Facile molten salt synthesis of zirconia whiskers

Tao Wang¹, Jianmin Liu², Weihui Jiang¹,²*, Guo Feng², Lifeng Miao², Ting Chen², Qian Wu², Huidong Tang¹, Wei Luo¹

¹School of Material Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen, Jiangxi 333403, China
²National Engineering Research Center for Domestic and Building Ceramics, Jingdezhen, Jiangxi 333001, China

Received 17 April 2018; Received in revised form 22 July 2018; Accepted 17 August 2018

Abstract

ZrO₂ whiskers have been synthesized by a facile molten salt method using ZrOCl₂·8H₂O and Na₃PO₄·12H₂O as the zirconium source and molten salt, respectively. Differential thermal and thermogravimetric analyses, X-ray diffraction analysis, field emission scanning electron microscope and transmission electron microscope were employed to characterize the heating process of the precursor mixture, phase composition of the as-synthesized ZrO₂ whiskers and the effect of reaction temperature on the synthesis of ZrO₂ whiskers. The results show that the ZrO₂ whiskers synthesized at 900 °C have an average aspect ratio of 30 and preferentially grow along [010] direction. The formation of sodium zirconium phosphate [Na₉₋₄ₓZrₓ(PO₄)₃] (x = 1, 2) and the reaction temperature play an important role in the growth of ZrO₂ whiskers. This work also suggests an effective route for mass production of high quality ZrO₂ whiskers.

Keywords: molten salt method, zirconia whisker, crystal growth, sodium zirconium phosphate

I. Introduction

Zirconia has been extensively studied in high-temperature structural materials, ceramic tools, biomaterials, solid fuel cells, oxygen sensors and catalytic materials due to its valuable physical and chemical properties, such as high melting point, high resistance to thermal shock, low thermal and electrical conductivity, excellent wear resistance, and biocompatibility [1–3]. Whisker is a kind of fibrous single crystal and has theoretical strength close to perfect crystal owing to its highly complete internal and external structure [4]. In view of the merits of ZrO₂ and whisker, ZrO₂ whisker will show broad prospects in reinforcing and toughening areas, especially for ceramic materials, since they are often quite brittle, limiting their applications in some instances. In addition, zirconia whisker is also expected to be applied in improving sensitivity of chemical sensors due to its high aspect ratio and small size [5].

Up to now, preparation methods for ZrO₂ whiskers are mainly focused on high pressure and high temperature method [6], chemical vapour deposition (CVD) method [7,8], and hydrothermal method [9,10]. Compared with the strict preparation conditions or long experimental period in above methods, molten salt method has been developed as a promising route for preparation of ZrO₂ whiskers [11], but the complex preparation process of precursor and the low aspect ratio (about 18) limit its further application. Molten salt method is reported to be one of the simplest methods and widely used in the synthesis of powders [12], nanorods [13], whiskers [14] and other materials due to its excellent molten salt flux in favour of crystal growth [15].

For typical molten salt synthesis, in this work we developed a novel ZrO₂ whiskers preparation strategy by means of using raw materials without pretreatment. The as-synthesized ZrO₂ whiskers showed an improved quality. The effect of reaction temperature on the synthesis of ZrO₂ whiskers is systematically investigated and the formation mechanism of ZrO₂ whiskers is also discussed.

II. Experimental

Analytically pure ZrOCl₂·8H₂O, Na₃PO₄·12H₂O and NaF were used as starting materials. The powders
of 2 g ZrOCl₂·8H₂O, 2 g Na₃PO₄·12H₂O and 0.2 g NaF were weighed and mixed. After being ground homogeneously, the precursor mixture was transferred into a corundum crucible and calcined at different temperatures for 5 h, then cooled down to room temperature. The product was washed 3 times with deionized water to remove residual salt and dried at 70 °C for 6 h.

The DTA-TG analysis of the precursor mixture was performed by NETZSCH STA449C (air atmosphere, heating rate: 10 °C/min). The phase composition of the as-synthesized samples was studied by XRD (Bruker D8 Advance). The morphology of ZrO₂ whiskers was observed by FE-SEM (SU8010) and TEM (JEM-2010). Crystal structure and growth direction of ZrO₂ whiskers were characterized by SAED and HR-TEM.

**III. Results and discussion**

Figure 1 shows the DTA-TG curves of the precursor mixture. In the TG curve two obvious stages can be observed in temperature ranges of 20–500 °C and 820–1170 °C. The first weight loss is about 45.29% and can be divided into two parts. The first part is from room temperature to 230 °C, which is the main weight loss part caused by the evaporation of crystalline water present in Na₃PO₄·12H₂O [16] and ZrOCl₂·8H₂O [17]. The second weight loss is about 17.77%, corresponding to the volatilization of molten salt. In the DTA curve, a sharp endothermic peak at 131 °C can be attributed to the evaporation of crystalline water. The endothermic peak at 751 °C is caused by the formation of liquid molten salt, confirmed by no obvious weight loss in TG curve. The broad endothermic peak from 820 to 1170 °C is due to the volatilization of molten salt.

The phase composition of the as-synthesized samples prepared at different temperatures is examined by XRD (Fig. 2). Only tetragonal zirconia (t-ZrO₂) appears at 300 °C and the broad diffraction peak demonstrates a poor crystallinity and tiny size of the obtained sample. Not only diffraction peaks of t-ZrO₂ and small amount of monoclinic zirconia (m-ZrO₂), but Na₂Zr(PO₄)₂ and NaZr₂(PO₄)₃ are observed at 500 °C. The occurrence of t-ZrO₂ at room temperature is due to the crystallite size effect (below 30 nm). The increased grain size will lead to the phase transformation of t-ZrO₂ to m-ZrO₂ with the increase of heat treatment temperature [18]. The phase of Na₂Zr(PO₄)₂ and NaZr₂(PO₄)₃ can be classified as sodium zirconium phosphates, Na₉₋₄ₓZrₓ(PO₄)₃,
(x = 1, 2), which shows an extensive solid solution of ZrO₂ in Na₃PO₄ [19]. Diffraction peaks of m-ZrO₂ and Na₉₋₄ₓZrₓ(PO₄)₃ (x = 1, 2) are detected at 700 and 800 °C. As the temperature rises to 900 and 1000 °C, only m-ZrO₂ is present and no secondary phase is observed, indicating that Na₉₋₄ₓZrₓ(PO₄)₃ will dissolve in liquid molten salt and release ZrO₂ at high temperature. The whole process can be divided into following three stages: i) the decomposition of ZrOCl₂·8H₂O (equation 1); ii) the formation of Na₉₋₄ₓZrₓ(PO₄)₃ (x = 1, 2) (equation 2); iii) the release of ZrO₂ from Na₉₋₄ₓZrₓ(PO₄)₃ (equation 3).

\[
\begin{align*}
\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} & \rightarrow \text{ZrO}_2 + 7\text{H}_2\text{O} + 2\text{HCl} \quad (1) \\
x\text{ZrO}_2 + 3\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O} & \rightarrow \quad (2) \\
\text{Na}_{9-4x}\text{Zr}_x(\text{PO}_4)_3 & \rightarrow x\text{ZrO}_2 + 3\text{Na}_3\text{PO}_4 \quad (3)
\end{align*}
\]

FE-SEM micrographs of the samples synthesized at different temperatures are presented in Fig. 3. When the reaction is carried out at 700 °C (Fig. 3a), the sample is made of particles and tiny bars. Compared with the short ZrO₂ whiskers obtained at 800 °C (Fig. 3b) and the stump ZrO₂ whiskers obtained at 1000 °C (Fig. 3d), ZrO₂ whiskers synthesized at 900 °C (Fig. 3c) show better quality and have an average aspect ratio of 30, which is comparable with the aspect ratio of ZrO₂ whiskers synthesized by chemical vapour deposition [8].

Low-magnification FE-SEM micrograph of ZrO₂ whiskers prepared at 900 °C is shown in Fig. 4a. Well dispersed ZrO₂ whiskers with 100–250 nm in diameter have a uniform length ranging from 4 µm to 6 µm. The TEM image (Fig. 4b) reveals that the as-synthesized ZrO₂ whisker presents a flat and smooth surface. Three legible spots in the SAED pattern (Fig. 4c) are indexed as (101), (010) and (111) planes (PDF#65-1025) and the zone axis of the SAED is in [01] direction, which indicates the single crystalline nature of the ZrO₂ whisker. The HR-TEM image (Fig. 4d) corresponding to SAED pattern shows the lattice fringe of 0.528 nm, which is in good agreement with the (010) lattice spacing of the m-ZrO₂. It can be concluded from above results that the ZrO₂ whisker preferentially grows along [010] direction.

The reaction temperature has a great influence on the preparation of ZrO₂ whiskers. When the reaction temperature is 700 °C, the molten salt has not been melted completely or it is too viscous to flow, thus it cannot take the role of flux and effectively promote the one dimensional crystal growth. Although the molten salt has been melted at 800 °C, the negligible volatilization of molten salt (Fig. 1) and the incomplete dissolution of NaZr₂(PO₄)₃ (Fig. 2) result in the significantly low supersaturation, which is not beneficial for the growth of ZrO₂ whiskers. In comparison, a little volatilization of molten salt (Fig. 1) and the complete dissolution of NaZr₂(PO₄)₃ (Fig. 2) at 900 °C lead to the proper supersaturation, which is favourable for the one dimensional preferential growth of zirconia whiskers [20]. In addition, the excessive volatilization of molten salt at 1000 °C (Fig. 1) causes too high supersaturation, which is not beneficial for the preparation of high quality zirconia whiskers.
A schematic diagram of the growth mode is presented in Fig. 5. Most of the reactions in salt medium generally follow nucleation and growth process of an oxide compound through the dissolution of precursors and precipitation of oxide product [21]. The first step is key for the following crystal growth and it is usually difficult to find a proper molten salt for the dissolution of precursor, especially for ZrO₂. In this work, ZrOCl₂·8H₂O and Na₃PO₄·12H₂O are used as the precursor and molten salt, respectively. During the heating process, ZrOCl₂·8H₂O is first converted into ZrO₂ and exists in t-ZrO₂ due to the size effect (Fig. 5a) [18]. Then Na₉₋₄Zrₓ(PO₄)₃ (x = 1, 2) is formed by the solid reaction between small amount of ZrO₂ and Na₃PO₄·12H₂O (Fig. 5b). Afterwards, the release of ZrO₂ from the dissolved Na₉₋₄Zrₓ(PO₄)₃, combined with the volatilization of molten salt, leads to the supersaturation of ZrO₂ in liquid molten salt. From then on, the supersaturation fosters the precipitation and one dimensional growth of ZrO₂ on the surface of undissolved zirconia nuclei (Fig. 5c). Finally, the ZrO₂ grows into high quality ZrO₂ whiskers (Fig. 5d).

IV. Conclusions

In this work we developed a facile molten salt method to prepare ZrO₂ whiskers. The DTA-TG analysis reveals the melting and volatilization temperature of molten
salt. The XRD results show that the sodium zirconium phosphate Na$_{4+x}$Zr$_x$(PO$_4$)$_3$ ($x = 1, 2$) is formed at low temperature and gradually disappears with the elevating temperature. The DTA-TG analysis combined with XRD results is in good agreement with the morphology changes presented in FE-SEM micrographs. The ZrO$_2$ whiskers synthesized at 900°C have an uniform length ranging from 4µm to 6µm with average aspect ratio of 30 and preferential growth along [010] direction. The reaction temperature and the formation of Na$_{4+x}$Zr$_x$(PO$_4$)$_3$ ($x = 1, 2$) is favourable for the growth of ZrO$_2$ whiskers by adjusting the dissolution and precipitation of ZrO$_2$. Furthermore, this work suggests a valuable way for mass production of high quality ZrO$_2$ whiskers.

Acknowledgement: The authors are grateful for the Fund for National Natural Science Foundation of China (51662016), the Fund for Distinguished Young Scholars of Jiangxi Province (20171BCB23071), the Fund for Science Foundation of Jiangxi Province (GJJ160881).

References