Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 4421–4427

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Research on the grain growth and the mechanism of $(U,Ti)O_2$ dispersion fuel microspheres

Hui Wang[a,*], Junyan Liang[a], Chao Lu[b], Huawei Huang[a], Junbo Ren[a]

[a]National Key Laboratory for Nuclear Fuel and Materials, Nuclear Power Institute of China, Chengdu 610041, PR China
[b]College of Materials Science and Engineering, Sichuan University, Chengdu 610064, PR China

Received 21 August 2013; received in revised form 26 August 2013; accepted 26 August 2013
Available online 21 September 2013

Abstract

This paper studies the preparation of UO_2 dispersion fuel microspheres with 0.3 wt% of doped titanium by the sel–gol method. The experimental results show that between 1250 °C and 1450 °C, grain growth speeds are different with a rapid growth of some grains and a “double peaks” feature of grain sizes distribution, while at 1550 °C, the grain sizes have normal distribution with the average grain size of about 42 μm. Based on the calculation, between 1250 and 1550 °C, the average activation energy of the grain growth of $(U,Ti)O_2$ microspheres, Ea, was 232.79 kJ/mol, which is significantly lower than that of the UO_2 microspheres. In the later sintering period of $(U,Ti)O_2$ microspheres, U_4O_9 is formed in some parts of the microspheres, accelerating the U-atom diffusion rate and the grain growth.

Keywords: B. Grain size; UO_2 microspheres; Activation energy; Dispersion fuel

1. Introduction

In order to improve the efficiency of nuclear power, alleviate the handling and disposal pressure of spent fuel, developing fuel elements with high burnup and a long life is a long-term goal for nuclear power plants. Compared with the UO_2 ceramic pellets rod fuel elements used in the current water reactor power plants, the fuel particles dispersing in metal matrix form metal–ceramic dispersion fuel (Fig.1), a characteristic of low core temperature, inherent high safety, high radiation resistance, deep burn-up, long service life etc. [1–6], thus making it have broad application prospects in water power reactors also [7–9]. Metal–ceramic dispersion fuel is made up of the fuel phase and matrix phase. Nuclear fuel particles are evenly distributed in the base material. As far as fuel phase particles are concerned, the ideal dispersion fuel phase should have the following advantages: (1) the spherical particle; (2) higher relative theoretical density and mechanical strength; and (3) good microstructures. Therefore, it is more complex and difficult to prepare than the UO_2 pellets in nuclear power rod typed fuel element.

Although metal–ceramic dispersion nuclear fuel combines the advantages of ceramic fuel and metal fuel [10], overcomes the shortcomings of each fuel, thus improving the irradiation stability and increasing burnup depth, the pure UO_2 fuel dispersion phase has been difficult to meet higher requirements. Because the further deepening of burnup can lead to sharp increase in release rate of fuel fission products, UO_2 fuel irradiation swelling will be worse [11–15]. So it has become an important research direction to add other metal elements to UO_2 to inhibit fission gas release and improve the irradiation resistance and corrosion resistance of fuel phase so as to improve the fuel burnup [16,17].

At present, $(U,Ti)O_2$ fuel spheres prepared by the sol–gel process are considered good ceramic fuel, which can improve fuel burnup and irradiation stability under high burnup. The microstructure of UO_2 has a great influence on the irradiation behavior inside the reactor. Therefore, in order to guarantee the stable safe running of fuel elements in the reactors, there are certain requirements for the microstructure of UO_2, especially the fuel grain size.

*Corresponding author. Tel.: +86 13709081432.
E-mail address: qinghe5525@163.com (H. Wang).

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2013.08.114

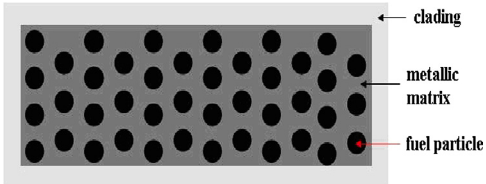

Fig. 1. Metal–ceramic composite dispersion fuel.

The larger the grain size of UO_2 pellets, longer the fission gas migration distance and lower the fission gas release rate. Lowering the pellets-cladding interaction (PCI) can significantly improve the safety margin of the fuel in the reactor in the process of running. In early experimental research work, we found that $(U,Ti)O_2$ fuel microspheres can be prepared with uniform distribution of titanium by using the sol–gel method [18]. A small amount of doped titanium can effectively promote the grain growth of UO_2 microspheres. In the same sintering conditions, the grain size of $(U,Ti)O_2$ fuel microspheres is much bigger than that of the UO_2 microspheres without doped titanium. The grain growth behavior between $(U,Ti)O_2$ fuel microspheres and UO_2 microspheres is definitely different; so the study on the grain growth mechanism of $(U,Ti)O_2$ fuel microspheres has certain theoretical guiding significance and academic value for improving and controlling the quality of $(U,Ti)O_2$ fuel microspheres, optimizing the process parameters as well as doing research on the dispersion nuclear fuel with high intrinsic safety in a water power reactor. Based on in-depth research and analysis about the grain growth of $(U,Ti)O_2$ fuel microspheres, the distribution of different grain sizes, microstructure morphology, titanium distribution inside the microspheres and grain growth kinetics, etc the grain growth mechanism of $(U,Ti)O_2$ fuel microspheres is discussed.

2. Experimental method

2.1. Preparation of $(U,Ti)O_2$ microspheres

The doping content of titanium is fixed as 0.3 wt%. The sol–gel method is used to prepare ADUN sol containing titanium. Take a certain amount of acid, deionized water titanium compound ADUN and mix them in the beaker and prepare 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 $(U,Ti)O_2$ fuel microspheres. The sintering atmosphere is H_2 and the sintering temperatures are 1250 °C, 1350 °C, 1450 °C and 1550 °C. The sintering time is 4 h.

2.2. Analysis and measurement

After the sintering of $(U,Ti)O_2$ fuel microspheres, sand paper is used to gradually grind (until 800 mesh) 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 reveal all the grain boundaries for metallographic observation and image acquisition. Image instrument is used for statistical measurement of the mean grain size. Scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) are used to observe the microstructures of $(U,Ti)O_2$ fuel microspheres, titanium element distributions as well as the titanium content on the grain boundary at different sintering temperatures.

3. Discussion of grain growth mechanism of $(U,Ti)O_2$ fuel microspheres

3.1. Calculation of grain growth activation energy of $(U,Ti)O_2$ fuel microspheres

For general material, the grain growth conforms to the classic Arrhenius formula:

$$k = A\exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

In the formula, k is grain growth speed, A refers to the pre-exponential factor, E_a is grain growth activation energy, R refers to the gas constant and T is the heat treatment temperature.

If $k = dG/dt$, and k is a constant within a certain temperature range, integral calculation on both sides goes like

$$\int_{t_1}^{t_2} k\,dt = \int_{G_1}^{G_2} dG \Rightarrow k = \frac{G_2 - G_1}{t_2 - t_1} \tag{2}$$

That is $\left((G_2-G_1)/(t_2-t_1)\right) = A\exp\left(-\left(E_a/RT\right)\right)$, take logarithm on both sides to get:

$$\ln\left(\frac{G_2 - G_1}{t_2 - t_1}\right) = \ln A - \frac{E_a}{RT} \tag{3}$$

Between the 2 temperatures T_1 and T_2, the average activation energy is

$$E_a = \frac{RT_1T_2}{T_1 - T_2}\ln\left(\frac{G_2 - G_0}{G_1 - G_0}\right) \tag{4}$$

In the formula, G_1 and G_2 are the average grain sizes at the temperatures of T_1 and T_2.and G_0 is the average grain size of samples before annealing. $(U,Ti)O_2$ fuel microspheres in the present study keep thermal preservation for 4 h at 1250 °C, 1350 °C, 1450 °C and 1550 °C respectively with the average grain sizes of 3.3 μm, 6.8 μm, 25.4 μm and 41.9 μm (Fig. 2). According to the formula (4), the average grain growth activation energy of $(U,Ti)O_2$ fuel microspheres, E_a, can be calculated between 1250 °C and 1550 °C. Calculation results are listed in Table 1.

According to Table 1, between 1250 °C and 1550 °C, the average grain growth activation energy of $(U,Ti)O_2$ fuel microspheres, E_a=(181.72+361.7+154.95)/3=232.79 kJ/mol.

The average grain growth activation energy of UO_2 microspheres E_{a0}=518.32 kJ/mol. Nichols [19] proposed a phenomenological dynamic equation for the normal grain growth (5), which can also be applied to the grain growth kinetics when the second phase impurities are present at the same time.