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Publication Date

1976

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January 1976

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

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HOMOGENIZATION OF MIXED OXIDE FUELS

by D. R. Olander

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(U,Pu)O₂ fuels for plutonium recycle in light water reactors or for LMFBRs are usually prepared from mechanically blended powders of the two pure oxides. Sintering conditions of 1600 - 1700°C in hydrogen gas provide acceptable porosity reduction and O/M control but are not sufficient to produce heavy metal mixing on an atomic scale. The presence of discrete particles of PuO₂ in the resulting fuel impairs performance by causing hot spots near the cladding and by influencing irradiation-induced processes such as creep and swelling. In addition, dissolution of PuO₂ in the conventional head-end reprocessing step is considerably more difficult than dissolving UO₂.

One possible method of promoting atomic dispersion of the heavy metals in a mixed oxide (other than by using feed prepared by coprecipitation) is by annealing the sintered pellets at sufficiently high temperature that intimate mixing is achieved by interdiffusion of plutonium and uranium cations. The purpose of this note is to apply classical diffusion theory to assess the kinetics of the annealing process.

We assume that the initial mixture consists of N plutonium dioxide particles of radius R per unit volume uniformly dispersed in a matrix of uranium dioxide. The average enrichment of the fuel (plutonium atoms per heavy metal atom) is:

$$q_{av} = \left(\frac{4}{3} \pi R^3\right) N \quad (1)$$

The two-phase solid is represented as a collection of spherical unit cells with one PuO₂ particle at the center of each. The unit cell radius, $\mathcal{R}$, is determined

by the relation $4\pi R^3 N/3 = 1$, or, on eliminating N by use of Eq. (1),

$$\frac{R}{R} = q_{av}^{1/3} \quad (2)$$

The diffusion process during annealing may be described as follows. At zero time, the temperature is raised to a value at which the mutual diffusion coefficient of Pu and U cations in the mixed oxide is D . The subsequent redistribution of plutonium in the unit cell is governed by the solution of the transient diffusion equation:

$$\frac{\partial q}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) \quad (3)$$

where r is the radial position in the spherical unit cell and $q(r,t)$ is the plutonium cation fraction at r and time t . The initial condition is:

$$q(r,0) = \begin{cases} 1 & \text{for } 0 \leq r \leq R \\ 0 & \text{for } R \leq r \leq R \end{cases} \quad (4)$$

In addition to requiring that q be finite at $r = 0$, there can be no flux of plutonium across the outer boundary of the unit cell:

$$\left(\frac{\partial q}{\partial r} \right)_{R} = 0 \quad (5)$$

The solution to Eq. (3) subject to Eqs. (4) and (5) is given by Carslaw and Jaeger¹:

$$\frac{q}{q_{av}} = 1 + \sum_{j=2}^{\infty} C_j \exp(-\alpha_j^2 \tau) \left(\frac{\sin \alpha_j \eta}{\alpha_j \eta} \right) \quad (6)$$

where

$$\tau = Dt/R^2 \quad \text{and} \quad \eta = r/R \quad (7)$$

are dimensionless time and position, respectively, and α_j are the roots of:

$$\tan \alpha = \alpha \quad (8)$$

The first few roots of Eq. (8) are¹: $\alpha_1 = 0$, $\alpha_2 = 4.4934$, $\alpha_3 = 7.7253$

The coefficients C_j are given by

$$C_j = 2(\alpha_j^2 + 1) \left[\frac{\sin(\alpha_j \beta) - (\alpha_j \beta) \cos(\alpha_j \beta)}{(\alpha_j \beta)^3} \right] \quad (9)$$

where $\beta^3 = q_{av}$.

Figure 1 shows the evolution of the plutonium distribution for 5% enriched fuel.

The extent of homogenization can be characterized by the ratio of the maximum to the average plutonium concentrations, which occurs at the center of the original PuO_2 particle. Figure 2 shows that this ratio decreases with increasing dimensionless time. The effect of enrichment is quite small, especially for long times.

Of practical interest is the time required for the ratio q_o/q_{av} to reach a specified value as a function of annealing temperature. Because the time required for q_o/q_{av} to reach an acceptable level (say 2) is quite long, only the first term in the sum of Eq. (6) is significant. Therefore, Eq. (6) at $\eta = 0$ can be solved for τ and this value may be substituted into Eq. (7) to determine the time t . The result is:

$$t = - \frac{\ln \left[\frac{C_2}{(q_o/q_{av}) - 1} \right] R^2 e^{E/RT}}{\alpha_2^2 q_{av}^{2/3} D_o} \quad (10)$$

The coefficient C_2 depends upon q_{av} according to Eq. (9). D_o and E are the preexponential factor and activation energy for mutual diffusion of plutonium and uranium ions in the mixed oxide. The values given by Bober et al.²,

$D_0 = 0.34 \text{ cm}^2/\text{sec}$ and $E = 460 \text{ kJ/mole}$, have been used. Figure 3 shows the time-temperature plots for $100 \text{ }\mu\text{m}$ radius PuO_2 particles for $q_0/q_{av} = 2$. According to these curves, a sintered compact containing 5% plutonium in the form of $100 \text{ }\mu\text{m}$ radius particles requires annealing at 2500°K for 350 hrs if the plutonium fraction at the original PuO_2 particle center is to be reduced to twice the average value. If the temperature is lowered to 2200°K , the required annealing time is 7600 hrs. To achieve the same degree of homogenization in less than 100 hours would require temperatures in excess of 2600°K . These annealing times vary as the square of the PuO_2 particle radius but are not very sensitive to the average plutonium content of the mixture.

The required times and temperatures appear to be impractically large to render high temperature annealing a useful manufacturing method for homogenization of mixed oxide fuels fabricated from blended powders. The numerical results cited above, however, depend very strongly on the cation diffusion coefficient in the mixed oxide. The values suggested in Reference 2 are based upon diffusion measurements in nominally stoichiometric fuel. Available evidence^{2,3} suggests that: (a) the mutual diffusion coefficient of U and Pu in the mixed oxide is sensibly the same as the tracer diffusivity of U in UO_2 ; (b) the diffusivity of U in UO_2 is markedly enhanced by increasing the oxygen-to-metal ratio to values greater than two. In hyperstoichiometric fuels, theory⁴ suggests that the cation diffusion coefficient in MO_{2+x} should increase as x^2 . Variations of this magnitude are experimentally observed³. (c) the disagreement between the diffusion data obtained by different investigators is substantial. The set of measurements which Belle³ believes to be the most reliable are ~ 2 orders of magnitude lower than Bober's choice² in the temperature range from 2000 to 2600°K . The diffusion coefficient upon which Bober's suggested values rest may actually represent hyperstoichiometric material.

In view of the substantial uncertainty in the U-Pu mutual diffusion coefficient, it appears worthwhile to experimentally verify the feasibility of high temperature homogenation of mixed oxide fuels on production-grade samples. To capitalize on the beneficial effect of large oxygen-to-metal ratios on the cation diffusion coefficient, the homogenization anneal should be performed prior to hydrogen reduction.

Acknowledgement

This work was conducted under the auspices of the Energy Research and Development Administration.

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FIGURE CAPTIONS

1. Change in the plutonium distribution in the unit cell during homogenization.
2. Decrease in the central plutonium concentration with time.
3. Time-temperature plots for fuels originally containing discrete PuO_2 particles 100 μm radius to homogenize to the extent that the maximum plutonium concentration is twice the average value.

XBL7512-9234

Fig. 1

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Fig. 2

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Fig. 3

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