Solid State Phenomena
ISSN: 1662-9779, Vol. 159, pp 153-156
doi:10.4028/www.scientific.net/SSP.159.153
© 2010 Trans Tech Publications, Switzerland

Nanosized Silicon Carbide Obtained from Rice Husks

Dimitar Radev, Ivan Uzunov

Institute of General and Inorganic Chemistry, BAS "Acad. G. Bontchev" str.,Bl.11, 1113 Sofia, Bulgaria

ddradev@gmail.com, iuzunov@svr.igic.bas.bg

Keywords: Silicon carbide, nanosized materials, synthesis, rice husks

Abstract. Two ways to obtain nanosized silicon carbide (SiC) powders from the products of thermal decomposition of rice hulls and posterior thermal and chemical treatment of SiO_2-C precursors are shown in the present paper. The reagents and products were analyzed using BET, DTA, IR, XRD and SEM/TEM. Precursors obtained from rice husks containing pure SiO_2 and a controlled SiO_2-C ratio were used for the synthesis of SiC. The synthesis of SiC proceeded for 30-45 min in a graphite heater furnace under protective Ar atmosphere at relatively low temperatures (1450^oC-1550^oC). Nanosized dimensions of reagents obtained from rice husks and their high activity allow obtaining SiC in relatively milder thermal regimes. TEM and XRD analysis revealed synthesis of nanostructured mainly β-SiC with a mean crystallite size of 40-100 nm. Due to their purity and nano-scale properties, the products obtained are appropriate for production of bulk SiC or design of SiC–based ultra high-temperature materials using the methods of powder metallurgy.

Introduction

Great deal of interest has been created among the materials scientists in developing structure of materials of specific nanomorphologies [1]. The different nanoforms of inorganic materials play a vital role as they exhibit unique mechanical, physical and technological properties [2]. The properties of silicon carbide (SiC), such as high chemical and high-temperature stability, wide bandgap, high breakdown electric field strength, high saturated electron drift velocity and high thermal conductivity make the material suitable for production of electronic devices operating under extreme conditions as high temperature, high power and harsh environments [3,4]. The high thermal conductivity coupled with low thermal expansion and high strength gives this material exceptional thermal shock resistant qualities. Silicon carbide ceramics with little or no grain boundary impurities maintain their strength to very high temperatures, approaching 1600°C with no strength loss. Chemical purity, resistance to chemical attack at high temperature, and strength retention at high temperatures have made this material very popular as wafer tray supports and paddles in semiconductor furnaces. Various synthesis methods such as laser ablation, physical evaporation, chemical vapor deposition (CVD), self-propagating high-temperature synthesis (SHS), sol-gel, plasma, microwave irradiation, etc have been explored to produce SiC nanomaterials [5-9]. Silicon oxide (SiO_2), silicon poly-silane polymer precursor and different carbon sources have been utilized with these methods as reagents for the synthesis of SiC. Rice husks (RH) which are a natural agricultural waste product containing 18-20% SiO_2 and the products of their thermal and chemical treatment could be a valuable source for synthesis of SiC. Here we show two simple ways to produce nanosized SiC from products of thermal treatment of RH, namely pure SiO_2 and SiO_2/C precursor.

Experimental

The phase composition of reagents and products and their structural peculiarities were studied by FTIR, XRD, SEM and TEM. The specific surface area of the products was measured using the Brunauer-Emmett-Teller (BET) method. After water washing and chemical treatment with hydrochloric acid (1:1) RH were subjected to oxidation burning at 800°C or pyrolysis at 450°C. The oxidation burning of RH at 800°C leads to high-purity SiO_2 with a highly developed surface area. These properties make it appropriate as a reagent for synthesis of SiC. The products of thermal treatment of RH, pure SiO_2 or SiO_2-C precursor were admixed with carbon black or an additional amount of SiO_2, to achieve a stoichiometric SiO_2:C ratio equal to 1.67 in stainless steel bawls using a *Puverizette Fritsch* planetary ball mill. The exact carbon ratio in the products of pyrolysis was determined by thermal analysis. The quantity of impurities in the composirtion of SiO_2 was determined by atomic absorption spectroscopy (AAS). A stoichiometric mixture of reagents was shaped into pellets by cold pressing at 100 MPa using 2 wt.% paraffin as plasticizer. The corresponding amount of SiO_2 was added to keep the optimum Si:C ratio of the reagents. The pellets were placed into graphite crucible. Synthesis of SiC proceeded at 1550°C or 1450°C for 30 min in a high-temperature vacuum furnace *Degussa,* equipped with a graphite heater. The temperature was measured using an optical pyrometer. The phase changes and microstructure evolution of reagents were examined by X-ray diffraction (XRD). The spectra were obtained by a *Philips APD 15* X-ray diffractometer with mounted graphite monochromator operating with Cu K_{α} radiation. The JCPDF standards were used for that purpose. X-ray data were also utilized to estimate the nanograin (crystallite) sizes of the phases obtained. A computer program was used to separate and calculate the effects of lattice strain and grain refinement. The morphology and sizes of powder particles were studied by scanning electron microscopy (SEM, *Jeol 357*) and transmission electron microscopy (TEM, *Jeol 200 CX*).

Results and discussion

The thermal treatment (oxidation burning or pyrolysis) leads to a high purity SiO_2 or SiO_2-C precursor which could be used as reagents for the synthesis of materials having a significant industrial meaning, such as silicon nitride (Si_3N_4), polycrystalline silicon (Si) and silicon carbide (SiC). Fig.1 shows the product after oxidation burning of RH at 800°C. XRD analysis shows that the thermal treatment of rice husks in an oxygen medium at 800°C leads to partially crystallized SiO_2 (Figure 2). The main impurities in the composition of SiO_2 were Na, K, and Fe and according to data from AAS, their level was: $370 \pm 10\ \mu g.g^{-1}$; $580 \pm 10\ \mu g.g^{-1}$ and $330 \pm 10\ \mu g.g^{-1}$ respectively. BET data show a specific surface area of $34\ m^2.g^{-1}$. The high purity of SiO_2 and its large surface area are a precondition for the synthesis of a pure product at relatively low temperatures.

Fig.1. SiO_2 obtained from RH

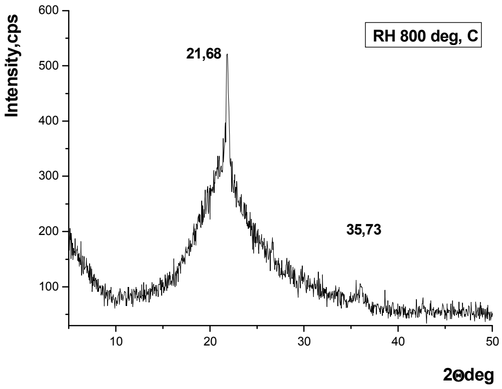

Fig.2. XRD of partially crystallized SiO_2

Fig.3 shows the TEM image of SiO_2 admixed with the necessary amount of carbon black after 60 minutes of homogenization in a planetary ball mill. The picture reveals particles with sizes of about 10-20 nm. Intense mechanical treatment in high-energy milling apparatuses such as attritors and planetary mills leads to a perfect homogenization and closer contacts between the particles. Fig.4

shows XRD patterns of the product obtained after thermal treatment of the reagents at 1550°C. The picture reveals the presence mainly of β-SiC and some amount of α-SiC.

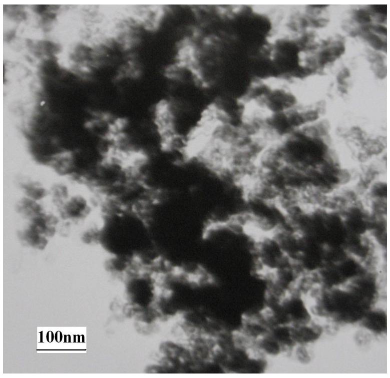

Fig.3.TEM of SiO_2-C admixture, X100 000

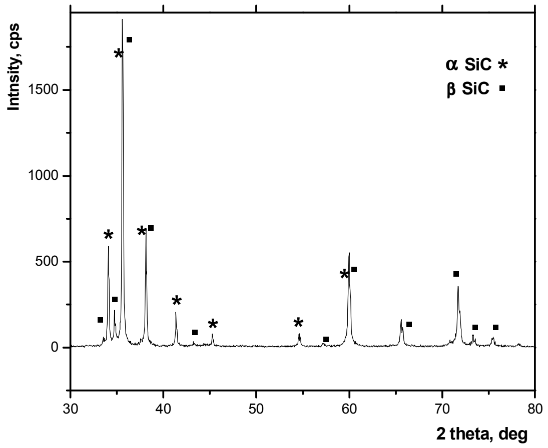

Fig.4. XRD patterns of SiC obtained from SiO_2 and C at 1550°C

A TEM image of the product obtained from nanosized SiO_2 and carbon black is shown on Fig. 5. The SiC particles preserve nano-scale dimensions of the reagents. They are characterized by well formed walls and a mean particle size of about 40-60 nm.

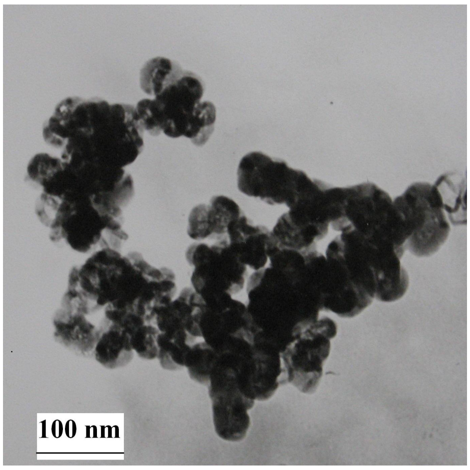

Fig.5.TEM of SiC, obtained from SiO_2-C admixture at 1550°C, X 100 000.

The circumstance that the SiO_2 obtained after the process of pyrolysis is embedded into the hydrocarbon matrix of the RH favors the synthesis of SiC. Using appropriate thermal conditions one can control the Si:C ratio, which makes the rice hulls an attractive source for the synthesis of pure SiC. The thermal analysis data show that the SiO_2-C precursor obtained after pyrolysis of RH at 450° C contains 62.3% C and 37.7% SiO_2, which means that an additional SiO_2 admixture is necessary to obtain an optimal composition of reagents [10]. The XRD patterns of the products reveal the formation of β-SiC with a mean crystallite size of 90 nm (Figure 6). Figure 7 shows a TEM image of SiC particles obtained after a 30 min thermal treatment at 1450°C of a SiO_2-C precursor mixed with the necessary amount of SiO_2. The particles possess a mean size of about 80-100 nm. Nanosized SiC is valuable because of its enhanced sinterability and the possibility to obtain bulk SiC products and tools using a conventional sintering process and avoiding expensive and low-efficient methods for densification such as hot-pressing or hot isostatic pressing.

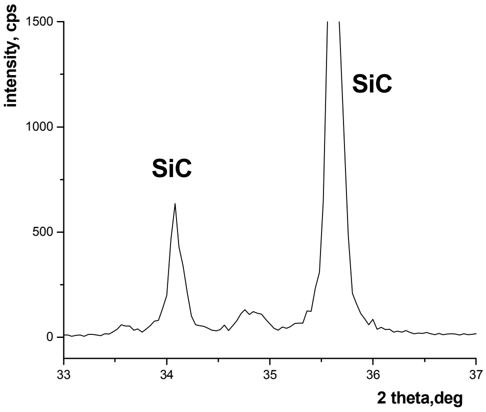

Fig.6. XRD of SiC obtained from a SiO_2/C precursor at 1450°C

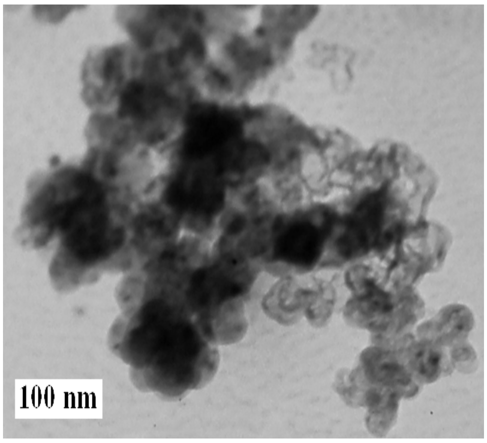

Fig.7.TEM of SiC obtained from a SiO_2/C precursor at 1450°C X60 000

Nanosized SiC could play an irreplaceable role in the creation of new ultra-high temperature composite materials. Since 1891, when Acheson invented the industrial production of SiC from SiO_2 and C at 2800-3300°C, the modern technology for SiC production differs in minor details [11,12]. The present study shows the possibility for low-temperature synthesis of nanosized SiC using products of RH pyrolysis. The method described in the present work proceeds with a significantly lower consumption of energy, utilizing a waste product from rice production, thus solving some ecological problems of the rice-productive agricultural districts.

References

[1] S. Iijima: Nature Vol. 354 (1991), p. 56

[2] C.M. Lieber: Solid State Commun. Vol. 107 (1998), p. 607

[3] S. Madapura, A.J. Steckl, M. Loboda: J. of the Electrochem. Soc. Vol. 146 (3) (1999), p. 1197

[4] N.E. Korsunka, I. Tarasov, V. Kushnirenko, S. Ostapenko: Semicon. Sci. Tecnol. Vol. 19 (2004), p. 833

[5] W. Shi, Y. Zheng, H. Peng, N. Wang, C.S. Lee and T. Lee: J. Am. Chem. Soc. Vol. 83 (2000), p. 3228

[6] Z.S. Wu, S.Z. Deng , J. Chen, J. Zhou: Appl. Phys. Lett. Vol. 80 (2002), p. 3829

[7] H.F. Zhang, C.M. Wang, S.L. Wang: Nano Lett. Vol. 2 (2002), p. 941

[8] J. Narayan, R. Raghunathan, R. Chowdhury, K. Jagannadham: J. Appl. Phys. Vol.75 (1994), p. 7252

[9] K. Nagarajan, S. Kumar Raman: Bulg. J. Phys. Vol. 35 (2008), p. 53

[10] V. Vikulin, I. Shkarupa, T. Gurina, M. S. Paizulahanov, Sh. Faiziev, G. Adilov: Patent RU 2299177 (2007)

[11] E.H.P. Wecht in: *Applied Mineralogy*, Springer, Vienna, (1977) p. 21.

[12] K. Winnacker, L. Koehler in: *Chemische Technologie*, 4-th ed., volume 2, Hanser, Munich, (1982) p. 627