Middle-East Journal of Scientific Research 12 (9): 1250-1253, 2012
ISSN 1990-9233

DOI: 10.5829/idosi.mejsr.2012.12.9.366

Changing ph to Improve Efficiency of SiC Nano-Particles Produced by Chemical Method

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Abstract: Nanopowder silicon carbide (SiC) was produced in this research through chemical method. Saccharose and TEOS were used as precursors of C and Si. Gels were prepared by mixing the raw materials with different pH values followed by drying them. They were pyrolyzed at 650°C and then reduced using carbothermal operation. XRD results indicated that the produced powders under these conditions were only composed of β-SiC. Analysis on Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) micrographs has revealed that pH value of 4 has yielded spherical grains and maximum efficiency with minimum grain size and agglomeration.

Key words: Nanopowder · Silicon dioxide · Synthesis · Chemical method

INTRODUCTION

SiC has been emphasized as a promising ceramic material during the last decades due to it's unique properties of stability at high temperatures although it's low toughness is an important problem as for many other ceramics [1]. Many studies have been launched in recent years in order to solve this problem by devising fibers and whiskers or producing multiphase structures. However the toughness of SiC and other ceramic materials have been improved to some extent, this parameter is still lower than that of practical metals. Production of nano-particles and controlling their size, binding energy in structure, surface and interface have introduced hopeful opportunities to make strong ceramic with high toughness content [2-12].

Nanopowder SiC is the proper choice for reinforcing composite materials and high temperature applications such as thermal elements and refractory materials because of it's following interesting characteristics: high hardness and strength, high resistance against corrosion and oxidation, low thermal expansion coefficient, high thermal conductivity [13]. Meanwhile, SiC is being used as a semi-conductor in designing electronic chips with the ability to operate at elevated temperatures, high electrical power and frequency and high stress environments [15].

Carbothermal reduction of silica (Achson Process) is well-known as a conventional method to produce SiC powder. This technique produces silicon carbide by a solid-state reaction between silica and raw cock at significantly high temperatures (2500°C). The SiC produced in this way is considerably large sized and involves high content of impurities [1]. In order to produce a part with desired properties one would need high purity, spherical shape, very small size of particles, controlled size distribution and low intensity of agglomeration. Such a nanopowder can be earned from various techniques namely sol-gel [16], thermal plasma [17], milling [15] and carbothermal reduction of SiO_2 [14]. Sol-gel and carbothermal reduction methods are almost similar, although the former produces a mixture with much higher homogeneity regarding different mixing conditions of the two reactants (SiO_2 and C). Having a homogenous mixture will increase rate of the reaction and decrease temperature of it, thereby conditions would be ready to produce fine grain powder [18].

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Table 1: Proportions of materials with different pH values

Sample	TEOS/Eth	TEOS/Sac	Sac/H_2O	TEOS/H_2O	Time (hr)	pH
P1	5	4	0.5	2	4	3
P2	5	4	0.5	2	4	3.5
P3	5	4	0.5	2	4	4
P4	5	4	0.5	2	4	4.5

Experimental: Tetra Ethyl Ortho Silicate (TEOS) with chemical formulas of Si ($C_2H_5O_4$), ethanol, saccharose ($C_{12}H_{22}O_{11}$) and distilled water were used as the raw materials. They were mixed according to proportions listed in Table 1 for 4hr at 30°C using rotation speed of 250rpm. The obtained solution was kept for some 18hr in closed environment for the purpose of finishing the hydrolysis reactions. The produced gels were then exposed to 60°C temperature to be completely dried.

To implement the pyrolysis, samples were stored in a vacuum atmosphere furnace at 650°C for 1.5hr using heating rate of 15°C/min, while the samples were kept for 1.5hr at 1500°C in an argon atmosphere furnace using heating rate of 20°C/min. For burning the excessive carbon, the samples were roasted for 1hr at 650°C while HF acid was employed to remove remaining Si and SiO_2 from the samples. A step of milling was accomplished in neutral environment since the samples were agglomerated.

Samples were then investigated using XRD phase analysis technique after being classified. They were also studied and photographed by SEM and AFM methods in order to discover their morphology and phase distribution in addition to justify or reject the expected theories.

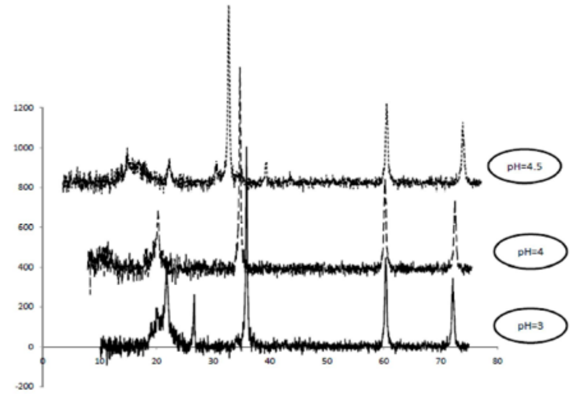

Fig. 1: XRD patterns of the samples produced

RESULTS AND DISCUSSION

Effect of pH Value on the Amount of SiC Produced: Figure1 depicts XRD patterns of the samples.

It is obvious from figure1 that the SiC formed in pH=4 has been more than other samples, since intensity of the recorded peaks are higher for SiC. This fact can be justified by more complete hydrolysis reactions at this pH which has produced more SiO2 and led to formation of SiC along with carbon resources. When pH goes higher or lower than this value, less proportion of the reactions will be implemented due to variation in their rates.

Effect of pH Value on the Shape of SiC Produced: Figure2 illustrates SEM micrographs of SiC samples after being heated at 1500°C for 1hr in argon atmosphere. Studying

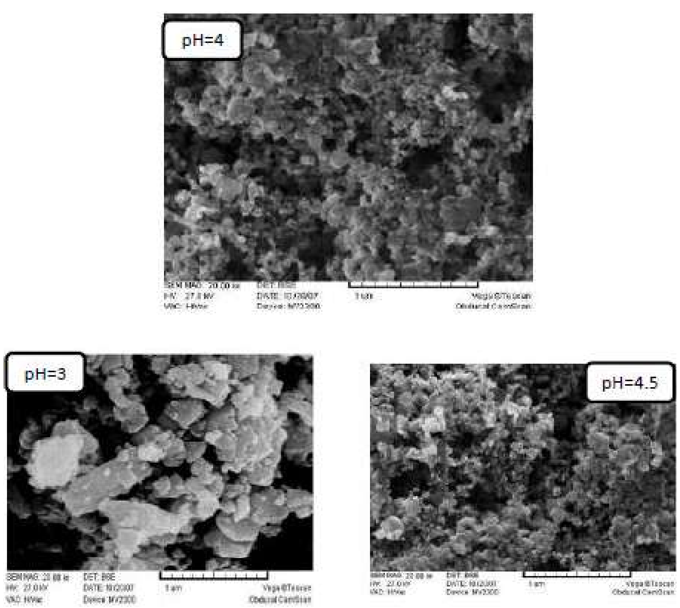

Fig. 2: SEM micrographs of the final samples

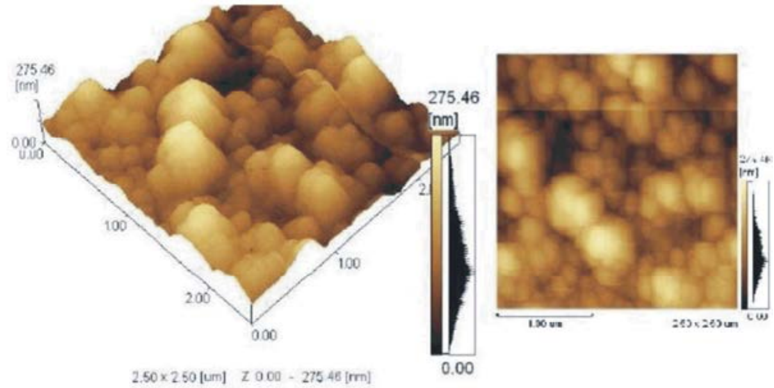

Fig. 3: AFM micrograph of the final sample

the images reveals that the powder morphology will change from spherical to planar when pH value of the solution is reduced from 4-4.5 to more acidic values. It should be noted that the hydrolysis reaction would be accelerated with increased acidity or basicity. In fact, final shape of the hydrolyzed silica is dependent to pH content of the solution to a great extent. Transformation to metal oxide from a mid state is accompanied by losing water and alcohol. At low pH values, namely strong acidic state, silica has much tendency to form linear molecules which are connected in width.

The oxygen atom on alcoxide group will absorb electrophile reagents or H^+ protons. Linear chains bear lower density than transverse connections and this can lead to formation of a soft and reversible gel which is able to redistribute within solution. Once the pH content is decreased, actually the transverse connections are increased between polymeric chains. Thus, at small pH values, linear polymers will branch more and there would be more transverse connections. On the other hand, at higher pH values, hydrolysis and polymerization will occur by attack and strike of nucleophilic reagents to Silicon ion (Si^{4+}). The result would be a hydrated gel which is indeed a special form of 3D polymer rather than a colloidal dispersion. Increased pH will enhance hydrolysis and polymerization with the small parts being solved and precipitated on larger chains. Therefore, number of small molecules will be decreased and large molecules will grow instead.

This fact is attributed to the try for reaching minimum energy. The evolution process is called Stowald in which smaller particles are absorbed by larger particles in order to achieve the minimal energy content. SEM evaluations for this purpose have uncovered that any deviation from equilibrium pH (4 in this case) can cause growth of the particles and finally change from spherical state. Figure3 (AFM micrograph of the final sample) shows that the ideally produced materials have lower than 100nm grain size with an almost uniform distribution.

CONCLUSIONS

The highest efficiency of producing SiC is realized at pH=4 while this efficiency is decreased at either higher or lower pH contents. When pH value of the initial gel solution is reduced, shape of the obtained powder will transform from spherical to planar. All XRD patterns include other phases which are amorphous in some points, so they can be removed by pickling.

Among all effective variables of this research, pH has been identified as the most effective one whose small variation will change conditions of the process significantly. However, results of this experiment were accompanied by some deviation due to the existing conditions and constraints.

REFERENCES

1. Raman, V., O.P. Bahl and U. Dhavan, 1995. Synthesis of Silicon Carbide Through the Sol-Gel Process from Different Precursors, National Physical Laboratory, New Delhi, India.
2. Tong Ramana, L. and G. Reddy, 2005. Thermal Plasma Synthesis of SiC Nano-Powders/Nano-Fibers, Department of Metallurgical and Materials Engineering, The University of Alabama, USA.
3. Satapathy, L.N., P.D. Ramesh, D. Agrawal and R. Roy, 2005. Microwave synthesis of phase-pure, fine silicon carbide powder", Materials Research Bulletin 40: 1871-1882.

4. Gupta, A., T. Ghosh and C. Jacob, 2006. The influence of diluents gas composition and temperature on SiC nanopowder formation by CVD, J. Mater Sci.
5. Du, K., H. Yang, R. Wei, M. Li, Q. Yu, W. Fu, N. Yang, H. Zhu and Y. Zeng, 2007. Electric-pulse discharge as a novel technique to synthesize β-SiC nano-crystallites from liquid-phase organic precursors, Materials Research Bulletin.
6. Intarasiri, S., T. Kamwanna, A. Hallen, L.D. Yu, M.S. Janson, C. Thongleum, G. Possnert and S. Singkarat, 2006. RBS and ERDA determinations of depth distributions of high-dose carbon ions implanted in silicon-carbide synthesis study, Nuclear Instruments and Methods in Physics Research B, 249: 859-864.
7. Chen, C.C., C.L. Li and K.Y. Liao, 2002. A cost-effective process for large-scale production of submicron SiC by combustion synthesis, Materials Chemistry and Physics, 73: 198-205.
8. Larpkiattaworn, S., P. Ngernchuklin, W. Khongwong, N. Pankurddee and S. Wada, 2006. The influence of reaction parameters on the free Si and C contents in the synthesis of nano-sized SiC, Ceramics International, 32: 899-904.
9. Lin, Y.J. and C.M. Chuang, 2007. The effect of transition metals on carbothermal synthesis of β-SiC powder, Ceramics International, 33: 779-784.
10. Kogler, R., F. Eichhorn, A. Mucklich, W. Skorupa, C. Serre and A.P. Rodriguez, 2007. Effect of excess vacancies in ion beam synthesis of SiC nanoclusters, Vacuum, 78: 177-180.
11. Tong, L. and R.G. Reddy, 2006. Thermal plasma synthesis of SiC nano-powders/nano-fibers, Materials Research Bulletin, 41: 2303-2310.
12. Raman, V., O.P. Bahl and U. Dhawan, 1995. Synthesis of silicon carbide through the sol-gel process from different precursors, Journal of Materials Science, 30: 2686-2693.
13. Pampuch, R., G. Gorny and L. Stobierski, 2004. Synthesis of One-Dimensional Nanostructured Silicon Carbide by Chemical Vapor Deposition, University of Science and Technology, AGH, Krakow, Poland.
14. Konno, H., T. Kinomura, H. Habazaki and M. Aramata, 2003. Synthesis of Submicrometer-Sized SiC Particles from the Precursors Composed of Exfoliated Graphite and Silicone, Lab. Of Advanced Materials Chemistry, Japan.
15. Ronald William, R.W., 1989. Fundamental Principles of sol-gel Technology.
16. Li, J., J. Tian and L. Dong, 2000. Synthesis of SiC Precursors by a two-step Sol-Gel Process and their conversion to SiC powders, Journal of the European Ceramic Society, pp: 1853-1857, 77.
17. Pierre, A.C., 1991. Sol-Gel Processing of Ceramic Powders, Ceramic Bulletin, 70: 1281-1288.
18. Brinker, C.J. and G.W. Sherrer, 1990. Sol-Gel Science, Academic Press, NY.