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Preparation of ZrO_2/Gd_2O_3 composite ceramic materials by coprecipitation method

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Abstract

High burnup is a goal for further development of advanced nuclear power in the future. However, along with the increase of burnup, it becomes more diffidult to control reactor reactivity, which affects the operation safety of the nuclear reactor. Al_2O_3/B_4C burnable poison materials widely used in pressurized water reactor currently will not meet the requirements of burnable poison materials in high burnup nuclear power. Because of the better performance of ZrO_2/Gd_2O_3 burnable poison materials than that of Al_2O_3/B_4C, this paper studies the preparation of ZrO_2/Gd_2O_3 composite ceramic materials by the coprecipitation method. The experimental results show that at the sintering temperature of 1500–1650 °C, ZrO_2/Gd_2O_3 composite ceramic grains are small, compact and uniform with the generation of homogeneous solid solution. At 1600 °C, ZrO_2–10%Gd_2O_3 has the highest density and mechanical strength.

Keywords: D. ZrO_2; Gd_2O_3; Composite ceramic materials; Coprecipitation method

1. Introduction

Al_2O_3/B_4C burnable poison materials is widely used in nuclear power reactors at home and abroad, especially PWR cores, to control the initial reactivity, realize flattening core power distribution, improve fuel burn-up and prolong refueling cycle, which can thereby reduce nuclear power operation cost, improve operation safety and reliability [1–6]. But because of high nuclear reactor burn-up and the core power, Al_2O_3/B_4C burnable poison materials not only accelerate swelling, but also reduce its chemical stability, which influences the operation safety and economy of nuclear reactors [7,8]. Compared with Al_2O_3/B_4C, ZrO_2/Gd_2O_3 burnable poison materials have three advantages [9]. First, the swelling rate is lower. Second, ZrO_2 matrix and Gd_2O_3 can form solid solution easily, reducing uniformity of burnable poison materials to a minimum. Third, ZrO_2 matrix leaves good chemical stability to cladding alloy and the main coolant. Thus, research on ZrO_2/Gd_2O_3 burnable poison materials get positive attention of some researchers both at home and abroad.

At present, PWR nuclear fuel elements design adopts zirconium alloy cladding [10,11], large open porosity of ZrO_2/Gd_2O_3 composite materials leads to the adsorption of water vapor, which results in hydrogen embrittlement corrosion of zirconium alloy cladding materiasl. The solid solubility between ZrO_2 matrix and Gd_2O_3 has an important influence on the performance of ZrO_2/Gd_2O_3 composite materials at high temperatures. Therefore, it is an important research direction of the performance of ZrO_2/Gd_2O_3 burnable poison composite materials to improve the material density, the uniformity of phase and reduce its porosity.

Ball-milling method, powder metallurgy method, etc. can be used for the preparation of ZrO_2/Gd_2O_3 composite ceramic materials. Although ball-milling method and powder metallurgy method bring better economical efficiency, the preparation of composite ceramic materials meets lots of problems, such as the uncontrollability of internal uniformity, difficult densification, more pores and defects, a lot of dust, environmental pollution and damage to people's health. However, preparation of ZrO_2/Gd_2O_3 composite ceramic materials by chemical coprecipitation reactions can, in theory, get composite materials with uniform

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chemical composition, high purity and good crystal structures at low sintering temperatures. But there is almost no research report on preparation of ZrO_2/Gd_2O_3 composite ceramic materials by the coprecipitation method.

Gd_2O_3 and $ZrO(NO_3)_2$ are initial raw materials in the experiments in this paper. By the method of coprecipitation, ZrO_2/Gd_2O_3 composite ceramic materials with different content of Gd_2O_3 (mass fraction: 0, 5%, 10%, 15%) are preparaed and sintered at different sintering temperatures (1500 °C, 1550 °C, 1600 °C, 1650 °C). The paper studies the influence of the sintering temperatures and the content of Gd_2O_3 on the sintering densification and crushing strength. In addition, it also analyzes its microstructure and phase composition. The results provide certain technological and theoretical basis for the preparation and application of ZrO_2/Gd_2O_3 burnable poison composite ceramic materials with high burn-up and inherent safety in advanced nuclear power.

2. Experimental method

$ZrO(NO_3)_2 \cdot 5H_2O$ and Gd_2O_3 are initial raw materials. Raw materials are calculated according to the mass fraction of Gd_2O_3, 5%, 10%, 15%, in the final product. Zirconium oxynitrate is dissolved in moderate deions and Gd_2O_3 in moderate analytically pure nitric acid solution. Prepared gadolinium nitrate solution is mixed with oxygen zirconium nitrate solution by double drop method, which is stirred to prepare uniform mixed solution. The ammonia water is dropped into the mixed solution, the pH value of which is adjusted to be 6～8. During the dropping, the solution is stirred forcefully to make it react fully with white precipitate, which will continue to be stirred for two hours. Then the mixed solution is kept static and undergoes aging treatment for thirteen hours. After the absorption of supernatant liquid, ammonia water is added into it for washing until it no longer produces white precipitate in the solution. Aging products undergo deionised water washing repeatedly and suction filtration to get filter cake. The filter cake is dried to get the precursor powder at 140 °C. The precursor is put in box-type furnace for heat preservation for 3 h at 750 °C. After air cooling, it is taken out and grounded to ZrO_2/Gd_2O_3 composite ceramic materials powder. At last, after compression molding of the dry calcined powder, it undergoes vacuum sintering to get dense ZrO_2/Gd_2O_3 composite ceramic materials. The sintering temperatures are 1500 °C, 1550 °C, 1600 °C and 1650 °C. Soaking time is 2 h and the heating rate is 20 °C/min.

Archimedes method is used to measure the density of pellets, type D/max22400X X-ray diffractometer is used to determine surface phase structure of ZrO_2/Gd_2O_3 composite ceramic materials. FE I NOVA Nano SEM400(American) field emission scanning electron microscopy SEM is used to observe material microstructures.

3. Results and discussion

3.1. Phase analysis of ZrO_2/Gd_2O_3 composite ceramic materials

Fig. 1 is XRD diffraction pattern for ZrO_2/Gd_2O_3 composite ceramic materials which are sintered with different content of Gd_2O_3. As can be seen from Fig. 1, in the XRD diffraction pattern, only tetragonal phase ZrO_2 diffraction peaks can be seen, which means that substitutional solid solution is formed in ZrO_2/Gd_2O_3 composite ceramic materials with different content of Gd_2O_3.

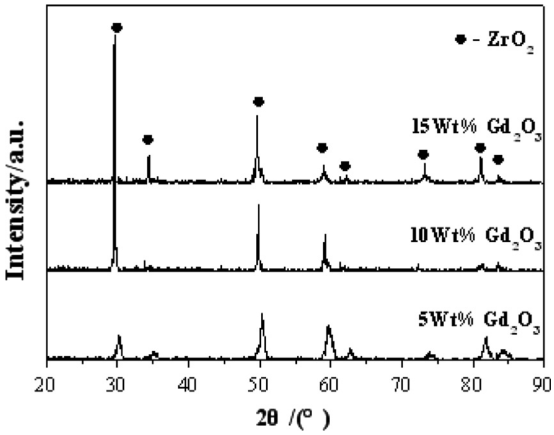

Fig. 1. XRD diffraction pattern for composite ceramic materials with different content of Gd_2O_3.

Fig. 1 also shows that with the increase of the content of Gd_2O_3, there are tiny changes about the diffraction angle θ in XRD diffraction pattern. The θ value of composite ceramic materials containing 10% of Gd_2O_3 is 0.3° smaller than that with 5% of Gd_2O_3. The θ value of composite ceramic materials containing 15% of Gd_2O_3 is 0.3° smaller than that with 10% of Gd_2O_3. According to the Bragg equation and interplanar spacing formula, the diffraction direction formula for tetragonal crystal system is as follows:

$$\sin^2\theta = \frac{\lambda^2}{4\alpha^2}(h^2+k^2+l^2) \tag{1}$$

From Formula (1), it is known that the larger the α of solid solution is, the smaller the θ is. Because ion radius of Gd^{3+} is larger than that of Zr^{4+}, the higher the content of Gd_2O_3 in ZrO_2/Gd_2O_3 composite ceramic body is, the greater the α of solid solution in composite material is, and the fewer chances θ has. This conclusion from the Formula is proved directly in the data in Fig. 1. And because the proportion of substitutional solid solution in ZrO_2/Gd_2O_3 composite ceramic body is higher along with the increase of the content of Gd_2O_3, it also confirms the conclusion in Fig. 1 that substitutional solid solution is formed in ZrO_2/Gd_2O_3 composite ceramic materials with different content of Gd_2O_3.

3.2. The influence of sintering temperatures and the content of Gd_2O_3 on sintered density of composite materials

Fig. 2 shows that when the sintering temperature is between 1500 °C and 1600 °C, the sintered density of ZrO_2/Gd_2O_3 composite materials with four different contents of Gd_2O_3 rises with the increase of the temperature. At 1600 °C, the sintered theoretical density of ZrO_2/Gd_2O_3 composite materials with 10% Gd_2O_3 is over 96%, which reaches the highest degree of densification. But when the sintering temperature rises to

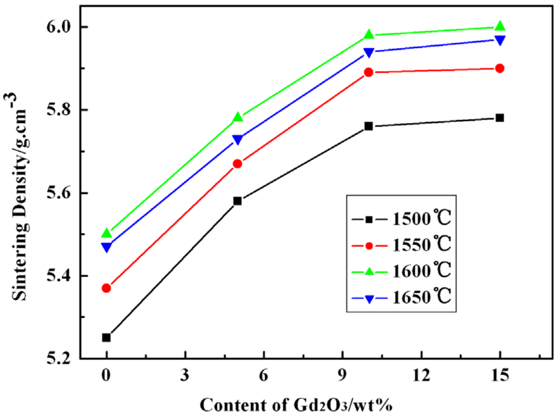

Fig. 2. The influence of sintering temperatures and the content of Gd_2O_3 on the sintered density of composite mterials.

1650 °C, sintered density of composite ceramic fuel has a downward trend. Fig. 2 also shows that at different sintering temperatures of 1500 °C, 1550 °C, 1600 °C and 1650 °C, the sintered density of ZrO_2/Gd_2O_3 composite materials with four different contents of Gd_2O_3 are basically identical with the changes of contents of Gd_2O_3. At each sintering temperature, sintered density of composite ceramic materials rises with the increase of the content of Gd_2O_3. More Gd_2O_3 leads to more ZrO_2/Gd_2O_3 composite powder in ceramic body prepared by the coprecipitation method. It is conducive to sintering diffusion and mass transfer of ZrO_2/Gd_2O_3 composite powder in the sintered body and more pores are filled for better densification so as to improve the sintered density of ceramic body.

From the data analysis in the figure, it is believed that the densification process of composite ceramic with different contents of Gd_2O_3 stops at 1600 °C. Ceramic density depends on the size and content of the internal pores. Fig. 3 shows that in composite ceramic materials with different contents of Gd_2O_3 there are a small number of small pores. When the sintering temperature is 1600 °C, the sintered density of composite ceramic body is the highest. With the increasing content of Gd_2O_3 in the composite ceramic body ZrO_2/Gd_2O_3, the number of pores decreases in the sintered body. Therefore, at 1600 °C, the sintered density of ZrO_2/Gd_2O_3 composite ceramic with three different contents of Gd_2O_3 reaches its maxmum point. Along with the increase of the content of Gd_2O_3, the maximum sintered density of composite materials increases as well. When the sintering temperature continues to increase, the pores in ceramic body will grow, making the density of the composite ceramic body drop slightly.

3.3. The microstructure of ZrO_2/Gd_2O_3 composite ceramic materials

Fig. 3 shows the microscopic structures (SEM) of ZrO_2/Gd_2O_3 composite ceramic materials with 15%, 10% and 5% of Gd_2O_3 at the sintering temperature of 1600 °C. In Fig. 3, obvious ZrO_2 and Gd_2O_3 free phase is not seen in ZrO_2/Gd_2O_3 composite ceramic sintered body with different contents of Gd_2O_3. Composite ceramic body grains are small and evenly arranged close with good density. It also suggests that stable solid solution with good sintering performance is formed in ZrO_2/Gd_2O_3 composite ceramic sintered body with different content of Gd_2O_3.

3.4. The influence of the content of Gd_2O_3 and sintering temperatures on the strength of composite mterials

Fig. 4 shows the influence of the content of Gd_2O_3 and sintering temperatures on the flexural strength of composite mterials. At 1500 °C, 1550 °C, 1600 °C and 1650 °C, the strength of ZrO_2/Gd_2O_3 composite ceramic materials changes basically in accordance with the content of Gd_2O_3 which means that when Gd_2O_3 in the composite ceramic materials increases from 5% to 10%, the strength of the sample greatly increases. When Gd_2O_3 increases from 10% to 15%, the strength of the sample varies little with a slightly downward trend. From Figs. 2 and 3, when there is 10% of Gd_2O_3 in composite ceramic materials, the densification degree of the sample is high. Therefore, the sample has higher flexural strength. The composite ceramic materials with 10% of Gd_2O_3 sintered at 1600 °C has the highest flexural strength, 72.5 MPa. The continuous increase of Gd_2O_3 has little effect on the sintering and strength of composite materials. This is basically consistent with the influence of the content of Gd_2O_3 on sintering density.

From the analysis of Fig. 4, we can also shows that at the sintering temperatures of 1500 °C, 1550 °C, 1600 °C and 1650 °C, flexural strength of the composite ceramic sample with 5% of Gd_2O_3 is low. But the flexural strength of the composite ceramic samples with 10% and 15% of Gd_2O_3 at each sintering temperature is higher with approximate numbers. This is connected with the formation of ZrO_2/Gd_2O_3 composite ceramic, anisotropic heat shrink tiny crack, doping activation sintering of ZrO_2 and so on. It is consistent with the influence of the content of Gd_2O_3 on the sintering density.

In view of the influence of the content of Gd_2O_3 and sintering temperatures on the sintered density and flexural strength of composite ceramic samples, good sintering effect with higher sintered density and flexural strength can be obtained in ZrO_2/Gd_2O_3 composite ceramic samples with 10% of Gd_2O_3 at each sintering temperature. 10% of Gd_2O_3 and the sintering temperature of 1600 °C are suitable for the preparation of ZrO_2/Gd_2O_3 composite ceramic materials with high density and strength.

4. Conclusion

(1) At 1500–1650 °C, the grains in ZrO_2/Gd_2O_3 composite ceramic samples with 5–15% of Gd_2O_3 are small and evenly arranged close with good density. ZrO_2 and Gd_2O_3 free phase is not seen and uniform substitutional solid solution is formed.

(2) With the increase of the content of Gd_2O_3 in ZrO_2/Gd_2O_3 composite ceramic sample from 5% to 10%, the sintering performance of the sample is obviously improved. However, when it is increased from 10% to 15%, the sintering performance of the sample is more similar.

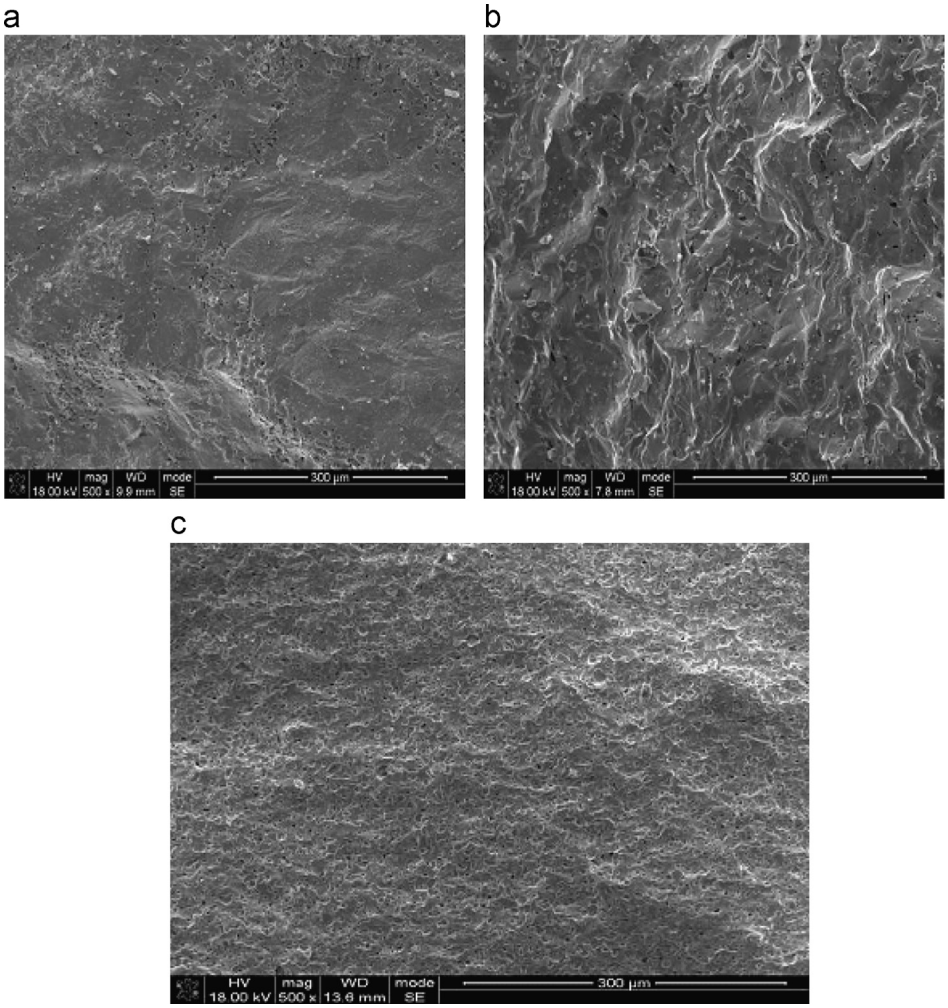

Fig. 3. SEM of ZrO_2/Gd_2O_3 composite ceramic materials with different content of Gd_2O_3 sintered at 1600 °C. (a) 5% Gd_2O_3, (b) 10% Gd_2O_3 and 15% Gd_2O_3.

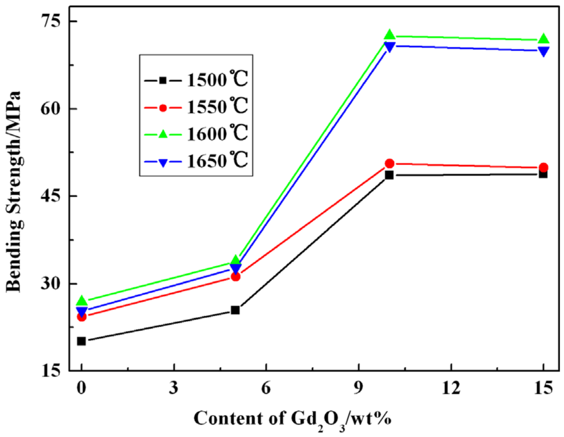

Fig. 4. The influence of the content of Gd_2O_3 and sintering temperatures on the flexural strength of composite mterials.

(3) With the increase of the content of Gd_2O_3 in ZrO_2/Gd_2O_3 composite ceramic sample from 5% to 10%, the flexural strength of the sample is obviously improved. However, when it is increased from 10% to 15%, there are few variations in the strength of the sample.

(4) In view of the influence of composite material composition and sintering temperatures on the sintering performance of materials, 10% of Gd_2O_3 and the sintering temperature of 1600 °C are suitable for the preparation of ZrO_2/Gd_2O_3 composite ceramic materials with high density and strength.

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