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Magnesiothermic Reduction Synthesis of Silicon Carbide with Varying Temperatures: Structural and Mechanical Features

Nurul Hidayat^{1,*}, Ardiansyah¹, Abdulloh Fuad¹, Nandang Mufti¹, Anggun Amalia Fibriyanti¹, Chusnana Insjaf Yogihati¹, Bambang Prihandoko²

¹ Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia

² Research Center for Physics, Indonesian Institute of Sciences (LIPI), Kawasan PUSPITEK Serpong, Banten 15310, Indonesia

*Corresponding author's email: nurul.hidayat.fmipa@um.ac.id

Abstract. The search for finding effective ways to produce high quality of nanostructured materials have always been the never-ending work of many scientists and engineers from time to time. Important issues to address are reducing fabrication expense and lowering energy utilization to complete the synthesis. A specific circumstance is an investigation of using relatively low temperature to fabricate pure silicon carbide (SiC), one of the most notable materials due to its excellent properties, from naturally appearing minerals. In this current study, silicon carbide was prepared by means of magnesiothermic approach at some adjusting temperatures using argon gas furnace. The source of silicon and carbon were respectively initiated from naturally purified silica and sucrose. The X-ray diffraction (XRD) assessment clearly uncovered the pure moissanite-3c phase of silicon carbide, having a cubic crystal structure. The disappearing of magnesium, otherwise in the form of magnesium oxide, was also validated by the X-ray fluorescence (XRF) test. Furthermore, the chemical functional groups were clarified by Fourier-transform infrared (FTIR) spectroscopy, and the silicon-carbide interaction was evidently detected from the FTIR spectrum. Besides, the SiC products exhibited high Vickers hardness values, nearly 150 MPa for the sample with temperature synthesis of 800 °C.

Keywords: Magnesiothermal, silicon carbide, chemical structure, hardness

1. Introduction

The discovery of silicon ability, in the late 1990s, to capture visible light emission encouraged a great deal of scientists to explore silicon nanocrystals attributable to their quantum confinement effect [1]. Until then it was found that nanostructured silicon carbide, compared to silicon nanocrystals, offered more outstanding performances, mainly for its mechanical strength, thermal conductivity, thermal stability, chemical inertness, electronic saturation velocity, bandgap, and mechanical strength [2-4]. In other words, studies on silicon carbide related topics, from the very fundamental of structural investigation to advanced applications, contribute to many fields in science and engineering. The progressive features of silicon carbide have opened up the opportunities in solving problems of elevated conditions in power, temperature, and frequency applications. Silicon carbide has been exposed to take full advantages of huge range of applications, from ceramics industries [5] to high-energy physics, astronomy, and space applications [6].



Despite the fact that silicon carbide that contains silicon and carbon can be found in nature, the mineral is extremely rare. The mass production of SiC is, therefore, a necessity to fulfill human needs in life. Silicon carbide can be fabricated by sintering at a very high temperature to form a compact ceramic. The SiC nanostructures were built through the direct chemical reaction of mesoporous carbon and silicon above 1300 °C [7]. Others employed carbothermal reduction using heating temperatures up to 1400 °C [8], sonochemical method at a sintering temperature of 850 °C [9], chemical vapor deposition at temperatures from 1200 °C to 1800 °C [10], and sol-gel at 1200-1500 °C [11]. However, sintering and grain growth control related problems arose when counting against the creation of ordered structures at very high temperatures.

A breakthrough to overcome those problems is to employ magnesiothermic assisted synthesis to produce silicon carbide from silica/carbon composite at reasonably low temperatures, e.g., around 750 °C [12] and 600-900 °C [13]. The sources of silica to prepare silicon carbide may come from tetraethyl orthosilicate, polycarbosilane, resorcinol formaldehyde, or any materials containing silicon and carbon. Herein, we preferred the use of crystalline silica from natural limestone as the source of silicon and sucrose as the source of carbon. The magnesium was introduced to the silica/carbon composite in an argon gas furnace. The magnesiothermic reduction can break silica chemical bonding at lower temperatures which in turns offer better control of the building block arrangements [2]. On top of that, the magnesiothermic synthesis is more economical by virtue of the use of the natural mineral, and it requires low temperature to complete the silicon carbide fabrication.

2. Methods

To start with, a 2 g crystalline silica was mixed with a 1.14 g sucrose. The crystalline silica, with nanometric size, was initially extracted and purified from a naturally occurring material which was reported elsewhere [14]. The mixture was added by sulfuric acid and distilled water with proper concentrations previous to drying at 100 °C for 6 h and 160 °C for the other 6 h to attain silica/carbon composite. The dried powder was then carbonated at 700 °C for an hour using an argon gas furnace. After reaching room temperature, a magnesium powder was introduced into the dried silica/carbon powder. The compositional calculation obeys Equation 1. These procedures lead to magnesium exothermic reaction, yielding temperatures nearly 2000 °C and implying the formation of silicon carbide crystals [5].



The mixture of silica/carbon and magnesium powders were reacted at varying temperatures, from 700 °C to 1000 °C, by means of the argon gas furnace. The magnesiothermic process was controlled for 18 h. The as-prepared silicon carbide product was then leached by hydrofluoric acid (10 wt%) and nitric acid (4 M) for 3 h on a hotplate with stirring speed of 600 rpm and temperature of 100 °C. The use of strong acid for leaching is sufficient to remove magnesium oxide and silicon dioxide. The precipitate was filtered and cleaned with distilled water and dried for a half hour on a hot plate with the same stirring speed and temperature as the previous setting.

The SiC characteristics were finally tested by virtue of (a) X-ray fluorescence (XRF) for elemental analysis, (b) X-ray diffraction (XRD) for crystalline phase and structural determination, (c) scanning electron microscopy (SEM) for morphological exploration, (d) Fourier-transform infrared (FTIR) spectroscopy for chemical bonding study, and microhardness Vicker's hardness test for mechanical performance evaluation.

3. Results and Discussion

The XRD patterns for the as-produced silicon carbide powders are represented in Fig. 1(a). All samples clearly show the same trend of XRD patterns which are in an excellent agreement with the moissanite-3c phase of silicon carbide. According to PDF reference code number 01-073-1708, silicon carbide crystallizes in cubic structure in a space group of $F\bar{4}3m$ (216) with lattice parameter, crystal density, and cell volume of 4.3480 Å, 3.24 g/cm³, and 82.20 Å³, respectively. This type of silicon carbide phase

is well recognized as β -SiC or 3c-SiC. The diffraction data of the β -SiC are listed in detail in Table 1. The sharpest peaks are found in Bragg angles of around 35°, 60°, and 75°, with which respectively refer to (111), (220), and (222) crystal planes. The d -spacing, in Table 1, dictates the distance between adjacent Bragg planes.

To ensure that there were no magnesium or magnesium oxide-based phases in the silicon carbide products, the XRF test was conducted. The results revealed that there was no magnesium or magnesium oxide detected in all samples. Meanwhile, the silicon atoms within the samples with varying temperatures of 700 °C, 750 °C, 800 °C, 900 °C, and 1000 °C, were respectively 96.7%, 96.2%, 97.0%, 98.2%, and 96.2%. Hence, these XRF data supported the XRD analysis in justifying the only silicon carbide existence in all synthesis products.

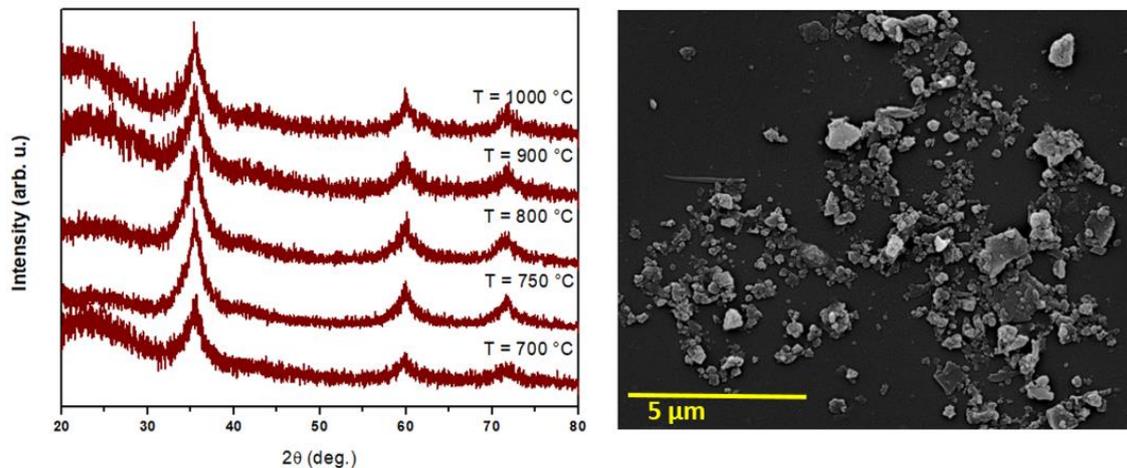


Figure 1. (a) XRD profiles of the as-prepared silicon carbide via magnesiothermic approach at different temperatures and (b) SEM image of silicon carbide sample for $T = 900$ °C.

Table 1. XRD data for cubic structured silicon carbide (PDF code: 01-074-2307).

No.	h	k	l	d -spacing (Å)	2θ (°)	Intensity (%)
1	1	1	1	2.51635	35.651	100.0
2	2	0	0	2.17922	41.400	17.4
3	2	2	0	1.54094	59.985	35.3
4	3	1	1	1.31412	71.772	23.6
5	2	2	2	1.25818	75.502	3.3
6	4	0	0	1.08961	89.975	3.9

Taking into consideration the values of peak intensity and full width at half maximums (FWHM), the temperature did not seem to have a linear relationship with those crystallographic parameters. As the temperature increased, the highest peak intensity for (111) plane started to form 125 counts at 700 °C and went up to 196 counts when $T = 750$ °C. The peak intensity fell slightly to 169 counts at 800 °C and again diminished 48 counts at 900 °C. But then it rose up to 132 counts at the last temperature setting. The FWHM also varied as the temperature changed, implying the non-linear change of the crystallite size, from 8.57 nm to 13.16 nm. These findings indicate that there is an optimum parameter for silicon carbide fabrication. This is in line with other reports in using low temperature to form silicon carbide through magnesiothermic assistance [13,15-16]. Furthermore, the morphological characteristic of the silicon carbide is given in Fig. 1(b). Some particles have already been in a very small size (below 100 nm), but some others are captured in bigger shapes. It is due to the fragmentary grinding of the samples before scanning by electrons. The grain size of silicon carbide, from the SEM image, supported the crystallite size, which was derived from the FWHM.

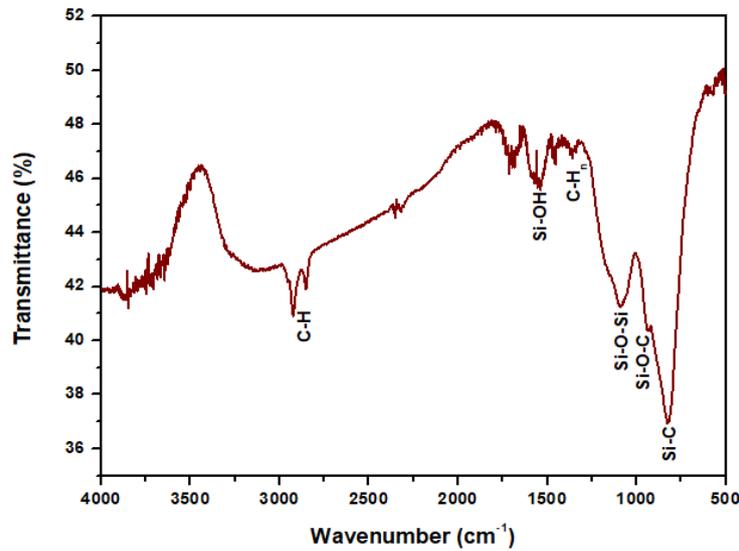


Figure 2. FTIR spectrum for silicon carbide produced by magnesiothermic method at $T = 900$ °C.

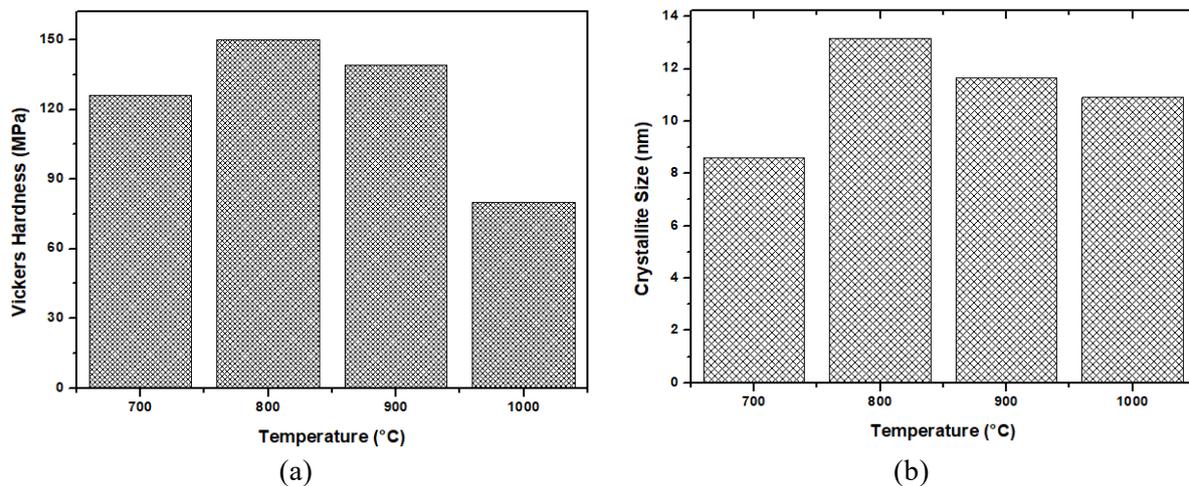


Figure 3. (a) Vickers hardness and (b) crystallite size of silicon carbide at various temperature produced by magnesiothermic synthesis

Fig. 2 shows the FTIR profile of the as-prepared silicon carbide at temperature synthesis of 900 °C. The intense and sharp band near 650 cm^{-1} refers to Si-C stretching [17]. It strongly indicates the presence of the silicon carbide compound. The silicon-oxygen-carbon interaction is depicted by the absorption peak at 999 cm^{-1} [9]. The Si-O-Si functional group also occurred at 1100 cm^{-1} [18]. The C-H and CH_n functional groups, that correspond to $\text{CH}_2\text{-Si}$ and $\text{CH}_3\text{-Si}$ stretching, are found in wavenumbers of 1300 cm^{-1} and 2800 cm^{-1} [17]. The hydrogen oxide interaction with silicon appears in 1500 cm^{-1} [19]. The absorption peaks which emerge around 1600 cm^{-1} are due to the manifestation of moisture in the silicon carbide [20]. As it should be, the magnesium-based functional groups are not identified in the FTIR spectrum. Thus, all these vibration modes clarify the formation of silicon carbide with proper chemical interactions.

Though it is not a fundamental physical characteristic, hardness represents the material's resistance to strong indentation. The Vickers hardness values of the silicon carbide are shown in Fig. 3(a). The crystallite sizes, calculated by taking into account the FWHM of the silicon carbide diffraction profiles, are drawn in Fig. 3(b). Visibly from Fig. 3, the crystallite size influences the Vickers hardness of SiC.

They were likely to be linearly proportional when the crystallite increased, the Vickers hardness also enhanced. Compared to the hardness of α -SiC, the hardness of β -SiC is, however, smaller in value. Besides the influence of the crystallite size on the Vickers hardness, the strong covalent bond in the SiC is also accountable to its mechanical strength [2].

4. Conclusion

Silicon carbide nanopowders have been successfully synthesized by means of magnesiothermic reduction approach, with temperature variation from 700 °C to 1000 °C. The incorporation of magnesium during heating enabled the release of silicon from silica, and its oxygen was bound by magnesium in such a way that crystalline silica carbide was established. It was possible since the magnesium underwent an exothermic reaction to create higher temperature for formation of silicon carbide inside the argon gas furnace. The cubic structure of silicon carbide, known as 3c-SiC or β -SiC, was captured by the XRD profiles. The XRF, SEM, and FTIR data altogether supported the formation of nanostructured silicon carbide, with fairly remarkable hardness characteristics.

References

- [1] Canham L T 1990 Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers *Appl. Phys. Lett.* **57** 1046
- [2] Mojarad B S, Nourbakhsh A, Kahrizsangi R E, Masoud M and MacKenzie K J D 2015 Synthesis of nanostructured SiC by magnesiothermal reduction of silica from zeolite ZSM-5 and carbon: the effect of carbons from different sources *Ceram. Int.* **41** 5287–5293
- [3] Zhu J, Liu Z, Wu X L, Xu L L, Zhang W C and Chu P K 2007 Luminescent small-diameter 3c-SiC nanocrystals fabricated via a simple chemical etching method *Nanotechnology* **18** 365603
- [4] Pujari and Sidharam P 2013 *Covalently attached organic monolayer onto silicon carbide from 1-alkynes: molecular structure and tribological properties* pubs.acs.org/langmuir: Laboratory of organic chemistry Waganing Universty
- [5] Shi L, Zhao H, Yan Y, Li Z and Tang C 2006 Synthesis and characterization of submicron silicon carbide powders with silicon and phenolic resin **169**(2) 71-76
- [6] Rafi J M, Pellegrini G, Godignon P, Quirion D, Hidalgo S, Matilla O, Fontserè A, Molas B, Takakura K, Tsunoda I, Yoneoka M, Pothin D and Fajardo P 2018 Four-quadrant silicon and silicon carbide photodiodes for beam position monitor applications: electrical characterization and electron irradiation effects *JINST* **13** C01045
- [7] Shi Y, Wan Y and Zhao S 2011 Ordered mesoporous non-oxide materials *Chem. Soc. Rev.* **40** 3854–3878
- [8] Yang Z X, Xia Y D and Mokaya R 2004 High surface area silicon carbide whiskers and nanotubes nanocast using mesoporous silica *Chem.Mater.* **16** 3877–3884
- [9] Sivasankaran S and MJ K K 2015 A novel sonochemical synthesis of nano-crystalline silicon carbide ceramic powder and its characterization *Int. J. Recent Sci. Res.* **6** 2630–2633
- [10] Yang X, Wei L, Song W and Zhao-hui C 2012 Effects of the single layer CVD SiC interphases on the mechanical properties of the C/SiC composites fabricated by PIP process *Mater. Sci. Eng., A* **558** 451–455
- [11] Simonenko E P, Simonenko N P, Derbenev A V, Nikolaev V A, Grashchenkov D V, Sevastyanov V G and Kuznetsov N T 2013 Synthesis of nanocrystalline silicon carbide using the sol-gel technique *Russ. J. Inorg. Chem.* **58**(10) 1143–1151
- [12] Shi Y, Zhang F, Hu Y S, Sun X, Zhang Y, Lee H I, Chen L D and Stucky G 2010 Low-temperature pseudomorphic transformation of ordered hierarchical macro-mesoporous SiO₂/C nanocomposite to SiC via magnesiothermic reduction *J.Am.Chem.Soc.* **132** 5552–5553

- [13] Zhao B, Zhang H, Tao H, Tan Z, Jiao Z and Wu M 2011 Low temperature synthesis of mesoporous silicon carbide via magnesiothermic reduction *Materials Letters* **65**(11) 1552–1555
- [14] Fuad A, Mufti N, Diantoro M and Subakti 2016 Synthesis and characterization of highly purified nanosilica from pyrophyllite ores, in: *AIP Conf. Proc.*, *AIP Publishing* **1719** 030020
- [15] Liu S T, Yan K K, Zhang Y H, Jin S Di, Ye Y and Chen X G 2015 Magnesiothermic reduction of rice husk ash for electromagnetic wave adsorption *J. Magn. Magn. Mater.* **394** 266–273
- [16] Saeedifar Z and Nourbakhsh A A, Kalbasi R J and Karamian E 2013 Low-temperature magnesiothermic synthesis of mesoporous silicon carbide from an MCM-48/polyacrylamide nanocomposite precursor *J. Mater. Sci. Technol.* **29** 1-6
- [17] Vasin A V, Kolesnik S P, Konchits A A, Rusavsky A V, Lysenko V S, Nazarov A N, Ishikawa Y and Koshka Y 2008 Structure, paramagnetic defects and light-emission of carbon-rich α -SiC:H films *J. Appl. Phys.* **103** 123710–123717
- [18] Liu Z, Shen W, Bu W, Chen H, Hua Z, Zhang L, Li L, Shi J and Tan S 2005 Low-temperature formation of nanocrystalline β -SiC with high surface area and mesoporosity via reaction of mesoporous carbon and silicon powder *Microporous Mesoporous Mater.* **82** 137–145
- [19] Yu W, Lu W, Han L and Fu G 2004 Structural and optical properties of hydrogenated amorphous silicon carbide films by helicon wave plasma-enhanced chemical vapour deposition *J. Phys. D Appl. Phys.* **37** 3304–3308
- [20] Smith B 1999 *Infrared spectral interpretation, A systematic approach* CRC Press Florida

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