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Preparation and characterization of amorphous boron powder with high activity

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Abstract: The amorphous boron powders with high activity were prepared by the high-energy ball milling−combustion synthesis method. The effects of the milling rate and milling time on the crystallinity, microscopic morphology and reactivity of amorphous boron powder were studied. The results show that the crystallinity of amorphous nano-boron powder is only 22.5%, and its purity reaches 92.86%. The high-energy ball milling can significantly refine boron powder particle sizes, whose average particle sizes are smaller than 50 nm, and specific surface areas are of up to 70.03 m^2/g. When the transmission electron beam irradiates the samples, they rapidly melt. It can be seen that the monomer amorphous boron size is less than 30 nm from the specimen melting traces, which indicates that the samples have high reactivity.

Key words: amorphous nano-boron powder; high activity; high-energy ball milling; combustion synthesis

1 Introduction

The traditional metal thermal reduction methods which are used to prepare boron powders have some shortcomings, such as low purity, large particle size and high cost [1−5]. Its purity is only less than 90.0% and the size is larger than 2 μm [6−8]. However, the amorphous nano powder has aroused the great academia interests because of its unique nature. Recently, with the developments of aviation, aerospace, rocket launchers fuel, automotive airbags and nano materials, the demands of amorphous boron powders are increasing [9−11], and especially the demands for the amorphous boron powders with high activity [12]. Now, the qualities of amorphous boron powders have been unable to meet the requirements, so the preparation of the amorphous boron powder with high activity has become the hot topic. The researches mainly concentrate on theoretical calculations of the boron nanotubes and boron nanofibers [13−15]. The preparations and performance characterizations on amorphous boron powders with high reactivity are scarcely.

As for the shortcomings of the large particle size and the low activity of amorphous boron powder prepared by the magnesium thermal reduction, the high-energy ball milling−combustion synthesis method was used to prepare the amorphous nanometer boron powders with high reactivity.

2 Experimental

2.1 Sample preparation

The raw materials included magnesium powder with 99% purity within the particle size less than 149 μm and B_2O_3 powder with 99% purity and particle size less than 149 μm. The materials were weighed stoichiometrically according to the following Equation (1) and then mixed by high-energy ball milling (mode:P4 of Fritsch Company made in Germany). The milling conditions were: balls of 5−15 mm and the volume ratio of reactants to balls of (1−2):1. Before combustion synthesis reactions, the reaction raw materials were mixed, and the details were as follows: for No. A, ordinary tank mixing for 3 h; for No. B, high-energy ball milling for 15 min with 300 r/min; for No. C, high-energy ball milling for 20 min with 300 r/min; for No. D, high-energy ball milling for 20 min with 250 r/min;

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for No. E, high-energy ball milling for 20 min with 30 r/min. The detailed experiment conditions are listed in Table 1. The mixed powders were placed in a SHS reactor. And the ignitor of $KClO_3$ and magnesium were placed on the surface of reactants to ignite the combustion synthesis reaction to get the coarse products with MgO by-products.

$$3Mg+B_2O_3=2B+3MgO \quad (1)$$

Table 1 Experiment conditions

Sample No.	$n(Mg)/n(B_2O_3)/n(KClO_3)$
A	3.0:1:0
B	3.0:1:0
C	3.0:1:0.1
D	3.0:1:0.1
E	3.0:1:0

The combustion products were leached with 10% HCl in mass fraction at 45 °C for 24 h and amorphous boron powders were obtained after filtration and drying.

2.2 Characterization

The phase compositions of the amorphous boron powder were determined by an X-ray diffractometer (XRD, Rigaku D/max III B) and then the crystallinity was calculated. The microscopic morphology of amorphous boron powder was observed by a scanning electron microscope (SEM, SSX−550 and FEI, NavoSEM). The specific surface area of amorphous boron powder was obtained with a specific surface area and bore diameter tester (ASAP2020M). The amorphous boron powder microscopic morphology was analyzed by a transmission electron microscope (TEM, H800). The reactivity of amorphous boron powders was characterized on their crystallinity and specific surface areas and chemical reaction temperature.

3 Results and discussion

3.1 XRD pattern

Figure 1 shows the XRD patterns of the amorphous boron powders prepared in different conditions. For the sample A, the reactants were mixed by milling for 3 h in ordinary mixing tank. For the samples B−E, the reactants were milled by high-energy ball milling for 15−20 min (the experimental conditions for the samples A−E in Figs. 2−4 and Table 2 were the same as those in Fig. 1, so these were not explained repeatedly).

Figure 1 shows that samples A−D have some obvious diffraction peaks of crystal boron at the 2θ of

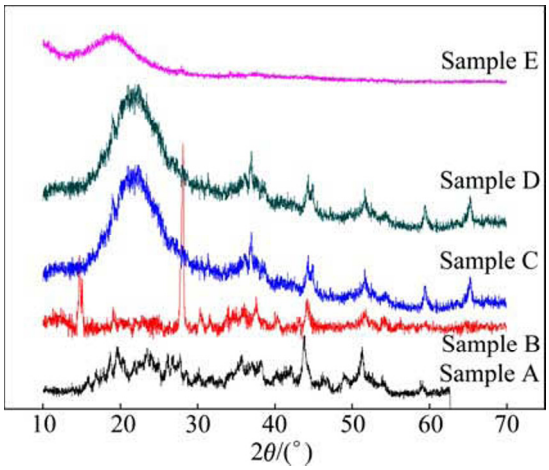

Fig. 1 XRD patterns of boron powders

36.96°, 44.32°, 51.64° and 59.48° which do not appear in sample E. But sample B has a great diffraction peak at 2θ of 28.12° of the crystalline diffraction peak of impurity magnesium borate ($Mg_3B_2O_6$) attributed to the inadequate acid leaching. By comparing the XRD patterns of samples A−D, it is found that the crystal boron diffraction peak intensity in amorphous boron will reduce significantly if the reactants are pretreated through the high-energy ball milling, and the crystallinity of amorphous boron powder declines obviously with the increase in high-energy ball milling time and the high-energy ball milling rate. By comparing XRD patterns of sample C and sample E, it can be seen that the crystallinities of amorphous boron powders will increase with reaction temperature increasing. There is an obvious diffraction peak of crystal boron in the sample C, but there is not in the sample E. Because the heating agent $KClO_3$ was added to the reactants when preparing the sample C, the reaction temperature became high, which provided a completely thermodynamic and kinetic condition for crystal boron to form and grow up. The crystallinities of samples A−E are 72.46%, 32.4%, 31.0%, 29.4% and 22.5%, respectively, which are calculated by software Diffrac.Suite.Eva. By combining XRD and calculated crystallinities, it is found that the samples B−E are mainly amorphous boron. So, the high-energy ball milling for the reactants is necessary to obtain the lower crystallinity amorphous boron powders.

3.2 Morphology

Figure 2 shows the SEM images of the amorphous boron powders made under different conditions. It can be seen from Fig. 2 that boron powder particle sizes are of micron degree and a large number of rod-like crystals appear (the length of about 1 μm, the diameter of