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Grain growth and Ostwald ripening in chromia-doped uranium dioxide

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The use of solid solution additives such as "corundum" types oxides is a practical mean for enhancing grain growth of stoichiometric uranium dioxide. The present paper deals with chromia-doped UO_2 samples. Large-grain sized fuels can be produced by addition of less than 1000 ppm of chromia to UO_2 powder prior to sintering. Above the solubility limit, excess of insoluble Cr_2O_3 precipitates from solid solution to create second phase inclusions in UO_2 matrix. These inclusions coalesce by an Ostwald ripening phenomenon.

INTRODUCTION

A better uranium dioxide utilization is needed to reduce fission product release from pellets during irradiation. Improvement of fuel performances could be achieved by increasing the diffusion path length of volatile fission products, and dispersing precipitates which are able to pin individual fission gas bubbles in UO_2 matrix. Studies have been performed to create new fuel microstructures, mainly characterized by a large grain size, and a dispersion of second phase inclusions.

GRAIN GROWTH

The use of sintering additives is necessary to promote stoichiometric uranium dioxide grain growth. A recent complete study [1] has been made on UO_2 samples doped with "corundum" type oxides showed in table 1.

Table 1: Solubility limit of different "corundum" structure type oxides in UO_2 at 1700°C.

OXIDE	Cation radius (nm)	Solubility limit (ppm)	Grain size (μm)
Al_2O_3	0,0535	70	35
Ti_2O_3	0,0670	1000	65
V_2O_3	0,0640	400	40
Cr_2O_3	0,0615	700	65

In this paper, we will focus on mechanisms reported for chromia-doped uranium dioxide, but these phenomena can be applied to the previously mentioned oxides.

Experimentally, the thermodynamic conditions of the sintered treatments were defined to control the oxidation state of doped cations, to preserve M^{3+} ions.

Figure 1: Thermodynamic presentation of chromia-doped UO_2 system with some reducing sintering atmospheres [2].

At high temperature, under reducing atmosphere, chromium can be maintained in Cr_2O_3 chemical state (figure 1). This favourable condition allows the dissolution of the dopant in the host matrix, and the development of a large grained fuel microstructure.

Figure 2: Oxygen potential influence on Cr_2O_3 -doped samples (4 hours at 1700°C).

In figure 2, the grain size of pellets is plotted as a function of initial doped oxide concentration. A solubility limit of additives in UO_2 can be found at the upper grain diameter. At 1700°C , the solubility limit yields 700 ppm for chromia in uranium dioxide.

Two different behaviours must be considered :

- in domain A, for quantity of Cr_2O_3 lower than the solubility limit, the dopant oxide is soluble in fluoritic uranium dioxide and forms a substitutional solid solution. It promotes the grain growth. The average maximum grain size reaches $65\ \mu\text{m}$. In the same time, an acceleration of specimen densification seems to be influenced by an abnormal grain growth process;

- with an increasing concentration of chromia, above the solubility limit, in domain B, excess of insoluble Cr_2O_3 precipitates to form small second phase particles. These inclusions can inhibit grain growth by limiting grain boundaries mobility, such as in a Zener drag type mechanism. When Cr_2O_3 concentration increases, the presence of a liquid phase can explain the emphasis of the pellets density and grain growth, showed by the second maximum on figure 2. At high temperature, Tokar and all.^[2] propose in a new phases diagram, the existence of an eutectic composition " CrO " between Cr_2O_3 and Cr. The coalescence of large grains takes place by dissolution and diffusion of uranium in the intergranular liquid phase.

OSTWALD RIPENING

The chromium oxide micrometric precipitates are almost spherical (figure 3), and located principally within grains.

Figure 3: Cr_2O_3 precipitates (SEM, BEI X2000)

When heat treatment annealing times reach several hours at 1700°C , it appears that inclusions coalesce by an Ostwald ripening phenomenon.

Figure 4: Schematical approach of Ostwald ripening.

The driving force is derived from the consequent reduction in total interfacial energy. The large precipitates grow by diffusion of Cr^{3+} atoms from small ones through the supersaturated host matrix. In the case of chromia-doped samples, with small fraction of second phase noninteracting particles, lower than 1 weight percent, LSW theory [3] can be used. The rate equation is found to be a $1/3$ power time law expressed as $G^3 - G_0^3 = Kt$; where G is the particle size and K is a constant which depends on $D_{\text{vol}}(\text{Cr}^{3+})$, the solute Cr^{3+} volume diffusion coefficient.

Experimental SEM observations of doped pellets, associated with image analysis and then calculations, have been performed to determine the shape of the precipitate size distributions (figure 5) and the diffusion coefficient of Cr^{3+} (figure 6).

Figure 5: Shapes of the precipitate size distributions, Cr_2O_3 -doped samples (1700°C).

Figure 6: Position of Cr^{3+} experimental volume diffusion coefficient.

DISCUSSION

The experimental distributions, stationary with increasing time, do not agree with the theoretical LSW one, based on coarsening of solid precipitates in a liquid or a gaseous medium. These discrepancies were thought to be due to elastic coherency strains and to the presence of grain boundaries short circuit diffusion path. These factors, not included in LSW model, must be considered in polycrystalline solid system.

The Cr^{3+} volume diffusion coefficient is in the same range value than the uranium grain boundary diffusion coefficient in stoichiometric UO_2 . However, it is higher by 7 orders of magnitude than uranium volume diffusion coefficient. The value of $D_{\text{vol}}(\text{Cr}^{3+})$ estimated by this original method, is of great interest to predict the irradiation behaviour of chromia-doped fuel.

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