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Research on the preparation and sintering process of (U,Ti)O_2 dispersion fuel microsphere

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A B S T R A C T

This paper discusses the preparation of titanium-doped UO_2 microsphere by the method of sol–gel, its microstructure, pore distribution, grain sizes, and the titanium element distribution through metallographic microscope, scanning electron microscope (SEM) and energy diffraction spectrum (EDS) as well as its density with water immersion method. The experimental results show that at a certain sintering temperature, the adding of a small amount of titanium can obviously improve the sintering performance. In the experimental conditions, the optimum amount of doped titanium is under 0.3% (mass fraction) and the sintering temperature is 1250–1350 °C. After the study on the activated sintering mechanism, it is proved that the material transfer mechanism may be the joint action of strengthening cation diffusion and residual oxygen. With regard to the titanium element distribution, in addition to the solid solution of some on the outside of UO_2 microspheres, the other titanium oxides gather in the grain boundary in the form of free phase particles.

1. Introduction

In order to improve the efficiency of nuclear power, alleviate the handling and disposal pressure of spent fuel, a long-term goal for nuclear power plants is to develop high burn-up fuel with a long life. Compared with UO_2 ceramic pellets rod fuel elements used in the current water reactor power plants, the fuel particle dispersion in metal matrix forms the ceramic metal dispersion typed composite nuclear fuel which is characteristic of low core temperature, the inherent high safety, high radiation resistance, deep burn-up, long service life etc., making it also have broad application prospects in water power reactors [1–3].

The continuous improvement of burn-up can accelerate the irradiation swelling of UO_2, or even produces the foaming of fuel elements, which reduce the operation safety of the reactor. Researchers in the United States added the additive titanium in fuel particles of UO_2-SS (SS refers to stainless steel) dispersion fuel elements, making the foaming temperature of UO_2-SS dispersion fuel elements increase 50 °C to improve the fuel irradiation performance and increase the safety of the reactor operation. UO_2 microscopic structure has a great influence on its irradiation behavior in the reactor. Therefore, in order to ensure the stable and safe operation of fuel elements in the reactor, there are certain requirements on the UO_2 microstructure, especially fuel grain size, sintered density, etc. The doping of metal oxide in the fuel particles can increase the grain size of UO_2 fuel particles and improve the irradiation performance. At the same time, the doped metal oxide can be used as a sintering aid [4] to improve the sintered density and speed up the sintering rate [5].

Since the design feature of dispersion fuel elements is high fuel consumption, the ideal dispersion fuel phase should have the following disadvantages: (1) the spherical particle; (2) higher relative theoretical density and mechanical strength; (3) good microstructures, uniform distribution of small pores and fine grains. In order to further deepen the fuel burn up and improve the safety and economy of nuclear power, developing (U,Ti)O_2 dispersion fuel sphere with a high density and a good microstructure will have some scientific significance and provide technical support for the research on dispersion fuel element with high performance in nuclear power.

There are many methods to prepare spherical UO_2 particles with high density, such as sol–gel method, ball milling, and powder metallurgy method. Ball milling and powder metallurgy have good economical efficiency, but during the preparation of spherical fuel grain, there are some defects, such as the difficulty of controlling the spherical degrees, the unstable density and a large amount of dust. But sol–gel method has lots of advantages, such as the uniformity and purity of the material chemical composition, good crystal structure, easy control of spherical degrees and low sintering temperatures, which make it a research and development focus for preparation of ceramic fuel particles of UO_2, PuO_2 and ThO_2 at home and abroad. The sol–gel process has been recognized as the advanced technology for preparing ceramic nuclear fuel. But there

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is little research on the preparation of $(U,Ti)O_2$ microspheres by the method of sol–gel. In this paper, UO_2 microspheres are prepared through sol–gel with different amount of doped titanium (mass fractions are 0.3%, 0.5%, 0.7% and 0.9%) and sintered at different sintering temperatures (1250, 1350, 1450, 1550 °C), by which we will know the influence rules of the doped titanium compounds on sintering properties and microscopic structure of UO_2 microspheres.

2. The experimental method

2.1. Preparation of titanium-doped UO_2 microsphere

Take a certain amount of acid, deionized water and titanium compound, mix them in the beaker to prepare stable titanium sol through continuous stirring. Then mix adequate amount of uranyl nitrate (ADUN) with prepared titanium sol together to get transparent titanium-doped ADUN sol after uniform stirring for a period of time. Through sol dispersion, gelling, washing, calcination, reduction sintering and other processes titanium-doped ADUN sol will change to titanium-doped UO_2 microspheres. The sintering atmosphere is H_2 and the sintering temperatures are 1250, 1350, 1450 and 1550 °C. The sintering time is 4 h.

2.2. Analysis and measurement

Water immersion method is used to measure the density of titanium-doped UO_2 microspheres. Sand paper is used to gradually grind (until 800 meshes) the samples of microspheres. Cr_2O_3 turbid liquid is used for mechanical polishing. The volume fraction of 50% concentrated HNO_3 + 50% H_2O with high purity is used for chemical etching for 1–3 min to make all the grain boundaries revealed for metallographic observation and image acquisition. Image instrument is used to measure grain sizes. Scanning electron microscopy (SEM) and energy diffraction spectrum (EDS) are used to observe pore sizes and distributions of samples which are polished but without etching as well as the microstructures of samples and titanium element distributions after polishing and etching.

3. The experimental results and discussion

3.1. The influence of the content of doped titanium and sintering temperatures on the density of the microspheres

Fig. 1 shows that when the sintering temperature is 1250–1350 °C, doped titanium can significantly improve the rate of sintering UO_2 microspheres. When it is above 1350 °C, there is little impact on the compacting of UO_2 microspheres. When the content of doped titanium is more than 0.3%, the densities of microspheres increase slowly, then the densities decline slightly. When the sintering temperature is 1450 °C, with the increase of doped titanium the densities of microspheres increase slightly, but the increase rate is very small. When the sintering temperature reaches 1550 °C, the densities of titanium-doped UO_2 microspheres drop instead. From Fig. 2 it shows that when the content of doped titanium is 0.3%, 0.5%, 0.7% and 0.9%, the densities of microspheres begin to decline with the increase of sintering temperatures. When the temperature is over 1350 °C, microspheres densities increase as the sintering temperatures increase. But when the sintering temperature is 1450–1550 °C, there are few changes of microspheres densities, which is different from the densification law that with the increase of sintering temperatures, microspheres densities rise. Therefore, the sintered densities of UO_2 microspheres do not always rise with the increase of the content of doped titanium and sintering temperatures. The doped content of 0.3% and the sintering temperature of 1250 °C influence the densification of UO_2 microspheres most.

According to the literature [6], the positive role that TiO_2 plays in sintering is liquid phase sintering (liquid eutectic temperature of 1600 °C). When the highest sintering temperature is 1550 °C, UO_2 and TiO_2 cannot fully form eutectic liquid phase. Due to the small amount of doped titanium, liquid phase produced in sintering process of the titanium oxide will drop accordingly. Therefore, although the liquid phase sintering can effectively promote the sintering densification, it should not be the main factors to promote the sintering in the study of this paper. The following study shows that titanium ions are varying. Sintered in the reduction of H_2, TiO_2 can be restored into low titanium oxides (TiO, Ti_2O_3, Ti_3O_5, etc.) to release oxygen ions which come into the UO_2 interstitial void, making the UO_2 excess oxygen concentration increase so as to promote the sintering.

But when the doped titanium is more than 0.3%, the densities of UO_2 microspheres basically have no change. When it is more than 0.7%, the densities decline slightly. This may be due to titanium solution to the UO_2 during a small amount of doping, (Fig. 3). In Fig. 3, it is known that the titanium oxides are mostly distributed in the grain boundary. The content of titanium in grains is very low. In the solid solution state, titanium, mostly as a free phase dispersed particle, has an effect on material transfer, so this impedes the sintering densification of UO_2, leading to lower sintering densities.

3.2. The effect of the content of doped titanium and sintering temperatures on grain sizes of microspheres

Fig. 4 shows that the doping of titanium can effectively promote the grain growth of UO_2 microspheres. In the initial stage, with the

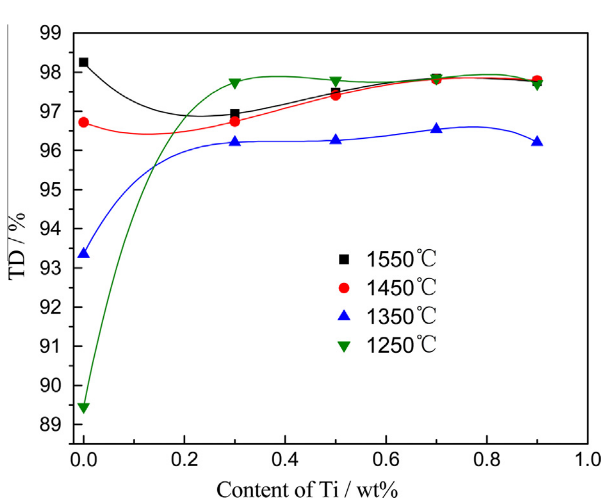

Fig. 1. The effect of the doped titanium on the density of UO_2 Microspheres.

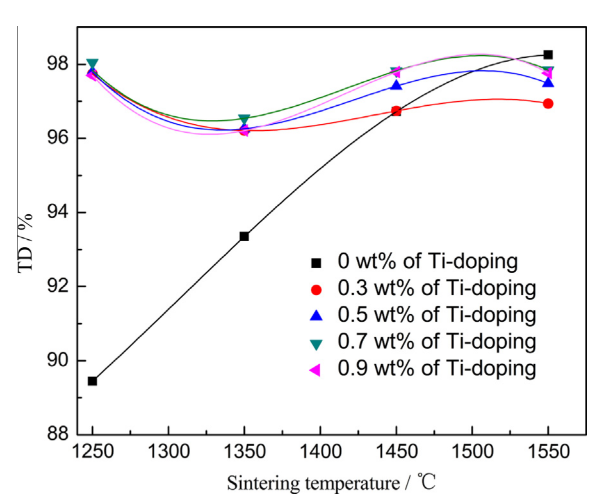

Fig. 2. The effect of sintering temperatures on the density of doped-titanium UO_2 microspheres.