PURIFICATION OF AMORPHOUS BORON POWDER BY USING THE SOLUBLE TRANSFORMATION OF ACID-INSOLUBLE BORON MAGNESIUM COMPOUNDS

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Abstract

At present, amorphous boron powder is considered to be the best fuel for solid fuel-rich propellants due to its extremely high volume calorific value and mass calorific value. Amorphous boron powder produced by magnesium thermal reduction contains many impurities that are insoluble in acids as well as defects such as low purity, excessive particle size, and poor chemical activity, which seriously hinder its large-scale application in the military and aerospace fields. In this paper, the soluble transformation mechanism of insoluble boron magnesium compounds into amorphous boron powder during calcination and a method for purification boron powder were studied. In order to remove insoluble boron magnesium compounds in amorphous boron powder, the insoluble impurities $Mg_5B_2O_5$ and MgB_4 were converted into soluble MgB_4O_7 and MgO during calcination. The samples were then subjected to either water leaching or acid leaching to convert the crude amorphous boron powder products into high-purity amorphous boron powder products. SEM-EDS, XRD, XPS, and other techniques were used to determine the occurrence states of the impurity phases. The transformation of impurity phases after calcining water leaching and acid leaching was monitored. The results showed that the magnesium content in the amorphous boron powder was reduced to 0.96%, and the purity of the boron powder was increased to 97.34% by subjecting the amorphous boron powder to a combined calcination technique and either water leaching or acid leaching treatment.

Keywords: Amorphous boron powder; Purification; Magnesium removal; Boron magnesium compounds; Soluble transformation

1. Introduction

Amorphous boron powder is an important fine chemical product widely used in high-tech fields such as high-energy solid fuels, aerospace, space technology, nuclear power, and superconducting materials [1–5]. Amorphous boron powder is usually prepared by the self-propagating metallurgy, in which B_2O_3 is reduced with magnesium powder [6-10]. However, some acid-insoluble boron magnesium compounds, such as $xMgO·yB_2O_3$ and MgB_x, are formed during the reduction process [11]. With the continuous development of hypersonic vehicles for missiles, countries around the world attach great importance to the research of solid ducted motors, and fuel-rich propellants for solid ducted motors have also developed rapidly. Due to the high mass calorific value and volume calorific value of boron powder, amorphous boron powder is widely used in fuel-rich propellants. The quality of amorphous boron powder for fuel-rich propellants directly affects the performance of rocket propellant, but the amorphous boron powder produced by magnesium thermal reduction method has low purity. Therefore, magnesium impurities must be removed from the amorphous boron powder prepared by magnesium thermal reduction.

The existing purification methods of boron powder are mainly physical or chemical methods that exploit the different physical and chemical properties of the impurity phases in boron powder. Jain [4] et al. proposed the use of water leaching and acid leaching to purify electrodeposited boron powder, and the purified boron powder could be applied to the control rods of fast reactors. Yoo et al. [12] improved the size of boron particles prepared by magnesium thermal

reduction by adding NaCl, which improved the combustion properties of the boron particles. Sreedhara et al. [13] showed that the activity of boron powder after low-temperature grinding was improved. The boron powder by-product obtained by Capra et al. [14] by treating MgB_2 with glacial acetic acid had a smaller particle size and lower of crystalline boron content than commercial boron powder.

In this paper, we analyze the existing state of impurities in amorphous boron powder and perform thermodynamic analysis and calculations of the soluble transformation of boron magnesium compounds. Based on this, a method of adding B_2O_3 into amorphous boron powder is proposed, so that insoluble boron magnesium compounds can be transformed into soluble substances. This procedure made it possible to purify amorphous boron powder by water leaching and acid leaching to meet the application requirements of amorphous boron powder in high-tech fields.

2. Experimental method
2.1. Raw material analysis of amorphous boron powder

Amorphous crude boron powder with a purity of 90.18% prepared by magnesium thermal reduction was used as the raw material, in which the magnesium content impurity was 5.67% and the oxygen content impurity was 4.15%. The main phase composition of crude amorphous boron powder was determined by XRD analysis. The XRD pattern of the amorphous boron powder is shown in Fig. 1, and the phase composition was crystalline B, H_3BO_3, $Mg_2B_2O_5$, and MgB_4. The impurities in crude amorphous boron powder were mainly boron magnesium compounds, which were insoluble in acids.
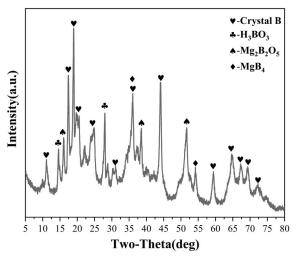

Figure 1. XRD pattern of amorphous boron powder

2.2. Experimental scheme design

Crude boron powder and dried B_2O_3 powder were respectively weighed, ground, grind, and homogenized in an agate mortar. The mixed sample was then placed into an iron crucible, which was placed in a horizontal atmosphere resistance furnace, as shown in Fig. 2. The air in the furnace was flushed with argon, and after continuous ventilation for 10 minutes, heating began. Under the protection of the flowing argon atmosphere, the furnace temperature was raised to 800 °C at a rate of 10 °C/min and maintained for 4 hours. After the experiment, the resistance furnace was cooled to room temperature while maintaining an argon atmosphere. Then, the argon flow was closed, and the solidified sample was water leached for 3 h before filtration. After filtration, the filter cake was dried in a vacuum drying oven. After drying, the purified boron powder was analyzed
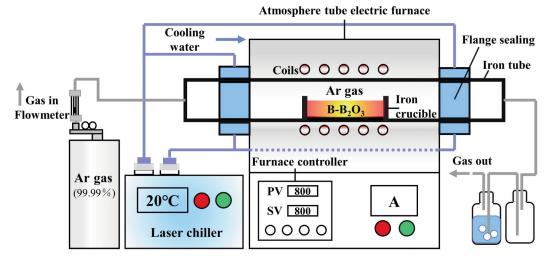

Figure 2. Schematic diagram of the calcining device

and tested.

To further remove the residual soluble boron magnesium compounds in the amorphous boron powder, the calcining treated boron powder was subjected to water leaching, followed by a mixed HNO_3-HCl acid leaching experiment. In the subsequent analysis, purified boron at high temperature refers to the powder treated by water leaching after roasting, and purified boron after acid leaching refers to the powder treated by acid leaching after roasting. The experimental conditions are shown in Table 1. A magnetic stirrer was used to stir the dissolution process to improve the dissolution rate of the boron magnesium compounds phase. Scanning electron microscope (SEM) and energy-dispersive spectrometry (EDS) were used to observe and analyze the morphology of the boron powder samples after acid leaching. Finally, the magnesium content of the boron powder samples after acid leaching was determined by ICP-OES, and the purity of boron powder was determined by chemical titration. The contents of Mg and O in the samples were determined by inductively coupled plasma emission spectrometer (ICP-OES) and an oxygen nitrogen hydrogen analyzer (ONH analyzer).
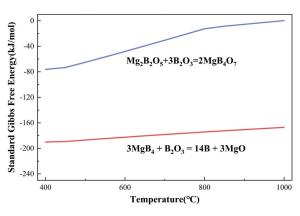

Figure 3. *Standard Gibbs free energy changes for main chemical reaction at different temperatures*

B_2O_3 began to melt at 450 °C. Choosing 800 °C as the experimental temperature is to improve the reaction rate and ensure the smooth progress of the reaction. At 800 °C, B_2O_3 reacts with $Mg_2B_2O_5$ and MgB_4 in the crude boron powder to form MgB_4O_7, MgO, and B. MgB_4O_7 is soluble in water [15], allowing it to be removed by water leaching, while MgO can be easily removed by acid leaching. Therefore, controlling the purification temperature,

Table 1. *Experimental conditions of HNO_3-HCl mixed acid leaching*

Mixed acid (mol/L)		The ratio of liquid to solid	Temperature (°C)	Time (h)
HNO_3	HCl			
0.25	0.5	10:01	80	3

3. Results and discussion

3.1. Thermodynamics and mechanism of the soluble transformation of insoluble boron magnesium compounds

B_2O_3 reacts with the boron magnesium compounds $Mg_2B_2O_5$ and MgB_4 in amorphous boron powder. The boron magnesium compounds are converted into MgB_4O_7 and MgO, which are readily soluble in acid, as expressed by chemical reaction equations (1) and (2).

$$Mg_2B_2O_5 + 3B_2O_3 = 2MgB_4O_7 \qquad (1)$$

$$3MgB_4 + B_2O_3 = 14B + 3MgO \qquad (2)$$

The HSC Chemistry software (Outokumpu Research OY, Pori, Finland) was designed for calculating the thermodynamic data of various chemical reactions. The standard Gibbs free energy changes ΔG for each reaction at different temperatures could be obtained by HSC Chemistry software. The results are shown in Fig 3.

B/B_2O_3 mass ratio, and holding time can be used to realize the soluble transformation of boron magnesium compounds.

Fig. 4 describes the mechanism of boron magnesium compounds soluble transformations in amorphous boron powder. After B_2O_3 is melted at 450 °C, it reacts with the boron magnesium compounds in amorphous boron powder particles and is converted into soluble MgB_4O_7 and MgO, thus removing the magnesium impurity.

3.2. Impurity distribution in amorphous boron powder

In order to clarify the soluble transformation behavior of boron magnesium compounds during calcining and acid leaching, the crude boron powder, the calcining treated boron powder was subjected to water leaching treated samples, and calcining treated + acid leached boron powder samples were selected for comparative analysis. The sample physical diagram is shown in Fig. 5. The crude amorphous boron powder with a purity of 90.18% was black and
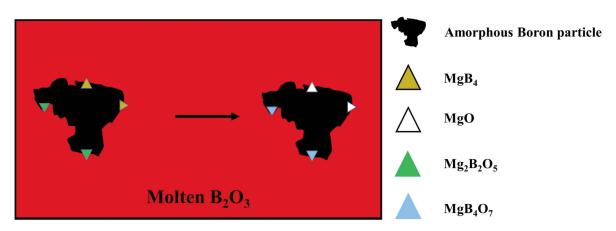
Figure 4. Schematic diagram of the mechanism of the soluble transformation between boron magnesium compounds and B_2O_3 in amorphous boron powder
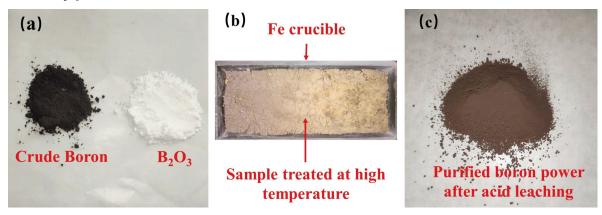

Figure 5. Sample of boron powder (a) raw boron powder and B_2O_3, (b) samples subjected to calcining, (c) calcining + acid leaching boron powder

gray. B_2O_3 melted at 800 °C. The boron powder was evenly distributed in it, and the sample formed a yellow-brown frit after cooling. After further acid leaching, the boron powder became reddish-brown, which is completely consistent with the color of high-purity amorphous boron powder.

The distribution and purification effect of impurity elements during calcining water leaching and calcining acid leaching as well as the raw material crude boron powder were studied. The SEM characterization of the boron powder samples and the distribution of B, Mg, and O are shown in Fig. 6. Most of the solid particles were formed by the agglomeration of fine boron powder, while the Mg and O impurities were uniformly dispersed in the fine particles boron.

The corresponding Mg distribution maps in Fig. 6 (b) and (c) are lighter than those in Fig. 6 (a). The ICP-OES analysis revealed a magnesium content of 1.30% and 0.96%, in Fig. 6 (b) and (c), respectively, which proves that calcining transformed acid-

insoluble boron magnesium compounds, allowing them to be removed from the boron powder by water leaching and acid leaching. The oxygen content increased significantly after water immersion treatment.

Compared to the oxygen distribution in Fig.6 (a), the aggregate of oxygen impurities in Fig.6 (b) was more obvious. In Fig. 6 (c), the red circle in the corresponding oxygen distribution image was a small aggregate of oxygen impurities. Combined with the morphology analysis of the boron powder, this shows the presence of impurities remaining in the reaction blind areas of the irregular boron powder particles during acid leaching and were difficult to remove by simple acid leaching.

Overall, the color of the oxygen was lighter, and the oxygen contents in (b) and (c) were 5.30% and 1.31%, respectively. The results show that the oxygen-containing impurities were removed, and the purity of the boron powder was further improved by the further acid leaching of the boron powder.
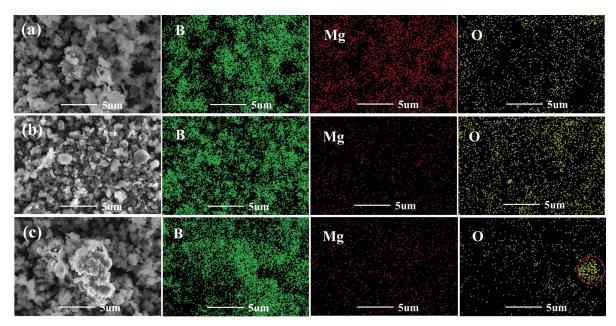
Figure 6. SEM characterization of boron powder samples and the distribution of B, Mg, and O (a) raw boron powder, (b) calcining treated and water leached boron powder, (c) calcining treated and acid leached boron powder

3.3. The soluble transformation of acid-insoluble boron magnesium compounds

The XRD patterns of raw boron powder, calcining treated and water leached samples, and calcining treated and acid leached samples are shown in Fig. 7. After calcining and water leaching, the diffraction peaks of MgB_4 and $Mg_2B_2O_5$ in boron powder decreased, while the diffraction peaks of B and B_2O_3 increased. The calcining and water leaching process removed the MgB_4 and $Mg_2B_2O_5$ impurities from crude boron powder. However, due to the addition of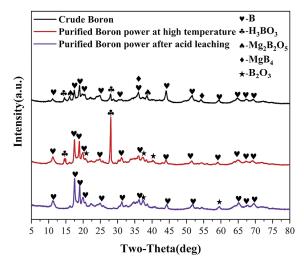 excess B_2O_3 for boron magnesium compounds soluble transformation, excess B_2O_3 could not be completely removed after the purified sample was subjected to water leaching, so some B_2O_3 remained in the boron powder. Fig. 7 shows that after calcining and water leaching and further acid leaching, the B_2O_3 diffraction peak in the boron powder disappeared, and the intensity of the B diffraction peak increased. The boron powder sample after calcining and water leaching was further pickled by mixed-acid leaching, and the remaining B_2O_3 was removed. The results show that the calcining and water leaching process removed acid-insoluble boron magnesium compounds in crude boron powder. Further acid leaching removed the residual B_2O_3, further improving the purity of the amorphous boron powder.

The XPS spectra of raw boron powder, calcining treated and water leached boron powder samples and calcining treated and acid leached boron powder samples are shown in Fig. 8. Fig. 8(a) shows that, in addition to elemental boron, Mg and O elements were also detected in raw boron powder, namely in the form of B_2O_3, B_xO, MgO, and Mg, respectively. Mg may have formed a stable intermetallic compound with B. Fig. 8(b) shows that the elemental composition of the boron powder after calcining and water leaching was the same as that of crude boron powder. The single peak strength of Mg decreased obviously, which proves that calcining and water leaching removed magnesium impurities from amorphous boron powder. The increase in B_2O_3 peak intensity was due to the addition of excess B_2O_3 during purification, so that B_2O_3 was not completely

Figure 7. Comparison chart of crude boron powder before and after calcining
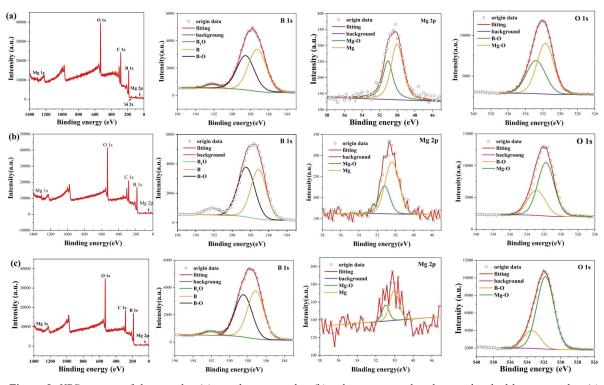
Figure 8. XPS spectra of the samples (a) raw boron powder, (b) calcining treated and water leached boron powder, (c) calcining treated and acid leached boron powder
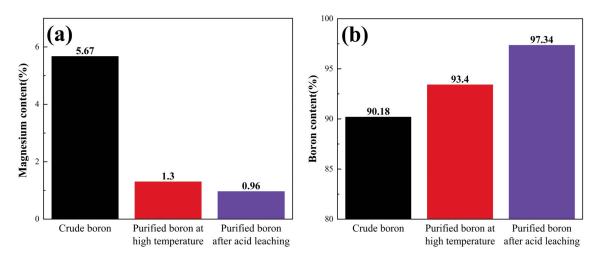

Figure 9. Effect of acid leaching on boron powder purification (a) the magnesium content in boron powder, (b) purity of boron powder

removed after water leaching the sample. The oxygen content of the raw boron powder is 4.15 %, and the B_2O_3 in the water-immersed boron powder reacts with water to generate a small amount of boric acid, resulting in an increase in oxygen content after water immersion. It can be seen from Fig. 8(c) that the single peak strength of Mg decreased after further acid leaching of the boron powder treated by calcining and water leaching. This shows that the acid leaching

removed Mg further. The B_2O_3 peak intensity also decreased, showing that the acid leaching process further improved the purity of the boron powder.

3.4. Effect of acid leaching on boron powder purification

After calcining and water leaching, the boron powder was subjected to acid leaching with HNO_3-

HCl mixed acid. The acid leaching conditions are shown in Table 1, and the acid leaching results are shown in Fig. 9. The results show that the magnesium content in the crude amorphous boron powder was 5.67%, which was reduced to 1.30% after calcining and water leaching. The magnesium content was also reduced to 0.96%, and the total separation efficiency reached 83.07%. The purity of boron in the crude boron powder was 90.18% and increased to 93.40% after calcining and water leaching. The purity of boron powder reached 97.34% after calcining water leaching and acid leaching. Acid leaching played an important role in removing magnesium from crude amorphous boron powder and improving the purity of boron powder.

4. Conclusion

The acid-insoluble impurities $Mg_2B_2O_5$ and MgB_4 were converted into soluble MgB_4O_7 and MgO by adding B_2O_3 into crude amorphous boron powder for calcining at 800 °C. Impurities in the boron powder were then removed by water leaching and acid leaching to purify the boron powder. After calcining and water leaching, the magnesium content in the crude boron powder was reduced to less than 1%. After calcining and water leaching, the boron powder was subjected to further acid leaching, the magnesium content was reduced to 0.96%, and the purity of the boron powder reached 97.34%. The crude boron powder and B_2O_3 were treated at calcining, the acid-insoluble impurities were removed, and the purity of boron powder was improved by water leaching and acid leaching. This advanced purification process provides a new way to produce amorphous boron powder with low cost and high performance.

Acknowledgment

Data Availability Statement

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Conflict of interest statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author's'contributions

Shuxuan Lv: Writing-review & editing, Writing-original draft, Visu-alization, Validation, Supervision, Conceptualization. Jijun Wu:Writing-original draft, Validation, Funding acquisition, Formal anal.ysis, Data curation. Zhen Cao: Visualization,Formal analysis.

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PREČIŠĆAVANJE AMORFNOG BORA U PRAHU KORIŠĆENJEM RASTVORLJIVE TRANSFORMACIJE KISELINSKO-NERASTVORLJIVIH BOR-MAGNEZIJUMSKIH JEDINJENJA

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Apstrakt

Trenutno se amorfni bor u prahu smatra najboljim gorivom za čvrste pogonske materijale zbog njegove izuzetno visoke zapreminske i masene kalorijske vrednosti. Amorfni bor u prahu proizveden termičkom redukcijom magnezijuma sadrži mnogo nečistoća koje su nerastvorljive u kiselinama, kao i defekte poput niske čistoće, prevelike veličine čestica i slabe hemijske aktivnosti, što ozbiljno ometa njegovu široku primenu u vojnim i svemirskim oblastima. U ovom radu su istraživani mehanizam konverzije nerastvorljivih bor-magnezijumskih jedinjenja u amorfni bor u prahu tokom kalcinacije i metoda za prečišćavanje borovog praha. Da bi se uklonila nerastvorljiva bor-magnezijumska jedinjenja u amorfnom boru u prahu, nerastvorljive nečistoće $Mg_2B_2O_5$ i MgB_4 su tokom kalcinacije pretvorene u rastvorljive MgB_4O_7 i MgO. Uzorci su zatim podvrgnuti ispiranju vodom ili kiselinom kako bi se sirovi proizvodi amorfnog bora u prahu pretvorili u proizvode amorfnog bora u prahu visoke čistoće. SEM-EDS, XRD, XPS i druge tehnike korišćene su za određivanje stanja faza nečistoća. Praćena je transformacija faza nečistoća nakon kalcinacije, ispiranja vodom i ispiranja kiselinom. Rezultati su pokazali da se sadržaj magnezijuma u amorfnom boru u prahu može smanjiti na 0,96%, a čistoća borovog praha može se povećati na 97,34% primenom kombinovane tehnike kalcinacije i ispiranja vodom ili kiselinom.

Ključne reči: Amorfni bor u prahu; Prečišćavanje; Uklanjanje magnezijuma; Bor-magnezijumska jedinjenja; Rastvorljiva konverzija