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Initial Stages of Phase Formation in the C–Si, C–Si–Cu, and C–Si–Al Systems

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Abstract—The initial stages (2–6 s) of reaction in the C–Si system and the influence of Cu and Al additives on this process were studied by x-ray diffraction analysis. The average grain size of silicon carbide was found to attain 500 Å after just 6 s of reaction.

INTRODUCTION

The wide application of C–SiC composites in modern technology is due to their unique physicochemical properties [1–4]. These materials are usually prepared by reaction of ultrafine carbon powders with the silicon melt. The phase-formation kinetics in the C–Si system were studied for relatively late stages of reaction. Tarabanov *et al.* [1] suggested that SiC formation is a diffusion-limited process. However, the diffusion model is incapable of adequately describing the initial stages of reaction: the content of SiC formed during the first 60 s is about one order of magnitude higher than that predicted by the model. The aim of this work was to study the initial stages of crystal formation in the C–Si system and the influence of Cu and Al additives on this process.

EXPERIMENTAL

The USB-15 isotropic carbon-based glass-ceramic was used to investigate phase formation at the interface between carbon and Si + M (M = Cu, Al) melts during the first seconds of reaction. A uniform layer of silicon powder or a silicon + 30 wt % M powder mixture was applied to a glass-ceramic plate (25 × 5 × 3 mm), which was then heated to 1500°C under a vacuum of 10^{-2} Pa in a VUP-4 vacuum system. The temperature was measured with a W/W–Re thermocouple. The holding time τ was 2, 6, 12, 24, 60, or 120 s. In some experiments, SiC was synthesized by immersing porous graphitized carbon into Si–Cu or Si–Al melts. X-ray diffraction studies were carried out with a DRON-3 diffractometer (CuK_α or CoK_α radiation). Diffraction profiles were recorded at a θ scan speed of 1/8 and 1/16 deg/min with rutile as a standard.

The average size of coherently scattering domains (CSD) was assessed by a conventional procedure [5] and by fourth-moment analysis [6]. Interplanar spacings were determined by the method of centroids. The SiC content of the samples was estimated from the integrated intensity ratio of the 111 β-SiC peak to the nearest B_4C peak 220. According to Frantsevich *et al.* [7], B_4C does not decompose in the presence of SiC, and its content remains unchanged.

RESULTS AND DISCUSSION

Our XRD data show that the surface layer of the carbon-based glass-ceramic plate consists of graphite, β-SiC, silicon metal, and boron carbide. In addition, the intermetallic ε-phase close in stoichiometry to Cu_4Si is found in the Cu-doped samples. The phase composition and average particle size depend strongly on τ and on the type of additives.

The most rapid reaction occurs in the Al-doped samples (Fig. 1). Under the experimental conditions, the maximum content of silicon carbide is observed after 24 s of reaction (Table 1). In the Cu-doped samples, SiC formation proceeds more slowly.

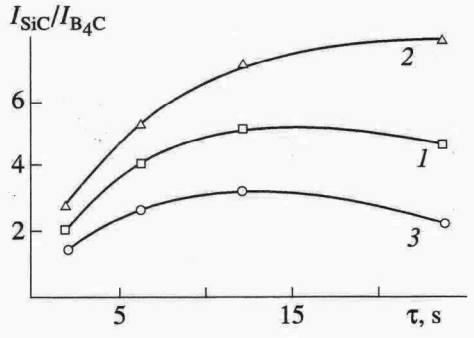

Fig. 1. Integrated intensity of the 111 β-SiC reflection vs. holding time for materials prepared by reaction of carbon with the (*1*) Si, (*2*) Si + 30 wt % Al, and (*3*) Si + 30 wt % Cu melts.

†Deceased.

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Table 1. Structural characteristics of SiC as a function of holding time τ for samples prepared by reaction of carbon with the Si, Si + 30 wt % Al, and Si + 30 wt % Cu melts

System	d_{111}, Å				L_{111}, Å				I_{SiC}/I_{B_4C}			
	2 s	6 s	12 s	24 s	2 s	6 s	12 s	24 s	2 s	6 s	12 s	24 s
C–Si	2.519	2.518	2.518	2.518	420	500	560	730	2.04	3.87	5.16	4.63
C–Si–Al	2.526	2.522	2.522	2.522	370	540	590	780	2.18	4.83	6.84	7.34
C–Si–Cu	2.523	2.517	2.516	2.516	180	220	390	420	1.75	2.67	3.48	1.91

At τ = 2 s, the average size of SiC grains estimated from the diffraction peak width (without considering microstrains) is 180, 370, and 420 Å in the systems C–Si–Cu, C–Si–Al, and C–Si, respectively, while the CSD size assessed by the more accurate fourth-moment analysis is ≈2.5 times larger. By τ = 24 s, the average grain size increases almost twofold (Fig. 2). The growth rate and CSD size are maximal in the C–Si–Al system (780 Å) and minimal in the C–Si–Cu system (420 Å) (Table 1).

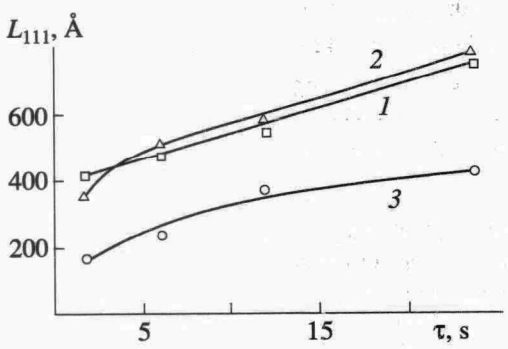

Fig. 2. Average CSD size of β-SiC vs. holding time for materials prepared by reaction of carbon with the (*1*) Si, (*2*) Si + 30 wt % Al, and (*3*) Si + 30 wt % Cu melts.

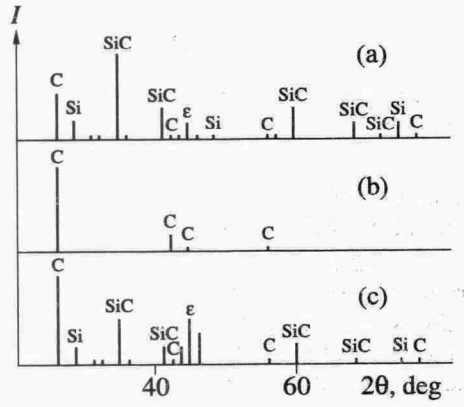

Fig. 3. Schematic x-ray diffraction patterns of the sample prepared by reaction of carbon with the 60 wt % Si + 40 wt % Cu melt: (a) uniform portion of the composite, (b) unreacted carbon, (c) intermediate region.

The structural parameters of carbon also change during the first seconds of reaction (Table 2). In the C–Si–Al system, the average size of graphite CSDs along the *c* axis, L_c, increases most rapidly, from 98 to 114 Å in 24 s. In the C–Si and C–Si–Cu systems, L_c attains 109 Å in 12 s. Initially, the interplanar spacings d_{002} of graphite and d_{111} of β-SiC exceed the values given in the JCPDS Powder Diffraction File. With increasing τ, the *d*-spacings and the average microstrains $\overline{|\Delta d|}/d$ in CSDs gradually decrease (Tables 1, 2). Calcining the carbon-based glass-ceramic without the silicon melt under the same conditions for 120 s has no effect on its structural characteristics.

The model experiments above enable a more detailed understanding of interactions between porous graphitized carbon and Si–Al or Si–Cu melts. Under the action of capillary forces, the melt infiltrates the porous material and reacts with carbon to give a C–SiC composite. When heavily doped melts (≈40 wt % Cu or ≈10 wt % Al) are used, the phase uniformity of the composite degrades owing to the formation of macrodomains containing only graphitized carbon (Fig. 3). In the Cu-doped composite, these macrodomains are surrounded by Cu-rich regions, as evidenced by the appearance of diffraction peaks due to the ε-phase (Cu_4Si), which forms only if the melt contains more than 88 wt % Cu [8]. Therefore, the spatial nonuniformity of the composite is caused by the increase in Cu content at the carbon–melt interface. As a result, the contact angle increases, preventing the melt from penetrating deeper into capillaries. The average CSD size of SiC in the Cu-rich regions is almost half that in the uniform material.

Table 3 demonstrates how the phase composition of the C–SiC composite prepared by reaction of carbon with the Si + 10 wt % Al melt varies across the reacted layer. The width (the ratio of the integrated intensity to the peak height) of the β-SiC 111 peak (100%) remains constant at 0.18° across the whole mixed-phase layer. This implies that the average CSD size (≈700 Å) of silicon carbide is also constant throughout the layer.

Table 2. Structural characteristics of graphite as a function of holding time τ for samples prepared by reaction of carbon with the Si, Si + 30 wt % Al, and Si + 30 wt % Cu melts

	τ, s	0	2	6	12	24	60	120
C–Si	I, arb. units	9600	2560	2470	3490	3740	4110	4050
	d_{002}, Å	3.471	3.453	3.451	3.451	3.451	3.449	3.449
	β_{002}, deg	1.11	1.06	1.03	1.02	1.03	1.03	1.04
	L_c, Å	98	104	107	109	107	107	106
	D_c, Å	320	390	510	560	420	390	410
	$(\overline{\lvert\Delta d\rvert}/d) \times 10^2$	1.74	1.42	1.44	1.46	1.43	1.42	1.43
C–Si–Al	I, arb. units	9600	2530	1820	2690	3630	5640	5590
	d_{002}, Å	3.471	3.453	3.452	3.451	3.447	3.447	3.447
	β_{002}, deg	1.11	1.04	1.01	1.00	0.98	0.97	0.98
	L_c, Å	98	106	110	111	114	115	114
	D_c, Å	320	600	760	870	740	590	610
	$(\overline{\lvert\Delta d\rvert}/d) \times 10^2$	1.74	1.59	1.42	1.56	1.55	1.55	1.54
C–Si–Cu	I, arb. units	9600	1630	2510	3260	3690	3620	3610
	d_{002}, Å	3.471	3.453	3.449	3.450	3.451	3.449	3.450
	β_{002}, deg	1.11	1.07	1.06	1.02	1.03	1.03	1.03
	L_c, Å	98	103	104	109	107	107	107
	D_c, Å	320	420	520	550	420	380	380
	$(\overline{\lvert\Delta d\rvert}/d) \times 10^2$	1.74	1.70	1.59	1.56	1.56	1.55	1.55

Note: The average CSD size L_c was assessed from the peak width; D_c and $\overline{\lvert\Delta d\rvert}/d$, by the fourth-moment analysis.

Table 3. Structural characteristics of the major phases (reflections 002 C, 111 Si, and 111 SiC) in the sample prepared by reaction of carbon with the 90 wt % Si + 10 wt % Al melt at different distances h from the carbon–composite interface

	h, mm	8	6	3.5	2.5	0
SiC (111)	β, deg	0.18	0.18	0.18	0.18	–
	d, Å	2.526	2.527	2.527	2.529	–
	I, arb. units	716	704	532	480	–
C (002)	d, Å	3.376	3.382	3.388	3.388	3.388
	I, arb. units	672	752	1300	1505	5280
	L_c, Å	464	437	341	341	328
Si (111)	d, Å	3.145	3.149	3.153	3.153	–
	I, arb. units	210	145	65	52	–

The SiC content estimated from the intensity of β-SiC reflections gradually decreases with decreasing h (distance to the carbon–composite interface). The spacing d_{111} of silicon in the composite varies from 3.145 to 3.153 Å and exceeds that of pure silicon (3.135 Å). The Al content of silicon (estimated from Vegard's law) is ≈7 wt % at h = 8 mm and increases to ≈13 wt % at the interface. Therefore, the spatial nonuniformity of the C–(Si + Al) composite can be attributed to the higher rate of reaction between C and Si (leading to the formation of a thick layer of products inside the capillaries, which prevents further infiltration) as well as to the substantial Al enrichment of the silicon melt.

The content and structural parameters of polycrystalline graphite also vary with h. The average size L_c of graphite CSDs assessed from β_{002} increases from 330 to 460 Å as the distance to the carbon–composite interface rises. The spacing d_{002} decreases from its maximum value (3.388 Å) in the carbon region to 3.376 Å at h = 8 mm (Table 3).

Thus, SiC grains with an average size greater than 500 Å are formed in the system C–Si for $\tau < 2$ s. The content of the new phase increases with τ, while

the average size of CSDs increases only twofold. The rapid increase in SiC content can be explained by heat evolution (63 ± 12 kJ/mol) accompanying SiC formation. As in other ultrafine-particle systems [9, 10], the heat released at the interface causes local heating in the reaction zone. Assuming that the reaction is adiabatic, we find that the local superheating in the reaction microdomain may exceed 500°C, which promotes reaction and growth of SiC grains. The addition of 40 wt % Cu inhibits the increase in the average CSD size of SiC. In the presence of 10 wt % Al, reaction in the C–Si system proceeds more actively, probably because aluminum reacts with carbon to form metastable aluminum carbides [2], the subsequent decomposition of which contributes to SiC grain growth. Simultaneously, the starting carbon undergoes structural changes: the average CSD size increases, while d_{002} and $\overline{|\Delta d|}/d$ decrease.

CONCLUSION

The fast growth of SiC grains at the initial stages of reaction (2–6 s) is promoted by the heat of SiC formation. The addition of copper to the melt (40 wt %) inhibits growth of SiC grains, while aluminum (10 wt %) has the opposite effect.

The spatial nonuniformity of the composite prepared from fine-particle carbon and the silicon melt containing 40 wt % Cu or 10 wt % Al is caused by the enrichment of the melt with the dopant in the reaction zone, which prevents further melt infiltration.

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