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**HOT-ISOSTATIC PRESSING OF U-10Zr BY GRAIN BOUNDARY DIFFUSION
AND CREEP CAVITATION - PART II: THEORY AND DATA ANALYSIS**

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Hot-isostatic pressing (HIP) experiments performed at 700°C on U-10Zr samples with different impurity phase contents (Part I) are analyzed in terms of several creep cavitation models. The coupled diffusion/creep cavitation model of Chen and Argon shows good quantitative agreement with measured HIP rates for hydride- and metal-derived U-10Zr materials, assuming that pores are uniformly distributed on grain boundaries and are of "modal" size, and that far-field strain rates are negligible. The analysis predicts, for the first time, an asymmetry between HIP and swelling at identical pressure-induced driving forces due to differences in grain boundary stresses. The differences in compressibility of hydride- and metal-derived U-10Zr can be partially explained by differences in pore size and spacing. The relevance of the experiments to description of in-reactor densification under external pressure or contact stress due to fuel/cladding mechanical interaction is discussed.

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1. Introduction

Uranium - 10 wt % zirconium (U-10Zr) is a fuel alloy that has been used in the Experimental Breeder Reactor - II (EBR-II) at Argonne National Laboratory [1]. The high burnup that was desired in this fuel system made high demands on the mechanical compatibility between fuel and cladding both during normal operation and during safety-related transients when rapid differential expansion may cause high stresses. In general, this mechanical stress can be reduced by cladding deformation if the cladding is sufficiently ductile at high burnup, and/or by fuel hot-pressing. Fortunately, the fuel is very porous when it contacts the cladding, but this porosity gradually fills with solid fission products (primarily lanthanides) that may limit the fuel's compressibility [2]. If the porosity remains open, gaseous fission products are released and the porous fuel creeps rather than hot-presses under contact stresses. If the pores are closed by sintering or by solid fission products, the porous fuel will hot-isostatic press (HIP), as represented by the models to be discussed. The HIP experiments described in Part I [3] produced the first primary data available for this alloy system, but they required more extensive analyses than previous experiments of the same type [4-11]. These analyses are presented here as Part II. For clarity, the background and salient results from Part I will be reviewed first.

Specimens of U-10Zr were prepared under purified argon from mixtures of uranium hydride with zirconium hydride powders ("hydride-derived" specimens) and of uranium microspheres with zirconium metal ("metal-derived" specimens). The processing methods are described elsewhere [3,12,13]. The hydride- and metal-derived samples were sintered under pressure in a purified argon atmosphere at 1100°C and 1200°C, respectively. This high-pressure sintering method, developed by Abbott and Solomon [4], generates gas-filled pores or bubbles on the grain boundaries. Both types of specimens were successfully hot-pressed by increasing the ambient pressure to create a driving force for densification at 700°C (γ -phase U-10Zr). HIP was also attempted at 600°C but no densification was detectable.

The initial HIP strain rates taken at 1 minute after the onset of densification are shown in Fig. 1 vs. the initial HIP driving force. The driving force is given by $F = P - p + 2\gamma/r_p$, where P is the ambient pressure; p is the internal pressure of the gas-filled pores; $2\gamma/r_p$ represents the pore surface pressure due to the surface tension, γ ; and r_p is taken to be the modal pore radius of curvature from the log-normal pore size distribution. (It was reported that the mode best represented the porosity distribution during swelling and HIP [8].) The hydride-derived specimens hot-pressed at higher strain rates than the metal-derived specimens under the same driving force, in spite of the significantly higher concentration of impurity particles and lower amount of dissolved Zr in the hydride-derived material.

As discussed in Part I [3], the measured driving force dependence of the HIP strain rate and the measured HIP activation energy point to opposing conclusions. It is apparent from the data in Fig. 1 that the driving force dependence of the initial HIP rate is nonlinear.* A power law of the form $\dot{\epsilon} \sim F^n$ was used to determine an empirical driving force dependence (n -value) of 3.7 ± 0.5 [3] for both materials ($\dot{\epsilon}$ is the HIP strain rate and F is the pressure driving force for HIP). An independent measure of n was also made through small pressure perturbations during the HIP experiments. These experiments yielded $n = 3.4 \pm 0.3$ for the metal-derived specimens and 3.2 ± 0.5 for the hydride-derived specimens [3], in good agreement with the previous determination. This nonlinear dependence on the driving force was not seen in our previous HIP and swelling experiments on nonmetallic materials under similar conditions [4-10] but was detected for pure Ni [11]. Together, these two observations suggests the possibility that, under these conditions, power-law creep is significant in the HIP of metals.

On the other hand, a different indication is given by the HIP activation energy (Q), which was measured for both types of specimens through temperature cycling during HIP transients. There was good agreement between the Q -values measured for the hydride- and metal-derived materials, with an overall mean Q -value of 187 ± 10 kJ/mole (45 ± 3 kcal/mole) [3,12,13]. This value is consistent with the reported activation energy of 186.6 kJ/mole (44.6 kcal/mole) for grain

* The log-log plot of the same data is included in Fig. 4.

boundary diffusion of uranium in pure γ -uranium [14], which suggests that grain boundary diffusion dominates the HIP process. Thus, the activation energy results indicate that HIP should be unrelated to power-law creep under the present conditions.

Despite the different implications of the measured n and Q values, the agreement in n and Q for the hydride- and metal-derived specimens strongly supports the idea that both types exhibit the same HIP mechanism. The purpose of this paper is to examine the applicability of the various available HIP models to explain our experimental results. It has been established that the phenomena of HIP and swelling of porous materials at elevated temperatures can be well described by models developed for creep cavitation [11]. These models for creep cavitation will be reviewed and then applied to the U-10Zr results presented in Part I.

2. Creep Cavity Growth Models

The models described below require the assumption of uniform cavity sizes and spacings on grain boundaries normal to the applied stress, so that a single representative volume element can be analyzed. While such models may capture the basic physics, some important interactions are omitted because pore sizes and spacings can vary in a real system [15]. Therefore, the simplified models should only be expected to give order-of-magnitude agreement with measurements for most real microstructures.

2.1 *Grain boundary diffusion controlled cavitation*

Hull and Rimmer [16] were the first to analyze the growth of grain boundary cavities by vacancy diffusion in response to an applied tensile stress. Cavities of identical size and spacing are assumed to nucleate or pre-exist on grain boundaries that are perpendicular to the applied tensile load. The stress-induced potential difference between the grain boundary and the cavity surface creates a driving force for vacancy diffusion from the boundary to the cavity surface (or a reverse

flow of atoms), inducing cavity growth. Diffusion on the cavity surface is assumed to be much more rapid than in the grain boundary, such that grain boundary diffusion is rate-limiting. It is also assumed that atoms are deposited uniformly over the entire boundary to minimize lattice strains. It is implicit in these assumptions that the grain boundary and cavity surfaces also act as perfect sources and sinks for vacancies.

The original Hull-Rimmer formulation for diffusion-controlled cavitation has been modified by several authors [17-22], but the fundamental concept has not changed. Important modifications have been made to the model geometry [17-20] and the boundary conditions [21,22]. A further modification to this diffusion-controlled mechanism was developed by Chuang *et al.* [23,24] for "crack-like" cavity growth during creep, which occurs when cavity surface diffusion is not much faster than grain boundary diffusion. However, crack-like cavity growth is typically not observed for HIP and swelling situations under the present conditions [3,5-11], so this model will not be considered.

The models for diffusional cavitation were later supplemented by coupled diffusion and creep models [25,26] in which diffusion dominates near the cavity and creep dominates far from the cavity. Figure 2 illustrates the geometry generally assumed for the coupled creep cavitation models. This geometry can be used to represent grain boundary diffusion controlled cavitation at one extreme and creep-controlled cavitation at the other, according to the formulation of Beere and Speight [25] and Chen and Argon [26], when both processes contribute to cavitation. The diagram shows a top and side view of two adjacent unit cells which are divided into two regions, one where grain boundary diffusion dominates (Region I) and one where creep deformation dominates (Region II). The unit cell geometry consists of a cavity* with a radius of curvature r_p in a cylindrical volume element with radius λ and height ℓ .

Chen and Argon [26] argue that the model presented by Speight and Beere [22] provides the most accurate and complete formulation for cavity growth controlled by grain boundary

* The terms "cavity," "pore," and "bubble" will be used interchangeably.

diffusion. When grain boundary diffusion dominates cavitation, Region I (Fig. 2) extends over the entire unit cell ($b \geq \lambda$) making the model geometry identical to the Speight-Beere geometry [22].

For a material containing spherical, gas-filled pores with an internal pore pressure p and an external tensile stress σ , the Speight-Beere expression for the rate of change of an individual pore's volume, v , is given as [22]

$$\left(\frac{dv}{dt}\right)_{gb} = \frac{2\pi \Omega D_b \delta_b}{kT f\left(\frac{r_p}{\lambda}\right)} \left[\sigma - p + \frac{2\gamma}{r_p} \right], \quad (1)$$

where γ is the pore surface energy, D_b is the grain boundary diffusion coefficient, δ_b is the effective "width" of the boundary, Ω is the atomic volume, k is Boltzmann's constant, and T is temperature. For the present situation, where the external stress state is a hydrostatic pressure P the grain boundary diffusion controlled rate of change is given by [3]

$$\left(\frac{dv}{dt}\right)_{gb} = \frac{2\pi \Omega D_b \delta_b}{kT f\left(\frac{r_p}{\lambda}\right)} \left[P - p + \frac{2\gamma}{r_p} \right]. \quad (2)$$

The term $f\left(\frac{r_p}{\lambda}\right)$ is a geometric function given by [22]

$$f\left(\frac{r_p}{\lambda}\right) = - \left[\ln\left(\frac{r_p}{\lambda}\right) + \frac{1}{4} \left(1 - \left(\frac{r_p}{\lambda}\right)^2 \right) \left(3 - \left(\frac{r_p}{\lambda}\right)^2 \right) \right] \quad (3)$$

It should be noted that under hydrostatic conditions, all grain boundaries have the same normal stress, which makes the model more relevant.

2.2 Creep-controlled cavitation

In the limit where grain boundary diffusion is limited, creep can dominate the pore growth rate. Beere and Speight [25] discuss the tensile creep of a cylindrical shell of material around the pores, assuming that ℓ (Fig. 2) is on the order of the pore diameter and thus Region II extends over the entire unit cell. Beyond this pore growth region, additional strain can occur by creep under the applied tensile stress. The pore growth rate resulting from the creep of the cylindrical shell is given by [25]

$$\left(\frac{dv}{dt}\right)_{\text{creep}} = 2\pi r_p^3 \dot{\epsilon}_c, \quad (4)$$

where $\dot{\epsilon}_c$ is the axial strain rate in response to the stress acting on the shell. In the models for creep cavitation and HIP that are governed by plastic deformation [25-30], creeping material is assumed to creep according to the constitutive relation

$$\dot{\epsilon}_c = B\sigma_e^n, \quad (5)$$

where $\dot{\epsilon}_c$ represents the creep strain rate of the material in response to an effective stress σ_e , and B and n are empirical constants.

Another example is the creep-controlled HIP model derived by Wilkinson and Ashby [27], which is based on earlier models of Murray *et al.* [28], Mackenzie and Shuttleworth [29], and Wolfe [30] and on Eq. 3. The model assumes a uniform, three-dimensional distribution of equisized pores. The unit cell geometry is defined as a spherical pore in the center of a creeping spherical shell with the outside diameter equal to the pore half-spacing. An applied hydrostatic stress acts on the exterior of the shell and a gas pressure acts on the inside. Wilkinson and Ashby derive the stress field within the shell to determine the effective stress, assuming an external hydrostatic pressure and an internal pore pressure. The applicability of such a uniform

densification model to a case in which pores exist only on the grain boundaries seems questionable. The initial hydrostatic stress at the grain boundary is perturbed by the surrounding rigid grains, and this perturbation causes the stress state to evolve into the Beere-Speight model in which the boundary pores densify under the normal stresses. Therefore, for creep-controlled cavitation, we considered only the Beere-Speight model.

2.3 Coupled diffusion/power-law creep controlled cavitation

Several authors have considered the simultaneous operation of the creep and grain boundary diffusion mechanisms. These combined models are referred to as "constrained" cavitation [31-33] or "enhanced" cavitation [15,25-26,34-36]. The term "constrained" is used when cavities are isolated on a boundary that is surrounded by adjacent boundaries having no cavities. The growth of widely-spaced cavities under a tensile load requires long-range diffusion unless the material far from the cavities can creep [31-33]. Thus, the surrounding material is considered to act as a "constraint" to diffusive cavitation, and creep can relax this constraint. Thus, creep aids or "enhances" cavitation. Therefore, the distinction between "constrained" or "enhanced" is semantic only and arises when the assumption of uniform cavity spacing is relaxed [15].

When cavity spacing is uniform, a representative volume element allows simple modeling of the coupled creep/diffusion process. As discussed in Part I, Beere and Speight [25] treat this coupled mechanism by assuming that diffusion alone occurs near the cavity and that diffusion is negligible over the rest of the grain boundary, while creep alone occurs outside Region I (Fig. 2). For the diffusive region, the assumed rigid grains move apart when atoms migrate to the grain boundary in a process called "jacking" [22]. For strain compatibility at the cell boundary, it is assumed that the vertical creep strains in Region II match the strains produced by jacking in Region I over the cell height. The cell height, ℓ , is taken as $2b$, which is equivalent to assuming a hole exists in the material the size of the diffusion zone because all stresses are assumed to be relaxed by diffusion in Region I.

Beere and Speight [25] derive a system of equations based upon assumed boundary conditions to calculate the parameters b , σ_I , and σ_{II} , where σ_I is the average stress over region I (including the cavity) and σ_{II} is the stress on the boundary in Region II. Because the system of equations is complex, Beere and Speight subsequently presented an approximation for the pore rate of volume change by summing the two limiting cases in which diffusion alone ($b \geq \lambda$) or creep alone ($b \leq r_p$) is dominant [25]. This approximation was later rejected as an oversimplification by several authors [26,34-36].

A significant improvement to the coupled model came from Chen and Argon [26], who advanced a similar, but more elegant, model that directly calculates the size of the diffusional zone. They also extended the model to include nonequilibrium, crack-like pores, similar to the model of Chuang *et al.* [23,24]. The complex system of equations presented by Beere and Speight [25] becomes unnecessary because the size of the diffusion zone, b , is calculated from the "diffusion distance" or "characteristic length" (Λ in Fig. 2) as derived by Rice [35]

$$\Lambda = \left(\frac{D_b \delta_b \Omega \sigma_\infty}{kT \dot{\epsilon}_\infty} \right)^{1/3}, \quad (6)$$

where σ_∞ and $\dot{\epsilon}_\infty$ represent the far-field creep stress and creep rate, respectively. Chen and Argon [26] estimate the diffusion zone radius by setting $b = r_p + \Lambda$ and then calculate the pore growth rate due to the jacking of Region I. Therefore, the pore growth rate for the coupled process may be directly calculated from

$$\left(\frac{dv}{dt} \right)_{cp} = \frac{2\pi \Omega D_b \delta_b}{kT f \left(\frac{r_p}{b} \right)} \left[P - p + \frac{2\gamma}{r_p} \right]. \quad (7)$$

which is identical to Eq. 2 with b substituted for λ . The structure function, $f\left(\frac{r_p}{b}\right)$, is strongly stress dependent. Therefore, the stress dependence of the model rises from $n=1$ at low stresses to the creep exponent of the material at high stresses (assuming dislocation creep dominates diffusive creep). Chen and Argon compare their model with the exact finite element calculation of Needleman and Rice [36] and their own exact solution of the Beere-Speight system of equations, and the model shows excellent agreement with both.

3. Comparison of Data with Theoretical Models

According to Solomon and Hsu [9], the expressions presented for the rate of volume change for individual pores may be translated to an overall linear rate for HIP or swelling by using

$$\dot{\epsilon}_L = \frac{1}{3} N_v \left(\frac{dv}{dt} \right), \quad (8)$$

where dv/dt may be calculated from the pure diffusional or creep models, or the coupled models. For all models, this study assumes spherical pores, consistent with the microstructural observations in Part I [3]. Tables 1 and 2 summarize the measured values and the diffusion parameters assumed for U-10Zr that were used in the models to calculate HIP behavior.

3.1 Grain boundary diffusion controlled HIP of U-10Zr

When combined with Eq. 8, the Speight-Beere model (Eq. 2) for diffusional pore shrinkage during HIP becomes

$$\left(\dot{\epsilon}_L \right)_{gb} = \frac{2\pi}{3} \frac{N_v \Omega D_b \delta_b}{kT f\left(\frac{r_p}{\lambda}\right)} \left[P - p + \frac{2\gamma}{r_p} \right]. \quad (9)$$

Figure 3 shows the diffusional HIP rates of U-10Zr predicted by Eq. 9, compared with the measured initial HIP rates shown in Fig. 1 for the hydride- and metal-derived materials. Although the model predictions and the measured HIP rates are within one order of magnitude at low driving forces, at higher driving forces there is a difference of almost three orders of magnitude. Therefore, simple diffusional models do not adequately predict the magnitude or stress dependence of the HIP rates for U-10Zr under the observed conditions, despite the excellent agreement between the measured activation energy (187 ± 10 kJ/mole [3]) and the reported value for uranium grain boundary diffusion (186.6 kJ/mole [14]).

3.2 Power-law creep controlled HIP of U-10Zr

Before the creep models can be applied to the U-10Zr HIP conditions, a constitutive creep expression of the form given by Eq. 5 must be established for U-10Zr. In the absence of primary creep data for U-10Zr, an approximate uniaxial creep expression was generated [13]:

$$\dot{\epsilon}_c = (4 \times 10^{-10}) \sigma^5 \text{ s}^{-1}, \quad (10)$$

where σ is in units of MPa. This expression was determined by using a correlation for creep in metals developed by Stocker and Ashby [38] and Derby and Ashby [39]. The correlation was developed through an empirical fit of creep data from a wide variety of metals to a constitutive creep equation. In the absence of primary data, the uncertainty of this correlation is high. However, Eq. 10 was found to agree with unreported creep data for a similar uranium alloy within an order of magnitude [13]. Therefore, Eq. 10 was adopted as a first approximation for creep of U-10Zr.

The Beere-Speight creep cavitation model [25] may be translated into a HIP strain rate using Eqs. 4 and 8 to yield

$$(\dot{\epsilon}_L)_{\text{creep}} = \left[\frac{2}{3} \pi r_p^3 N_v \right] \dot{\epsilon}_c, \quad (11)$$

where $\dot{\epsilon}_c$ is computed from Eq. 10 using the average stress, σ_{av} , acting on the creeping boundary shell. Therefore, a further approximation is required for σ_{av} . Based upon the free-body diagram in Fig. 4, the average stress on the grain boundary of a typical unit cell (Fig. 2) that has a single gas-filled pore and is subjected to an external pressure, P , may be written as

$$\sigma_{av} = \frac{P \lambda^2 + \left(\frac{2\gamma}{r_p} - P \right) r_p^2}{(\lambda^2 - r_p^2)}. \quad (12)$$

The predictions of the creep-controlled cavitation model are shown in Fig. 5. The model exhibits reasonable quantitative agreement with the strain rate data, but it is inconsistent with the measured HIP activation energy of 187 ± 10 kJ/mole. Dislocation core diffusion might be used to explain an activation energy of this order, but no measurements are available. Typically, the measured activation energy for dislocation creep is the same as that for volume diffusion, and should therefore be dependent upon the U-10Zr matrix alloy composition. From the data in Table 2, the activation energy for uranium diffusion in a U-Zr alloy with between 5 and 10 wt % Zr should be between 134 and 113 kJ/mole, but the measured value is well above that range. Also, if creep were completely controlling the HIP process, we would expect to see an effect from the hard impurity phases in the hydride-derived material, but in fact that material densifies faster than the purer metal-derived material.

3.3 Coupled diffusion/power-law creep controlled HIP of U-10Zr

The lack of full agreement between the U-10Zr HIP results and either the pure diffusional or pure creep model raises the possibility of a coupled process. For the present results, the model

of Chen and Argon [26] (Eq 7) was selected and translated to a linear HIP strain rate (using Eq. 8), which is given as

$$\left(\dot{\epsilon}_L\right)_{cp} = \frac{2\pi}{3} \frac{N_v \Omega D_b \delta_b}{kT f\left(\frac{r_p}{b}\right)} \left[P - p + \frac{2\gamma}{r_p} \right] \quad (13)$$

The structure function, $f\left(\frac{r_p}{b}\right)$, is the only difference between this equation and the diffusion-controlled model described by Eq. 9, but the calculation of the diffusion zone radius, b , requires several assumptions. First, the characteristic length, Λ , defined in Eq. 6 must be evaluated. Using the parameters in Table 2 for U-10Zr at 700°C and substituting Eq. 10 into Eq. 6, Λ is given by

$$\Lambda = 18.9 \sigma_{\infty}^{-4/3} \mu\text{m} \quad (14)$$

when σ_{∞} is given in MPa. For the calculation of the HIP rate, σ_{∞} was taken to be σ_{av} , as defined by Eq. 12 and Ω was taken to be 10^{-29} m^3 [13]. As stated in connection with Eq. 6, b is calculated as the sum of the pore radius and the characteristic length, again assuming spherical pores.

The variation of the diffusion zone radius, b , with external HIP pressure is shown in Fig. 6 for the two types of U-10Zr specimens. The pore radii (r_p) and pore half-spacings (λ) are indicated along the vertical axis for reference. This calculation of b shows that a coupled mechanism is likely for both types of U-10Zr specimens between external pressures of approximately 5 to 30 MPa. Below 5 MPa, b becomes greater than λ , indicating that the diffusion length is large enough for diffusion-controlled cavitation to dominate HIP. Above 30 MPa, b is nearly equivalent to r_p , indicating that the diffusion length is small and creep-controlled cavitation dominates HIP.

Figure 7 shows the comparison of the coupled model prediction with the experimental HIP data, which indicates good quantitative agreement between model predictions and the data. The

model predicts a variation in the stress dependence from $n=1$ to $n=5$ as the diffusion zone shrinks from $b=\lambda$ down to $b=r_p$. (It is important to note that an apparent transition in n was also observed for swelling in nickel [8].) The U-10Zr HIP results were all generated between 5 and 30 MPa, and in that range the predicted n -value is between the two extremes [3]. For the calculated HIP rates between 5 and 30 MPa, the predicted n -values are $n=3.8$ and $n=3.6$ for the hydride- and metal-derived materials, respectively. These values agree well with the measured n -values [3].

The HIP activation energy should show a similar transition, as boundary diffusion becomes less dominant and power-law creep becomes dominant. However, all of the experimental measurements for Q were made at lower driving forces (~ 8 MPa), where diffusion begins to become dominant. This helps to explain why the activation energy corresponded more closely to grain boundary diffusion. Therefore, considering the good agreement with the measured n -values and the qualified agreement with the measured Q -values, it can be concluded that the HIP of U-10Zr is best modeled by a coupled mechanism of diffusion and dislocation creep. It is also reassuring, but possibly fortuitous, that the magnitudes of the overall HIP rates are as well-predicted as they are in view of the uncertainty in the primary data and simplification of the models. No attempt was made to improve the fit, however.

4. Discussion

4.1 Implications of coupled model

An important feature of the coupled model is the potential for asymmetry between HIP and swelling behavior under similar conditions. Previous applications of cavitation models to HIP and swelling assumed the two processes to be reversible [8-11], which is true if they are controlled by grain boundary diffusion [11]. However, creep deformation over all or a portion of the grain boundary is dependent upon the stress acting upon the boundary, not upon the diffusional driving

force. The coupled model described above uses the average stress on the grain boundary (Fig. 4 and Eq. 12) to evaluate Λ , and σ_{av} is dramatically different for HIP and swelling.

Hot-isostatic pressing of the metal-derived U-10Zr (Table 1) with an external pressure of 20 MPa and an initial internal pressure of 1 MPa would generate a grain boundary stress of ~21 MPa, whereas swelling of the same material with an initial internal pressure of 20 MPa and an external pressure of 1 MPa would generate a stress less than 1 MPa. It is therefore feasible that HIP may be controlled by a coupled mechanism ($b < \lambda$) or even be dominated by plastic deformation because of high boundary stresses, while a similar swelling situation may be controlled by grain boundary diffusion ($b > \lambda$) when σ_{av} is small and Λ is large. Thus, the ability of a material to plastically deform may become much more important during HIP.

The coupled HIP model also provides insight into the reasons for the differences in the measured HIP rates for the hydride- and metal-derived U-10Zr specimens. The initial HIP rates for the hydride-derived specimens are about eight times higher than HIP rates for the metal-derived specimens at identical driving forces and temperatures (Fig. 7). The relevant differences between the two types of specimens, based upon the coupled HIP model (Eq. 13), are the structure function ($f \left(\frac{r_p}{b} \right)$) and the pore number density (N_v).

The hydride- and metal-derived specimens' structure functions (f) are nearly identical over the spectrum of pressures used in this study (e.g., for $P=20$ MPa and $p=1$ MPa, $f=0.84$ and 0.83 initially for the hydride- and metal-derived materials, respectively). Differences in N_v (Table 1) can partially explain the calculated HIP rates. The value of N_v for the hydride-derived material is 1.6 times greater than N_v for the metal-derived material. The grain boundary diffusivity ($\delta_b D_b$) may also differ between the two materials because of matrix composition differences and prevalent second phase boundaries in the hydride-derived material, but data are not available to verify that speculation. In addition, the expected reduction in plasticity for the hydride-derived material due to the hard impurity phases would tend to reduce its HIP rate relative to the purer metal-derived material.

4.2 Time dependence of the coupled HIP model

The model vs. data comparisons discussed above only consider the initial HIP rates vs. the initial pressure driving force. The pressure driving force for HIP will decrease with time as the pore volume changes. Eventually, a new pressure equilibrium is achieved and HIP-induced densification stops. This is also true for swelling, except when the driving force is so great that cavity interconnection and gas release occur before the new equilibrium is established [11]. The HIP/swelling strain rate should therefore decrease with time.

In swelling experiments on other materials [8-11], the strain rate was observed to follow

$$\dot{\epsilon}_L \sim t^m, \quad (15)$$

where $m \approx 1/3$, as determined experimentally. This value agrees well with the theoretical prediction of $m=2/5$ [11], which was made assuming that internal gas pressure and surface energy were negligible for swelling. However, these parameters could be significant for HIP as equilibrium is approached. The U-10Zr HIP results reported in Part I [3] indicate that the measured m -values varied from as low as 0.1 up to 0.8 with bi-linear behavior (two distinct regions of constant time-dependence on a logarithmic scale).

The coupled model (Eq. 13) was therefore used to predict the time-dependent HIP behavior of U-10Zr by means of a simple numerical integration method. The pore radius is decreased after a finite time step, Δt , by a linear first-order approximation in which the radial shrinkage rate is calculated from the volume rate of change. The characteristic diffusion length (Eq. 6) was calculated for each time step, Λ_i , and it increased as the internal pore pressure increased and σ_{av} decreased during the calculated transient. When the calculated diffusion zone radius, b_i , exceeds the unit cell radius, λ , the diffusion model of Speight and Beere (Eq. 9) [22] was used for the remainder of the calculated transient.

Calculated HIP transients are shown in Fig. 8. The calculations were made using the hydride-derived specimen parameters in Tables 1 and 2, assuming an initial sintering pressure of 2.5 MPa for each calculation. Hot-isostatic pressing was then numerically simulated for external pressures of 5, 10, 15, and 20 MPa ($\Delta P = 2.5, 7.5, 12.5,$ and 17.5 MPa) using time step intervals (Δt) of 10 seconds. The calculated transients show a continuous change in the time-dependence (m) rather than the observed bi-linear behavior.

For comparison, HIP strain rate vs. time data from one of the hydride-derived transients presented in Part I ($\Delta P = 10.5$ MPa) [3] is shown in Fig. 9 along with a calculated HIP transient that was generated using the experiment parameters. The calculated strain rates were lower than the measured strain rates by a factor of three, which is consistent with the difference between the calculated and experimental hydride-derived data shown in Fig. 7. Therefore, the calculated curve in Fig. 9 was normalized to match the initial measured HIP rate. Despite potential inaccuracies in the boundary stress assumption and the calculation of Λ and b , this normalized time-dependent calculation reproduces the HIP transient with reasonable accuracy. The calculated transient mirrors the experimental HIP transient through most of the test, but it drops off dramatically at extended time as the calculated driving force approaches 1 MPa. Below 1 MPa, the strain rates are very low and little specimen strain occurs. The strain rate resolution of the data measurement method [3] is 10^{-8} s^{-1} . The overall calculated strain (1.31%) is similar to the measured strain for this particular sample (1.33%). The ability of this model to so accurately predict the time-dependent HIP behavior of U-10Zr has significant implications for the modeling of nuclear fuel behavior.

The drop-off in the calculated strain rate is due to the changing driving force that results from the increases in the internal gas pressure and the surface energy as the calculated pore radius shrinks. This decrease implies that the specimen microstructure, i.e., the pore size and spacing, appears to be the most significant parameter for modeling HIP behavior. This conclusion is supported by the fact that the differences in HIP rates shown in Fig. 6 between the hydride- and metal-derived specimens can be almost totally rationalized by the pore size-to-spacing ratio, in spite of differences in impurity phase content and dissolved zirconium.

4.3 Relevance of ex-reactor models and experiments to nuclear fuels

Despite the general acceptance of ex-reactor densification models for representing in-reactor hot-pressing [40], the question arises whether the models should be modified for in-reactor conditions, or whether unique hot-pressing mechanisms exist within the reactor. During irradiation, a supersaturation of vacancies and interstitials exists in the fuel which enhances atom mobility. However, *if* local equilibrium is maintained at the pore surfaces and grain boundary sinks, then, as argued for radiation-induced creep [41] and fission-induced densification [42], enhanced diffusion cannot affect the HIP rate since the net flux of vacancies from source to sink is unchanged and the ex-reactor models are relevant.

However, as argued elsewhere [42], if local equilibrium at the grain boundaries cannot be maintained under irradiation as a result of the large point defect fluxes, effects of interface control may reduce the predicted rates. On the other hand, there is also the possibility that the creep component *could* be enhanced by radiation [41] causing an acceleration at high stresses and low temperatures, but there are no data available on the magnitude of the radiation-enhanced creep in U-10Zr. For the outer region of the fuel where temperatures are at or below 600°C and ex-reactor HIP was not detected, a radiation-enhanced creep component could make an important contribution in reducing fuel/clad mechanical interaction (FCMI), as it does in oxide nuclear fuels [42].

For the important case of open pores, where a pressure differential cannot exist to cause HIP, the plastic deformation of the fuel in response to FCMI becomes the dominant stress-reducing mechanism, and radiation-enhanced creep becomes crucial. The creep can occur by dislocation or diffusive transport, with the former possibly enhanced by radiation.

Another effect that may be important under irradiation is the fission-fragment-induced resolution of especially small pores that may be trapped within grains. The vacancies produced by resolution may then preferentially migrate to grain boundaries under compressive stresses. As agreed elsewhere [42], resolution alone is not sufficient to cause densification; the vacancies must

be absorbed at the grain boundaries. Also, if the normal vacancy sources at pore surfaces (ledges, etc.) are poisoned by fission product "impurities," the pores may not be able to emit vacancies thermally and fission-fragment-induced emission would become important.

If pores or tears in the fuel are stabilized by fission gas, then the fission-fragment-induced resolution of the gas and its motion to grain-boundary short-circuit paths for release will permit the vacancies to continue to be emitted from the pore and be absorbed at the grain boundary sinks. Thus, pressure-induced densification can continue rather than be arrested by the buildup of gas pressure within the pores.

A final effect that may be introduced during fission is enhanced diffusion in the wake of fission fragments due to intense localized heating (i.e., thermal rod). This effect was proposed to rationalize in-reactor sintering of unstable oxide fuels, where the heating is intense and of long duration in such poor conducting materials [42], but this effect may still play a role in metallic fuels at low temperatures.

The available data and models are insufficient to assess these in-reactor contributions to the HIP or densification rates, but since they generally augment the ex-reactor mechanism, the ex-reactor calculations are conservative in modeling these phenomena.

5. Summary

The results from hot isostatic pressing experiments performed on sintered hydride- and metal-derived U-10Zr samples were analyzed to quantitatively determine the dominant HIP mechanism. It was found that the model of Chen and Argon [26] for HIP controlled by coupled grain boundary diffusion and power-law creep agreed best with the HIP behavior of γ -phase U-10Zr. It was also shown that the coupled model predicts an asymmetry between HIP and swelling rates. The differences in HIP behavior between the hydride- and metal-derived samples are explained in part by differences in the pore number densities, but the magnitude of the HIP rate differences could not be fully rationalized.

The model of Chen and Argon was used to predict the time-dependent HIP behavior of U-10Zr using numerical integration. The result showed that HIP does not exhibit a characteristic time-dependence, in contrast to swelling, for which an exponential time-dependence of $m=2/5$ is predicted under typical conditions. Comparison of a calculated HIP transient with data from a hydride-derived HIP experiment showed good quantitative agreement between the calculated HIP rates and the measured HIP rates over most of the experimental transient.

Finally, a number of in-reactor phenomena were considered that could modify the ex-reactor mechanism or become important under special situations. These include radiation-enhanced creep, fission-fragment-induced resolution of small pores and fission gas atoms, localized heating, and enhanced diffusion in the wake of fission fragments.

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Table 1. Specimen parameters for hydride and metal-derived U-10Zr [3].

	Hydride-Derived U-10Zr	Metal-Derived U-10Zr
Pore number density, N_v	$9.3 \times 10^{14} \text{ m}^{-3}$	$5.8 \times 10^{14} \text{ m}^{-3}$
Modal diameter, r_p	$1.6 \pm 0.1 \text{ } \mu\text{m}^*$	$1.3 \pm 0.1 \text{ } \mu\text{m}^*$
Avg. spacing, λ	$10 \text{ } \mu\text{m}$	$7 \text{ } \mu\text{m}$
Grain size	$34 \text{ } \mu\text{m}$	$114 \text{ } \mu\text{m}$
Internal pressure, p	1.7 MPa^*	1.2 MPa^*

* Denotes post-sintering value prior to HIP at 700°C.

Table 2. Diffusion parameters for uranium and U-Zr alloys.

	γ (Uranium)		γ (U - Zr) [37]	
	Grain Boundary Diffusion [14]	Volume Diffusion [37]	Volume Diffusion of Zr (5 wt % Zr)	Volume Diffusion of Zr (10 wt % Zr)
$(D_b\delta_b)_0$ or $(D_v)_0$ (at $T = 0$ K)	$3.24 \times 10^{-11} \text{ m}^3/\text{s}$	$1.12 \times 10^{-7} \text{ m}^2/\text{s}$	$10^{-7} \text{ m}^2/\text{s}$	$10^{-8} \text{ m}^2/\text{s}$
Activation energy, Q	186.6 kJ/mole	112 kJ/mole	134 kJ/mole	113 kJ/mole
$D_b\delta_b$ or D_v at 700°C	$(3.1 \times 10^{-21} \text{ m}^3/\text{s})^*$	$(1.2 \times 10^{-13} \text{ m}^2/\text{s})^*$	$6.5 \times 10^{-15} \text{ m}^2/\text{s}$	$8.6 \times 10^{-15} \text{ m}^2/\text{s}$

* Values computed for data evaluation. However, for pure uranium, $\beta(\text{U})$ is the equilibrium phase at 700°C , not $\gamma(\text{U})$.

Figure 1. Initial HIP strain rates extrapolated to 1 minute vs. the initial pressure driving force at 700°C for hydride- and metal-derived U-10Zr.

Figure 2. Model geometry for coupled grain boundary diffusion and creep cavitation [3].

Figure 3. Comparison of diffusion-controlled HIP model with measured U-10Zr HIP rates.

Figure 4. Free-body diagram of grain boundary stresses during HIP.

Figure 5. Comparison of creep-controlled HIP model with measured U-10Zr HIP rates.

Figure 6. Diffusion zone radius: variation with external pressure and relation to pore half-spacing (λ) and pore radius (r_p).

Figure 7. Comparison of the coupled HIP model based on Chen and Argon [25] with measured U-10Zr HIP rates.

Figure 8. Time-dependence of hydride-derived U-10Zr HIP transients calculated by using the coupled model of Chen and Argon [25].

Figure 9. Comparison of a single hydride-derived HIP transient and a comparable, calculated HIP transient based upon identical conditions.

FIGURE CAPTIONS

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