Synthesis and sintering of SiC under high pressure and high temperature

S. K. Bhaumik, C. Divakar, S. Usha Devi, and A. K. Singh
High Pressure Laboratory, Materials Science Division, National Aerospace Laboratories, Bangalore 560 017, India

(Received 30 March 1998; accepted 17 August 1998)

Starting from elemental powders, simultaneous synthesis and compaction of SiC were conducted at 3 GPa pressure and temperatures in the range 2100–2900 K. The sintered compacts were characterized by x-ray diffraction, microhardness measurements, and microscopic studies. The efficiency of formation of SiC was dependent on the particle size of the silicon powder, crystallinity of the reactant carbon, molar ratio of silicon and carbon, and synthesis temperature and time. Carbon in excess of the stoichiometric amount was required to obtain compacts free from residual silicon. The SiC samples, with a Si : C molar ratio 1 : 1.05, prepared at 2100 K for 300 s had a density and hardness of 3.21 g/cm^3 (98.8% of theoretical density) and 22 GPa, respectively. The crystal structure of the SiC depended on the synthesis temperature. Pure β–SiC in the temperature range 2100–2500 K, and a mixture of α– and β–SiC above 2500 K were obtained. The β–SiC was highly crystalline and nearly defect-free.

I. INTRODUCTION

A highly exothermic reaction, once started, can run to completion by the propagation of combustion zone through the reactant mixture. Such reactions have been long since used in welding,[1] fabrication of cermets,[2] and ceramic composites.[3,4] More recently, Merzhanov and Borovinskaya[5] systematically exploited this principle in synthesizing a large number of compounds. This process, commonly known as the self-propagating high temperature synthesis (SHS), has now been used to synthesize over 200 compounds. Extensive reviews on SHS can be found in the literature.[6–9] The SHS process has two distinct advantages. As the heat of reaction is used to complete the reaction, considerable heat energy savings are expected. The reaction product is free from volatile impurities as these are driven out when the reaction zone reaches high temperature. The reaction product, however, is porous. The porosity is caused by a number of factors, such as, the volume change inherent in the reaction, short duration (insufficient for sintering) of the high temperature reaction zone, porosity present in the reaction mixture, and escape of the gases during the reaction. For any practical application, the product of SHS has to be compacted and sintered. Miyamoto *et al.*[10] suggested that the synthesis and compaction can be carried out in a single step if SHS is conducted under high pressure. This process is termed as high-pressure self-combustion sintering (HPCS). The HPCS of SiC at 3 GPa and 2270 K for 1 s gave compacts with 90% theoretical density which contained β-phase (cubic) and had high hardness (21 GPa).[11]

In this paper, we present the results of simultaneous synthesis and compaction of SiC under high pressure. A systematic study was carried out to establish the dependence of the starting mixture composition and synthesis temperature on the formation and crystal structure of SiC. The reaction mechanism and the microstructural features are also discussed.

II. EXPERIMENTAL

Silicon powder (99.999% pure from Koch-Light Ltd., UK) and amorphous carbon powders from three different sources: Philips carbon black (carbon-A), soot collected by burning camphor (carbon-B), and activated charcoal, GR grade marketed by Sarabhai Chemicals, India (carbon-C) were used as the starting materials. The carbon powders were heated to 1700 K under inert atmosphere for 8.6×10^4 s to remove the volatile matter. The x-ray diffraction analysis of these powders showed that carbon-C was least crystalline (Fig. 1). The Si + C mixtures were prepared by both dry and wet milling. Dry milling was performed in a Spex mill-8000 in argon atmosphere for 2.4×10^3 s. Wet milling was carried out in a Fritsch Pulverisette-5 centrifugal mill in hexane medium for 8.6×10^4 s. The milled powder was dried and stored under vacuum. The average particle sizes of the dry- and wet-milled powders were 8.6 and 3.2 μm, respectively.

The simultaneous synthesis and sintering experiments at high pressures and high temperatures were carried out using a cubic anvil apparatus (anvil face: 10 mm square) capable of generating pressures up to 6.5 GPa. A high pressure–high temperature cell[12] capable of producing sample temperatures up to 3300 K was used (Fig. 2). The reactant mixture was packed in a graphite tubular heater fitted in a pyrophyllite cube. The

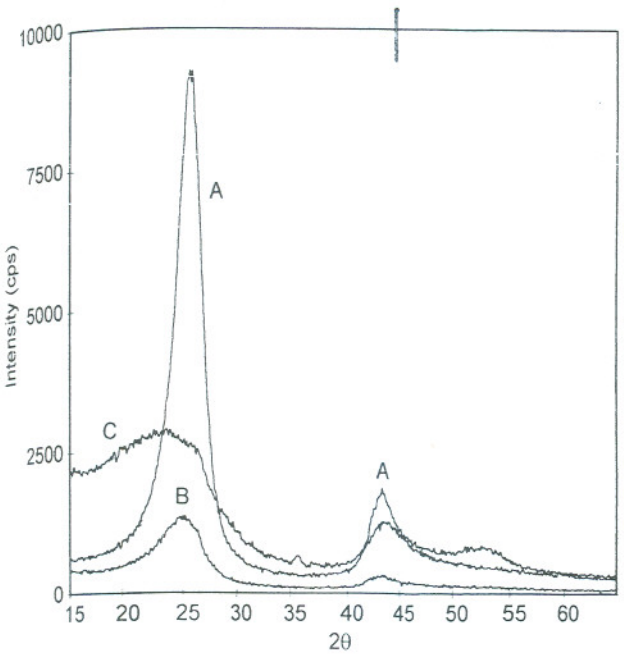

FIG. 1. X-ray diffractograms of the carbon powders: (a) Philips carbon black, (b) soot collected by burning camphor, and (c) activated charcoal. Activated charcoal has the least crystallinity. (Radiation used: Cu K_α of $\lambda = 1.542$ Å.)

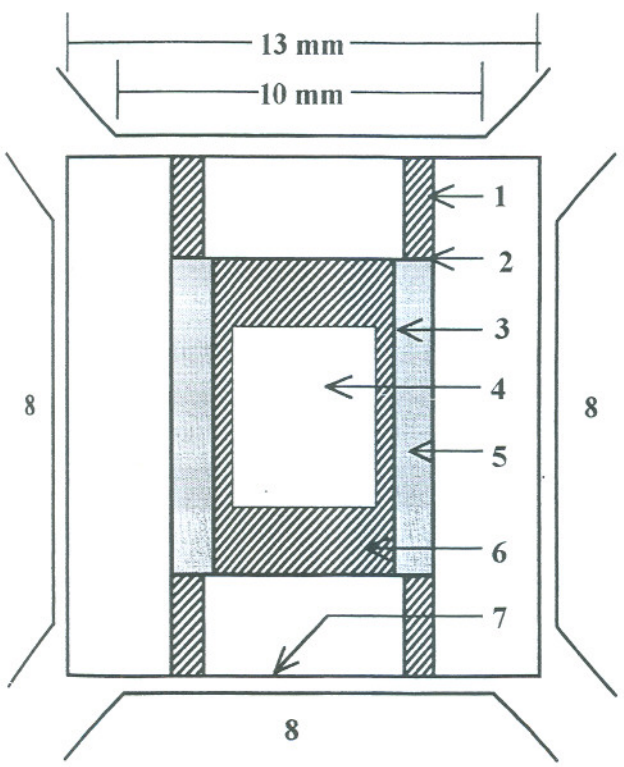

FIG. 2. High pressure–high temperature cell: (1) current ring (graphite), (2) graphite disk, (3) graphite heater, (4) sample, (5) zirconia liner, (6) graphite plug, (7) tantalum disk, and (8) WC anvils; remaining portion of the cell is pyrophyllite.

cube filled with the reactant mixture was degassed at 673 K in vacuum (~10^{-4} Torr) for 7.2 × 10^3 s before the experiments.

The oil pressure in the hydraulic rams versus sample-pressure curve was obtained using the Bi I → II (2.55 GPa) and Yb fcc → bcc (4.0 GPa) transformations. The heater-power versus sample-temperature curve was obtained up to 1900 K using a Pt–Pt 10% Rh thermocouple. Heater-power versus sample-temperature plot above 1900 K was established by using the melting point (or decomposition temperature) of Al_2O_3, Y_2O_3, TiB_2, and SiC. The details of the high pressure–high temperature cell and the temperature calibration are reported elsewhere.[12]

In a typical experiment, the sample was first pressurized to 3 GPa, heated to the required temperature (2100–2900 K), and cooled after a waiting period (30–300 s). Two types of heating schedules were adopted: (i) heating to desired temperature (one-step heating) and (ii) holding the temperature at 1500 K for 600 s followed by heating to the desired temperature (two-step heating). In both types of experiments, the heating rate was 40 K/s.

The surfaces of the recovered samples (in the form of disks, ~3.5 mm in diameter and ~4 mm thick) were flattened by wet polishing on a cast iron wheel using coarse diamond paste (~50 μm). This was followed by fine polishing with diamond paste of decreasing grit size (~25, 5, 1 μm). The SiC phases were identified by x-ray diffraction studies using Cu K_α radiation of wavelength 1.542 Å. To identify unreacted silicon, the polished samples were etched with a solution containing 50 ml HF, 50 ml HNO_3, and 10 ml H_2O. The microstructures of the polished and etched samples were examined under optical (Neophot-2) and scanning electron (JEOL 840A) microscopes. The volume fraction of the unreacted silicon was determined by the point-counting method.[13] One hundred measurements were performed on each sample and the average values are reported. The hardnesses of the compacts were determined at a load of 1.96 N (Shimadzu HSV-20 microhardness tester). The densities of the sintered compacts were measured by water-displacement method.

III. RESULTS AND DISCUSSION

A. One-step heating

The microstructures of the sintered compacts prepared at 2100 K for 60 s with the reactant mixtures having different carbon powders are shown in Figs. 3(a)–3(c). Three distinct phases which appear as grey, white, and black regions are seen in the micrographs. The phases were identified by microhardness measurements and metallographic observations. The grey regions had high hardness (~22 GPa) and were identified as SiC. The white regions had low hardness (~11 GPa) and were identified as unreacted silicon. The black regions were unreacted carbon and pores. The fraction of the SiC formed in the sintered compacts, prepared under identical conditions, was maximum when carbon-C was used.

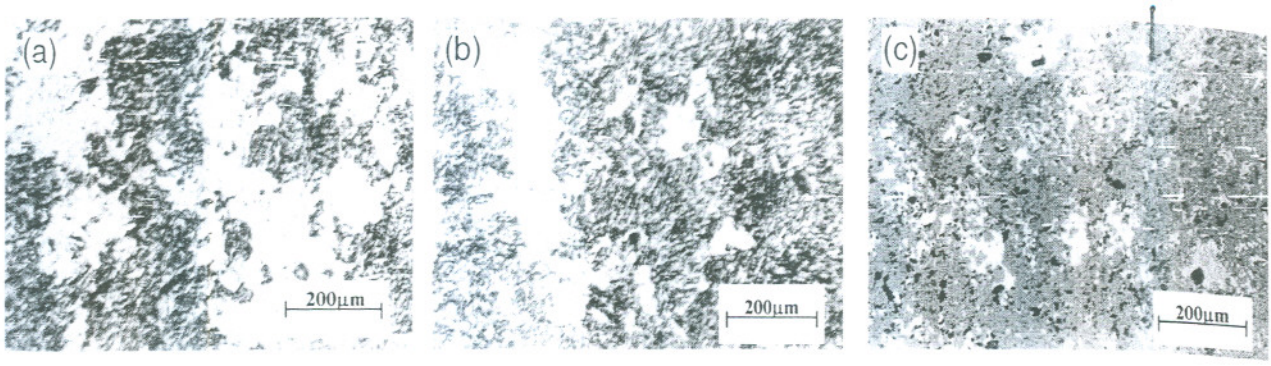

FIG. 3. Optical micrographs of the samples (Si : C = 1 : 1) prepared with various carbon powders: (a) Philips carbon black, (b) soot collected by burning camphor, and (c) activated charcoal. The synthesis and sintering were carried out at 2100 K for 60 s. The amount of unreacted silicon (white phase) is lowest in (c).

The microstructures of the sintered compacts prepared from the dry- and wet-milled powders are shown in Figs. 4(a) and 4(b). While the dry-milled powder compact [Fig. 4(a)] contains a substantial amount of unreacted phases (white and black regions), the wet-milled powder compact [Fig. 4(b)] shows predominantly the grey phase (SiC). Further, the dry milling resulted in the clustering of carbon in the reactant mixture [Fig. 4(a)]. In a finer powder mixture, the contact area between the reactants is larger and provides more sites for the initiation of the reaction. Also, the distances through which the reactants have to diffuse are smaller. Both these factors result in a faster rate of reaction.

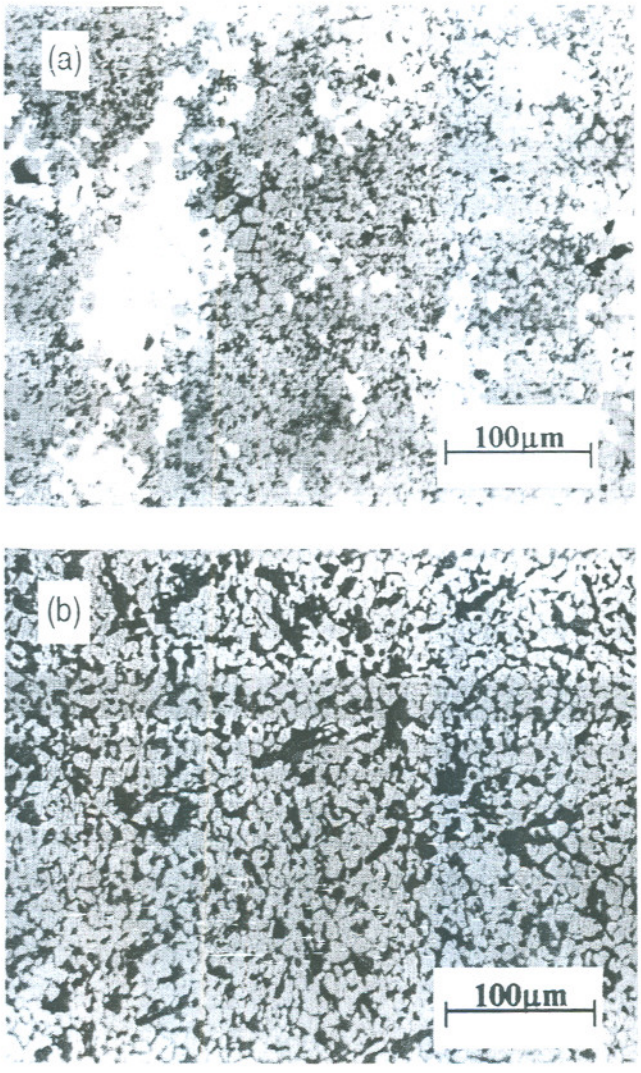

FIG. 4. Optical micrographs of the samples (C-1) sintered at 2200 K for 30 s: (a) dry milled and (b) wet milled. The SiC (grey), Si (white), and carbon (black) phases are seen.

The results indicate that the formation of SiC is enhanced if the carbon is less crystalline and the reactant powders are of small particle size. In view of this, further experiments were carried out with the wet-milled powder mixture containing carbon-C only. Powder mixtures with Si : C molar ratio 1 : 1, 1 : 1.02, and 1 : 1.05 were used. These are referred to as C-1, C-2, and C-3, respectively.

The microstructures of the compact (C-1) prepared at 2300 K for 60 s are shown in Figs. 5(a)–5(c). These contain a large fraction of unreacted silicon and carbon. The heat of formation of SiC is relatively low (69 kJ/mol) and is insufficient for the spontaneous propagation of the reaction. Also, the application of high pressure establishes good contact between the reactants leading to enhanced heat loss by conduction. Therefore, if the reactant mixture is ignited, with no further supply of energy, the reaction progresses through the whole compact but is limited to the surfaces of the reactants. At the start of the reaction, silicon melts and reacts with solid carbon. Initially, several nuclei of SiC form at the Si–C interface, which with time, grow and impinge on each other. Thus, a solid SiC rim is formed around the molten silicon pool and physically separates the reactants [Figs. 5(a) and 5(b)]. For the reaction to proceed, carbon atoms diffuse through the grain boundaries in this SiC layer [Fig. 5(c)]. Since the diffusion coefficient of carbon in SiC is low, it is essential to maintain high temperature until the reaction is completed.

The powders contain a substantial amount of adsorbed oxygen due to high surface area. In addition, the silicon powder contains a thin layer of SiO_2 on the surfaces. At high temperatures, both chemically combined

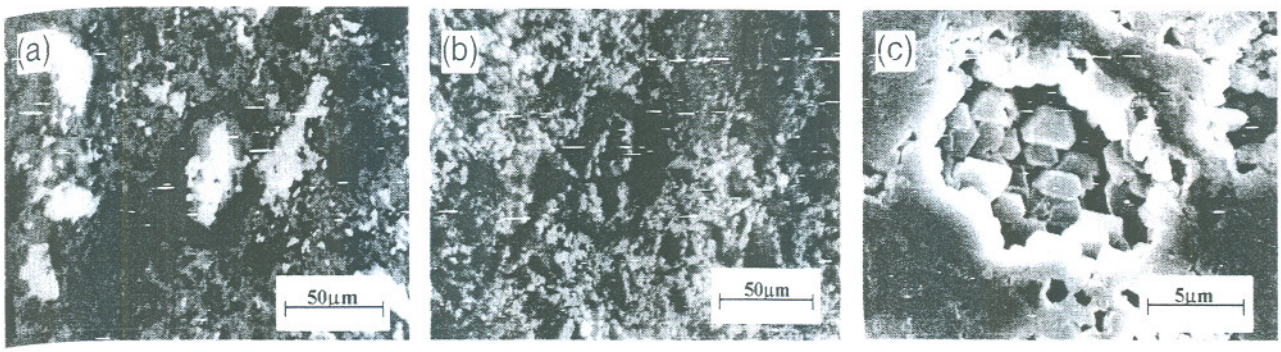

FIG. 5. Microstructures of HPCS compacts (2300 K, 60 s): (a) SiC (grey), silicon (white), and carbon (black) phases, (b) after etching, and (c) scanning electron microstructure showing faceted crystals of β–SiC grown into silicon melt.

and adsorbed oxygen react with carbon and produce CO_2/CO gas. The resulting carbon loss gives rise to free silicon in the compacts. To avoid this, carbon in excess of the stoichiometric amount has to be provided in the reactant mixtures.

The increase in synthesis time to 300 s resulted in a higher fraction of SiC in the compact [Fig. 6(a)], but it contained some unreacted silicon. The fraction of unreacted silicon decreased when the carbon content in the reactant mixtures was more than the stoichiometric amount [Figs. 6(a)–6(c)]. Typically, compacts prepared from powder mixtures with Si : C molar ratios 1 : 1, 1 : 1.02, and 1 : 1.05 contained 8.9, 2.6, and 0.9 vol% free silicon, respectively.

The compacts prepared in the temperature range 2100–2500 K contained β–SiC (Fig. 7). At the onset of the reaction, many β–SiC nuclei form at the Si–C interface and with the progress of the reaction, the faceted SiC grains grow inside the liquid silicon pool [Fig. 5(c)]. The microstructure of the compact after the completion of the reaction is given in Fig. 8(a). At temperatures >2500 K, the microstructure changes to a mixture of equiaxed (β–SiC) and elongated grains (α–SiC) [Figs. 7 and 8(b)]. The elongated grains with high aspect ratio (platelike morphology) is known to develop[14] when β–SiC transforms to α–SiC. This indicates that initially molten silicon reacts with carbon to form β–SiC which transforms to α–SiC at temperatures ~2500 K. The $\beta \rightarrow \alpha$ transformation is completed at 2500 K in ~300 s. Further increase in temperature or synthesis time results in the coarsening of α–SiC platelets. Around 2800 K, the decomposition of α–SiC to silicon and carbon is observed [Fig. 8(c)]. Above this temperature, the microstructure contains α–SiC platelets, silicon, and carbon phases.

The densities of the compacts prepared at various processing conditions are listed in Table I. These are also expressed in terms of percent theoretical density (% TD). However, it may be noted that the sintered compacts have unreacted silicon and carbon which have fewer densities than SiC. Therefore, the actual porosities in the compacts are less than those reported in Table I. Taking into account the unreacted silicon (2.33 g/cm^3) and carbon (1.7 g/cm^3) present, the calculated densities of the sintered compacts prepared from powder mixtures with Si : C molar ratios 1 : 1, 1 : 1.02, and 1 : 1.05 are 3.08, 3.20, and 3.23 g cm^{-3}, respectively.

The present results indicate that the reaction takes place in two stages. On reaching ~2100 K, the reaction is self-propagating but limited to the surfaces of the reactants. On subsequent holding at this temperature, the reaction is completed by the diffusion of carbon through SiC. Therefore, the time required for the completion of the reaction is dependent on the synthesis temperature.

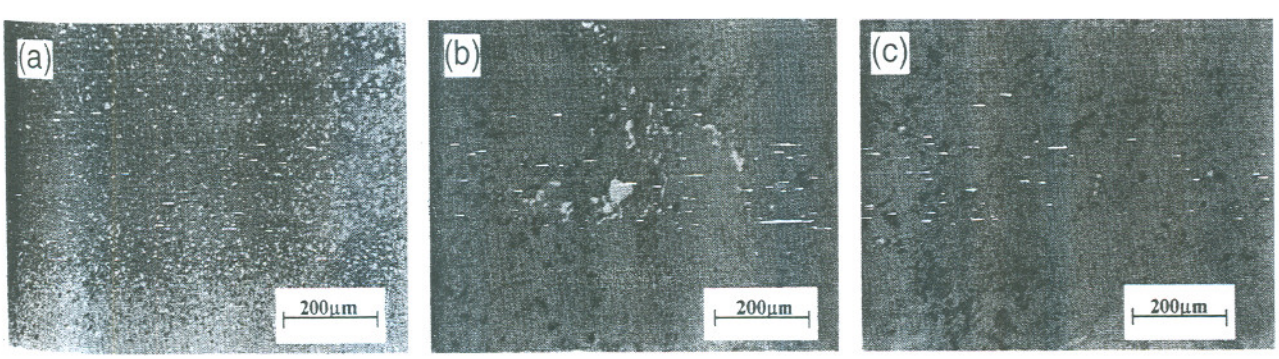

FIG. 6. Optical microstructures of the sintered compacts prepared at 2300 K for 300 s with Si : C molar ratios (a) 1 : 1, (b) 1 : 1.02, and (c) 1 : 1.05. The volume fraction of unreacted silicon decreases with the increase in carbon content.

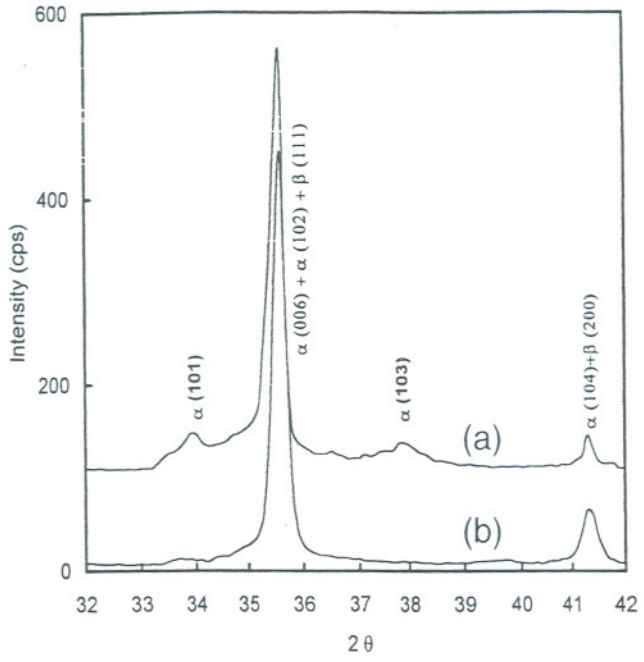

FIG. 7. X-ray diffractograms of the samples (C-3) synthesized at (a) 2500 K and (b) 2200 K for 300 s. (Radiation used: Cu K_α of λ = 1.54 Å.)

This observation is in variance with that reported by Yamada *et al.*[11] This may be due to the differences in the heating rate and the size of the high pressure cell. The higher heating rate (2300 K/s) and larger pyrophyllite cell (20 mm cube) used by Yamada *et al.*[11] might have led to the reduction in heat loss from the reaction zone. However, the SiC compact obtained by Yamada *et al.*[11] had ~10% porosity, and may have contained a substantial amount of unreacted silicon and carbon. In contrast, the density of the SiC compacts obtained in present experiments was 98.8%.

B. Two-step heating

It is observed that the porosity is less when the heating is done in two steps (Table I). The compacts (C-3) prepared at 2100 K for 300 s had a maximum density of 3.21 g/cm^3 (98.8% of TD). The porosity in the sintered compacts is due to the release of adsorbed gases and gaseous products at high temperatures. In pressureless sintering, most of the gaseous phases come out of the sample. In high pressure sintering, the compact is completely isolated from the atmosphere and, therefore, no gaseous phase can escape. The amount of gaseous products as well as the gas pressure inside the pores increase with the increase in temperature. Both these factors hinder densification and result in higher porosity in the sintered compacts. When the temperature is held at 1500 K for 600 s, the reactant mixture gets densified due to deformation of silicon particles. This hinders the evolution of gaseous products leading to denser compacts.

The hardness value of the compacts synthesized in the temperature range 2100–2500 K (β–SiC) is 23 ± 1 GPa. Compacts synthesized in the temperature range 2500–2700 K have a hardness of 30 ± 1 GPa in the α–SiC regions. Irrespective of the heating schedule (one-step or two-step), the compacts have similar hardness values.

IV. SUMMARY

In the HPCS of SiC, the reaction between silicon and carbon does not go to completion due to the weak exothermicity (69 kJ/mol) of the reaction and enhanced conduction losses under high pressure. Completion of the reaction requires externally supplied heat. Also, carbon in excess of the stoichiometric amount has to be provided in the reactant mixture to obtain compacts free from residual silicon. After the reaction commences and the solid SiC product is formed, the reaction proceeds by the diffusion of carbon atoms through the SiC layer into silicon melt. The crystal structure of the SiC is dependent on the synthesis temperature. It is pure β–SiC in the temperature range 2100–2500 K, and a mixture

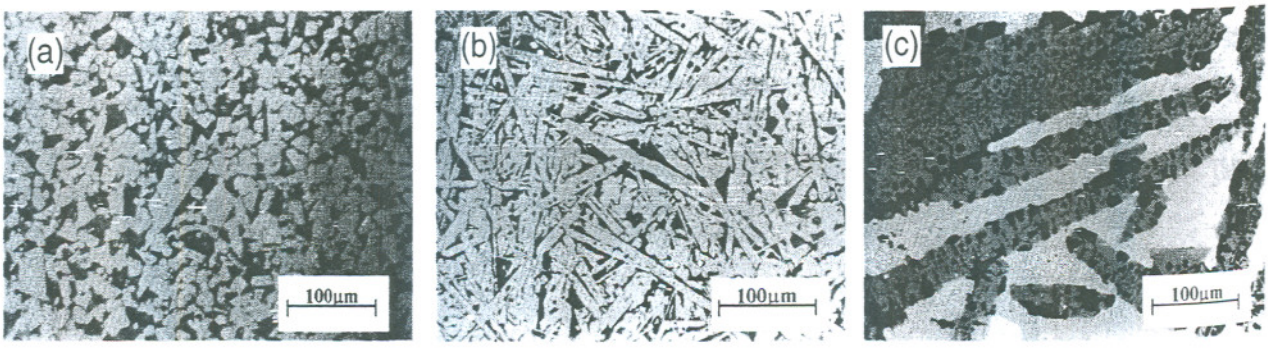

FIG. 8. Microstructures of the samples (C-3) sintered at (a) 2100, (b) 2500, and (c) 2900 K for 300 s. The microstructures show (a) the equiaxed grains of β–SiC, (b) the $\beta \rightarrow \alpha$ transformation, and (c) the decomposition of α–SiC. The α-phase has a platelike morphology. The white and black regions are silicon and carbon, respectively.

TABLE I. Density values of SiC samples processed at different temperatures. Processing was carried out at 3 GPa for 300 s. % TD is the percent theoretical density. I and II denote, respectively, the one-step and two-step heating schedules used to prepare the samples.

Starting mixture (Si:C molar ratio)	Processing temperature (K)	Density, g/cm^3 (% TD)	
		I	II
1:1.02	2100	3.13 (96.4)	3.18 (97.8)
	2300	2.93 (90.2)	
	2500	2.87 (88.5)	3.15 (97.1)
	2700	2.80 (86.2)	
1:1.05	2100	3.12 (96.0)	3.21 (98.8)
	2300	2.89 (89.0)	

of α- and β-SiC above 2500 K. The β-SiC obtained is highly crystalline and defect-free.

ACKNOWLEDGMENTS

The authors thank P.M. Jaman for assistance in the fabrication of the high pressure cells. This work was funded by BRNS, India (Grant No. 34/2/96-R&D-II/1066).

REFERENCES

1. *The Cambridge Encyclopedia*, edited by D. Crystal (Cambridge University Press, Cambridge, 1994).
2. J.D. Walton, Jr. and N.E. Poulos, J. Am. Ceram. Soc. **42**, 40 (1959).
3. S. Krapf, Ber. deut. keram. Ges. **31**, 18 (1954).
4. R.A. Abramovici and M. Enache, Keram. Z **19**, 699 (1967).
5. A.G. Merzhanov and I.P. Borovinskaya, Dokl. Chem (Eng. Trans.) **204**, 429 (1972).
6. J.F. Crider, Ceram. Eng. Sci. Proc. **3**, 519 (1982).
7. Z.A. Munir, Am. Ceram. Soc. Bull. **67**, 354 (1988).
8. J.B. Holt and S.D. Dunmead, in *Annual Review of Materials Science*, edited by R.A. Huggins, J.A. Giordmaine, and J.B. Wachtman, Jr. (Annual Reviews Inc., CA, 1991), Vol. 21, p. 305.
9. J. Subrahmanyam and M. Vijayakumar, J. Mater. Sci. **27**, 6249 (1992).
10. Y. Miyamoto, M. Koizumi, and O. Yamada, Commun. Am. Ceram. Soc. **67**, C-224 (1984).
11. O. Yamada, Y. Miyamoto, and M. Koizumi, Am. Ceram. Soc. Bull. **64**, 319 (1985).
12. S.K. Bhaumik, C. Divakar, M. Mohan, and A.K. Singh, Rev. Sci. Instrum. **67**, 3679 (1996).
13. J.E. Hillard, in *Quantitative Microscopy*, edited by R.T. DeHoff and F.N. Rhines (McGraw-Hill Book Company, New York, 1968), p. 45.
14. M. Lancin, F. Anxionnaz, J. Thibault-Desseaux, D. Stutz, and P. Griel, J. Mater. Sci. **22**, 1150 (1987).