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FABRICATION DEVELOPMENT OF U-Mo-UO_2 AND U-Mo-UC DISPERSION FUELS FOR THE ENRICO FERMI FAST-BREEDER REACTOR

S. A. Rabin
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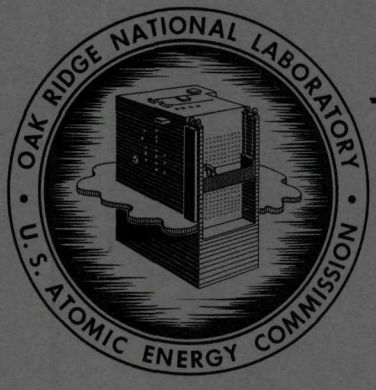

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ABSTRACT

The fabricability of dispersion fuels using UO_2 or UC as the dispersoid and uranium combined with 10 to 15 wt % Mo as the matrix was investigated. Cores containing 17.8 wt (25 vol) % UO_2 dispersed in U–15 wt % Mo were successfully fabricated to about 80% of theoretical density by cold pressing at 50 tsi, sintering at 1100°C, and cold coining at 50 tsi. Comparable results were obtained with UC as the dispersoid.

Core fabrication results varied greatly with the type of matrix powder used. Occluded gases, pour density, and surface cleanliness bore important relations to the fabrication behavior of powders. Suitable pressing and sintering results were obtained with prealloyed, calcium-reduced U-Mo powder and with molybdenum and calcium-reduced uranium as elemental powders. Shotted prealloyed powders were difficult to press and sinter, as were elemental and prealloyed powders prepared by hydriding.

The cores containing UO_2 were picture-frame, hot-roll-clad as miniature plates. Molybdenum, Fansteel 82, and Zr–3 wt % Al were investigated as cladding materials. While each bonded well to itself, only the molybdenum-clad core (rolled at 1150°C to 10/1 reduction) resulted in dispersions free of ruptures and UO_2 fragmentation and in strong bonding to the core (evaluated by metallography, mechanical peel, and thermal shock tests). The matrix phase was homogeneous, but the UO_2 dispersoid showed stringering characteristic of cores worked by hot rolling. Core densities as high as 99% of theoretical were obtained.

INTRODUCTION

The fuel fabrication work presented in this report constitutes one of the tasks undertaken in the Oak Ridge National Laboratory (ORNL) Fast-Breeder Assistance Program. The general purpose of this program

was to develop improved fuels for fast reactors, and the specific objective was to provide assistance in the materials field to Atomic Power Development Associates (APDA), designers of the nuclear system for the Enrico Fermi atomic power plant. This study, initiated in the latter part of 1959, was terminated in October 1960 when the adaptation of oxide fuels to an operational fuel element became a more immediate prospect. However, the program reorientation did not reflect a diminished nuclear attractiveness of the dispersion fuel.

The principal criteria for the proposed Fermi fuel included nuclear burnups in excess of 50,000 Mwd/ton at an operating temperature of 650°C or higher, a high fuel density, good thermal performance as reflected in permissible power density and thermal stability, compatibility with coolant and cladding, and high functional integrity. For this program it was specified that the fuels be of a plate design and consist of a dispersion of enriched UO_2 or UC in an isotopically depleted γ-uranium alloy matrix. Such a design capitalizes upon the high burnup potential of the dispersion-type fuel while exploiting the fertile metal matrix to achieve high nuclear conversion and thermal performance.

Pertinent design data, as established by APDA, are listed in Table 1. Two cermet elements were proposed, one consisting of 25.4 vol (18.1 wt) % UO_2 dispersed in U–15 wt % Mo matrix, and the other a 19.3 vol (16.3 wt) % UC–bal U–15 wt % Mo dispersion. Uranium carbide is superior to UO_2 in uranium density and thermal conductivity, but its application to dispersion fuels was not so fully developed; therefore emphasis was placed on developing the oxide-containing element. A zirconium alloy was originally suggested for the cladding material, but was eventually discarded in favor of other materials.

Although these fertile-matrix fuel elements appear to offer much potential merit in performance characteristics, fabrication constitutes a formidable problem because of (1) the radiological and pyrophoric nature of uranium-bearing powders, necessitating dry-box operations, (2) limited availability and high cost of the desired powders, (3) scarcity of developed materials for cladding application that are compatible with the core constituents and sufficiently oxidation-resistant in air at the fabrication temperatures, and (4) lack of previous fabrication work on this fuel system.

Table 1. Fertile-Matrix Fuel Element Design Parameters

Core composition: 19.3 vol (16.3 wt) % UC in U–15 wt % Mo, or 25.4 vol (18.1 wt) % UO_2 in U–15 wt % Mo

Reactor power, Mw (thermal)	430
Core power, Mw (thermal)	400
Sodium inlet temperature, °C	290
Average sodium temperature rise, °C	170
Number of core subassemblies	130
Core pressure drop, psi	75
Breeding ratio	> 1.000
Fuel element geometry	Plates
Number of plates per subassembly	12
Plate length, in.	49.5
Core length, in.	48.0
Plate width, in.	2.450
Core width, in.	2.200
Plate thickness, in.	0.131
Core thickness, in.	0.121
Clad thickness, in.	0.005
Throughput burnup, fissions/cc	
UC	14.3×10^{20}
UO_2	10.5×10^{20}
Enrichment, %	
Matrix	0.35
Dispersoid	93
Center-line fuel temperature, °C	320 to 640
Matrix fission rate, fissions cc^{-1} sec^{-1}	0.2 to 1.3×10^{13}

To limit the development work, roll cladding of fuel cores by the conventional picture-frame technique was selected as the reference fabrication method. Both elemental and prealloyed powders were investigated as potential matrix materials. For the fissile phase, spherical particles having a size of about 150 μ were deemed the best compromise between the competing factors of irradiation stability and ease of fabrication.[1–3] Another significant consideration was that the dispersed particles be mechanically strong in order to resist stringering during fabrication.

Experience in roll cladding of dispersion-type fuels indicated that compact densities no greater than 80% of theoretical would be required.[4,5] Accordingly, emphasis in the powder metallurgy work was placed on obtaining interparticle bonding, homogeneity, and dimensional control rather than on gross shrinkage through sintering.

Procedures for rotary swaging U-Mo powders were also investigated. The purposes of this study were to develop procedures for fabricating wrought forms in the γ-uranium alloys (10 to 15 wt % Mo range) and to provide needed materials for irradiation and mechanical properties tests. This work is described in another report.[6]

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[1]C. E. Weber, Progr. Nucl. Energy (5)2, 295–362 (1959).

[2]J. R. Weir, A Failure Analysis for the Low-Temperature Performance of Dispersion Fuel Elements, ORNL-2902 (May 27, 1960).

[3]D. R. Gurinsky and G. J. Dienes, Nuclear Fuels, Van Nostrand, Princeton, 1956.

[4]D. L. Keller, "Dispersion Fuels," in Reactor Handbook, vol I, Interscience, New York, 1960.

[5]J. H. Cherubini, R. J. Beaver, and C. F. Leitten, Jr., Fabrication Development of UO_2-Stainless Steel Composite Fuel Plates for Core B of the Enrico Fermi Fast Breeder Reactor, ORNL-3077 (Apr. 4, 1961).

[6]S. A. Rabin, A. L. Lotts, and J. P. Hammond, Swaging of Uranium-Molybdenum Alloy Powders Containing 10 to 15 wt % Mo, ORNL-TM 455 (in preparation).

REVIEW OF THE LITERATURE

The fabrication of dispersions of UO_2 in various matrices has been extensively investigated. However, little has been done on the powder metallurgy of U-Mo alloys or on dispersions of UO_2 in U-Mo alloy matrices.

Kalish[7,8] has described the preparation by powder metallurgy techniques of U-Mo alloys containing up to 12 wt % Mo. Uranium powder produced by the hydride method was used as the base material. The coarsest material that could be pressed and sintered to a dense, homogeneous product with reasonable sintering temperatures and times was −325 mesh uranium powder. Fine molybdenum powder, preferably −325 mesh, was also essential. Cold compaction and sintering of elemental powders resulted in alloy homogeneity comparable to that obtained by hot pressing, but to achieve very high densities (better than 97% of theoretical), temperatures very near to or exceeding the melting point were required. It was not reported whether these densities were determined geometrically or by immersion; values for the latter might be considerably higher. Camphor, which proved to be an ideal powder lubricant for cold pressing and sintering, was added as a benzene solution, and a slurry was made of the powders. The mixture was vacuum-dried prior to compacting. The optimum compacting pressures appeared to be 40 to 50 tsi. Sintering was conducted in a vacuum of about 1×10^{-4} mm Hg. Kalish quoted[8] a density of 97.2% of theoretical for the U–12 wt % Mo alloy.

Lloyd and Williams[9] also prepared U-Mo alloys by powder metallurgy. Cold-compacted mixtures containing 9 and 60 wt % Mo gave alloys of over 90% of theoretical density when sintered for 2 hr at 1100°C in a vacuum. Equilibrium structures were produced provided that the initial particle sizes of the elemental powders were below about 60 μ (approximately −230 mesh).

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[7]H. S. Kalish, p 141 in Powder Metallurgy in Nuclear Engineering, Proceedings of the Conference on Powder Metallurgy in Atomic Energy, Philadelphia, Oct. 20, 1955, ASM, Cleveland, 1958.

[8]A. L. Eiss and H. S. Kalish, Dimensionally Stable Alloys, SCNC-249 (Oct. 30, 1957).

[9]H. Lloyd and J. Williams, Proc. U.N. Intern. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva, 1958 6, 426–437 (1958).

Fabrication studies on cermet fuels consisting of UO_2 dispersed in a U-Mo alloy matrix were conducted at BMI for APDA.[10,11] This investigation resulted in a procedure for fabricating small, unclad specimens consisting of 27 wt (36.7 vol) % UO_2 in a U–10 wt % Mo matrix. Natural uranium alloy powder of –100 +325 mesh size, prepared by the hydriding process, was blended with –200 +325 mesh enriched UO_2 and tap-packed into a preformed type 304 stainless steel can. The can, which was lined with molybdenum foil to prevent reaction between it and the powder, was sealed by welding in an inert atmosphere. This composite was then press-forged at 925°C between heated plates to a 40% reduction in thickness, annealed for 3 hr at 925°C, hot-rolled at 815°C to an additional 30% reduction, and water-quenched. The sheath was stripped from the core, and the specimens were hand-ground from the fabricated material. Densities of these specimens ranged from 89.5 to 93.5% of theoretical.

Results of the literature survey on cladding materials for the U–15 wt % Mo–base dispersion fuel system have been published.[12]

DESCRIPTION OF MATERIALS

Powders

Pertinent data concerning the matrix powders used in the present work are given in Tables 2, 3, and 4. Table 2 lists the powders with their source, grade, mode of preparation, mesh size, and composition. Some of the chemical analyses were furnished by the suppliers; the others were obtained at ORNL. Table 3 presents x-ray diffraction data for some of the powders. Tap densities of various U-Mo matrix powders are given in Table 4.

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[10] A. A. Shoudy, Review of UO_2-Uranium-Molybdenum Cermet Fabrication and Irradiation, memorandum to D. O. Leeser, APDA (Jan. 22, 1959).

[11] D. L. Keller et al., Fabrication Development and Irradiation of Uranium-Molybdenum Alloy-UO_2 Dispersions, BMI-APDA-647 (Mar. 12, 1959).

[12] M. M. Martin and R. J. Beaver, Cladding Survey for the Enrico Fermi Reactor U–15 wt % Mo Base Dispersion-Type Fuel Element, ORNL CF-60-4-118 (Apr. 29, 1960).

Table 2. Information on Powders for Fertile-Matrix Fuel Cores

Nominal Composition	Type	Grade and Mesh Size	Chemical Analysis									
			U (%)	Mo (%)	O_2 (ppm)	H_2 (ppm)	Inert Gas+N_2 (ppm)	C (ppm)	Fe (ppm)	Mg (ppm)	Ca (ppm)	Si (ppm)
U–10 wt % Mo	Prealloyed shot (N[a])	Spherical; –100 and –70 +100	89.85	10.0	580			175	535	90		70
U–15 wt % Mo	Prealloyed shot (N[a])	Spherical; –100	84.91	13.7[b]				158	464	3		35
U–15 wt % Mo	Co-reduction with calcium (U[a])	Irregular; –325 (50% < 20μ)	84.39	15.2	2500	500	65		150		40	80
Uranium	Hydride (U[a])	Irregular; –325 (av, ~ 5μ)	97.82		42,000	2500	2000	446	150	2	40	135
Uranium	Calcium-reduced (U[a]) Batch No. 94	Spheroidal; –325 (50% < 16μ)	99.26		1430			136	460	> 190	125	
Uranium	Calcium-reduced (U[a]) Batch No. 95	Spheroidal; –325 (50% < 15.5μ)	99.44		4000	180	42	120	80	103	75	
Molybdenum	Hydrogen-reduced (M[a])	Good commercial grade; –325		99.85	1900			200				
Molybdenum	Hydrogen-reduced (W[a])	Standard grade; –325 (av, ~ 4μ)		99.9	400			140				

[a]N: National Lead Company of Ohio; U: Union Carbide Nuclear Company; M: Molybdenum Corporation of America; W: Wah Chang Corporation.

[b]National Lead value: Mo = 14.9%.

Table 3. X-Ray Diffraction Analyses on Some Uranium and U-Mo Powders

Composition	Powder Type	Phases	Intensity[a]
Uranium	Hydride	α-U	Medium-strong
		β-UH_3	Medium-strong
		UO_2	Medium-strong
Uranium	Calcium-reduced Batch No. 94	α-U	Strong
		UO_2	Medium
U–13.7 wt % Mo	Shot	γ-U(Mo)	Strong
		Mo	Medium
		UO	Strong
U–15.2 wt % Mo	Calcium-reduced	γ-U(Mo)	Very strong
		α-U	Medium-strong
		Mo	Medium
		UO_2	Medium-faint

[a]Diffractograms taken on Debye-Scherrer camera.

Table 4. Tap Density of Various Matrix Powders

Composition	Constituents	Density (g/cc)	Percent of Theoretical
U–10.0 wt % Mo	Prealloyed shot	10.54	61.3
U–13.7 wt % Mo	Prealloyed shot	10.49	62.4
U–15 wt % Mo	Hydride uranium + Mo[a]	4.55	27.1
U–15 wt % Mo	Calcium-reduced uranium + Mo[a]	9.09	54.1
U–15.2 wt % Mo	Prealloyed by calcium-reduction	9.76	58.4

[a]From Molybdenum Corporation of America.

Since the fabricability of powders is directly related to such characteristics as gas content, particle size and shape, and surface condition, a more detailed description of the processing and properties of the various powders is given below.

Prealloyed U-Mo Powders

Several methods for making U-Mo alloy powder have received attention. The more prominent techniques that have been investigated are hydriding,[11] shotting,[13] atomizing,[13] and calcium reduction.[14]

Shotting Method.– Because of its relative availability and low cost, powder prepared by the spinning-disk shotting method was used as the matrix material in the early work. However, considerable difficulty was experienced in producing a satisfactory powder, and modification of the equipment and techniques is required to improve the quality of the product. The formation of a tenacious oxide film appears to be inherent to this method of powder preparation.

In the shotting process as conducted at the National Lead Company of Ohio, chunks of uranium and high-purity molybdenum powder were initially vacuum-induction-melted in a graphite crucible washed with beryllia. The shotting tank was backfilled with helium to give efficient cooling under protective conditions. The molten alloy was then bottom-poured onto a rapidly spinning (approximately 8000 rpm), 5-in.-diam zirconia disk, which dispersed the metal within a 12-ft-diam tank, where the droplets solidified. The interior of the chamber was made of mild steel. Pouring temperatures were approximately 1450°C for the U–10 wt % Mo shot and 1650°C for the U–15 wt % Mo shot.

The powder thus obtained was spheroidal, as shown in Fig. 1. The particle size was –100 mesh, with most of the yield in the –100 +200 mesh range. As would be expected, the shot has a cored dendritic structure (Fig. 1a). The vendor reported molybdenum contents of 10.0 and 14.9 wt % for the intended U–10 wt % Mo and U–15 wt % Mo materials, respectively.

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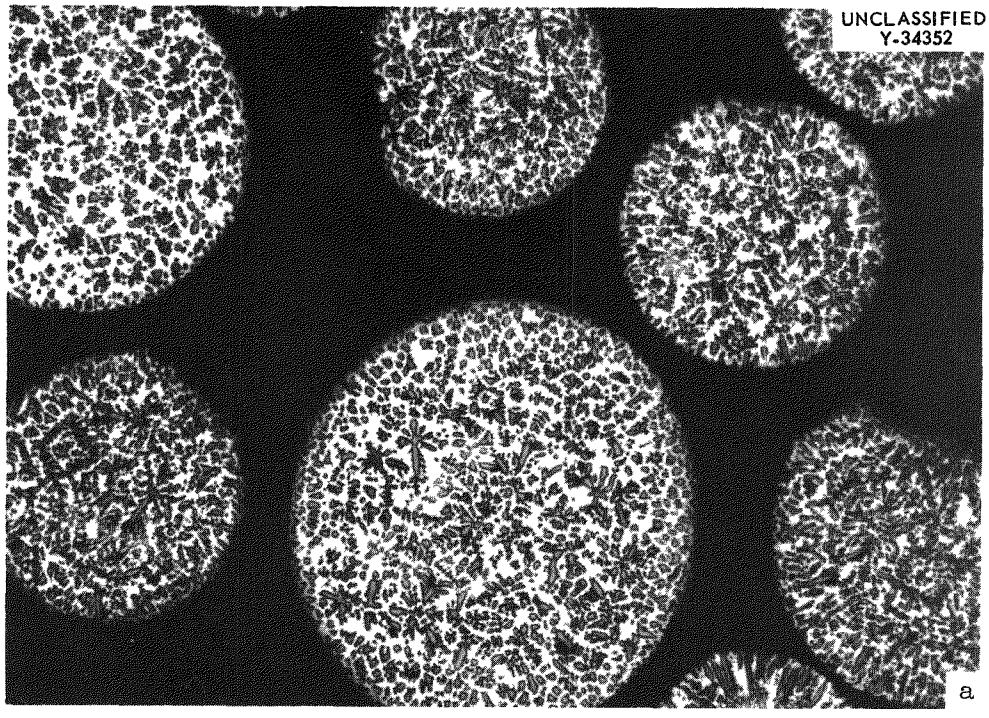
[13]R. H. Barnes et al., Engineering and Nuclear Design Phases of a Paste-Fuel Irradiation Experiment, BMI-APDA-642 (June 4, 1958).

[14]R. H. Myers and R. G. Robins, Proc. U.N. Intern. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva, 1958 6, 91–95 (1958).



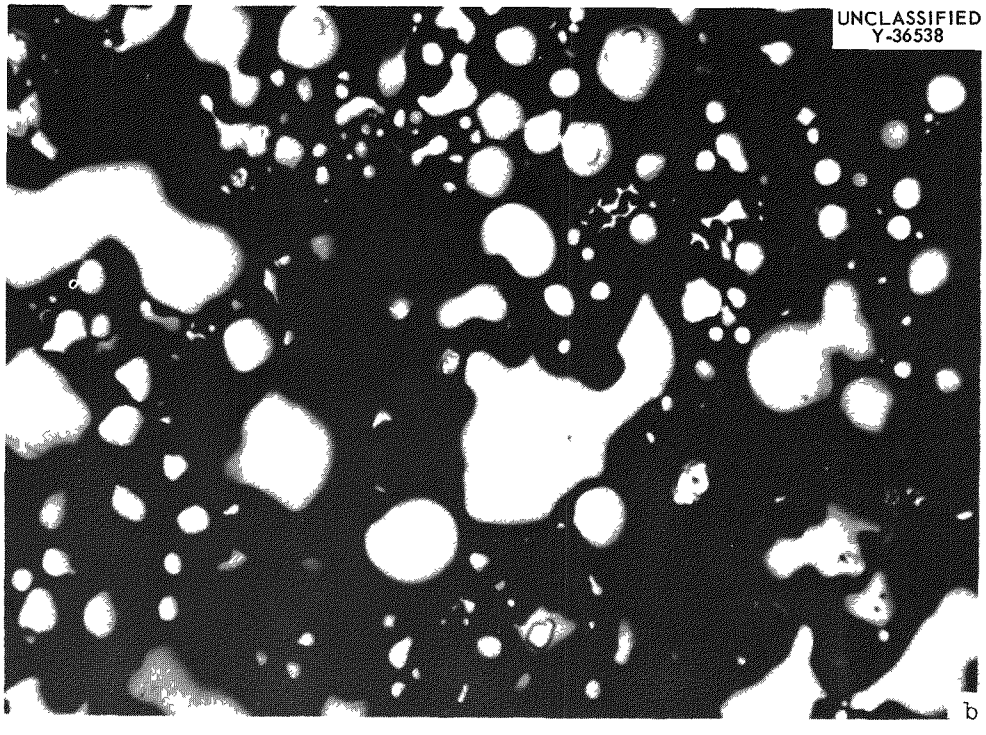


Fig. 1. Effect of Preparation Route on Prealloyed U-Mo Powder Characteristics. 500X. (a) U–13.7 wt % Mo shot, –100 mesh; polished cross section; etchant: 50% HNO_3–50% $HC_2H_3O_2$. (b) U–15 wt % Mo made by calcium reduction of UO_2 and molybdenum, –325 mesh; polished cross section; as-polished. Reduced 5%.

While an ORNL analysis on the former agreed with the intended composition, check analyses on several samples of the nominally U–15 wt % Mo alloy indicated the molybdenum content to be 13.7 wt %. The latter value is used in this report.

Calcium-Reduction Method.– Prealloyed U–15 wt % Mo powder (procured from the Union Carbide Nuclear Company Y-12 Plant) was made by the calcium-bomb reduction of mixtures of UO_2 and molybdenum. Powder prepared by this method contained rather large quantities of oxygen and hydrogen (Table 2). The particles were small and irregular in shape, as illustrated in Fig. 1b. Powders having –325 mesh particle size range were selected for use. Although duplicate analyses on the same batch yielded values of 15.2 wt % Mo, metallographic examination indicated a wide variation in composition from particle to particle. Microinhomogeneity was confirmed by x-ray diffraction analyses given in Table 3. In addition to the γ-U(Mo) phase, substantial amounts of undissolved molybdenum and α-uranium were observed, together with a small amount of UO_2. Further development no doubt would improve the quality of this product.

Hydriding Method.– Prealloyed powders produced by the hydriding method were not initially included in the program because of high costs anticipated for their production and the discouraging experience of others in producing U–10 wt % Mo powder by this means.[11] However, in view of impurity problems associated with other commercial powders, it was ultimately decided to prepare at ORNL laboratory quantities of U-Mo powders by this method.

Studies by others at ORNL[15] revealed that if the material is in the proper structural condition U-Mo alloys can be hydrided more easily than indicated by earlier work. No hydrogen absorption occurred when alloys were in the gamma-quenched condition. However, when the alloys were heat-treated to transform the metastable gamma phase to the equilibrium constituents, that is, $\alpha + \gamma'(U_2Mo)$, the amount of hydrogen absorbed increased in proportion to the amount of alpha phase present.

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[15]H. Inouye, Met. Div. Ann. Progr. Rept. May 31, 1961, ORNL-3160, pp 146–147.

The process involved heat treating the gamma-stabilized alloys at temperatures near the nose of the isothermal transformation curve to produce a partially transformed structure and then hydriding them at 200°C. The hydride powder was ground in a ball mill for 64 hr, vacuum-decomposed at 450°C, and reground to −325 mesh in a ball mill.

Elemental Uranium Powder

The various methods of producing uranium powder include direct-reduction processes, hydriding, electrolysis of fused salts, and breakup of the massive metal.[16] Uranium powders employed in this investigation were prepared by both the hydride process and the reduction of UO_2 with calcium.

Hydride Process.— This process involves the embrittlement of massive uranium by the absorption of high-purity hydrogen. Uranium metal chips were hydrided in a fluidized bed at 300 to 350°C under pressure. The hydride was sufficiently friable to be rendered into very fine powder. The resultant powder was decomposed in a helium atmosphere between 350 and 550°C.

The particles were −325 mesh with an average size of about 5 μ (Table 2). The particle shape was irregular, as shown in Fig. 2a. The tap density of the powder was comparatively low (see Table 4), as was its uranium content (approximately 97 wt %). As noted in Table 2, the amount of gaseous impurities was substantial, being predominantly oxygen, nitrogen, and hydrogen.

Calcium-Reduction Process.— Uranium powder made by calcium reduction of UO_2 was also acquired from the Y-12 Plant. The particles were spheroidal after reduction, as depicted in Fig. 2b. The particle size of this material also was fine, with a predominance of particles less than 20 μ in diameter. Both the uranium analysis and tap density were comparatively high; principal impurities are given in Table 2. Comparison with the hydride powder (Fig. 2) reveals substantially less oxide on the calcium-reduced uranium particles.

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[16]P. Chiotti and H. A. Wilhelm, p 31 in Powder Metallurgy in Nuclear Engineering, Proceedings of the Conference on Powder Metallurgy in Atomic Energy, Philadelphia, Oct. 20, 1955, ASM, Cleveland, 1958.

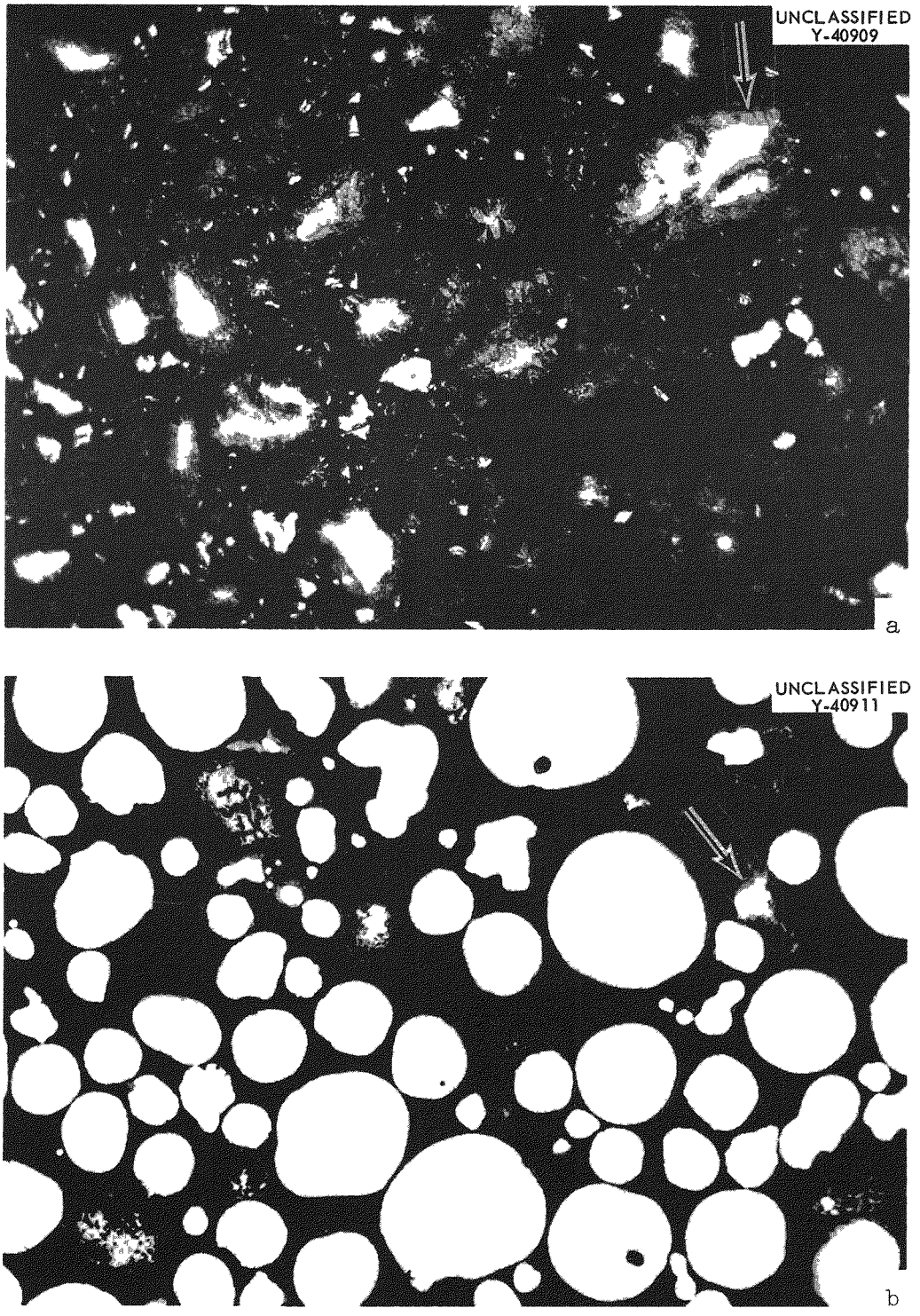

Fig. 2. Unetched Polished Cross Section of −325 Mesh Uranium Powder Produced by the (a) Hydride Process (1000X) and (b) Calcium-Reduction Process (500X). Note that particles produced by calcium-reduction are spheroidal and have oxidized less than those by the hydride process (see surfaces at arrows).

Molybdenum Powder

Properties of the commercial molybdenum powders, produced by hydrogen reduction, are presented in Table 2. The primary difference between these powders was in particle size. The extremely fine Wah Chang powder was incorporated in the program when it became apparent from swaging studies[6] that homogeneity was a problem.

Uranium Dioxide

Commercial high-fired spheroidal UO_2 shot was used as one of the dispersoid materials. The powder was made by United Nuclear Corporation by a proprietary process. A −80 +120 mesh particle size distribution was selected as a compromise between fabricability and anticipated irradiation behavior. The oxygen uranium ratio was 2.005. A photomicrograph of this material is shown in Fig. 3.

Uranium Monocarbide

Small quantities of uranium monocarbide were obtained from four vendors, although all could not supply UC in spheroidal form. The powders obtained were as follows: UC shot of −70 +270 mesh particle size from United Nuclear Corporation; spheroidal shot in the −80 +120 mesh range, produced in a high-intensity arc, from Vitro Chemical Company; fused and ground UC, −70 +270 mesh, from Spencer Chemical Company; and Davison Chemical Company UC sponge which was subsequently rendered in powder form at ORNL by crushing in a diamond mortar under an inert atmosphere.

Cladding Materials

Potential cladding materials for the flat-plate fuel element were surveyed[12] for strength and compatibility with the core, coolant, and protective sheathing materials, as well as for feasibility of fabrication by rolling. Fast-neutron-capture cross sections, status of development, and cost were also considered. From the many items assessed, the materials selected for further evaluation were molybdenum, Zr–3 wt % Al alloy, Cb–33 wt % Ta–0.7 wt % Zr (Fansteel 82), Cb–1.8 wt % Cr alloy, and Inconel or "A" nickel with prebonded molybdenum barrier. Some

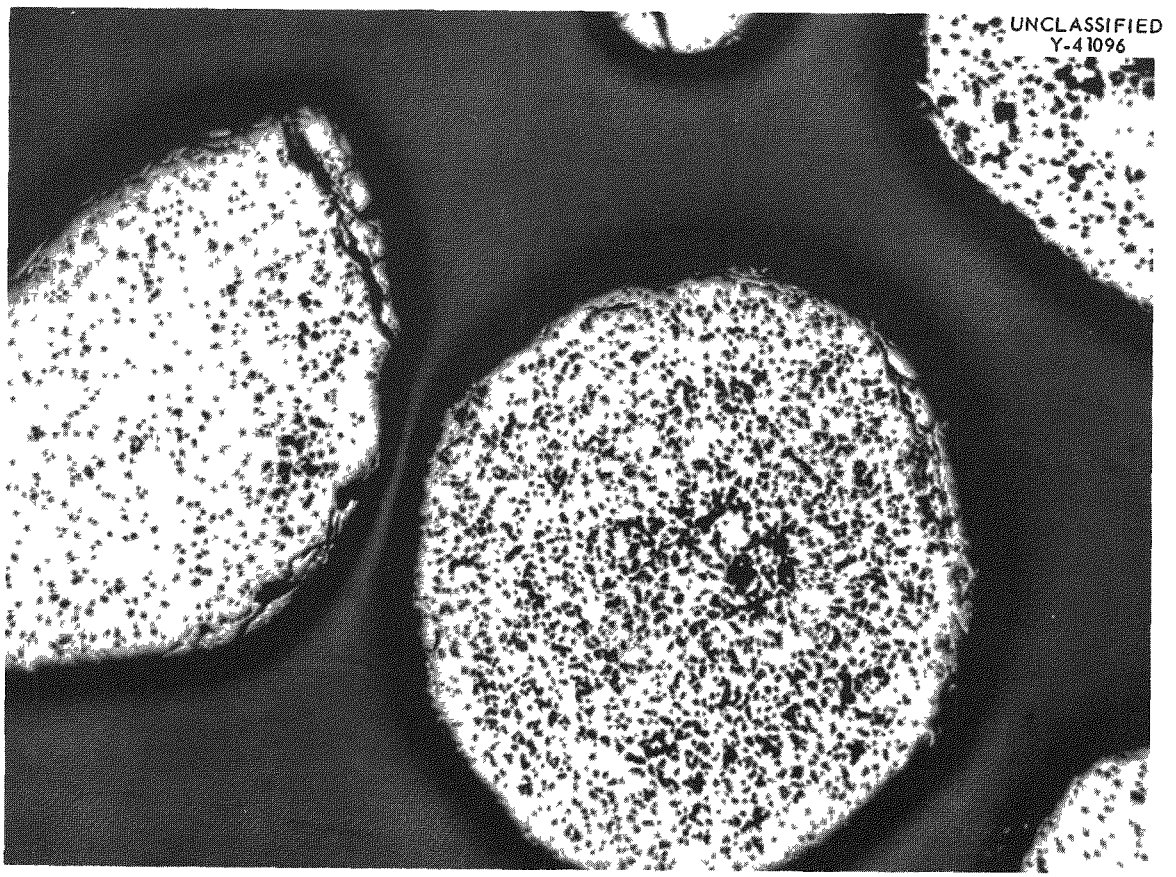

Fig. 3. Photomicrograph of High-Fired (United Nuclear) UO_2 Shot, −80 +120 Mesh. Unetched polished cross section. The shot is estimated to be about 95% of theoretical density. Black areas represent voids. 500X.

advantages and disadvantages associated with these materials are summarized in Table 5. A description of the materials used in this investigation is given below. The program was terminated prior to evaluating the last-mentioned material.

Molybdenum

Commercially pure molybdenum (containing 0.03 wt % C + < 0.4 wt % other impurities) was procured from the Westinghouse Electric Corporation. The material was fabricated by the powder metal process and was received as warm-rolled plates in thicknesses of 0.5 and 0.25 in.

Zr–3 wt % Al Alloy

Two forged and face-machined slabs, each 1 in. thick, were supplied by the Carborundum Metals Company. Hammer forging was used to fabricate the slabs from a 6-in.-diam cast ingot. Mechanical property data from Carborundum are as follows:

Tensile strength	98,000 psi
Yield strength	78,500 psi
Elongation in 2 in.	15%

Fansteel 82

Fansteel Metallurgical Corporation supplied a small rectangular sample of Fansteel 82. The material was fabricated directly from an arc-cast ingot by cold rolling.

Cb–1.8 wt % Cr Alloy

Attempts to purchase a Cb–1.8 wt % Cr alloy in fabricated plate form from commercial vendors were unsuccessful. However, an arc-cast slab, weighing 330 g, was prepared by the Melting and Casting Group of the Metals and Ceramics Division.

Because of its high volatility, chromium was charged 25% in excess and melted under a positive pressure of argon. Notwithstanding, chemical analyses indicated a 44% loss of chromium. The as-cast alloy was extremely brittle and unmachinable. Efforts to work the material by hot rolling were unsuccessful, and no other fabrication techniques were attempted.

Table 5. Advantages and Disadvantages of Potential Cladding Materials

Cladding Material	Advantages	Disadvantages
Fansteel 82	Possibility of rolling in air; high strength; yield strength ~40,000 psi at 870°C; core compatibility expected	High fast-neutron-capture cross section; high cost; ~$80/lb; possible limited temperature in sodium because of internal oxidation
Cb–1.8 wt % Cr	High strength; yield strength ~68,700 psi at 800°C; core compatibility expected; single-phase alloy	Technology limited; possible limited temperature in sodium because of internal oxidation; high cost; ~$60/lb
Zr–3 wt % Al	Less expensive than Cb-base alloys; ~$30/lb; basic technology known; may have sufficient strength; yield strength ~20,000 psi at 800°C	May not be compatible with core; sheathing problems if rolled above 900°C
"A" nickel (molybdenum barrier) or Inconel (molybdenum barrier)	Less expensive than Zr-base alloys; ~$2/lb; sheathing may not be required during rolling; technology known	Possible eutectic formation during rolling; possible intermetallic formation during bonding; may require tapered-end design
Molybdenum	Relatively low cost; ~$8/lb; core compatibility expected; technology developed; yield strength ~16,000 psi at 1105°C	Sheathing problem; difficult to fabricate

FABRICATION DEVELOPMENT OF U-Mo MATRIX DISPERSIONS

The fabrication development on U-Mo–base cermets containing UC or UO_2 involved compact preparation and composite plate fabrication.

Compact Preparation

Equipment and General Procedure

Because of differences in properties of the various matrix materials used, no single compact fabrication procedure was applicable to all the systems investigated, but the methods employed were generally similar. All operations which involved the handling of pyrophoric, toxic, or oxidation-prone powders were executed in a dry box which had been filled with high-purity (99.995% min) argon.

The individual powders were weighed and blended either mechanically in a modified oblique blender or manually to achieve a homogeneous mixture of the constituents. In some cases a binder was added to assure homogeneity and enhance interparticle bonding during cold pressing.

After blending, the powders were transferred to a $\frac{1}{2}$-in.-diam single-action steel die for the cold-pressing operation. The die walls and punches were lubricated with a thin film of 10% stearic acid–carbon tetrachloride solution. Compacting pressures ranged from 25 to 65 tsi. The green compacts were ejected from the die by applying a light load to the die punch. In later work a split die was constructed to facilitate this step.

The compacts, placed in tantalum, fused magnesia, or beryllia combustion boats, were vacuum-sintered in a Globar tube furnace capable of pressures down to 10^{-5} mm Hg. The furnace system was provided with means for introducing an inert atmosphere. Compacts were placed in the sintering furnace at room temperature, and the furnace chamber was evacuated before heat-up. Specimens were cooled before removal from the furnace. The organic binders were evaporated in a separate vacuum furnace at lower temperatures prior to sintering, which was performed at temperatures as high as 1200°C. This procedure of fabrication hereinafter will be referred to as "dynamic sintering."

In some instances static sintering was used to improve the quality of the vacuum. In this method, compacts were enveloped in either molybdenum or tantalum foil prior to evacuating in quartz capsules and sealing with a torch. Thus the only available oxygen was that initially present.

The compacts generally were coined after sintering to increase density and achieve the desired dimensions. When swelling occurred incident to sintering, the compacts were ground to size before reinsertion in the die for coining.

Results on U-Mo-UO_2 Cores

As previously noted, several types of powder were used in the investigation. Typical pressed, sintered, and coined densities as a function of the type of matrix powder are presented in Table 6. Although the core fabrication procedure varied somewhat for the various powders, it was nevertheless evident that marked differences in behavior result from differences in the powders used.

Prealloyed Shot.- The first powder examined for the matrix was the prealloyed U-Mo shot. It was not possible to press this powder dry without incurring cracking during the subsequent handling operations. The poor compactibility of the shot was attributed to a combination of an oxide film on the particles and their lack of plasticity. To overcome this problem, it was necessary to either paste blend the powders or clean the U-Mo shot before cold pressing.

In the paste-blending technique, as-received shot and UO_2 powder were weighed individually, then blended with a copious amount of binder to form a slurry. The blended powders were dried by moderate heating prior to compacting. Of a number of binders investigated (paraffin-carbon tetrachloride; stearic acid-carbon tetrachloride; lauryl alcohol; camphor-methanol; camphor-acetone; polyox-water; Carbowax 600), lauryl alcohol and stearic acid dissolved in carbon tetrachloride proved to be the most suitable.

Representative results for the prealloyed shot are presented in Table 7. As shown, densification generally did not occur during sintering and frequently the compacts swelled. The microstructures revealed that

Table 6. Typical Densities of Compacts of 25 vol (17.8 wt) % UO_2 Plus U-Mo Cold-Pressing and Coining Operations at 50-tsi pressure

Matrix Powder Specifications[a]		Cold-Pressing Theoretical Density (%)	Sintering Operation			Coining Theoretical Density (%)	Comments
			Temperature (°C)	Time (hr)	Theoretical Density (%)		
Composition	Type						
U–13.7 wt % Mo	Prealloyed shot (as-received)	77.6[b]	1100[c]	24	77.5	78.5	No sintering
U–10.0 wt % Mo	Prealloyed shot (acid-cleaned)	79.2	1100	16	76.6	81.5	Good green strength; meager interparticle bonding after sintering
	Prealloyed by hydride process	56.8	1100	24	58.8	60.8	Initial density too low
U–15.2 wt % Mo	Prealloyed by Ca reduction	e	1100	24	71.3	82.3	Good bonding; swelling
U–15 wt % Mo[d]	Ca-reduced U (Batch No. 94) + Mo (as-received)	78.7	1100	24	64.7	75.8	Good bonding; blistering
	Ca-reduced U (Batch No. 95) + Mo (as-received)	e	1100	24	78.6	81.5	Good bonding; blistering
	Ca-reduced U (Batch No. 95) + Mo (vacuum-degassed)	e	1100	20	78.5	81.0	Good bonding; no blisters
	Elemental hydride U + Mo	61.5	1150	2	53.4	68.8	Poor results because of low tap density and contamination of uranium powder

[a]Dispersoid: UO_2 shot, –80 +120 mesh. [b]Pressed under 40 tsi; lauryl alcohol binder; other compacts listed prepared with no binder. [c]Presintered in vacuo at 525°C. [d]Intended composition. [e]Too fragile to be determined.

Table 7. Density of Cold-Pressed and Sintered Compacts Containing 25 vol (17.8 wt) % of UO_2 and 75 vol % of U–13.7 wt % Mo and Made with Prealloyed Shot

Binder	Pressure (tsi)	Green Density (% of Theoretical)	Evaporation[a] Temperature (°C)	Sintering[a] Temperature (°C)	Sintering Time (hr)	Sintered Density (% of Theoretical)
Paraffin-CCl_4	30	b	450	1100	4	73.7
	55	b	450	1100	4	63.4
Lauryl alcohol	35	b	400	1100	5	82.3
	40	76.5	525	1100	18	77.1
		78.4	525	1150	4	73.7
		77.6	525	1100	24	77.5
Stearic-CCl_4	35	b		1100	24	74.7
	45	74.5	250	1100	6	69.7
		74.6	375	1150	4	68.4

[a]Evaporation of binder and sintering done in vacuo at 10^{-4} mm Hg.

[b]Too fragile to be measured.

only meager interparticle bonding had occurred, even for a compact which had a density of 82.3% of theoretical (Fig. 4). Also, many adjacent particles failed to make contact.

The lack of sintering was primarily attributed to the oxide film initially on the particles. Additional oxygen was absorbed during sintering, forming a flaky, black oxide scale on the compacts. An unidentified reaction product resembling UO_2 was observed on certain U-Mo particles, especially at junctures between the UO_2 particles and U-Mo shot (see Fig. 4).

A second procedure for improving the pressing characteristics of the U-Mo shot involved chemically treating the material prior to blending with the UO_2. This method made it feasible to press powders without binder. Cleaning agents composed of 20 vol % HNO_3–80 vol % H_2O or of 194 ml of 3% H_2O_2–6 g $Na_2C_2O_4$ buffered to pH of 4.5 with oxalic acid and heated to 90°C produced the best results, with the latter method being superior.

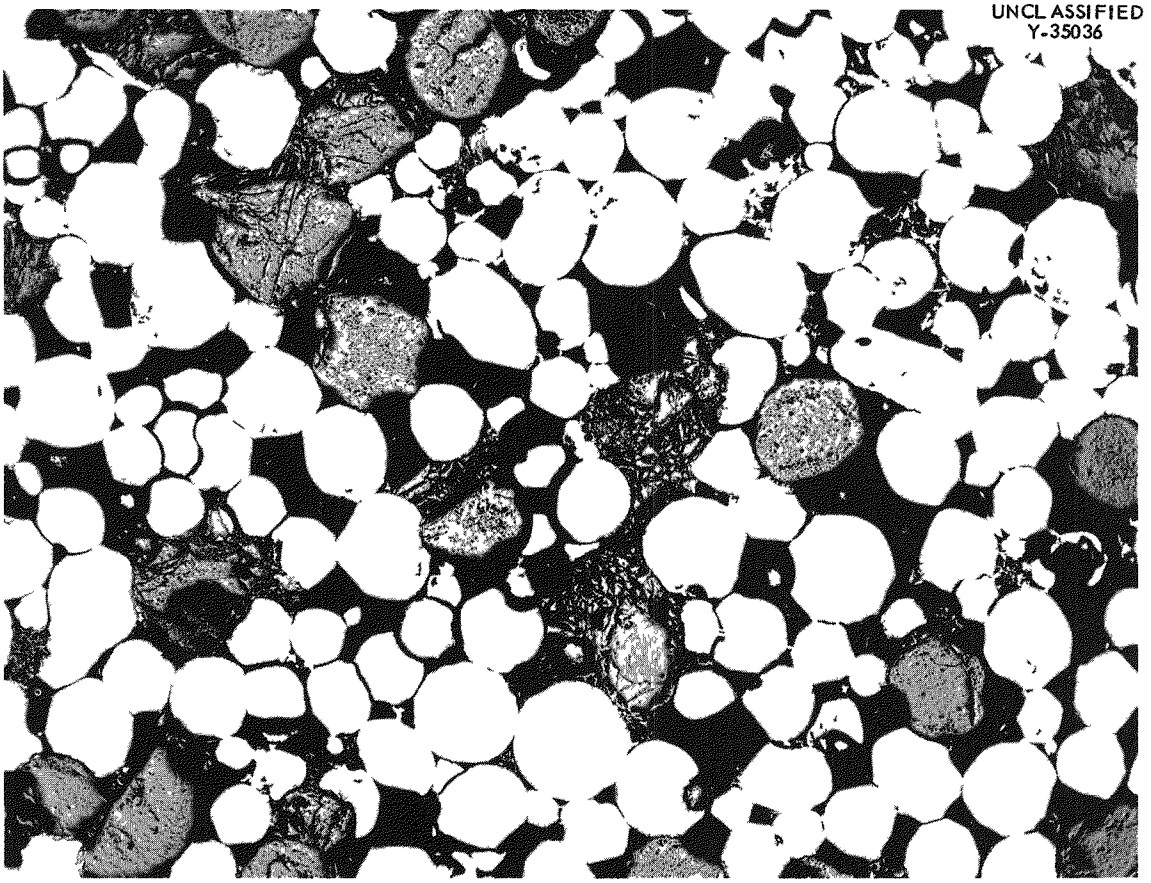

Fig. 4. Photomicrograph of Compact Containing 25 vol (17.8 wt) % UO_2–75 vol % Prealloyed U–13.7 wt % Mo Shot. Pressed with dodecyl alcohol binder at 35 tsi and sintered for 5 hr at 1100°C. Dark particles, UO_2; light particles, U–13.7 wt % Mo. Note absence of interparticle bonding. As-polished. 100X.

Cleaning the U-Mo powder enabled pressing to densities as high as 79% of theoretical (50 tsi used), but the sintering was not improved (Table 6). Therefore efforts in this direction were terminated.

Calcium-Reduced Powder.— Only a cursory examination was made of compact fabricability using prealloyed U–15.2 wt % Mo powder prepared by calcium reduction. A typical result is given in Table 6. Compacts incorporating this matrix powder were friable after cold pressing but could be handled. Although the compacts grew or blistered during the sintering treatment, interparticle bonding resulted and the compacts were mechanically strong. Thus it appears that cohesion resulting from interparticle bridging (first-stage sintering[17–19]) had occurred.

Upon controlled heating of these compacts under conditions representing dynamic vacuum sintering, substantial gas release occurred between 400 and 600°C, as evidenced by a sudden rise in system pressure. Samples of this gas were collected and analyzed with a mass spectrometer (Table 8). These data show that the gas released in the greatest quantity was hydrogen. This hydrogen no doubt was introduced incident to the acid leaching of the powder — a step required to remove the calcium. Swelling of compacts by the liberation of hydrogen has been observed by many investigators.[10, 20, 21]

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[17]G. C. Kuczynski, L. Abernethy, and J. Allan, p 1 in Proceedings of the Plansee Seminar "De Re Metallica," 3rd, Reutte/Tyrol, 1958, Metallwerk Plansee A. G., 1959.

[18]F. M. Rhines, p 38 in Proceedings of the Plansee Seminar "De Re Metallica," 3rd, Reutte/Tyrol, 1958, Metallwerk Plansee A. G., 1959.

[19]R. G. Bernard, Powder Met. 3, 86–103 (1959).

[20]L. R. Williams and T. J. Heal, p 350 in Proceedings of the Plansee Seminar "De Re Metallica," 3rd, Reutte/Tyrol, 1958, Metallwerk Plansee A. G., 1959.

[21]G. L. Miller, p 303 in Proceedings of the Plansee Seminar "De Re Metallica," 3rd, Reutte/Tyrol, 1958, Metallwerk Plansee A. G., 1959.

Table 8. Gas Released from Various Uranium-Base Powders During Heating from Room Temperature to 1000°C in Vacuum (at STP)

Gas	Amount of Gas Released (cc/g)		
	From Hydride Uranium	From Calcium-Reduced Uranium (Batch No. 95)	From Calcium-Reduced Prealloyed U–15.2 wt % Mo
H_2	7.65	2.11	5.39
He	11.94		
CH_4	0.07	0.01	0.02
H_2O	0.89	0.01	0.01
HC	0.01		0.01
N_2 + CO	0.26	0.01	0.02
O_2	0.01		
Ar	0.01		
CO_2	0.04		
Total	20.88	2.14	5.45

By grinding off the blister end of the compacts and coining, densities as high as 82.3% of theoretical were achieved (Table 6). The photomicrograph shown in Fig. 5 illustrates the increased soundness of the pressed, sintered, and coined compacts as compared with the material shown in Fig. 4.

Hydride Powder.– A typical result for a UO_2-γ (U-Mo) compact prepared with prealloyed (10 wt % Mo) powder made by the hydride process at ORNL was given in Table 6. Some shrinkage occurred during sintering. Unfortunately, however, the tap density of this powder was very low, and the green density was only about 57% of theoretical for a compacting pressure of 50 tsi. Because of the inferior compactibility of the hydride powder, a burden of high sintering shrinkage is imposed. As a result inferior dimensional control is to be expected.

A resintering treatment of 24 hr at 1150°C was conducted on compacts after the coining operation. However, this gave little improvement in density or compact appearance. Although it is possible that acceptable

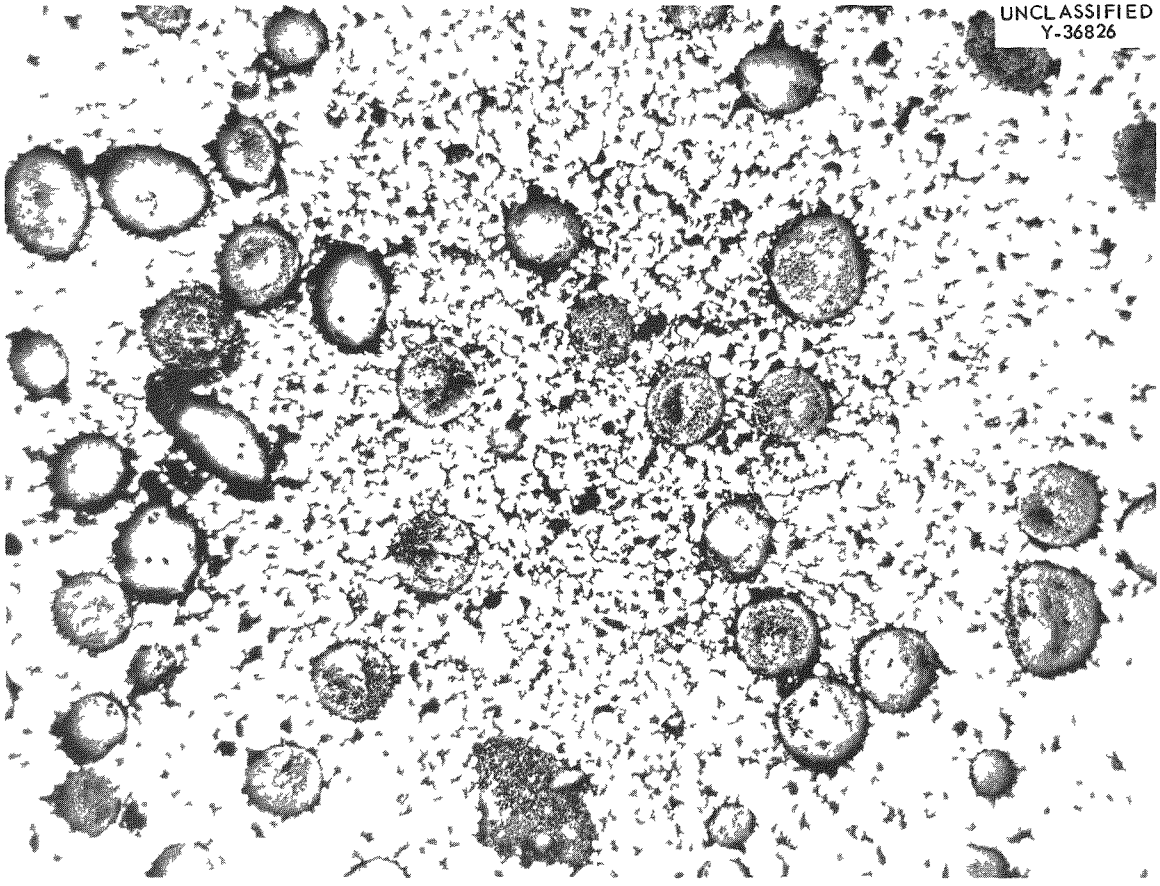

Fig. 5. Photomicrograph of Compact Containing 25 vol (17.8 wt) % UO_2–75 vol % Prealloyed (Calcium-Reduced) U–15 wt % Mo. Pressed at 50 tsi, sintered in vacuo at 1100°C for 24 hr, and coined at 50 tsi to 80% of theoretical density. Gray particles, UO_2; light particles, U-Mo; black areas, voids. As-polished. 75X.

density could be achieved with a more effective hydrogen degassing treatment and use of still higher sintering temperatures, the problem of dimensional control would remain.

Elemental Powders.— Elemental uranium powders prepared by both the hydride and the calcium-reduction method were mixed with hydrogen-reduced molybdenum and investigated as potential matrix materials.

Much higher green densities were achieved with the calcium-reduced uranium than with the hydride uranium because of its relatively high tap density as contrasted to the flocculent quality of the hydride powder. Although sintering produced strong compacts with calcium-reduced uranium powders, densification was impeded by the contained gases.

The mass spectrometric analyses on gases released from these powders also are given in Table 8. The main gases in the hydride powder were hydrogen, helium, and some water vapor. Hydrogen was the principal gas in the calcium-reduced uranium. The presence of helium in the hydride uranium was surprising and its source was never determined. A volumetric analysis revealed the total gases removed from the calcium-reduced powder to be about one-tenth of that released from the hydride powder.

Mainly because of superior pressing characteristics, most of the work with elemental powders was done with the calcium-reduced uranium. Table 9 shows the effects of sintering time and temperature on the density of compacts prepared with as-received calcium-reduced uranium. It may be noted that substantial swelling occurred, increasing with temperature from 600 to 1050°C. Only at 1130°C did the shrinkage of sintering begin to offset the swelling. However, after 96 hr at 1130°C or 2 hr at 1200°C the sintered density was still rather moderate (70.4 and 71.7% of theoretical, respectively). Cold coining after sintering at 1200°C resulted in 80.7% of theoretical density, a value subsequently shown to be acceptable for roll cladding.

The microstructure of a core, sintered for 2 hr at 1200°C followed by coining, is shown in Fig. 6. The structure shows UO_2 dispersed in a homogeneous matrix phase with a small amount of oxide outlining the grain boundaries. As will be shown in a subsequent section, hot-roll cladding for the most part resulted in the elimination of the grain-boundary oxide

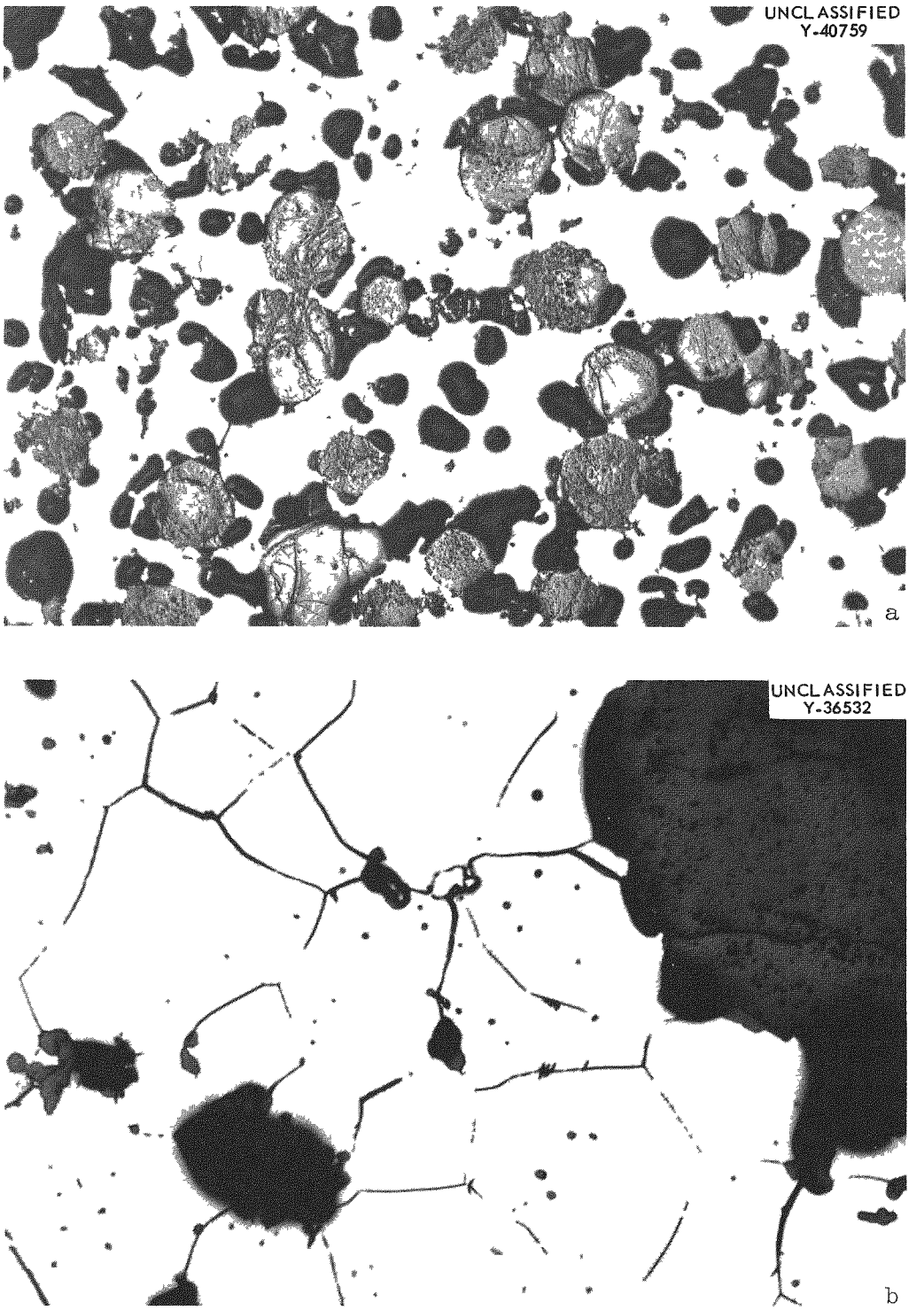

Fig. 6. Microstructures of Compact [(a) As-Polished, 75X and (b) 500X, Etched with 50% H_2O_2–50% NH_4OH] Containing 25 vol (17.8 wt) % UO_2 Dispersed in Calcium-Reduced U–15 wt % Mo Matrix Powders Pressed at 50 tsi, Sintered at 1200°C for 2 hr in Vacuo, and Coined at 50 tsi to 80.7% of Theoretical Density. Gray particles, UO_2; white particles, U-Mo; black areas, voids.

Table 9. Densities of 25 vol (17.8 wt) % UO_2–75 vol % Elemental U–15 wt % Mo Powder Compacts as a Function of Sintering Time and Temperature[a]

Sintering[b] Temperature (°C)	Time (hr)	Sintered Density (% of Theoretical)	Coined Density[c] (% of Theoretical)
Green		78.7	
600	2	74.5	d
750	2	67.4	d
950	2	62.3	d
1050	2	61.8	77.3
1130	2	64.4	76.5
1130	16	67.6	76.5
1130	24	66.9	75.8
1130	96	70.4	76.5
1150	24	65.0	76.5
1200	2	71.7	80.7

[a]Calcium-reduced uranium (Batch No. 94).

[b]Initially cold-pressed at 50 tsi.

[c]Coined at 50 tsi.

[d]Not coined; too fragile.

as well as the matrix porosity. It is possible that there may have been incipient melting in the U-Mo matrix at this temperature (1200°C) and that this is prerequisite for obtaining high densities.

The effect of sintering atmosphere (dynamic vs static vacuum) was investigated with this powder, and the results are summarized in Table 10. It is to be observed that, in spite of the gas contained in the uranium powders, static sintering for 24 hr at 1150°C resulted in an acceptable density of 81.5%, an increase of about 3% over the pressed density. Sintering at the same time and temperature under dynamic conditions gave a density of only 65.0%, a value indicative of substantial compact swelling. Resintering of compacts after coining (Table 10) again in a static atmosphere resulted in a substantial improvement in shrinkage as compared with the dynamic condition. In addition to the improved shrinkage, sintering under the static condition resulted in much brighter compacts.

Table 10. Effect of Type of Vacuum on Densities of Compacts Containing 25 vol (17.8 wt) % of UO_2 and 75 vol % of U–15 wt % Mo and Prepared from Elemental Powders[a]

Sintered[b]			Coined[c]	Resintered		
Temperature (°C)	Time (hr)	Theoretical Density (%)	Theoretical Density (%)	Temperature (°C)	Time (hr)	Theoretical Density (%)
			In Static Vacuum			
1150	4	70.0	77.0			
	24	81.5	81.5			
1130				1100	110	84.3
			In Dynamic Vacuum			
1150	24	65.0	76.5			
1130	24	66.9	75.8			
	16	67.6	76.5	1100	100	77.9

[a]Calcium-reduced uranium (Batch No. 94).

[b]Initially cold-pressed at 50 tsi to 78.7% of theoretical density.

[c]Coined at 50 tsi.

Since work with most of the powders examined indicated the need for more efficient removal of gases, an endeavor was made to develop effective gas-removal heat treatments. Unfortunately this work had proceeded only a short while when the project was terminated. A treatment which showed promise for the calcium-reduced uranium powder consisted of the following: The UO_2 and elemental powders were weighed and blended, then vacuum-degassed for 8 hr at 400°C. The blend was portioned and weighed for pellet compaction. Data for a compact prepared in this fashion and sintered at 1100°C are shown in Table 6. Higher sintering temperatures should result in higher densities. Probably of even greater importance than the ultimate density obtained was that the degassing treatment produced a uniform blister-free core.

If it is desirable to achieve substantially higher densities than were obtained in the present work, higher sintering temperatures and finer powders should be used. Sintering temperatures near the melting temperature of the matrix alloy are recommended. For the present application, calcium-reduced elemental uranium or prealloyed powder is

preferable because of the superior compaction qualities of these powders and because highly dense compacts are not deemed essential for subsequent roll cladding.

Results on U-Mo-UC Cores

Since the effort directed on dispersion cores incorporating UC as the dispersoid was very limited, only a few remarks of a general nature are warranted.

The compact fabrication results with UC from several suppliers and elemental powders for the matrix are presented in Table 11, together with results for a compact incorporating UO_2 for comparative purposes. Representative microstructures of the UC-containing compacts are shown in Fig. 7.

Table 11. Effect of Dispersoid on Densities of Compacts Containing UO_2 or UC Dispersed in Elemental U–15 wt % Mo Matrix

Dispersoid Material[a]			Theoretical Density (%)		
Composition	Grade and Size	Supplier	Pressed[b]	Sintered[c]	Coined[d]
25 vol (17.8 wt) % UO_2	Spherical shot; –80 +120 mesh	United Nuclear	78.7	72.3	78.1
20 vol (16.8 wt) % UC	Fused and ground; –70 +270 mesh	Spencer	e	76.1	78.7
	Shot; –70 +270 mesh	United Nuclear	e	76.6	78.4
	Ground sponge	Davison	e	70.4	73.9
	Spherical (arc-melted); –80 +120 mesh	Vitro	e	70.8	76.9

[a] Matrix materials: Calcium-reduced (Batch No. 94) uranium, Wah Chang molybdenum.

[b] Pressed at 50 tsi.

[c] Sintered in vacuo at 1130°C for 24 hr.

[d] Coined at 50 tsi.

[e] Too fragile to measure.

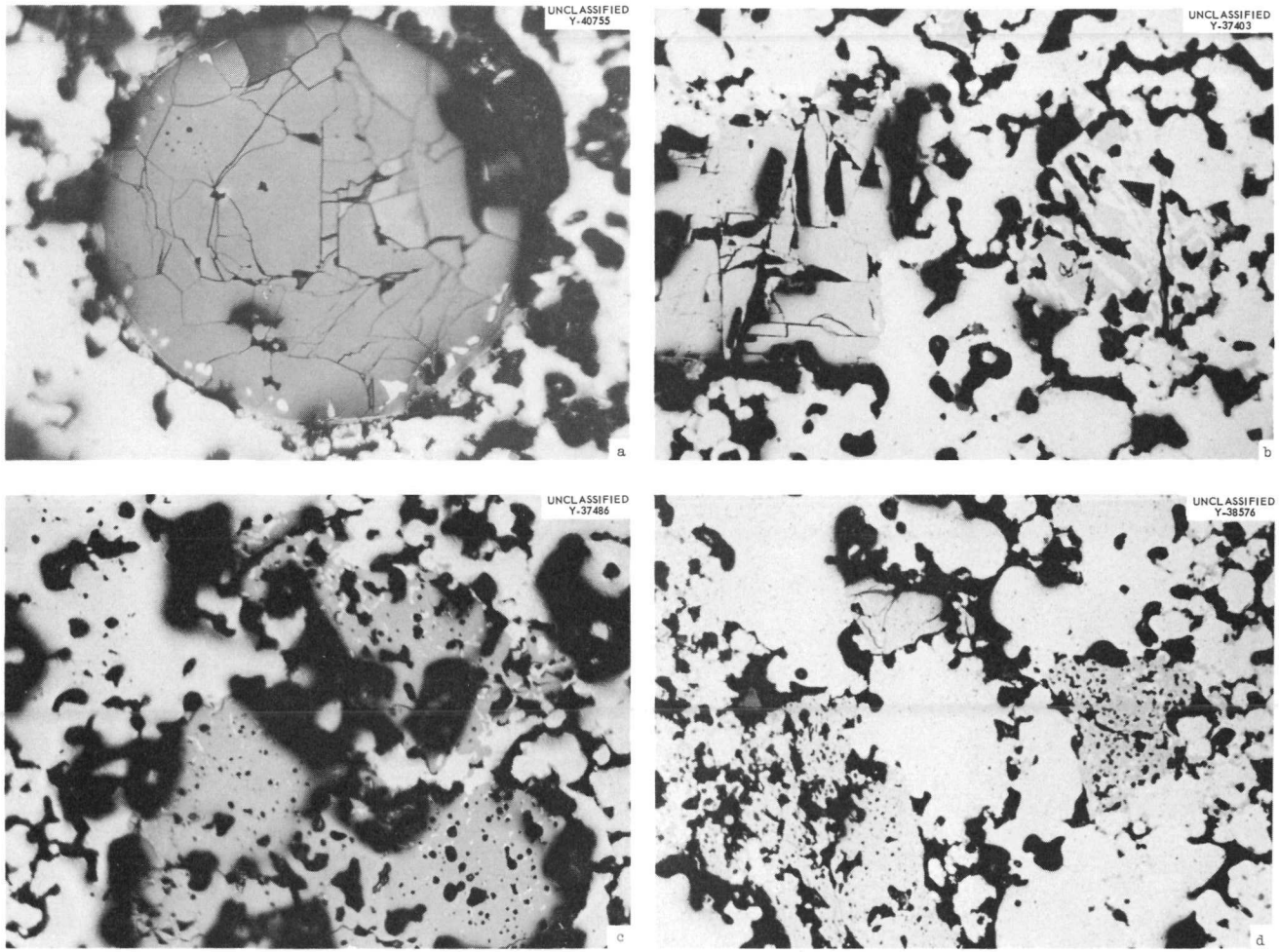

Fig. 7. Compacts Containing (a) Vitro UC Shot, (b) Spencer Fused and Ground UC, (c) United Nuclear UC Shot, or (d) Davison Ground Sponge UC, Each Dispersed in Elemental U–15 wt % Mo Matrix, Pressed at 50 tsi, Sintered in Vacuo at 1130°C for 24 hr, and Coined at 50 tsi. White particles, U-Mo matrix; gray particles, UC; black areas, voids. As-polished except for (a) which was etched with 1 HNO_3–1 $HC_2H_3O_2$–1 H_2O. 500X. Reduced 45%.

For the same pressing and sintering conditions it will be noted that compacts prepared with UC supplied by Spencer and United Nuclear Corp. gave densities in excess of those obtained with the UO_2-containing standard (Table 11). However, metallography revealed the dispersoids of these compacts to be unusually porous and quite irregular in shape (Fig. 7b, 7c). Although the Vitro dispersoid gave the best appearing dispersion structure (Fig. 7a), it appeared that some reaction had occurred between the dispersoid and the matrix.

These cursory tests suggest that compacts incorporating UC as the dispersoid are fabricable. While the densities reported here are not as high as desired, adjustments in sintering temperature should bring about acceptable results. The properties of the UC, or possibly the method of preparing compacts, need to be improved to increase green strength. In improving the quality of the UC dispersoid, attention should be given to chemical composition, density control, geometry, and strength.

Composite Plate Fabrication

Preparation of Cladding Components

The cladding billets, illustrated in Fig. 8, consisted of two cover plates, a frame, and a right cylindrical compact containing 25 vol (17.8 wt) % of UO_2 and 75 vol % of U–15 wt % Mo. The dimensions of the cladding billets were 5.5 × 5.5 × ~0.850 in., and the compacts were 0.5 in. in diameter and ~0.5 in. in height. The outer cover plate and frame constituted the sheathing assembly.

The roll-bond test billets were similar to the cladding billets, the only difference being that a solid section of the cladding alloy was substituted for the inner frame and core.

As noted previously, the cladding materials evaluated included molybdenum, Zr–3 wt % Al, and Fansteel 82 (Cb–33 wt % Ta–0.7 wt % Zr). After machining, the cladding components were degreased in trichloroethylene and annealed in suitable protective atmospheres.

The fuel cores consisted of 25 vol (17.8 wt) % UO_2 dispersed in a U–15 wt % Mo matrix of elemental powders (calcium-reduced uranium and

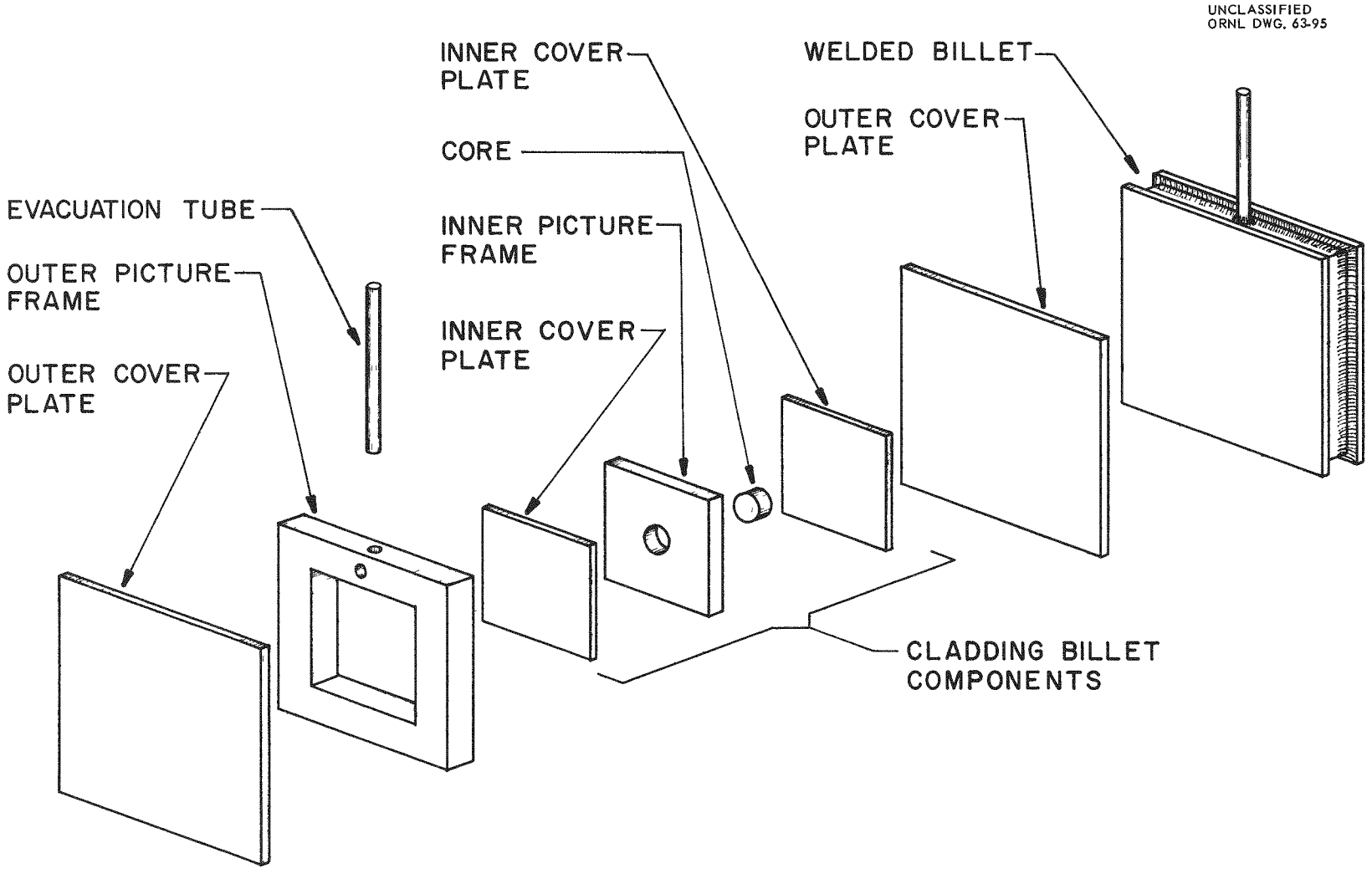

Fig. 8. Fuel Plate Billet Assembly.

Wah Chang molybdenum). The compacts were pressed at 50 tsi, sintered for 2 hr at 1200°C in dynamic vacuum, and coined at 50 tsi to densities of about 80% of theoretical.

Preparation of Billets for Roll-Bonding Studies

In the selection of suitable sheathing materials for the respective cladding alloys, a number of preliminary tests were made. A low-carbon titanium-killed steel (Ti-Namel) ordinarily used as a sheathing for Zircaloy-2 proved to have insufficient strength at the temperatures required to roll clad Zr–3 wt % Al to the UO_2-U-Mo core. Type 347 stainless steel was tried and subsequently accepted as the sheathing material for the Zr–3 wt % Al alloy. While some alloying of iron with the zirconium alloy was anticipated at 850°C and higher, such contamination did not interfere with the interpretation of the fabrication experiments.

A simulated rolling experiment was conducted to determine whether Fansteel 82 could be fabricated at 1100°C without protective sheathing. Seven cycles of heating to 1100°C followed by brief exposure in air resulted in over twofold hardening of the material to depths in excess of 0.005 in. Metallographic examination revealed that the contamination had resulted in the formation of a fine precipitate in the hardened zone. Thus protection by sheathing was deemed essential for Fansteel 82. Type 304 stainless steel was selected as the sheathing material for Fansteel 82; it was also used for sheathing the molybdenum cladding.

Machined surfaces were cleaned in trichloroethylene and then wire-brushed prior to assembly of the cladding components into billet form to facilitate bonding. Billet welding (Fig. 8) was done by the inert-gas tungsten-arc method, with chill-block cooling used to minimize contamination to the encased parts. For the same purpose, continuous helium purging was provided within the billet during the welding.

Preparatory to welding, billets were outgassed by evacuating to about 1×10^{-4} mm Hg pressure and heating for 15 to 20 min with an acetylene torch. While heating, the pressure rose to about 5×10^{-1} mm Hg before subsiding to the initial value. During cooling the evacuation tube was sealed by hammer forging.

Roll-Bonding and Evaluation Procedures

Billets were preheated for approximately 50 min in a Globar furnace and then rolled on a two-high mill (20-in.-diam × 30-in.-face rolls). Rolling temperature, reduction per pass, and total reduction are given in Tables 12 and 13 for the roll-bonding and fuel-plate rolling tests, respectively.

The bonded specimens were extracted from the steel jacket by machining the excess steel from the sides and ends of the rolled plates and removing the sheathing. Metallographic examinations were made of polished and etched sections taken from areas of interest. Geometric density determinations were made of the core components after rolling by machining parallelepipeds from the core and measuring their dimensions and weight.

Results

Examination of the roll-bonding tests conducted with molybdenum, Fansteel 82, and Zr–3 wt % Al indicated that when suitable rolling temperatures are used good metallurgical bonds are obtained in each material (Table 12). Photomicrographs of the bond interfaces of the respective specimens (Plates 3, 5, and 6 of Table 12) are shown in Fig. 9.

Recrystallization and grain growth across the interface, features generally associated with good bonding, were obtained for each material. For molybdenum, rolling at 1150°C did not significantly improve the bonding obtained with rolling at 1090°C, nor were reductions of 30% per pass an improvement over reductions of 10 to 20% (Table 12). Excellent bonds were achieved with the Zr–3 wt % Al alloy at 840°C as well as at 910°C. Acceptable joints were also obtained with Fansteel 82.

After the preliminary roll-bonding tests were completed, cylindrical cores of 25 vol (17.8 wt) % UO_2 in U–15 wt % Mo were clad with molybdenum or Zr–3 wt % Al alloy at rolling temperatures of 1150 and 910°C, respectively (Table 13). Very promising results were obtained with the molybdenum cladding but not with the Zr–3 wt % Al alloy. With the molybdenum cladding, good metallurgical bonding was obtained both between the cladding and core and the cladding and frame, as determined by metallographic examination, mechanical peel, and thermal shock tests. Densities approaching theoretical were obtained in the core pieces.

Table 12. Roll-Bonding Test for Potential Cladding Materials

Plate No.	Interface	Rolling Variables: Temperature (°C)	Rolling Variables: Reduction per Pass[a] (%)	Microexamination
1	Mo to Mo	980	7–15	Complete lack of bond
2	Mo to Mo	1090	30	Excellent bond; no inclusion visible
3	Mo to Mo	1100	10–20	Good bond; a few thin segmented inclusions in bond
4	Mo to Mo	1150	10–25	Excellent bond; no interface visible
5	Fansteel 82 to Fansteel 82	1100	30	Good bond; a few short segmented inclusions in bond
6	Zr–3 Al to Zr–3 Al	840	8–15	Excellent bond; no interface visible
7	Zr–3 Al to Zr–3 Al	875	8–15	Excellent bond; no interface visible
8	Zr–3 Al to Zr–3 Al	910	8–15	Excellent bond; no interface visible

[a]Total reduction, ~90%.

Table 13. Results of Miniature Fuel Plate Rolling Experiments

Plate No.	Interface	Rolling Variables: Temperature (°C)	Rolling Variables: Reduction per Pass (%)	Rolling Variables: Total Reduction (%)	Core Theoretical Density[a] (%): Initial	Core Theoretical Density[a] (%): Rolled	Microexamination
1	Mo to Mo	1150	10–18	92			Good bond
	Mo to UO_2–(U–15 wt % Mo)[b]	1150	10–18	92	79.5	97.3	Good bond; grain structure of Mo finer near the core-clad interface; UO_2 stringered and fragmented but no evidence of separation
2	Mo to Mo	1150	15–25	92.5			Same as for Plate No. 1
	Mo to UO_2–(U–15 wt % Mo)[b]	1150	15–25	92.5	80.6	98.7	Same as for Plate No. 1
3	Zr–3 Al to Zr–3 Al	910	10–15	89			Excellent bond
	Zr–3 Al to UO_2–(U–15 wt % Mo)[b]	910	10–15	89	83.0	96.9	Very poor bond; profuse diffusion layer at Zr–3 Al interface; intermittent separation at interface; large cracks in core; UO_2 stringered and fragmented
4	Zr–3 Al to Zr–3 Al	910	8–20	88			Same as for Plate No. 3
	Zr–3 Al to UO_2–(U–15 wt % Mo)[b]	910	8–20	88	79.8	97.3	Same as for Plate No. 3

[a] Theoretical density = 15.3 g/cc.

[b] Calcium-reduced uranium and hydrogen-reduced (Wah Chang) molybdenum.

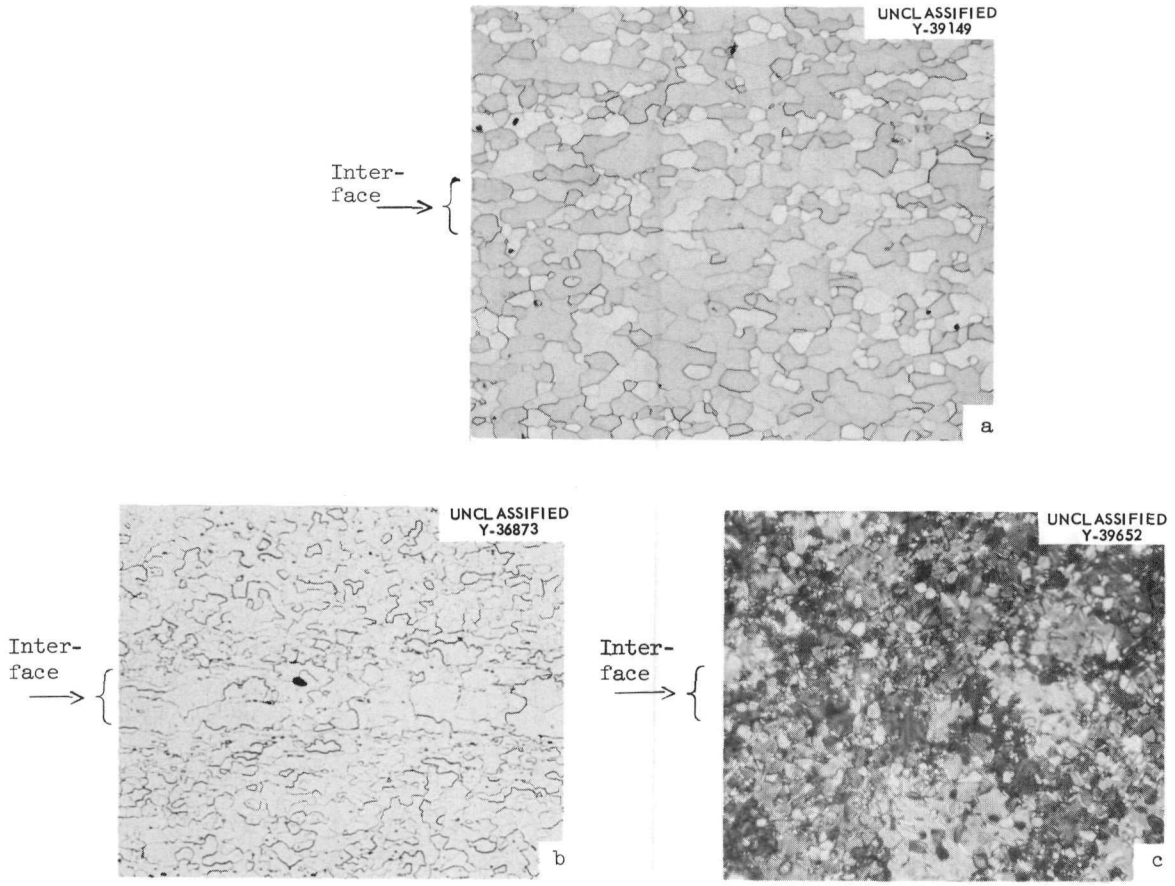

Fig. 9. Bond Interfaces of Molybdenum, Fansteel 82, and Zr–3 wt % Al Roll Bond Tests. Specimens reduced 90% in thickness. (a) Molybdenum, rolled at 1100°C, bright field 100X; etchant: NH_4OH–H_2O_2; (b) Fansteel 82, rolled at 1100°C and annealed at 1100°C, bright field 200X; etchant: H_2O–HNO_3–H_2SO_4–HF; (c) Zr–3 wt % Al, rolled at 840°C, polarized light 500X; etchant: disapol. Reduced 21.5%.

Photomicrographs of the core and cladding-core interface for this combination of materials are given in Fig. 10, which shows that the UO_2 experienced considerable stringering but resisted breakup. The core structure was free of rupture planes, and continuous bonding was obtained along the cladding-core interface. The interfaces were free of not only oxide but also diffusion voids, which are characteristic of unequal diffusion rates across a metal couple (Fig. 10c). The molybdenum adjacent to the bond interface had recrystallized as fine, equiaxed grains.

The roll-cladding experiments conducted with the Zr–3 wt % Al alloy as the cladding resulted in severe ratcheting of the core pieces (Plates 3 and 4 of Table 13). Uneven deformation between core and cladding resulted in large separations both at the core-cladding interface and within the core component itself (Fig. 11). The UO_2 particles showed some fragmentation and a significant diffusion layer penetrated into the Zr–3 wt % Al cladding.

An examination of the respective plates after rolling emphasized the importance of matching of yield strengths between cladding and core during rolling. In addition to the ratcheting noted in the Zr–3 wt % Al-clad plates, core edge effects were observed which bore a relation to the relative amount of reduction incurred between the core and cladding.

In the case of the molybdenum cladding at the 1150°C rolling temperature, the cladding was stronger than the core and consequently was reduced less. For the Zr–3 wt % Al-clad plates the cladding was weaker than the core at 910°C, resulting in a greater percent reduction in the cladding than in the core; further, the portion of the plate containing the fuel section was thicker than those areas around the periphery of the core. Transverse sections from the plates showed that rolling of the molybdenum-clad plate resulted in a concave shape at the end of the fuel section, whereas the Zr–3 wt % Al-clad plate exhibited a convex edge effect ("fishtail"), as would be expected with the observed changes in relative core and cladding thickness.

For the molybdenum-clad plates, it is clear that the core material afforded less resistance than the cladding to deformation during rolling. Lowering of the rolling temperature below 1150°C would be expected to

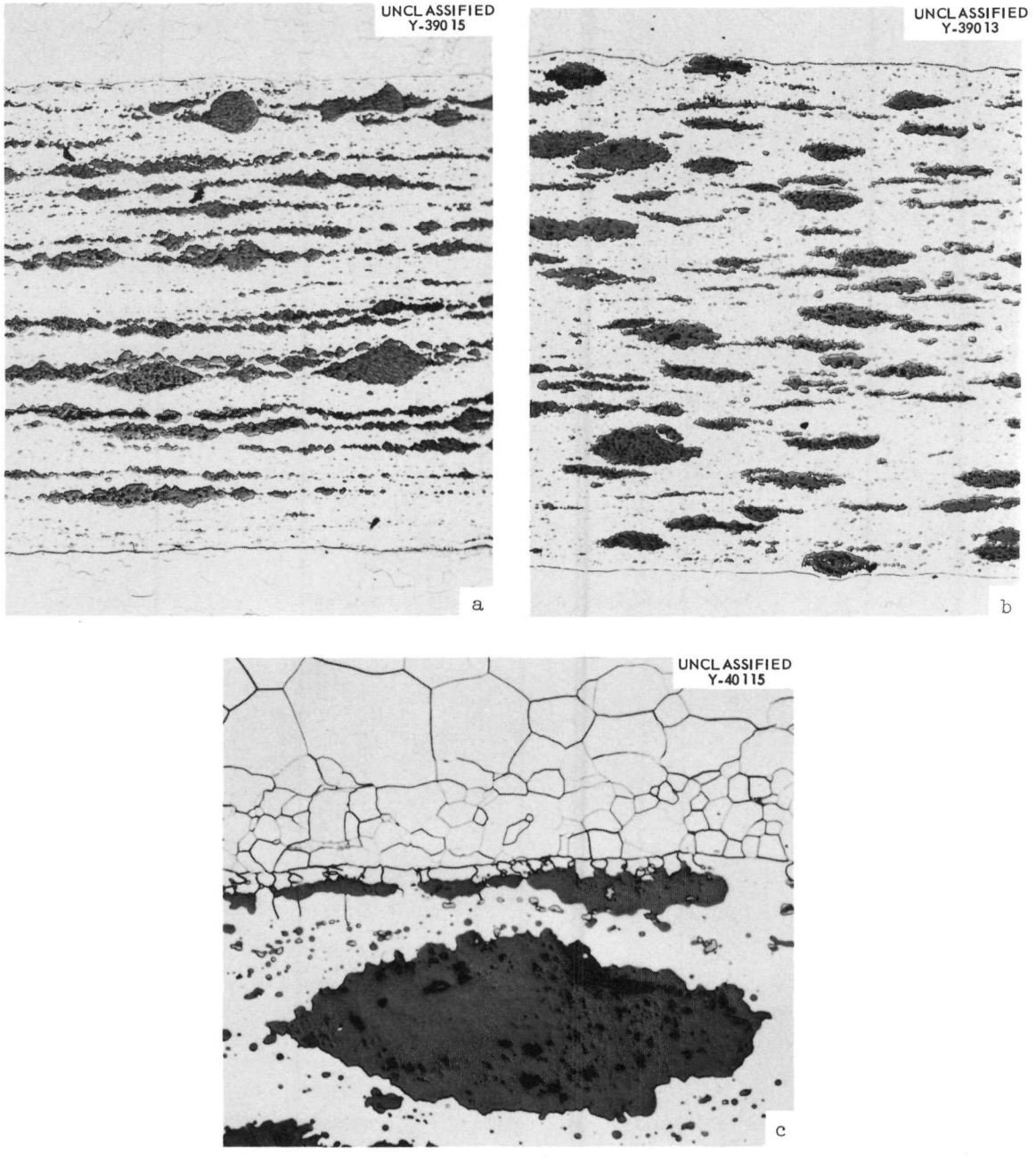

Fig. 10. Typical Microstructures of the 25 vol (17.8 wt) % UO_2-(U–15 wt % Mo) Plate Roll-Clad with Molybdenum at 1150°C (Plate 2 of Table 13). (a) Longitudinal section; as-polished; 100X; (b) transverse section; as-polished; 100X; (c) transverse section; core-cladding bond at 500X; etchant: 1% NH_4OH–1% H_2O_2. Reduced 16%.

Fig. 11. Transverse Cross Section of a Zr–3 wt % Al-Clad Plate Showing Large Cracks in the Core and a Diffusion Layer Extending into the Cladding (Plate 4 of Table 13). As-polished. 100X.

strengthen the core in relation to the cladding and thus alleviate the concave edge effect as well as cause greater uniformity of plate thickness. Conversely, an analysis of the relative reductions between core and cladding for the Zr–3 wt % Al-clad plates indicated the yield strength of the core to be greater than that of the cladding during rolling. Raising the fabrication temperature or lowering the molybdenum content of the core matrix constituent, which would bring yield strengths (cladding and core) more closely in balance, would no doubt improve the fabricability. However, raising the rolling temperature would not be practical, as the stainless steel sheathing would begin to alloy with the Zr–3 wt % Al alloy cladding, and lowering of the matrix-phase molybdenum content is undesirable because of the likely decreased irradiation resistance of the fuel. Because of these discouraging aspects of the Zr–3 wt % Al-clad fuel, investigations of the bonding integrity of the cladding were limited to the molybdenum-clad plates.

In mechanical peel tests (an attempt to manually tear the cladding from the core component with a pair of pliers) conducted on the molybdenum-clad plates, good bonding was shown. However, the molybdenum behaved in ductile or brittle fashion, depending upon the test temperature used. For tear tests conducted at room temperature the molybdenum exhibited brittle fracture. However, with heating to as little as 100°C the molybdenum cladding became tougher and severed in a ductile fashion before the bond was separated.

The molybdenum-clad specimens also were subjected to cyclic thermal shock by repeated heating to 650°C and water quenching to 95°C. The test specimens were encapsulated in Pyrex glass, backfilled with argon. After 17 cycles of heating and quenching there was no visual indication of parting at the cladding interface. Thus both the peel and thermal shock tests revealed sound and strong bonding between the molybdenum cladding and the UO_2-(U-Mo) core.

Several additional encouraging aspects of the molybdenum-clad fuel plates are worthy of note. Although the UO_2-(U-Mo) compacts used in the cladding experiment possessed considerable surface oxide, the bond interfaces were unusually clean and free of oxide. So striking was this

observation as to suggest that some phenomenon was active in transporting the oxide away from the bond interface. The clean interface no doubt contributes measurably to the strength of the clad-to-core bond.

While not pertinent to the molybdenum-clad plates alone, mention is made of the fact that rolling resulted in a high density for the core structure. With initial densities (after coining) near 80% of theoretical (Plates 1 and 2, Table 13), rolling resulted in densities in excess of 97%. In spite of elemental powders in the formulation of the matrix constituent having been used, the γ-uranium phase was obtained and proved to be homogeneous on the basis of x-ray diffraction and metallographic examination.

Equally encouraging was the facility with which the type 304 stainless steel jacketing material was removed from the plates after roll cladding. After the edges of the rolled billet were trimmed, the sheathing was readily separated from the cladding.

SUMMARY AND CONCLUSIONS

Dispersion fuel compacts using 25 vol (17.8 wt) % UO_2 as the dispersoid and γ-uranium alloy (10–15 wt % Mo) as the matrix were prepared, clad with molybdenum, and fabricated into fuel elements by the conventional picture-frame, roll-cladding technique.

The use of as-received prealloyed U–10 wt % Mo and U–13.7 wt % Mo shot in the cold pressing of UO_2-(U-Mo) compacts was not successful without the addition of large amounts of organic binder. The difficulty was attributed to surface oxide on the powder. The compactibility of the shot was improved by chemically cleaning the powder, but interparticle bonding with sintering still was not achieved.

Compacts with good strength after both sintering and coining were obtained with prealloyed U–15.2 wt % Mo powder prepared by calcium reduction. Coined densities to 84.5% of theoretical were achieved. Suitable UO_2 + (U-Mo) compacts also were prepared with elemental calcium-reduced uranium and hydrogen-reduced molybdenum. Hydride uranium, on the other hand, gave poor compactibility and low sintering shrinkage. This inferior behavior was attributed to its flocculent character and high

gas content. Fabrication of compacts based on hydrided prealloyed powder also resulted in low compactibility and inferior sintering and is ascribed to similar causes.

Vacuum degassing of the powders prior to compaction alleviated the swelling or blistering generally incurred by cold-pressed compacts during the vacuum sintering operation. Despite the swelling problem, good mechanical strength resulted with the nontreated calcium-reduced prealloyed or elemental uranium powder.

Dispersion cores with 20 vol (16.8 wt) % UC as the dispersoid were also prepared; however, time did not permit roll cladding these into plate form. The fabrication technique for the UC-(U-Mo) compacts was similar to that used for the UO_2-containing cores.

The work on the U-Mo dispersion cores points to the following factors having an important bearing on sintering behavior: cleanliness of matrix powders, notably gas content; size and shape of matrix powders; a good-quality inert atmosphere and/or vacuum for conducting all operations; and a sintering temperature just below the melting temperature of the matrix alloy.

Compacts were assembled into rolling billets with molybdenum (type 304 stainless steel sheathing), Fansteel 82 (type 304 stainless steel sheathing) or Zr–3 wt % Al (Ti-Namel or type 347 stainless steel sheathing) used as the cladding materials. The effects of core composition, cladding and sheathing materials, rate of reduction, and rolling temperature on microstructure and bonding at the interfaces were studied. Of the various combinations investigated, only the billets with molybdenum cladding gave promising results.

With molybdenum used as the cladding, UO_2-(U-Mo) cores based on either calcium-reduced prealloyed or elemental uranium powders and 1150°C as the rolling temperature, plates with good metallurgical bonding between cladding and core and cladding and frame were achieved. The strength of the clad-to-core bond was assessed as good by mechanical peel and thermal shock tests. Core pieces removed from the rolled plates showed densities approaching 99% of theoretical and were free of ruptures and UO_2 cracking.

RECOMMENDATIONS

In view of the encouraging results realized in the fabrication of the UO_2-(U–15 wt % Mo) and UC-(U–15 wt % Mo) dispersion fuels and their very attractive properties for fast reactor application, work on these fuel systems should be continued. Additional work is needed to develop the fabrication of these dispersions and to further validate by in-pile testing the suitability of gamma-stabilized U–15 wt % Mo alloy as the matrix material.

Because the fabrication procedure for the fertile-matrix dispersion fuels had not been well developed before inception of this program and since the project was terminated before its completion, additional work is required in a number of areas. Specifically, the following items should be considered:

1. use of improved matrix powders, particularly in purity (especially minimal gaseous contamination),
2. improved spheroidal UC, with special significance given to the chemistry, strength, control of density, spheroidicity, and cost,
3. effect of UO_2 and UC quality on fragmentation and stringering (similar to characterization studies on UO_2 stainless steel dispersion fuels currently in progress[22]),
4. plate fabricability as a function of compact preparation (e.g., compact density and dispersion characteristics),
5. optimized rolling parameters with the reference cladding material recommended as molybdenum jacketed in stainless steel,
6. compatibility of UC and U–15 wt % Mo under conditions representing fabrication and reactor performance,
7. irradiation testing on miniature dispersion fuels.

Finally, it is suggested that a reevaluation be made to ascertain whether pin subassemblies, as compared with plates, might be desirable from a performance point of view.

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[22]A. J. Taylor et al., pp 354–364 in Meeting on Characterization of Uranium Dioxide, TID-7637 (Oct. 1, 1962).

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