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WHAN-SA-79

From : MATERIALS TECHNOLOGY
Date : October 8, 1970
Subject:

To: Clearance Personnel

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J. A. Christensen
Technical Analysis
and Program Development

cbn

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STRUCTURE EVOLUTION IN AN OXIDE FUEL PIN*

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A Subsidiary of Westinghouse Electric Corporation
Post Office Box 1970
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October 8, 1970

For presentation at the West Coast Regional Meeting
of the American Ceramic Society to be held at
San Francisco, California, October 27-29, 1970.

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The net picture is very complicated - materials with time and space varying compositions operating for long times at extreme temperatures in an irradiation environment effects of which are largely unknown and impossible to estimate with confidence. Multi-coupled-current mass transport processes, activated by thermal and, perhaps, flux gradients determine the long-term behavior of these materials. These require empirical study in environments which can be specifically related to those in which they are used.

Direct application of laboratory results to such a complex system is rarely possible. A more productive approach is to combine out-of-reactor experimentation, which defines the separate processes, with irradiation experiments designed to determine interrelationships among processes. Identification of critical parameters and estimation of their interaction can be made tractable through use of the various analytical material behavior models being developed.

Categorization of separate transport processes in fuels is not realistic because of the almost universal interaction between these processes. For clarity, an arbitrary grouping of the current program into 1) fuel restructuring; 2) redistribution of fuel constituents; 3) energy transport; 4) fission gas effects; and 5) analytical modeling is employed in the following discussion.

Fuel Restructuring

Materials science is primarily concerned with the relationship between structure and properties. In oxide nuclear fuels, the structural changes which derive from service are especially interesting. The bulk of existing fuel materials information consists, in fact, of observations of these structural changes. Studies of structural changes are useful because these changes are easily observed, direct manifestations of the transport mechanisms which control all of the kinetic processes of practical importance in fuels. General application of the results of these studies is, however, usually frustrated by the difficulty in quantitatively

correlating structure type with a specific property. To compensate this, the intermediary parameter "temperature" is evoked to cross-correlate structure with specific properties. This represents only an approximation of course since other variables function independently of, as well as in interaction with, temperature in determining structure-property relationships (e.g., time, temperature gradient, neutron flux, fission rate, chemical composition, impurity content, pressure). Also, it is difficult to precisely assign temperatures to discrete structural features - partly because of interference from the above effects and partly because accurate in-reactor fuel temperature distribution measurements are impeded by the high temperature and steep thermal gradients. Enough information has been accumulated, however, to permit the requisite structure-temperature-property correlations for some important properties.

Examination of a representative cross-section of a highly rated cylindrical oxide fuel element reveals as many as six regions with distinctly different grain morphologies (Figure 1). An equal number of mobile or stable pore types can also be identified. Grain morphology and associated pore type can be roughly correlated with temperature as has been done in Table I. The correlation is crude because grain boundary and pore movements are kinetic processes. Structure thus varies continuously with time. Table I applies to the steady-state achieved in a UO_2 -25 wt% PuO_2 fuel shortly after irradiation is initiated. Superficially, analyses of such a complex system of structures appears overwhelming. In fact, however, only two processes appear to be very important: 1) nominally equiaxed grain growth involving mass transport by point defects and 2) formation of grains by pores traveling along the thermal gradient. The first process can be represented by an Arrhenius relationship with an activation energy of approximately 125 kcal/mole. The second process involves movement of pores up the thermal gradient by oxide vaporization from the hot side of the pore and condensation on the cold side. This mechanism is unimportant at low temperatures because the vapor pressure is negligible. Vapor-deposited-grain growth rate also increases

FIGURE 1
 Structure Development in Highly Rated Mixed Oxide Fuels
 Material is Sintered, 0.257 in. Diam (0.75U, 0.25Pu)O_{2.00} with an Initial Bulk
 Density of 94% T.D. Irradiated to 6×10^{18} f/cc with a Fuel Surface Temperature
 of 900°C and a Centerline Temperature Slightly Above Melting

TABLE I. *Temperature, Grain Type, Pore Type Correlation for Lightly Irradiated, Highly Rated Oxide Fuels**

<u>Temperature</u>	<u>Grain Morphology</u>	<u>Grain Size</u>	<u>Pore Morphology</u>	<u>Approximate Pore Size</u>	<u>Illustrated By</u>
900 °C- 1200 °C	Equiaxed, As-sintered	~20 μ	Equiaxed, Random Distribution	5 μ	Figure 1F
1200 °C- 1700 °C	Equiaxed, Normal Grain Growth	20 μ -40 μ	Radially Migrating or Grain Boundary Spheres	5 μ	Figure 1E
1700 °C- ~2000 °C	Columnar Grains	20 μ x 80 μ	Lenticular	3 μ x 50 μ	Figure 1D
~2000 °C- Melting	** Radially Elongated	150 μ x 600 μ	Random Spheres, Chevrons	10 μ -30 μ 1 μ x 50 μ	Figure 1C
Molten Region,** Outer Portion	Radially Elongated	150 μ x 600 μ	No Pores		Figure 1B
Molten Region,** Central Portion	Radially Elongated		Random Tubular	20 μ x 100 μ	Figure 1A

* Observations made on 94% T.D., 0.26 in. diameter UO_2 -25 wt% PuO_2 irradiated at ~30 kW/ft to 6×10^{18} f/cc. Observations apply in general to other oxide fuels but temperatures and dimensions may differ.

** Grains in these regions are mutually epitaxial from one region to the next or may extend through all three regions.

exponentially with temperature, however, and with an activation energy equal to the enthalpy of vaporization which is significantly higher than the activation energy for ordinary grain growth. At some intermediate temperature vaporization controlled grain growth thus becomes the dominant process. The rate of pore movement by vaporization-condensation is also a function of the thermal gradient. The gradient decreases to zero at the thermal center of a fuel core, thus in the central region of the fuel, diffusion controlled grain growth again predominates. This competitive interaction between diffusion and vaporization controlled grain growth, illustrated diagrammatically by Figure 2, gives rise to the familiar fuel structure consisting of central and circumferential regions of normal grain growth separated by an annulus of narrow columnar grains formed by migrating pores. Pore formation and migration requires a source of pores. In a virgin fuel, on the order of 5% porosity seems to be required to yield significant columnar grain growth. Thermal stresses established during thermal cycling of fuels which are not too heavily restrained cause circumferential cracks which serve as regenerative sources of migrating pores. Fission gas bubbles may function in this capacity also.

A second type of mobile porosity is shown in Figure 1E. Small ($<5\mu$) spherical pores are observed to form and migrate up the thermal gradient in the equiaxed grain region adjacent to the outer edge of the columnar grains. These are not fission gas bubbles - the specimen shown had a burnup too low to attribute the volume in the pores to fission gas. Many of these pores become trapped on grain boundaries but some escape and proceed into the matrix of the adjacent grain. These pores, which have been observed only in nearly stoichiometric urania-plutonia fuels of fast reactor compositions, are of a size appropriate for migration by a surface diffusion mechanism. They do not form new grains in their wake presumably because to do so would require an increase in grain surface area. These pores may be instrumental in fuel redistribution and fission product migration processes, and their transport characteristics can probably be related to fission gas

ln (Grain Volume Function) = ln f(V)

FIGURE 2
Interaction Between Different Growth Mechanisms to Yield
Columnar Grain Annulus Characteristic of High-Rated Oxide Fuels

bubble movements. They do not, however, cause apparently important structural modifications.

On a finer scale, fission gas porosity is the subject of intensive study. Transmission, replica, and scanning electron microscopy are being applied toward characterizing bubble size distributions in irradiated oxide fuels.

Redistribution of Fuel Constituents

In addition to restructuring, complex chemical redistribution occurs as a product of the high temperature, high thermal gradient irradiation environment. Redistribution of fuel components or fission products may occur by some of the same transport mechanisms responsible for grain restructuring or may reflect parallel processes which may or may not interact with restructuring. The potentially most important effect is oxygen migration. Thermodynamic calculations illustrate the feasibility of oxygen redistribution in fuels with an initial average O/M $\neq 2.00$ ⁶. Since UO_2 - PuO_2 fast fuels characteristically are fabricated with O/M's less than 2.00 and irradiation to burnups of several percent causes a thusfar undefined shift in O/M, measurements of oxygen distributions characteristic of typical fuel operating conditions are required.

Radial sampling and analyses of irradiated UO_{2+x} specimens showed that when partial fuel melting occurred the excess component (uranium or oxygen) migrated toward the fuel center⁷. This was interpreted in terms of an expected increased solubility of the excess component in the melt relative to the solid which it contacted. A subsequent analysis considered the existence of small quantities of carbon - an unavoidable impurity - which on oxidizing creates an oxygen pressure which varies with radial position in the fuel because of the temperature dependence of the $\text{CO}_2 \rightleftharpoons \text{CO} + 1/2 \text{O}_2$ reaction⁸. In agreement with the experiments, this mechanism predicts an oxygen concentration gradient of the same sign as the thermal gradient for hypostoichiometric fuel and of opposite sign for hyperstoichiometric fuel. A critical test to differentiate between the two proposed mechanisms is to determine the direction of

STRUCTURE EVOLUTION IN AN OXIDE FUEL PIN

NOMINAL HEAT RATING= ~ 13 kw/FT THROUGHOUT LIFE

WHAN-SA-79

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Richland, Washington
for the U.S.A.E.C.
under contract no. AT(45-1)-2170

- As H but with Family of New Cracks Formed on Shutdown
- Retains large voids formed Early in Life in Columnar Grains
- Pore Size Refined Beyond Columnar Grains (Fission Gas Bubbles)
- No Gap Reopening for Large Hg ($< \sim 2000$ BTU/HR-FT² °F)
- ▲ Voids Between 75 and 1000 Å Depending on Clad Temperature; Void Density Increases with Burnup; Void Size Increases with Temperature; Uniform Void Distribution with Slight Grain Boundary Denudation
- ▲ Dislocation Loops Commensurate with Atoms Displaced from Void Sites
- ▲ Possible Recrystallization with 900°F Na Outlet Temperature
- ▲ Grain Boundary σ Phase Concentration Saturated at 5-7%
- Heat Rating Reduced by Fissile Depletion
- Largest Holes and Old Cracks Replaced by Fine ($< 1\mu$) Gas Bubbles and Inclusions
- Extensive Fission Product and Clad Derived Inclusions
- Fission Product Oxides in Equiaxed Grains; Fission Product Metals in Columnar Grains Concentrated Near Edge
- ▲ Localized Clad Strain Near Cracks
- ▲ Clad Swelling Severe ($\sim 10\%$, May Cause Gap to Reopen?), Maximum Pin Diameter
- ▲ Ductility Decreased to Zero
- Maximum Impurity and Irradiation Effect on Thermal Conductivity and Melting Point

During Operation
After Shutdown

- Fuel-Clad Gap
- Pores, Voids, Cracks
- Metallic Fission Fragments
- Non-Metallic Fission Fragments
- Clad
- Structural and Dimensional Features
- Temperature Distribution Effects
- ▲ Effects on Clad (10^3 MWD/MTM $\approx 10^{21}$ nvt > 1 MeV)

- Small ($\sim 10\mu$) Equiaxed Grains
- Equilibrium Pores to 50μ
- Large Voids, $\sim 200\mu$
- Small Cracks, Crevices, etc.
- Gap Large (~ 3 mil) and Uniform, He Filled
- Radial and Circumferential Cracks from Thermal Shock
- Startup Cracks Taper Inward
- Gap Partly and Irregularly Closed from Thermal Expansion and Cracking; He Contaminated by Desorbed Gases.
- Reduction in Thermal Conductivity Because of Cracks

- Columnar Grain Formation by Lenticular Pore Migration
- Central Void Formed from Pores Displaced from Columnar Grain Region
- Some Equiaxed Grain Growth, Pores Move to Grain Boundaries
- Large Stable Central Pores — Increase in Size and Density Toward Center
- Small Migrating Spherical Pores
- Crack & Hole Healing to Beyond Grain Growth Region
- Gap Unchanged from "B" (or Perhaps Enlarged by Sintering or Closed by "Bloating")
- ▲ Grain Boundary Carbide Precipitate Concentration Reaches Limiting Value with 1100°F Na Outlet Temperature

- New Family of Cracks Which Taper Outward Formed During Shutdown
- Gap Opens Some Compared with "C" but Not to Condition in "A" Because Thermal Expansion Strains (cracks) Remain and are Partially Redistributed Toward Center
- Thermal Conductivity Increased Because of Porosity Depletion in Higher Temperature Regions
- ▲ Observable Grain Boundary σ Phase with 1100°F Na Outlet Temperature

- Gap Closes Further
- New Cracks Heal — Associated Void Redistributes Toward Center
- Gap Conductance Decreases from Xe and Desorbed Gas Contamination
- "Stable" Residual Crack Pattern Achieved After several Cycles
- Grain Growth Proceeds; Columnar Grain Growth "Temperature" Decreases Continuously During Life
- Central Void Diameter Increases Continuously During Life

- Gap Conductance Reaches Maximum, Steady-State Value
- ▲ 1% Swelling from Voids; He at Grain Boundaries Reduces Ductility to $\sim 1/2$ Pre-Irradiation Value
- ▲ Grain Boundary Carbide Precipitation with 900°F Na Outlet Temperature Reaches Limiting Concentration
- ▲ Recrystallization with 1100°F Na Outlet Temperature
- ▲ Observable Grain Boundary σ Phase with 900°F Na Outlet Temperature

- Gap Closed by Crack-Ratcheting After Several Cycles or Accelerated Fission Gas Swelling at Intermediate Temperatures (1300-1500°C)
- ▲ Clad Strain from Mechanical Interaction with Fuel on Cycling
- Residual Cracks Narrower Because of Clad Restraint and Swelling Accommodation
- Slight Irradiation Decrease in Thermal Conductivity
- ▲ Ductility Decreased Because of He in Grain Boundaries (~ 1 PPM He/ 10^{21} nvt)

- Bubble Steady State Achieved in Warmer Portions
- Large Voids and Old Cracks Begin to Close from Swelling
- Fission Fragments and Clad Derived Inclusions Appear
- Thermal Conductivity Further Decreased