NUCLEAR SCIENCE AND ENGINEERING: 22, 111-124 (1965)

Letters to the Editors

On the Fission-Gas Retention Ability of Uranium Dioxide Pellets Produced with Different Techniques

Uranium dioxide pellets used to fuel nuclear power reactors are usually manufactured by sintering pressed bodies of ceramic-grade UO_2 powder in pure hydrogen or cracked ammonia. Since temperatures to be maintained in the soaking period are comparatively high, other atmospheres or different techniques have been tried, with the purpose of reducing the cost of the operation. The alternative atmospheres used in place of hydrogen have been steam[1-3] and carbon dioxide[4]. Techniques include the use of sintering aids (mostly titanium dioxide)[5,6] and the pressing of mixtures of UO_2 and U_3O_8 (the latter usually obtained by roasting the former)[7,8], with sintering taking place in inert gas (high purity nitrogen or argon). The effectiveness of sintering aids may be in doubt, while with the other methods, reductions of at least 300°C in the soaking temperature (and sometimes increases in the final density) are claimed. It must be observed that all of these essentially consist in increasing the sintering rate through the effect of nonstoichiometric oxygen introduced in the UO_2 lattice; as a consequence, the final product should be over-stoichiometric, and, since this is not desirable, it must be reduced at high temperature in hydrogen.

Morphologically, the pellets sintered in hydrogen with the conventional technique do not differ from the others; however, some doubts are left as to the fission-gas retention capacity, especially because the final reduction of the nonstoichiometric product is a volume-increasing transformation and might cause micro-cracks in the material if it is not plastic enough at the reduction temperature.

For testing the fission-gas retention ability of sintered pellets, we have installed, in a 10-cm lead cell at the SORIN Nuclear Center in Saluggia (Vercelli), a post-irradiation annealing apparatus which includes a molybdenum tube furnace already described elsewhere[9]. Pellets are irradiated at low temperature in a flux of 5×10^{12} n/cm^2-sec in the SORIN Avogadro RS-1 swimming-pool reactor to a standard dose (approximately 10^{18} nvt); then they are tested in the hot cell as follows:

1) 6 h diffusion anneal at 1400°C in a tantalum crucible under helium atmosphere and
2) subsequent melting in potassium pyrosulphate.

Gases released during both stages are carried to a charcoal trap by a 2 cm^3/sec flow of pure helium. The trap is positioned over a NaI(Tl) scintillation crystal connected to a single-channel gamma-ray spectrometer, and Xe^{133} released from the samples is determined from its 81 keV gamma-ray emission. The fractions of Xe^{133} released during diffusion are calculated from the count rates at this stage and that at the melting stage (where it is assumed that all remaining gases are completely released), and the macroscopic diffusion coefficient[10] D' is derived from the linear portion of the plot of the fraction released vs the square root of diffusion time.

For this study pellets of nearly equal density, weighing approximately 4 g, were made from a ceramic UO_2 powder purchased from the French Commissariat a l'Energie Atomique (Grenoble). This powder, whose properties are listed in Table I, was prepared by calcining the ammonium

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[6] J. F. WATSON and D. R. WILDER, USAEC Report IS-221 (1960).

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TABLE I

Properties of the Natural UO_2 Powder Lot Received From C.E.A. (Grenoble)

Real density (CCl_4) g/cm^3	10.42
Tap density, g/cm^3	2.87
Average particle diam (Fisher), μm	0.90
Total surface area (BET), m^2/g	4.60
External surface area, m^2/g	0.65
Roughness factor	7.07
D.T.A.: 1st oxidation peak, °C	215
temperature difference between 1st and 2nd oxidation peaks, °C	131
O/U ratio	2.11

Typical Spectrographic Analysis, parts/10^6:	
Al	50
B	0.1-0.2
Cu	10
Cr	8
Fe	70
Mn	4
Mo	50
Ni	15
P	100
Pb	15
Si	60

diuranate at 380-400°C to obtain the UO_3 powder which was subsequently reduced in a rotary-tube furnace by hydrogen[11] at 600-700°C. In order to avoid the reoxidation of UO_2 powder in air, the batch was treated with carbon tetrachloride vapor at room temperature[12].

The UO_2 powder was mixed with 2 wt% camphor and 0.75 wt% stearic acid, and cold pressed at 5 ton/cm^2 to a green density of 5.5 g/cm^3. The sintering cycles were the following:

1) hydrogen sintering (stoichiometric UO_2): presintering at 800-900°C for 10 h and sintering at 1700°C for 3 g; cooling to 600°C in hydrogen and to room temperature in inert gas;

2) steam sintering (stoichiometric UO_2): raise to 800°C in inert gas (extra pure nitrogen); raise to soaking temperature in hydrogen: 3 h soaking in steam at 1400°C; cooling to 600°C in hydrogen and to room temperature in inert gas;

3) CO_2 sintering (stoichiometric UO_2): raise to soaking temperature in inert gas; 3 h soaking in CO_2 at 1450°C; cooling to 600°C in hydrogen and to room temperature in inert gas;

4) $UO_2 + U_3O_8$ (O/U = 2.20) sintering: raise to soaking temperature in inert gas; soaking 1 h at 1275°C in nitrogen plus 2 h reduction in hydrogen; cooling to 600°C in hydrogen and to room temperature in inert gas.

In all cases, the heating and cooling rates were kept as low as 5°C/min. The final material was always practically stoichiometric.

The characterization of the pellet specimens was done by determining the fired density, the open-porosity distribution (pressurized mercury technique), the grain size and the closed porosity (micrography). For all specimens, the open-pore-size distribution was similar and mostly in the range 0.1 - 0.3 μm whereas the closed pores were very fine and randomly distributed with larger pores (≈1μm) at the grain boundaries. The average grain diameter resulting was approximately 10 μm for hydrogen-sintered pellets and within the range

TABLE II

Release Rate Parameters at 1400°C*

Sample No.	Powder	Sintering Atmosphere	Pellet Density (per cent theor)	D' 1400°C (sec^{-1})
1	UO_2	H_2	94.3	2.7×10^{-14}
2	UO_2	H_2	94.3	7.4×10^{-14}
3	UO_2	H_2O	94.3	3.3×10^{-14}
4	UO_2	H_2O	94.4	9.2×10^{-14}
5	UO_2	CO_2	94.2	2.9×10^{-15}
6	UO_2	CO_2	94.3	3.6×10^{-15}
7	$UO_2 + U_3O_8$	$N_2 + H_2$	94.1	4.5×10^{-14}
8	$UO_2 + U_3O_8$	$N_2 + H_2$	93.7	1.3×10^{-13}

*Irradiation dose approximately 10^{18} nvt.

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[11] R. DELMAS and J. HOLDER, in *New Nuclear Materials Including Non-Metallic Fuels, Conf. Proc.*, Prague, (July 1-5, 1963), Vol. I, pp. 95-108, IAEA, Vienna, (1963).

[12] Y. CARTERET, P. CHENEBAULT and R. DELMAS, Brevet/D 1030 PV 833191 (June 1960).

5-7 μm for other specimens. Sintering in CO_2 did not lead to any carbon pickup[4], so the overall carbon content in any one of the sintered pellets should have been less than 100 parts/10^6, as usual.

The results of the fission-gas release experiments are listed in Table II.

The release rate parameters obtained by us at 1400°C are less or of the same order of magnitude as those obtained in earlier work by other investigators (see, for instance, Refs. 13 and 14). It should be noticed that this might be due to the somewhat higher irradiation dose adopted by us and the consequent decrease of the D' coefficient[15].

The reproducibility of data from duplicate specimens recorded in Table II is satisfactory. The release rates from pellets made by other techniques are never significantly higher than those of pellets made by the usual hydrogen-sintering method. On the contrary, the pellets sintered in carbon dioxide seem to have a better fission-gas retention capacity, even though we are inclined to feel that this feature is due to chance. Fission-gas release mechanisms have not yet been identified with certainty. The thermal diffusion process, however, is no doubt responsible for a substantial fraction of the total release. The extent to which this mechanism is affected by the structural conditions and purity of the specimens is not known. Although further work is required to test the fission-gas behavior in operating conditions in a power reactor, it is believed that our preliminary results substantiate the use of pellets made with one of the unconventional methods, if this method leads to economic gain.

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Received August 10, 1964
Revised November 30, 1964

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[14] W. H. STEVENS, J. R. MacEWAN and A. M. ROSS, USAEC Report TID-7610 (1961).

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Large Reactor Excursions Starting at Operating Conditions

The present note is an extension of previous work[1] on large excursions in reactors, to include those starting at operating, steady-state conditions. The previous work was limited to excursions starting at zero power.

Consider a *critical* reactor whose power, power due to delayed neutron precursors, and temperature are $(n,C,T) = (n_0,C_0,T_0)$. This steady state is characterized by the constant control reactivity, which balances exactly the reactor reactivity feedback, $\rho_c = -f(T_0)$, where $f(T)$ is the temperature-dependent reactivity feedback. If at a given instant, $t = 0$, a large reactivity step is inserted and all coolant is lost, the energy released in such an excursion is contained entirely in the core, and the reactor is described by the following kinetic equations[1]:

$$\begin{aligned} \frac{dn}{dt} &= \frac{\rho_0 - \beta + f(T)}{\ell}\, n + \lambda C \\ \frac{dC}{dt} &= \frac{\beta}{\ell}\, n - \lambda C \\ \frac{dT}{dt} &= \gamma n. \end{aligned} \qquad (1)$$

With the above initial conditions, at $t = 0$, the total reactivity equals the step insertion ρ_0 and $(n,C,T) = (n_0,C_0,T_0)$. The notation of system (1) is given in Ref. 1.

The first integral of system (1) found in Ref. 1 reads

$$n + C - \frac{\rho_0}{\gamma\ell}\, T - \frac{1}{\gamma\ell} \int f(T)dT = A. \qquad (2)$$

Here A is an arbitrary constant giving the initial condition. In our case this is

$$(n,C,T) = (n_0,C_0,T_0),$$

so that

$$A = \left(1 + \frac{\beta}{\lambda\ell}\right) n_0 - \frac{1}{\gamma\ell} \left[\int f(T)dT\right]_{T=T_0}, \qquad (3)$$

noting that $C_0 = \frac{\beta}{\lambda\ell}\, n_0$.

From here and using Eq. (3), one can follow exactly the treatment of Ref. 1 to obtain *all* the results corresponding to the general ones presented there for excursions starting at shutdown, where the initial condition was $(n,C,T) \approx (0,0,0)$ and

$$A = -\frac{1}{\gamma\ell} \left[\int f(T)dT\right]_{T=0}.$$

To illustrate this fully we have carried through the procedure in the simplest case where $f(T) = -a_1 (T-T_0)$ (constant temperature coefficient). Only in this linear case, it is possible and convenient to translate the temperature scale by T_0, so that $f(T) = -a_1 T$ and the temperatures calculated from Eq. (1) are temperature increases over the initial one,

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