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Chemical synthesis of niobium diboride nanosheets by a solid-state reaction route

A new process was developed to synthesize niobium diboride (NbB_2) nanosheets with the dimension of about 500 nm and thickness of about 10 nm by using metal niobium, iodine and sodium borohydride as starting materials in an stainless steel autoclave at 700 °C. Iodine was used to facilitate the exothermic reaction between metal niobium and sodium borohydride and the formation of NbB_2. X-ray powder diffraction pattern indicated that the obtained product is hexagonal phase NbB_2 with the calculated lattice constants a = 110 Å and c = 3.2929 Å. The obtained product was also studied by thermogravimetric analysis. It had good oxidation resistance below 400 °C in air.

***Keywords**: solid state route, X-ray diffraction, niobium diboride, nanosheets, chemical synthesis.*

INTRODUCTION

Niobium boride (NbB_2) is an important ceramic material and has been used in many fields for their excellent mechanical properties, such as high melting point, high chemical stability, good electrical and thermal conductivity, and high hardness [1–4]. In addition, $Nb_{1-x}B_2$ (x = 0–0.48) was a superconductor with the maximum superconducting transition temperature at 9.2 K [5].

Up to now, several synthetic methods had been developed to synthesize NbB_2 materials, such as, the carbothermal reduction of niobium pentoxide, boron and cornstarch at 1700 °C [6], borothermal reduction of niobium pentoxide and boron at 1600–1650 °C [7], borothermal reduction of niobium chloride, boron and acetic acid at 1300 °C [8], self-propagating high temperature synthesis (SHS) [9], mechanochemically assisted preparation [10], solid-state reaction of noibium and boron [11]. NbB_2 nanorods were prepared by a solid-state reaction of niobium chloride and sodium borohydride at 550–650 °C [12]. Ran et al. have prepared NbB_2 nanocrystallines by borothermal reduction of niobium pentoxide and boron in molten salt at 800–1000 °C [13]. A general rout towards metal boride nanocrytals had been developed by ionothermal process at a relatively mild temperature (500–900 °C) [14]. Torabi et al. developed a mechanical-thermal approach to synthesize NbB_2 powder from $Mg/B_2O_3/Nb$ powder mixture [15]. Herein, NbB_2 nanosheets were prepared from metal niobium and sodium borohydride via an iodine-assisted synthesis process at low temperature of 700 °C in a stainless steel autoclave.

Experimental procedure

All the reagents used in the experiments were purchased from Shanghai Chemical Reagents Company. All manipulations in our experimental were carried out in a glove box purged with flowing argon gas. In a typical procedure, metal niobium (0.23 g), iodine (0.60 g) and sodium borohydride (1.00 g) were mixed and load into a stainless steel autoclave with a capacity of about 20 mL. The autoclave was sealed and heated in an electric stove with a heating ramp rate of 10 °C/min from room temperature to 700 °C. The autoclave was kept at 700 °C for 10 h, and then followed by cooling to room temperature in the furnace naturally. The product collected from the autoclave was washed by absolute ethyl alcohol, distilled water and dilute HCl aqueous solution for several times to remove the impurities. Finally the final product was dried under vacuum at 60 °C for 10 h for further characterization.

X-ray diffraction (XRD) pattern of the obtained product was performed with a Philips X′Pert X-ray powder diffractometer using Cu*K*α radiation (λ = 1.54178 Å). The microstructure of the obtained product was investigated with a field-emitting scanning electron microscope (FE-SEM, JEOL-JSM-6700F), a transmission electron microscope (TEM, H7650), and a high-resolution transmission electron microscope (HRTEM, JEOL-2010) with an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) profile was performed on a Shimadzu-50 thermoanalyzer apparatus under flowing air below 700 °C at a rate of 10 °C/min.

RESULTS AND DISCUSSION

XRD was used to check the crystal structure and the phase purity of the obtained product. A typical XRD pattern of the obtained product was shown in Fig. 1. All the peaks in Fig. 1 of the (001), (100), (101), (002), (110), (102), (111), (200), and (201) reflections can be indexed to pure hexagonal NbB_2 with lattice constants of a = 3.1170 Å and c = 3.2929 Å, which were consistent with the reported values of hexagonal NbB_2 (Joint Committee on Powder Diffraction Standards (JCPDS) cards, No. 35-0724, a = 3.1113 Å and c = 3.2742 Å). No impurity peaks were detected in Fig. 1, suggesting the NbB_2 product with the high purity. All peaks with strong diffraction intensity indicated the obtained NbB_2 with excellent crystallinity.

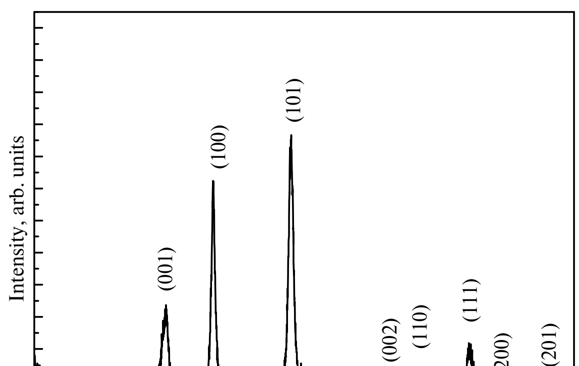
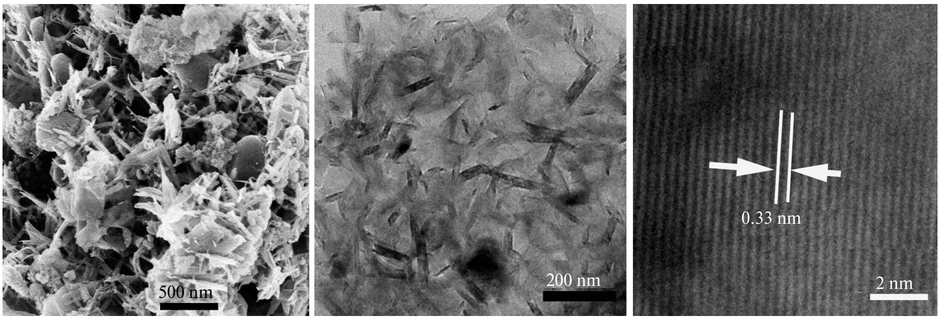


Fig. 1. XRD pattern of the obtained NbB_2.

FE-SEM, TEM and HRTEM were used to investigate the microstructure of the obtained NbB_2 product. The FE-SEM image of the obtained NbB_2 nanosheets was shown in Fig. 2, *a*. The FE-SEM image revealed that the obtained NbB_2 product was composed of nanosheets with a dimension of about 500 nm. The TEM image (see Fig. 2, *b*) of the NbB_2 product showed the average thickness of NbB_2 nanosheets was about 10 nm. The HRTEM image of the obtained NbB_2 was shown in Fig. 2, *c*. Well-resolved lattice fringes of the NbB_2 nanosheets were observed in Fig. 2, *c* with an average distance of 0.33 nm, which corresponded to the (001) planes of hexagonal phase NbB_2.



a *b* *c*

Fig. 2. SEM image of NbB_2 nanosheets (*a*), TEM image of NbB_2 nanosheets (*b*), HRTEM image of NbB_2 nanosheets (*c*).

The oxidation resistances of materials determine their application conditions. To investigate the oxidation resistance of the obtained NbB_2 product, the thermogravimetric analysis (TGA) was carried out from room temperature to 700 °C with a heating ramp rate of 10 °C/min under flowing air. The TGA curve of the NbB_2 was shown in Fig. 3. The TGA curve showed that the weight of the product had not changed below 400 °C. The onset of the oxidation of the NbB_2 product is found to begin at about 400 °C. The oxidation rate is very slow within 400–550 °C, which may be due to the produced oxide (niobium oxide and diboron trioxide) layer coating on the surface of the product. When the temperature is over 550 °C, the weight gain increases significantly. This may be due to the formed protective oxide layer is destroyed and the oxidation rate increases rapidly. The result of the TGA demonstrates that the obtained NbB_2 has a good oxidation resistance below 400 °C.

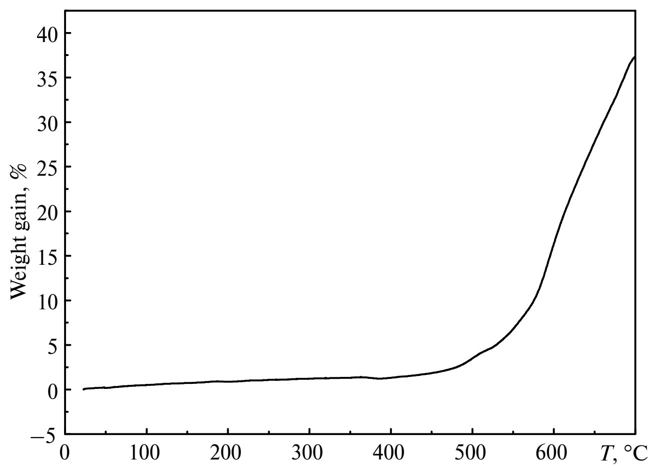


Fig. 3. TGA profile of the NbB_2 product under flowing air.

CONCLUSIONS

In summary, we have developed an iodine-assisted approach to prepare NbB_2 nanosheets with the dimensions of about 500 nm and thickness of about 20 nm in an autoclave through the reaction of metal niobium, sodium borohydride and iodine as reactants. The exothermic reaction between sodium borohydride and iodine was favorable for the final formation of NbB_2 nanosheets. The NbB_2 nanosheets obtained by our designed route have anti-oxidation under 400 °C.

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Розроблено новий процес синтезу наношарів дибориду ніобію (NbB_2) розмірами ~ 500 нм і товщиною ~ 10 нм з використанням металічного ніобію, йоду і боргідриду натрію як вихідних матеріалів у автоклаві з нержавіючої сталі при 700 °С. Йод використовували для полегшення екзотермічної реакції між металічним ніобієм і боргідридом натрію для утворення наношарів NbB_2. Рентгенограма порошку показала, що отриманий продукт є гексагональною фазою NbB_2 з розрахованими константами решітки а = 110 Å і с = 3,2929 Å. Отриманий продукт також вивчали термогравіметричним аналізом. Він мав гарну стійкість до окиснення в повітрі за температури нижче 400 °С.

***Ключові слова**: твердотільний шлях, рентгенівська дифракція, диборид ніобію, наношари, хімічний синтез.*

Разработан новый процесс синтеза нанослоев диборида ниобия (NbB_2) размерами ~ 500 нм и толщиной ~ 10 нм с использованием металлического ниобия, йода и боргидрида натрия в качестве исходных материалов в автоклаве из нержавеющей стали при 700 °С. Йод использовали для облегчения экзотермической реакции между боргидридом натрия и ниобием для получения нанослоев NbB_2. Рентгенограмма порошка показала, что полученный продукт представляет собой гексагональную фазу NbB_2 с рассчитанными постоянными решетки а = 110 Å и с = 3,2929 Å. Полученный продукт также изучали с помощью термогравиметрического анализа. Он имел хорошую стойкость к окислению на воздухе при температуре ниже 400 °С.

***Ключевые слова**: твердотельный путь, дифракция рентгеновских лучей, диборид ниобия, нанослои, химический синтез.*

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