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FACTORS INFLUENCING THE PREPARATION OF ULTRA-FINE ZrB2 POWDERS VIA CARBOTHERMAL REDUCTION

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The effect of different molar ratio between Zr^{4+} and citric acid, different pH values, temperatures and dispersant (polyethylene glycol) contents on amorphous precursor of zirconium diboride (ZrB_2) and synthesized powders were investigated. The fourier transform infrared spectroscopy showed that the optimal condition of complexation is Zr^{4+}/citric acid molar ratio of 2 and pH value is 1. Field emission scanning electron microscopy (FESEM) showed that synthesized powders exhibited near-spherical morphology with a low temperature (50 ^{o}C) with the increase of temperature, ZrB_2 powders proceeded with the growth process which was complied with the Ostwald ripening model and the Ostwald-Freundlish equation. Transmission electron microscopy (TEM) showed, besides the dispersing function, polyethylene glycol could also facilitate crystal grains to reunite, and result in the ordered arrangement of crystal grains, the synthesized powders with excellent homogeneity and dispersity, especially with the polyethylene glycol content of 2 wt.%. The following particle size distribution measured by laser particle size analyzer had also provided clear evidence for this.

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Keywords: Sol-gel; Carbothermal reduction; Amorphous precursor; Zirconium diboride powders; Ostwald ripening model

1. Introduction

As an important member of ultra-high-temperature ceramics, ZrB_2 ceramics have great potential for application in the field of high-temperature structural material [1-3], because of its unique chemical stability and excellent physical properties, such as high melting temperature, low density, high strength, high thermal conductivity, resistance to high-temperature oxidation, ablation and thermal shock [4-9]. In previous studies, it has been found that high purity fine ZrB_2 powders as raw materials could enhance the mechanical properties and increase the driving force for sintering [10-11]. Therefore, in the last decade, there has been an increasing focus on the production of ceramic powder with ultrafine or nano-scale particles and nano-grained sintered particles. Exceptional properties such as excellent sinterability and improved mechanical properties of the formed nano-grained particles are the motivation for this focus [12-13].

Presently, ZrB_2 powders could be synthesized by these methods of solid-state reaction, electrochemical, mechanical alloying and self-propagating high-temperature synthesis. However, these methods either require a high temperature or a long production period, besides, the powders synthesized from these methods also have a relatively larger particle size and poor sinterability. There is thereby an urgent need but it is still a significant challenge to develop ideal ZrB_2 powders. For purpose of fabricating ultra-fine ZrB_2 powders with ideal size and high purity, many researchers have adopted sol-gel method which is high intimacy at atomic-scale or molecular-scale. In our previous study, ZrB_2 powders with particle size range of 0.2~0.6μm and specific surface area of 88.14 m^2/g had been synthesized successfully from inorganic-organic hybrid precursors via carbothermal reduction [14]. However, the effect of some factors on the synthesis and growth process of ZrB_2 powders remains obscure now and needs further investigation.

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The present study attempts to further clarify the effect of different Zr^{4+}/citric acid molar ratio, different pH values, temperatures and polyethylene glycol contents on amorphous precursor of ZrB_2 and synthesized powders.

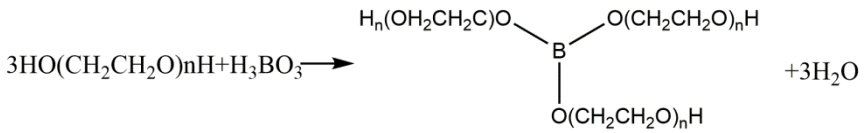
2. Experimental

Firstly, the solution of zirconium nitrate pentahydrate (Kermel Chemical Reagent Co., Ltd. Tianjin, China), boric acid(Sailboats Chemicals Co., Ltd. Tianjin, China), citric acid(Sailboats Chemicals Co., Ltd. Tianjin, China) all with the molar concentration of 0.5 mol/L were prepared by dissolving them in deionized water. The mixture of the solution of zirconium nitrate pentahydrate and boric acid was continually stirred at certain temperature (50℃, 60℃, 70℃) for 1h, after that, polyethylene glycol with different contents was added under continual stir. 20 minutes later, Citric acid dissolved in ethanol was dropwise added to form stable sol. Ammonia-water, which was used to adjust different pH values (pH=1, 4, 8), were introduced into the mixed solution obtained in the previous step to form a Zr-B-C-O gel. Finally, the Zr-B-C-O-containing gel was dried at 110℃ for 10~12h and then ground. Therefore, ZrB_2 precursors had been prepared. The subsequent heat treatment was performed at a heating rate of 2℃ /min to the target temperature of 1600℃ and then hold for 2h in alumina tube furnace under flowing argon atmosphere (Ar).

Microstructure was characterized by field emission scanning electron microscope (FESEM, JSM-7800F, Japan) and transmission electron microscope (TEM, JEM-2100, Japan). The structure of amorphous precursor of zirconium diboride was characterized by infrared spectroscopy (IR). Particle size distribution of synthesized powders was measured by laser particle size analyzer (OMEC Easysizer20, China).

3. Results and discussion

In general, the stability of sol is influenced by the concentration of sol directly. The raise of solid content can result in that the stability of sol reduces gradually. However, the sol stability can be promoted with stabilizer which changes the composition of three-dimensional network. The former research has indicated that the network structure is formed by zirconium hydrolysis and condensation reactions during the synthesis process of ZrB_2 precursors [15]. Nevertheless, the influence of boron on sol network structure could not be ignored, which could further affect the morphology and composition of ZrB_2 powders. In this research, boron was introduced into the sol network by adding polyethylene glycol as bridge bond. As a result, boron participated in the reaction process of building up of network, which increases the stability and uniformity of sol. According to the former researches [16, 17], boric acid could react with polyhydric alcohol and then formed chelate complex, and the solubility of boric acid in solvent was effectively improved through the coordination reaction, which significantly improved yield of ZrB_2 products. Boron atom, lack of electron, can react with polyhydric alcohol and then generates boron complex by releasing proton (Eq.1).



Scheme 1. Boron complex generated by the reaction of boric acid and polyhydric alcohol

Fig.1 shows FTIR spectra of the precursor powders with different Zr^{4+}/citric acid molar ratios, hereinafter referred to as R. There existed obvious characteristic absorption peak at 1420 cm^{-1}, which belonged to the characteristic peak of B-O-C bond, near by the characteristic absorption peak of B-OH (1370cm^{-1}) [18]. The reaction between boric acid and polyhydric alcohol

resulted in the transformation of B-OH into B-O-C bond. In addition, there existed several obvious peaks formed by hydrolysis of Zr^{+4} complex anions at low wavenumbers (i.e. 645cm^{-1} and 537cm^{-1}). From FTIR spectrum as shown in Fig.1, the characteristic absorption peaks of 819cm^{-1}, 1033cm^{-1}, 1188cm^{-1} were assigned to Zr-O-Zr, Zr-O-C and Zr-O-C-B bond, respectively [18]. With the proceeding of hydrolysis and condensation reaction, Zr-O-Zr and Zr-O-C-B networks were formed in the sol. Compared to single Zr-O-Zr network structure, the sol consisting of Zr-O-Zr and Zr-O-C-B networks became more stable and uniform in our research [19]. By contrast, the whole characteristic vibrating peaks gets maximum intensity when R is 2. Therefore, the optimal ratio of Zr^{4+}/citric acid was experimentally determined as 2 in our research.

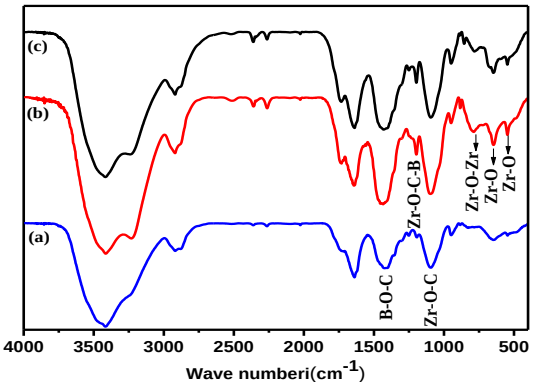


Fig. 1. Infrared analysis of the precursor with different molar ratio between Zr^{4+} and citric acid (a) R=3; (b) R=2; (c) R=1

Fig. 2 shows FTIR spectra of the precursor powders with different pH values. For reference, the infrared analysis of citric acid was also included (Fig. 2(d)). In experimental process, with gradual addition of ammonium hydroxide, there firstly generated milky precipitation and then turned to be colorless transparent. In the early stage of the reaction, after adding certain amount of ammonia-water equivalent to citric acid, then continued to increase the pH value of reaction system, there would form coordinate band between Zr^{4+} and citrate ions generated from completely acidolysis of citric acid. Moreover, this coordination compound displays electrically neutral and thus generated colloidal precipitate. When the reaction system turns to be alkaline, there formed the combination of Zr^{4+} and a certain amount of hydroxyl, this coordination compound become negatively charged accordingly and thus colloidal precipitate dissolved to be transparent. There existed obvious characteristic absorption peak at 1720cm^{-1}, which was assigned to the C=O (carbonyl group) antisymmetric stretching vibration of —COOH (fig. 2(d)). Close to the characteristic absorption peak of C=O, There existed another characteristic peak at 1667cm^{-1} originated from the carbonyl group of COO- complexing with Zr^{4+} [20]. It could be observed clearly that these characteristic peaks were weakened gradually with the increase of pH value, it reaches the strongest when pH value is 1 (Fig. 2(a)). Nonetheless, when the pH value is 8, these characteristic peaks of Zr-O and Zr-O-Zr became weaker and even disappeared (Fig. 2(c)), namely that the alkaline condition goes against the complexation reaction of Zr^{4+} and citric acid. Taken together, it demonstrated that the pH value is crucial as it exerts significant influence on the stability of sol, especially in the acidic reaction system. Therefore, the optimal pH value is 1 in this synthesis reaction system.

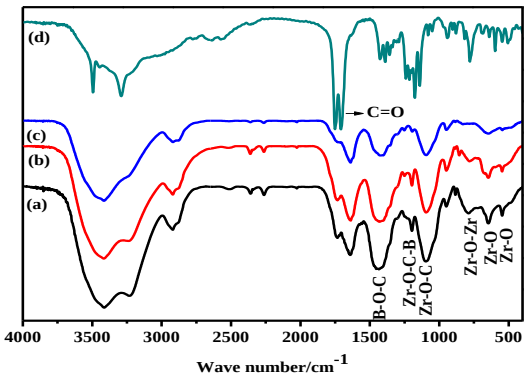


Fig. 2. Infrared analysis of the precursor with different pH
(a) pH=1 ; (b) pH=4 ; (c) pH=8

FE-SEM micrographs of ZrB_2 powders obtained with different temperatures provide insight into the particle morphology in Fig.3. Trends in the product morphology are clearly observable. The particle size of ZrB_2 increased from about 150-430nm (Fig.3(a)) for the lowest sol-gel temperature, to submicron values for the highest sol-gel temperature (Fig.3(c)). When the temperature was low (50℃), it can nucleate rapidly and generally avoid secondary nucleating, Therefore, ZrB_2 powders with a narrow size range exhibited near-spherical morphology (Fig.3(a)). Upon heating to a relatively high temperature (60℃), ZrB_2 particles, which exhibited irregular morphology, gradually increased and distributed nonuniformly. Meanwhile, there existed some smaller particles (Fig.3(b)). As temperature increased to 70℃, there were much more smaller ZrB_2 particles deposited onto the surface of big ZrB_2 particles (Fig.3(c)). According to the Ostwald Ripening model, this thermodynamically-driven spontaneous process occurs because larger particles are energetically favored than smaller particles [21]. This stems from the fact that molecules on the surface of a particle are energetically less stable than the ones in the interior. As the system tries to lower its overall energy, as shown in Fig.4, molecules on the surface of a small ZrB_2 particle will tend to detach from the particle and diffuse into the solution. When all small ZrB_2 particles do this, it increases the concentration of free molecules in solution. When the free molecules in solution are supersaturated, the free molecules have a tendency to condense on the surface of larger ZrB_2 particles. Therefore, all small ZrB_2 particles shrink while larger ZrB_2 particles grow, and overall the average size will increase.

According to Ostwald-Freundlish equation:

$$S = S_0 \exp(\frac{2\gamma_{SL} V_m}{R_g T_r}) \tag{2}$$

Where S is the solubility of small particles with a radius of r; S_0 is the constant; γ_{SL} is the molar ratio of solid phase materials; R_g is the ideal gas constant; T_r is the temperature. Thus, with the increase of temperature, the solubility of small ZrB_2 particles decreases and they redeposit onto the surface of those big particles (Fig.3(c)). Increase in temperature also weaken the intermolecular interactions in liquids so that the viscosity of liquids decreases, this leads to molecular collision happening more frequently and the probability of particles agglomeration increase. Finally, size of ZrB_2 particles increase with high-temperature pyrogenation [22]. Besides, for hydrolysis reaction belonging to endothermic reaction, the increase of temperature also contributes to hydrolysis reaction, increase crosslinking points, accelerate the aging of colloidal particles in the solution and ultimately make the size of colloidal particles increase [23].

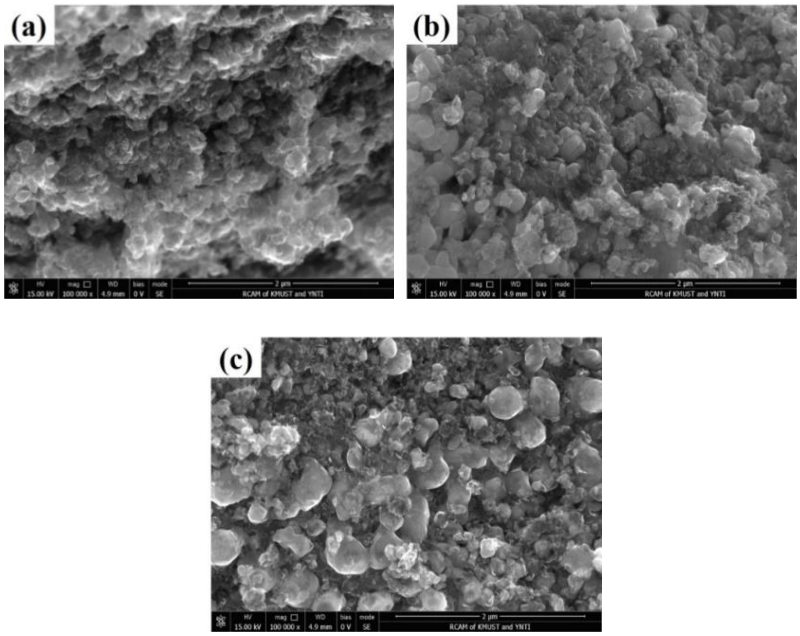


Fig. 3. FE-SEM images of ZrB_2 powders with different temperatures.
(a)50 ℃；(b)60 ℃；(c)70 ℃

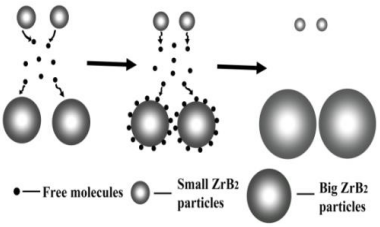


Fig. 4. Schematic of ZrB2 particles Ostwald ripening

Fig.5 shows TEM images of ZrB_2 powders with different polyethylene glycol contents. Without polyethylene glycol, ZrB_2 grains aggregated heavily and arranged irregularly (Fig. 5(a)). When polyethylene glycol content was 1 wt.%, ZrB_2 grains' dispersion had been improved and it displayed some of regularity (Fig. 5(b)). For polyethylene glycol additions up to 2 wt.%, these ZrB_2 grains dispersed better overall, especially that individual grain could be observed clearly (Fig. 5(c)). Addition of polyethylene glycol content higher than 2 wt.% resulted in that ZrB_2 grains aggregated heavily again, reunited and finally formed big ZrB_2 particles. Moreover, small grains contained in individual ZrB_2 particles showed the similar arrangement orientation (Fig. 5(d)).

Polyethylene glycol in the product phase is located as a coating on the formed ZrB_2 grains' surface. The formed ZrB_2 grains are surrounded by polyethylene glycol and are embedded in the round shaped formation of polyethylene glycol, which plays a key role in the refining of the ZrB_2 particle size by keeping apart the ZrB_2 grains. Addition of polyethylene glycol not only prevents the growth of colloidal grains, but also makes colloids crosslink in order for "bridging effect" of citric acid and polyethylene glycol. Finally, it forms chain or annulus structure in the sol-gel system, which could contribute to the colloid stability [24, 25]. Under the influence of surface hydroxyl groups of polyethylene glycol, small grains coated with excessive amount of polyethylene glycol reunite and form small particle clusters, subsequently these small ZrB_2 particle clusters collide and permeate with each other to form big particle clusters, just as we observed in Fig.5(d). Taken together, polyethylene glycol can not only coat the surface of particles to achieve dispersion effect, but also can be a "guide" to the cross linking of the clusters in the sol.

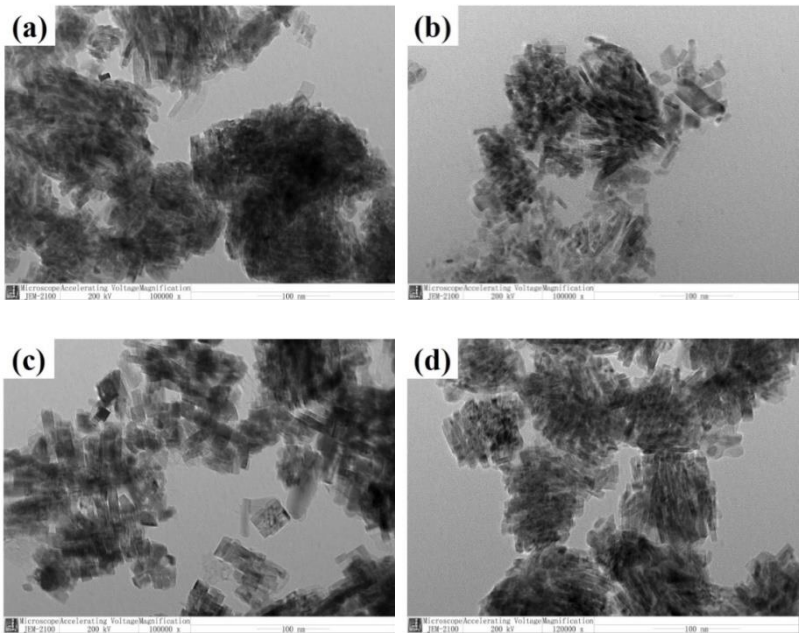


Fig. 5. TEM images of the products with different polyethylene glycol contents.
(a) no added,(b) 1 wt.%,(c)2 wt.%, (d) 3 wt.%.

Fig. 6 shows the patterns of particles size distribution of ZrB_2 powders obtained with 0 and 2 wt.% polyethylene glycol contents. Table.1 shows the characteristic size values of ZrB_2 particles. With the addition of 2 wt.% polyethylene glycol content, The average particle size of ZrB_2 decreased from 260nm to 190nm and the distribution range of ZrB_2 particles size narrowed further (Fig. 6, Table.1). It proves that proper addition of polyethylene glycol plays a key role in the refining of the ZrB_2 particle size by keeping apart the ZrB_2 grains.

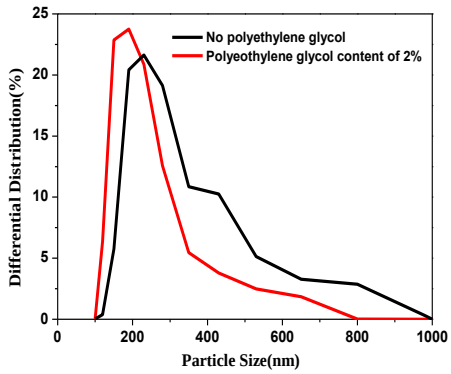


Fig. 6. The patterns of differential distribution of ZrB_2 powders.
(a) r=2,pH=4,T=50 ℃; (b) r=2,pH=4,T=50 ℃, c=2%

Table 1. Characteristic values of ZrB_2 powders particle size

Content/nm	D50	D10	D25	D75	D90
(a)	260	160	180	340	450
(b)	190	120	140	230	290

4. Conclusions

Effects of the molar ratio of Zr^{4+} to citric acid, sol-gel temperature, pH value and content of polyethylene glycol on ZrB_2 powders synthesized by carbothermal reduction were investigated. It was discovered that, the optimum condition of complexation reaction was Zr^{4+}/citric acid molar ratio of 2 and pH value of 1. When the temperature was low (50℃), ZrB_2 powders exhibited near-spherical morphology and dispersed well, the increase of temperature resulted in the growth of ZrB_2 powders which process complied with the Ostwald ripening model and the Ostwald-Freundlish equation. Besides the disperse function, polyethylene glycol can also guide sol grains to reunite, this resulted in the ordered arrangement of crystal particles and synthesized powders with good homogeneity and dispersity, especially with polyethylene glycol content of 2 wt.%.

Acknowledgement

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