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Studies on the Reactive Melt Infiltration of Silicon and Silicon-Molybdenum Alloys in Porous Carbon

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STUDIES ON THE REACTIVE MELT INFILTRATION OF SILICON AND

SILICON-MOLYBDENUM ALLOYS IN POROUS CARBON

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SUMMARY

Investigations on the reactive melt infiltration of silicon and silicon-1.7 and -3.2 at.% molybdenum alloys into porous carbon preforms have been carried out by process modeling, differential thermal analysis (DTA), and melt infiltration experiments. These results indicate that the initial pore volume fraction of the porous carbon preform is a critical parameter in determining the final composition of the reaction-formed silicon carbide and other residual phases. The pore size of the carbon preform is very detrimental to the exotherm temperatures due to liquid silicon-carbon reactions encountered during the reactive melt infiltration process. A possible mechanism for the liquid silicon-porous (glassy) carbon reaction has been proposed. The composition and microstructure of the reaction-formed silicon carbide has been discussed in terms of carbon preform microstructures, infiltration materials, and temperatures.

INTRODUCTION

Research and development on silicon carbide based advanced ceramics and composites have attracted a great deal of attention in recent years (refs. 1 to 8). The potential applications of these materials include components for advanced propulsion systems, energy conversion devices, and other high temperature structures. The residual silicon in commercially available silicon carbide ceramics is very detrimental to its high temperature strength especially around 1400 °C (m.p of Si = 1410 °C). In addition, there are other critical issues in the fabrication of silicon carbide based ceramics which are mainly related to complex shape fabricability, and processing time and temperatures. A combination of these factors lead to the high manufacturing cost of the final components. Owing to these considerations, there is a strong need to develop cost-effective processing approaches for silicon carbide based advanced ceramics and composites which yield low silicon content, high strength and toughness, high thermal conductivity, and good oxidation resistance.

We have used a *reaction forming process* for the processing of these ceramics. This process has near-net-shape capabilities, shorter processing times and lower processing temperatures in comparison to other conventional processes. In this process, a micro-porous carbon preform is infiltrated with molten silicon or a silicon-molybdenum alloy. The final products are silicon carbide with some free silicon or silicon carbide and molybdenum disilicide with some silicon-rich alloy and with amounts depending on the preform porosity and alloy composition. The reactive infiltration can lead to complete conversion of the carbon to a fully dense silicon carbide. However, in actual experimental conditions it is quite possible to have some residual free carbon and/or free silicon or alloy infiltrant and a small amount of porosity in the final material. The properties of the carbon preform i.e., pore size, pore volume, and carbon particle size are important in determining the final composition and microstructure of the reaction-formed silicon carbide ceramics. In addition, the infiltration length (thickness of the infiltrated sample) depends mainly on the wetting behavior, reaction kinetics and mechanism, and other processing variables such as infiltration times and temperatures.

The main objective of this paper is to study the effect of some critical parameters of the porous carbon preform which affect the amount of free silicon in the reaction-formed silicon carbide ceramics. These critical parameters include initial pore volume fraction and pore size of the porous carbon preform. In this study, the effects of carbon preform pore size and the type of infiltration material on the exothermic reaction temperature have been evaluated. Also, the effect of silicon-molybdenum alloy infiltration on the final composition and microstructure of silicon carbide is discussed.

PHYSICOCHEMICAL CONSIDERATIONS

In reactive melt infiltration, contact angle and work of adhesion between the melt and solid are very important parameters. In our processing approach, we do not apply any external pressure to the system and infiltration takes place by capillary action only (refs. 1 and 3). The rate of infiltration of the molten materials depends in part on the wetting of the preform by the melt which generally increases with increasing infiltration temperature. The wetting behavior of silicon with carbon and silicon carbide has been reported by a number of authors (refs. 9 to 12). The contact angle of silicon on silicon carbide was reported to be 38° at 1430° C (ref. 10). Using the values of surface tension at this temperature the work of adhesion is calculated to be 1311 mJ m^{-2} for the Si-SiC system at 1430 °C. A recent report by Nikoloupoulos et al. (ref. 12) indicates that the α-SiC is wetted better than the β-SiC by molten silicon. This behavior is attributed to the surface restructuring of β-SiC which may be caused by a partial transformation of β to α modification of SiC. The data on the wetting behavior of silicon-molybdenum alloys with carbon or silicon carbide are not available in the literature. Iseki and Ozumi (ref. 13) reported that the alloying of aluminum with transition elements such as molybdenum and niobium increases its wetting with β-SiC due to their tendencies to form carbides. Thus one might expect that silicon-molybdenum alloys would wet carbon better than pure silicon.

We have developed a simple model to determine the initial pore volume fractions of porous carbon desired for both silicon or silicon-molybdenum alloy infiltration (refs. 5 and 6). Experimental studies have shown that the external dimensions of the preform do not change during the reactive melt infiltration. For the pore size of the carbon preforms used in this study, the reaction rate between carbon and silicon was observed to be faster than the infiltration rate. In this case as the infiltration proceeds, the channels through which the infiltrating silicon or alloy melt must travel become narrowed reducing the flow. For initial pore volume fractions less than a critical value, the channels will be completely closed and the flow will stop. This phenomena is called choking-off of the infiltration and is due to the increase in the specific volume resulting from the conversion reaction. The infiltration model is centered on this choking-off point and the specific volumes of carbon, pores, and the reactants and products.

EXPERIMENTAL DETAILS

A mixture of high-char-yield resin, a liquid pore-forming reagent, and a catalyst is polymerized to form a porous solid polymer. This is heated slowly up to a high enough temperature to pyrolyze the polymer which gives a porous carbon preform. By varying the ratios of the constituents in the polymer system, carbon preforms with a wide variation of pore volumes, pore sizes, and morphologies can be obtained. The porous carbon precursor matrix is converted to silicon carbide by infiltration with molten silicon or silicon-1.7 and -3.2 at.% molybdenum alloys at temperatures of 1430 to 1500 °C using various schemes. The selection of processing time and temperature is critical to avoid cracking of the specimens due to thermal expansion mismatch and volume change. After infiltration, samples were cross-sectioned and polished for metallographic studies.

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Differential thermal analysis (DTA) studies were carried out in a Netzsch STA differential thermal analyzer system using a heating rate of 10 °C/min in a flowing helium atmosphere. Calculated amounts of infiltration materials (silicon and silicon-molybdenum alloys) were placed at the top of the porous carbon preforms. These amounts were based on the weight of the carbon in the preforms. Porous carbon preforms with two pore sizes i.e., 0.5 and 2-3 μm were used for DTA studies. In order to make comparisons among the DTA traces valid, the weight of each carbon preform sample was kept identical.

RESULTS AND DISCUSSION

Process Modeling

In the case of molten silicon infiltration, silicon reacts with the carbon forming silicon carbide and any remaining pores will be filled with silicon depending on the initial pore volume fraction of the carbon preforms. The modeling results obtained for the silicon infiltration are given in figure 1(a). This plot shows the dependence of the volume fractions of reaction products i.e., silicon carbide (V_{SiC}) and free silicon (V_{Si}) in the reaction formed material on the initial pore volume fraction of carbon preform. According to these results, for initial pore volume fractions less than 0.562, the porous carbon preform will not be completely converted due to choking-off of the infiltration. This phenomena is attributed to the fact that the infiltration passages are narrowed and closed as a result of the specific volume change due to conversion of carbon to silicon carbide. If the initial pore volume fraction of porous carbon preform is greater than 0.562, the final material will contain some free silicon along with the silicon carbide phase.

In the silicon-1.7 at.% molybdenum alloy infiltration, the final material will contain silicon carbide, molybdenum disilicide, and residual silicon-rich alloy, depending on the initial pore volume fraction of the carbon preform. In the alloy infiltration analogous to pure silicon infiltration, there is an initial pore volume fraction ($V_P{}^i$) below which choking-off will occur. In this case, the critical pore volume fraction below which choking-off occurs depends on the amount of molybdenum in the infiltrating alloy. Figure 1(b) shows the volume fractions of silicon carbide, molybdenum disilicide, and the residual alloy for an infiltrating alloy containing 1.7 at.% molybdenum in silicon. The concentrations of molybdenum chosen for this study are in the silicon-rich eutectic region of the silicon-molybdenum system. Modeling results indicate that the initial pore volume fractions below which choking-off occurs are 0.576 for silicon-1.7 at.% molybdenum and 0.59 for silicon-3.2 at.% molybdenum alloy.

Melt Infiltration Studies

A scanning electron micrograph of the fracture surface of a porous carbon preform with initial pore volume fraction of about 0.55 is given in figure 2(a). This microstructure shows uniform struts and pores indicating the ability of this process to produce microstructurally uniform carbon preforms. Figure 2(b) shows a cross-section of a silicon infiltrated preform with 0.55 pore volume fraction showing evidence of choking-off during infiltration. The liquid silicon was introduced from the bottom of the carbon preform and penetrated about 0.45 cm before the infiltration passages were choked-off. This choking-off occurred due to unavailability of enough pore volume to accommodate the volume increase during the conversion of carbon to silicon carbide. Figure 3(a) shows the microstructure of the fracture surface of a porous carbon with a fine pore and carbon particle size ($\sim 1 \mu$m) with initial pore volume fraction of about 0.58. This preform was infiltrated with a silicon-1.7 at.% molybdenum alloy at 1430 °C for 4 hr. The optical micrograph in figure 3(b) shows the complete conversion of carbon by the melt infiltration of the alloy and the uniform distribution of second phase throughout silicon carbide matrix. The uniformity of this

microstructure indicates that this processing approach is quite useful for controlling the distribution and morphology of the second phases in reaction-formed materials.

A clear understanding of the effect of pore and particle size of the carbon preform on the exothermic reaction temperature during the reactive melt infiltration is of prime importance. Pampuch et al. (refs. 14 to 16) reported that the conversion rates of different carbon reactants are a function of their BET surface area. Since the pores are filled by liquid silicon or alloy in very short times, the initial reaction rate can be assumed to be a function of internal surface area of carbon. Carbon preforms with two pore and particle sizes were used to evaluate their effect on the exothermic reaction temperatures via DTA studies, resulting microstructures and second phase morphologies. A scanning electron micrograph of the fracture surface of a carbon preform with a pore and particle size of about 0.5 μm is given in figure 4(a). The microstructure developed at the top of the infiltrated sample, given in figure 4(b), shows the faceted growth of silicon carbide. It appears that the growing silicon carbide nuclei thicken and begin to coalesce to produce serrated type structures. Progressive growth and coalescence produce the overlayer morphologies from which the final evolution of faceted crystals occurs. Ness and Page (ref. 17) observed the same kind of phenomena in their work on REFEL silicon carbide. Further studies on the factors leading to this microstructural evolution are in progress and will be reported elsewhere (ref. 18).

A scanning electron micrograph of the fracture surface of a porous carbon preform with an initial pore volume fraction of about 0.64 is shown in figure 5(a). Figure 5(b) shows a polished cross-section of the silicon infiltrated sample showing the uniform distribution of silicon phase. The x-ray diffraction analysis of this material indicated the amount of free silicon in this material to be about 10 percent. There is a marked difference in the second phase morphology in comparison to figure 3(b) due to the differences in pore shape and size of the carbon preforms. The amount of residual silicon in the final materials can be controlled by changing the initial pore volume fraction of the carbon preforms and by using silicon-molybdenum alloy infiltration. The morphology of the second phase can be engineered according to the requirements by changing the pore shape and size of the porous carbon preforms.

The observation of choking-off phenomena and the absence of infiltrants in the unreacted regions of the preform suggest that the reaction rate between carbon and silicon is faster than the infiltration rate. The reaction between porous carbon and the infiltration materials (silicon, silicon-molybdenum alloys) has been studied by DTA and results are described in the following sections.

DTA Studies

Our experimental results (refs. 5 and 6) and literature data (refs. 14 to 16) confirm that the reaction of porous carbon with molten silicon and silicon alloys is exothermic and the reaction time is very short. The degree of exothermicity of this reaction depends on a number of parameters including the surface area of the reactants (pore size and pore volume of porous carbon preforms) and its wetting behavior with infiltration materials. DTA curves for the reaction of small pore size (~ 0.5 μm) carbon with silicon and silicon-3.2 at.% molybdenum alloy is given in figure 6(a) and (b). It is evident from this figure that the exothermic temperature in the case of alloy infiltration is lower than for pure silicon infiltration. In the case of silicon infiltration, there is another endotherm at 1430°C in addition to one due to melting of silicon. However, there is no such endotherm in the reaction of carbon with silicon-3.2 at.% molybdenum alloy. This phenomena is controlled by the thermochemistry of the liquid silicon and carbon reaction and the nucleation and growth of the second phase. The main reactions occurring at various interfaces in the silicon-carbon system are as follows:

$$Si(l) + C(s) = SiC(s) \tag{1}$$

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$$Si(l) + C(s) = Si/C(soln.) \tag{2}$$

$$Si/C(soln.) = SiC(s) \tag{3}$$

Thermodynamic data for reactions (1) and (2) indicate that they are exothermic and reaction (3) is endothermic. The reaction (1) leading to the formation of primary silicon carbide takes place. Due to volume misfit with carbon, this silicon carbide spalls off and goes into suspension in the molten silicon solution. In addition, high temperature is generated due to exothermic reactions which also leads to higher solubility of carbon in molten silicon. When the concentration of silicon carbide reaches a critical limit in solution, then solution-reprecipitation of secondary silicon carbide takes place according to reaction (3). Recent studies on liquid silicon-carbon reaction by various authors (refs. 7, 11, and 14) also confirm that the primary silicon carbide dissolves in the molten silicon and then reprecipitates as secondary silicon carbide. Due to low coefficients of diffusion of carbon and silicon in silicon carbide, the growth of SiC by solid state reaction at the carbon-liquid silicon interface should be insignificant. The exothermic reaction temperatures observed in the DTA studies for the reaction of medium pore size (~2-3 μm) carbon preform with silicon and silicon-3.2 at.% molybdenum alloy is given in figure 7(a) and (b). In figure 7(a), there is an initial incubation period in the reaction observed in DTA before the exotherm starts. This phenomena has been speculated by Chiang et al. (ref. 7) in the case of carbon fiber-liquid silicon reaction. In porous carbon preforms, the mechanism for silicon carbide formation is a combination of interface limited reaction (in the incubation period) and of solution-reprecipitation (final product).

The exothermic temperature in the case of silicon-3.2 at.% molybdenum alloy is relatively lower than that for the pure silicon. There are a number of factors influencing the silicon-molybdenum alloy infiltration. First, due to molybdenum alloying of silicon, the wetting behavior of silicon-molybdenum alloy with carbon might be improved as suggested by Choh and Oki (ref. 13). Second, the molybdenum may act as a nucleation site during the solution-reprecipitation and growth. The combination of these factors might be the cause for the lower exothermic reaction temperature in the case of silicon-molybdenum alloys.

The exotherm temperature due to reaction of liquid silicon with medium (~2-3 μm) pore size carbon is higher than in the reaction with small pore size carbon preform. This phenomena is attributed to the fact that in small (~0.5 μm) pore size carbon preforms, the reaction and infiltration fronts move almost at the same time. The reactions become more nearly isothermal since heat can be dissipated. But in the case of a medium pore size preform, infiltration materials can be delivered rapidly ahead of the reaction front. Infiltration material goes all over in the preform and there is no control over the reaction. This leads to the high exothermic reaction temperatures since heat can not be so easily dissipated. In some cases, cracking of the preforms has been observed due to thermal stresses resulting from rapid local heating. These cracks are filled with silicon producing silicon veins. In addition, silicon carbide grain coarsening can also occur from solution-reprecipitation during these temperature excursions.

CONCLUSIONS

Using the combination of modeling, melt infiltration, and DTA results it has been concluded that the initial pore volume and pore and particle size of the carbon preform are critical parameters in the melt infiltration process. Pore volume controls the choking-off phenomenon. Modeling results, confirmed by experiments, indicate that carbon preforms with initial pore volume fractions of 0.562 and higher can be infiltrated with molten silicon. In the case of silicon-molybdenum alloy infiltration, the initial pore volume needed to prevent the choking-off increases with increasing content of molybdenum in the alloy.

Carbon pore and particle size control the reaction kinetics. The reaction mechanism of carbon with silicon is a combination of interface limited and solution-reprecipitation depending on the pore and particle size of the carbon. DTA results indicate that the reaction exotherms can be lowered by using silicon-molybdenum alloy infiltration instead of pure silicon and by using small pore size ($\sim$0.5 μm) carbon preforms. From the results of this study it can be further concluded that the combination of two factors, namely the carbon preform properties (pore and particle size) and infiltration materials, can significantly reduce the exothermic reaction temperatures.

ACKNOWLEDGMENTS

REFERENCES

1. Fitzer, E. and Gadow, R.: Am. Ceram. Soc. Bull., Vol. 65, No. 2, pp. 325-35, 1986.

2. Lamicq, P.J., Bernhart, G.A., Dauchier, M.M., and Mace, J.G.: Am. Ceram. Soc. Bull., Vol. 65, No. 2, pp. 336-338, 1986.

3. Hucke, E.E.: AMMRC Report, TR-83-5, 1983.

4. Washburn, M.E. and Coblenz, W.S.: Ceramic Bull., Vol. 67, No. 2, pp. 356-363, 1988.

5. Behrendt, D.R., Singh, M., and Dacek, R.F.: The 16th Annual Conference on Advanced Composites, Materials and Structures, Cocoa Beach, Florida, NASA CP-3175, 1992.

6. Behrendt, D.R. and Dacek, R.F.: 4th HITEMP Review, NASA CP-10082, Vol. 74, pp. 1-14, 1991.

7. Chiang, Y-M., Messner, R.P. Terwilliger, C. and Behrendt, D.R.: Mater. Sci. Eng., A144, pp. 63-74, 1991.

8. Messner, R.P. and Chiang, Y-M.: J. Am. Ceram. Soc., Vol. 73, No. 5, pp. 1193-1200, 1990.

9. Naidich, Ju. V.: "The Wettability of Solids by Liquid Metals," in Progress in Surface and Membrane Science Eds, D.A. Cadenhead and J.F. Danielli, Academic Press, NY, pp. 353-484, 1981.

10. Li, J.G. and Hausner, H.: J. Mater. Sci. Letters, Vol. 10 pp. 1275-1276, 1991.

11. Gnesin, G.G. and Raichenko, A.I.: Poroshk. Metall., Vol. 5, No. 125, pp. 35-43, 1973.

12. Nikolopoulos, P., Agathopoulos, S., Angelopoulos, G.N., Naoumidis, A., and Grubmeier, H.: J. Mater. Sci., Vol. 27, pp. 139-145, 1992.

13. Choh T. and Oki, T.: Mater. Sci. Technol., Vol. 3, pp. 378-385, 1987.

14. Pampuch, R., Walasek, E., and Bialoskorski, J.: Ceram. Intern., Vol. 12 pp. 99-106, 1986.

15. Pampuch, R., Bialoskorski, J., and Walasek, E.: Ceram. Intern., Vol. 13, pp. 63-68, 1987.

16. Pampuch, R., Stobierski, L., Lis, J., and Racza, M.: Mater. Res. Bull., Vol. 22 pp. 1225-1231, 1987.

17. Ness, J.N. and Page, T.F.: J. Mater. Sci., Vol. 21, No. 4, pp. 1377-1397, 1986.
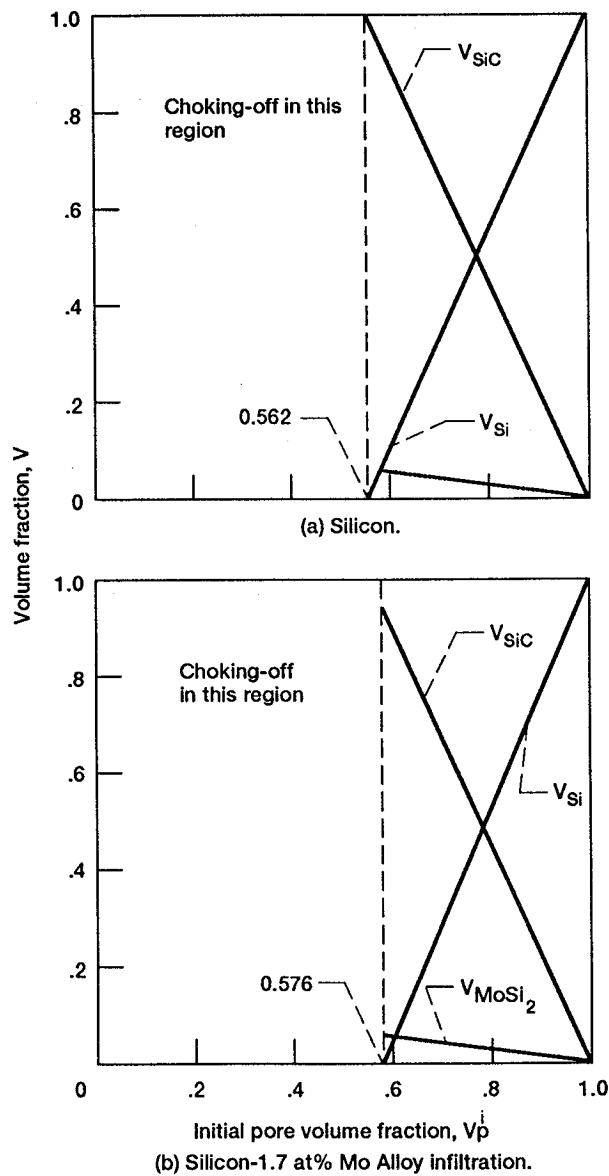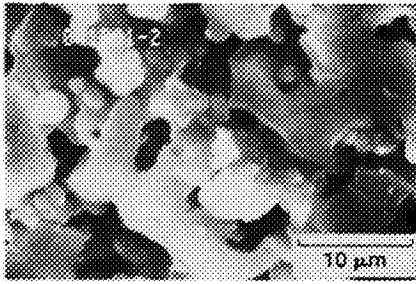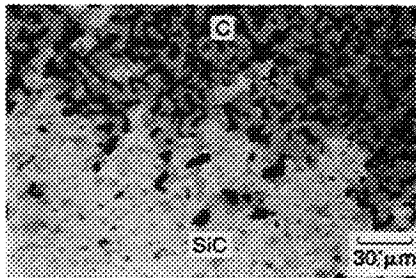
18. Singh, M. and Behrendt, D.R., Unpublished work.

(a) Silicon.

(b) Silicon-1.7 at% Mo Alloy infiltration.

Figure 1.—Effect of initial pore volume fraction of carbon preform on the volume fraction of reaction products.

(a) Microstructure of the fracture surface of a porous carbon preform (V_p^i = 0.55).

(b) Micrograph showing choked-off region during silicon infiltration (dark areas are carbon or pores, grey areas are SiC and white areas are Si).

Figure 2.—Microstructure of the porous carbon preform and silicon infiltrated material.
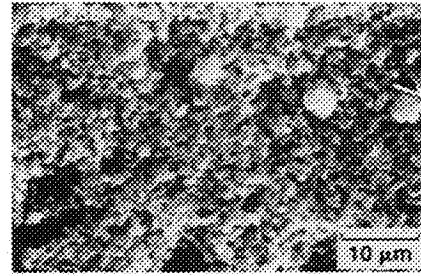
(a) Microstructure of the fracture surface of a porous carbon preform (V_p^i = 0.58).
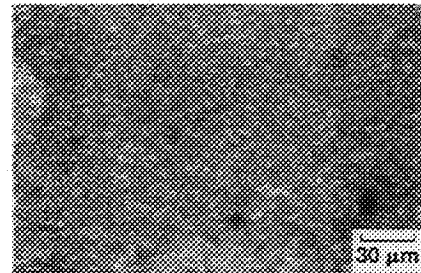
(b) Si-1.7 at % Mo alloy infiltrated material showing the uniformity of the micro-structure (grey areas are SiC and white areas are $MoSi_2$ plus Si).

Figure 3.—Microstructure of the porous carbon preform and silicon - 1.7 at% Mo alloy infiltrated material.
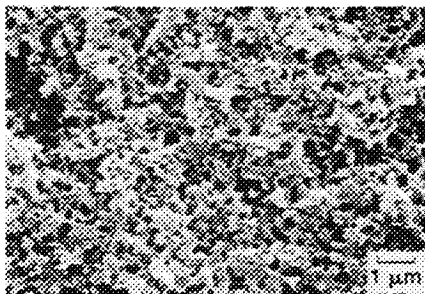
(a) Microstructure of the fracture surface of a porous carbon preform (V_p^i = 0.59).
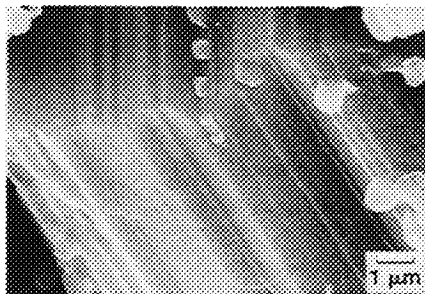
(b) Faceted growth of silicon carbide crystals on the surface due to solution-reprecipitation.

Figure 4.—Microstructure of the porous carbon preform and silicon carbide.

(a) Microstructure of the fracture surface of a porous carbon preform (V_p^i = 0.64).
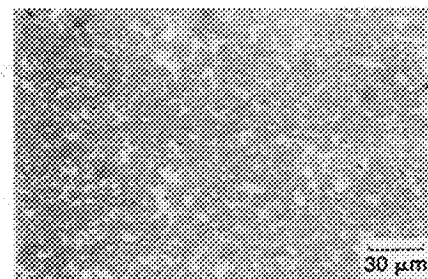
(b) Uniform microstructure of silicon carbide without any porosity (white areas are silicon).

Figure 5.—Microstructure of the porous carbon preform and silicon carbide.

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(a) Silicon.
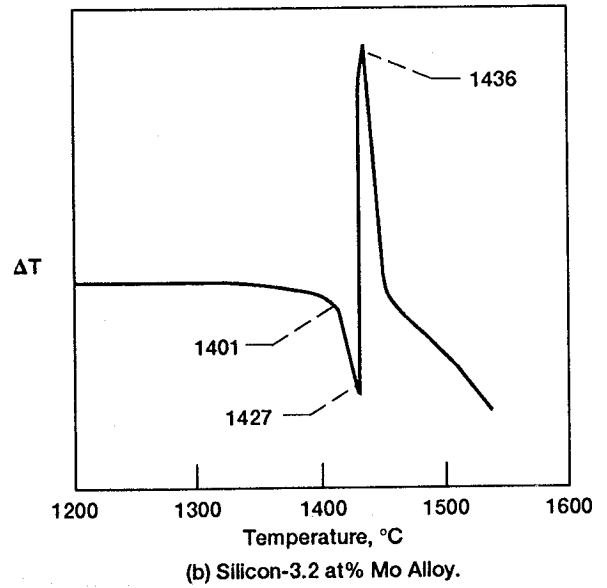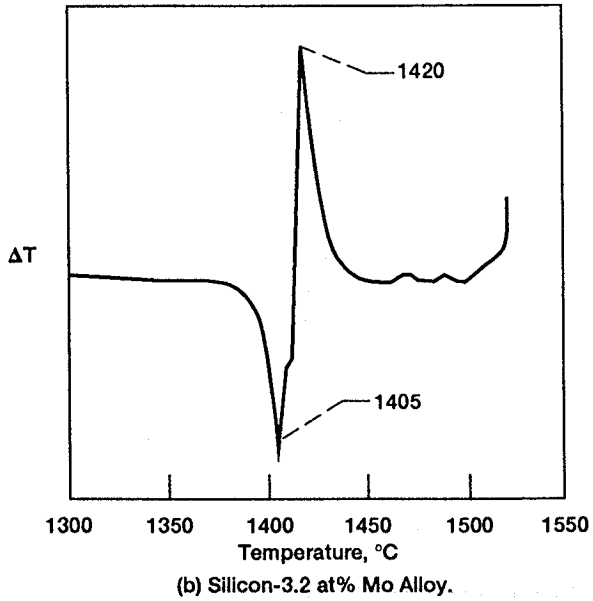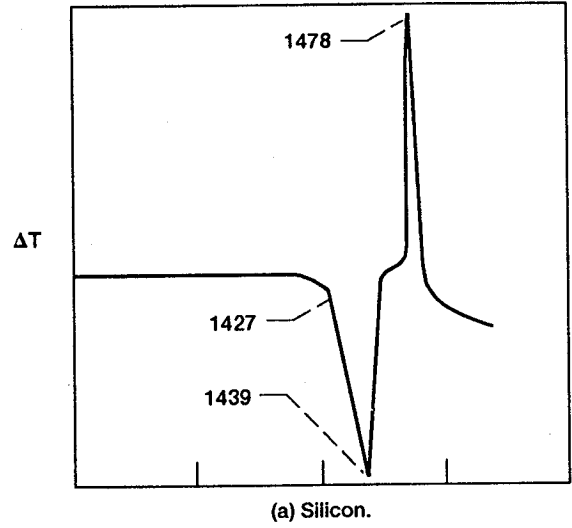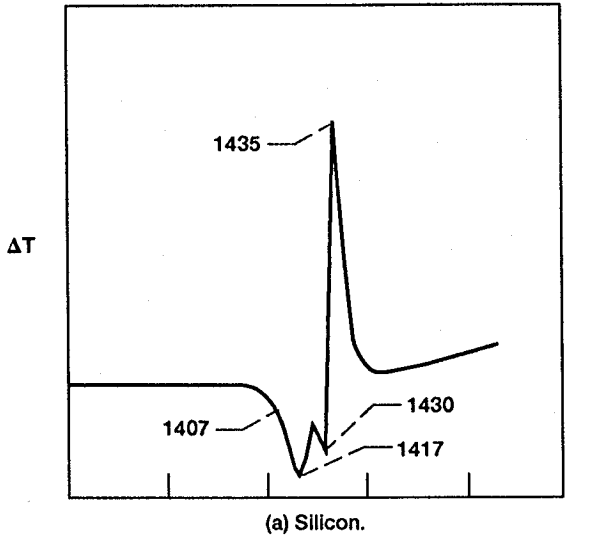

(a) Silicon.

(b) Silicon-3.2 at% Mo Alloy.

Figure 6.—DTA curves for the reaction of small (~ 0.5 μm) pore size carbon preform.

(b) Silicon-3.2 at% Mo Alloy.

Figure 7.—DTA curves for the reaction of medium (~ 2-3 μm) pore size carbon preform.

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13. ABSTRACT *(Maximum 200 words)*

Investigations on the reactive melt infiltration of silicon and silicon-1.7 and 3.2 at % molybdenum alloys into porous carbon preforms have been carried out by process modeling, differential thermal analysis (DTA) and melt infiltration experiments. These results indicate that the initial pore volume fraction of the porous carbon preform is a critical parameter in determining the final composition of the raction-formed silicon carbide and other residual phases. The pore size of the carbon preform is very detrimental to the exotherm temperatures due to liquid silicon-carbon reactions encountered during the reactive melt infiltration process. A possible mechanism for the liquid silicon-porous (glassy) carbon reaction has been proposed. The composition and microstructure of the reaction-formed silicon carbide has been discussed in terms of carbon preform microstructures, infiltration materials, and temperatures.

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