International Journal of Minerals, Metallurgy and Materials
Volume 19, Number 10, Oct 2012, Page 969
DOI: 10.1007/s12613-012-0656-5

Synthesis of $Mg_2B_2O_5$ whiskers *via* coprecipitation and sintering process

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(Received: 22 October 2011; revised: 2 November 2011; accepted: 8 November 2011)

Abstract: $Mg_2B_2O_5$ whiskers with high aspect ratio were synthesized by coprecipitation and sintering process using $MgCl_2·6H_2O$, H_3BO_3, and NaOH as raw materials and KCl as a flux. Their formation process was investigated by thermogravimetry and differential scanning calorimetry (TG-DSC), X-ray diffraction (XRD), and scanning electron microcopy (SEM). It is found that the products synthesized at 832°C are monoclinic $Mg_2B_2O_5$ whiskers with a diameter of 200-400 nm and a length of 50-80 μm. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) analyses show that the whiskers obtained at 832°C are single crystalline and grow along with the [010] direction. The growth mechanism of $Mg_2B_2O_5$ whiskers was also presented.

Keywords: magnesium borate; coprecipitation; sintering; crystal whiskers; crystal growth; microstructure

[*This work was financially supported by the Department of Science and Technology of Qinghai Province of China (Grant No.2010-G-208).*]

1. Introduction

Whiskers are filamentary single crystals with almost idea strength due to their perfect geometrical structure [1-2]. Therefore, they are the ideal reinforcing skeletons of composite materials. During the past several decades, SiC whiskers have been the most widely used whisker reinforcements for ceramic matrix composites as well as metal matrix composites. However, SiC whiskers have some drawbacks [3], such as sensitive to oxidizing at high temperature, incompatible with a lot of materials, and high cost. Therefore, it is necessary to develop novel whiskers with excellent properties and low cost. $Mg_2B_2O_5$ whiskers meet these expectations [4] based on their excellent mechanical properties and attractive thermal properties. Furthermore, compared to SiC whisker, $Mg_2B_2O_5$ whiskers' production cost is much lower since they can be synthesized from the byproducts of seawater desalting or the compounds containing Mg and B originating from saline.

$Mg_2B_2O_5$ whiskers are usually synthesized by the flux technique [5-6] or the hydrothermal method [7-8]. However, the whiskers prepared *via* the traditional flux technique generally have a low purity and a wide size distribution, while the hydrothermal method needs unfavorable high pressure.

Herein, a simple method to synthesize $Mg_2B_2O_5$ whiskers with high aspect ratio, high purity, and uniform morphology was reported using $MgCl_2·6H_2O$, H_3BO_3, and NaOH as raw materials and KCl as a flux in this paper, which involved coprecipitation and sintering process. Compared to single mechanical mixing in the traditional flux technique, coprecipitation process could make the raw materials blend more uniformly. Due to the improved blending effect of raw materials, whiskers with high purity and uniform morphology could be formed after the subsequent sintering process.

2. Experimental

All chemicals were of analytical grade and used without further purification. In a typical procedure, 0.2 mol $MgCl_2·6H_2O$, 0.2 mol H_3BO_3, and 0.4 mol NaOH were dis-

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solved in 100 mL distilled water under constant magnetic stirring at 60°C. The solution turned turbid immediately, and a white precipitate formed. The precipitate was washed with distilled water for several times and then baked at 100°C for 8 h. The obtained precipitate was the reaction precursor.

About 10 g precursor was mixed with 4 g H_3BO_3 and 20 g KCl, and ground into a fine powder. The powder was first placed in a muffle furnace and sintered for 5 h at 655, 832, and 988°C, respectively, and then cooled down to room temperature. Finally, the sintered powder was washed with distilled water for several times and dried at 100°C for 6 h.

The thermogravimetry and differential scanning calorimetry (TG-DSC) curves were measured on the NETZSCH STA 449F3. The structure and morphology of products were examined by X-ray diffraction (XRD, Rigaku, D/max-2500), scanning electron microcopy (SEM, JSM-5610LV), transmission electron microscopy (TEM, JEOL 2010), and selected area electron diffraction (SAED).

3. Results and discussion

Fig. 1 shows the TG-DSC curves of the reaction mixture (precursor, H_3BO_3, and KCl). Four endothermic peaks can be noticed in the DSC curve, respectively, at about 655°C, 725°C, 832°C, and 988°C. The endothermic at 655°C peak is weak, and the weight decreases at a slow rate, which indicates that a small amount of products are formed by reaction. Accompanied by a fast rate of weight loss, the endothermic peak at 725°C could be attributed to the melting and evaporation of KCl. The endothermic peak at 832°C is relatively broad, which is probably due to the fact that mass products were formed and grew up after KCl being melted.

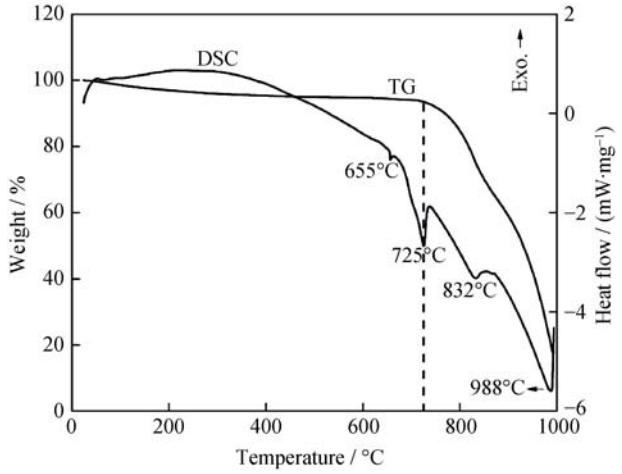


Fig. 1. TG-DSC curves of the reaction mixture (precursor, H_3BO_3, and KCl).

The endothermic peak at 988°C may be connected with the phase transition [9].

To confirm the above analysis and understand the formation of $Mg_2B_2O_5$ whiskers, the precursor and the as-synthesized products obtained at 655, 832, and 988°C were systematically surveyed by XRD and SEM. The XRD pattern of the precursor is shown in Fig. 2(a). It can be indexed as $Mg_7B_4O_{13}·7H_2O$ (PDF No.19-0754). The weak diffraction peaks indicate that the precursor has a poor crystallinity. The precursor content also was determined by TG and chemical analysis. It is shown that the weight ratio of crystal water is 23.43% and the molar ratio of Mg and B is 1.75 in the precursor, which agree well with the theoretical values of $Mg_7B_4O_{13}·7H_2O$. Fig. 2(b) shows the XRD pattern of the product obtained at 655°C. All diffraction peaks can be indexed as a monoclinic $Mg_2B_2O_5$ (m-$Mg_2B_2O_5$) with the lattice parameters of a=0.9197 nm, b=0.31228 nm, and c=1.2303 nm, which are consistent with the parameters of the bulk $Mg_2B_2O_5$ (PDF No. 86-0531, space group: $P2_1/c$). All diffraction peaks at 832°C in Fig. 2(c) can also be attributed to m-$Mg_2B_2O_5$ (PDF 86-0531). However, compared with bulk $Mg_2B_2O_5$, the diffraction intensities of the (201), (400), $(40\bar{2})$, and $(60\bar{2})$ planes increase significantly. Therefore, it is supposed that the product sintered at 832°C has a preferential growth orientation. No XRD peaks arising from the other products can be detected, indicating that the

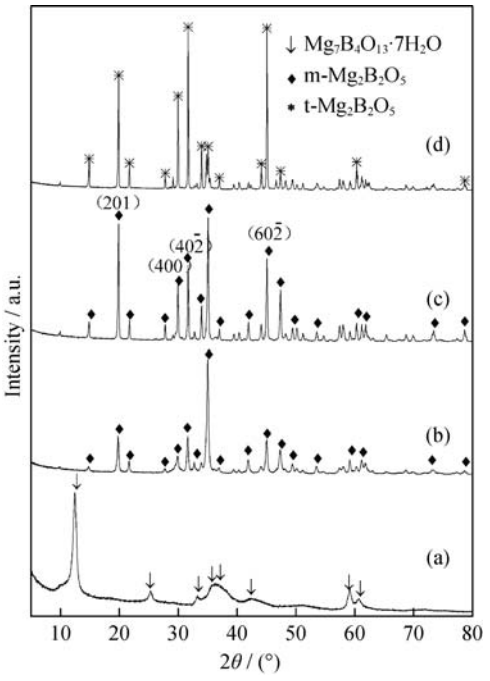


Fig. 2. XRD patterns of the precursor (a) and products sintered at different temperatures: (b) 655°C; (c) 832°C; (d) 988°C.

product is of high purity. Fig. 2(d) shows the XRD pattern of the product obtained at 988°C. All diffraction peaks can be indexed as a triclinic $Mg_2B_2O_5$ (t-$Mg_2B_2O_5$, PDF No.73-2232, space group: $P\bar{1}$). With the temperature increasing, m-$Mg_2B_2O_5$ transforms into t-$Mg_2B_2O_5$.

Fig. 3(a) shows the SEM image of the precursor. It can be observed that it is mainly composed of floc-like materials. After sintering at 655°C for 5 h, the SEM image shows that a lot of short columnar-like particles and some irregular materials are formed in Fig. 3(b). When the temperature rises to 832°C, the short columnar-like particles grow into uniform whiskers. The whiskers in Fig. 3(c) have the typical diameters in the range of 200-400 nm and the lengths of 50-80 μm. However, as the temperature further increases to 988°C, the diameter of the whiskers becomes larger obviously, as shown in Fig. 3(d). Thus, it is believed that the optimized calcination temperature is about 832°C.

TEM was also employed to study the structure and morphology of the whiskers. Fig. 4(a) shows the TEM image of an individual $Mg_2B_2O_5$ whisker obtained at 832°C. The diameter of the whisker is about 200 nm, which is in agreement with the SEM result in Fig. 3(c). The corresponding

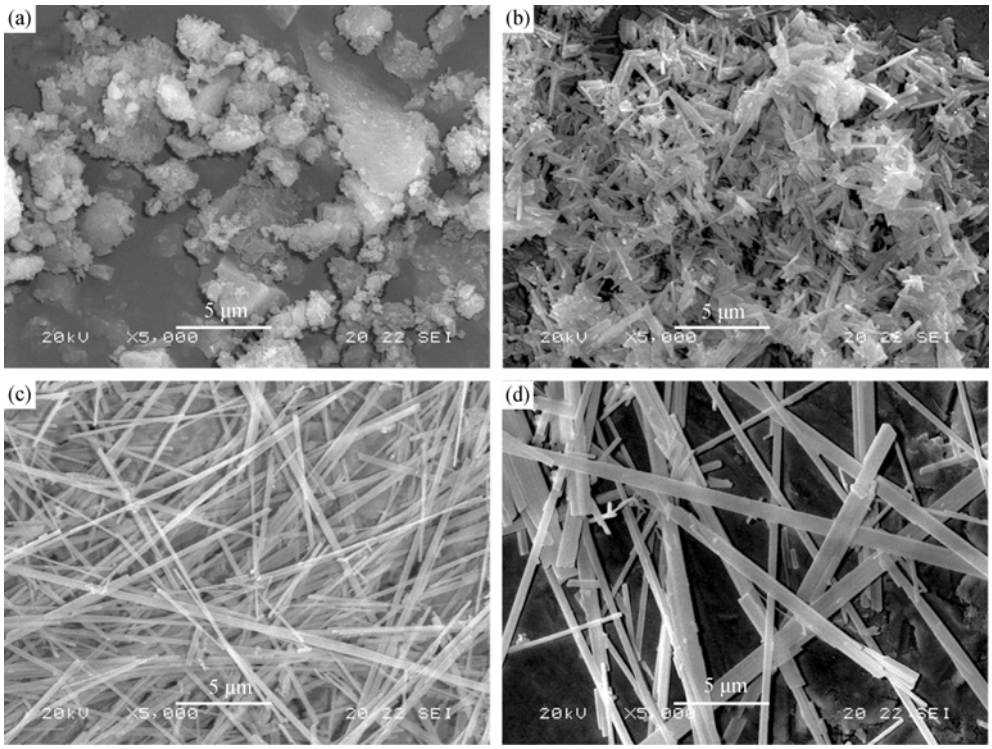


Fig. 3. SEM images of the precursor (a) and products sintered at different temperatures: (b) 655°C; (c) 832°C; (d) 988°C.

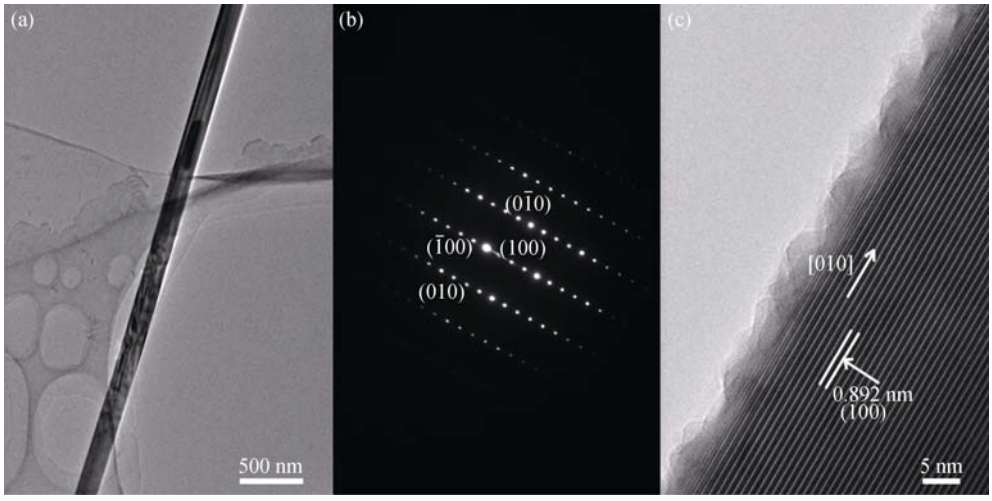
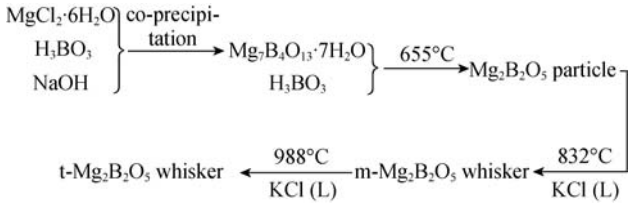


Fig. 4. TEM image (a), SAED pattern (b), and HRTEM micrograph (c) of the whisker obtained at 832°C.

SAED pattern of the individual whisker in Fig. 4(b) conforms that the whisker is single crystalline in nature and has a monoclinic crystal structure [10]. From the corresponding HRTEM micrograph in Fig. 4(c), it can be clearly shown that the whisker is well crystallized. The distance between parallel fringes is about 0.892 nm, corresponding to the (100) planes of m-$Mg_2B_2O_5$. It indicates that the whisker grows along with the [010] direction, which can conform the supposition of XRD analysis.

Based on the XRD and SEM analyses of the precursor, the formation process of $Mg_2B_2O_5$ whiskers can be illustrated as follows:



In the experiments, no tips were found at the whisker end, which was the characteristic of the vapor-liquid-solid (VLS) mechanism [11]. Therefore, the VLS mechanism is not suitable for the growth of as-synthesized whiskers. Based on the results, it is believed that the anisotropic growth mechanism [12-13] is responsible for the whiskers' growth. The crystal structure of m-$Mg_2B_2O_5$ is composed of B_2O_5 (double-triangle) groups, holding together by magnesium atoms that are in the middle of the distorted oxygen octahedral. Such an intrinsic anisotropic crystal structure leads to m-$Mg_2B_2O_5$ growing along one dimension at low concentration [14]. During the process, H_3BO_3 first decomposes into B_2O_3 at about 250°C and then melts at about 450°C [15]. With the increase of temperature, $Mg_7B_4O_{13}·7H_2O$ loses the crystal water, dissolves into molten droplets of B_2O_3, and then reacts with it. When the liquid droplets become saturated, $Mg_2B_2O_5$ particles precipitate from the droplets and disperse in the solid-state salt (KCl). Until the KCl melts, $Mg_2B_2O_5$ particles are deposited onto the high-energy surfaces of the existed particles to form $Mg_2B_2O_5$ whiskers.

4. Conclusion

$Mg_2B_2O_5$ whiskers with high aspect ratio were successfully synthesized by a facile route, using $MgCl_2·6H_2O$, H_3BO_3, and NaOH as raw materials and KCl as a flux. With the temperature increasing, the formation of $Mg_2B_2O_5$ whiskers goes through from floc-like $Mg_7B_4O_{13}·7H_2O$ to short columnar-like particles and then to uniform m-$Mg_2B_2O_5$ whiskers. When the temperature further increases to 988°C, t-$Mg_2B_2O_5$ whiskers with large diameter form. The m-$Mg_2B_2O_5$ whiskers obtained at 832°C with a diameter of 200-400 nm and a length of 50-80 μm have a uniform morphology, and they are single crystalline and grow along with the [010] direction. The whiskers' growth can be attributed to the anisotropic growth mechanism.

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