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Comparison of different methods to prepare MgO whiskers

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Abstract

Magnesia whiskers have been made by hydrolysis of $MgCl_2$–KCl melt and conversion of magnesium hydroxide whiskers. The morphology of MgO whiskers was examined by SEM and TEM. Composition of products was identified by XRD. Comparisons have been made on the morphology and quality of the products by different methods. Discussions have been made on the efficiency, product quality control and scale-up feasibility of these methods. Whiskers prepared by hydrolysis have uniform diameter but other shapes of magnesia are often found. Conversion of $Mg(OH)_2$ whiskers to MgO whiskers is simple and easy to scale-up, but the product often has many defects caused by decomposition. Nevertheless, the single crystal structure can be reserved as revealed by electron diffraction. XRD results show that the purity of products by hydrolysis is better than that by conversion. The conversion method is more hopeful for industrial production.

Keywords: A. Calcination; B. Whiskers; C. MgO

1. Introduction

MgO whiskers can be widely applied in various fields due to their predominant characteristics, such as high melting point, high modulus of rupture and high corrosion-resistance. It was reported that the incorporation of MgO whiskers into superconducting composites can improve the superconducting and mechanical properties [1]. The manufacture methods of MgO whiskers can be classified into two general categories: the direct ways and the indirect ways. The direct ways include carbothermal reduction of magnesia with aluminum [2] and hydrolysis of melts containing magnesium chloride [3], in which magnesia whiskers were prepared directly. The manufacture method by hydrolysis of magnesium chloride with flux has been studied broadly since it was first patented in 1973 by Dow chemical company in USA [3]. In the indirect ways, magnesia whiskers are prepared by decomposition of precursor whiskers, such as magnesium sulfate oxide whiskers [4]. Recently, the indirect manufacture methods have attracted more widespread attention. Nevertheless, no comparison has been made between these two kinds of ways. In this work, MgO whiskers have been prepared by two different ways and detailed comparison has been made in respect of the efficiency, costs, product quality control and scale-up feasibility of these methods.

2. Experimental procedure

2.1. Preparation of MgO whiskers by hydrolysis of melts

$MgCl_2$ is prone to hydrolysis before melting, so anhydrous $MgCl_2$ was used in experiments. A mixture of anhydrous analytical $MgCl_2$ and KCl with a molar ratio of 1:1 was placed in an alumina boat, which was then placed at the center of an alumina tube (Φ45 mm). The tube was inserted in a conventional horizontal tube furnace and flushed with 0.2 m^3/h dry N_2 (99.5%) for half an hour beforehand. Considering that anhydrous $MgCl_2$ is highly hydroscopic and quickly absorbs water when exposed to the air, it was weighted in a glove box and transferred into the tube carefully. Then the furnace was heated to 1000 °C in half an hour, and held at this temperature for an hour while 0.2 m^3/h wet N_2 was flowing through the tube. Wet N_2 was saturated with water vapor by bubbling in pure water of 26–30 °C, corresponding to the vapor pressure of 3.36–4.24 kPa. The tube was taken out after the tube was cooled down below 100 °C naturally. It was found that the edge and inner wall of boat was covered with a thick white deposit. Product was peeled off and washed with

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deionized water until no chlorine ion was detected by $AgNO_3$ solution. Then it was washed with ethanol and dried in 50 °C. The process is similar to that of [3].

2.2. Preparation of MgO whiskers by conversion of magnesium hydroxide whiskers

The preparation process includes three reactions as follows:

$$6MgCl_2 + 5Ca(OH)_2 + 8H_2O = 2Mg_3(OH)_5Cl \cdot 4H_2O + 5CaCl_2 \quad (1)$$

$$Mg_3(OH)_5Cl \cdot 4H_2O + NaOH = 3Mg(OH)_2 + NaCl + 4H_2O \quad (2)$$

$$Mg(OH)_2 = MgO + H_2O \quad (3)$$

5.93 g calcium hydroxide powder was added bit by bit to 250 mL 4.0 M aqueous magnesium chloride solution with a molar ratio of 1 $Ca(OH)_2$ to 10 $MgCl_2$ under constant stirring. Then the suspension was agitated in 45 °C bath. Suspension became a gel after several hours. It was found through an optical microscopy the gel contained lots of fibers after 30 h. The precipitation was washed with deionized water, ethanol and isopropanol, respectively and filtered with suction to remove the unreacted magnesium chloride and gel. Product after filtering was dried in 35 °C under normal pressure. Dried product thus obtained was suspended in 256 mL mixture solution with a volume ratio of 3 mL ethanol to 1 mL water, and then reacted with 85 mL 1 M aqueous sodium hydroxide. The suspension was heated to and held at 62 °C for 3 h under constant stirring. It was reported that a 3:1 mixture of ethanol and water seems to be the best solvent for the preservation of the whisker morphology and relative high reaction temperature (around 60 °C) and short reaction time helps to preserve the morphology [5]. At last the suspension was filtered and washed with ethanol several times and dried at 50 °C. It was found that the solid products were kept in fibrous shape with an optical microscopy. The composition of final product was identified by XRD.

At last, the dried powder was first heated to 150 °C (3 °C/min), and then slowly from 200 to 800 °C (1.5 °C/min) before the temperature was ramped to 1000 °C in flowing N_2. The powder was calcined at 1000 °C for an hour to finish the conversion to magnesia whiskers.

3. Results and discussion

3.1. Characterization of the products

The composition of products was identified by XRD. Fig. 1 shows that the product prepared by hydrolysis is only composed of magnesia phase. Fig. 2 presents the evidence of the conversion from $Mg(OH)_2$ whiskers (brucite) to MgO whiskers. It can be seen that the final product was also composed of magnesia phase. A little impurity is attributed to forsterite, probably introduced by the silica tube.

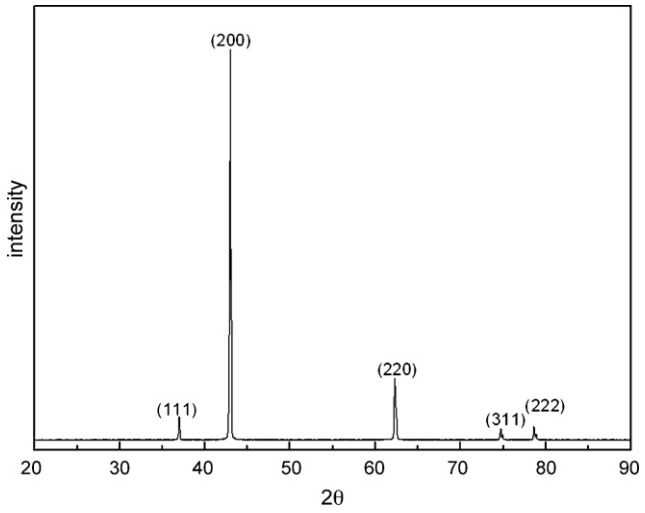


Fig. 1. XRD pattern of MgO whiskers prepared by hydrolysis of melts.

Fig. 3 shows the SEM images of the product prepared by hydrolysis of melts, revealing that it mainly consists of magnesia whiskers with diameter of 1–3 μm and length mainly of 130–300 μm. However, the morphology of products varies

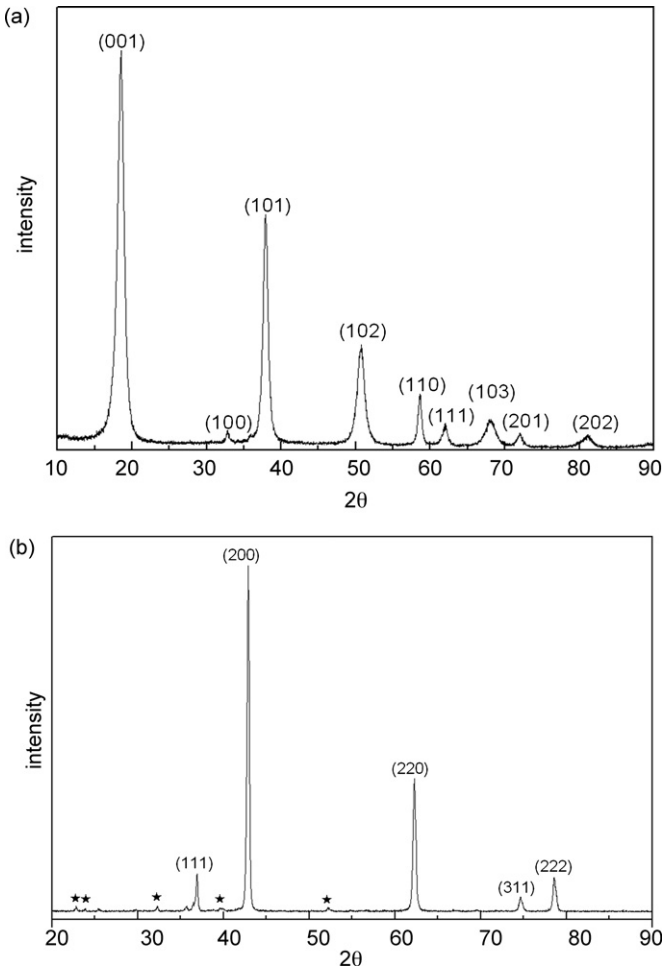
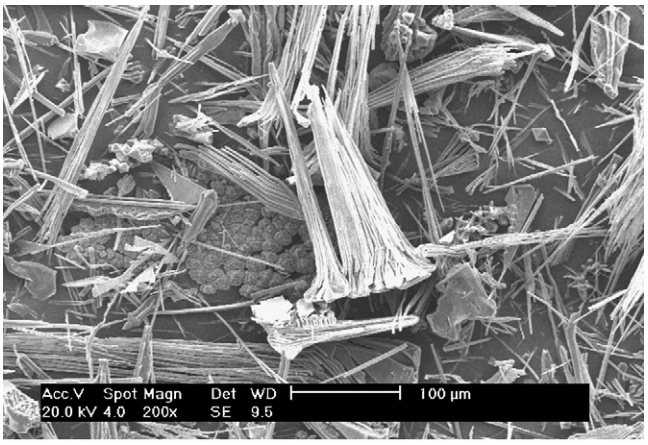


Fig. 2. XRD verification of conversion from $Mg(OH)_2$ whiskers to MgO whiskers: (a) XRD patterns of $Mg(OH)_2$ whiskers; (b) XRD patterns of MgO whiskers converted from $Mg(OH)_2$ whiskers, the peaks is attributed to the impurity forsterite denoted by (★).



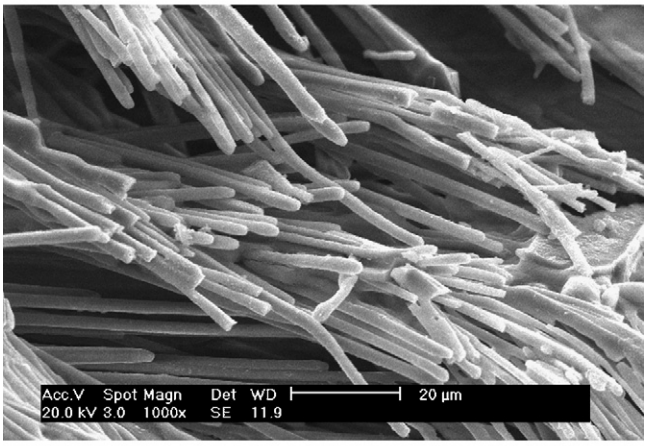


Fig. 3. SEM images of product prepared by hydrolysis of melt.

greatly. Some platelets and whiskers with branches are found and most whiskers are found growing in bundles. A large part of whiskers have kinks and uniform diameter. Dispersed short whiskers may be due to mechanical damage. There are two ways to verify whether products are single crystal or not, X-ray diffraction and electron diffraction, which demands the size of crystals to be larger than 10 μm and less than 1 μm, respectively. Unfortunately, the size of the whiskers falls beyond these ranges. It is difficult to verify whether they are single crystals or not in our experiments. Nevertheless, it has been reported that small magnesia whiskers prepared in this way are single crystal with a growth direction of [1 0 0] [6].

The yield of hydrolysis of melt is often less than 40%. Considering that $MgCl_2$–KCl has a marked vapor pressure of species containing $MgCl_2$ at 900 °C [7] and the water vapor pressure is low, the reaction probably took place in the vapor phase and some products were carried away by the gas flow. When a crucible was put near the alumina boat in the down-stream direction, white deposit was found on the crucible. So the fact that the reaction took place in the vapor phase was verified. The Vapor–Liquid–Solid (VLS) and Vapor–Solid (VS) mechanisms are usually used to explain the growth of whiskers from vapor. The growth mechanism of magnesia whiskers by hydrolysis is only reported in the cases of hydrolysis of magnesium chloride with no additives and hydrolysis of Mg [8]. It is believed that magnesia whiskers grow by a VLS mechanism in hydrolysis of Mg and by a VS mechanism in hydrolysis of $MgCl_2$ [8]. Since there are no globules found at the end of whiskers, VS may be the mechanism taking place in our experiments.

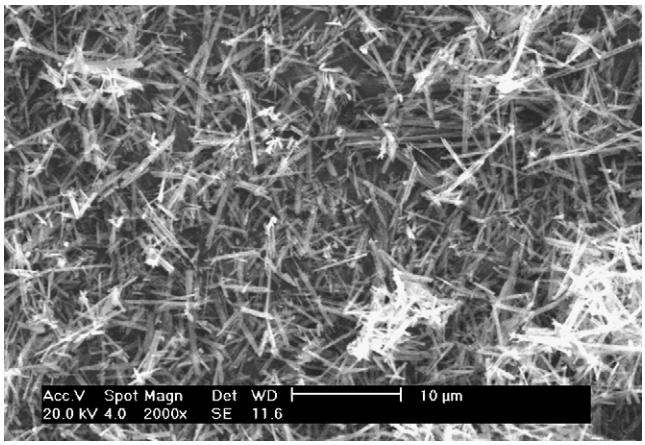


Fig. 4. SEM image of MgO whiskers prepared by conversion of $Mg(OH)_2$ whiskers.

Fig. 4 shows the SEM images of the product prepared by conversion of magnesium hydroxide whiskers. It has been found that they are completely composed of magnesia whiskers with diameter of 0.1–0.4 μm and length of 3–10 μm. Whiskers seem uniform and straight. Taking a close look it could be found that thick whiskers are consisted of several thin whiskers. Fig. 5 shows the HRTEM images of the product prepared by conversion. Fig. 5(a) and (b) show that whiskers obtained by conversion often have a length-to-diameter ratio of 30 or more. The diameter of thin whiskers is not uniform and ranges from 10 to 200 nm. The surface of whiskers is rough. Short crystals may be broken whiskers during ultrasonic dispersion before HRTEM study. Fig. 5(c) shows that the interlayer spacing is 0.24 nm and the growth direction is about 54 degrees with the interlayer. It was deduced that the growth direction is ⟨1 1 0⟩. Electron diffraction pattern in Fig. 6 reveals that the single crystal structure can be retained after conversion.

3.2. Comparison of whiskers made by different methods

The XRD patterns show that the purity of the product prepared by hydrolysis is better than that prepared by conversion of magnesium hydroxide whiskers. From the images it can be found that magnesia whiskers made by hydrolysis are thicker and longer. The surface is smoother and the size is more uniform. But except the whiskers, some platelets and grains are also found in the hydrolysis product. It is difficult to separate them from whiskers. The morphology of the product by conversion is more uniform but irregular diameters are often found.

The hydrolysis method is simple, efficient and low-cost, but the quality of product is difficult to control. Though it has been studied for many years, industrial production of magnesia whiskers by this method has never been reported. Large part of magnesia whiskers is formed in bundles and it is difficult to disperse them. The yield was often less than 40% in our

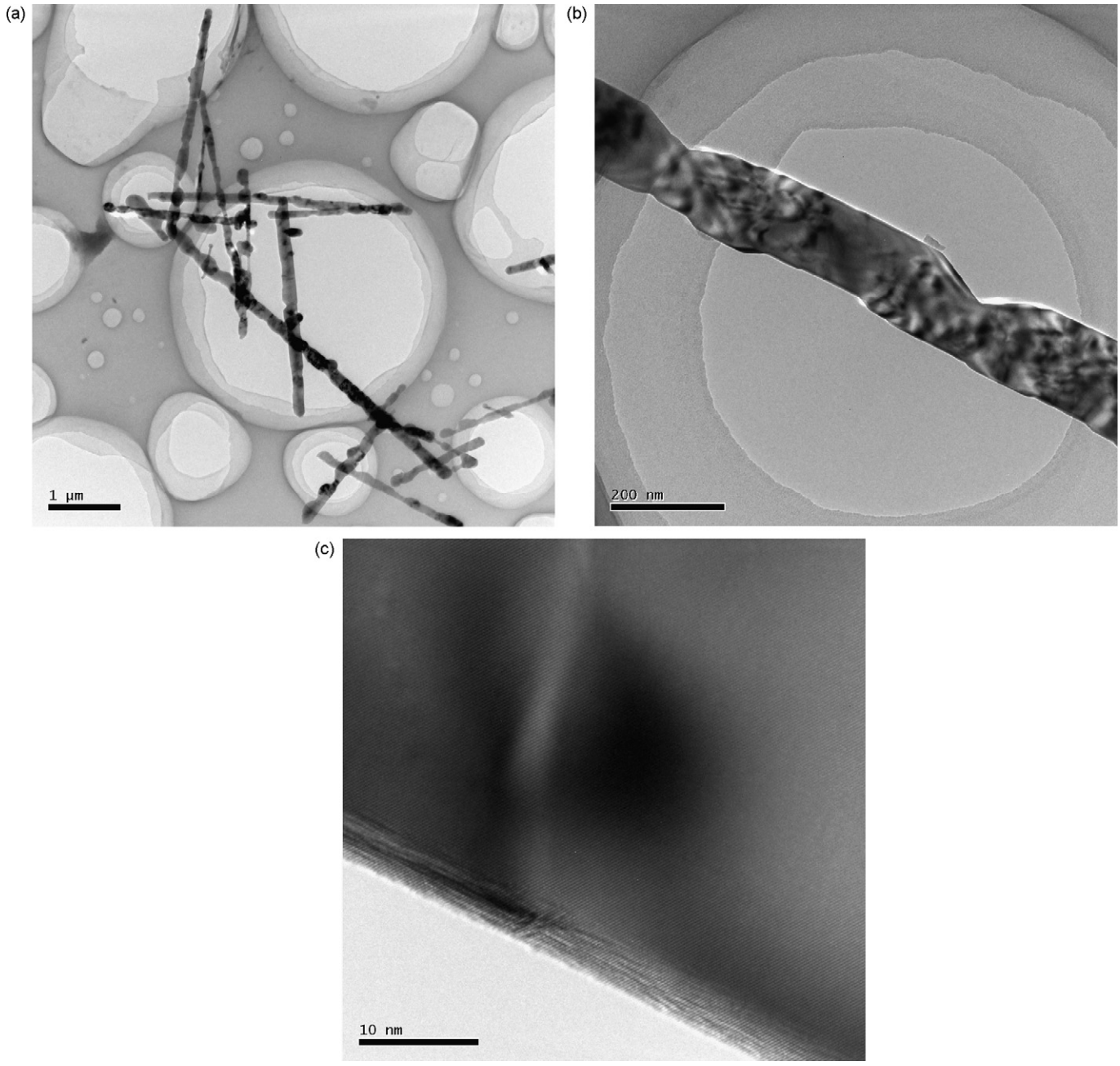


Fig. 5. HRTEM of the MgO whiskers obtained by conversion.

experiments and it is believed that this is because the reaction has taken place in gas phase and some products are carried away by nitrogen flow. The supersaturation of gas is influenced by gas flow and the geometry of the reactor and so on, which makes the reaction complicated to control and scale-up. Besides, the reactants of molten salt and the byproduct HCl are highly corrosive.

The method of conversion of magnesium hydroxide whiskers is simple and easy to obtain fibrous product. No platelet and grains were found under optimized conditions and the quality of product is easy to control. It is easy to scale-up and suitable for industrial production of magnesia whiskers. The key of this method is how to keep the single crystal structure and avoid aggregation during calcination. In addition, preparation of $Mg(OH)_2$ whiskers is also time-consuming, so better methods need to be further developed. Conversion of other magnesium-containing whiskers, for example, magnesium oxysulfate whiskers [4], has been reported, but magnesium hydroxide whisker may be the best precursor. First, it is found that $Mg(OH)_2$ decompose topotatically to yield porous pseudomorphic MgO with a single orientation relationship under vacuum, which could be considered an imperfect single crystal with high porosity [9]. The defects may be eliminated by sintering at high temperature [10]. Secondly, among the precursors, $Mg(OH)_2$ liberates the least amount of gas during conversion. When the gas molecules are liberated, the surface of whiskers is prone to be broken, especially when the gas volume evolved is large and the evolution quick. The

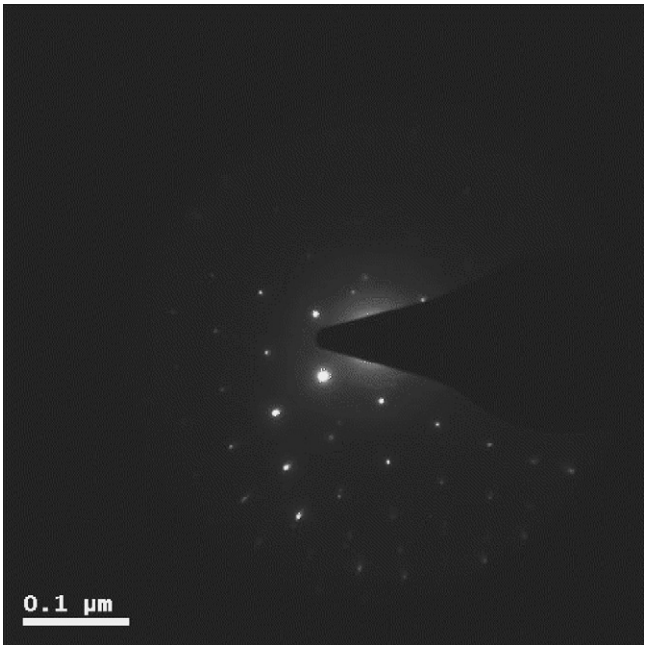


Fig. 6. Electron diffraction pattern of MgO whiskers obtained by conversion.

more gas molecules are liberated, the more prone the surface of precursor whiskers will be broken. More important, magnesium hydroxide crystal has a layered structure and the forces between layers of $Mg(OH)_2$ are relatively weak hydrogen bonds. When magnesium hydroxide whiskers are heated slowly, the water vapor will be liberated easily through the channels between layers in $Mg(OH)_2$ without destruction of the needle shape. Besides, only water vapor is formed in the conversion of magnesium hydroxide while some corrosive gases are often evolved in conversion of other precursors, which may cause serious corrosion to the equipment. Direct decomposition of magnesium hydroxide chloride whiskers will result in the destruction of the needle shape [11].

4. Conclusions

Two main methods for preparation of MgO whiskers were compared. Whiskers prepared by hydrolysis of melt have uniform diameter, straight stem and smooth surface. The equipment and process is simple and efficient. But the quality of the product is difficult to control because the supersaturation is influenced by many factors, which makes the scale-up and industrial production of MgO whiskers very complicated. Besides, corrosive reactants and byproduct may be detrimental to the equipments.

Conversion of magnesium hydroxide whiskers is a prospective way to produce magnesia whiskers industrially. Though the shape of MgO whiskers by this method is rough and some whiskers are aggregated, single crystal structure can be preserved as verified by electron diffraction. Great care must be taken to keep the single crystal structure and avoid aggregating during heating and calcinations. More studies should be made hopefully to compare the mechanical properties and strengthening effects of the whiskers.

References

[1] Y.S. Yuan, M.S. Wong, S.S. Wang, Superconducting properties of MgO-whisker reinforced BPSCCO composite, Physica C: Superconduct. 250 (3–4) (1995) 247–255.
[2] A. Yamaguchi, S. Hashimoto, Growth of magnesia whiskers, Ceram. Int. 18 (5) (1992) 301–305.
[3] B.D. Brubaker. (The Dow Chemical Company), US patent 3 711 599, 13 April 1970.
[4] Z. Wei, H. Qi, P. Ma, J. Bao, A new route to prepare magnesium oxide whisker, Inorg. Chem. Commun. 5 (2) (2002) 147–149.
[5] Q. Wei, Synthesis, properties and applications of nanorods and nanowires, Ph.D. thesis of Harvard University, 2001, 23–29.
[6] B. Soylu, N. Adamopoulos, D.M. Glowacka, J.E. Evetts, Composite reaction texturing of superconducting ceramic composites, Appl. Phys. Lett. 60 (25) (1992) 3183–3185.
[7] E.E. Schrier, H.M. Clark, Interaction in salt vapors and activity coefficients in the potassium chloride-magnesium chloride system, J. Phys. Chem. 67 (1963) 1259–1263.
[8] S. Hayashi, H. Saito, Growth of magnesia whiskers by vapor phase reactions, J. Cryst. Growth 24–25 (1974) 345–349.
[9] M.G. Kim, U. Dahmen, A.W. Searcy, Transformations in the decomposition of $Mg(OH)_2$ and $MgCO_3$, J. Am. Ceram. Soc. 70 (3) (1987) 146–154.
[10] N. Thangaraj, K.H. Westmacott, U. Dahmen, HVEM studies of the sintering of MgO nanocrystals prepared by $Mg(OH)_2$ decomposition, Ultramicroscopy 37 (1–4) (1991) 362–374.
[11] S. Xia, P. Xing, S. Gao, Studies on the basic compounds of magnesia cement: the thermal behavior of magnesium oxychlorides, Thermochim. Acta 183 (5) (1991) 349–363.