Preparation of SiC Powders by Carbonthemal Reduction Method at Low Temperature

Zhao Wang[1], Xiao-Yuan Dai[1], Shao-Peng Xu[1]and Man Xu[1, 2, a]

[1] *School of materials science and Engineering. Wuhan Institute of Technology. Wuhan, Hubei 430073*
[2] *Energy saving materials and Membrane Technology Institute.Wuhan Institute of Technology. Wuhan, Hubei 430073*

Abstract: The stable slurry was prepared by ball-milling with a certain proportion of silica fume as silicon source,glucose as carbon source and metal niobium (Nb) as additives mixed with alcohol water. After the slurry was dried and pulverized, put the powder into a tubular furnace heated to 650℃ for 2h under nitrogen atmosphere to prepare precursor, the heating rate was 5℃/min. Treated the precursor under vacuum by carbothermal reduction method to prepare silicon carbide (SiC) powder. The effect of temperature and additive content on the morphology of synthesised silicon carbide and the impurity removal order on product purity were explored. After firing at 1300℃,1400℃,1500℃ for 2 h, the 3C-SiC powders are detected, and as the temperature increased, the crystallinity of the product become better. When the content of the additive is 1% of the quality of the silica fume, the particle size of the silicon carbide synthesized at the temperature of 1500℃ is even and the dispersion is better. As for the impurity removal order, removed SiO2 first, then removed C can effectively remove the impurities in the product.

1 Introduction

Silicon carbide (SiC) is one of the most important non-oxide ceramics due to its unique characteristics such as high melting point, excellent oxidation resistance, high chemical inertness, high thermal conductivity, good microwave absorbing ability, wide energy band gap, and high mechanical strength. It is considered as a promising material in many fields including aerospace structures, biomaterials, high temperature semi-conducting devices, membrane supports, and catalysis in harsh environments [1–6].

The carbothermal reduction method has the advantages of high purity, simple preparation process and low cost of raw materials, so it has broad prospects for development of SiC powder. But the traditional carbonthermal reduction is often simply using quartz mixed with carbon black, which makes the reaction time too long and the synthesis temperature too high. In addition, the effect of the impurity removal order on product purity are seldom reported in the literature. So this paper explores the influence of reaction temperature and additive content on SiC powder preparation system and the effect of impurity removal order of reaction product purity on the base of carbonthermal reduction

a Corresponding author.Tel.:18707123506
E-mail address:1733784513@qq.com

reaction of the original preparation of SiC powders.

In this paper, SiC powder was prepared by carbothermal reduction method with silicon powder as silicon source, glucose as carbon source and Nb as additive.The effect of temperature and additive content on the synthesis of SiC morphology and the impurity removal order on product purity were explored.

2 Experimental

2.1 Experimental preparation

Took a certain amount of silica fume powder, glucose and Nb with the carbon silicon ratio of 1:4 (amount of substance ratio), amount of Nb was the quality of silica fume powder respectively l %, 2%, 3%. The glucose was completely dissolved in the mixed solution of distilled water and absolute ethyl alcohol first, then the silica fume powder was added into the mixed liquid, and finally, an appropriate amount of Nb was added, then ball milled the slurry at high speed for 4h. Then put the slurry in the oven under 100℃ for 24 h. After the slurry was dried and pulverized, put the powder into a tubular furnace heated to 650℃ for 2h under nitrogen atmosphere to prepare precursor, the heating rate was 5℃/min. The precursor was heated to reaction tempeture under vacuum for 2h. The synthesized powders were washed with hydrofluoric acid (HF) to remove unreacted silica and metal impurities, then heated the powders to 650℃ in atmosphere for 2h to remove the residual carbon in the product. Finally, the SiC powder could be obtained by washing, filtering and drying.

2.2 Sample characterization

The phase composition and crystallinity of the materials were characterized by powder XD-5A x-ray diffraction（XRD）which was produced by Japan Island Company[7].

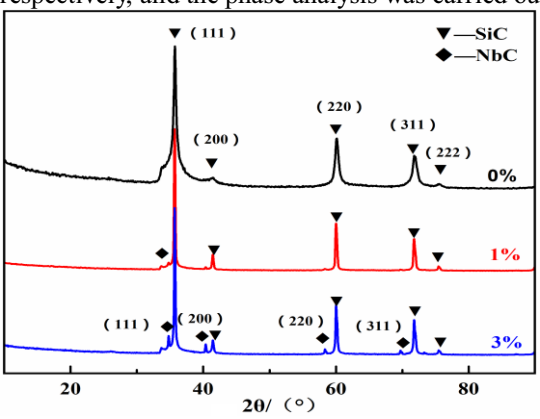
The investigation for chemical bonds was performed via a Fourier transform infrared（FT-IR）spectrometer which was produced by British Renishaw Company[7].

Microstructures of the products were observed on a JSM-5510LV Scanning Electron Microscope（SEM）which was produced by Japan[7].

3 Results and discussion

3.1 Effect of Nb on the formation silicon carbide

The samples with the Nb addition amount of 0%, 1%, 2%, 3% are fired at 1300℃ and 1500℃ respectively, and the phase analysis was carried out. The results were shown in Fig.1 and Fig. 2.



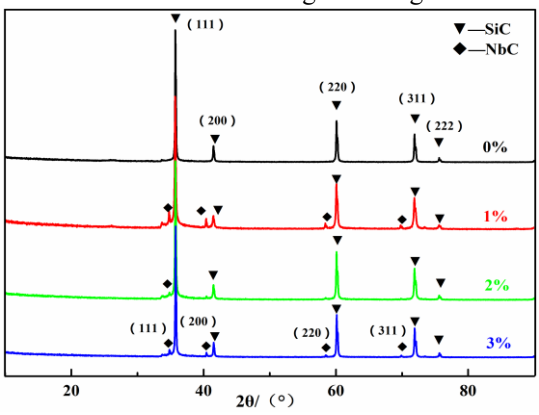


Figure 1. Effect of different content of Nb on the products reaction at 1300℃

Figure 2. Effect of different content of Nb on the products reaction at 1500℃

As shown in Fig.1, without adding Nb firing at 1300℃ for 2h, the product is SiC, and the diffraction peak is wide, indicating that the crystallization degree of SiC is not high. When the addition amount of Nb is 1%, the characteristic diffraction peak of NbC appears in addition to the characteristic diffraction peak of SiC. With the increase of Nb addition amount, the diffraction peak intensity of SiC is enhanced, the results showed that the crystallinity of SiC increased, indicating that the addition of Nb could promote the formation and growth of SiC. When the content of the metal niobium powder was 3%, the characteristic peak of NbC increased obviously and the peak of SiC in the product was not further enhanced, which indicated that the amount of NbC was increased and the amount of Nb is reasonable when the addition amount is 1% . It can be seen from Fig. 2 that when the amount of Nb is added, the diffraction peak of NbC appears and the diffraction peak of SiC increases, and with the addition of Nb increasing, the diffraction peak of SiC is not further enhanced, which is the same as Fig.1 shows.

3.2 Effect of impurity removal order on product purification

The products of 1400℃ were treated in three different ways（①: the product was first removed SiO_2 then removed C; ②: the product was first removed C then removed SiO_2; ③: the product do not do any processing）. Infrared and Raman tests were used to analyze the effect of impurity removal order on the purity of the product, and the results were shown in Fig. 3 and Fig. 4.

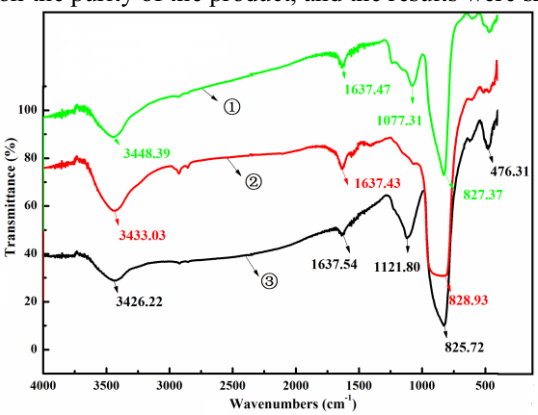


Figure 3. The Infrared test of the 1400℃ products after different treatment

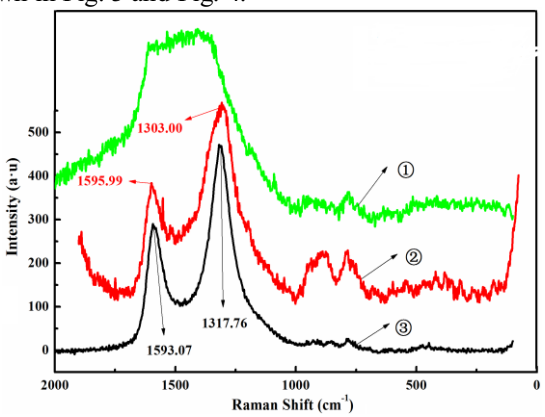


Figure 4. The Raman testof the 1400℃ products after different treatment

In accordance with the FTIR spectrum indicated in Fig. 3③, the bands at 3426.22 and 1637.54cm^{-1} represent hydroxyl groups. There is a band at 1121.80 cm^{-1} which corresponded to siloxane bonds (Si-O-Si) which are formed by unreacted silica fume. A band presented at 825.72 cm^{-1} corresponded to (Si-C) bonds that originated from the products containing silicon carbide. As shown in Fig.3②, after hydrofluoric acid treatment, the silicon dioxide disappeared. As shown in Fig.3①, the product was first removed SiO_2 then removed C , there is a band at 1077.31 cm^{-1} which corresponded tosiloxane bonds (Si-O-Si) which are formed by product oxidized. In accordance with the Raman spectrum indicated in Fig.4②③, the bands at 1593.07,1317.76,1595.99 and 1303.00cm^{-1} which corresponded (C-C) bonds. As shown in Fig.4①, there is no C-C bonds, it can be concluded that removed SiO_2 first, then removed C can effectively remove the impurities in the product.

3.3 Effect of temperature on Preparation of SiC powder

XRD patterns of the as-received products after the carbothermal reduction at different temperatures are shown in Fig.5. [7]

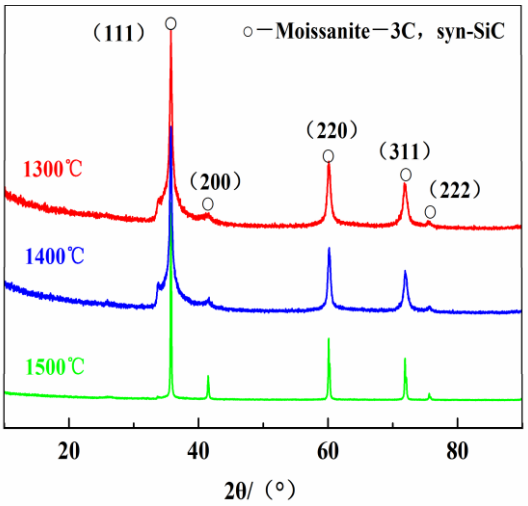


Figure 5. XRD analysis of products at different temperatures

Comparing XRD patterns shows that the crystalline phases of the products synthesized at 1300-1500℃ are quite similar, and the crystallinity of the products increases slightly with increasing reaction temperature. From the XRD patterns, it can be easily observed that there are four sharp diffraction peaks located at 35.6°(111), 41.4°(200), 60.0°(220), 71.8°(311) and 75.5°(222), all of which are attributed to β-SiC(3C-SiC). No other obvious diffraction peak is found. Therefore, it can be concluded that the products synthesized at 1300-1500℃ are relatively pure β-SiC(3C-SiC)[7].

3.4 Morphology of synthetic products

During the experiment, the results of the SEM analysis of the vacuum sintered products of the powder which does not contain the additive of the Nb at 1300℃, 1400℃ and 1500℃ are used to illustrate the influence of the temperature on the SiC, which are shown in Fig. 6.

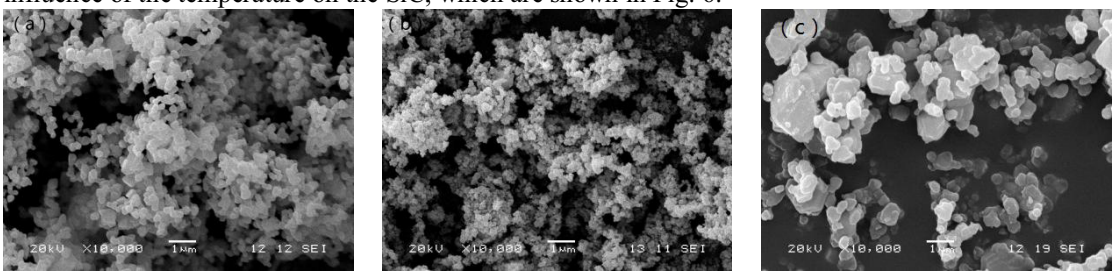
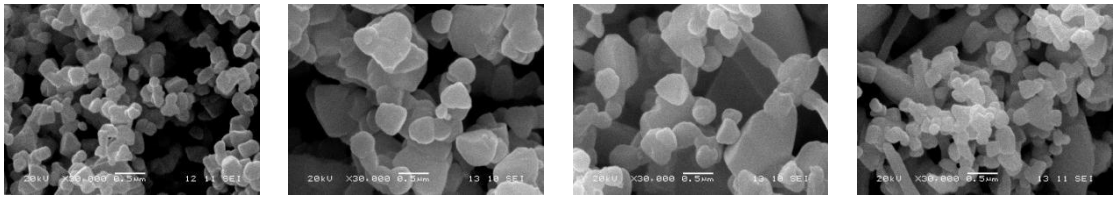


Figure 6. SEM images of SiC powder at different temperatures: (a) 1300℃; (b) 1400℃ and (c) 1500℃

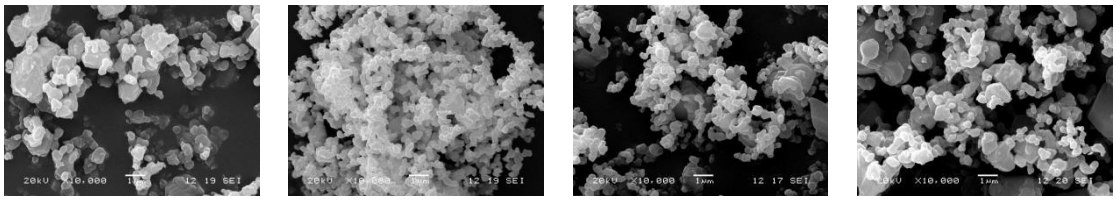
As shown in Fig.6 (a), when the reaction temperature is 1300℃, the SiC is granular, and the single particle diameter is about 250nm, when the temperature is 1400℃, the SiC has irregular particle distribution, particle agglomeration together and poor dispersion, when the temperature is 1500℃, SiC morphology generated large and small particles together, and compared with 1300℃ and 1400℃, the particle size increased, this is due to that the increase of temperature can promote the crystallization of SiC, which is consistent with XRD analysis results.

The effect of Nb content on the morphology of the synthesized SiC powder was investigated by SEM analysis of different samples at the same temperatures.The amount of Nb used in the four groups was 0%, 1%, 2%, 3% (the mass ratio of silica fume). The SEM images are shown in Fig.7 and Fig.8.



0% 1% 2% 3%

Figure 7. SEM images of SiC powder at 1300 ℃ with different content of Nb vacuum sintering



0% 1% 2% 3%

Figure 8. SEM images of SiC powder at 1300 ℃ with different content of Nb vacuum sintering

As shown in Fig.7, at 1300℃, when the Nb is not added, the SiC powder is granular, and the particle diameter is about 250nm, when the content of Nb is 1%, the particle size of SiC powder is slightly increased, the dispersion is improved, and the development of SiC crystal is perfect, when the addition amount of Nb is 2%, the SiC particles increase obviously, the particle diameter is about 400nm, when the content of Nb is up to 3%, the SiC with large particles can be seen more and more, and the SiC will gradually grow into rods. It can be inferred that with the increase of the content of Nb, the size of the SiC powder will increase.

As shown in Fig.8, at 1500℃, when the powder content of Nb is 1%, the generated SiC powder has uniform size and good crystal growth, and compared to 1300℃, the dispersion of product is better. This is due to the high temperature is beneficial to the nucleation and growth of SiC, thus relatively homogeneous particles are formed. With the increase of Nb content, the product gradually increased and the homogeneity become worse.

4 Conclusions

(1) Silica fume powder and glucose as raw material, under vacuum conditions at 1300 ℃ for 2h can produce 3C-SiC.
(2) The morphology and crystallinity of SiC can be significantly improved by adding Nb powder, and the particle size of SiC increases with the increase of niobium content at the same temperature.
(3) In this experiment, the best process for the synthesis of SiC is that under vacuum conditions at 1500℃ for 2 h, the content of Nb is 1% of the mass of silica fume powder.
(4) The removal of impurities in the product can be effectively removed by using the method of removing SiO_2 first then removing C.

Acknowledgments

This work was supported by the Postgraduate Innovation Education Fund (CX2016013), Hubei Province Science and Technology Support Project (Grant No.2014BAA102) and Project of Technology Innovationin Hubei Province (Grant No.2016ACA160).

References

1. A. Najafi, F.Golestani-Fard, H.R.Rezaie, N.Ehsani, J.Sol-Gel Sci.Technol. **59**, 205-214(2011).

2. V.G. Lutsenko, ActaMater. **56**, 2450-2455(2008).
3. H.P. Martin, R. Ecke, E. Müller, J.Eur.Ceram.Soc. **18**, l737-l742(1998).
4. B. Li, C.R. Zhang, H.F. Hu, Y.B. Cao, G.J. Qi, R.J. Liu, J.Mater.Eng.Perform. **16**, 775-778(2007).
5. P.V. Prabhakaran, K.J. Sreejith, B. Swaminathan, S. Packirisamy, K.N.Ninan, J.Mater.Sci. **44**, 528-533(2009).
6. A. Najafi, F.Golestani-Fard, H.R.Rezaie, N.Ehsani, PowderTechnol. **219**, 202-210(2012).
7. B.Li, Y.C.Song, C.R.Zhang, J.S.Y, J.Ceram. Int. **40**, 12613-12616(2014) .