DISPERSED (COATED PARTICLES) AND MONOLITHIC (ZIRCALLOY-4 CLADDING) U-Mo MINIPLATES.

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Abstract.

Uranium 7% (w/w) molybdenum (U-7Mo) particles were coated with silicon base material. Chemical vapour deposition (CVD) of silane and high temperature contact diffusion (HTCD) of silicon processes were employed. Hydrided, milled and dehydrided (HMD) particles annealed and centrifugal atomized powder were coated and the results compared. Miniplates were elaborated with both kinds of particles.

A third type of miniplate was elaborated incorporating silicon powder in the initial blending of the U-7Mo and Al powders instead of using an alloyed aluminum powder.

Monolithic miniplates of U-7Mo with zircaloy-4 cladding were also fabricated by hot rolling. The different steps of this picture and frame process are detailed and the method is shown to be versatile, can be easily scaled up, is performed with small modifications of usual equipment in fuel plants and seams to be a possible alternative for high flux reactors conversion from HEU to LEU fuels.

1. Introduction

The selection of U-7%(w/w)Mo as the more promising high density dispersed nuclear fuel compound emerged after the performance evaluation [1] and irradiation testing of several alternatives [2]. Recently, the appearance of undesired porosity detected between the interaction layer and the aluminum matrix at high heat fluxes [3,4], enforces the design of correction options with old and emerging proposals, simultaneously with the evaluation of the origin and causes of this problem. New testings have been and are being planned. Alloying of the aluminum in the matrix with Si is one of the alternatives that are being actually tested. Si can also be incorporated as a powder during the blending of the U-Mo and Al powders. Coating U-7Mo particles could also be an alternative to minimize the growing kinetics of the interaction layer acting as a diffusion barrier or as a stabilizing interphase material.

Since U-Mo alloys are ductile, monolithic fuels were revisited [5], and alternative technologies are being developed [6]. These processes are essentially different than colamination because of the big difference in thermomechanical properties of aluminum and U-Mo alloys. One way to go back to colamination processes by hor rolling is changing the aluminum cladding by a zircalloy-4 one.

2. Coated particles

Physical and chemical methods have been used since many years ago for coating refractory nuclear particles (oxides, carbides, nitrides) from a vapor phase [7]. The coating

of ductile and low melting compounds, such as uranium-molybdenum alloys, has not been so extensively explored. Medium melting point alloys can be coated also by interdiffusion in the solid phase. Ductile particles coated with brittle coatings have to adequately match thermo-mechanical properties of both materials so as to avoid surface breakage during processing of the powder and further manipulation.

Centrifugally atomized particles from KAERI and hydrided, milled and dehydrided (HMD) particles from CNEA were coated with silicon. Two different techniques were used: low pressure chemical vapour (CVD) deposition of silicon [8] from the decomposition of silane (SiH_4) and high temperature contact diffusion (HTCD) of silicon.

In the CVD method, silane was produced at low pressure from the reaction of magnesium silicide (Mg_2Si) and hydrochloric acid (HCl, 1N):

$$Mg_2Si + 4HCl\ (1N) \rightarrow SiH_4 + 2MgCl_2$$

The reaction was controlled drop by drop in a three liter glass balloon externally refrigerated with ice to maintain a low partial pressure of water vapor. The pressure was maintained lower than 25 mbar by pumping the reaction product gases threw a dry ice (CO_2) condenser. The pumping was performed by a mechanical pump threw a one liter volume stainless steel (AISI 310) hot chamber (750 °C) at a pressure of half milibar where the deposition took place in moving (tapping and vibrated) U-7Mo particles. In the deposition reaction, hydrogen is liberated:

$$SiH_4\ (>500\ °C) \rightarrow Si + 2H_2$$

The total quantity of silane gas in the glass reactor was always maintained at concentrations lower than 1.4 %, avoiding any explosive condition in case of leakage or breakage [9]. Before exhaust, excess silane and derivatives, and the reaction products after deposition, were diluted in air using a gas compressor and evacuated threw absolute filters.

The rate of deposition was controlled by the pumping system at programmed pressures in the reaction vessel and hot chamber. With the used equipment, half a litter of solution was poured in approximately 2 hours.

Figure 1 shows centrifugally atomized powder uncoated (left) and CVD silicon coated (right). Particles have an average size of 80 microns and total silicon after chemical analysis is 0.4% w/w. The presence of silicon was also corroborated by semiquantitative EDAX analysis. A uniform coating thickness slightly smaller than 1 micron can be estimated from metallographic observations and calculations. The electronic photograph in the middle of the bottom row shows that some coatings are broken. This can be attributed to the different thermo-mechanical properties of the coating and kernel materials. In the three higher magnification photographs of the coated particles it can be clearly observed a precipitate phase growing at the expense of the surrounding material. This phase could not be identified using semi-quantitave analysis. Since there is shrinkage in the precipitation of this phase, it is more probable to correlate it with the precipitation of a uranium mixed oxide than with a uranium silicide compound.

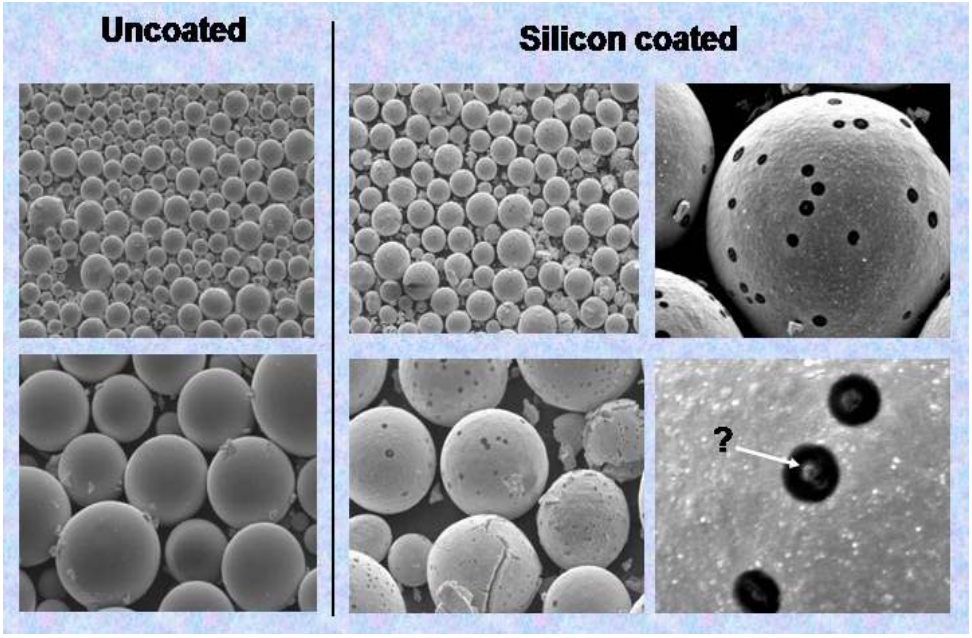


Figure 1. *Scanning electron microraphy of U-7Mo centrifugally atomized powder (80 microns mean size) uncoated and low pressure CVD silicon coated.*

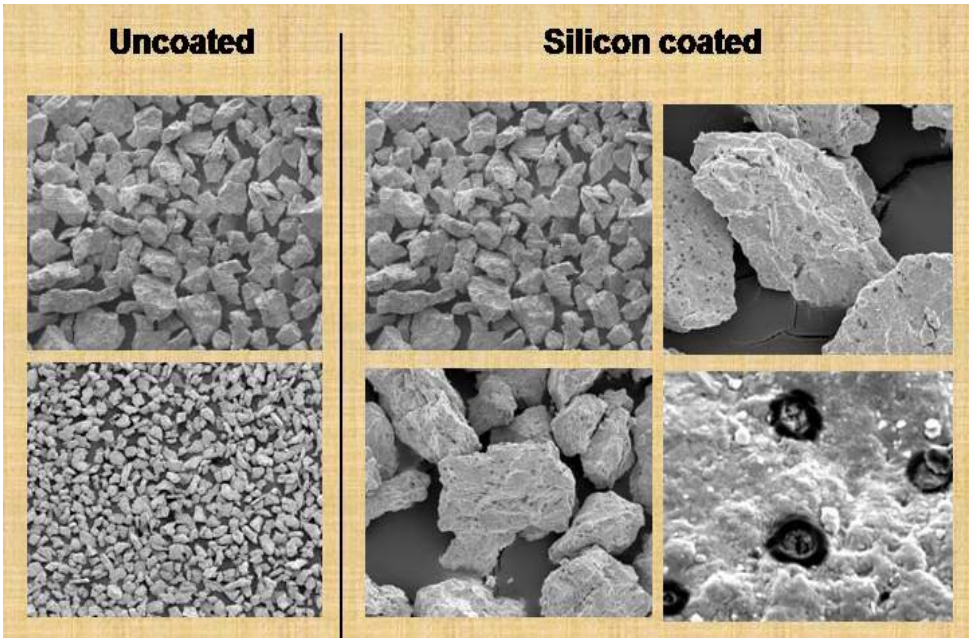


Figure 2. *Scanning electron microraphy of U-7Mo HMD powder (85 microns mean size) uncoated and HTCD silicon coated.*

Another method of coating particles was tested by high temperature (950 °C) contact diffusion (HTCD) between silicon powder (< 32 μ) and HMD U-7Mo powder during 2 hours. The basic idea was not only to diffuse silicon in the uranium alloy, but also to allow for the metallurgical transformation to obtain a U_3Si_2 coverage. This process was performed in a high vacuum previously oxidized zircalloy chamber to avoid undesired reactions between the mixing powders and the walls of the vessel.

The HMD powder produced [10] with 20% enriched uranium after the elaboration of the alloy in an induction furnace had a composition of 92.41 ± 0.09 % w/w U and 6.99 ± 0.07 % w/w Mo and a density of 17.3 g/cm^3. A powder size range of + #325 / - #120 was selected and heat treated during 4 hours at 1000° C in the same chamber used for the posterior coating; after this annealing treatment the density was 17.1 g/cm^3. At the left of figure 2 are two micrographs showing the appearance of the UMo powder.

An initial quantity of 1% w/w Si powder (- #400) was used for the coating by the HTCD process. The final composition of the coated particles was 91.58 ± 0.09 % w/w U, 6.77 ± 0.07 % w/w Mo and 0.82 ± 0.01 % w/w Si. The final density of the particles was 16.3 g/cm^3. The high magnification SEM photographs in figure 2 show a similar precipitation in the coating as that observed in the CVD coated particles.

Coating thicknesses of nearly one micron were obtained with the two methods employed for the silicon coverage of U-Mo particles; i.e. CVD and HTCD. X-ray diffraction (XRD) of particles coated by the two different methods (figure 3) show an enhanced presence of uranium dioxide attributed to contamination during the covering process. These contaminations were smaller in the case of diffusion coverage because of better control of equipment leakages. Silicon or other compounds could not be characterized by XRD, although some unidentified peaks are present in the spectra; special attention was given looking for the presence of U_3Si_2. The general appearance of the results show that no big difference is evident from the two employed methods. Further characterization is needed to corroborate what kind of coating and structure were obtained.

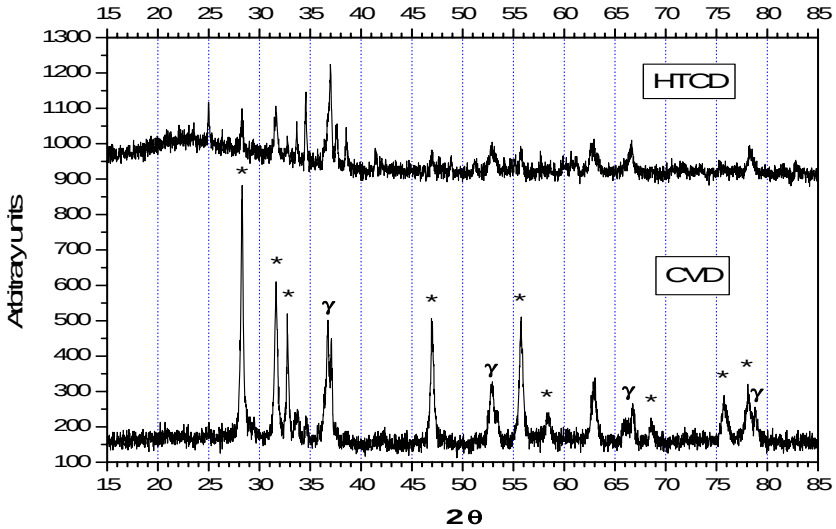


Figure 3. *XRD of coated particles by CVD and HTCD processes. Peak positions indicated with γ and * correspond to γ - UMo and UO_2 structures; other peaks are unidentified.*

3. Silicon incorporation

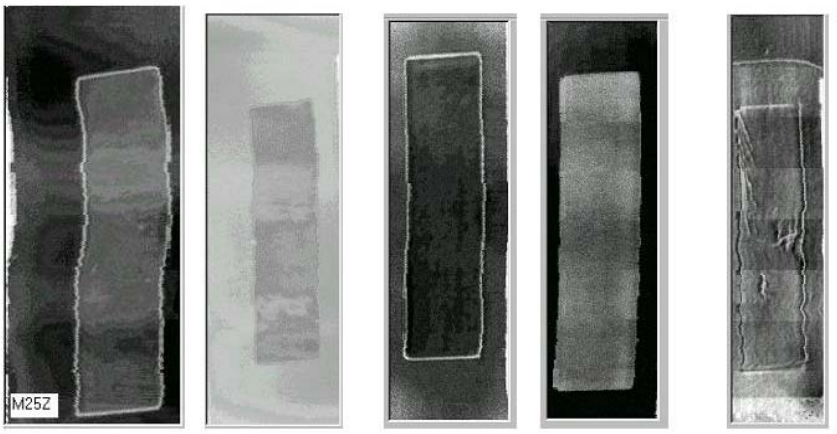
The coated U-7Mo particles, CVD and HTCD, were mixed with aluminium powder in a proportion such as to have a 7 gU/cm3 miniplate meat final density. Also, uncoated annealed HMD powder was blended with aluminum and silicon (<32 μ) powders and pressed. Si/Al powder proportion was 5.1 % w/w; its behavior should be similar to an alloyed aluminum after hot rolling. Two pairs of each dispersed fuel were prepared.

Pressed probes (compacts) of all dispersed fuel had side dimension of 21.0 x 28.6 mm and a thickness of approximately 1.9 mm.

Lids and frames of Al-6061 were machined and etched; the sandwich of each plate was TIG welded by the sides. The sandwiches were hot rolled at 440/455 °C in 6 passes with intermediate heatings of 5/7 minutes to obtain a final thickness dimension of 1.5 mm. All the rolling was performed in less than one hour time. The hot rolled plates were finally cold rolled and straightened. No unusual defects were detected in radiographies.

4. Monolithic U-Mo/Zr-4 miniplates

Miniplates with monolithic U-7Mo and zircalloy-4 cladding were also elaborated by hot rolling using the picture and frame process. Previous investigation of the feasibility of this process was analized by interdifussion couples, Zr-4/Zr-4 and UMo/Zr-4 colamination set up, testing of temperature and adequate deformation passes, and calculation analysis of stresses coming from the different thermal expansion coefficient of both materials. The alloy was melted in an induction furnace and casted in a graphite mold to obtain a plate of 2 mm thickness. Coupons of 18 x 20 mm were machined with this thickness for the elaboration of miniplates with a 0.5 mm meat thickness after hot rolling. For the elaboration of thinner meat thickness miniplates, coupons were machined after casted plates were hot rolled at 650 °C to the adequate thickness with intermediate etching passes.



. MZ25 (back) | MZ25 (2nd interph) | MZ50 (back) | MZ50 (2nd interph) | No bond

Figure 4. *Ultrasonic Scan-C of three different monolithic miniplates. The miniplate at the extreme right evidences no bonding and overlapped meat material.*

The U-7Mo coupons before hot rolling had a composition of 92.91 ± 0.09 % w/w U and 7.04 ± 0.07 % w/w Mo. The density was 17.53 ± 0.02 g/cm^3. Lids and frames were machined and, after assembling the sandwiches, they were TIG welded. Hot rolling was performed with six different miniplates using depleted and 20% enriched UMo alloys. Hot rolling was performed in eight steps with intermediate heating between 655/675 °C during 6/7 minutes in a furnace without controlled atmosphere. The whole lamination process for each plate was performed in less than one hour. Special precautions were developed for cleaning the UMo and Zr-4 bonding surfaces. In some cases blistering was observed during the rolling process because of unsatisfactory initial mechanical match between frame and kernel. Debonding was noticed in the first rolling steps if the plates cooled excessively after deformation because of differential contraction. The cooling to room temperature produces less than 1% deformation and this can be sustained if a complete bonding is achieved. Also the lowest temperatures were chosen to avoid excessive contamination of the zircalloy surface.

Monolithic miniplates were surface finished to a final thickness of 1 mm by wet abrasion with SiC paper of 320 and 400 mesh. Plates could be obtained with no defects detected in radiographies and ultrasonic scanning after rolling. In figure 4 are shown the ultrasonic Scan-C of miniplates totally bonded and one with several defects.

In figure 5 it is shown a U-Mo monolithic miniplate with zircaloy-4 cladding elaborated with depleted uranium for feasibility purposes. The overall dimensions are 100 x 25 x 1 mm^3 with a 0.5 mm meat thickness.

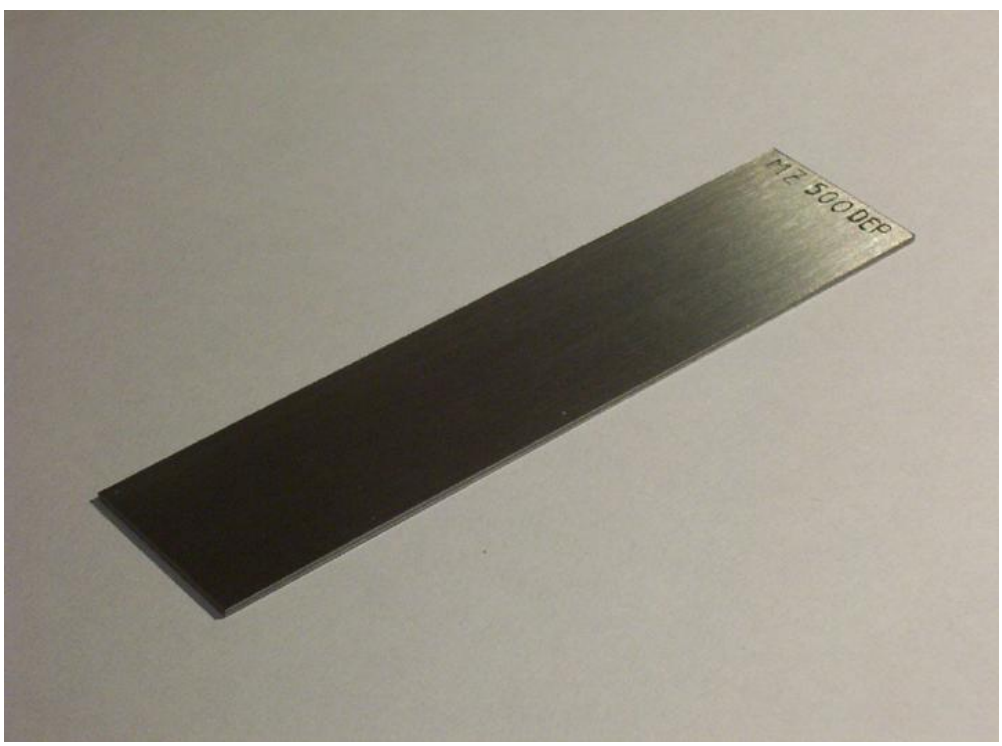


Figure 5. *Monolithic miniplate of U-7Mo with zircaloy-4 cladding.*

5. Miniplates characteristics

A total set of 12 miniplates were elaborated; half of them with dispersed fuel and the other half with monolithic nucleus. They are shown in figure 6.

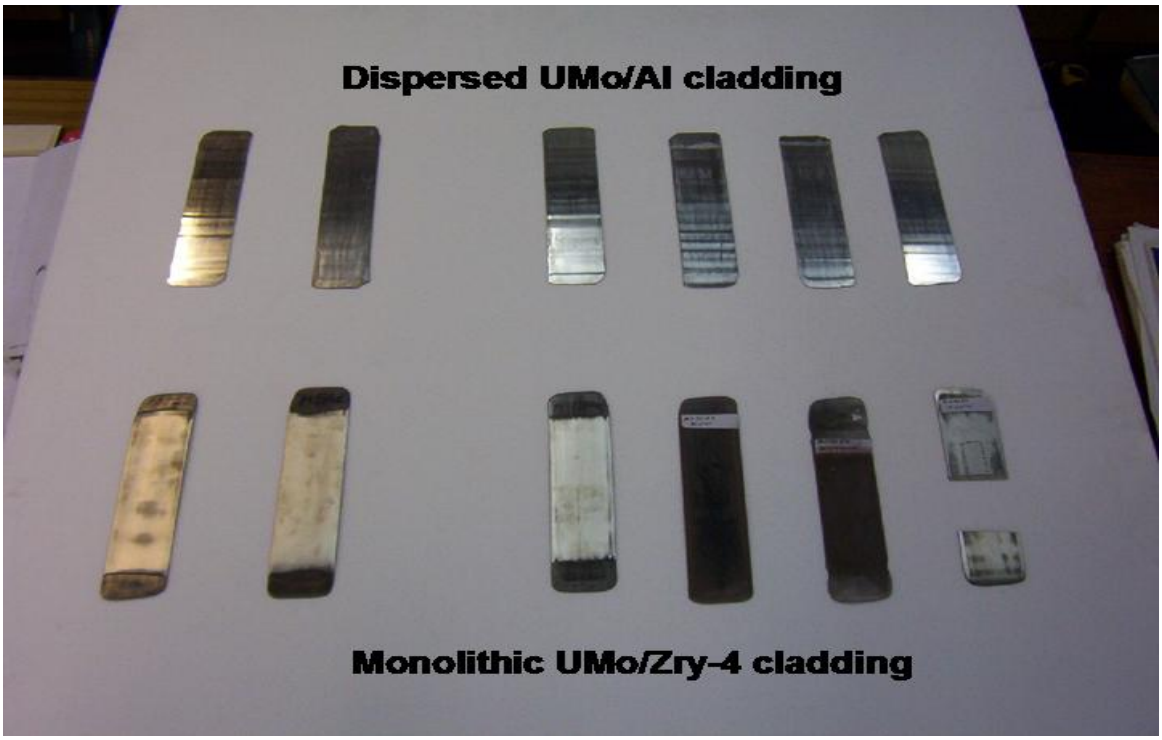


Figure 6. *Dispersed and monolithic fuel miniplates after hot rolling by the picture and frame process. Cladding in each case is Al-6061 and Zr-4, respectively.*

The dispersed fuel miniplates have aluminum cladding with a total thickness of approximately 1.4 and are ready for cutting to final dimensions and posterior cleaning. The monolithic miniplates with zircaloy-4 cladding have a nominal thickness of 1 mm; the three miniplates at bottom left have already been cleaned by wet abrasion and are ready for final cutting. The one at the bottom right was used for cleaning set up and cut for metallographic studies. All U-Mo alloys were casted with the same LEU with an enrichment of 19.86 % ^{235}U. Some testing for monolithic miniplates was done with UMo with depleted uranium.

In Table 1 are specified the characteristics of four of the elaborated miniplates with dispersed fuel -coated and uncoated- and monolithic with .25 and .5 mm meat thickness. These four miniplates were shipped from Buenos Aires to INL for the possibility of irradiation in the RERTR-7 experiment.

The characteristics of the four miniplates, the two ones at the left of the upper and lower rows in figure 6, are detailed in table 1. The name of miniplates correspond to the following description:

1. **MZ50.** Monolithic miniplate with zircaloy-4 cladding and .50 millimeter nominal meat thickness.
2. **MZ25.** Monolithic miniplate with zircaloy-4 cladding and .25 millimeter nominal meat thickness.
3. **HMDC.** High temperature heat treated U-7Mo HMD particles coated with silicon by HTCD and Al-6061 cladding.
4. **HMDS.** High temperature heat treated U-7Mo HMD, aluminum and silicon powders cold pressed and Al-6061 cladding.

Table 1. Dispersed and monolithic miniplates.

CNEA´s MINIPLATES	MZ50	MZ25	HMDC	HMDS
Plate thickness [mm]	1.01	0.99	1.45	1.45
Meat thickness [mm]	0.51	0.26	0.64	0.65
Meat width [mm]	18.6	18.8	21.4	21.9
Meat longitude [mm]	71.0	73.0	80.7	87.0
Total U [g]	10.9	5.9	7.50	8.34
Meat density [gU/cm^3]	16.2	16.5	6.8	6.7
Ratio U/surface [gU/cm^2]	0.41	0.21	0.22	0.22
Porosity [%]	-	-	5	7

Testings of curvature were performed in a monolithic miniplate. A hot bending with a curvature of 25 mm was performed after 1 hour heat treatment at 850 °C. In figure 7 it is shown the curved miniplate after cutting it for metallographic purposes. The metallography at right shows the higher curved zone were an interaction layer of approximately 5 microns is present.

It has to be enfasized that all mentioned miniplate with dispersed and monolithic fuel were elaborated by hot rolling using the picture and frame process. Difference arises only in rolling temperature and surface cleaning. The same equipment was used in all cases.

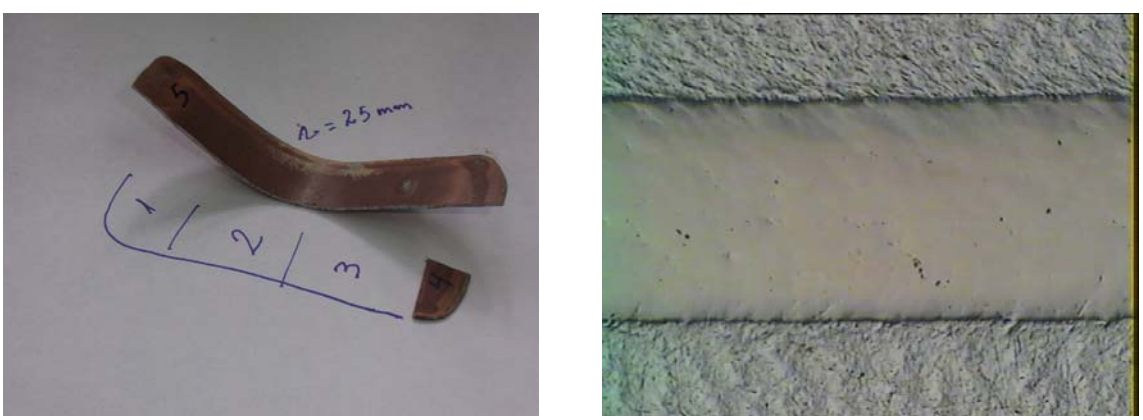


Figure 7. *Hot curved monolithic UMo/Zr4 miniplate after 1 hr at 850 °C and metalography at the higher curvature (r = 25 mm) zone.*

6. Conclusions

Efficient coating of UMo particles have been shown that can be performed by silane chemical vapor deposition and high temperature contact diffusion. Better deposition yields and control can be achieved with the latter. Good oxygen evacuation is needed to avoid growing oxides at the coating surfaces. Not wanted metallurgical transformations have occurred in the coated surface. Coating layers thicker than one micron of brittle materials seem to be thermo-mechanically incompatible with ductile UMo. Additional characterization of coatings has to be performed such as to asses on its structure and composition. In the particular case of silicon deposits several compounds can be present, such as silicon oxide. Mixed uranium-silicon oxides, silicides, in crystalline or amorphous structures can be present. Similar results are expected to be obtained if nitride coatings are performed. Coatings in UMo particles are believed that can stabilize the interaction layer and/or be a diffusion barrier to slow down diffusion kinetics. It seems reasonable to attempt to perform thicker coatings using more ductile materials such as nickel and niobium that have been tested previously in other nuclear fuel developments.

In the case of dispersed Si powder in the Al matrix it seams to be a reasonable alternative process for alloing the matrix. Metallographic characterization is being performed of the fabricated miniplates to confirm if good bonding have been achieved during hot rolling.

The fabrication of monolithic U-Mo with zircalloy-4 cladding is a flexible technology where special forms can be adapted. It looks that it is easily scalable to full size plates and should be considered as a possible candidate for conversion of high flux reactors from HEU to LEU. Minor modifications of usual equipment of plate production plants are needed for their elaboration at industrial scale. Probable economic benefits can come out from thorough evaluation of the whole fuel cycle, including storage and back end options. Higher surface heat flows can be used accounting for higher flexibility in the materials used and the possibility of higher reductions in cladding and plate thicknesses.

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9. References

1. J. L. Snelgrove, G. L. Hofman, C. L. Trybus, and T. C. Wiencek. Development Of Very-High-Density Fuels By The Rertr Program. 19th International Meeting on Reduced Enrichment for Research and Test Reactors (RERTR). Seoul, Republic of Korea. October 7-10, 1996.
2. M. K. Meyer, C. L. Trybus, G. L. Hofman, S. M. Frank, T. C. Wiencek. Selection and Microstructures of High Density Uranium Alloys. 20th International Meeting on Reduced Enrichment for Research and Test Reactors (RERTR) Jackson Hole, WY (US), 10 Oct 1997.
3. G.L. Hofman, Y.S. Kim, M.R. Finlay, J.L. Snelgrove. S.L. Hayes, M.K. Meyer, and C.R. Clark. Recent Observations at the Postirradiation Examination of Low-Enriched U-Mo Miniplates Irradiated to High Burnup. 25th International Meeting on Reduced Enrichment for Research and Test Reactors (RERTR). Chicago, Illinois. October 5-10, 2003.
4. P. Lemoine, J. L. Snelgrove, N. Arkhangelsky, L. Alvarez. U-Mo Dispersion Fuel Results and Status of Qualification and Licensing Programs. 8th International Topical Meeting on Research Reactor Fuel Management (RRFM). Munich, Germany. March 2004.
5. T. C. Wiencek and I. G. Prokofiev. Low-Enriched Uranium-Molybdenum Fuel Plate Development. International Meeting on Reduced Enrichment for Research and Test Reactors. October 1-6, 2000, Las Vegas, Nevada, USA.
6. C.R. Clark, G.C. Knighton, M.K. Meyer, G.L. Hofman. Monolithic Fuel Plate Development at Argonne National Laboratory. 25th International Meeting on Reduced Enrichment for Research and Test Reactors (RERTR). Chicago, IL, USA. 5-10 Oct 2003.
7. Dispersión-Fuel Nuclear Reactor Elements. A. G. Samoilov, A. I. Kashtanov and V. S. Volkov. Israel Program for Scientific Translations Ltd., Jerusalem 1968.
8. Handbook of Thin-Film Deposition Processes and Techniques. Principles, Methods, Equipment and Applications. Ed. K. K. Schuegraf. Noyes Publications. Park Ridge, NJ, USA. 1988.
9. Materials Safety Data Sheet (Silane).
10. E. E. Pasqualini, J. Helzel Garcia, M. López, E. Cabanillas and P. Adelfang. Powder Production Of U-Mo Alloy, HMD Process (Hydriding-Milling-Dehydriding)¨, 6th International Topical Meeting on RRFM, Ghent, Belgium (2002).