NOTE

Fibrous boron carbide prepared from electrospun condensed boric acid-poly(vinyl alcohol) product fibers

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Fibrous crystalline boron carbide (B_4C) was fabricated by carbothermal reduction starting from electrospun condensed boric acid (H_3BO_3)-poly(vinyl alcohol) (PVA) product fibers. The addition of hydrochloric acid to a H_3BO_3 -PVA/dimethyl sulfoxide solution resulted in electrospinnability of the solution; thus, condensed H_3BO_3 -PVA product fibers were prepared by electrospinning. The fibrous B_4C precursor was prepared by the thermal decomposition of the electrospun H_3BO_3 -PVA product fibers in air. The fibrous B_4C was obtained by heat treatment of the fibrous precursor at 1400 °C in an Ar flow. The structure of fibers in fibrous B_4C consisted of connected particles.

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Fibrous ceramics are attractive for use as a highly anisotropic filler for ceramic/ceramic or ceramic/polymer composite materials. Boron carbide (B_4C) is an important nonoxide ceramic with attractive properties (high melting temperature, low specific weight, excellent hardness, and high chemical stability) and superior functions (high thermal neutron absorption cross section and excellent high-temperature thermoelectric properties).¹⁾ Hence, fibrous B_4C is expected to be used in a nonwoven structure and as reinforcing fiber. The formation of fibrous B_4C using specialized techniques and/or raw materials was previously reported.^{2)–6)} We successfully fabricated fibrous crystalline B_4C consisting of connected particles by carbothermal reduction [Eq. (1)] via electrospinning.⁷⁾

This is an evolutionary method of our low-temperature synthesis method of boride powders by carbothermal reduction,^{8)–18)} and is a preferred approach because carbothermal reduction is the conventional manufacturing process for B_4C . In our method of fabricating fibrous B_4C ,⁷⁾ the fibrous B_4C precursor consisting of boron oxide (B_2O_3) particles and a carbon matrix is prepared by the

thermal decomposition of electrospun condensed boric acid (H_3BO_3)-poly(vinyl alcohol) (PVA) product fibers in air. A spinning solution, H_3BO_3 -PVA/dimethyl sulfoxide (DMSO) solution, had no electrospinnability owing to its high viscosity, and thus the blending of glycerin, as a plasticizer, in the solution is needed to enable electrospinning.⁷⁾ In this study, we attempted to prepare condensed H_3BO_3 -PVA product fibers by electrospinning without a plasticizer.

PVA (PVA-117) was supplied by Kuraray Co., Ltd., Japan. H_3BO_3 (99.5%), DMSO (99.0%), and hydrochloric acid (HCl, 1 mol/L) were purchased from Wako Pure Chemical Industries, Ltd., Japan. These materials were used as received. PVA was dissolved in DMSO (5 wt %) by stirring and heating at 120 °C for 1 h, followed by slow cooling at room temperature (RT). HCl was added to the PVA/DMSO solution (5–15 wt % relative to the PVA/DMSO solution), and then H_3BO_3 was added, followed by stirring at RT for 1 h. The above-mentioned processes were performed in a closed beaker. The condensed H_3BO_3 -PVA product fibers were prepared by electrospinning of the H_3BO_3 -PVA/DMSO solution. The obtained solution was electrospun at a fixed voltage and flow rate of 20 kV and 2.5 mL/h, respectively. The inner diameter of the nozzle (stainless-steel needle) and the distance between the needle tip and the rotating collector were 0.50 mm and 15 cm, respectively. The collector, which was covered with

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Fig. 1. FE-SEM images of condensed H_3BO_3 -PVA product fibers prepared with various amounts of HCl.

aluminum foil, was rotated at a speed of 20 m/min. The temperature throughout the process was 45 °C. The obtained electrospun condensed H_3BO_3 -PVA product fibers were peeled off from the aluminum foil, dried at 120 °C for 12 h in vacuum, and thermally decomposed at 580 °C for 2 h in air. A fibrous B_4C precursor obtained by the thermal decomposition of the condensed product fibers in air was placed in a graphite boat and heated at 1400 °C for 5 h in an Ar flow (200 mL/min) at a heating rate of 10 °C/min.

HCl was used to decrease the viscosity of the spinning solution because acid weakens the interaction between H_3BO_3 and PVA. The H_3BO_3 -PVA/DMSO solution without HCl was a heterogeneous solution including aggregates and had no electrospinnability. The homogeneous solution was prepared by adding HCl. The viscosity of the H_3BO_3 -PVA/DMSO solution decreased with increasing amount of HCl, resulting in the electrospinnability of the solution, probably because of the moderate degradation of borate ester (B–O–C) bonds between H_3BO_3 and PVA. **Figure 1** shows field-emission scanning electron microscope (FE-SEM) images of the electrospun fibers prepared from H_3BO_3 -PVA/DMSO solutions with different amounts of HCl. The formation of B–O–C bonds in the electrospun fibers was identified by the thermogravimetric measurements and attenuated total reflectance Fourier transform infrared measurements, indicating the formation of condensed H_3BO_3 -PVA product fibers. The electrospun fibers prepared from the H_3BO_3 -PVA/DMSO solution with 5 wt % HCl had an inhomogeneous structure owing to its higher solution viscosity. Fiber diameter decreased with increasing amount of HCl owing to decreasing solution viscosity. **Figure 2(a)** shows a photograph of the obtained fibrous B_4C precursor prepared by the thermal decomposition of the electrospun condensed H_3BO_3 -PVA product fibers (10 wt % HCl) in air. The precursor having a nonwoven structure was obtained. The fiber in the fibrous precursor consisted of nanosize B_2O_3 particles and a fibrous carbon matrix [Fig. 2(b)], similarly to that prepared using the H_3BO_3 -PVA/DMSO solution with glycerin.⁷⁾ This B_2O_3 /carbon structure is the characteristic morphology of the precursor prepared from a condensed H_3BO_3 -PVA product.^{9),12),17)} Thus, the addition of HCl to the spinning solution does not affect the precursor structure, i.e.,

Fig. 2. (a) Photograph of fibrous B_4C precursor prepared by thermal decomposition of electrospun condensed H_3BO_3 -PVA product fibers (10 wt % HCl) in air. (b) FE-SEM image of fibrous B_4C precursor after removal of B_2O_3 by washing in hot water, leaving the carbon structure (pores where B_2O_3 previously existed).

the obtained fibrous B_4C precursor has higher reactivity.¹⁷⁾ Consequently, the fibrous B_4C precursor was prepared from the electrospun condensed H_3BO_3 -PVA product fibers. In contrast, the fibrous precursor prepared using the H_3BO_3 -PVA/DMSO solution with 15 wt % HCl had an inhomogeneous B_2O_3 /carbon structure owing to excess weakening of the interaction between H_3BO_3 and PVA in the solution.

Figure 3 shows the X-ray diffraction (XRD) pattern of the product obtained from the fibrous B_4C precursor prepared using the H_3BO_3 -PVA/DMSO solution with 10 wt % HCl after heat treatment at 1400 °C for 5 h in an Ar flow. Peaks corresponding to a rhombohedral B_4C crystal were observed, indicating that crystalline B_4C with little free carbon was synthesized. The obtained product had the fibrous structure [Fig. 4(a)]. Consequently, fibrous crystalline B_4C was formed from the electrospun condensed H_3BO_3 -PVA product fibers. The structure of fibers in the fibrous B_4C consisted of connected microparticles [Fig. 4(b)], in which the morphology was similar to that of B_4C particles obtained from a condensed H_3BO_3 -PVA product.^{9),12)} This structure was also observed for B_4C fibers prepared from the electrospun condensed H_3BO_3 -PVA product fibers with glycerin.⁷⁾ These results suggest that this structure is characteristic of B_4C fibers prepared from condensed H_3BO_3 -PVA product fibers.

Fig. 3. XRD pattern of product obtained from fibrous precursor prepared using H_3BO_3 -PVA/DMSO solution with 10 wt % HCl after heat treatment at 1400 °C for 5 h in an Ar flow.

Fig. 4. (a) Digital microscopy and (b) SEM images of obtained fibrous B_4C .

In conclusion, we fabricated fibrous crystalline B_4C by carbothermal reduction starting from electrospun condensed H_3BO_3 -PVA product fibers. The electrospun condensed H_3BO_3 -PVA product fibers were prepared from the H_3BO_3 -PVA/DMSO solution with an adequate amount of HCl added to decrease the solution viscosity. The B_4C precursor was prepared by the thermal decomposition of the electrospun condensed H_3BO_3 -PVA product fibers in air and had the fibrous structure. Fibrous crystalline B_4C ,

in which the structure of fibers consisted of connected particles, was obtained by heat treatment of the fibrous B_4C precursor at 1400 °C in an Ar flow.

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References

- 1) F. Thévenot, *J. Eur. Ceram. Soc.*, **6**, 205–225 (1990).
- 2) D. Zhang, D. N. McIlroy, Y. Geng and M. G. Norton, *J. Mater. Sci. Lett.*, **18**, 349–351 (1999).
- 3) M. J. Pender and L. G. Sneddon, *Chem. Mater.*, **12**, 280–283 (2000).
- 4) J. Wei, B. Jiang, Y. Li, C. Xu, D. Wu and B. Wei, *J. Mater. Chem.*, **12**, 3121–3124 (2002).
- 5) R. Ma and Y. Bando, *Chem. Phys. Lett.*, **364**, 314–317 (2002).
- 6) D. T. Welna, J. D. Bender, X. Wei, L. G. Sneddon and H. R. Allcock, *Adv. Mater.*, **17**, 859–862 (2005).
- 7) M. Kakiage and T. Kobayashi, *Mater. Lett.*, **254**, 158–161 (2019).
- 8) M. Kakiage, N. Tahara, I. Yanase and H. Kobayashi, *Mater. Lett.*, **65**, 1839–1841 (2011).
- 9) M. Kakiage, N. Tahara, S. Yanagidani, I. Yanase and H. Kobayashi, *J. Ceram. Soc. Jpn.*, **119**, 422–425 (2011).
- 10) M. Kakiage, Y. Tominaga, I. Yanase and H. Kobayashi, *Powder Technol.*, **221**, 257–263 (2012).
- 11) M. Kakiage, N. Tahara, Y. Tominaga, S. Yanagidani, I. Yanase and H. Kobayashi, *Key Eng. Mat.*, **534**, 61–65 (2013).
- 12) M. Kakiage, N. Tahara, R. Watanabe, I. Yanase and H. Kobayashi, *J. Ceram. Soc. Jpn.*, **121**, 40–44 (2013).
- 13) N. Tahara, M. Kakiage, I. Yanase and H. Kobayashi, *J. Alloy. Compd.*, **573**, 58–64 (2013).
- 14) M. Kakiage, S. Shiomi, I. Yanase and H. Kobayashi, *J. Am. Ceram. Soc.*, **98**, 2724–2727 (2015).
- 15) M. Kakiage, T. Shoji and H. Kobayashi, *J. Ceram. Soc. Jpn.*, **124**, 13–17 (2016).
- 16) M. Kakiage, S. Shiomi, T. Ohashi and H. Kobayashi, *Adv. Powder Technol.*, **29**, 36–42 (2018).
- 17) M. Kakiage, *J. Ceram. Soc. Jpn.*, **126**, 602–608 (2018).
- 18) M. Kakiage, T. Ohashi, S. Shiomi and H. Kobayashi, *Adv. Powder Technol.*, **30**, 644–648 (2019).