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Preparation of Magnesium Borate Whisker by Novel High Temperature-Flux-Wet Method

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Abstract

High-quality magnesium borate whisker was synthesized by novel high temperature-flux-wet method process with $MgCl_2 \cdot 6H_2O$ and borax as raw materials. The synthesized samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Effects of amount-of-substance ratio of boron to magnesium, calcination temperature and calcination time on whisker's quality were investigated systematically. The growth mechanism of magnesium borate whisker was discussed as well. Results showed that smooth-faced magnesium borate whisker with diameter of at 0.5~1 μm and length of at 10~60 μm could be synthesized while calcination temperature was 800℃ calcination time was 6 h, amount-of-substance ratio of boron to magnesium was 2:1, and dosage of flux was 4:1. The growth mechanism of magnesium borate whisker was solid-liquid-solid (S_1-L-S_2) mechanism.

Key words

Magnesium borate whisker; high temperature-flux-wet method; preparation; growth mechanism

1. Introduction

Magnesium borate whisker, a white fluffy solid, presents the shape of fibrous single crystal under the microscope. The light, wear-resistant, heat-resistant and corrosion-resistant material with high toughness and cheaper price than other whiskers is widely researched as a novel composite enhancer [1-3].

Primary synthesized methods for magnesium borate whisker include high temperature molten-salt methods [4-6], microwave irradiation [7], hydrothermal synthesis method [8-11], sol-gel process [12] and chemical vapor deposition method [13-15]. Among them, microwave irradiation and hydrothermal synthesis method are still at the stage of laboratory research for their rigorous process and low production; sol-gel process fails to produce magnesium borate whisker with large length-diameter ratio, but produces magnesium borate powder and nanorods currently; chemical vapor deposition method requires a specific protective atmosphere and a high synthesis temperature, leading to difficulty in mass industrial production. In contrast, characterized by accessible raw materials, simple process, low cost, and applicability to industrial production, high temperature molten-salt methods has become the leading method for research and production of magnesium borate whisker. Prevailing high temperature molten-salt methods are divided by high temperature-flux-dry method and high temperature-flux-wet method. For the former one, despite the simple technology, it is hard for the whisker to reach single-crystal nanoscale, leaving alone low length-diameter ratio and serious agglomeration. For the high temperature-flux-wet method, despite clear-cut fibration and high length-diameter ratio, such problems as the generation of whisker particles and blocks resulting from quantities of impurities [16-18], and high energy consumption resulting from spray drying technology restrict the promotion and usage of magnesium borate whisker as composite enhancer.

Based on existing research work, the paper discussed the optimum process for preparation of magnesium borate whisker by novel high temperature-flux-wet method, and analyzed the growth mechanism of magnesium borate whisker as well. Compared to current process, this process overcame such problems as serious agglomeration and low length-diameter ratio. Meanwhile, as the spray drying process is excluded, energy consumption is significantly reduced. The magnesium

borate whisker produced by the method herein has coordinated size and appearance, high length-diameter ratio, optimized crystallinity, and good dispersibility.

2. Materials and Methods

2.1 Experimental materials

$MgCl_2•6H_2O$ with the analytical purity of no less than 98.0%, from Beijing Chemical Works; borax ($Na_2B_4O_7•10H_2O$), NaCl and KCl with the analytical purity of no less than 99.5%, from Beijing Chemical Works; homemade deionized water by Milli-Q-type pure water, from MilliPore Co., USA.

2.2 Experimental methods

The flux is binary compound of NaCl and KCl with the molar ratio of 1:1. The flux volume is determined to render the molar ratio of (NaCl+KCl)/Mg equal to 4:1. The experimental materials of $MgCl_2•6H_2O$, $Na_2B_4O_7•10H_2O$, NaCl and KCl are weighed respectively according to certain amount-of-substance ratios. Add proper amounts of deionized water until the materials dissolve. Stir the slurry evenly. Pour the blended slurry into a box-type resistance furnace. Increase its temperature at a rate of 5~10℃/min until to the designated temperature. Let the slurry react for a certain period at this temperature before natural cooling to the room temperature. Rinse the calcinate for multiple times and dry it to become magnesium borate whisker.

2.3 Analytical methods

Calcine the samples by the SX2-8-16 box-type resistance furnace from the Tianjin Central Furnace Co., Ltd. Analyze the phase composition of the samples by X'Pert PROMPD (Cu Kα1) X-ray diffractometer from PANalytical Co., Ltd. Observe the appearance of sample particles by JSM6700F SEM. Analyze the surface morphology of the whisker by ESCALAB 250Xi XRS.

3. Results and Discussion

3.1 The influence of B/Mg (molar ratio) on whisker

Under the temperature of 800℃ and the calcination time of 6h, the experiment analyzed the influence of B/Mg (molar ratio) on whisker. Figure 1 and Figure 2 show XRD patterns and SEM patterns, respectively. According to Figure 1, when the B/Mg (molar ratio) is 1:1, the principal phase is $Mg_2B_2O_5$ and the impurities are $Mg_3B_2O_6$ and MgO; the increasing B/Mg (molar ratio) leads to dropping diffraction peaks of $Mg_3B_2O_6$ and Mg. when the B/Mg (molar ratio) exceeds 2:1, there is only the diffraction peak of $Mg_2B_2O_5$.

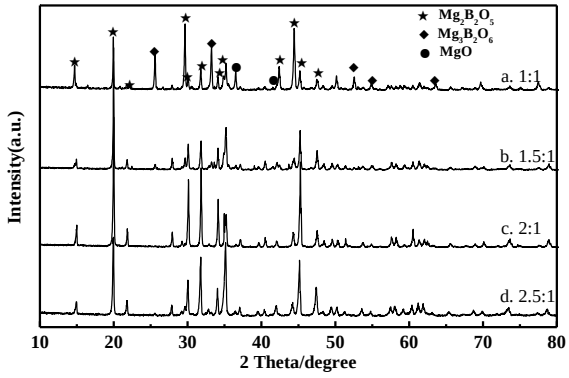


Fig.1. XRD patterns of the products obtained at different B/Mg (molar ratio)

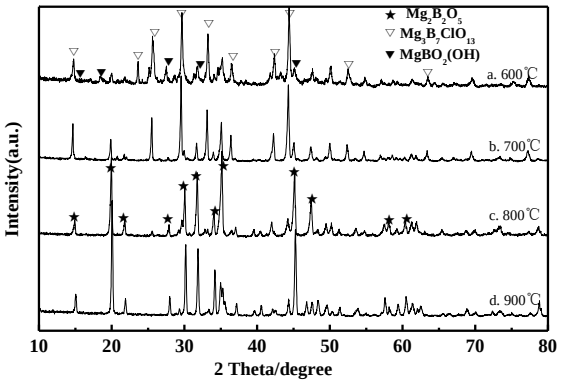


Fig.3. XRD patterns of the products obtained at different sintering

Figure 2 shows SEM images of the products obtained at different B/Mg (molar ratio). When the B/Mg (molar ratio) is 1:1, there are apparently quantities of broken crystal, crystal fragments and particles. When the B/Mg (molar ratio) is 1.5:1, in spite of the decrease of crystal fragment and particles, the whisker still has poor appearance and uneven thickness. When the B/Mg (molar ratio) is over 2:1, the whisker has uniformed appearance and size at the length of around 10~60 μm and the diameter of around 0.5~1 μm. Therefore, to a certain scope, the larger the B/Mg (molar ratio) is, the more smooth-faced, purer, and with larger length-diameter ratio the magnesium borate whisker becomes.

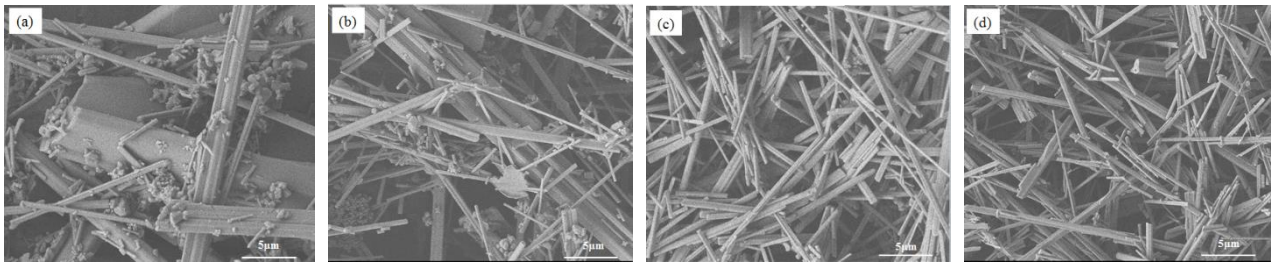
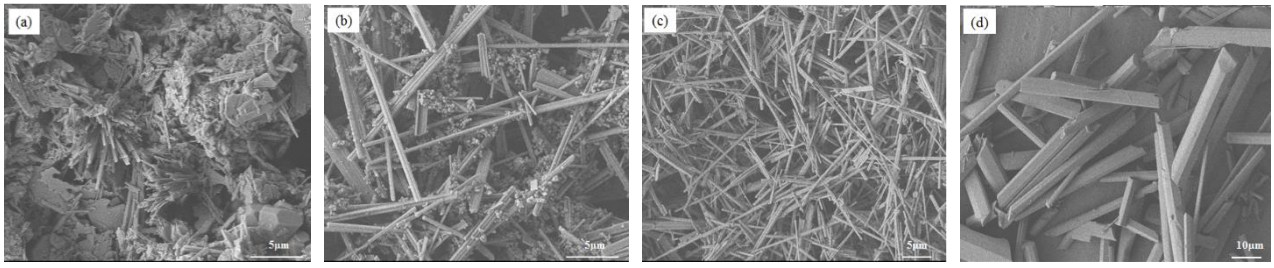


Fig.2. SEM images of the products obtained at different B/Mg (molar ratio a,1:1； b,1.5:1； c,2:1； d,2.5:1)

3.2 The influence of calcination temperature on whisker

Under the B/Mg (molar ratio) of 2:1 and the calcination time of 6h, the experiment analyzed the influence of calcination temperature on whisker. Figure 3 and Figure 4 show XRD patterns and SEM patterns, respectively. According to Figure 3, at the calcination temperature of 600℃, the products are quantities of $Mg_3B_7ClO_{13}$ and $MgBO_2(OH)$, with minor $Mg_2B_2O_5$. As the calcination temperature rises, $Mg_2B_2O_5$ increases, but $Mg_3B_7ClO_{13}$ and $MgBO_2(OH)$ decrease. At the calcination temperature of 800~900℃, the diffraction peak appears only for $Mg_2B_2O_5$, denoting that the product is a high-purity $Mg_2B_2O_5$. According to Figure 4, at the calcination temperature of 600℃, the products are found to be crystal blocks. At the calcination temperature of 700℃, the number of whisker expands. However, there is still a mixture of particles and crystal fragments. At the calcination temperature of 800℃, crystal blocks and particles disappear, and the obtained whisker is smooth-faced at the length of 10~60 μm and at the diameter of 0.5~1 μm. At the calcination temperature of 900℃, the whisker thickens as the length-diameter ratio drops.



(a) 600 ℃ (b) 700 ℃ (c) 800 ℃ (d) 900 ℃

Fig.4. SEM images of the products obtained at different sintering temperature

The influence of calcination time on whisker

Under the B/Mg (molar ratio) of 2:1 and the calcination temperature of 800 ℃, the experiment analyzed the influence of calcination time on whisker. Figure 5 and Figure 6 show XRD patterns and SEM patterns, respectively. According to Figure 5, at the calcination time of 2h, the principal phases are $Mg_2B_2O_5$ and $Mg_3B_2O_6$. As time goes, the diffraction peak of $Mg_2B_2O_5$ rises and that of $Mg_3B_2O_6$ drops. When the materials are calcined for 6-8h, the diffraction peak appears only for $Mg_2B_2O_5$, denoting that the product is a high-purity $Mg_2B_2O_5$. According to Figure 6, as calcination time is prolonged within a certain scope, the appearance and uniformity of whisker improve, and the length-diameter ratio increases. However, at the calcination time of 8h, quantities of rough crystals emerge, and the length-diameter ratio decreases. Therefore, overlong calcination time may potentially cause change of growth mechanism to the disadvantage of preparation of high-quality whisker.

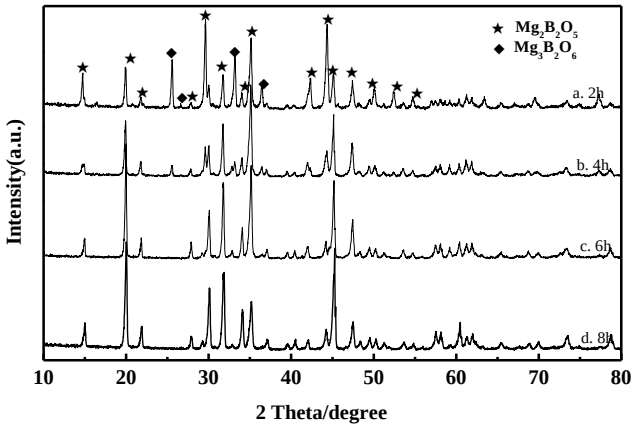
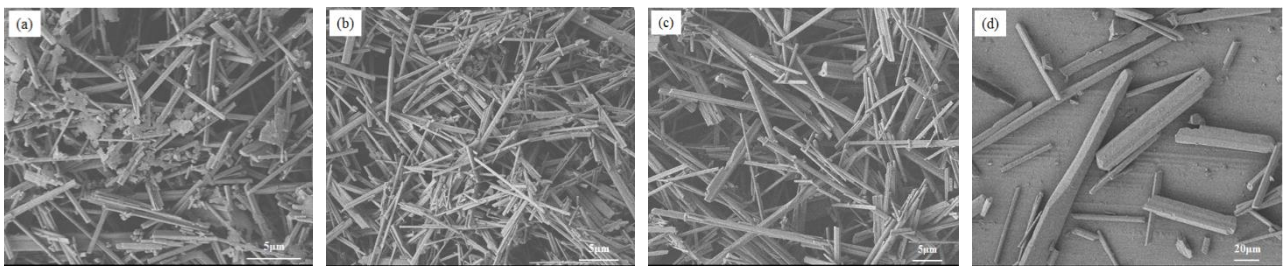


Fig.5. XRD patterns of the products obtained at different sintering time



(a) 2 h (b) 4 h © 6 h (d) 8 h

Fig.6. SEM images of the products obtained at different sintering time

4. The growth mechanism of $Mg_2B_2O_5$ whisker

For research of the growth mechanism of $Mg_2B_2O_5$ whisker at high temperature, the experiment analyzed XRD images of the products formed at different stages. At a low temperature of from 600 ℃ to 700 ℃, the principal products are $Mg_3B_7ClO_{13}$, $MgBO_2(OH)$, with the mixture of a little $Mg_2B_2O_5$ whisker. At the calcination temperature of 800 ℃, the only product is $Mg_2B_2O_5$. Within a short reaction time, the products contain $Mg_2B_2O_5$ and $Mg_3B_2O_6$. When the calcination time is prolonged to 6h, the only product is $Mg_3B_2O_6$. Thus, it can be deducted that borax is decomposed into B_2O_3 during the process of reaction. When the calcination temperature reaches about 500℃, the state of B_2O_3 transforms completely to the liquid state, and $MgCl_2•6H_2O$ is decomposed into fine MgO particles that disperse in the molten B_2O_3. Also, under the influence of water vapor, $MgBO_2(OH)$ is generated by the reaction of B_2O_3 with MgO, following the immediate generation of $Mg_3B_7ClO_{13}$ by the reaction between $MgBO_2(OH)$, Cl^- and B_2O_3. At high temperature, $Mg_3B_7ClO_{13}$ is decomposed into $Mg_2B_2O_5$ [19-20]. If the amount of B_2O_3 fails to meet the reaction demand, the generated $Mg_2B_2O_5$ will combine with MgO into $Mg_3B_2O_6$. This reaction corresponds to the result that there are quantities of diffraction peaks of $Mg_3B_2O_6$ in the XRD pattern of the products formed at the calcination time of 2h, proving that the growth of whisker requires abundant B.

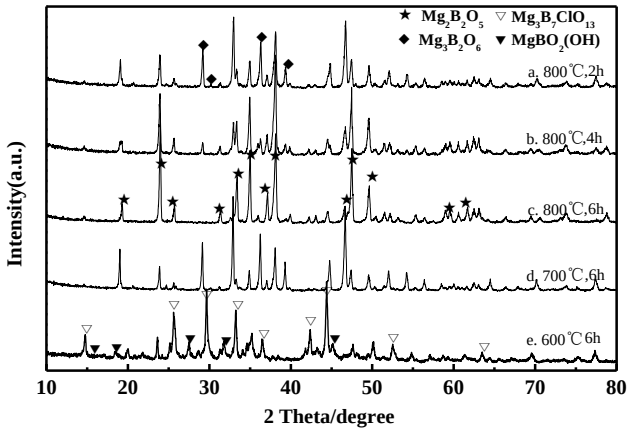


Fig.7. XRD patterns of the products formed at different stages

Under the B/Mg (molar ratio) of 2:1, the calcination temperature of 800 ℃, and the calcination time of 2h, the experiment analyzed XPS spectra of the prepared $Mg_2B_2O_5$. The results are shown in Figure 8. As can be seen, there is only Mg, B and O in the spectra, where the combination between

Mg 2P, B 1s and O 1s are respectively 50.53 eV, 192.47 eV and 531.98 eV, which means that their valence state are +2, +3 and -2, respectively. The quantitative result of peak area for each of the element in Figure 8 is n(Mg):n(B):n(O)=2:2.1:2.49, which fits the stoichiometric ratio of $Mg_2B_2O_5$. This shows that the intermediate products under this condition have finally transformed into pure $Mg_2B_2O_5$ whisker.

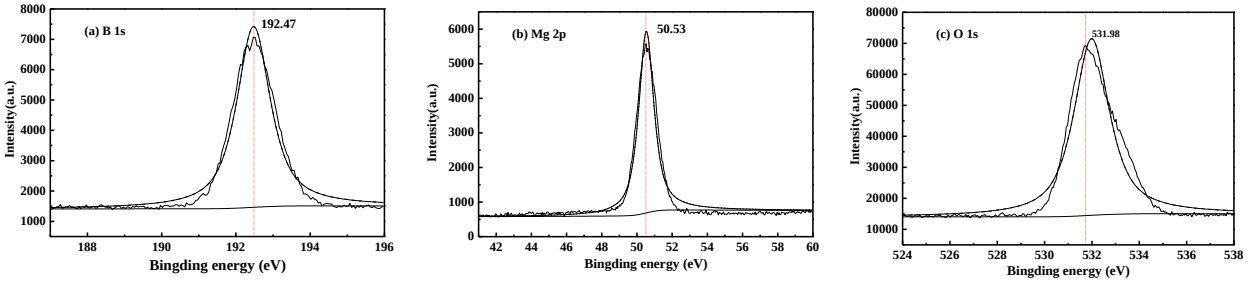


Fig.8. XPS spectra of the product prepared under the best condition

The axial screw dislocation contained in the crystal nucleus determines the direction of rapid growth of whisker [21-22]. As can be seen from the aforementioned SEM pattern, the synthesized whisker in the experiment is rodlike with even radial growth. Combined with the above analysis, it is deemed that the $Mg_2B_2O_5$ whisker that is synthesized by novel high temperature-flux-wet method matches the solid-liquid-solid (S_1-L-S_2) mechanism [5], where S1 denotes solid MgO particles, L denotes molten B_2O_3 and molten $Mg_2B_2O_5$, and S2 denotes solid $Mg_2B_2O_5$ nucleus. The formation of magnesium borate whisker is composed of nucleus formation and whisker growth. For whisker growth, it is required that there should be one substrate with screw dislocation. In the experiment, the substrate is selected to be Solid MgO particles, which react to molten B_2O_3 to form supersaturated liquid. It follows the precipitation of solid $Mg_2B_2O_5$ nucleus from the molten $Mg_2B_2O_5$. The molten NaCl and molten KCl carry B_2O_3 continuously as a necessary reactant for $Mg_2B_2O_5$ nucleus to grow gradually into magnesium borate whisker.

5. Conclusion

With $MgCl_2$•$6H_2O$ and borax as raw materials, smooth-faced and high-purity magnesium borate whisker with diameter of at 0.5~1 μm and length of at 10~60 μm could be synthesized while calcination temperature was 800 ℃, calcination time was 6 h, amount-of-substance ratio of boron to magnesium was 2:1, and dosage of flux was 4:1. Reaction at high temperature (＞800℃)

facilitates the growth of magnesium borate whisker, while overlong calcination time （＞8h）can accelerate the radial growth of whisker, with the appearance of quantities of rough crystals at a decreasing length-diameter ratio in the products. The growth of whisker requires abundant B. Preparation of magnesium borate whisker by novel high temperature-flux-wet method matches the solid-liquid-solid (S_1-L-S_2) mechanism.

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