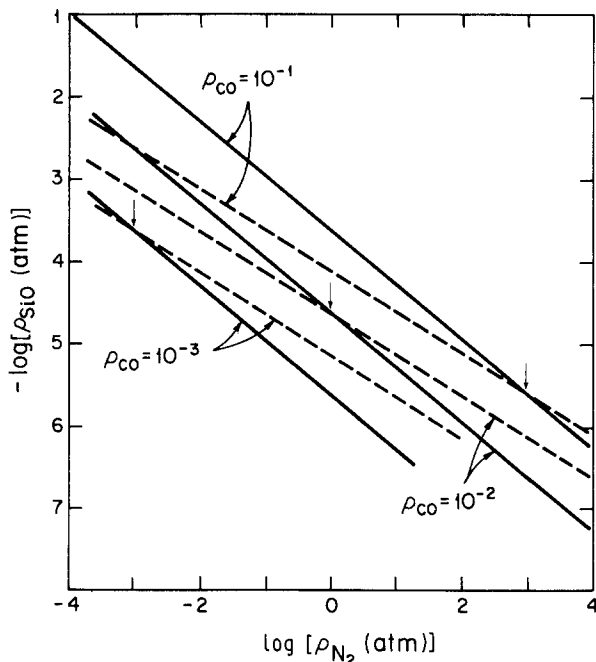


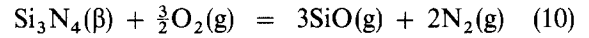
Figure 1 Logarithms of p_{N_2} and p_{SiO} for (—) $\beta\text{-Si}_3\text{N}_4$ and (---) $\text{Si}_2\text{N}_2\text{O}$ formation from $\text{SiO}(\text{g})$ at 1623 K and $a_{\text{C}} = 1$.

0.001 atm for each carbon activity. Fig. 1 shows the calculated results for $\log p_{\text{SiO}}$ and $\log p_{\text{N}_2}$ pairs at $a_{\text{C}} = 1$ for both Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$ formation. When Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$ are in equilibrium, the two lines share the same p_{N_2} and p_{SiO} values. This equilibrium p_{N_2} is expressed as a function of p_{CO} and a_{C} by combining Equations (5) and (7) as

$$\log p_{\text{N}_2} = 6 + 3 \log p_{\text{CO}} - 3 \log a_{\text{C}} \quad (9)$$

Calculated values of $\log p_{\text{N}_2}$ are marked with arrows in Fig. 1. Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$ are in equilibrium at $p_{\text{N}_2} = 10^3$ when $p_{\text{CO}} = 10^{-1}$, while $p_{\text{N}_2} = 10^{-3}$ when p_{CO} is reduced to 10^{-3} , i.e. Si_3N_4 is a stable phase for nitrogen pressures as low as $p_{\text{N}_2} = 10^{-3}$ when $p_{\text{CO}} = 10^{-3}$, while when p_{CO} increases to 10^{-1} it is stable only at higher nitrogen pressures. This implies that if $a_{\text{C}} = \text{constant}$, Si_3N_4 becomes more stable than $\text{Si}_2\text{N}_2\text{O}$ with decreasing p_{CO} . Since the decrease in p_{CO} from 10^{-1} to 10^{-3} reduces the equilibrium p_{N_2} from 10^3 to 10^{-3} , controlling the nitrogen pressure is more effective in controlling the $\text{Si}_3\text{N}_4/\text{Si}_2\text{N}_2\text{O}$ equilibrium than controlling p_{CO} .

Because one of the controllable variables in the experiment involving the Si-N-C-O system is oxygen pressure, the equilibrium p_{O_2} is calculated as follows [3, 4]:



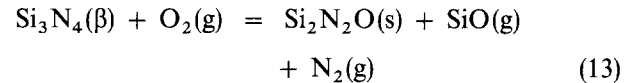
$$\begin{aligned} \log K_{10} &= \log \left(\frac{p_{\text{SiO}}^3 p_{\text{N}_2}^2}{a_{\text{Si}_3\text{N}_4} p_{\text{O}_2}^{3/2}} \right) \\ &= (-31\,382/T) + 36.04 \end{aligned} \quad (11)$$

The logarithm of p_{O_2} can be calculated by the following equation for each pair of equilibrium p_{SiO} and p_{N_2} values:

$$\log p_{\text{O}_2} = -\frac{2}{3} \log K_{10} + \frac{4}{3} \log p_{\text{N}_2} + 2 \log p_{\text{SiO}} \quad (12)$$

In Fig. 2, $\log p_{\text{N}_2}$ and the corresponding p_{CO} and p_{SiO} are plotted against $\log p_{\text{O}_2}$. The Si_3N_4 phase is stable on the upper side of the $\log p_{\text{N}_2}$ line, while $\text{Si}_2\text{N}_2\text{O}$ is the stable phase on the other side of the line.

Two phases are in equilibrium on the $\log p_{\text{N}_2}$ line which can be written as



$$\log K_{13} = \log \left(\frac{a_{\text{Si}_2\text{N}_2\text{O}}}{a_{\text{Si}_3\text{N}_4}} \right) + \log \left(\frac{p_{\text{SiO}} p_{\text{N}_2}}{p_{\text{O}_2}} \right) \quad (14)$$

Since Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$ form practically no solid solution, there are only three possibilities for the first term of Equation 14: (a) if the two phases are in equilibrium, $\log (a_{\text{Si}_2\text{N}_2\text{O}}/a_{\text{Si}_3\text{N}_4}) = 0$; (b) if $\text{Si}_2\text{N}_2\text{O}$ is the only stable phase, $\log (a_{\text{Si}_2\text{N}_2\text{O}}/a_{\text{Si}_3\text{N}_4}) > 0$; and (c) if Si_3N_4 is the only stable phase, $\log (a_{\text{Si}_2\text{N}_2\text{O}}/a_{\text{Si}_3\text{N}_4}) < 0$. To suppress the $\text{Si}_2\text{N}_2\text{O}$ formation, which corresponds to case (c), the second term must be higher than that of the $\text{Si}_3\text{N}_4/\text{Si}_2\text{N}_2\text{O}$ equilibrium, either by lower oxygen partial pressures or lower $p_{\text{SiO}}/p_{\text{N}_2}$ ratios. The carbon activity has no direct effect on that. Therefore, to eliminate $\text{Si}_2\text{N}_2\text{O}$ phase formation in either the whisker formation or reaction sintering of Si_3N_4 , the

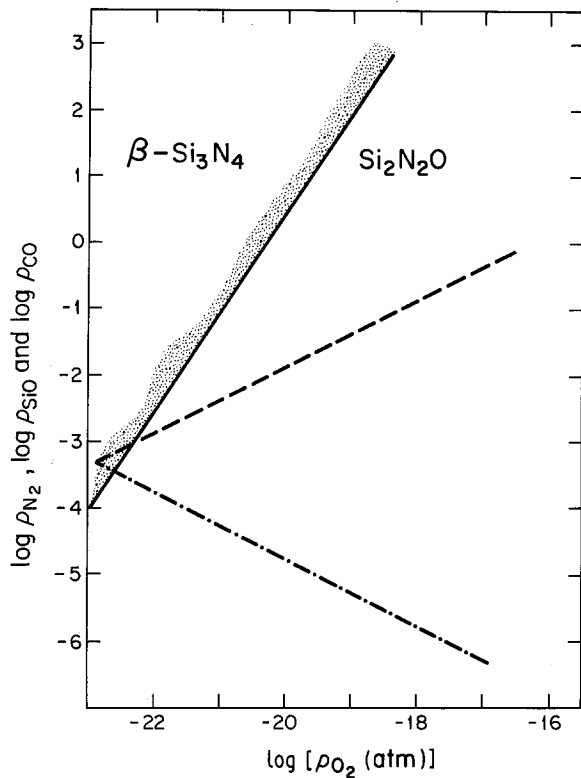
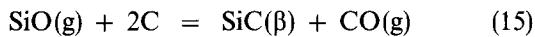


Figure 2 Logarithms of (—) equilibrium p_{N_2} and corresponding (---) p_{CO} and (-·-) p_{SiO} (atm) for β - Si_3N_4/Si_2N_2O equilibrium at 1623 K and $a_C = 1$.

p_{SiO}/p_{N_2} ratio must be maintained at adequately low values as well as keeping the oxygen pressure low.

2.3. Gas/SiC/ Si_3N_4 equilibrium

SiC formation can be expressed by the following reaction based on the same reasoning as Equation 1 [3, 4]:



$$\begin{aligned} \log K_{15} &= \log \left(\frac{a_{SiC} p_{CO}}{p_{SiO} a_{C^2}} \right) \\ &= (4277/T) - 0.16 \end{aligned} \quad (16)$$

When SiC is a stable solid phase, $a_{SiC} = 1$ and $\log p_{SiO}$ is calculated as a function of p_{CO} and a_C as

$$\log p_{SiO} = -\log K_{15} + \log p_{CO} - 2\log a_C \quad (17)$$

When both the Si_3N_4 and SiC phases are coexisting, $a_{SiC} = a_{Si_3N_4} = 1$. By combining Equations 5 and 17, the equilibrium p_{N_2} is obtained as

$$\log p_{N_2} = -0.17 + \frac{3}{2}\log a_C \quad (18)$$

A pair of equilibrium p_{N_2} and p_{SiO} values is determined for each set of a_C and p_{CO} .

The oxygen partial pressure is calculated as follows [4]:



$$\begin{aligned} \log K_{19} &= \log \left(\frac{p_{SiO} p_{CO}}{a_{SiC} p_{O_2}} \right) \\ &= (7966/T) + 8.93 \end{aligned} \quad (20)$$

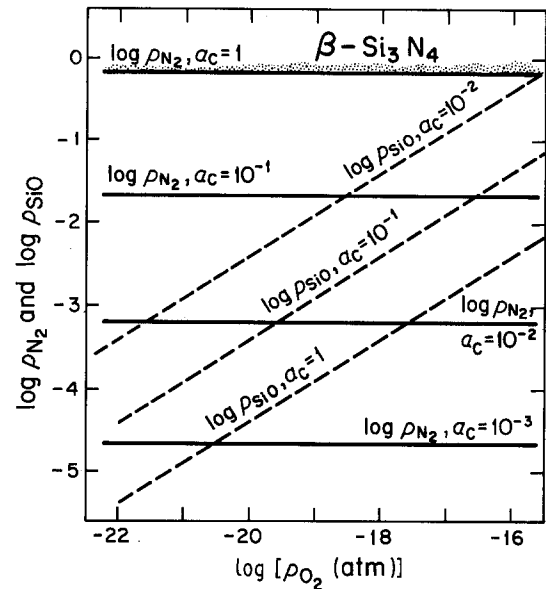
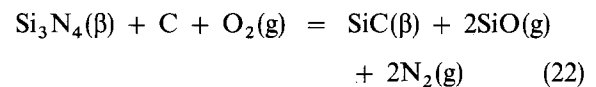


Figure 3 Logarithms of equilibrium p_{N_2} and corresponding p_{SiO} (atm) for β - Si_3N_4/SiC equilibrium at 1623 K for various a_C levels.

The equilibrium p_{O_2} can be calculated for each pair of equilibrium p_{SiO} and p_{CO} values at 1623 K as

$$\log p_{O_2} = -13.69 + \log p_{SiO} + \log p_{CO} \quad (21)$$

The equilibrium p_{N_2} and corresponding p_{SiO} are shown in Fig. 3. The Si_3N_4 is a stable solid phase along the upper side of the $\log p_{N_2}$ line for each carbon activity, while SiC is a stable phase along the lower side of the line. The Si_3N_4/SiC equilibrium can be expressed by the equation



$$\log K_{22} = \log \left(\frac{a_{SiC}}{a_{Si_3N_4}} \right) + \log \left(\frac{p_{SiO}^2 p_{N_2}^2}{p_{O_2} a_C} \right) \quad (23)$$

Because $\log(a_{SiC}/a_{Si_3N_4}) < 0$ when Si_3N_4 is a stable phase, the values of $(p_{SiO}^2 p_{N_2}^2 / a_C)$ must be higher than those at the Si_3N_4/SiC equilibrium at a known p_{O_2} . As seen in Fig. 3, $(p_{SiO}^2 p_{N_2}^2 / a_C)$ is basically controlled by a_C : the lower the a_C the higher the $(p_{SiO}^2 p_{N_2}^2 / a_C)$, while the p_{SiO}/p_{N_2} ratio decreases. The p_{SiO}/p_{N_2} ratio must therefore be lower than that of the equilibrium value to form the Si_3N_4 phase only. However, controlling a_C is more effective in controlling the Si_3N_4/SiC equilibrium than controlling the p_{SiO}/p_{N_2} ratio.

2.4. Gas/SiC/ Si_2N_2O equilibrium

The same calculation is carried out for the SiC/ Si_2N_2O equilibrium. Combining Equations 7 and 17, a pair of equilibrium p_{SiO} and p_{N_2} values are calculated for each set of p_{CO} and a_C , while $\log p_{O_2}$ is calculated from Equation 21 for these p_{SiO} values. The equilibrium p_{N_2} is a function of both p_{CO} and a_C :

$$\log p_{N_2} = -2.23 + 3\log a_C - \log p_{CO} \quad (24)$$

The final result is summarized in Fig. 4. The SiC is a stable solid phase along the lower side of the $\log p_{N_2}$ line at each carbon activity, while the Si_2N_2O phase is stable along the upper side of the line. The equilibrium

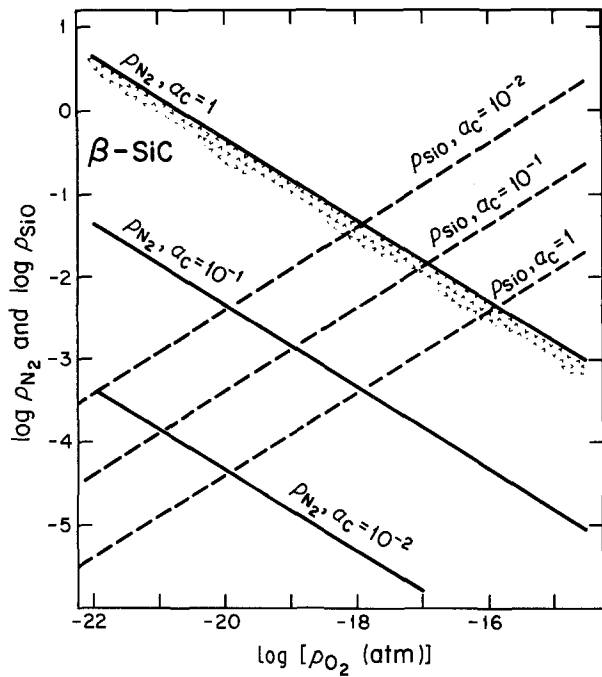
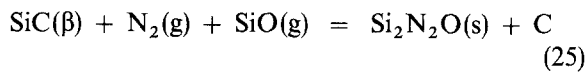


Figure 4 Logarithms of equilibrium p_{N_2} and corresponding p_{SiO} (atm) for SiC/Si₂N₂O equilibrium at 1623 K for various a_C levels.

can be expressed as



$$\log K_{25} = \log\left(\frac{a_{Si_2N_2O}}{a_{SiC}}\right) + \log\left(\frac{a_C}{p_{SiO}p_{N_2}}\right) \quad (26)$$

When SiC is the only stable solid phase, the first term of Equation 26 must be $\log(a_{Si_2N_2O}/a_{SiC}) < 0$, which requires that either a_C must be higher or p_{SiO}/p_{N_2} ratios must be lower than those at the SiC/Si₂N₂O equilibrium. Fig. 4 shows that $p_{SiO}p_{N_2} = \text{constant}$ as far as $a_C = \text{constant}$ and decreases with decreasing a_C , while p_{SiO}/p_{N_2} increases with decreasing a_C . Therefore, to suppress Si₂N₂O formation, the $p_{SiO} \cdot p_{N_2}$ ratio must be higher than that in the SiC/Si₂N₂O equilibrium, but keeping a_C higher is more effective in ensuring the formation of only β -SiC phase.

2.5. Ratio p_{SiO}/p_{N_2} in gas phase

A calculation of gas phases has shown that the solid phase stability is closely related to the p_{SiO}/p_{N_2} ratio. Logarithms of p_{SiO}/p_{N_2} in the gas phase which is in equilibrium with either Si₃N₄/Si₂N₂O, Si₃N₄/SiC or Si₂N₂O/SiC are plotted against $\log p_{O_2}$ in Fig. 5 for a_C levels 1.0, 0.1 and 0.01. All solid-phase equilibria are shown by solid lines for $a_C = 1.0$; these lines change to dashed and dot-dashed lines as a_C changes to 0.1 and 0.01, respectively: from A to B and then to C. The values of the p_{SiO}/p_{N_2} ratio are increased more than 100 times when a_C decreases 10 times. The Si₃N₄/Si₂N₂O equilibrium requires the lowest p_{SiO}/p_{N_2} ratio among these three equilibria. The Si₃N₄ phase is a stable phase on the lower sides of the lines at all levels of carbon activity. At $a_C = 1$ and $\log p_{O_2} = -20$, the Si₃N₄ phase is a stable phase below the solid line, and the Si₂N₂O phase becomes a stable

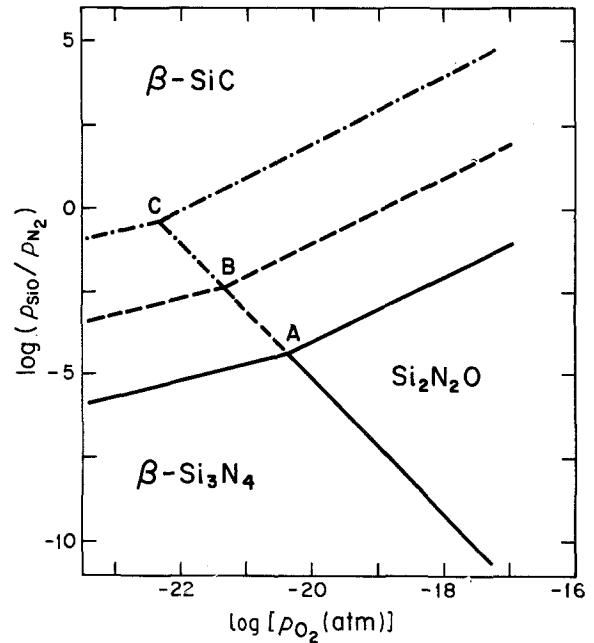
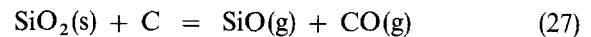


Figure 5 Effect of p_{SiO}/p_{N_2} ratio in the gas phase on the stability of phases at 1623 K for various a_C levels: (---) 10^{-2} , (----) 10^{-1} , (—) 1.

phase until $\log(p_{SiO}/p_{N_2})$ reaches the next solid line at about $\log(p_{SiO}/p_{N_2}) = -4$, above which the SiC phase is the most stable phase.

In our current study [1], SiO(g) is produced by the decomposition of SiO₂(s). The value of p_{SiO} is estimated as -2.53 atm at 1623 K by substituting p_{CO} with the average measured values of $\log p_{CO} = -1.7$ in Table II in our current work [1], and $a_C = 1$, into Equation 28 [4]



$$\log K_{27} = (-35261/T) + 17.50 \quad (28)$$

As mentioned in Section 1, there are two possible causes for Si₂N₂O formation in the lower area of charged material: p_{N_2} and p_{SiO} . The nitrogen pressure in the lower area can be one of the following: the same p_{N_2} as the flowing gas, or the equilibrium p_{N_2} of the Si₃N₄/Si₂N₂O two solid phase equilibrium, or the equilibrium p_{N_2} of the Si₂N₂O single solid phase formation. The values of p_{N_2} are calculated as $\log p_{N_2} = -0.013$ for the first case, and $\log p_{N_2} = 0.9$ for the second case by Equation 9, and $\log p_{N_2} = -3.8$ for the third case by Equation 6. Since the N₂ gas pressure was given by $\log p_{N_2} = -0.013$, all three cases were possible, but the first and second cases were more likely to occur than the third case because a mixture of Si₃N₄ and Si₂N₂O was always obtained in the lower area.

The p_{SiO}/p_{N_2} ratios are estimated for each case as $\log(p_{SiO}/p_{N_2}) = -2.5, -3.4$ and 1.3 , respectively. From Fig. 5, it can be concluded that either the first or second case is likely to occur in the lower area, depending on the fluctuating SiO(g) evolution. It might not be caused only by the fluctuation in SiO(g) but possibly affected by a fluctuation in p_{CO} as well. In the third case, the estimated p_{SiO}/p_{N_2} ratio is far beyond the Si₂N₂O stable area when $\log p_{N_2} = -3.8$,

and SiO_2 must remain as a stable phase at this $p_{\text{SiO}}/p_{\text{N}_2}$ ratio. However, solid SiO_2 phase was never found at the end of the whisker formation. The higher $p_{\text{SiO}}/p_{\text{N}_2}$ ratio consequently increases p_{O_2} in the lower area. In Fig. 5, the lowest oxygen pressures, which correspond to $\log(p_{\text{SiO}}/p_{\text{N}_2}) = -2.5$ and -3.4 , are in the range of $\log p_{\text{O}_2} = -18.5$ to -19.5 .

Some whiskers grown in the bottom area of the wool yarn-like upper whiskers, the area between the upper and the lower areas, formed polycrystalline knots as shown in Fig. 12 of our current study [1]. Fluctuation in the $p_{\text{SiO}}/p_{\text{N}_2}$ ratio also seems to be related to this morphological change in the silicon nitride whiskers, but further analysis of the gas phases is necessary to clarify the observation.

3. Summary

Phase stability among $\beta\text{-Si}_3\text{N}_4$, $\text{Si}_2\text{N}_2\text{O}$ and SiC is analysed based on the $p_{\text{SiO}}/p_{\text{N}_2}$ ratio in the gas phase. The following results are obtained:

1. To suppress $\text{Si}_2\text{N}_2\text{O}$ during Si_3N_4 formation, the $p_{\text{SiO}}/p_{\text{N}_2}$ ratios as well p_{O_2} should be kept adequately low. Controlling the nitrogen pressure is most effective for that purpose and the carbon activity has no direct effect on that.

2. To suppress $\text{Si}_2\text{N}_2\text{O}$ formation in the SiC processing, on the other hand, the $p_{\text{SiO}}/p_{\text{N}_2}$ ratios should be higher than that in the $\text{Si}_2\text{N}_2\text{O}/\text{SiC}$ equilibrium,

but keeping a higher carbon activity is more effective.

3. In the $\text{Si}_3\text{N}_4/\text{SiC}$ equilibrium such as in the $\text{SiC(w)}/\text{Si}_3\text{N}_4$ composite formation, the $p_{\text{SiO}}/p_{\text{N}_2}$ ratios must be close to the equilibrium value, but controlling the carbon activity is more effective for this purpose than controlling the nitrogen pressure.

4. $\beta\text{-Si}_3\text{N}_4$ is stable when the $p_{\text{SiO}}/p_{\text{N}_2}$ ratio in the gas phase is lower than the equilibrium values in both $\text{Si}_3\text{N}_4/\text{Si}_2\text{N}_2\text{O}$ and $\text{Si}_3\text{N}_4/\text{SiC}$ equilibria.

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