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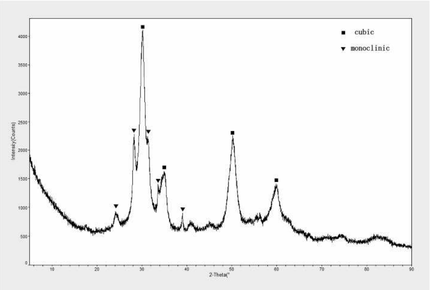

Cubic phase ZrO_2 can be synthesized with amorphous carbon as a phase transition promoter.

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ARTICLE

Preparation of t-ZrO_2 by sol-gel process with carbon as a phase transformation promoter

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The cubic and tetragonal ZrO_2 were synthesized by sol-gel method using ethanol and glycerol as solvents and $ZrOCl_2$•$8H_2O$ as zirconium source. The effect of phase stabilization with amorphous carbon was observed and discussed. The structure evolution, phase transformation and morphological characteristic of powders were investigated by thermogravimetric analysis(TG), differential scanning calorimetric analysis (DSC), powder X-ray diffraction (XRD) X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Cubic and tetragonal phase could be generated in this system.

1. Introduction

Zirconia (ZrO_2) ceramic is one of the advanced ceramic materials. It has a series of outstanding properties, such as high melting point, high specific strength, excellent corrosion resistance, low thermal conductivity and low heat capacity.[1,2] Zirconia ceramics are used for production of catalysts, dielectric materials, chemical sensors, high-performance ceramic materials, solid oxide fuel cells and functional coatings.[3-5] Pure ZrO_2 presents three forms of crystal structure: monoclinic phase (m-ZrO_2), tetragonal phase (t-ZrO_2) and cubic phase (c-ZrO_2).[6,7] The m-ZrO_2 is stable at room temperature, while the t-ZrO_2 and c-ZrO_2 are commonly observed in high temperature environments. The transitions between them usually happen in particular circumstances. The m-ZrO_2 reversibly transforms to t-ZrO_2 and then to c-ZrO_2 at 1170℃ and 2370℃, respectively. However, the mechanical property of m-ZrO_2 is too poor for use. In most cases, t-ZrO_2 or c-ZrO_2 ceramics are more suitable for application. Therefore, the preparation of them has become a challenge in research now.

For obtaining t-ZrO_2 ceramics, various methods have been developed and investigated, including rare earth stabilization method, annealing method, low temperature calcination method and sol-gel method.[8] The homogeneous mixture of the components makes sol-gel method an outstanding synthesis, which allows obtaining the powder with well-controlled homogeneity, purity, reactivity, particle morphology and microstructure.[9-11] However, the ZrO_2 ceramics synthesized by sol-gel method are commonly mixed with tetragonal and monoclinic phase in most cases. Storing energy in the system could be a way to stabilize t-ZrO_2 and c-ZrO_2, and to solve this problem.

This paper discusses the sol-gel system with alcohols as solvent and origin of phase transformation component in the synthesis of c-ZrO_2 and t-ZrO_2 from $ZrOCl_2$•$8H_2O$ by thermal decomposition. Suitable alcohols could be able to change into amorphous carbon and provide the energy of c-ZrO_2 generation. The addition of Y_2O_3 would benefit the stability of t-ZrO_2.

2. Experimental

The zirconia ceramics were synthesized using the sol-gel process. 0.4mol/L zirconium oxychloride octahydrate($ZrOCl_2{\cdot}8H_2O$, 99.9%, Aladdin Industrial Corporation) was dissolved in the mixture of anhydrous ethanol and glycerol(C_2H_6O, $C_3H_8O_3$, 99%, Beijing Chemicals) with a volume ratio of 1:3 (sample Z1). For the comparative experiment, 3 weight. % of Nanometer yttrium oxide (Y_2O_3, 99.99%, Aladdin Industrial Corporation) was added to stabilize tetragonal or cubic phase (sample Z2). Sols fully transform into gels under 500W ultrasound and 50℃ water bath assisted for 20 minutes. Additionally, Nano carbon powder (99.5%, Aladdin Industrial Corporation) and m-ZrO_2 (99%, Aladdin Industrial Corporation) were mixed in 1:1 mass ratio (sample MS) to check the role of amorphous carbon as phase transformation promoter.

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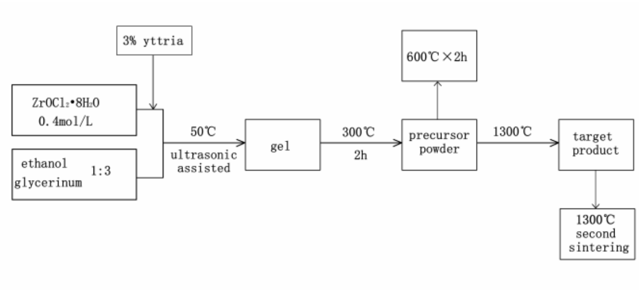


Fig. 1 Flow diagram for synthesis of ZrO_2 powders.

The precursor powders were produced by heating the sols above the fully weight loss point. The weight loss point has been determined by thermogravimetric analysis (TG, Netzsch TG-209F-3) in N_2 atmosphere with a heat rate of 10℃/min. The powders were calcined at 1300℃ in N_2 atmosphere for phase and structure evolution study. Thermal analyses of the phase variation were carried out by differential scanning calorimetric analysis (DSC, Netzsch DSC-404F-3) in N_2 atmosphere with a heat rate of 10℃/min. Morphological characteristic of powders were investigated by scanning electron microscopy (SEM, HITACHI S-4700). The crystalline phases of ZrO_2 powders calcined at different conditions (600℃, 1300℃ and 1300℃ second sintering) and MS calcined at 1300℃ were identified by powder X-ray diffraction (XRD, Bruker D8 Advance). The scans were taken within the 2θ between 20° and 90°, and operated at an accelerating voltage of 40 kV and an emission current of 40 mA. The powders of sample MS after calcination at 1300 ℃ were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250) with Monochromated Al Kalph (150W). The spot size was focused to~500 μm.

3. Results and discussion

3.1. Generation of c-ZrO_2

Sample MS (C: m-ZrO_2=1:1) was designed to investigate the generation process of c-ZrO_2. Fig. 2 shows the XRD patterns of sample MS calcined at 1300℃. After the heat treatment m-ZrO_2 partly transformed into c-ZrO_2 and remained stable in the cubic phase after natural cooling to room temperature. Fig. 3(a) shows the DSC curve of the process. Under normal conditions, m-ZrO_2 would first become t-ZrO_2 at around 1170℃, and change back in the cooling process. However, the crystal form transition process underwent in sample MS was completely different (Fig. 3(b)). The phase transformation from monoclinic to tetragonal phase was entirely prevented in the heating process. The only peak corresponded to the endothermic behavior of nano carbon powder (Fig. 3(c)) is observed in the heating process of sample MS. The steep curves in Fig. 3(b) &(c) indicate the great amount of heat absorbed by nano carbon powder. The following next heat release rapidly increase the internal energy of the m-ZrO_2 in sample MS and provide it transformation into c-ZrO_2. The energy stored in amorphous carbon increase the surface energy of ZrO_2 phase, th stabilizes the c-ZrO_2 and overlap the bulk energy difference of c-ZrO_2–m-ZrO_2 transformation. Thus, c-ZrO_2 is not able to transform back into t-ZrO_2 or m-ZrO_2 and keep stable. However, the nonuniform mixing of the two powders makes

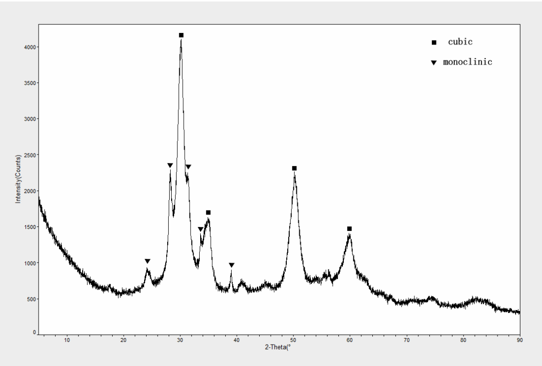
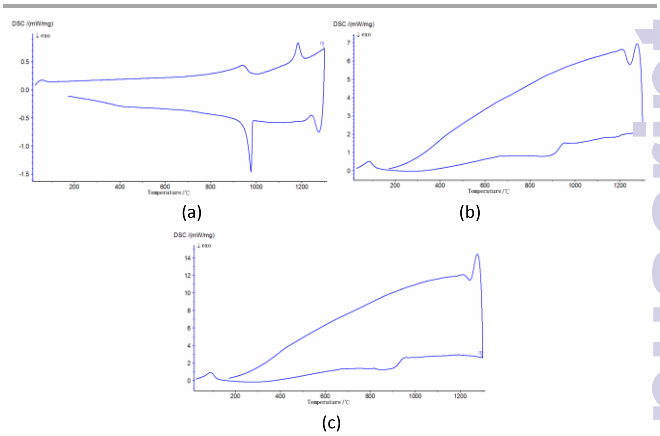


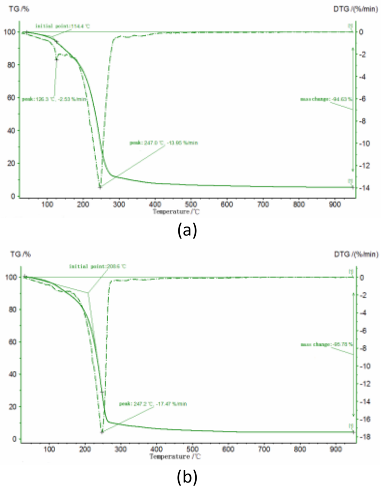
Fig. 2 XRD patterns of sample MS calcined at 1300℃.



(a) (b)

(c)

Fig. 3 DSC curves of (a) ZrO_2; (b) sample MS; (c) nano carbon powder.



(a)

(b)

Fig. 4 TG curves of (a) the Z1 ZrO_2 gels.; (b) the Z2 ZrO_2 gels.

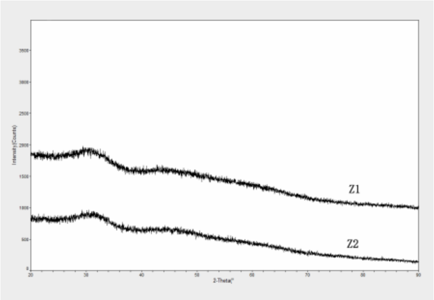


Fig. 5 XRD patterns of the ZrO_2 sols calcined at 300℃.

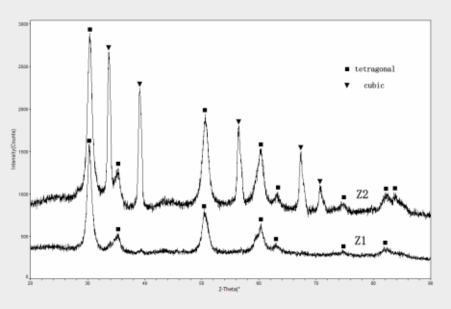


Fig. 7 XRD patterns of the ZrO_2 powders calcined at 1300℃.

the m-ZrO_2 presence possible.

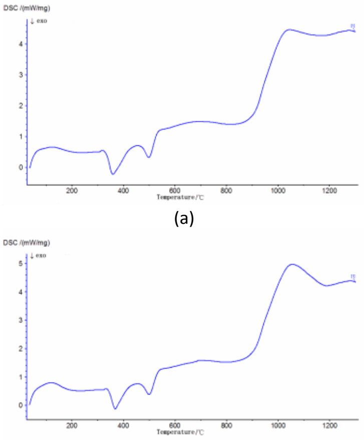
3.2. Characterization of ZrO_2 precursor powders

The precursor powders are used to provide homogeneously mixed carbon and ZrO_2. Sol-gel method could mix carbon and ZrO_2 in molecular level to make better use of the energy that carbon stored. Fig. 4 shows the TG curves of sample Z1 and Z2. The weight loss peaks at around 247℃ correspond to the evaporation of solvents and the reduction of the organic phase of the gels. The solid phase was generated at around 247℃ and had no more weight loss with the temperature increasing, indicating the molecular level mixed precursor powders of amorphous carbon and ZrO_2 were prepared. As it is shown in Fig. 5, no crystalline substance could be observed in the precursor powders.

3.3. Crystallization process of ZrO_2 ceramics

Fig. 6 shows the DSC curves of sample Z1 and Z2. There are two exothermic peaks and one endothermic peak in both of the two curves. The exothermic peaks at around 350℃ and 500℃are associated with the structural variation of the ZrO_2 powders. These peaks might be attributed to the energy of chain scission or bond breaking. Organic substance of the system vanished completely after calcination at 300℃. The structure of the ZrO_2 powders might be the chain of -Zr-O-Zr- or the bulk of Zr and O. The morphology of these structures is amorphous as it can be seen in Fig. 5. These structures were destroyed in the heating process from 300℃ to 550℃ with energy release. The endothermic peaks at around 1000℃ should be related to endothermic peak of carbon in Fig. 3(c). Affected by the energy stored in amorphous carbon, we could not detect the crystal form of sample Z1 and Z2 in the heating process.

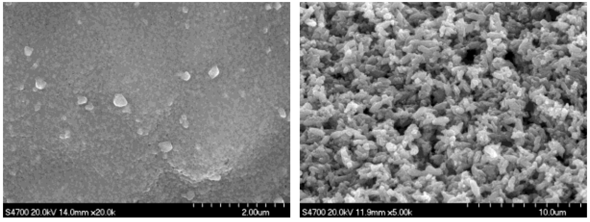
Shown in Fig. 7 is the XRD patterns of ZrO_2 powders calcined at 1300℃. The ZrO_2 sample of Z1 was in a fully stabilized tetragonal state, while the sample of Z2 was in a heterogeneous state formed by tetragonal and cubic phase. As it has been mentioned above (see in 3.1), cubic phase should be generated in the cooling process, and the energy source is amorphous carbon. In sample Z1, the energy that amorphous carbon provides was able to form cubic phase, but not high enough to stabilize the c-ZrO_2 at low temperature, which is caused by the low ratio of C:ZrO_2. In normal cases, t-ZrO_2 would transform back into m-ZrO_2 in cooling procedure. However, no evidence of monoclinic phase could be observed in these samples, because the transformation from c-ZrO_2 to t-ZrO_2 would release energy and slow down or inhibit the transition from t-ZrO_2 to m-ZrO_2. For sample Z2, the Y_2O_3 as a stabilizer could form liquid phase in the sample. During the heat treatment, the Y_2O_3 doping could diffuse into the ZrO_2 crystal lattice. [12,13] In the process of temperature reduction, the Y_2O_3 could slow down the crystal structure transformation which cause the stabilization of the cubic phase of sample Z2 in room temperature.



(a)

(b)

Fig. 6 DSC curves of (a) the Z1 ZrO_2 powders.; (b) the Z2 ZrO_2 powders.



(a) (b)

Fig. 8 SEM images of (a) Z1 ZrO_2 powders (b) Z2 ZrO_2 powders calcined at 1300℃.

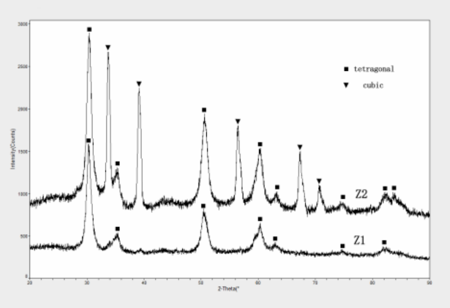


Fig. 9 XRD patterns of the ZrO_2 powders calcined at 1300℃ × 2h as a second sintering.

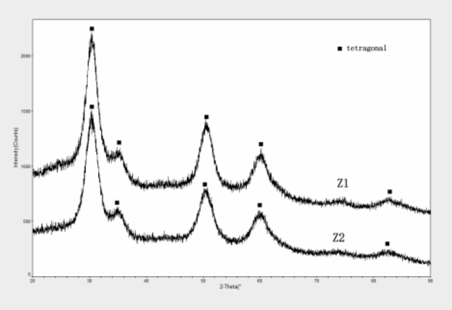


Fig. 11 XRD patterns of the ZrO_2 powders calcined at 600℃

Furthermore, the surface morphology of the samples has been investigated. The SEM images of these two samples are shown in Fig. 8. It is observed that the fine structure was affected by whether adding yttria or not. For sample Z1, the SEM reveals a flat and loose morphology of ZrO_2 surface (see Fig. 8 (a)). And the morphology of sample Z2 is rough and uneven (see Fig. 8 (b)). It is affected by the volume differences of t-ZrO_2 and c-ZrO_2.

3.4. Stabilization process of tetragonal phase

To investigate the principle of stabilization of tetragonal phase, the crystalline structure under other thermal conditions was taken into consideration. The XRD patterns of ZrO_2 samples went through second sintering are shown in Fig. 9. No cubic peaks but trace amount of monoclinic peaks could be observed in these XRD patterns. Tetragonal and cubic phases were still unstable during additional heat treatment without the addition of Y_2O_3. Amorphous carbon could largely prevent the change to m-ZrO_2, but the trace of the variation still could be found. And yet, the ratio of monoclinic in sample Z2 was obviously lower than Z1. It would be attributed to the effect of Y_2O_3, and the energy released by the transformation from c-ZrO_2 to t-ZrO_2.

In former studies, amorphous carbon was found to have the ability to diffuse into the ZrO_2 crystal lattice and stabilize tetragonal phase. The XPS peaks at around 282.9eV which were assigned to C 1s binding energy from Zr-C bonds could be a proof of it.[14] However, this phenomenon could not be detected in all cases.[15] For sample MS after calcined 1300℃, as it can be seen in Fig. 10, no Zr-C bindings, which would be respected by a C 1s binding energy at 281.1eV or 282.1eV, was detected. There are no chemical reactions between ZrO_2 and C. It proves that the stored energy of amorphous carbon played an important role in stabilizing tetragonal and cubic phases in sample Z1 and Z2.

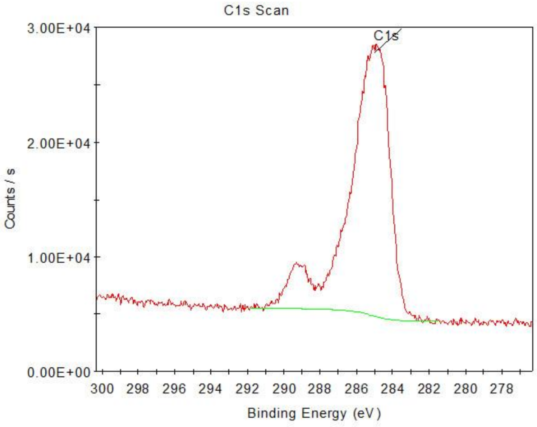


Fig. 10 XPS analysis of sample MS after calcined at 1300℃.

The XRD patterns of ZrO_2 powders calcined at 600℃ ar displayed in Fig. 11. Clearly, there is no evidence of monoclinic phase in the samples. The broadening of diffraction peaks was attributed to the amorphous component of the ZrO_2 samples. It was clear that for the ZrO_2 powders prepared by Z1 and Z2 system, calcination of 600℃ would transform part of the ZrO_2 powders from amorphous phase to tetragonal phase. Amorphous carbon could also store and release energy to make ZrO_2 crystal. But the energy value would be much lower than it was in 1300℃.

Through the above analysis, there are ways to generate better crystalized and more stable t-ZrO_2 or c-ZrO_2 by increase the ratio of C/ZrO_2. Choosing the higher carbon content solvents or just adding some carbon powder would be useful.

4. Conclusions

ZrO_2 ceramics were synthesized by sol-gel method using ethanol and glycerol as solvent and $ZrOCl_2 \cdot 8H_2O$ as zirconium source. It could synthesize and stabilize t-ZrO_2 and c-ZrO_2 at a low temperature. The energy source is the amorphous carbon in the system. The energy release from carbon and the transformation from c-ZrO_2 to t-ZrO_2 could slow down inhabit the transformation from t-ZrO_2 to m-ZrO_2. Y_2O_3 in the sample as a stabilizer would also stabilize the tetragonal phase.

Notes and references

1 Xiaoxuan Pian, Bingbing Fan, Hao Chen, Preparation of m-ZrO_2 compacts by microwave sintering, Ceramics International, 2014, **40**, 10483-10488
2 Lingqian Kong, Shengyu Zhu, Qinling Bi, Friction and wear behavior of self-lubricating $ZrO_2(Y_2O_3)$-CaF_2-Mo-graphite

composite from 20℃ to 1000℃, Ceramics International, 2014, **40**, 10787-10792

3 Thammanoon Sreethawong, Supachai Ngamsinlapasathian, Susumu Yoshikawa, Synthesis of crystalline mesoporous-assembled ZrO_2 nanoparticles via a facile surfactant-aided sol–gel process and their photocatalytic dye degradation activity, Chemical Engineering Journal, 2013, **228**, 256-262

4 S. Jaenicke, G. K. Chuah, V. Raju, Structural and Morphological Control in the Preparation of High Surface Area Zirconia, Catalysis Surveys from Asia, 2008, **12**, 153-169

5 Qibing Chang, Jian-er Zhou, Yongqing Wang, Formation mechanism of zirconia nano-particles containing pores prepared via sol-gel-hydrothermal method, Advanced Powder Technology, 2010, **21**, 425-430

6 Wenzhi Huang, Jili Yang, Xiangsheng Meng, Effect of the organic additions on crystal growth behavior of ZrO_2 nanocrystals prepared via sol-gel process, Chemical Engineering Journal, 2011, **168**, 1360-1368

7 Rongjun Zhang, Huimin Liu, Dehua He, Pure monoclinic ZrO_2 prepared by hydrothermal method for isosynthesis, Catalysis Communications, 2012, **26**, 244-247

8 Vishwanath G, Deshmane, Yusuf G, Synthesis of thermally stable, high surface area, nanocrystalline mesoporous tetragonal zirconium dioxide (ZrO_2): Effects of different process parameters, Microporous and Mesoporous Materials, 2012, **148**, 88-100

9 Huiming Ji, Ming Yang, Minmin Li, Low-temperature synthesis of ZrB2 nano-powders using a sorbitol modified sol–gel processing route, Advanced Powder Technology, 2014, **25**, 910-915

10 H. Bensouyad, H. Sedrati, H. Dehdouh, Structural, thermal and optical characterization of TiO_2:ZrO_2 thin films prepared by sol-gel method, Thin Solid Films, 2010, **519**, 96-100

11 Ricardo Caruso, Oscar de Sanctis, Antonio Macias-Garcia, Influence of pH value and solvent utilized in the sol-gel synthesis on properties of derived ZrO_2 powders, Journal of Materials Processing Technology, 2004, **152**, 299-303

12 Nadia Mamana, Antonio Díaz-Parralejo, Angel L. Ortiz, Influence of the synthesis process on the features of Y_2O_3-stabilized ZrO_2 powders obtained by the sol-gel method, Ceramics International, 2014, **40**, 6421-6426

13 A. L. Ortiz, A. Díaz-Parralejo, O. Borrero-López, Effect of ion nitriding on the crystal structure of 3 mol% Y_2O_3-doped ZrO_2 thin-films prepared by the sol–gel method, Applied Surface Science, 2006, **252**, 6018-6021

14 Huiming Xiang, Xinpo Lu, Jingjing Li, Influence of carbon on phase stability of tetragonal ZrO_2, Ceramics International, 2014, **40**, 5645-5651

15 N. Laidani, V. Micheli, M. Anderle, Carbon effect on the phase structure and the hardness of RF sputtered zirconia films, Thin Solid Films, 2001, **382**, 23-29