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Growth and characterization of dumbbell-shaped MgO nanowhiskers

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Abstract

By depositing Mg vapor generated by carbothermal reduction onto boron powder, dumbbell-shaped MgO nanowhiskers were obtained. The diameters of these whiskers and balls are 50–150 nm and 1.4–2 μm, respectively. EDS analysis results reveals that the compositions of whiskers are Mg, O and small amount of B and Si. While the compositions of balls are Si, O and small amount of Al, B, C, Mg, K, Ca. SEM and TEM observation indicates that interfaces between balls and whiskers are very smooth. Experimental result shows that whiskers should grow in advance, and then balls grew by depositing silicon oxide and other vapor species onto the surface of these whiskers. The presence of silicon oxide was considered to play a key role in the formation of this peculiar morphological product.

Keywords: B. Whiskers; D. MgO

1. Introduction

Magnesium oxide has been widely used as refractory material in steel manufacture due to its high corrosion-resistance and high melt point. Also, MgO is a valuable crystal and an excellent catalyst in the application of optical transmitters and substrates for thin film growth. MgO whiskers have been used to reinforce ceramic composite materials. Recently, it was found that it could improve the superconducting properties in addition to improve the mechanical properties when it was added into superconducting composites [1].

Different morphologies of MgO crystalline fibers such as MgO nanorods [2,3], MgO fishbone fractal nanostructures [4] and nanobelts [5] have been obtained. In this paper, a dumbbell-shaped MgO nanowhisker formed by the deposition of Mg vapor onto boron powder was reported. From the view of bionics, these dumbbell-shaped whiskers could reinforce ceramic composites well than those straight and smooth fibers [6]. Bai et al. have studied the preparation of dumbbell-shaped SiC whisker and found that it actually is a good reinforcement for composites [7]. In addition, VLS and VS growth mechanism were usually used to explain the formation of ceramic whiskers such as SiC [8], TaC [9,10], NbC [11], Si_3N_4 [12] and etc. In this paper, the growth mechanism of dumbbell-shaped MgO nanowhiskers was also investigated.

2. Experimental procedure

About 2 g mixture of fine activated carbon and analytical-grade magnesium oxide powder with a molar ratio of 6.7:1 were placed in an alumina boat, which was then placed in the center of an alumina tube (24×800 mm^2). Amorphous ground boron powder with 98% purity (the molar ratio of MgO:B = 2:1) and a bit of silicon powder were mixed and placed in another alumina boat which was placed near the first boat with a distance of 10 mm in a down-stream direction. Then the tube was inserted in a conventional tube furnace. The setup is similar to that of Ref. [13].

Before heating, the tube was flushed with pure argon flow (150 mm/min) for 20 min to eliminate the residual air. Then the furnace was heated to 1250 °C in an hour

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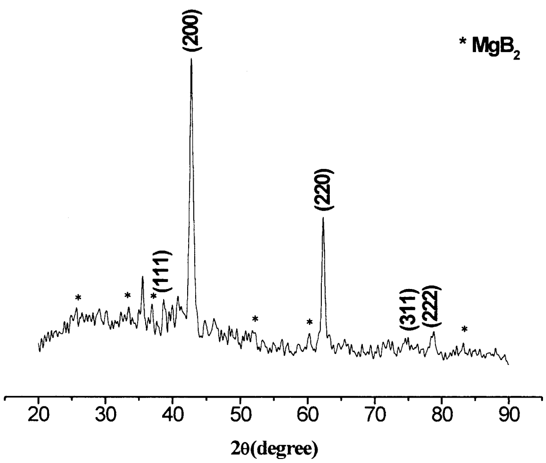

Fig. 1. The XRD patterns of the product, which indicating the main phase of MgO and small amount of MgB_2 phase.

and held at this temperature for an hour. After that, the furnace was cooled down to room temperature. During the whole process, an Ar flow of 20 mm/min was introduced to the tube serving as carrier gas and protective gas. After the second boat was taken out of the furnace, it was found that the color of the up-layer of boron powder (with thickness of about 5 mm) changed from black to white-gray. This white-gray product was then characterized by field emission scanning electronic microscopy (FE-SEM) with model of JSM-6301F and transmission electronic microscopy (TEM) with model of JEM-200CX. respectively. Its composition was identified by X-ray diffraction (XRD) (nickel-filtered CuK_α radiation) and X-ray energy dispersive spectrometer (EDS) attached with SEM (Link ISIS-300).

3. Results and discussion

3.1. Characterization of the product

The XRD pattern of the product was shown in Fig. 1. It clearly shows that the product is mainly composed of MgO phase. In addition, MgB_2 phase can also be indexed. Fig. 2 is the SEM images of the product. Fig. 2a shows that the product mainly consists of whiskers. However, in most cases, there are balls grew on whisker surfaces which looks like dumbbells. Sometimes there are many balls located at one whisker. Generally, the balls and whisker of a dumbbell have a same axis line. However, sometimes balls deviated from the axis of the whisker. At the same time, it can be seen that the sizes of balls and distances between two balls are different even in the same whisker. A closed view of a dumbbell-like object (Fig. 2b) clearly showed that the ball

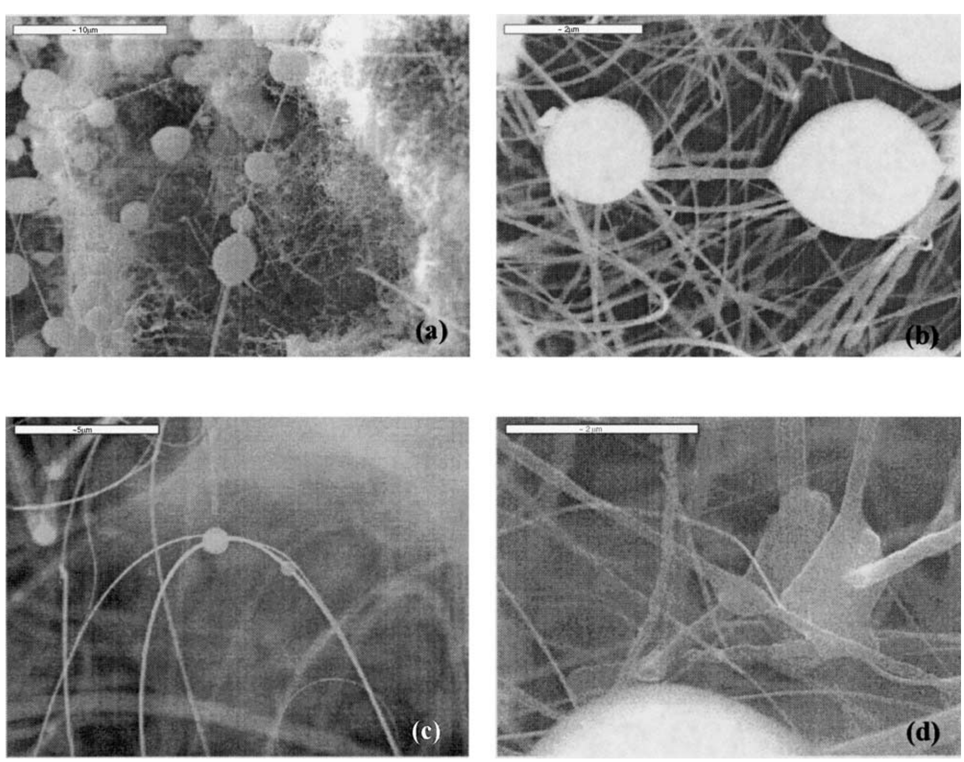

Fig. 2. SEM images of the product: (a) a general view of the product; (b) a closed view of the product displaying a dumbbell-shaped whisker; (c) a bent dumbbell-shaped whisker; (d) in addition to the ball or quasi-ball, plate-like and pear-like (or hemisphere) objects were also observed on whisker surfaces.

surface is rather smooth while the whisker surface is rough. The whiskers and balls have diameters of 50–150 nm and 1.4–2μm, respectively. Fig. 2c shows that a dumbbell-shaped whisker bent extremely into a bow. In addition to the ball or quasi-ball, pear-like (or hemisphere-like) and plate-like objects can also be observed (Fig. 2d). Obviously, they are the growing dumbbells.

As shown in Fig. 3a, EDS analysis result reveals that the compositions of whiskers are mainly composed of Mg, O, which is well consistent with the XRD result. In addition, a small amount of B and Si were also observed. Fig. 3b shows the main compositions of balls are Si and O. However, Al, B, C, K and Ca were also identified. The presence of Al is possibly a product of the reduction reaction of Al_2O_3 and Mg. This can be confirmed by the fact that the initial relative smooth alumina boat surface became coarse after the experiment. K and Ca should be impurities involved by raw material. Whereas the presence of C must derive from the conducting rubber that was used in SEM observation. Therefore, it can be concluded that the whisker composition is MgO and the ball composition is silicon oxide.

Fig. 4 is the TEM images of the dumbbell-like MgO whiskers. Fig. 4a shows that the ball surface and the interface between balls and whisker are very smooth. The diameters of whisker and balls are about 14 μm and 180–240 nm, respectively. The inset SAED (selected area electron diffraction) patterns further confirmed that it is a crystalline MgO whisker. Similar to the SEM result (Fig. 2a), Fig. 4b clearly displays a ball deviated from the axis of the whiskers. The SAED patterns (inset image) indicate that the ball is a polycrystalline particle, which also consisted with the EDS result.

3.2. The growth mechanism

VLS and VS mechanism were usually used to explain the growth of whiskers. Although a bit of silicon powder was added in the preparation of dumbbell-shaped MgO whiskers, the ends of whiskers have no sphere-like caps, which was considered as a sign of VLS process. Moreover, although at the reaction temperature (the location temperature is about 1100 °C) Si and Mg can form a liquid alloy due to their low eutectic point (637.6 °C) [14], Si was mainly consumed by the formation of silicon oxide balls. So these

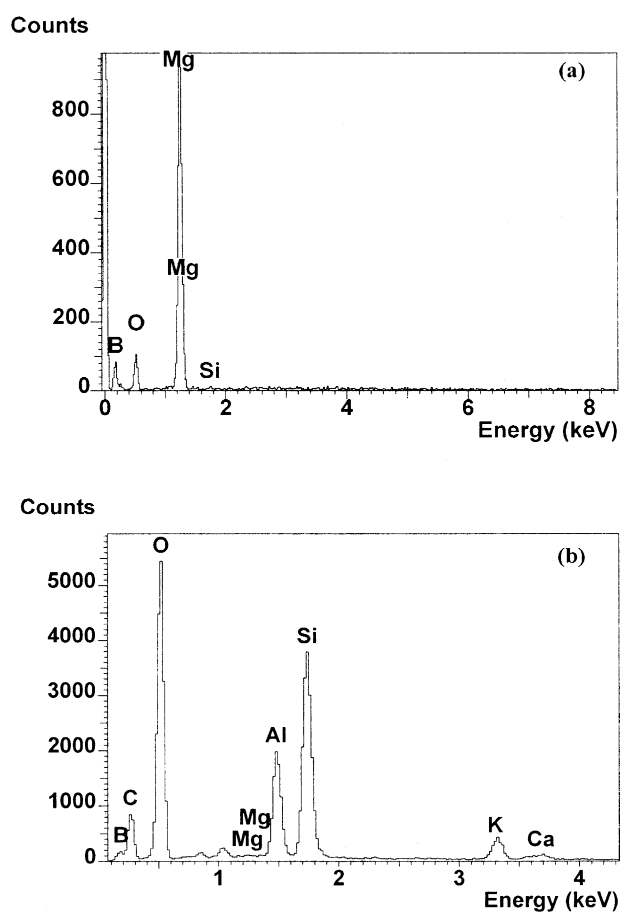

Fig. 3. EDS results of (a) a whisker and (b) a ball in a dumbbell.

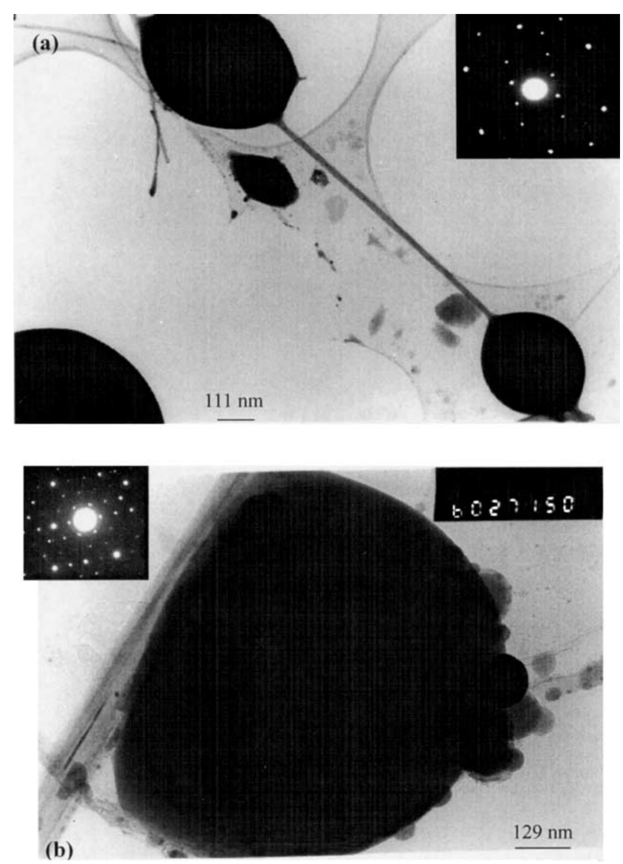

Fig. 4. TEM images of (a) a dumbbell-shaped whisker, the inset SAED patterns indicating the crystalline characterization and (b) a dumbbell-shaped whisker in which the ball deviated from the axis of the whisker. The SAED patters inset indicates that the ball is a polycrystalline particle.

dumbbell-shaped MgO nanowhiskers did not grow via VLS mechanism.

From the SEM images, it can be seen that on both sides of a ball the whisker surfaces are very similar and the interfaces between whisker and balls are very smooth, which indicates that the whisker and the ball did not form at the same time. The deviation of balls from the axis of whisker (Fig. 4b) and the growth process of balls on whisker surface (Fig. 2d) further reveal this fact. Actually, MgO whiskers formed in advance, then balls grew by depositing silicon oxide and other vapor species (eg. Al, Ca, K and etc.) onto the surface of whiskers. It was believed that the stacking faults and twinning in whiskers provide preferential sites for the deposition of silicon oxide and other vapor species [7]. Therefore, it can be concluded that this dumbbell-shaped whiskers formed via a VS mechanism. To completely understand the growth mechanism of this dumbbell-shaped whisker further investigation is needed. In addition, boron powder in the experiment merely serves a supporter for the growth of MgO whiskers though our original intension is to prepare MgB_2.

4. Conclusion

By depositing Mg vapor generated via carbothermal reduction onto boron powder, dumbbell-shaped MgO nanowhiskers were prepared. The whiskers and balls of these dumbbells have diameters of 50–150 nm and 1.4–2 μm respectively. The ball surface and the interface between ball and whisker are very smooth but the whisker surface is rough, which indicates that whiskers formed in advance and balls formed later by depositing silicon oxide and other vapor species onto the grown-whisker surface. A small amount of added silicon powder in boron powder and the whisker defects such as stacking faults and micro-twinning were believed to play important roles in the formation of this peculiar morphological MgO whiskers. However, the detailed reaction mechanism needs further investigation.

Acknowledgements

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