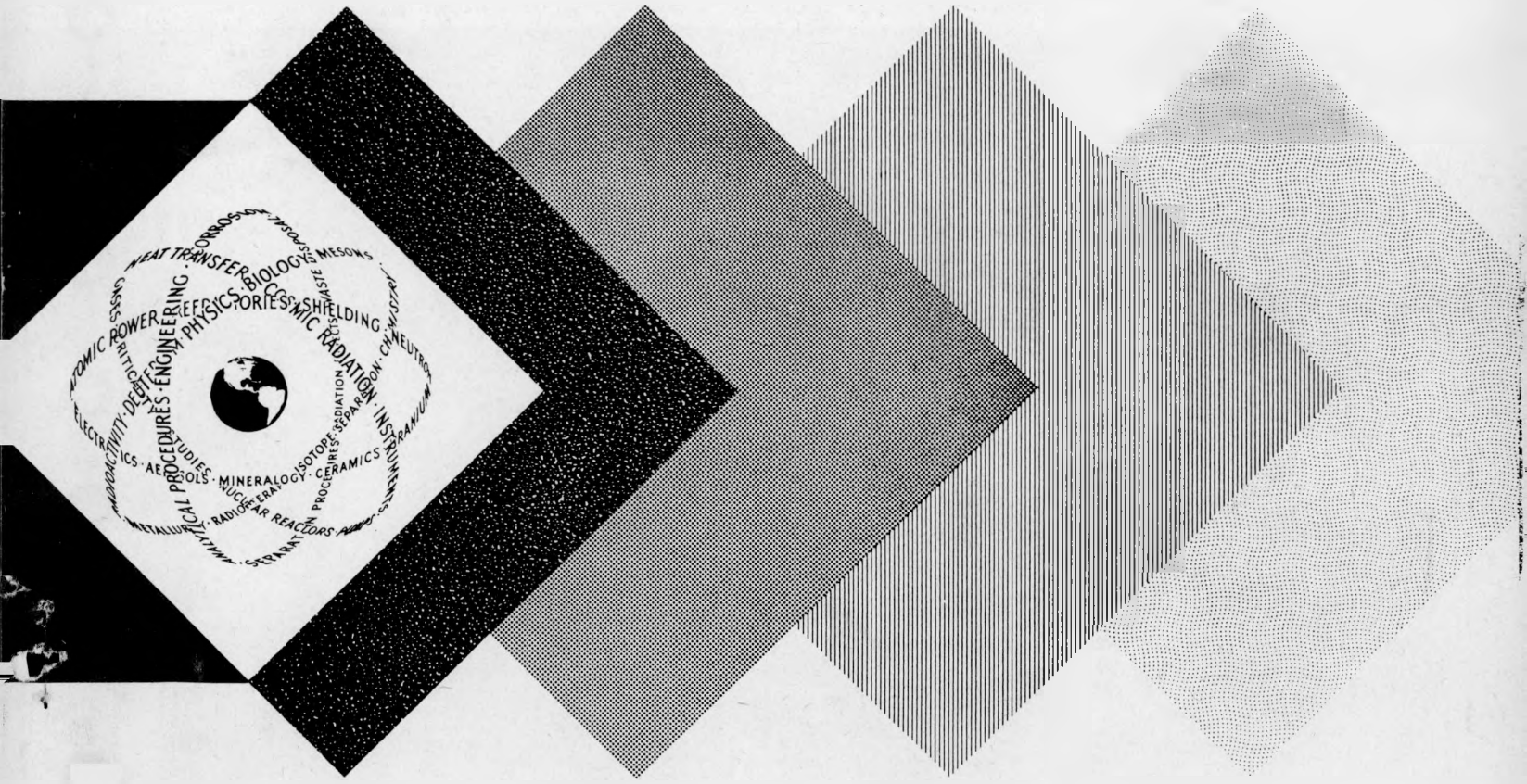
SCNC-306

METALLURGY AND CERAMICS

QUARTERLY TECHNICAL PROGRESS REPORT FOR PERIOD ENDING DECEMBER 31, 1959

February 1960

Sylvania-Corning Nuclear Corporation
Bayside, New York



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SCNC-306

QUARTERLY TECHNICAL PROGRESS REPORT

FOR PERIOD ENDING

December 31, 1959

J. L. Zambrow, Director of Engineering

Contract: AT-30-1 Gen-366
Division of
Reactor Development

Issued: February, 1960

SYLVANIA-CORNING NUCLEAR CORPORATION
Bayside, Long Island, New York

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I. LOW COST CERAMIC FUEL ELEMENTS BY ISOSTATIC PRESSING

(I. Sheinhartz and J. Fugardi)

Objective: The objectives of this program are the fabrication of low cost, high quality ceramic rod-type fuel elements through the application of hot isostatic pressing techniques.

The work performed during the past quarter was directed at improving the density of the hot isostatically pressed, fused UO_2 compacts, and determining the changes in the structure of the cladding due to hot isostatic pressing.

A. Improvement of the Hot Isostatic Pressing Density by Classification of the Powder

The data listed in Table I contain the optimum results of work performed to date. The as-received properties of the powder are listed for comparative purposes. To improve the hot isostatic pressing density, various fractions were selected and blended to determine the optimum blend on the basis of tap density. Table II lists the various blends and the tap density of each blend. Blend No. 12 (consisting of 64 w/o -20 +100, 9 w/o -140 +200, and 27 w/o -325) was selected as the maximum based on this limited study. In comparing the apparent density and the cold compacted density of blend No. 12 with that of the as-received powder there was only slight improvement although a significant increase in the tap density was obtained. After hot isostatic pressing at 1200°C, 12,000 psi for one hour the density was only 1.1% better than that of the as-received material. Sectioning of this sample revealed interconnecting porosity within.

A sample of the as-received material was ball milled for 5 minutes and its properties were characterized. The apparent density, tap density, and cold compacted

TABLE I

DENSITY OF FUSED UO_2 POWDER
(All densities in g/cc)

Material	Spencer fused UO_2 As-received	Spencer fused UO_2 Blend No. 12	Spencer fused UO_2 Ball mill 5 min.	Spencer fused UO_2 & ceramic	Norton fused UO_2 & ceramic	Norton same particle size distribution as Spencer
Apparent density	5.45	5.50	5.20	-	-	-
Tap density	7.37	7.90	7.15	-	-	-
Cold compacted density, 40 tsi	9.26	9.30	8.96	-	-	-
H.I.P. 12,000 psi 60 minutes						
1200°C	9.93	10.04	10.09	10.06	10.72	-
1275°C	9.95	-	-	10.35	-	-
1300°C	10.11	-	9.87	10.32	10.79	10.27

TABLE II

TAP DENSITIES OF VARIOUS BLENDS OF FUSED UO_2

Blend No.	-20 +100, %	-100 +140, %	-140 +200, %	-200 +230, %	-230 +325, %	-325, %	-20 +80, %	-80 +200, %	-20 +30, %	-30 +200, %	Tap density, g/cc	Theo. density, %
As-Recv'd.	50	9.8	8.7	4.2	4.8	22.1	-	-	-	-	7.37	67.2
1	100	-	-	-	-	-	-	-	-	-	6.25	56.9
2	91	9	-	-	-	-	-	-	-	-	6.27	57.1
3	91	-	9	-	-	-	-	-	-	-	6.36	57.9
4	91	-	-	9	-	-	-	-	-	-	6.45	58.7
5	91	-	-	-	9	-	-	-	-	-	6.65	60.9
6	91	-	-	-	-	9	-	-	-	-	6.80	62.0
7	83	-	-	-	-	17	-	-	-	-	7.24	65.9
8	76.9	-	-	-	-	23.1	-	-	-	-	7.62	69.4
9	71.4	-	-	-	-	28.6	-	-	-	-	7.82	71.2
10	66.7	-	-	-	-	33.3	-	-	-	-	7.86	71.6
11	64	9	-	-	-	27	-	-	-	-	7.89	71.9
12	64	-	9	-	-	27	-	-	-	-	7.90	72.0
13	64	-	-	9	-	27	-	-	-	-	7.83	71.4
14	64	-	-	-	9	27	-	-	-	-	7.87	71.7
15	-	-	-	-	-	-	40	60	-	-	6.59	60.0
16	-	-	-	-	-	-	-	-	40	60	6.88	62.7

density of the ball milled powder was less than that of the as-received material, but upon hot isostatic pressing a higher density was obtained. The appearance of this sample after sectioning was similar to that of blend No. 12, as it also had interconnecting porosity.

B. The Effect of Physical and Chemical Properties on the Hot Isostatic Pressing Density

Two samples of 75% fused plus 25% ceramic UO_2 powder were hot isostatically pressed at 12,000 psi for 60 minutes at 1200°C, and two other samples were hot isostatically pressed at 12,000 psi, 60 minutes at 1300°C.

One sample of each temperature group was made with Norton fused UO_2, and the second sample of each group was made with Spencer fused UO_2.

Since the blend of Norton fused UO_2 plus the ceramic grade powder gave consistently better results than the Spencer fused plus ceramic grade powder, a comparison of the chemical and physical properties of these powders was made.

1. Visual Examination (Binocular Microscope, 25X)

The particles of both the Norton fused powder and the Spencer fused powder had a similar particle shape, i.e. angular.

2. Internal Structure (100X)

Samples of both the Norton and Spencer fused powders were separately mounted in bakelite and polished. The examination of these powders at a magnification of about 100X showed no differences between the Norton fused and the Spencer fused powders in either the cross sectional shape of the particles, the internal structure, or the internal porosity.

3. U/O Ratio (Chemical Determination)

The U/O ratio of the Norton fused powder was 1:2.034 and the U/O ratio of the Spencer fused powder was 1:1.995.

4. Pycnometer Densities

The average pycnometer particle density for the Norton fused powder was 10.82 gm/cc and the average pycnometer density for the Spencer fused powder was 10.78 gm/cc.

A second series of pycnometer densities, taken after grinding the powders to a finer fraction, did not indicate any internal porosity.

5. Density After Hot Isostatic Pressing

A sample of 100% Norton fused powder, consisting of 50 w/o -50 +100 mesh, 30 w/o -100 +325 mesh and 20 w/o -325 mesh, was hot isostatically pressed at 1300°C and 12,000 psi for one hour. The density obtained was 10.27 g/cc.

A similar sample of Spencer fused powder, pressed at the same conditions, namely 1300°C, and 12,000 psi for one hour, densified to 10.11 g/cc.

6. Spectrographic Analysis

The spectrographic analysis, performed by Mr. H. Mullen of the A.E.C. New Brunswick Laboratory, on samples of both the Norton and Spencer fused powders indicated no gross impurity differences.

In summarizing the results, only two differences have been found between the Norton fused powder and the Spencer fused powder. These are: (1) the Norton powder has a higher U/O ratio; and (2) the Norton powder hot isostatically presses to a higher density. These two results appear to be related, as it has been reported in the literature that

nonstoichiometric $UO_{2.06}$ can be plastically deformed at temperatures above 800°C* while $UO_{2.0}$ deforms at 1600°C.

C. The Effect of Temperature on the Hot Isostatically Pressed Density

Several runs were hot isostatically pressed at various temperatures to determine the effect of temperature on the hot isostatically pressed density. A maximum of 1300°C was used for these tests as the sample cladding has a melting point of about 1400°C. In the limited temperature range available, there was no appreciable density increase resulting from increasing the hot isostatically pressed temperature from 1200°C to 1300°C. Some improvement was noticed, however, with the blend of Spencer fused UO_2 plus ceramic powder.

D. Vibratory Packing of Loose Powder

Samples are presently fabricated by tamping the powder directly into the cladding, vacuum welding to seal the sample and then hot isostatically pressing the sample for final densification. The limitations of tamping the powder are recognized and visible evidence of the tamping ridges can be seen in the hot isostatically pressed sample. The diametrical elevation of these ridges ranges from a maximum of 0.005" to less than 0.001".

By vibratory packing of the powder, using either sonic or ultrasonic vibrations, a superior product can be made yielding densities equal to that obtained by the tamping process.

A trip was made to Aeroprojects to discuss the consolidation of UO_2 powder in a tube, using ultrasonic

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* British report AERE M/R-2648, R. Scott, A. Hall and J. Williams, U.K.A.E.A., Research Group, Harwell, England, December, 1958.

vibrations. Mr. Tarpley of Aeroprojects suggested he would like to investigate the effect of column height. It was agreed that Sylcor would supply a special blend of fused UO_2, namely blend No. 12 of Table II. Compaction by ultrasonic vibration will be done using a fixed blend of powder with a high tap density which was previously developed. Blends No. 15 and 16 are similar to those used by General Electric to consolidate a fused UO_2 powder column using sonic vibrations.

E. Structure of the Cladding

Comparison studies have been made to determine if the hot isostatic pressing process has caused any structural defects of the cladding.

In comparing the cladding pressed at 1200°C with the as-received material some grain growth has taken place (see Figures 1 and 2). Cladding taken from samples hot isostatically pressed at 1250°C and higher showed excessive grain growth, penetration of oxide into the grain boundaries terminating at the surface (intergranular corrosion), and precipitation at the grain boundaries. A photomicrograph of the cladding after hot isostatic pressing at 1250°C is shown in Figure 3.

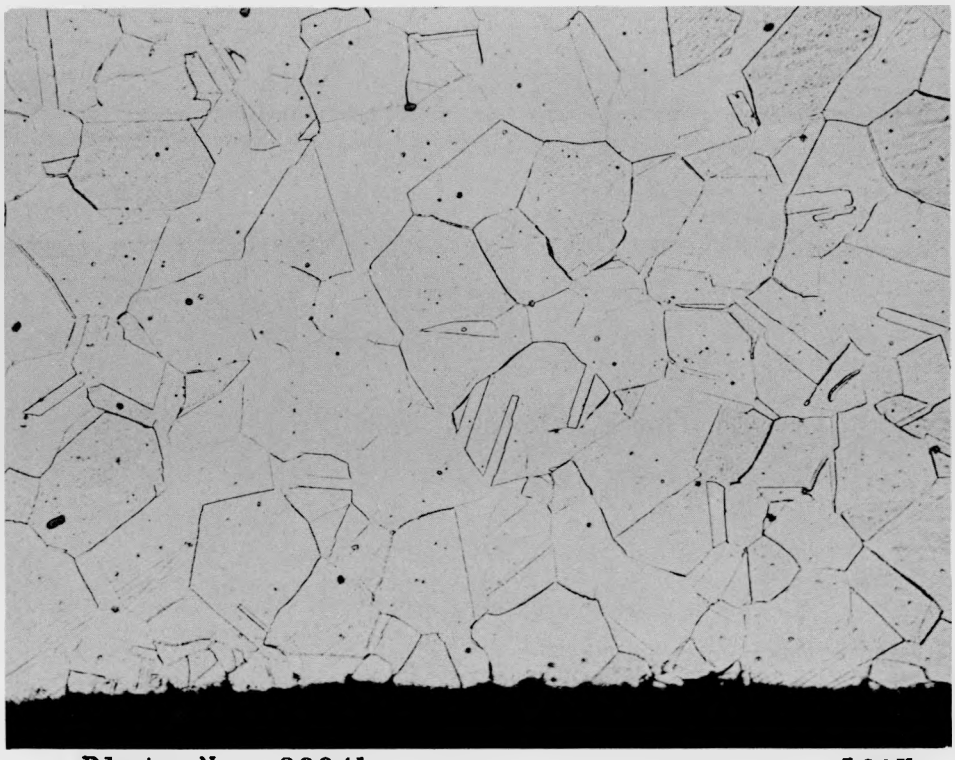

Plate No. 22941 500X

Fig. 1. As-received tubing - stainless steel type 304 LC.

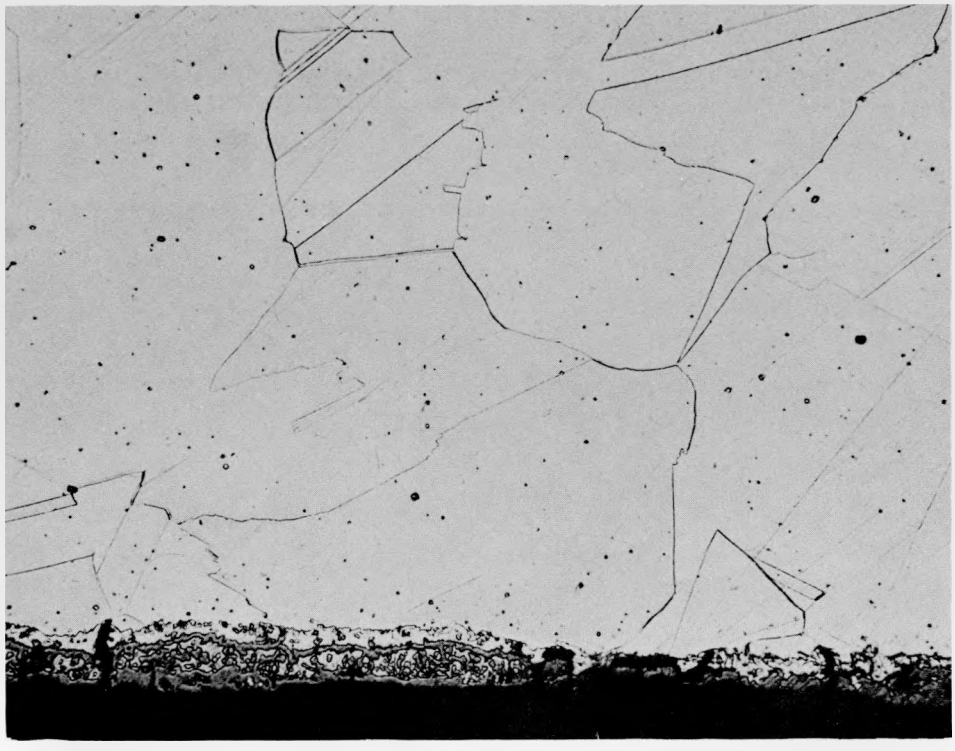

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Fig. 2. Cladding after hot isostatic pressing at 1200°C, 12,000 psi for 60 minutes.

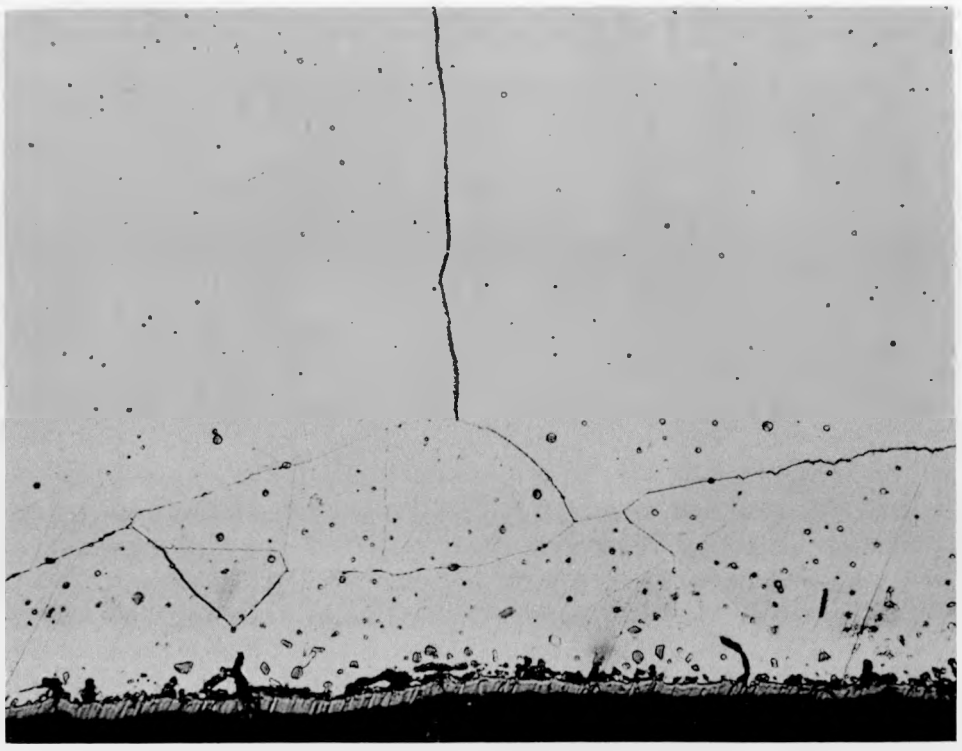

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Fig. 3. Cladding after hot isostatic pressing at 1250°C, 12,000 psi for 60 minutes.

II. URANIUM DIOXIDE FUEL ELEMENTS (R. M. Powers and H. Shapiro)

Objective: **A.** Improvement in the thermal conductivity of UO_2 pellets by the addition of small amounts of other oxides.

B. Reduction of the sintering temperature of urania-thoria compositions by coprecipitation.

A. UO_2 Plus Additives

Attempts to prepare dense samples for thermal conductivity tests, using 92 m/o UO_2-8 m/o Y_2O_3 rather than 96 m/o UO_2-4 m/o Y_2O_3 as in the previous period, were unsuccessful. A sample sintered in argon at 1300°C and reduced in argon-hydrogen was both low in density (80% of theoretical) and cracked. A second sample sintered in argon at 1500°C was not cracked, but was less than 90% of theoretical density. This sample was slowly reheated in argon to 1300°C and then reduced in argon-hydrogen at 1300°C. It then was found to have cracked, and showed a density of 84% of the calculated theoretical density. A third sample was sintered in hydrogen at 1620°C; it, too, was cracked, although its density was 99% of the theoretical density.

Photomicrographs of the first and third samples are shown in Figures 4 and 5. The oxygen-to-uranium ratio for each of these samples was about 2.1, and the lattice constants obtained by X-ray diffraction were 5.42 and 5.44 Å, respectively. These results indicate that the cracking takes place in the presence of hydrogen, but is not necessarily due to the removal of excess oxygen, and that increasing the Y_2O_3 content from 4 to 8 m/o raises the sintering temperature from 1300° to above 1500°C. Also,

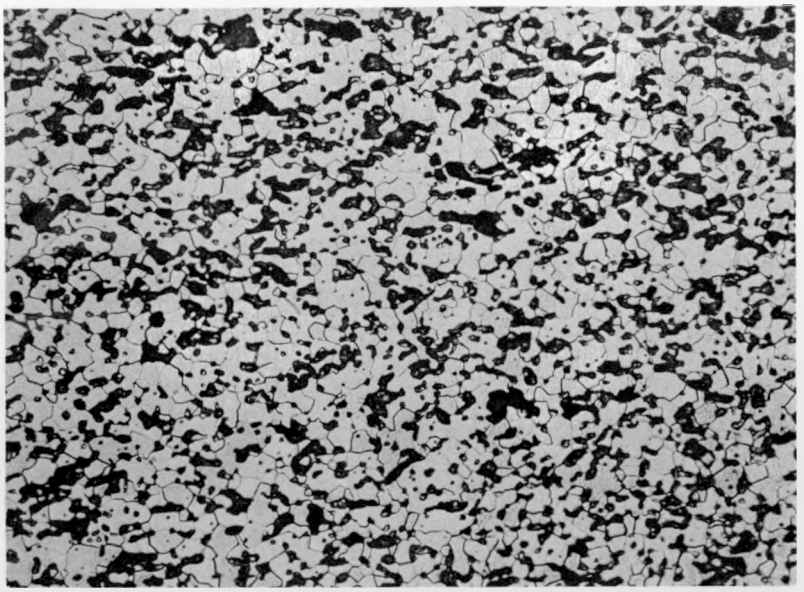

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Fig. 4. UO_2 + 8 m/o Y_2O_3, sintered and reduced at 1300°C, density 8.1 g/cc (80% of theoretical), 5-10 microns grain size.

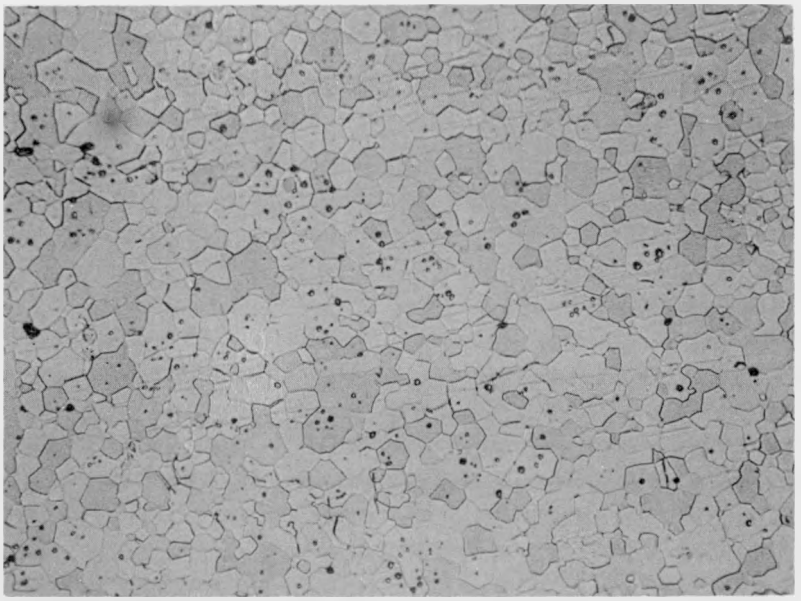

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Fig. 5. UO_2 + 8 m/o Y_2O_3, sintered in hydrogen at 1620°C, density 10.04 g/cc (99% of theoretical), 5-15 microns grain size.

some excess oxygen has been retained in the UO_2-Y_2O_3 lattice since X-ray diffraction and metallographic examination show only the cubic form of oxide. Samples for thermal conductivity measurements were prepared with 2 m/o and 8 m/o CaO additions. Difficulty with cracking was observed for the latter. Photomicrographs of these samples are shown in Figures 6 and 7, and the results with various additions and heat treatments are summarized in Table III. 2 m/o CaO adds the same number of calcium atoms as 1 m/o Y_2O_3 adds yttrium atoms to the UO_2, and from Table III it can be seen that the effects of a given amount of Y_2O_3 are about equal to the effects of twice as much CaO. Additions of more than 2 m/o CaO or 1 m/o Y_2O_3 begin to decrease the oxygen-to-uranium ratio and the lattice constant. More than 4 m/o Y_2O_3 decreases the sinterability and appears to stabilize excess oxygen in the lattice.

B. Thermal Conductivity Measurements

Attempts to standardize the thermal conductivity furnaces with three UO_2 samples are still unsuccessful. It has been shown that the cross-section of the furnace has a uniform temperature. Runs have been made in which crushed insulating fire-brick was packed around the samples to decrease heat transfer by radiation; the length of thermocouple wire at the same level as the bead was increased to decrease heat conduction along the wires, a constant output voltage transformer was installed to decrease supply voltage variations, and an ice-water cold junction was installed for the thermocouples. A complete thermal balance could not be obtained in all cases; only three of the four necessary positions could be balanced thermally.

C. Irradiation Capsules

During this period the machine shop prepared eight irradiation capsule assemblies, and one assembly has been sent to the Atomic Energy of Canada at Chalk River, Ontario for their inspection.

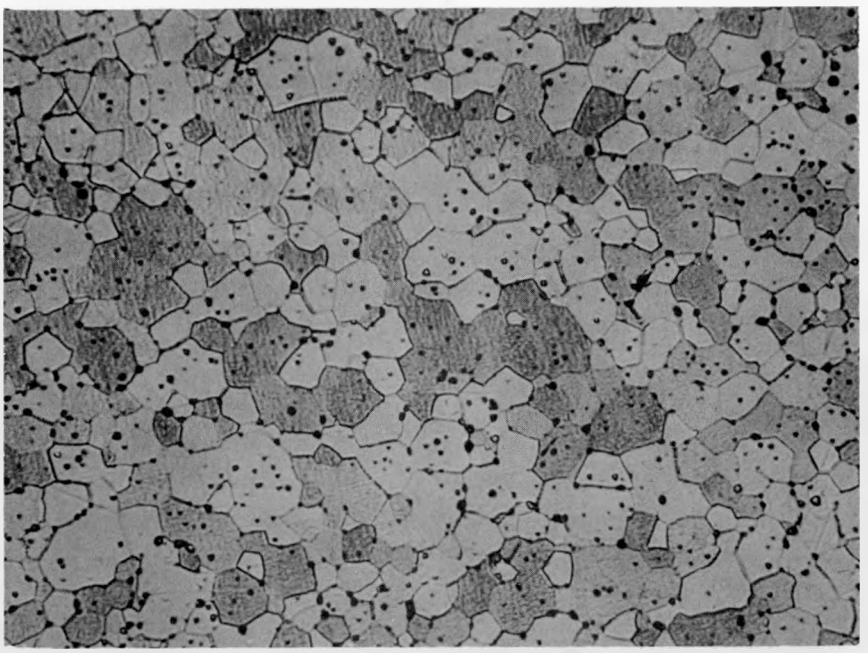

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Fig. 6. UO_2 + 2 m/o CaO, sintered and reduced at 1300°C, density 10.6 g/cc (97% of theoretical), 6-11 microns grain size.

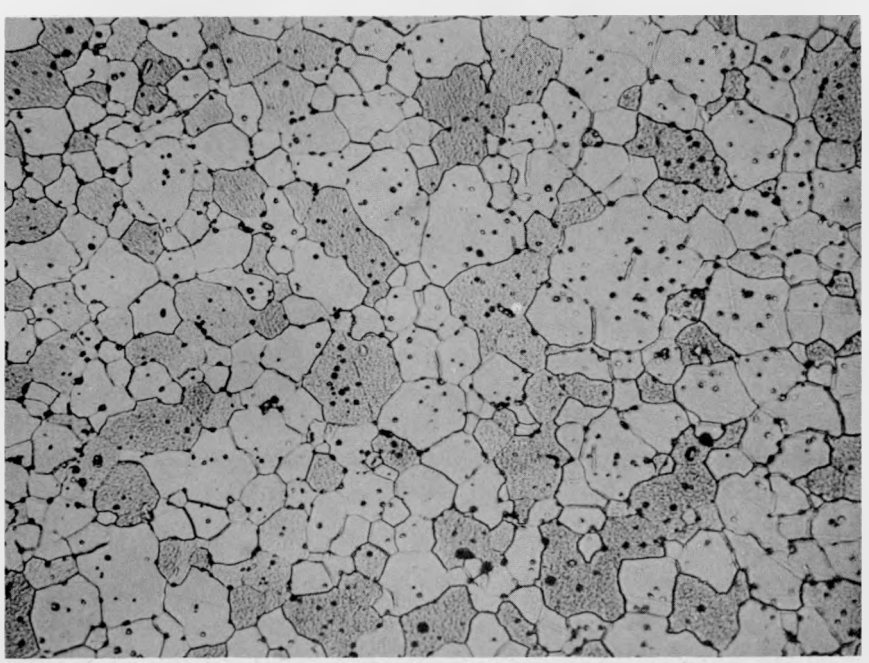

Plate No. 22877 500X

Fig. 7. UO_2 + 8 m/o CaO, sintered and reduced at 1300°C, density 10.0 g/cc (95% of theoretical), 9-23 microns grain size.

TABLE III

UO_2 PLUS ADDITIVES

Additive	Sintering temperature		Density g/cc	Density % of theoretical	O/U	Lattice constant Å
None	Argon	1300°C	10.7	97	2.00	5.47
1/4 m/o Y_2O_3	Argon	1300°C	10.5	96	-	5.47
1 m/o Y_2O_3	Argon	1300°C	10.6	97	2.00	5.47
4 m/o Y_2O_3	Argon	1300°C	10.0	95	1.97	5.45
8 m/o Y_2O_3	Argon	1300°C	8.1	80	2.09	5.42
8 m/o Y_2O_3	Hydrogen	1620°C	10.0	99	2.15	5.44
2 m/o CaO	Argon	1300°C	10.6	97	1.99	5.46
8 m/o CaO	Argon	1300°C	10.0	95	1.97	5.45

Mallinckrodt ceramic grade UO_2, low bulk density and 4.6% enriched in U-235, was used to prepare the UO_2 pellets for the irradiation tests. The UO_2 was oxidized to an oxygen-to-uranium ratio of 2.4. A granulation with 1/2% duPont Elvanol 51-05 as a binder and 1/4% zinc stearate as a lubricant was prepared and pressed in a 0.825 inch diameter die at 20 tsi. The pellets were sintered in argon at 1300°C and reduced in argon-hydrogen at 1300°C. Samples of the sintered pellets were taken for metallographic examination, and measurement of oxygen-to-uranium ratio and lattice constant. The sintered density of these pellets varied between 10.6 and 10.7 g/cc or 96-98% of theoretical density. The sintered oxygen-to-uranium ratio was 2.00, and the lattice constant 5.471 ± 0.002 Å (the value given in the literature is 5.468 Å). The grain size was 5-15 microns (see Figure 8).

Samples of 96 m/o UO_2-4 m/o Y_2O_3 were prepared as follows: enough fully enriched uranium (as a uranyl nitrate solution containing 0.1 grams uranium per milliliter) was added to the Mallinckrodt 4.6% enriched UO_2 to obtain material 3% enriched in U-235. Enough yttrium (as a yttrium nitrate solution containing 0.3 grams of yttrium per milliliter) was added to the UO_2 to give a batch equivalent to 96 m/o UO_2-4 m/o Y_2O_3. The batch was then calcined in argon at 900°C, reduced, and reoxidized to an oxygen-to-uranium ratio of 2.58. A granulation was then prepared using 1/2% duPont Elvanol 51-05 as a binder and 1/4% zinc stearate as a lubricant, and this was pressed in a 0.825 inch diameter die at 20 tsi. The pellets were sintered in argon at 1300°C and reduced in argon-hydrogen at 1300°C. The sintered density of these pellets varied between 10.0 and 10.2 g/cc or 95-97% of calculated theoretical density. The sintered oxygen-to-uranium ratio was 1.96 to 1.97, and the lattice constant 5.455 ± 0.002 Å. The grain size was 8-15 microns (see Figure 9). Metallographic examination showed larger pores than in the case of the UO_2 control.

The pellets are to be ground to 0.660 ± 0.0005 inches diameter and 0.454 ± 0.0005 inches long in order to fit into the radiation capsule.

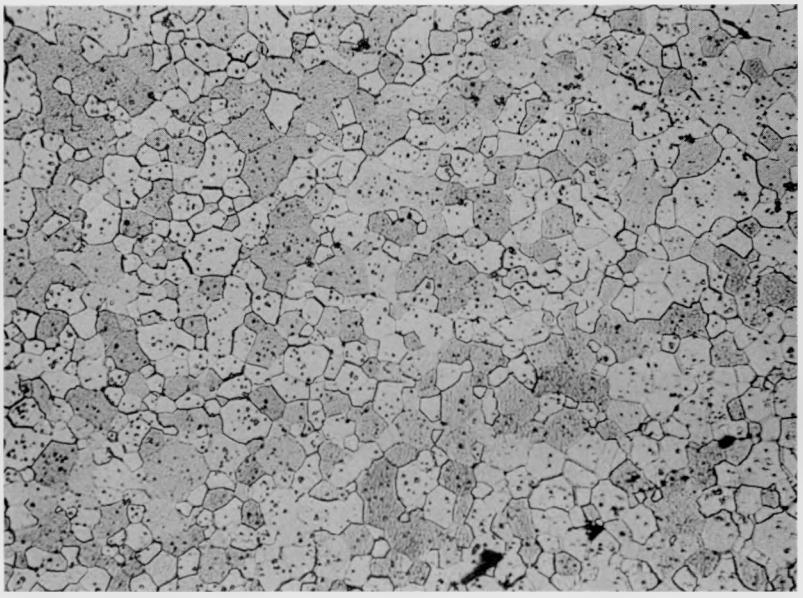

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Fig. 8 UO_2, 4.6% enriched, sintered and reduced at 1300°C, density 10.7 g/cc (97% of theoretical), 5-15 microns grain size.

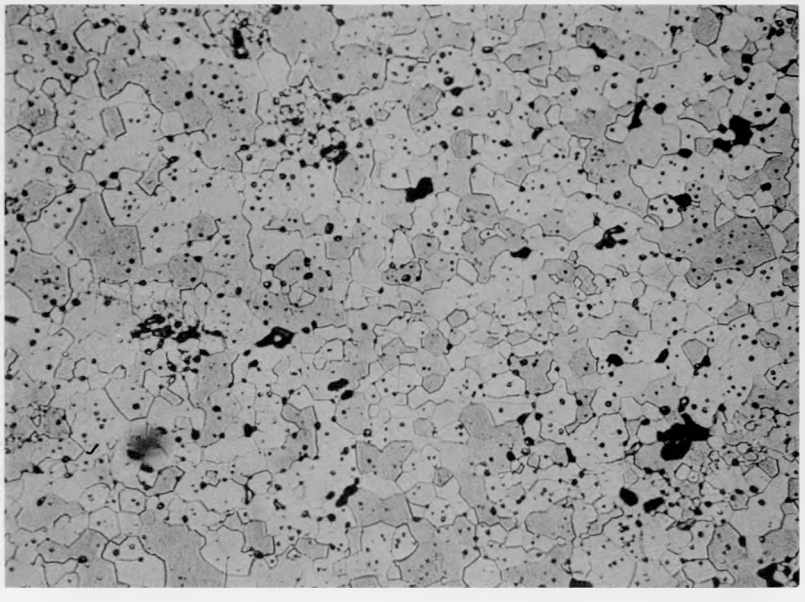

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Fig. 9. 96 m/o UO_2 (5% enriched)-4 m/o Y_2O_3, sintered and reduced at 1300°C, density 10.1 g/cc (96% of theoretical), 8-15 microns grain size.

III. IRRADIATION OF ISOSTATICALLY PRESSED OXIDE SAMPLES

(S. D. Strauss)

Objective: Determination of the behavior of stainless steel-clad, isostatically pressed oxide samples relative to that of standard, pelletized UO_2, under prolonged neutron irradiation.

All parameters of the irradiation samples and test have been determined in this initial quarterly period of the project. Isostatically pressed samples of both 100% fused uranium oxide and a mixture of 75% fused and 25% ceramic grade oxide, all clad in stainless steel, will be encapsulated together with samples of standard UO_2 pellets. Test conditions will be designed to create central temperatures in the range 2800°C to 2900°C, sufficient to produce a small melt zone at the sample centerlines, and burnups in the range 3,000 to 20,000 megawatt days per ton of oxide in the samples. A combination of 18% uranium enrichment and 0.400 inch oxide diameter was selected for this purpose. The required effective thermal neutron flux and irradiation period are 10^{13} neutrons/cm^2-sec and 2 to 11 months, respectively.

Procurement of fully enriched oxide has been initiated. This material will be blended with normal or depleted oxide in the proportions necessary to produce the desired U-235 density in the test samples. The isostatically pressed oxide density is expected to be approximately 92% of theoretical.

The Nuclear Development Corporation (NDA) has undertaken the design and construction of test capsules. Three single-walled, stainless steel capsules will be used. Each will accommodate four isostatically pressed samples and one pelletized sample 1.0 inch long by 0.430 inch diameter. Thermocouples and monitor wires will be incorporated to provide continuous monitoring of capsule temperatures and to indicate total

integrated neutron flux, respectively. The capsule design has been completed and tests are under way on a prototype sample to determine temperature drops across the wall and sodium heat transfer layer.

During the next quarter all samples will be fabricated and encapsulation will be started. Irradiation is scheduled to commence early in May, 1960. Discussions have begun with both MTR and WTR on the availability of facilities for the required period.

IV. IRRADIATION OF URANIUM-YTTRIUM ALLOYS (S. D. Strauss)

Objective: Determination of the dimensional stability of uranium-yttrium alloys under neutron irradiation at high temperatures.

In this initial quarterly period all material and test conditions were determined. Two alloys will be examined: 50 w/o uranium-50 w/o yttrium, and 25 w/o uranium-75 w/o yttrium. The uranium enrichments selected are 22% and 55% for the 50-50 and 25-75 alloys, respectively. Samples with diameters varying from 0.15 to 0.27 inches will be subjected to an effective thermal neutron flux of 8×10^{13} neutrons/cm^2-sec for approximately 60 days. This combination of enrichment, diameter and neutron flux is expected to produce central temperatures from 500°C to 900°C, and an integrated fission density of 4×10^{20} fissions per cubic centimeter of alloy.

Procurement of fully enriched uranium metal has been initiated. This material will be combined with the proper amount of normal uranium metal to produce the required enrichments. The uranium and yttrium metal will be hydrided separately in equipment now being prepared for use. The materials will then be blended, pressure compacted at 50 tsi, and sintered under vacuum. The process is expected to produce a U-235 density of approximately 0.75 gm per cubic centimeter of alloy in the test samples.

Design and construction of the temperature-controlled test capsules is being done by the Nuclear Development Corporation (NDA). Two capsules will be used, each containing five alloy samples of 0.75 inch length and varying diameter. One capsule will produce central temperatures from 500°C to 700°C; the other, from 700°C to 900°C. They will be equipped with control elements to maintain sample surface temperatures within $\pm$ 20°C of the design values. Thermocouples and monitor wires will be incorporated to provide continuous monitoring of capsule temperatures and to indicate total neutron flux, respectively. Design of the capsules is approximately 75% complete, and the calibration apparatus is being assembled.

All samples will be fabricated during the next quarter and encapsulation will be started. Irradiation is to start in May, 1960 and end in July. Arrangements are being made for the use of test facilities in either MTR or WTR for the required period.