Research on the preparation and sintering process of (U,Ti)O$_2$ dispersion fuel microsphere

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**ABSTRACT**

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, some on the outside of UO$_2$ microspheres, the other titanium oxides gather in the grain boundary in the form of free phase particles.

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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$_2$ microstructural 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 \((\text{U},\text{Ti})\text{O}_2\) microspheres by the method of sol–gel. In this paper, \(\text{UO}_2\) 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 \(\text{UO}_2\) microspheres.

2. The experimental method

2.1. Preparation of titanium-doped \(\text{UO}_2\) 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 \(\text{ADUN}\) sol will change to titanium-doped \(\text{UO}_2\) microspheres. The sintering atmosphere is \(\text{H}_2\) 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 \(\text{UO}_2\) microspheres. Sand paper is used to gradually grind (until 800 meshes) the samples of microspheres. \(\text{Cr}_2\text{O}_3\) turbid liquid is used for mechanical polishing. The volume fraction of 50% concentrated \(\text{HNO}_3 + 50\% \text{H}_2\text{O}\) 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 \(\text{UO}_2\) microspheres. When it is above 1350 °C, there is little impact on the compacting of \(\text{UO}_2\) 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 \(\text{UO}_2\) 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 \(\text{UO}_2\) 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 \(\text{UO}_2\) microspheres most.

According to the literature [6], the positive role that \(\text{TiO}_2\) plays in sintering is liquid phase sintering (liquid eutectic temperature of 1600 °C). When the highest sintering temperature is 1550 °C, \(\text{UO}_2\) and \(\text{TiO}_2\) 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 \(\text{H}_2\), \(\text{TiO}_2\) can be restored into low titanium oxides (\(\text{TiO}, \text{Ti}_2\text{O}_3, \text{Ti}_3\text{O}_5\), etc.) to release oxygen ions which come into the \(\text{UO}_2\) interstitial void, making the \(\text{UO}_2\) excess oxygen concentration increase so as to promote the sintering.

But when the doped titanium is more than 0.3%, the densities of \(\text{UO}_2\) 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 \(\text{UO}_2\) during a small amount of doping. 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 \(\text{UO}_2\), 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 \(\text{UO}_2\) microspheres. In the initial stage, with the
increase of doped titanium, the grain sizes increase, but when the
doped content is more than 0.3%, the grain sizes decrease with the
increase of doped titanium. The grain sizes of UO₂ microspheres
with the same amount of doped titanium increase when tempera-
ture rises, especially when the sintering temperature is more than
1350°C, the grain sizes increase more significantly. When the con-
tent of doped titanium is 0.3% and the sintering temperature is
1550°C, the grain size can reach 55 μm. From the experimental re-
result, a small amount of titanium is needed to get UO₂ microspheres
with big grain sizes. A large doping amount may hinder grain
growth. Temperatures have great influence on grain growth, which
means that the higher the temperature is, the faster the material
transfer rate is, the greater the grain size is. The experimental re-
results that Fig. 4 shows are consistent with the rules of other mate-
rial grain growth. That is to say, the higher the sintering
temperature is, the greater the grain size is (Fig. 5). From Fig. 5
we can also see that despite the fact that average grain sizes are
different at different sintering temperatures, the grain size distri-
bution is uniform.

According to oxide ceramics sintering theory, the material
transfer caused by lattice point defects will lead to the growth of
the grains. During the reducing sintering, the diffusion rates of oxy-
gen and metal cations are different, forming oxygen defect. By fill-
ing oxygen defects, material is transferred. Therefore, increasing
the concentration of oxygen defects can speed up the material dif-
fusion rate to boost the grain growth. If the cationic chemical va-
lence of doping oxide of is different from that of UO₂, cationic
vacancy appears to achieve the charge balance. There is more espe-
cially oxygen defect when the cationic sizes are similar and the
doped amount reaches solution limit. In reducing sintering, partial
TiO₂ is reduced into TiO, Ti₂O₃, Ti₂O etc. so that cationic vacancy
is formed so as to increase grain sizes. In the sintering of TiO₂ cations
have a stronger tendency to occupy the lattice space, which also
strengthens the diffusion of cations, and boost the grain growth.

Ploetz and other researchers [7] find that after adding 1% of TiO₂
into UO₂ liquid phase appears in the process of sintering. UO₂ and
TiO₂ form eutectic liquid phase (liquid eutectic temperature of
1600°C). The liquid phase infiltrates to the grain boundary, making

![Figure 3](image1.png)

**Fig. 3.** SEM and EPMA micrographs of UO₂ microspheres sintered at different temperatures.

![Figure 4](image2.png)

**Fig. 4.** Grain size of UO₂ microspheres as a function of Ti content.
the grain boundary migration easier, which reduces the grain boundary migration activation energy (Q) and contributes to the grain growth. At the same sintering temperature, when the titanium-doped content is more than 0.3%, the microsphere grain sizes begin to decrease with the increase of doped amount. The main reason may be that at the sintering temperature of 1650 °C and in the sintering atmosphere of H2, the solubility of TiO2 in UO2 is 0.07–0.13%. The sintering temperature of titanium-doped UO2 is 1250–1550 °C, lower than the liquid eutectic temperature of 1600 °C between TiO2 and UO2. Therefore, non-dissolved titanium oxide is free from the grain in the form of the second phase particles which enrich in grain boundary area (Fig. 3), having a “pinning” effect and thus inhibiting grain growth.

3.3. The pore changes in the sintering process of titanium-doped UO2 microspheres

According to Fig. 6, at the temperature of 1250 °C, the number of pores in titanium-doped UO2 microspheres is larger with smaller pore volume. When the sintering temperature reaches 1350 °C,
the number decreases slightly, but big pores increase a lot (Fig. 6b). When the temperature reaches 1450 °C, the number decreases further. Basically the pores are small with an obvious change to spheres (Fig. 6c). Within this sintering temperature range, the regularity of pores is similar to that of UO2 microspheres and the densification is higher. But when the sintering temperature reaches 1550 °C, although the number decreases a lot, the pore volume increases obviously (Fig. 6d). Therefore, compared with the sintering at 1450 °C, the density of titanium-doped UO2 microspheres does not rise like UO2 microspheres, but declines slightly (Fig. 1).

According to Fig. 7a and b, at the same sintering temperature, there are fewer pores with smaller volume and an obvious spherical tendency in UO2 microspheres than those in 0.3% titanium-doped microspheres. The densification of UO2 microspheres has almost finished (the relative theoretical density is 98.2%) and the pore size no longer reduces. Therefore, when 0.3% titanium-doped microspheres are sintered at 1550 °C, the densification reduces. From Fig. 7c and d, with the increase of titanium, the number of pores reduces significantly, but the spherical pores appear. Therefore, at 1550 °C, a small amount of doped-titanium in UO2 microspheres (<0.3%) can reduce the sintering density of UO2 microspheres. The increase of doped titanium in microspheres (mass fraction >0.3%) almost has no influence on the sintering densification of UO2 microspheres.

(2) At the sintering temperature of 1250–1350 °C, the reason why doping titanium can promote the densification of UO2 microspheres is that in the sintering process excessive oxygen and a small amount of liquid phase are formed. But at the sintering temperature of 1550 °C, the titanium oxide beyond the solid solubility mostly precipitates as a free phase dispersed particles, distributing in the pores of the grain boundary, which inhibits the densification of microspheres.

(3) Only a small amount of titanium is needed to get UO2 microspheres with big grain sizes. Too much titanium will hinder the grain growth. When the content of doped titanium is 0.3% and the sintering temperature is 1550 °C, the grain sizes of UO2 microspheres can reach 55 μm.

(4) When there is less titanium and the sintering temperature is within 1450 °C, the pore change rule of titanium-doped UO2 microspheres is basically the same as that of UO2 microspheres without titanium. But when the titanium is >0.3% and the sintering temperature is 1550 °C, the pore volume expands and the microspheres densification declines slightly.

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