

Research Article

Preparation and Characterization of Amorphous B Powders by Salt-Assisted SHS Technique

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To use the salt-assisted SHS technique to prepare B powders was proposed. Calculation results found that the adiabatic combustion temperature of the B_2O_3 -Mg reaction system was 2604 K, higher than the 1800 K criterion of self-propagating temperature, which meant that the SHS application was feasible. When 0, 10%, 20%, 30%, 40%, 50%, and 60% NaCl content were added, the adiabatic combustion temperature of the reaction system decreased linearly. When 60% NaCl content was added, the adiabatic combustion temperature was 1799 K (lower than 1800 K), unsuitable for self-propagating reaction, which was consistent with the experimental results. Through scanning electron microscope (SEM), energy disperse spectroscopy (EDS), and particle size analysis, the influence of different addition of NaCl on the morphology, average particle size, and purity of prepared B powder was investigated. EDS and chemical analysis indicated that the purity of prepared B powder was over 96% and the average particle size was within the range of 0.4~0.8 μm when the content of NaCl was 50%. The analysis of X-ray diffraction (XRD) and selected area electron diffraction (SAED) proved that the prepared B powder was amorphous.

1. Introduction

Amorphous boron is attractive material with applications in fuel additives [1, 2], dopant in solar cell [3, 4], and boron neutron capture therapy [5, 6]. In particular, amorphous boron is a very interesting material as a fuel additive because it has high mass and volume specific combustion energy [7, 8].

Traditional methods to prepare amorphous boron powder include molten salt electrolysis, diborane pyrolysis, boron hydrogen chloride reduction, and magnesium thermal reduction [9]. With the potassium chloride-potassium fluoroborate-boron oxide molten salt system, Song et al. [10] succeeded in preparing the boron powder with the purity over 90%. However, due to the limitations of low current use efficiency, poor working conditions, and discontinuous production, the molten salt electrolysis process failed to get any further development. Moreover, even though the diborane pyrolysis process and the boron hydrogen chloride reduction process can obtain boron high purity powder, the highly demanding working conditions and serious pollution

problems limit the applications of these methods. At present, boron powder with the content of boron less than 90% and the particle size above 2 μm can be only obtained by the metal thermal reduction, due to technical limitations [11–15].

SHS (self-propagating high-temperature synthesis) is a self-propagating process to realize reactions between the powders, which shortens and simplifies the procedures in comparison to traditional preparation processes. Once being started via ignition, no more outside energy is needed. Compared to other processes, this self-propagating technique has many advantages, such as simple process, high purity, small particle size, and high activity of product.

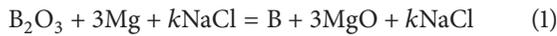
A new technique was proposed in this paper to produce boron powder and optimize the preparation process by combining the SHS technique and the traditional magnesium thermal reduction method and choosing NaCl as a diluter. The adiabatic temperature of SHS technique is rather high. The reaction occurs in a high-temperature state for a long time, which is liable to bring about the side reactions, reduce purity, and lead to particle aggregation. NaCl can effectively

reduce the adiabatic combustion temperature, suppress side reactions, increase product purity, and reduce particle size. Moreover, the process is easier to be applied and realize industrialization. In this paper, effect of NaCl addition on morphology, size, and phase of submicron amorphous boron powders was investigated.

2. Experiment

2.1. Preparation of Samples. Commercial grade B_2O_3 (>99.0 wt%, Liaoning Pengda Science and Technology Ltd., Yingkou), Mg (99.5 wt%, Kunshan Fuerbang New Material Technology Co., Ltd., Kunshan), and NaCl (99.0 wt%, Nanjing Dongde Chemical Technology Co., Ltd., Nanjing) were mixed in certain proportion. Materials were thoroughly mixed by a planetary ball mill and pressed into a cylinder. The tableting pressure was 10 Mpa. A self-made reactor was used to successfully produce the ultrafine boron powders via the salt-assisted SHS technique. The combustion synthesis of the 60% NaCl system was also tried in the experiment, which however resulted in incomplete reaction.

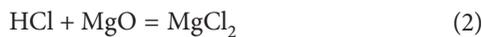
The main equation of combustion synthesis is as follows:



k refers to the percentage of NaCl among all ingredients; k is 0, 10%, 20%, 30%, 40%, 50%, and 60%, respectively. The content of Mg in the reaction materials was in excess of 10%.

If no NaCl was added in the reaction materials, the product obtained after combustion was relatively hard and needs grinding. This was because, without NaCl, severe agglomeration occurred. If NaCl was added, the product obtained was a fluffy, block-like material. This was because the product was coated by NaCl and thus easy to crush. The obtained products contained boron powder, diluter NaCl, byproduct MgO, and so forth. The acid leaching-alkali leaching-acid leaching-water leaching process was adopted to produce high purity boron powder. The leaching agents included HCl, NaOH, and distilled water. After filtration and drying, the amorphous B powder was finally obtained.

The leaching reaction equation is as follows:



2.2. Analytical Methods. The morphology and elementary composition of B powder were examined by scanning electron microscope (JSM-6700, JEOL) equipped with an energy dispersive spectrometer (EDS) and chemical analysis. The phase analysis of the powder samples was investigated by X-ray diffraction (XRD, D/max-2400, Rigaku) and selected area electron diffraction (SAED, JEM-1200EX, FEI USA). The average particle size of sample was measured by laser particle size analyzer (Nano Series Nano-ZS, ZETASIZER).

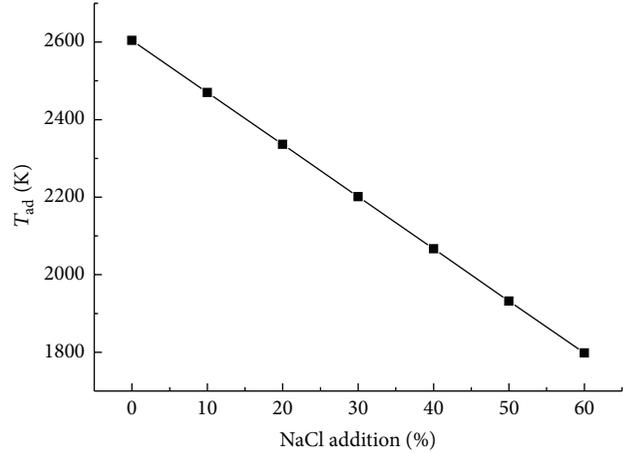


FIGURE 1: Change of T_{ad} with the addition of NaCl.

3. Results and Discussion

3.1. Calculations of Adiabatic Temperature. Adiabatic temperature (T_{ad}), thermodynamic parameter to describe the SHS characteristics, can not only serve as a criterion to judge whether reactions can occur, but also forecast the state of combustion products and provide a reference for the ingredient design of the reaction system. Merzhanov et al. proposed that only when $T_{ad} > 1800$ K, can SHS reaction be completed. Otherwise, the combustion wave of the reaction system cannot propagate.

T_{ad} is calculated as follows: the adiabatic temperature of reaction (1) was T_{ad} , and the cycle test algorithm was used [16]. If the temperature obtained after cycle test calculation is a phase-transition temperature, namely, $T = T_{tr}$, we need to judge the phase changes of the material [17]. The C language was used to write a program to calculate the relationship between the addition of NaCl and T_{ad} of the reaction system via the cycle test algorithm. During the calculation, relevant thermodynamic data of reactants and products were derived from literature [18].

Figure 1 shows the calculated T_{ad} with different k values. As can be seen from Figure 1, with the increase of k , T_{ad} demonstrates a linearly decreasing trend. As NaCl content increased from 0 to 50%, the calculated T_{ad} was higher than the criterion of self-propagating combustion temperature, namely, 1800 K. Therefore, it was feasible to use the salt-assisted SHS reaction. When the addition of NaCl was over 60%, the calculated T_{ad} was 1798 K, less than 1800 K, not feasible for self-propagating reaction. This was consistent with experimental results.

The NaCl melting point is 800.8°C, lower than the calculated adiabatic temperature. NaCl is in liquid state in reaction. It absorbs heat in the melting process, so the addition of NaCl can help in reducing T_{ad} . The melting points of reactants and products are shown in Table 1.

According to the measurement of the adiabatic temperature and the initial reaction temperature, the initial reaction temperature of B_2O_3 -Mg-NaCl system was higher than the melting points of B_2O_3 , Mg, and NaCl. We can therefore infer

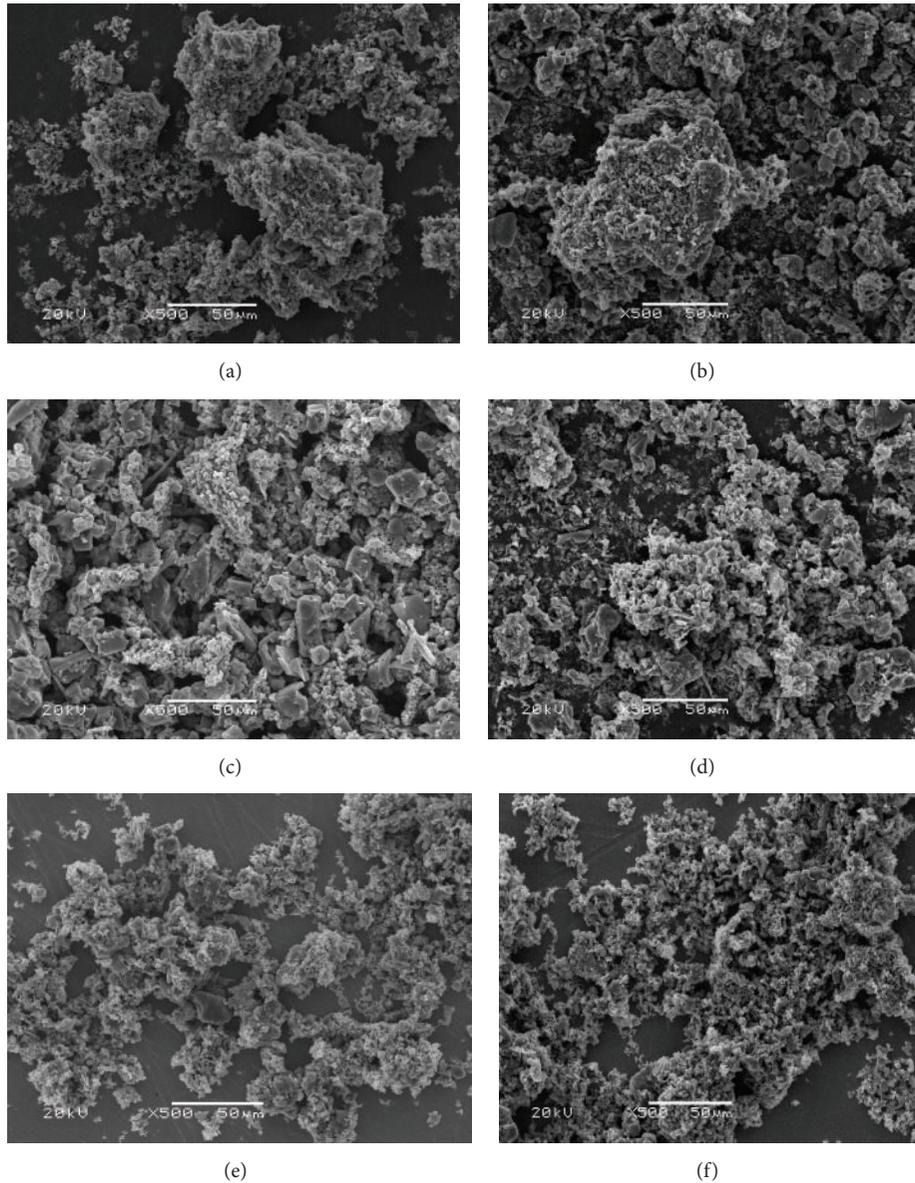


FIGURE 2: Morphologies of leached products obtained by salt-assisted SHS synthesis with different content of diluter. (a) 0% NaCl; (b) 10 wt% NaCl; (c) 20 wt% NaCl; (d) 30 wt% NaCl; (e) 40 wt% NaCl; (f) 50 wt% NaCl.

TABLE 1: Melting points of reactants and products.

Reactants and products	Melting points/ $^{\circ}\text{C}$
NaCl	800.8
Mg	650.0
B	2079.0
B_2O_3	450.0
MgO	2800 ± 13

that the salt-assisted SHS technique is a liquid-liquid reaction mechanism.

3.2. Morphology, Particle Size Distribution, and Purity of Products Obtained with Different Contents of NaCl. Figure 2 shows the morphology of leached products by adding

different amounts of NaCl to the materials. From Figure 2(a), we can see that without NaCl there was a serious agglomeration phenomenon and a poor dispersibility between sample particles. The five samples of adding NaCl all contained a large amount of small particles and only a very few large particles. In terms of morphology, large particles showed the shapes of irregular geometry, while small particles exhibited similar spherical shapes. In Figure 2(a), large particles were about $5 \mu\text{m}$, while small particles were within the range of hundreds of nanometers. With the increase of NaCl content, there were a decrease in the size of large particles in Figure 2(b) and an improvement in the dispersibility between particles. When the NaCl content reached 40%, only a very few particles were within the size of about $1 \mu\text{m}$, with others reaching submicron level. When the NaCl content reached 50%, particles were uniform in size, most of which

were within 0.5–0.8 μm . Only a small part of these particles exhibited nanosizes, with the presence of soft agglomeration phenomenon between the particles.

It indicates that the morphology and particle size could be controlled effectively through properly changing the addition of the diluter NaCl.

Figure 3 shows the diagrams about size distribution of leached products obtained by salt-assisted SHS synthesis with different contents of diluter. Figure 3 was obtained by using Ipwin32 software to make repeated statistics of SEM graphics first and then the graphics are drawn by the Origin software. Figure 3 shows clearly that with the increase of NaCl content the average particle size of products has a decreasing trend, with the increasing proportion of small-size particles. When NaCl increased from 10% to 40%, the average particle size of boron powder decreased from 2.07 μm to 0.8 μm . The average particle size of products decreased considerably. When NaCl increased from 40% to 50%, the average size of boron powder decreased from 0.8 μm to 0.50 μm . The average particle size of boron powder decreased less considerably.

When NaCl increased from 0% to 50%, the average particle sizes measured by laser particle size analyzer were 3.88 μm , 3.22 μm , 1.77 μm , 1.73 μm , 1.69 μm , and 1.64 μm , respectively. The reasons that average particle size increases compared with Figure 3 are as follows: (1) the samples were not saved in the inert gas, susceptible to oxidizing into B_2O_3 and liable to absorb impurities in the air, so that the particles increase; (2) hydration made particles increase in the process of ultrasonication.

From Figures 2 and 3, we can see that the diluter can effectively reduce the average particle size of products and weaken the agglomeration between the particles. The reason lies in that the salt-assisted SHS synthesis reaction is a liquid-liquid reaction process; the addition of NaCl reduces the adiabatic temperature and slows down the rate of diffusion of the produced solid B particles in the liquid phase, which effectively avoids the rapid agglomeration of solid B particles. In addition, as the combustion synthesis is completed, the system will cool down. During the cooling process, liquid NaCl will first reach saturation and then precipitate, forming a coating layer on the surface of product particles and further preventing the continual agglomeration of B particles.

Comparisons of particle sizes between amorphous B powder produced with 50% NaCl in this experiment with B powder produced by SB Boron are shown in Table 2.

From the comparison of B powder sample produced with 50% NaCl and those produced by SB boron in Table 2, we can see that these indexes well satisfy the requirements of the composite propellant of solid rocket-ramjet engine [19]. Therefore, the use of salt-assisted SHS technique to produce B powder is of great theoretical value and practical significance.

An EDS analysis of six samples was made. The statistical results are shown in Table 3, from which we can see that after adding the diluter the purity of samples increased. The reason lies in the fact that the diluter reduced the adiabatic temperature of the reaction system and hence avoided the side reaction that may occur under high temperatures. When the addition of diluter increased from 10% to 50%, the purity of leached boron powder barely changed. The prepared

TABLE 2: Comparison of particle sizes between amorphous B powder produced with 50% NaCl and B powder produced by SB boron.

Samples	Samples in this experiment	SB boron 90	SB boron 95
Average particle size/ μm	0.4~0.8	1.0	0.8~1.0
B content/%	>96	90~92	95~97

TABLE 3: Element contents in leached products prepared with different contents of diluter.

Samples (wt% NaCl)	B (wt%) EDS	O (wt%) EDS	Mg (wt%) EDS	B (wt%) Chemical analysis
0	94.08	2.32	3.59	94.72
10	96.09	0.15	3.77	96.02
20	96.01	0.43	3.56	96.00
30	98.22	0.25	1.53	97.96
40	97.43	0.44	2.13	97.12
50	96.26	1.16	2.58	96.16

products contained only three elements, namely, B, O, and Mg. The leached products contained over 96% boron powder, with other two elements less than 5.0%, consistent with the results of chemical analysis. With the increase of diluter content, the content of element B showed the first rising and then declining trend, reaching the maximum value when the content of diluter was 30%. However, the content of O and Mg elements changed in a trend opposite to that of element B, reaching the minimum value when the content of diluter was 30%.

Figure 4 is an X-ray diffraction pattern of leached products. There is no diffraction peak of B, indicating the B powder is amorphous. There are some unknown impurity peaks. The reason may be that after leaching B powder particles were in small size and had large specific surface area and high specific surface energy, susceptible to oxidizing into B_2O_3 and liable to absorb impurities in the air. Therefore, the produced B powder should be stored in the inert atmosphere.

Figure 5 is the diagram of selected area electron diffraction (SEAD) of leached products, indicating that the prepared B powder is amorphous.

4. Conclusion

To prepare submicron B powder by the salt-assisted SHS technique was proposed in this paper. Calculation results show that the addition of diluter NaCl into the B_2O_3 -Mg system can effectively reduce the adiabatic combustion temperature. With the increase of NaCl content, the adiabatic combustion temperature of the reaction system linearly declined. When 60% NaCl was added, the adiabatic combustion temperature was 1799 K, lower than 1800 K, unsuitable for the self-propagating reaction, which was consistent with results of experiment.

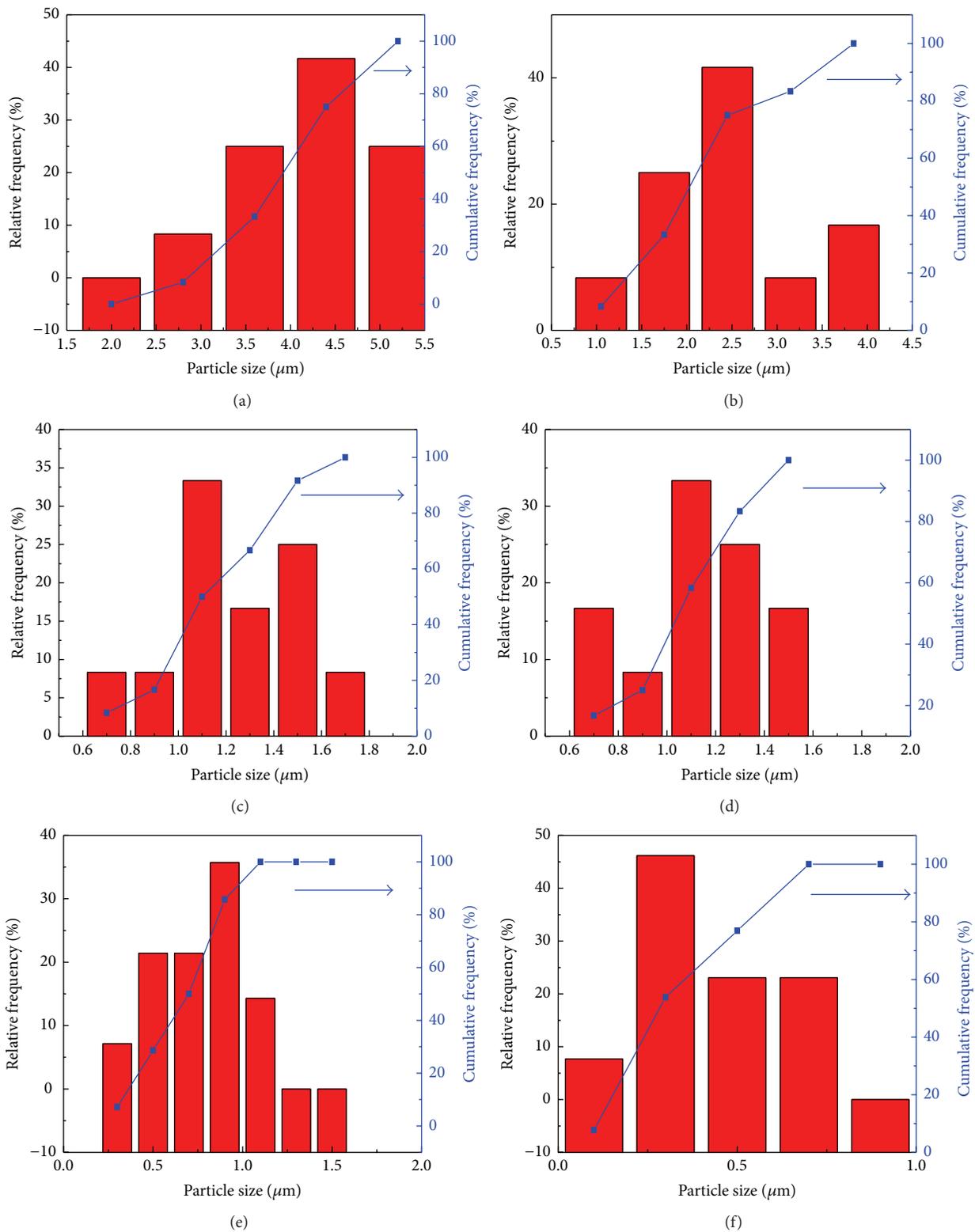


FIGURE 3: Particle size distribution of products obtained by combustion synthesis with different contents of diluter. (a) 0% NaCl; (b) 10 wt% NaCl; (c) 20 wt% NaCl; (d) 30 wt% NaCl; (e) 40 wt% NaCl; (f) 50 wt% NaCl.

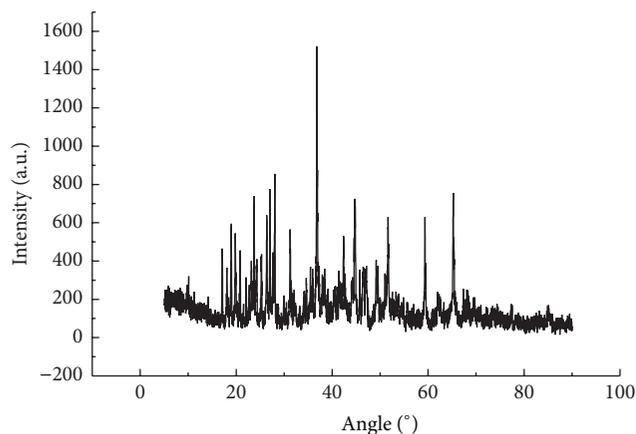


FIGURE 4: XRD patterns for leached boron samples.



FIGURE 5: SEAD chart of leached B powder.

With the increase of NaCl content, the average particle size of leached products decreased. When NaCl content increased from 10% to 50%, the average particle size decreased from $2.07\ \mu\text{m}$ to $0.69\ \mu\text{m}$. After adding the diluter, the product purity increased. When the content of diluter increased from 10% to 50%, the purity of leached products was over 96%.

The XRD and SEAD of products indicated that the prepared B powder was amorphous. The obtained B powder had small particle size and high activity and thus should be stored in the inert atmosphere.

This method could be further industrialization and become a common approach to prepare various inorganic materials. We hope that the present work is useful for the popularization and application of the amorphous boron powders.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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