

In-situ synthesis of ZrC@ZrO₂ core-shell high temperature thermal insulation nanopowders by precipitation method

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ZrC (shell) and ZrO₂ (core) (ZrC@ZrO₂) core-shell nanopowders were in-situ synthesized by precipitating method using zirconium dioxide (ZrO₂) and sucrose (C₁₂H₂₂O₁₁). C₁₂H₂₂O₁₁ was selected since it can be completely decomposed to carbon. Thus, carbon might be accounted precisely for the carbothermal reduction reaction. The ZrC@ZrO₂ core-shell nanopowders were obtained with a molar ratio of C / Zr = 2 for the starting materials at 1500 °C for 2 hrs. The SEM photomicrograph reveals that ZrC@ZrO₂ core-shell particles had an equiaxed morphology with a high surface rough. Furthermore, the size distribution of the particles was around 100 nm in diameter. Additionally, in the case of either C / Zr (mol.) > 1 or pyrolyzing temperature above 1400 °C, the thickness of ZrC shell could be increased. Moreover, the HR-TEM showed that the nanopowders possessed core-shell structure with ZrO₂ core and ZrC shell, and the thickness of ZrC was about 10 nm carbothermally reduced at 1500 °C for 2 hrs with a molar ratio of C / Zr = 2.

Key words: ZrC@ZrO₂, Core-shell, Nanopowders, In-situ, Thickness.

Introduction

At a high speed air vehicle thermal protection system, advanced thermal insulation materials with ultra-high porosity, low thermal conductivity, high temperature stability, and high resistance to chemical corrosion are urgently required [1-3].

Recently, as two kinds of the most promising advanced insulation materials till now, aerogel [4-7] and porous ceramics [8, 9] have absorbed more and more attention. For example, SiO₂ aerogel [10-15] has many excellent properties, such as high surface area, high porosity, low density, and small pore size. However, the poor stability limited the use of SiO₂ aerogel due to radiation sources and humidity [11]. Furthermore, the porous structure of SiO₂ aerogel could be destroyed as a result of mass transfer between solid particles at high temperatures. In the end, the porosity of SiO₂ aerogel was decreased and its thermal insulation was destroyed. On the other hand, ZrO₂ ceramic has also attracted much attention because of its high melting point and stability, high mechanical properties, good insulation and erosion resistance for functional applications, such as ceramic filters [16], catalysts support [17], and lightweight parts used at high temperatures [18, 19]. Moreover, ZrO₂ ceramic is also traditionally used for thermal barrier coatings in gas turbine engines, because it has low thermal

conductivity, high thermal expansion coefficient, and good erosion resistance [20]. However, at high temperatures, the porosity is decreased and the thermal conductivity is increased due to the sintering of ZrO₂. As a result, the use of ZrO₂ porous ceramic has been limited at high temperatures. Therefore, the outside of ZrO₂ porous ceramic need to be covered a protective layer of high temperature resistance in order that the performances of ZrO₂ are not destroyed.

ZrC as shell is a good choice because ZrC has a high melting point, a solid-state phase stability, a low evaporation rate, a high hardness, and a good thermal shock resistance. That is to say, ZrC@ZrO₂ core-shell porous ceramic may be used at high temperature (1500 °C) since ZrC could be used as a resistance to high temperature protective layer. Finally, the porosity and the thermal conductivity of ZrO₂ could not be damaged due to the existence of the protective layer at high temperature (1500 °C). However, the use of ceramics is sometimes determined by the features of the powder, such as size, purity, morphology etc. As far as we know, there are no literature reports about the synthesis of ZrC@ZrO₂ nanopowders.

In the present study, ZrC@ZrO₂ core-shell nanopowders were in-situ synthesized by precipitating method using zirconium dioxide (ZrO₂) and sucrose (C₁₂H₂₂O₁₁). C₁₂H₂₂O₁₁ was a source of pyrolyzed carbon. Here, C₁₂H₂₂O₁₁ was used since it can be completely decomposed to carbon. Thus, carbon might be accounted precisely and C / Zr molar ratio might be fixed. Additionally, the effects of C / Zr molar ratio of the starting materials and the temperature of carbothermal reduction on the ZrC thickness were

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investigated. Moreover, the structures of C@ZrO₂ and ZrC@ZrO₂ core-shell nanopowders were discussed.

Experimental and Method

Materials

ZrO₂ and C₁₂H₂₂O₁₁ were supplied by the Lanyi Reagents Co. Ltd., Beijing, China. The grade of all the above reagents was analytical. A general flow diagram for the synthesis of ZrC@ZrO₂ core-shell nanopowders is shown in Fig. 1. In a typical synthesis, 3.43 g of C₁₂H₂₂O₁₁ was dissolved in 40 ml of H₂O using a 80 ml beaker at room temperature. We refer to this solution as Solution 1. Then, 7.38 g of ZrO₂ was added with a molar ratio of C / Zr = 2 for the start materials and this resulting solution was continuously stirred for 4 hrs. We refer to this solution as Solution 2. Finally, it was dried at 110 °C for 12 hrs followed by a grind process using an agate mortar and a pestle. In this way, a precursor powder was prepared.

After that, the above precursor was firstly heated to

800 °C at a heating rate of 5 °C / min, then to 1200 °C at 3 °C / min and maintained at this temperature for 2 hrs in argon using an alumina tube furnace. Afterwards, the precursor powder was continued to heat from 1200 °C to 1500 °C at a heating rate of 2 °C / min and kept at this temperature for 2 hrs. Then, the sample was cooled to room temperature at a cooling rate of 5 °C / min. In the end, black powder was obtained. For purposes of comparison, sample with C / Zr molar ratio of 1 for the starting materials was prepared.

Characterization

The mass and heat flow of the samples were monitored by thermal analysis (TG-DSC, Beijing Hengjiu instrument Co. Ltd., Beijing, China). The crystallographic constitution was identified by means of an X-ray diffractometer (XRD) using graphite monochromatized CuK_α radiation (Rigaku, D/MAX 2200 PC). Crystallite size was estimated using the Debye-Scherrer equation,

$$D_{hkl} = 0.9 \lambda / \beta_{hkl} \cos \theta \quad (1)$$

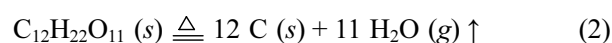
Where D_{hkl} is the crystallite size, λ is the wavelength of CuK_α radiation, β_{hkl} is the full-width at half maximum, and θ is the Bragg diffraction angle. The morphology of the final products was characterized by SEM using a JEOL JSM-6700F JAPAN microscope and TEM using a JEM-2100F microscope.

Results and Discussion

Thermal analysis of C₁₂H₂₂O₁₁

TG-DSC analysis in argon was conducted to understand the process of pyrolysis of C₁₂H₂₂O₁₁. The complementary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g. melting and crystallization) and those which involve a weight loss (e.g. degradation). TG analysis showed that a considerable weight loss occurred in a temperature range of 219 °C-337 °C for C₁₂H₂₂O₁₁ as shown in Fig. 2.

Taking the result into account, the thermal decomposition reaction between 219 °C-337 °C may be described as follows:



Theoretically, C₁₂H₂₂O₁₁ completely transformed to carbon and H₂O, accompanied with 58 % weight loss between 219 °C-337 °C (see eq. (2)). This magnitude is almost in agreement with the experimental weight loss of 57% between 219 °C-337 °C (see Fig. 2).

Alternatively, DSC curve in Fig. 2 reveals that an endothermic peak at about 193 °C. It might be attributed to the melting peak of C₁₂H₂₂O₁₁ [21, 22]. An

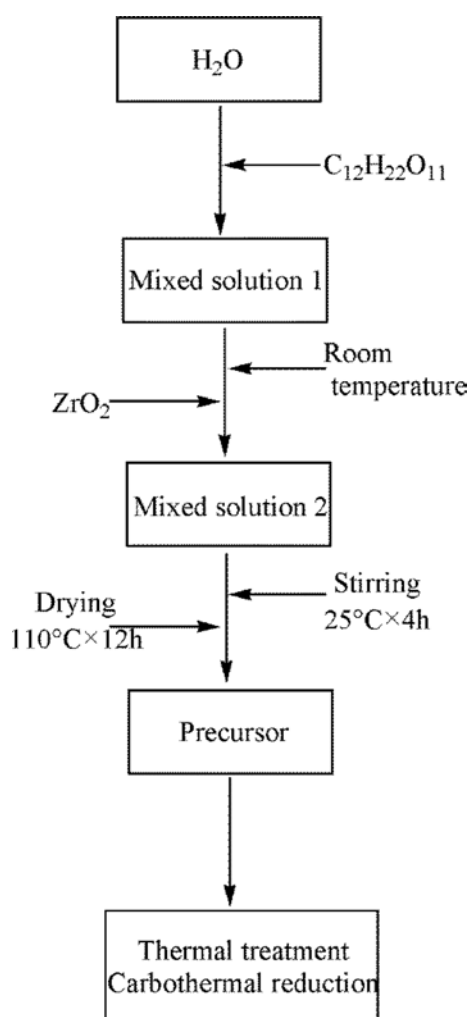


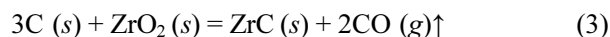
Fig. 1. General flow diagram for synthesis of ZrC@ZrO₂ core-shell nanopowders.

exothermic peak at about 219 °C could be attributed to the decomposition peak of $C_{12}H_{22}O_{11}$.

Influence of pyrolysis/calcination temperature on phase constitution

Fig. 3 shows XRD patterns of the powder precursor calcined at different temperatures with a molar ratio of $C / Zr = 2$ for the starting materials. Clearly, the precursor was only ZrO_2 phase without any ZrC peak in its XRD pattern. In the sample treated at 1400 °C for 2 hrs ZrO_2 and ZrC phases were identified. With the increasing of the calcining temperature, the XRD patterns show that the diffraction intensity of ZrC increased, and furthermore, the peak of ZrO_2 decreased at temperature of 1500 °C for 2 hrs. This means that a carbothermal reduction process was not able to complete at 1500 °C. However, this just matched our original target to synthesis $ZrC@ZrO_2$ core-shell nanopowders.

Theoretically, an idealized reaction to produce ZrC by carbothermal reduction in the present study is shown as follows:



Here, a carbothermal reduction process was able to complete with the stoichiometric proportion of $C / Zr = 3$, but a single phase ZrC was not necessary in the present study. Therefore, in order to prepare $ZrC@ZrO_2$ core-shell nanopowders, a lower C / Zr ratio for the starting materials that the stoichiometric proportion of $C / Zr = 3$ as shown in reaction (3) was necessary.

For purposes of comparison, Figs. 4 and 5 display the XRD patterns of the precursors pyrolyzed at 1500 °C for 2 hrs with molar ratios of $C / Zr = 2$ and 1, and at 1400 °C for 2 hrs with molar ratio of $C / Zr = 1$, respectively. It may be found that at 1500 °C the intensity of ZrC peaks increased with the increasing of the molar ratios of C / Zr from 1 to 2 (see Fig. 4(a) and (b)). At the same time, the intensity of ZrC peaks also increased with the increasing of the temperature from 1400 °C to 1500 °C with molar ratio of $C / Zr = 1$ (see Fig. 4(a) and Fig. 5). This means that the thickness of ZrC shell increased with the increasing of the temperature and molar ratio of C / Zr . In the present work, C / Zr (mol.) = 2 for the starting materials was given on the basis of experiments.

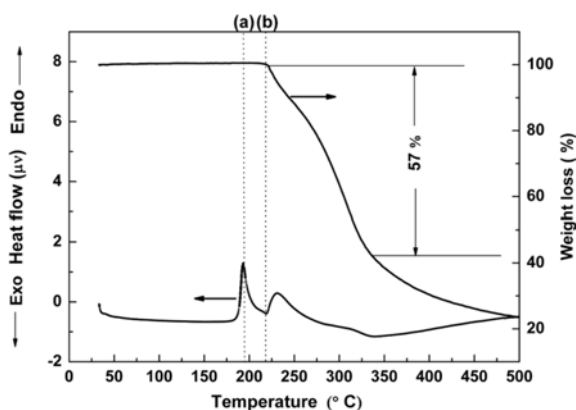


Fig. 2. TG-DSC thermal analysis curve for $C_{12}H_{22}O_{11}$ from room temperature to 500 °C: (a) 193 °C; (b) 219 °C.

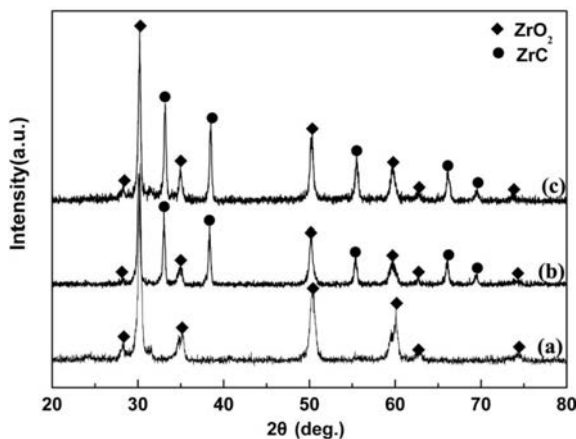


Fig. 3. XRD patterns of (a) precursor, and pyrolyzed the precursor at (b) 1400 °C; (c) 1500 °C for $C / Zr = 2$.

Morphology formation of $ZrC@ZrO_2$ core-shell

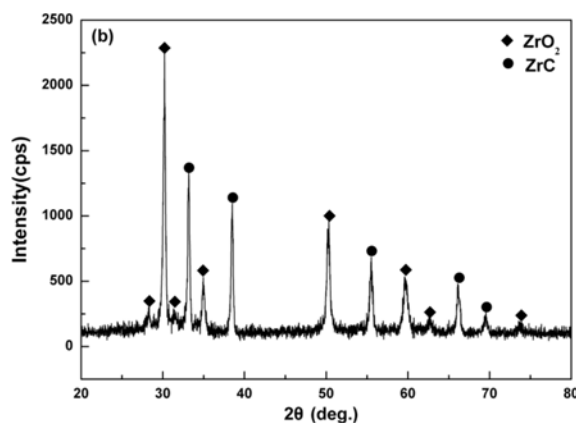
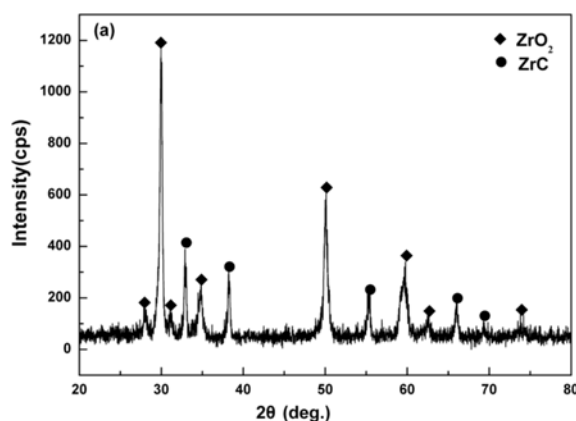


Fig. 4. XRD patterns of precursors pyrolyzed at 1500 °C for 2 hrs with molar ratios of C / Zr : (a) 1; (b) 2.

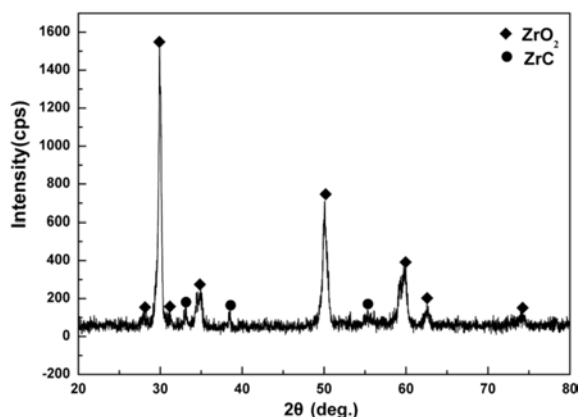


Fig. 5. XRD pattern of precursor pyrolyzed at 1400 °C for 2 hrs with molar ratio of C / Zr = 1.

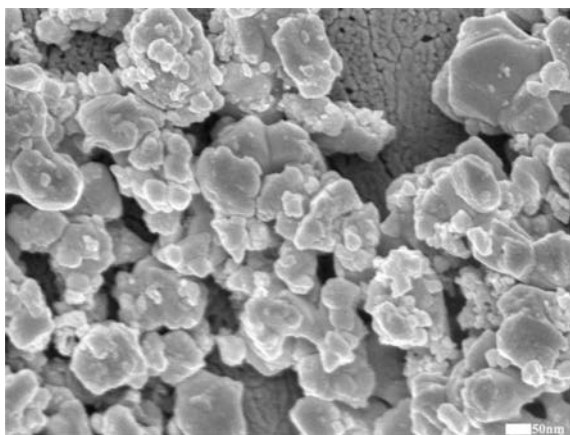


Fig. 6. SEM images of ZrC@ZrO₂ core-shell nanopowders pyrolyzed at 1500 °C for 2 hrs with a molar ratio of C / Zr = 2.

nanopowders

Generally, the morphology of particles is a comprehensive reflection of the synthesis methods and processes. Fig. 6 shows a SEM image of ZrC@ZrO₂ core-shell nanopowders synthesized and carbothermally reduced at 1500 °C for 2 hrs. The SEM photomicrograph reveals that ZrC@ZrO₂ core-shell particles had an equiaxed morphology with a high surface rough. Furthermore, the size distribution of the particles was around 100 nm in diameter.

A High-Resolution TEM (HRTEM) was conducted to clarify the microstructure of ZrC@ZrO₂ core-shell nanopowders. Fig. 7(a) showed that the nanopowders possessed core-shell structure, with ZrO₂ core and carbon shell carbothermally reduced at 800 °C. Additionally, Fig. 7(b) revealed that the nanopowders possessed core-shell structure, with ZrO₂ core and ZrC shell at 1500 °C. It also may be found from the HR-TEM image that ZrC and ZrO₂ particles shared {111} and {011} lattice fringes with interplanar spacings of 2.7 nm and 2.95 nm, respectively (see Fig. 7(b)). Furthermore, the thickness of ZrC was about 10 nm

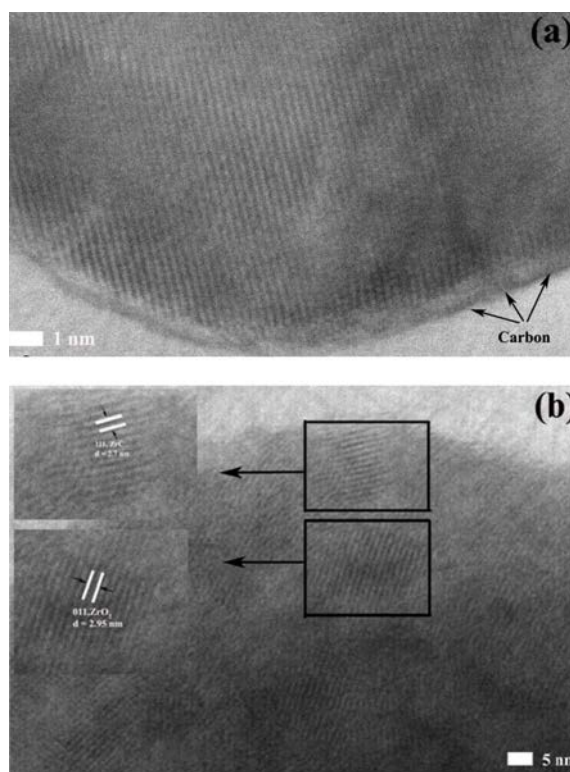


Fig. 7. HR-TEM image of ZrC@ZrO₂ core-shell particle reduced carbothermally with (a) 800 °C; (b) 1500 °C.

carbothermally reduced at 1500 °C for 2 hrs with a molar ratio of C / Zr = 2 (see Fig. 7(b)).

Conclusions

ZrC@ZrO₂ core-shell nanopowders with an equiaxed morphology were successfully in-situ synthesized by precipitating method. The average grain size of ZrC@ZrO₂ core-shell nanopowders was *ca.* 100 nm. Furthermore, in the case of either C / Zr (mol.) > 1 or pyrolyzing temperature above 1400 °C for C / Zr (mol.) = 2, the thickness of ZrC shell could be increased. Moreover, the HR-TEM showed that the nanopowders possessed core-shell structure, with ZrO₂ core and carbon shell, and ZrC shell carbothermal reduced at 800 °C and 1500 °C, respectively. Additionally, the thickness of ZrC was about 10 nm carbothermally reduced at 1500 °C for 2 hrs with a molar ratio of C / Zr = 2.

Acknowledgments

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