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Preliminary study on the growth mechanism of zircon whiskers prepared via non-hydrolytic sol-gel method combined with carbon black as reducing agent

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Abstract

Zircon whiskers were prepared at 700 °C via non-hydrolytic sol-gel method combined with carbon black as reducing agent, $Si(OC_2H_5)_4$ (TEOS) and $ZrCl_4$ as precursors and LiF as mineralizer. The whiskers were characterized and their growth mechanism was discussed. The results show that the introduction of carbon black is beneficial for the preferential axial growth of zircon crystals into whiskers. The diameter and aspect ratio of zircon whiskers are 30–40 nm and 6–15, respectively. The zircon whiskers grow along the [001] direction, which is c-axis oriented. The growth mechanism is revealed to be the screw dislocation mechanism with the mass transport mainly from the zircon crystal particle matrix.

Keywords: *non-hydrolytic sol-gel process, whiskers, zircon, growth mechanism*

I. Introduction

Whiskers are filament single crystals and have attracted much attention because of their near theoretical strength value, unique physical and chemical performance [1,2]. By adding whiskers into the ceramic tool composites, the strength and toughness can be significantly improved [3–5]. However, there are very few types of whiskers commercially available on a large scale [6,7]. Zircon whiskers can be a potential reinforcing phase for ceramic composites to enhance the comprehensive mechanical properties, due to their high strength, modulus, wear resistance, thermal stability and melting point, low thermal expansion coefficient and cost [8–11]. It has been demonstrated that zircon whiskers can be applied potentially in the fields of aviation, aerospace, automotive, energy etc. [8–11]. Currently, there are several zircon whiskers preparation methods of non-hydrolytic sol-gel method combined with: carbon black as reducing agent [8,9]; using ZrF_4 as catalyst [10]; molten salt method [11]. They are all developed previously by our group. However, the growth mechanism of zircon whiskers prepared via non-hydrolytic sol-gel method combined with carbon black as reducing agent has not been investigated. Based on our previous studies [8,9], the aim of this paper is to discuss the growth mechanism of zircon whiskers prepared via non-hydrolytic sol-gel method combined with carbon black as reducing agent.

II. Materials and methods

Zircon whiskers were prepared via non-hydrolytic sol-gel method combined with carbon black as reducing agent, $Si(OC_2H_5)_4$ (TEOS) and $ZrCl_4$ as precursors and LiF as mineralizer. All the chemical reagents used in this work were of analytical grade and purchased from Sinopharm chemical reagent Co. Ltd., Beijing, China.

With the Si/Zr and Li/Zr molar ratio being 1.2 and 0.36 [12], respectively, 8 ml of TEOS was mixed with $ZrCl_4$ and LiF. 30 ml of ethanol was added into the

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above mixture with stirring, and transparent solution was obtained. Zircon sol without carbon black formed after refluxing at 110 °C for 24 h.

For the sample prepared with carbon black, 30 ml of ethanol was placed in a beaker with 5 wt.% (mass percentage to ethanol) of polyvinyl butyral (PVB) for the carbon black suspension dispersivity and stirred for 12 h. After that, the carbon black was added and stirred for another 12 h to obtain carbon black suspension. Then carbon black suspension was poured into zircon sol and stirred for 12 h to form zircon sol with carbon black. These samples were dried at 110 °C. Finally, they were heat treated at 700 °C for 30 min in muffle furnace.

The phase composition of the samples was analysed by X-ray diffraction (XRD, D8 Advance, Bruker AXS Co. Ltd.) with Cu Kα radiation (λ = 0.154 nm), with 2θ scanning range of 5–70°. The morphologic information of the samples was obtained by transmission electron microscopy (TEM, JEM-2010, JEOL). TEM was also used to characterize and to analyse the microstructure and growth direction of whiskers.

III. Results and discussion

X-ray diffraction (XRD) patterns of the samples prepared with and without carbon black are presented in Fig. 1. In these two XRD patterns, only several very weak diffraction peaks of ZrO_2 are observed. The other diffraction peaks are in good agreement with those of tetragonal zircon phase, with the following cell parameters: $a = b = 0.6604$ nm, $c = 0.5979$ nm, $\alpha = \beta = \gamma = 90°$, and density of 4.60 g/cm^3, (JCPDS Card No. 06-0266). These results indicate that the synthesis products have high purity. It is worth pointing out that some differences are observed in these two XRD patterns. The strongest peak intensity appears for the (200) lattice plane. However, the peak intensity for it and peak intensity ratio $I_{(200)}/I_{(112)}$ of the sample prepared with carbon black are larger than that of the sample prepared without carbon black, indicating the preferential growth of sample prepared with carbon black. Meanwhile, the half-peak width of peaks in the XRD pattern of the sample prepared with carbon black is wider and more uneven than that of the sample prepared without carbon black, which indicates that there are more crystal defects in the sample prepared with carbon black [13].

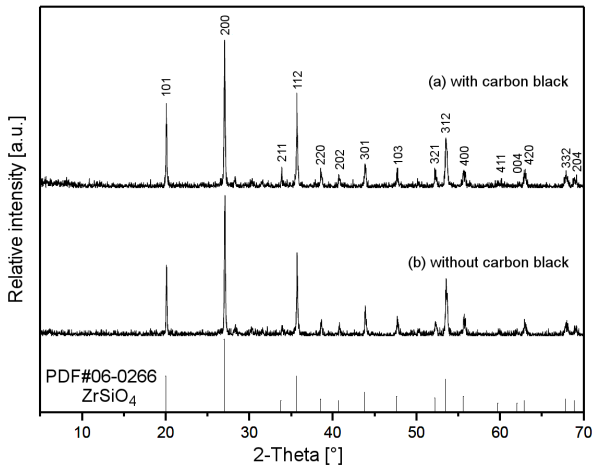

Figure 1. XRD patterns of samples prepared with and without carbon black

Figure 2 shows the morphologies of the samples without and with carbon black. Figure 2a is a typical morphology of zircon prepared by non-hydrolytic sol-gel method, which is mainly composed of particles with a bit of agglomeration [12]. The sample prepared with carbon black shown in Fig. 2b is mainly composed of whiskers; their diameter and aspect ratio are 30–40 nm and 6–15, respectively. Moreover, some smaller nanoparticles have also been observed in these whiskers. High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) analysis were also carried out to further investigate the microstructures of these whiskers. Figure 2c and 2d show the HRTEM images of the whiskers. The inset SAED pattern corresponding to the selected-area in Fig. 2c is related to a single crystal that can be indexed as tetragonal-structured zircon. This is consistent with the XRD results. Figure 2d displays a very high degree of order, which shows that the whisker has a highly crystalline structure. The inter space between neighbouring fringes along the axis of whisker is about 3.302 Å, which is very close to the theoretical value for (200) planes indicated by JCPDS Card (No. 06-0266) of zircon. Therefore, the preferred growth direction of crystal whiskers is along with the crystal direction of [001] in the lattice structure of zircon, which is c-axis oriented.

In order to discuss the growth mechanism of zircon whiskers prepared via non-hydrolytic sol-gel method combined with carbon black as reducing agent, further investigation by TEM was performed. Thus, Fig. 3 shows TEM images of some sparse regions of the sample prepared with carbon black and shorter holding time of 10 min at 700 °C. At the tip of zircon whisker shown in Fig. 3a, there is an obvious axial screw dislocation which can be indicated by the light and dark contrast, the dimple and bulge [14–18]. This axial screw dislocation provides a self-perpetuating growth step and greatly promotes the mass transport in the process of whisker growth [19–21]. The formation of screw dislocation is mainly caused by atmosphere [22], thermal fluctuation [23] and impurity [24] with the introduction of carbon black. However, the screw dislocation is in a metastable equilibrium and it would disappear in the whisker growth process because of continuous diffusion, offset between each other or different dislocation slip direction. Meanwhile, restricted by the observation range, it is often very difficult to observe the screw dislocation in the whisker test process [25,26]. Therefore, it is sparse among many zircon whiskers. Figure 4b reveals the growth process of zircon whiskers. As it can be seen from positions 1, 2, 3 and 4, the starting point

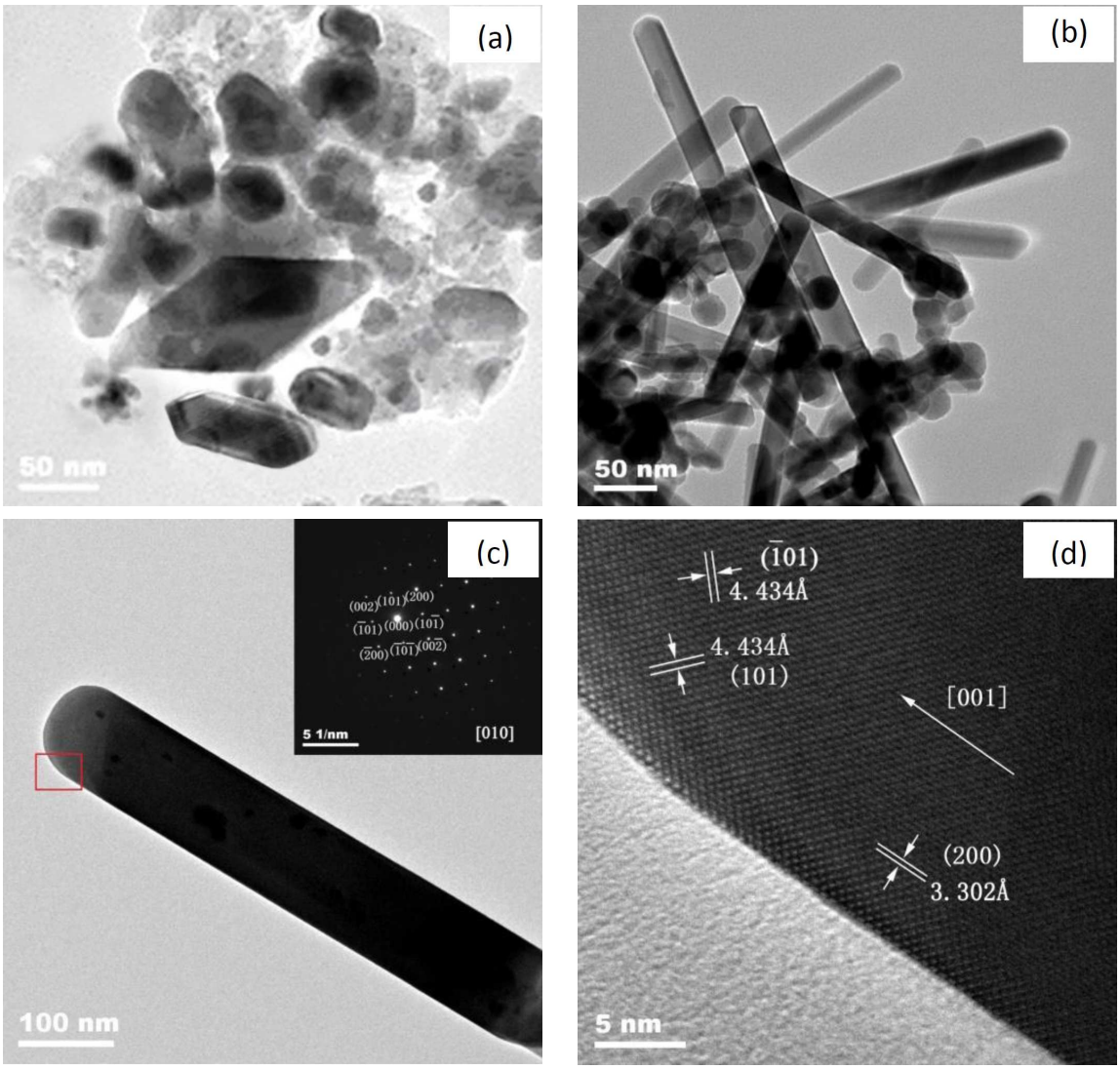

Figure 2. TEM, HRTEM images and SAED pattern of samples

of what is to become a zircon whisker is the formed zircon particle. This means that zircon particles (skeleton) form firstly, and they act as nuclei for the growth of zircon whiskers. There are bulges on the particle surface (such as positions 1 and 2 in Fig. 3b); there are also transient states in the whiskers growth process (such as positions 3 and 4 in Fig. 3b) and these characteristic positions indicate the Frank dislocation growth mechanism of zircon whiskers. In addition, for a screw dislocation, Frank [25,26] has suggested the formation of a bulge, which is a prerequisite for whisker growth. However, it is different from the general mass transport of adsorbing action of the centre axial screw dislocation in low vapour supersaturation [27]. The mass transport in the process of whisker growth is mainly from the particle matrix along direction indicated by the arrow, which can be deduced from the formation of the concave and the neck at the arrow.

Combining the above analysis and our previous reports [8–12] the possible growth mechanism of zircon whiskers might be as follows (Fig. 4): i) the NHSG reaction between precursors of $ZrCl_4$ and $Si(OC_2H_5)_4$ with the formation of ≡Si−O−Zr≡ in the wet gel and the elimination of alkyl halides C_2H_5Cl; ii) the exsolution of ZrO_2 from ≡Si−O−Zr≡ with the formation of ≡Si−O−Si≡ in the drying process and low temperature in the heat treatment; iii) from about 550 °C, LiF begins to exert its mineralizing agent role, promotes the formation of SiF_4 firstly and then urges crystallization of zircon. Meanwhile, carbon black uniformly adsorbs between the particles reacting with O_2 to form weak reducing atmosphere; iv) previously formed weak reducing atmosphere promotes the crystal defect formation of screw dislocation which urges the one-dimensional preferential growth of zircon to whiskers. The keys for zircon whiskers formation are NHSG process and the introduction of carbon black. The combination of NHSG process with the general mineralizer LiF can reduce the synthesis temperature of zircon to 600 °C which can provide suitable crystal growth rate and growth dynamic differences of three dimensions at 700 °C. The introduction of carbon black creates a reducing atmosphere during the nucleation and growth of zircon crystal, which is beneficial for the

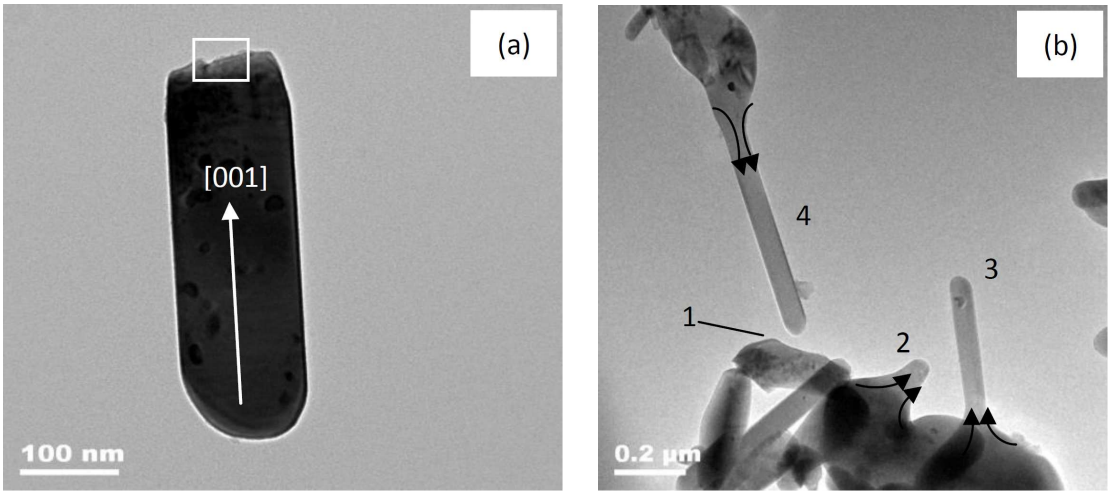

Figure 3. TEM images of some special regions of the sample with carbon black

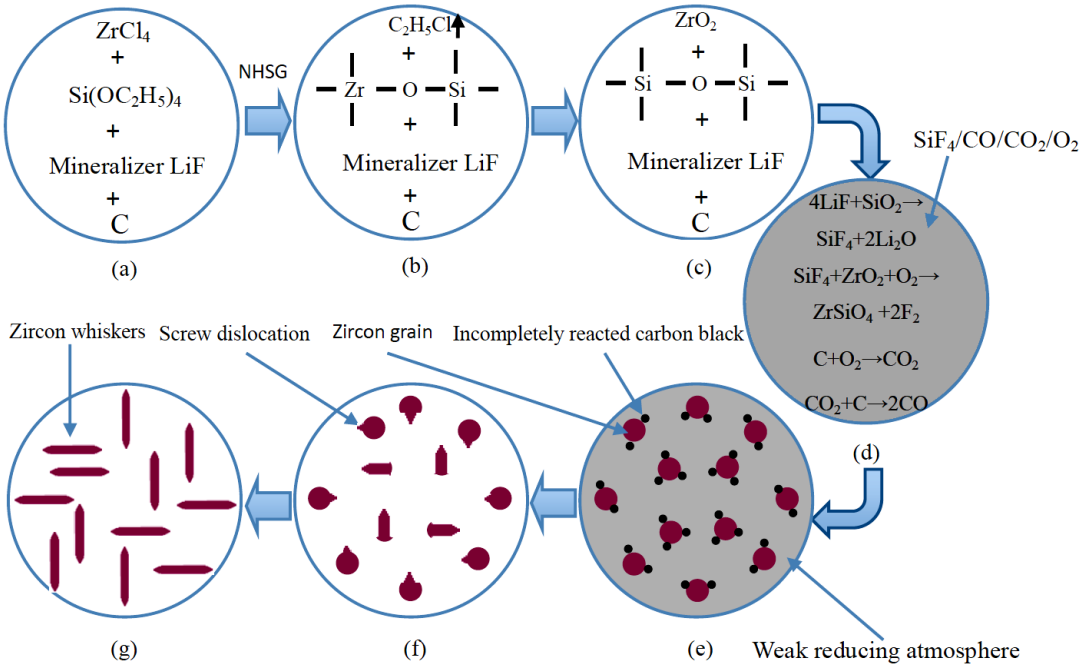

Figure 4. Schematic of the zircon whiskers growth mechanism

formation of crew dislocation and further promotes the one-dimensional preferential growth to form zircon whiskers.

IV. Conclusions

In this paper, zircon whiskers were successfully prepared at 700 °C via non-hydrolytic sol-gel method combined with using carbon black as reducing agent. XRD, TEM and the corresponding SAED pattern have been utilized to reveal the growth mechanism. The screw dislocation is probably the driving force for the whisker growth. Non-hydrolytic sol-gel method reduces the synthesis temperature of zircon. It also provides suitable crystal growth rate and three dimensions growth dynamic differences at 700 °C. Weak reduction atmosphere created by the introduction of carbon black is beneficial to the formation of crew dislocation. It further promotes the one-dimensional preferential growth to form zircon whiskers.

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