Preparation, characterization and formation mechanism of single-crystal zirconia micro-sheets

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Abstract

Zirconia micro-sheets were prepared by molten salt method using the salt mixture of NaCl and NaF. FE-SEM, TEM, EDS, DTA-TG, XRD, Raman and FT-IR techniques were employed to characterize the morphology, phase composition and formation mechanism of the ZrO₂ micro-sheets. The obtained monoclinic ZrO₂ micro-sheets with exposed {100} facets show an average thickness of 0.2 µm. The growth of the ZrO₂ micro-sheets is proved to be assisted by the addition of fluoride. On the one hand, the addition of fluoride promotes the mass transfer of zirconia through the formation of zirconium fluoride complexes (ZrF₃–). On the other hand, fluoride adsorbed on the surface of zirconia stabilizes {100} facets and lead to the exposure of {100} facets in the final product.

Keywords: zirconia micro-sheet, molten salt method, fluoride, crystal growth

I. Introduction

As a typical structural and functional material, ZrO₂ has been extensively used in the field of ceramic tools, catalysts and catalyst supports, oxygen sensors, solid fuel cells and biomaterials owing to its excellent physical and chemical properties, such as high melting point, good chemical and mechanical stability, high toughness, ionic conductivity, excellent wear resistance and biocompatibility [1–4]. Recently, micro-sized single-crystal zirconia with significant recoverable shape deformation has received growing interest in the field of shape memory ceramics because of its fewer defects and high specific surface area for the relaxation of transformation mismatch stress [5,6]. In view of this, the as-prepared ZrO₂ micro-sheets in this work may be a good candidate for the shape memory ceramics. Up to now, a wide range of ZrO₂ morphologies such as rods [7], tetragonal stars [8], fibres [9], belts [10] and flowers [11] have been prepared by using hydrothermal method and template method. However, little effort has been reported to fabricate ZrO₂ micro-sheets. Since the facile ionic-liquid environment is favourable for the fast mass transfer [12], molten salt method has been preferentially employed to prepare the ZrO₂ micro-sheets in this work. Moreover, molten salt method has been proved to be a practical way for the preparation of Y₂O₃-stabilized ZrO₂ [13], thus the further achievement of stabilized ZrO₂ micro-sheets can be better served as shape memory ceramics.

For typical molten salt synthesis, ZrO₂ micro-sheets were synthesized by the growth from salt mixtures of NaCl and NaF. The microstructure of the ZrO₂ micro-sheets was characterized and the formation mechanism was also discussed.

II. Experimental section

All the starting materials including ZrOCl₂ · 8 H₂O, NaCl and NaF were analytical reagents and used without further purification. The powders of 2 g ZrOCl₂ · 8 H₂O, 2 g NaCl and 0.2 g NaF (mass ratio 10 : 10 : 1) were mixed and ground for 15 min in an agate mortar, then the mixture was transported into a corun-
were obtained from Raman spectrometer (Renishaw in Via) with 532 nm incident photons from an Ar ion laser.

III. Results and discussion

FE-SEM images of the samples grown from NaCl and NaCl/NaF are shown in Figs. 1a and 1b, respectively. When NaF is introduced into the molten salt, the dramatic morphology changes from tiny particles to micro-sheets can be observed, suggesting that the addition of NaF plays an important role in the formation of the micro-sheets. The thickness of the obtained micro-sheets varies from 0.1 µm to 0.3 µm and the average thickness is about 0.2 µm. EDS analysis was performed on an aluminium foil and the EDS spectrum (Fig. 1c) has indicated that the sample is only composed of the element of Zr and O with a ratio of Zr to O approximately equal to 1 : 2, which is in agreement with the formula of ZrO$_2$. The typical TEM image (Fig. 1d) further confirms its sheet-shape structure with no distinct defects.

The legible SAED pattern (Fig. 1e) viewed from [100] zone axis indicates the single crystal nature of the micro-sheets and the three spots are indexed as (001), (010) and (011) facets of monoclinic zirconia (m-ZrO$_2$, JCPDS 97-065-8755). The lattice fringes (Fig. 1f and Fig. 1g) with an interplanar lattice spacing of 0.365 nm, 0.528 nm and 0.263 nm correspond to (011), (010) and (002) atomic planes, respectively. In addition, Fig. 2 shows the XRD patterns of the sample synthesized with different amount of NaF. All of the diffraction peaks of the samples can be indexed as monoclinic zirconia (m-ZrO$_2$). It can be seen that the peak intensity of (100) and parallel (200) atomic planes become stronger with the increase of NaF, whereas the peak intensity of (111) facet is reduced when the amount of NaF is be-
Beyond 0.4 g. To intuitively understand the peak intensity changes, Table 1 gives the variation of diffraction peak intensity with the increase of NaF. The peak intensity ratios of $I_{(100)}/I_{\overline{1}1\overline{1}}$ and $I_{(200)}/I_{\overline{1}1\overline{1}}$ get promoted with the increase of NaF. This phenomenon also suggests that the growth habit of $\text{ZrO}_2$ is greatly affected by the NaF. On the basis of above results, it can be confirmed that \{100\} facets are exposed on the bottom and top surfaces of the micro-sheets.

DTA-TG curves of the precursor mixture with the addition of NaF are shown in Fig. 3. There are two obvious weight loss stages at 30–500°C and 700–1100°C in TG curve. The first weight loss is about 26.36%, corresponding to the evaporation of $\text{H}_2\text{O}$ and $\text{HCl}$ produced by the decomposition of $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$ [14]. The second weight loss is about 54.21%, which is attributed to the volatilization of the molten salt. In DTA curve, two adjacent endothermic peaks centred at 83 and 147 °C are caused by the different dehydration stages of $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$ [15]. The distinct endothermic peak at 753 °C is assigned to the melting of salt mixture, paralleling with little weight loss in TG curve. The broad endothermic peak ranging from 874 to 945 °C can be attributed to the volatilization of the molten salt. Thus, a completely melted ionic-liquid environment can be achieved at 800 °C based on above analysis, which is greatly beneficial to the mass transfer and the crystal growth of $\text{ZrO}_2$.

XRD patterns of the samples synthesized with or without NaF are shown in Fig. 4. The sample synthesized without NaF shows diffraction peaks of t-$\text{ZrO}_2$. The t-$\text{ZrO}_2$ is produced by the decomposition of $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$ and exists in metastable forms due to the small size effect for which the critical size is about $28 \pm 6 \text{nm}$ [16]. The Scherrer equation $d = K \cdot \lambda/(\beta \cos \theta)$ [17] was applied to calculate the average crystallite size $d$ (θ is the diffraction angle, $K = 0.89$, $\lambda$ is X-ray wavelength, $\beta$ is the full width at half maximum). The average crystallite sizes of t-$\text{ZrO}_2$ and m-$\text{ZrO}_2$ are estimated to be 32 and 44 nm, respectively, where the average crystallite size of t-$\text{ZrO}_2$ satisfies the small size effect, explaining the existence of metastable t-$\text{ZrO}_2$, at room temperature. These XRD results reveal that the addition of NaF can effectively promote the crystal growth and crystallinity of the obtained $\text{ZrO}_2$, which has also been confirmed by the FE-SEM images.

Raman spectra of the samples synthesized with or without NaF are shown in Fig. 5. The Raman spectra of intensity of monoclinic zirconia (m-$\text{ZrO}_2$) and no secondary phase such as tetragonal zirconia (t-$\text{ZrO}_2$) is observed. However, the sample synthesized without NaF shows diffraction peaks of t-$\text{ZrO}_2$. The t-$\text{ZrO}_2$ is produced by the decomposition of $\text{ZrOCl}_2 \cdot 8 \text{H}_2\text{O}$ and exists in metastable forms due to the small size effect for which the critical size is about $28 \pm 6 \text{nm}$ [16]. The Scherrer equation $d = K \cdot \lambda/(\beta \cos \theta)$ [17] was applied to calculate the average crystallite size $d$ (θ is the diffraction angle, $K = 0.89$, $\lambda$ is X-ray wavelength, $\beta$ is the full width at half maximum). The average crystallite sizes of t-$\text{ZrO}_2$ and m-$\text{ZrO}_2$ are estimated to be 32 and 44 nm, respectively, where the average crystallite size of t-$\text{ZrO}_2$ satisfies the small size effect, explaining the existence of metastable t-$\text{ZrO}_2$, at room temperature. These XRD results reveal that the addition of NaF can effectively promote the crystal growth and crystallinity of the obtained $\text{ZrO}_2$, which has also been confirmed by the FE-SEM images.

Raman spectra of the samples synthesized with or without NaF are shown in Fig. 5. The Raman spectra of

### Table 1. Variation of diffraction peak intensity with the increase of NaF

<table>
<thead>
<tr>
<th>Amount of NaF [g]</th>
<th>$I_{\overline{1}1\overline{1}}$</th>
<th>$I_{100}$</th>
<th>$I_{200}$</th>
<th>$I_{100}/I_{\overline{1}1\overline{1}}$</th>
<th>$I_{200}/I_{\overline{1}1\overline{1}}$</th>
<th>Peak intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>757</td>
<td>62</td>
<td>121</td>
<td>0.082</td>
<td>0.160</td>
<td>0.160</td>
</tr>
<tr>
<td>0.2</td>
<td>890</td>
<td>75</td>
<td>145</td>
<td>0.084</td>
<td>0.162</td>
<td>0.162</td>
</tr>
<tr>
<td>0.4</td>
<td>889</td>
<td>98</td>
<td>288</td>
<td>0.110</td>
<td>0.324</td>
<td>0.324</td>
</tr>
<tr>
<td>0.6</td>
<td>754</td>
<td>118</td>
<td>646</td>
<td>0.156</td>
<td>0.414</td>
<td>0.414</td>
</tr>
</tbody>
</table>
both samples are almost the same in spite of the different peak intensities of Raman bands at 589 cm\(^{-1}\) marked as asterisks (*). Among 17 Raman bands observed in both samples, except two peaks at 264 and 589 cm\(^{-1}\) ascribed to t-ZrO\(_2\) [18], all other bands are assigned to vibration modes of m-ZrO\(_2\) [19]. Noticeably, the sample synthesized without NaF shows a relatively stronger peak intensity at 589 cm\(^{-1}\) than the sample synthesized with NaF, indicating the higher content of t-ZrO\(_2\) in the former, which is consistent with the XRD results. The existence of t-ZrO\(_2\) in micro-sheets detected by Raman unlike with XRD confirms again that Raman spectrum is a very useful technique for the determination of crystall phase of zirconia. In the ionic-liquid salt system, it has been proved that the addition of the fluoride can effectively promote the mass transfer process of ZrO\(_2\), which is achieved by the formation of chemical species ZrF\(_3^-\) as shown in following equation [20,21]:

\[
\text{ZrO}_2 + 7 \text{F}^- \rightarrow \text{ZrF}_3^- + 2 \text{O}^{2-}
\]

Thus, the crystal size of the obtained ZrO\(_2\) can rapidly grow from nanoscale to microscale. In addition, due to the small amount of fluoride in this work, ZrF\(_3^-\) species remain dissolved in the melt without forming other compounds [20], which is also confirmed by the XRD and Raman analysis.

Since the early growth stage of the ZrO\(_2\) below melting temperature is crucial to further understand the formation mechanism of sheet-shaped ZrO\(_2\), the XRD pattern and FT-IR spectrum of the sample synthesized at 300 °C for 5 h are given in Fig. 6. As shown in Fig. 6a, the pattern is mainly indexed as m-ZrO\(_2\) except for some diffraction peaks belonging to t-ZrO\(_2\). In addition, the broad diffraction peaks indicate the small size and low crystallinity of obtained m-ZrO\(_2\), which is favourable for the growth of ZrO\(_2\) micro-sheets relative to the highly crystalline ZrO\(_2\) [12]. Fig. 6b shows the FT-IR spectrum of the sample synthesized at 300 °C. The broad peak around 3475 cm\(^{-1}\) is attributed to the physically absorbed –OH with Zr\(^{4+}\). Bands at 2800–2980 cm\(^{-1}\) and 1460 cm\(^{-1}\) are assigned to the \(-\text{CH}_2\)– stretching vibration and \(-\text{CH}_3\) band vibration [22], respectively, which arise from the residual ethanol in the sample. The peak centred at 2360 cm\(^{-1}\) is due to the stretching and bending vibrations of \(-\text{OH}\) groups, while the band at 1635 cm\(^{-1}\) is associated with the bending vibrations of Zr–OH [23]. Accordingly, the weak peak at 472 cm\(^{-1}\) is assigned to the band of Zr–F, suggesting that the ZrO\(_2\) shows high affinity for F\(^-\) [24]. A growth mechanism for ZrO\(_2\) micro-sheets can be proposed based on the above analysis. As shown in Fig. 7, tiny m-ZrO\(_2\) is formed at the initial growth stage and its theoretical equilibrium shape is composed of four
Facets. The surface energies of these facets increase in the following order: \((\overline{1}1\overline{1}) < (11\overline{1}) < (01\overline{1}) < (00\overline{1})\) [25]. In addition, the facet with higher energy means faster growth rate in the crystal growth. Then, the adsorbed \(\text{H}_2\text{O}\) and bonded \(-\sigma\text{OH}\) on the surface of \(\text{ZrO}_2\) give a chance for the appearance of new (100) facet [25]. It should be noticed that (100) facet possesses higher surface energy than the former four facets [25,26]. So, (100) facets show stronger adsorption for \(\text{F}^-\) than other four facets. Correspondingly, the \(\text{F}^-\) adsorption leads to the inverse surface energy, of which the (100) facet is the lowest one. This similar phenomenon is also observed in the stabilization of highly reactive \{001\} facets in \(\text{TiO}_2\) by the addition of fluoride [27]. Finally, the sheet-shaped \(\text{ZrO}_2\) with exposed \{100\} facets is achieved via the further growth of \(\text{ZrO}_2\) in the liquid salt flux.

IV. Conclusions

This work has developed a facile molten salt method to fabricate \(\text{ZrO}_2\) micro-sheets. The as-prepared \(\text{ZrO}_2\) micro-sheets with average thickness of \(0.2\ \mu\text{m}\) show exposed \{100\} facets and are characterized with the monoclinic structure. The addition of \(\text{NaF}\), essential for the preparation of \(\text{ZrO}_2\) micro-sheets, is found to play an important role in accelerating the mass transfer of \(\text{ZrO}_2\) through the formation of \(\text{ZrF}_3^{3-}\) and controlling the sheet-shape by the \(\text{F}^-\) adsorption on the surface of \(\text{ZrO}_2\). Moreover, the special micro-sized single-crystal \(\text{ZrO}_2\) sheets will find application in the shape memory ceramics in the future.

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