Ultrafine SiC Synthesis Using Induction Plasmas: A Parametric Study

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Abstract

A parametric study was carried out to examine the influences of the process parameters on the synthesis of SiC powder through the reaction of elemental Si and CH_4 in an induction plasma. The powder obtained was composed of a mixture of α and β-SiC with varying amounts of free C and free Si. The experimental results support the view that the formation mechanism for ultrafine SiC is dominated by the reaction of Si vapor with the thermal decomposition products of CH_4.

1. Introduction

In our previous work [1], we have demonstrated that ultrafine SiC powders can be synthesized from elemental Si and CH_4 using the r.f. induction plasma techniques. Pressureless sintering of these powders [2] indicated that their sinterability was strongly dependent on the chemical composition of the powders. The presence of free Si and/or free C in the powders obtained, can be detrimental to their sintering properties. It was also noted that the processing parameters, such as plasma power level, plasma gas composition, reactants injection probe position, feed rates of injected Si and the C/Si molar ratio, significantly affect the conversion and the quality of the SiC powder obtained. In order to optimize the process and to ensure the reproducibility of powder quality, a systematic investigation into the effects of the process parameters on the formation of SiC, was carried out.

2. Experimental

The experimental apparatus used in the synthesis of ultrafine SiC powders is shown in Fig. 1. The experimental procedures followed were similar to those described in Ref. [1]. Two series of experiments were conducted for this parametric study. Run Nos. 1 to 11 employed coarse Si powder as starting material ($\overline{d_P}$ = 68 μm and σ = 21 μm). In this series of runs we investigated the influences of probe position and plasma gas composition on the conversion and the composition of the SiC powder obtained. Run Nos. 21 to 36 employed fine Si powder as starting material ($\overline{d_P}$ = 31 μm, σ = 9 μm). In the run Nos. 34 to 36 of this series of tests, CH_4 was used directly as carrier gas. This series of tests examine the effect of plasma power level, Si feed rate and C/Si molar ratio, and carrier gas. Table 1 shows a summary of the operating conditions for the reaction runs. In each of the experiment, powder was collected from the different sections of the reactor and filter system. These were identified as "RW", for reactor wall, "RB", for reactor bottom, "CB", for cyclone bottom, and "F", for filter. The weight fraction of the powders collected on each section in the total collected powders varied with the particle size of the starting Si powder. The powders collected at the different sections have different physical features and varying chemical compositions [1]. The filter powders were subjected to detailed examination in the present parametric study. The structure and composition of the powder collected on each of the above identified sections was analyzed by means of XRD. The free C content in the powder was determined by TGA, using air as the combustion atmosphere. The specific surface area of the powder

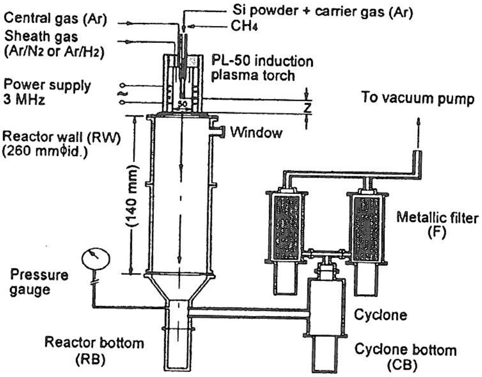


Fig. 1 Schematic of experimental set-up for SiC synthesis

Table 1 Operating conditions for the SiC synthesis runs

Run No.	Particle size of fed Si powder (μm)	Central gas Ar (slpm)	Operating conditions									
			Sheath gas (slpm)			Power level (kW)	Probe position z (cm)	Reactant feed rate			C/Si molar ratio	Feed time (min)
			Ar	N_2	H_2			Si (g/min	Carrier gas (slpm)	CH_4 (slpm)		
1	68 ± 21	41	51	52	-	43.2	9.3	3.89	5.0Ar	2.50	0.74	6
4		41	51	52	-	40.0	4.0	2.18	5.0Ar	1.31	0.68	10
5		41	51	52	-	40.0	7.2	2.18	5.0Ar	1.31	0.68	10
8		41	51	52	-	43.2	7.2	3.89	5.0Ar	2.50	0.74	10
9		41	90	-	8.7	40.0	7.2	2.18	5.0Ar	1.31	0.68	10
11		41	90	-	8.7	43.2	7.2	3.89	5.0Ar	2.50	0.74	10
21	31 ± 9	41	51	52	-	41.3	8.0	4.35	5.0Ar	2.0	0.53	5
25		41	51	52	-	52.2	8.0	4.35	5.0Ar	2.0	0.53	5
28		41	51	52	-	52.2	8.0	2.15	5.0Ar	3.20	1.70	5
29		41	51	52	-	52.2	8.0	2.38	5.0Ar	1.43	0.69	5
30		41	51	52	-	52.2	8.0	2.38	5.0Ar	2.50	1.20	5
32		41	51	52	-	52.2	8.0	4.40	5.0Ar	4.80	1.25	5
34		41	51	52	-	52.2	8.0	2.03	2.85CH_4	-	1.60	5
35		41	51	52	-	52.2	8.0	2.03	3.80CH_4	-	2.14	5
36		41	51	52	-	52.2	8.0	2.12	1.31CH_4	-	0.70	5

was measured by the BET method, using nitrogen as adsorbate.

3. Results and discussion

The mass balance data for the reaction runs are shown in Table 2. Table 3 lists the analysis results for the powders obtained (the results for "RW" and "CB" powders are listed only as examples). R_T in Table 2 is the total recovery of reactants in product powder. Si_{OC} in Table 3 is the overall conversion of the injected elemental Si to SiC. The calculation formulas for R_T, Si_{OC} and SiC_{WA} (the weighted average of the SiC contents in each part of the collected powder) had been described in Ref. [1].

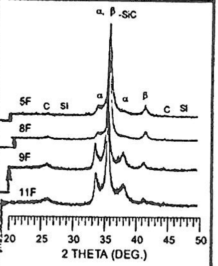
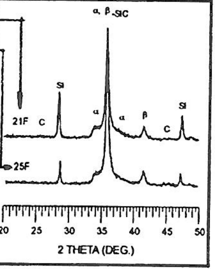
3.1 Influence of plasma gas composition It is of interest to note that whenever H_2 was used to replace N_2 as the plasma sheath gas, the characteristic peaks of α-SiC in XRD patterns of the product powders were substantially intensified, as it may be seen by comparing run Nos. 5 and 8 with run Nos. 9 and 11, respectively, shown in Table 3. The quantitative phase compositions of the powders indicate that the ratio of α- to β-phase in SiC powder with Ar/H_2 as plasma gas was always greater than 1.5, whereas the ratio of α- to β-SiC was consistently less than 1.0 for the powder produced with Ar/N_2 as plasma gas. The SiC_{WA} in powders from run Nos. 5 and 8 was higher than that in run Nos. 9 and 11. The surface area measurements shown in Table 3 are consistent with the powder composition since different components have different sizes (free C, 10 - 30 nm, free Si > 100 nm, and SiC, 40 - 80 nm) [1].

Table 2 Mass balance data

Run No.	Mass balance					
	Total Si injected (g)	Collected powders				R_T (%)
		W_{RW} (g)	W_{RB} (g)	W_{CB} (g)	W_F (g)	
1	23.3	14.8	3.4	4.0	3.3	83.0
4	21.8	16.5	3.2	4.2	2.2	92.6
5	21.8	14.5	4.6	4.5	3.0	94.4
8	38.9	25.0	5.6	5.9	5.3	81.6
9	21.8	15.7	3.3	5.0	2.3	93.3
11	38.9	31.1	2.2	4.0	4.6	81.8
21	21.8	15.2	~0	4.2	5.1	91.8
25	21.8	14.7	~0	4.1	5.4	90.6
28	10.7	8.9	~0	2.7	3.4	80.5
29	11.9	9.0	~0	1.4	3.4	89.5
30	11.9	9.6	~0	2.2	4.0	87.5
32	22.0	18.3	~0	6.9	5.9	92.0
34	10.2	7.6	~0	1.8	3.4	74.9
35	10.2	8.2	~0	2.1	3.9	72.9
36	10.6	7.9	~0	1.5	3.8	95.7

3.2 Influence of injection position of the reactants According to thermodynamic analysis, the synthesis yield of SiC was favored by relatively high temperature. Therefore, it was important to select an appropriate injection position for the reactants to ensure that they attained sufficiently high temperature and long residence time in the plasma for the Si particle melting and evaporation followed by reaction with CH_4. In comparing the analysis results of sample No. 4F with those of No. 5F and No. 8F with those of No. 1F as set out in Table 3, it is found that as expected, the insertion "depth", z, of the injection probe affected the chemical compositions of the powders obtained. In the case where z = 7.2 cm, the probe tip was further upstream in the discharge compared to case of z = 4.0 cm, providing a longer residence time and better reaction environment. As the probe tip was pushed up to a further higher position (the case z = 9.3 cm) close to the center of the discharge, powders collected in the filters were composed of nearly pure SiC even with the heavier reactant feed rates.

Table 3 Analysis results for ultrafine SiC powder obtained

Sam. No.	Phase composition (wt%)				α/β-SiC	SiC (wt%)	BET $(m^2/g$	Weighted average comp.			Si_{OC} (%)	XRD pattern
	α-SiC	β-SiC	Si_f	C_f				SiC	Si_f	C_f		
1F	46.4	52.8	0.3	0.5	0.9	99.2	43.8	50.8	44.8	4.4	44.2	
4F	44.3	48.5	0.2	7.0	0.9	92.8	-	-	-	-	-	
5RW	16.3	26.1	52.6	5.0	0.6	42.4	10.0	40.6	54.1	5.3	34.5	
5CB	13.3	23.8	47.9	15.0	0.6	37.1	18.7					
5F	46.3	53.3	0.3	0.1	0.9	99.6	35.0					
8F	41.2	52.6	0.2	6.0	0.8	93.8	-	47.1	43.2	9.7	43.3	
9RW	18.7	11.8	56.0	13.5	1.6	30.5	-	35.6	50.4	14.0	33.1	
9CB	32.1	18.2	23.2	26.5	1.8	50.3	29.4					
9F	54.1	35.5	0.4	10.0	1.5	89.6	67.4					
11F	53.0	31.7	0.3	15.0	1.7	84.7	75.9	33.0	45.8	21.2	33.6	
21F	39.7	53.9	6.3	0.1	0.7	93.6	-	72.1	25.5	2.4	66.5	
25F	41.2	55.7	3.0	0.1	0.7	96.9	38.0	77.8	20.5	1.7	72.7	
28F	38.6	59.0	0.4	2.0	0.7	97.6	35.0	84.5	7.8	7.7	88.3	
29F	44.7	54.4	0.8	0.1	0.8	99.1	34.3	82.8	17.0	0.2	77.3	
30F	41.4	57.0	0.6	1.0	0.7	98.4	43.0	84.7	13.2	2.1	81.8	
32F	47.3	48.8	3.4	0.5	1.0	96.1	36.8	74.4	16.1	9.5	76.4	
34F	48.6	50.7	0.2	0.5	1.0	99.3	-	91.1	6.6	2.3	90.6	
35F	45.1	53.7	0.2	1.0	0.8	98.8	37.5	91.5	5.5	3.0	92.0	
36F	38.8	57.0	4.1	0.1	0.7	95.8	36.5	86.9	13.0	0.1	82.4	

3.3 Influence of plasma power level From the XRD patterns for the filter powders for run Nos. 21 and 25 corresponding to 41.3 and 52.2 kW respectively, it is observed that with increasing power level, the intensity peak for free Si decreased, suggesting that the increase of power level and thus increased plasma temperature was favorable for the reaction. However, it should be noted that the influence of power level was not so strong under the condition of low C/Si molar ratios used in the present study. It can be reasonably expected that the influence of power level on carburization would be more apparent at higher C/Si ratios.

3.4 Influence of feed rates of reactants and C/Si molar ratio The injection rates employed for the input materials have a significant influence on the synthesis and chemical composition of the SiC powder. Although the plasma medium is a high temperature source, the in-flight melting, evaporation, and reaction of solid particles still face challenge. Excessive injection of reactants would only result in large amounts of unreacted Si and C in the products. Comparing the results for run Nos. 32 and 30, which were produced from near equivalent C/Si molar ratios but at different fine Si feed rates, it is found that the injection rates of 4.40 g/min Si gave rise to higher free Si and free C but lower Si_{OC} in the product powder than for 2.38 g/min. Under the condition of constant feed rate for Si, increasing the C/Si molar ratio of the injected reactants significantly increased the conversion of Si to SiC. This may be found by examining Table 3, for the cases in which either Ar or CH_4 was used as carrier gas (run Nos. 28 to 30 or run Nos. 34 to 36). This suggests that the optimum synthesis of SiC require the presence of certain excess of CH_4.

3.5 Influence of CH_4 used directly as the carrier gas for Si powder transport It is found from Table 3 that generally the Si_{OC} and the SiC_{WA} were both significantly increased with the use of CH_4 directly as the carrier gas for Si powder transport and injection (run Nos. 34 to 36 compared with run Nos. 28 to 30). At the level of C/Si molar ratio of 2.14 and with CH_4 carrier gas, the Si_{OC} and SiC_{WA} rose to 92.0% and 91.5 wt%, respectively. The overall advantage of using CH_4 directly as the carrier gas may lie in a combination of chemical and thermal aspects, which may be set down as the following points: 1) suppression of local cooling caused by the injection of Ar carrier gas; 2) improved pre-reaction mixing between the Si powders and the CH_4 gas and 3) reduced velocity of the Si powder transport and injection through reduced gas flow rate and thus relatively longer residence time for Si in the plasma.

Although some researchers claim [3] that the most favorable conditions for SiC formation exist when C reacts with liquid Si, a contention that is supported by the fact that liquid Si ideally wets graphite, thus creating the maximum possible surface area of reaction, the formation mechanism for SiC, by reaction of liquid Si with solid C, seems an unlikely explanation for the present synthesis route. Preliminary evaporation tests with the coarse Si particles indicated that the percentage evaporation accounted for around 30 - 40 wt% of input. This result was basically consistent with the SiC formation observations under the condition of CH_4 injection, meaning that the formation of SiC depends initially on the prior evaporation of the Si particles. The improvement to both the overall conversion of Si and the weighted average content of SiC with the use of the smaller Si particles are attributed to the increased rate and completeness of Si evaporation. The carburization of liquid Si particles was very insignificant when conducted in the present test run conditions. As one of the routes of confirmation, plasma reactive deposition was also performed, using graphite as the deposit substrate and coarse Si and CH_4 as input materials. The deposits obtained were mainly composed of Si, with a small portion of SiC. The XRD patterns for such deposits were very similar to those obtained for the powder collected on the reactor wall in the SiC synthesis tests. In the latter case, the major part of the formed SiC would not deposit on the substrate but scatter in the form of ultrafine powder. The carburization of liquid Si did not occur during the particle plasma in-flight period nor on the substrate.

The predominant formation mechanism for SiC indicated by the present study is proposed as the reaction of gaseous Si with the plasma decomposition products of CH_4. Due to the great vapor pressure over liquid Si [4], it is not unlikely that SiC formation could also occur at temperatures below the boiling temperature of Si, but it would represent only a small portion in the circumstance presented. The synthesis of ultrafine SiC powders through the mechanism of dissolution of C(s) in Si(l) and sublimation of the formed SiC(s) is also considered. Due to the rapid quenching and steep temperature gradients existing in the plasma as well as the smoothness of the obtained Si particle surfaces observed, such in-flight reaction-sublimation-condensation mechanism was also considered unlikely.

4. Summary and conclusion

The formation of SiC from elemental Si and CH_4 injected into an induction plasma relies on a number of process parameters such as; plasma plate power, plasma gas composition, injection position of reactants, feed rates and the reactants C/Si molar ratio, and carrier gas for Si powder transport. Generally, the increase in temperature favors the synthesis of SiC. The replacement of N_2 by H_2 as the plasma sheath gas substantially increased the formation of α-SiC, resulting in a ratio of α to β-SiC of >1.50 in product. To improve the conversion of Si to SiC and the adjustment of injection probe position to near the center of the discharge zone ($z = 7.2 - 8.0$ cm), excess of CH_4 (C/Si molar ratio ≈ 2) and the use of CH_4 directly as the carrier gas are some of the measures which resulted in an increase of Si conversion to SiC.

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