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Continuous synthesis of silicon carbide whiskers

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A two-step reaction scheme has been employed for the synthesis of SiC whiskers at 1450 °C under an argon or hydrogen flow. First, SiO vapour was generated via the carbothermal reduction of silica in a controlled manner. Second, the generated SiO vapour was reacted with carbon-carrying vapours such as CO and CH_4, which resulted in the growth of SiC whiskers on a substrate away from the batch. A higher growth rate was observed in the hydrogen atmosphere due to the formation of CH_4 which provides a more favourable reaction route. By the use of thermodynamic calculations, the preferred reaction routes have been selected for an efficient synthesis of SiC whiskers, and a continuous reactor has been designed. The system consists of a boat-train loaded with the silica–carbon mixture and iron-coated graphite substrate above it in an alumina-tube reactor. By pushing the boat-train into the hot zone at a fixed speed, SiO vapour is constantly generated. High-quality SiC whiskers have been grown on the substrate with diameters of 1–3 μm. The yield was about 30% based on the silicon input as SiO_2 and silicon output as SiC whiskers. This demonstrates the feasibility of continuous production of high-quality SiC whiskers which does not require additional processes such as purification and classification.

1. Introduction

SiC whisker is an effective material for the reinforcement of various composite materials, mainly due to its superb mechanical properties [1–3]. Its synthesis can take several routes; carbothermal reduction of silica [4–10], decomposition of organic silicon compounds [11–13] and reaction between silicon halides and CCl_4 [14]. At the present time, the preferred method for mass production appears to be by carbothermal reduction of silica [15, 16].

The carbothermal reduction has been used in many fields, such as ablation in rocket nozzles, ore processing, and synthesis of carbides and nitrides in powder or whisker form [17–20]. It is, however, well recognized that the reaction involves many steps and substeps which makes a clear understanding of it very difficult. However, numerous studies have generated a sizeable amount of data and the picture has now become clearer. The major findings on the synthesis of SiC whiskers via the carbothermal reduction of silica are summarized below.

1. To grow SiC in whiskers morphology, it is necessary to supply the reactants in a vapour form in the final step of the reaction [6, 21]. Otherwise, particulate SiC will result. The most common vapour species are SiO and CO in an inert atmosphere [4, 5, 9, 21], and SiO and CH_4 in a hydrogen atmosphere [6].

2. To achieve a reasonable growth rate of high-quality SiC whiskers, the process conditions, such as vapour pressures, temperature and catalyst addition, should be optimized fairly strictly [9, 22]. Otherwise, either the growth rate will be too slow or SiC will result in undesirable morphologies such as rosary-like, kinked, or of irregular form.

3. Iron appears to be the most effective catalyst making the vapour–liquid–solid (VLS) mechanism possible [6, 9]. The resultant whiskers are usually long (up to several millimetres) and thick (1–5 μm) and show a smooth surface with relatively little stacking fault [9]. SiC whiskers are generally of the cubic SiC structure grown in the ⟨1 1 1⟩ direction.

It was the intention of this study to ascertain the overall mechanism, especially in the presence of hydrogen, and to develop a continuous process for the synthesis of SiC whiskers via the carbothermal reduction of silica.

2. Experimental procedure

2.1. Thermodynamic calculation

The thermodynamic calculation using the SOLGASMIX computer program [23] was performed on the SiO_2–C–Ar and SiO_2–C–H_2 systems to identify the vapour and solid species at 1450 °C. The thermodynamic data were taken from the JANAF tables [24]. Based on this calculation, the stability diagram for the Si–C–O system was constructed.

2.2. Reactor for the continuous synthesis of SiC whiskers

The system designed for the continuous synthesis of SiC whiskers is shown in Fig. 1. The graphite boats containing silica (Aerosil 200, Degussa Corp., NJ) (40 wt %)–carbon (carbon black, N220, Lucky

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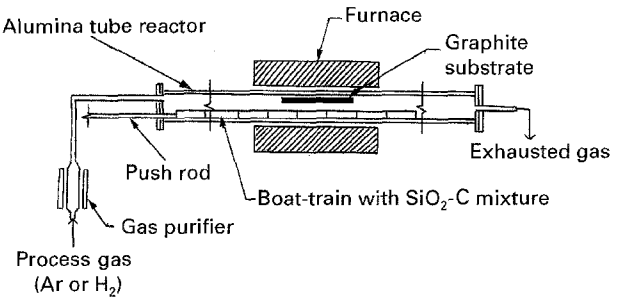

Figure 1 Schematic illustration of the reactor for the synthesis of SiC whiskers.

Continental Co. Ltd., Seoul) (60 wt %) mixture were placed at the left-hand end of the tube reactor at the beginning of each run. The substrate on which SiC whiskers grow was placed at the hot zone. The substrate was a high-purity graphite (NP60, PF Grade, Toshiba Ceramics Co. Ltd, Tokyo) or BN (99.9 %, Hoechst Ind., Korea Ltd, Seoul, Korea) which was treated with boiling hydrochloric acid (37%) for 4 h followed by uniform coating of iron powder (5 μm diameter) as catalyst. Argon gas was introduced to maintain the inert atmosphere during the heat-up period. At the reaction temperature (1450 °C), the process gas (argon or hydrogen) was introduced at the rate of 191 $cm^3 min^{-1}$ into the reactor, and the graphite boats were pushed forward to the hot zone at the predetermined rate of 0.25 g batch/min to generate SiO. At this set-up, the SiO generation rate from the batch was fixed to 9 $cm^3 min^{-1}$ by the following reaction

$$SiO_2(s) + 2C(s) \rightarrow SiO(v) + CO(v) \quad (1)$$

Another competing reaction also took place in the batch, forming SiC in particulate form as

$$SiO_2(s) + 3C(s) \rightarrow SiC_p(s) + 2CO(v) \quad (2)$$

Here, the subscript "p" refers to particle form. Therefore, the rate of SiO generation was calculated by weight loss and chemical analysis of batch at various intermittent reaction times and confirmed by the amount of SiC whiskers formed on the substrate.

2.3. Characterization

Upon completing the reaction in 15 h, the collected whiskers were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

3. Results and discussion

3.1. Thermodynamics

According to the scheme of this study, an efficient synthesis of SiC whiskers requires the conversion of SiO_2 not to SiC solid but to SiO vapour in the batch as much as possible. It also requires that the generated SiO should meet carbon-carrying species in the vapour phase which will be able to grow SiC in whisker form.

TABLE I The predominant vapour species in the SiO_2–C–Ar and the SiO_2–C–H_2 systems at 1450 °C

System	Vapour species	Equilibrium partial pressure (atm)
SiO_2–C–Ar	CO	1.95×10^{-2}
	CO_2	4.71×10^{-8}
	Si	1.55×10^{-8}
	SiO	8.63×10^{-5}
SiO_2–C–H_2	CH_2O	1.01×10^{-8}
	CH_3	4.13×10^{-6}
	CH_4	9.69×10^{-4}
	C_2H	1.82×10^{-8}
	C_2H_2	1.02×10^{-4}
	C_2H_3	3.59×10^{-8}
	C_2H_4	3.64×10^{-6}
	CO	1.95×10^{-2}
	CO_2	4.72×10^{-8}
	H	1.79×10^{-4}
	H_2O	8.26×10^{-6}
	Si	1.55×10^{-8}
	SiH	2.32×10^{-8}
	SiH_4	1.98×10^{-8}
	SiO	8.63×10^{-5}

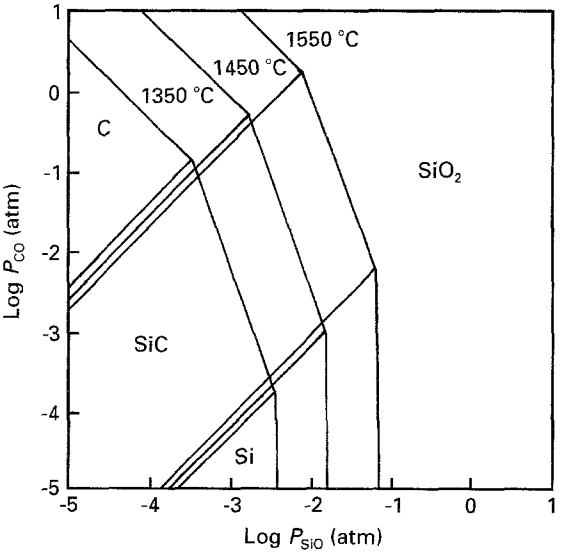

Figure 2 Stability diagram of the Si–C–O system at 1350, 1450 and 1550 °C.

Table I shows all possible vapour species in the SiO_2–C–Ar and the SiO_2–C–H_2 system that were identified by the SOLGASMIX computer program. It indicates that SiO and CO are the major vapours in the SiO_2–C–Ar system, and SiO, CO and CH_4 are the major vapours in the SiO_2–C–H_2 system.

Fig. 2 is a stability diagram for the Si–C–O system in terms of P_{CO} and P_{SiO} at temperatures of 1350–1550 °C. It shows that SiC has a fairly wide range of stability when P_{CO}/P_{SiO} is 1–10. Inside the batch, the SiC-stable zone should be avoided as much as possible to encourage the SiO generation rather than the SiC particle formation. On the substrate, however, the condition should return to the SiC-stable zone again to grow SiC whiskers. Two vapours, SiO and CO, will play critical roles in this regard.

3.2. The growth mechanism of SiC whiskers

In an argon atmosphere, the weight loss and chemical analysis of the batch at various intermittent reaction times showed that Reactions 1 and 2 were taking place inside the batch, forming SiC particles and generating SiO and CO vapour. The rate of SiO generation was $\sim 9\ cm^3\ min^{-1}$ at the charge rate of 0.25 g batch/min.

On the substrate, the generated SiO vapour reacted with CO vapour for SiC growth in whisker form by the following reaction

$$SiO(v) + 3CO(v) \rightarrow SiC_w(s) + 2CO_2(v) \quad (3)$$

Here the subscript "w" refers to whisker form. However, the SiC whisker-forming reaction was quite sluggish in an argon atmosphere. Only 10% of the generated SiO vapour participated in SiC whisker formation, leaving most of the SiO deposited at the cold zone of the reactor outlet. Furthermore, it was found that iron droplets were never formed at the tips of SiC whiskers, suggesting the VLS mechanism never took place. Consequently, the formed SiC whiskers were of irregular shapes.

Reaction 3 can proceed only if the generated CO_2 vapour can be reduced below its equilibrium partial pressure by excess carbon, e.g. graphite substrate or excess carbon powder in the batch as

$$2C(s) + 2CO_2(v) \rightarrow 4CO(v) \quad (4)$$

Hence, the overall reaction is

$$SiO(v) + 2C(s) \rightarrow SiC_w(s) + CO(v) \quad (5)$$

This critical role of excess carbon in the overall reaction was confirmed by a specially designed experiment using a BN boat and BN substrate, and introducing SiO vapour generated from a SiO_2–Si mixture, and CO vapour from a gas supply. In this arrangement, which eliminates any involvement of solid carbon in the reaction, there was no growth of SiC whisker under any favourable partial pressures of SiO and CO.

In a hydrogen atmosphere, it was assumed that the reactions in the batch were the same as those in an argon atmosphere, because hydrogen penetration into the batch is somewhat restricted at the hot zone due to the constantly evolving SiO and CO vapours. The SiC whisker-forming reaction on the substrate, however, was much faster in a hydrogen atmosphere, converting all of the generated SiO into SiC whiskers.

This enhanced growth of SiC whiskers in a hydrogen atmosphere could be attributed to the presence of CH_4 as a carbon-carrying vapour. At the gas-inlet, CH_4 can be readily formed by the reaction between hydrogen and carbon in the batch as

$$2H_2(v) + C(s) \rightarrow CH_4(v) \quad (6)$$

This will make an alternative route possible for the formation of SiC whiskers

$$SiO(v) + 2CH_4(v) \rightarrow SiC_w(s) + CO(v) + 4H_2(v) \quad (7)$$

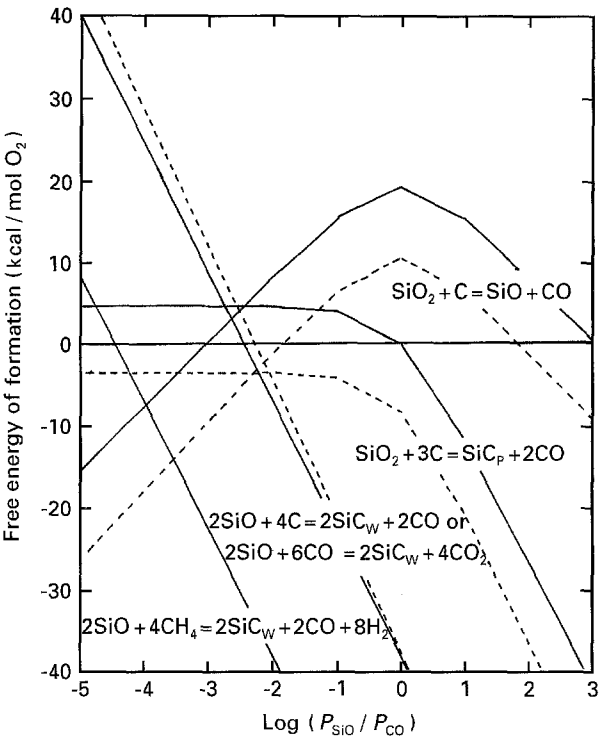

Figure 3 Plot of free energies of formation for the reactions involved as a function of P_{SiO}/P_{CO} at (———) 1450 °C and (- - -) 1550 °C.

Calculation shows that the equilibrium partial pressure of CH_4 is 7×10^{-2} atm at 800 °C and 8×10^{-4} atm at 1450 °C. However, it seems that the partial pressure of CH_4 at the hot zone was at least one order of magnitude higher than 8×10^{-4} atm, because the generated SiO is fully consumed by CH_4 forming SiC whiskers. This means that the formed CH_4 at the gas inlet did not fully crack at its equilibrium value at the hot zone.

Fig. 3 shows the detailed thermodynamic plots for these reactions taking place in terms of P_{SiO}/P_{CO}. The usual calculation at 1450 °C indicates that Reaction 2 is the only one feasible under the range of $P_{SiO}/P_{CO} = 1\text{–}10^{-3}$. However, it has been well documented that the equilibrium of carbothermal reduction of silica shifts by ~ 100 °C when the reactants are in a highly reactive amorphous form [4, 25–27], which is the case in this study. Considering this fact, the equilibrium for Reactions 1–3 is recalculated using data at 1550 °C instead of 1450 °C and presented as dashed lines in Fig. 3. Based on these corrections, the reaction sequence can be described as follows. (1) In the first 0.5 h of run when P_{CO} inside of the batch is lower than ~ 0.5 atm, SiC particles are forming by Reaction 2 in both argon and hydrogen atmospheres. (2) Once the P_{CO} inside the batch builds up to close to 1 atm, Reaction 1 becomes thermodynamically favourable and can proceed, generating SiO and CO vapour. (3) The generated SiO has three choices: (a) reacting with carbon in the batch to form SiC particles by Reaction 2, (b) leaving the batch and reacting with CO vapour to form SiC whiskers by Reaction (3), and (c) leaving the batch and reacting with incoming CH_4 to form SiC whiskers by Reaction

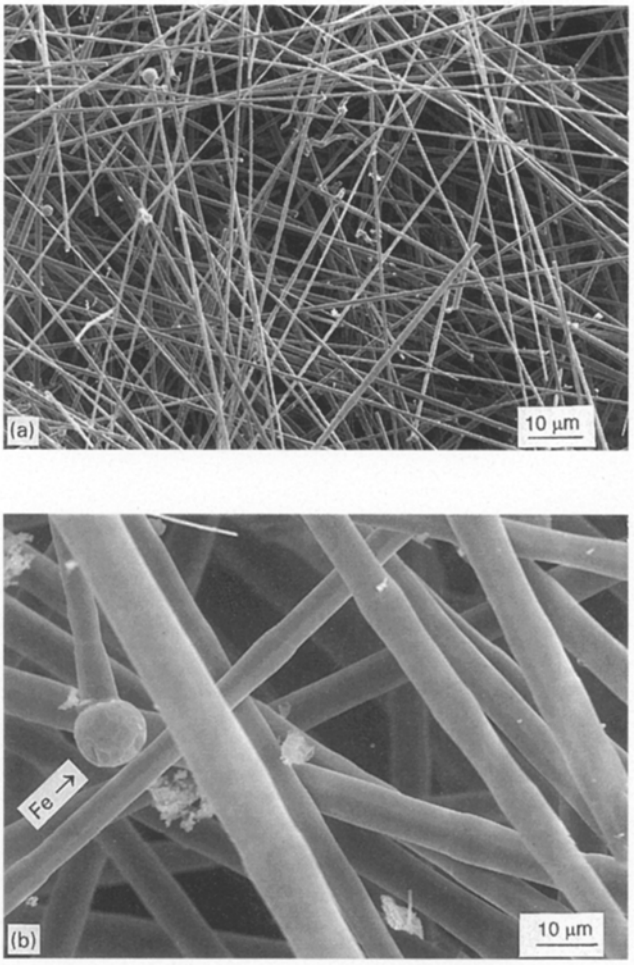

Figure 4 (a,b) Scanning electron micrographs of SiC whiskers synthesized in the continuous reactor.

7. Thermodynamic calculation in Fig. 3 suggests that Reaction 7 is the most favourable one when the P_{SiO}/P_{CO} is in the range of 0.1–0.001, assuming P_{CH_4} is maintained at higher than 8×10^{-3} atm.

It was also found that most of the whiskers were grown on the iron droplets, suggesting the VLS mechanism was taking place. The SiC whiskers formed were thick and straight, as shown in Fig. 4. In the VLS mechanism, it is generally assumed that iron dissolves silicon- and carbon-carrying vapours and acts as a reservoir of reactants for the precipitation of SiC in whisker form. Therefore, the diameter of SiC whisker is mainly limited by the sizes of the iron drops and their surface energy relationship, and undisturbed growth of whiskers is possible.

3.3. Continuous synthesis of SiC whiskers

Based on this study, a laboratory-scale reactor was constructed for the continuous synthesis of SiC whiskers as shown in Fig. 1. The system consists of a boat-train loaded with the silica–carbon mixture and iron-coated graphite substrate above it in an alumina-tube reactor. Hydrogen gas was introduced into the reactor at the rate of 191 $cm^3 min^{-1}$. By pushing the boat-train into the hot zone at a constant speed, SiO vapour was generated at the rate of 9 $cm^3 min^{-1}$ at 1450 °C.

It was found that the whiskers are β-SiC grown along the [1 1 1] direction with typical diameters of 1–3 μm and a smooth surface as shown in Fig. 4. The yield was about 30% based on the silicon input as SiO_2 and silicon output as SiC whiskers. This demonstrates the feasibility of continuous production of high-quality SiC whiskers which does not require additional processes such as purification and classification.

4. Conclusion

SiC whiskers were synthesized in a two-step process involving the generation of SiO followed by SiC growth. Consideration of the thermodynamics showed that both reactants, SiO_2 and carbon, should be in the highly reactive amorphous form to grow SiC whiskers successfully. It also showed that carbon should be supplied as CH_4 vapour into the sites of SiC growth. Using this concept, a continuous reactor was constructed and high-quality SiC whiskers were harvested without purification or classification.

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