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Abnormal grain growth of UO_2 with pores in the final stage of sintering: A phase field study

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ABSTRACT

The phase field formulation has been employed to investigate the abnormal grain growth behaviors for UO_2 with pores in the final stage of sintering. The microstructure evolution is found dependent on the total volume fraction and individual sizes of pores. The grain growth rate is evidently suppressed when the porosity is high and it is found independent of pore size at low porosity. Moreover, the smaller pores may cause worse abnormal grain growth at low porosities and more significant stagnation effect at high porosities in the sintering of UO_2. By further inspection on pore-boundary interaction in a bi-grain system designed in this work, the grain growth behavior is determined to be strongly correlated to the engulfment of pores by grains which may be described by the critical grain radius and critical time defined hereby. The data obtained may provide a new insight into the mechanism behind the sintering technology of nuclear fuels such as UO_2.

1. Introduction

As the most widely utilized nuclear fuel at present, UO_2 is of great importance in nuclear industry. The microstructure of UO_2 plays a decisive role in its performance in a nuclear reactor. By theories and experiments, it has been reported that UO_2 with large grains can suppress the emission of fusion gas during operation of the reactor, assisting to enhance the burn-up and extend the operating life of the fuel [1]. Therefore, in order to improve the performance of UO_2, one of the effective ways is the preparation of UO_2 with uniformly distributed large grains, which demands elaboration on the fabrication procedures, such as sintering. Nowadays, the investigation on UO_2 grain growth behaviors during the sintering process has attracted considerable attention. Particularly, the understanding of grain growth behavior in the final stage of sintering, which is significantly influenced by the interaction between the grain boundaries (GBs) and pores, is crucial to control the microstructure of UO_2 pellets.

Since 1960s, many studies have been reported on the grain growth of UO_2 during the process of sintering. Ainscough et al. [2] studied the isothermal grain growth kinetics of sintered UO_2 pellets, and found temperature had impact on the grain size limit. MacEwan et al. [3] claimed that pronounced grain growth was not observed in sintering processes until the total porosity decreased to 2–3% of the volume for the specimens. Brook [4] studied the interaction between GBs and pores and found that different mechanisms of pore-boundary interaction could lead to different grain growth exponents. During the sintering of UO_2, various ways of mass transport including surface, GB and bulk diffusion and evaporation-condensation (EC) can facilitate the pore-boundary interaction dependent on temperatures [5–8]. Bourgeois et al. [9] found surface diffusion was the predominant transport mechanism over EC for pore migration at around 1700 °C. Depending on the mechanisms of pore-boundary interaction, grain size distribution and sintering atmosphere, the grain growth behavior can be normal or abnormal [10]. Normal grain growth (NGG) is driven by the decrease of total grain boundary energy and evolves in a uniform manner. On the contrary, abnormal grain growth (AGG) is characterized by a subset of grains gaining some privilege to grow faster than others and tends to result in non-uniform microstructure. In fact, the anisotropy in the GB energy, GB mobility [11], GB complexion [12], free surfaces [13] and second phase particle distributions [14] may synergistically induce AGG. For polycrystalline materials, occurrence of AGG often has undesirable effects on the homogeneity of grain size [15]. During the final stage of

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UO_2 sintering, especially, pores located at GBs are likely to alter the motion of the GBs, leading to the occurrence of AGG the degree of which is dependent on the distribution of pore sizes and locations [5]. Bourgeois et al. [16] found that grain growth in the final stage of sintering of UO_2 could be considered as abnormal in the sense that the pores does not seem to pin the GBs. However, it is still an open question what impact the pore distribution has on AGG of UO_2.

To study the UO_2 grain growth behavior with pores, a number of methods have been adopted experimentally and theoretically. With the rapid development of super-computing, numerical modelling has become a major technique in this field recently. In particular, the phase field model is considered as a promising scheme to describe the microstructure evolution of UO_2 with pores from different perspectives, such as pore-boundary interaction during UO_2 GB migration [17], fission gas bubble evolution in UO_2 under post-irradiation thermal annealing [18], and features of faceted void morphologies in UO_2 [19]. Especially, Ahmed et al. [5–8] have recently developed a phase field model and accurately obtained the kinetics of grain growth in porous UO_2. This model can combine various diffusion mechanisms concerning the interaction between GB and pores. Moreover, by this model one can incorporate the GB diffusivity and surface diffusivity with respect to the specific material, such as UO_2. The predictions exhibit excellent agreement with the experimental results, demonstrating that this model is suitable to explore the porous grain growth. Nevertheless, the role of pore distributions in the AGG of UO_2 during the final stage of sintering has not been thoroughly studied and needs further investigation.

In this article, we use the phase field model to study the grain growth behavior of UO_2 with pores in the final stage of sintering, with emphasis on the characteristics of AGG. The roles of total pore volume fraction and individual pore size in AGG are elucidated. Particularly, to characterize the degree of abnormality for AGG, a five-level hierarchy system based on grain sizes is thereby applied.

2. Phase field model

Here, the phase field modeling in the framework provided by Ahmed et al. [5–8] is employed to study the microstructure evolution of UO_2. The free energy functional F for the non-uniform medium consisting of solid grains and pores is given as follows:

$$F = \int \left[f(\rho, \eta_1, \eta_2, \ldots, \eta_q) + \frac{k_\rho}{2}|\nabla\rho|^2 + \frac{k_\eta}{2}\sum_{\alpha=1}^{q}|\nabla\eta_\alpha|^2 \right] d^3\mathbf{r}. \tag{1}$$

Here $\rho(\mathbf{r}, t)$ is the conserved field as the function of position vector $\mathbf{r}$ and time t to distinguish grains ($\rho = 1$) and pores ($\rho = 0$). $\eta_\alpha(\alpha = 1, 2, \ldots, q)$ are the non-conserved order parameters with q as the total number of grains, being unity in the α-th grain and zero otherwise to distinguish different grains. The changes in these parameters reflect the microstructure evolution in the polycrystalline solid with pores [6]. k_ρ and k_η are the gradient coefficients. Consistent with Ahmed et al. [5–8], the bulk free energy density f is

$$f(\rho, \eta_1, \eta_2, \ldots, \eta_q) = B\rho^2(1-\rho)^2 + C\left[\rho^2 + 6(1-\rho)\sum_{\alpha=1}^{q}\eta_\alpha^2 - 4(2-\rho)\sum_{\alpha=1}^{q}\eta_\alpha^3 + 3\left(\sum_{\alpha=1}^{q}\eta_\alpha^2\right)^2\right]. \tag{2}$$

As discussed below, B and C, along with k_ρ and k_η in Eqs. (1) and (2), are structure-related constants determined by surface, GB energies and GB width. The free energy parameters are related to the material properties as [6]:

$$\begin{aligned} \gamma_{GB} &= 2\sqrt{Ck_\eta/3}, \\ \gamma_s &= \sqrt{2(k_\rho + k_\eta)(B + 7C)}/6, \\ l &= \sqrt{4k_\eta/3C} = \delta, \\ 6k_\rho C &= k_\eta(B + C), \end{aligned} \tag{3}$$

where γ_{GB}, γ_s and δ are the GB energy, surface energy, and GB width, respectively, and l is the diffuse interface width. In our simulation, specifically, for UO_2 with surface energy γ_s of 0.6 J/m^2, GB energy γ_{GB} of 0.3 J/m^2 and GB width δ of 1 nm [6], the free energy parameters take on the values: $B = 1.9176 \times 10^9$ J/m^3, $C = 1.128 \times 10^8$ J/m^3, $k_\eta = 6 \times 10^{-10}$ J/m and $k_\rho = 1.8 \times 10^{-9}$ J/m. According to the empirical potential calculations, the GB energy of UO_2 may be in the range of 1–1.9 J/m^2 at 0 K [20]. However, the GB energy can be largely decreased with the increasing temperature, especially at high temperatures, for example, above $0.5T_m$ in oxides [21,22] and metals [23]. In experiments, the sintering temperatures can be actually around 1700 °C [16,24]. Furthermore, the surface diffusion activation data obtained by experiments are relatively reliable between 1200 °C and 1800 °C [9]. Thus, 1700 °C is chosen as the sintering temperature in the current modelling study, which is close to 0.6 T_m. As a result, it is reasonable to choose GB energy to be 0.3 J/m^2 consistent with the previous simulations and experiments [6,24].

The governing equations for the field and order parameters are given by:

$$\begin{aligned} \frac{\partial\rho}{\partial t} &= \nabla\cdot\mathbf{M}\nabla\frac{\delta F}{\delta\rho}, \\ \frac{\partial\eta_\alpha}{\partial t} &= -L\frac{\delta F}{\delta\eta_\alpha}. \end{aligned} \tag{4}$$

In Eq. (4), L is Allen-Cahn mobility; $\delta F/\delta\rho$ and $\delta F/\delta\eta_\alpha$ are functional derivatives of the free energy with respect to ρ and η_α. $\mathbf{M} = \mathbf{D}\upsilon_m/RT$ is the chemical mobility tensor, with $\mathbf{D}$ as the mass diffusion tensor, $\upsilon_m = 24.5 \times 10^{-6}$ m^3/mol as the molar volume, R as the universal gas constant and T as the absolute temperature. This tensor accounts for multiple diffusion mechanisms, including bulk, GB and surface diffusions [5]. According to Ahmed et al. [6], surface diffusion is the dominant mechanism in the sintering of UO_2 at high temperatures and will be also considered as the major mechanism in our simulation. For UO_2 with only surface diffusion, $\mathbf{M} = \upsilon_m\mathbf{D_s}/RT$ with $\mathbf{D_s}$ as the surface diffusion tenor along the surface of pores. Specifically, $\mathbf{D_s} = D_s\rho^2(1-\rho^2)\mathbf{T_s}$, where D_s is the surface diffusion coefficient, chosen as $D_s = 50\exp(-450{,}000/RT)$ [24] and $\mathbf{T_s} = \mathbf{I} - \mathbf{n_s}\otimes\mathbf{n_s}$ with $\mathbf{I}$ being the identity tensor, $\otimes$ representing the dyadic product, and $\mathbf{n_s}$ the unit normal vector to the pore surface, calculated by $\mathbf{n_s} = \nabla\rho/|\nabla\rho|$. In order to determine L in Eq. (4), a relation of $L = \gamma_{GB}M_{GB}/k_\eta$ will be used, where $M_{GB} = D_a\upsilon_m/RT\delta$ is the GB migration mobility with GB migration coefficient D_a=1.38 × $10^{-7}\exp(-239{,}000/RT)$, which has been proved to be suitable for describing grain growth of UO_2 [6]. The key expressions used for calculating $\mathbf{M}$ and L in Eq. (4) are summarized in Table 1.

To implement convenient numerical governing equations, the coefficients k_ρ, k_η, B and C are simultaneously rescaled according to Eq. (3) to allow for the use of much thicker diffusive interface l' (e.g. $l' = 1.3$ μm in this article) while keeping the surface and GB energies as well as the grain growth kinetics invariant [6]. Thus, the dimensionless version of the kinetic equations is constructed by choosing $\varepsilon = B'$ (rescaled B), $l^* = 0.2l'$ and $t^* = 1/L\varepsilon$ as the reference energy density, length scale and time scale, respectively, expressed as follows [6]