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**Plasma Spraying of Diffusion Barrier Coatings for
LEU Monolithic Fuel**

K.J. Hollis

Materials Science and Technology Division

Los Alamos National Laboratory, PO Box 1663, Los Alamos, NM 87544 – USA

ABSTRACT

Zirconium and molybdenum metal coatings applied by inert plasma spraying have been investigated for use as a diffusion barrier coating on low enrichment uranium fuel for high flux nuclear test reactors. Diffusion barrier coatings are designed to prevent fuel structural damage from swelling which can result from the interaction of the uranium-molybdenum fuel with the aluminum fuel cladding. The coatings have been applied to both stainless steel (as a surrogate) and uranium alloy substrates. Spray parameter development accompanied by coating characterization has been performed. Coating density, chemical composition, microstructure, surface profiles and bonding characteristics as functions of spray parameters are presented.

1. Introduction

The purpose of the Department of Energy's National Nuclear Security Administration's Office of Global Threat Reduction's Conversion program, formerly known as the Reduced Enrichment for Research and Test Reactors (RERTR) program, is to work with research reactors operators worldwide in an effort to convert reactors from the use of highly enriched uranium (HEU) fuel to the use of low enriched uranium (LEU). In support of this effort, the Convert program is working to develop new fuels to allow for the conversion of high performance research reactors worldwide. One of the primary challenges in developing LEU monolithic fuel for high neutron flux test reactors is the insertion of a thin (10-100 μm) diffusion barrier to prevent the interaction of the U-Mo fuel with the aluminum (Al) cladding which can lead to fuel plate swelling and possible rupture during reactor operation. The diffusion barrier must be well bonded to the underlying U-Mo fuel foil and must have a top surface which promotes strong adhesion to the Al cladding which is hot isostatic press bonded to the fuel foil. Zirconium (Zr) is currently being used as the diffusion barrier in fuel development and testing activities due to its low neutron capture cross section and its ability to prevent uranium-aluminum interaction under reactor operational conditions. The baseline technique for applying the Zr to the fuel is by canned hot rolling of Zr foils on either side of the U-Mo fuel foil (co-rolling). The Zr is bonded to the U-Mo while both are at high temperature and pressure is applied by the rolling mill.

The use of a coating technique to apply the diffusion barrier after the U-Mo is bare rolled to final thickness has potential advantages over co-rolling. These advantages include: no waste from the rolling can material; the Zr surface roughness can be optimized for better bonding to the Al; there is no potential for parting agent contamination of the foil; the measurement of the final U-Mo foil thickness can take place without the Zr barrier reducing the complication and increasing the accuracy of the measurement; rolling parameters can be optimized for U-Mo rolling without considering the Zr/U-Mo bonding; and the U-Mo scrap can be recycled directly through a later stage in production since there is no diffusion barrier applied that would require additional processing steps to remove. Coating techniques are also not limited to material combinations that bond easily by co-rolling. The use of molybdenum (Mo) as a diffusion barrier has potential advantages over Zr but since Mo is a high melting point, it would not likely bond with U-Mo at the temperatures needed for U-Mo hot rolling (~600°C). The primary advantage of using Mo as the diffusion barrier pertains to the recycle or reprocessing of fresh or spent fuel. Unlike other potential diffusion barriers, Mo is the primary alloying element in the U-Mo fuel. Therefore, the Mo diffusion barrier need not be separated from the fuel before melt reprocessing but instead the Mo added to the melt to form the desired U/Mo ratio is adjusted based on the amount of Mo in the recycled fuel + diffusion barrier. This eliminates the separation of the diffusion barrier coating with accompanying reductions in cost, manufacturing footprint, waste stream and radiation exposure.

This paper describes recent progress in developing Zr and Mo diffusion barrier coatings for use on LEU fuels for high flux research reactors. Plasma spraying in an inert gas environment is used as the coating technique due to its ability to quickly coat surfaces and its ability to deposit reactive metals. The primary coating characteristics of interest for this application are the coating/substrate interface, the coating thickness and the coating roughness.

2. Experimental Procedure

Powders of 20-50 μm average diameter were used for depositing the Zr or Mo coatings. Coating system equipment and parameters have been published previously [1-3]. The coatings were deposited onto 21 Cr – 6 Ni – 9 Mn stainless steel (SS) or depleted uranium-10% Mo substrates each 19 mm x 83 mm x 0.4 mm. A two-dimensional (line type) triangulation laser displacement sensor (LJ-G015, Keyence Corp.) was used to measure coating surface profile and roughness. Cross sectional images of the coating were recorded using light optical microscopy (LOM) and scanning electron microscopy (SEM). Coating thickness was also measured by X-ray fluorescence (XRF) using a handheld analyzer (DP-2000, Olympus/Innov-X). A ratio of the line emission amplitude for Zr and Fe or Zr and U was used along with Zr thickness calibration standards to determine coating thickness. The spot size for the XRF device was 10 mm diameter. A Mo coating was deposited on a large SS foil with size 610 mm x 102 mm x 0.33 mm. This is similar to the size of the reactor fuel foil used for the LEU conversion.

3. Results and Discussion

3.1 Zirconium Coatings

Figure 1 shows a montage of LOM cross section images of a Zr coating on the top and bottom sides of a SS substrate. The average porosity in the coating was measured to be less than 0.5%

using 2-D image analysis to differentiate between pores and coating. The coating thickness as measured on the micrograph varies between 40 μm and 90 μm . There are no areas of uncoated substrate observed. A higher magnification view of an etched Zr coating is shown in Fig. 2. This coating has an equiaxed grain structure with an average grain diameter of 6.5 μm . An elemental inter-diffusion zone at the coating/substrate interface indicates the metallurgical nature of the bond.



Fig. 1 Zr coating on the top and bottom of a SS substrate. The width of foil shown (the entire image width) is 4.5 mm.

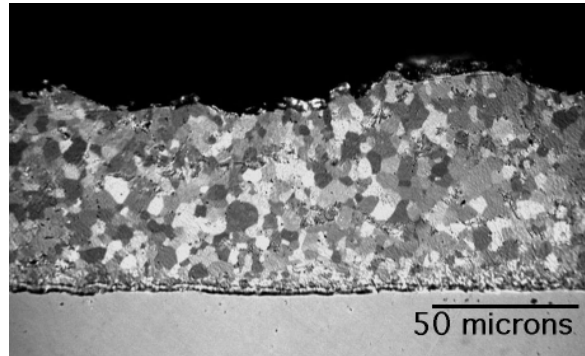


Fig. 2 Zr coating on SS etched to reveal the Zr grain structure.

SS and U-Mo foils were coated with Zr and then had coating thickness measurements performed using XRF. The purpose of the XRF measurement is to determine the coating thickness variation using a large sample size of 10 mm diameter compared to the smaller scale thickness measurements of microscopy. The results of the XRF measurement of Zr thickness on the SS foil are shown in Fig. 3 and for the U-Mo foil in Fig. 4. The measurement uncertainty for the

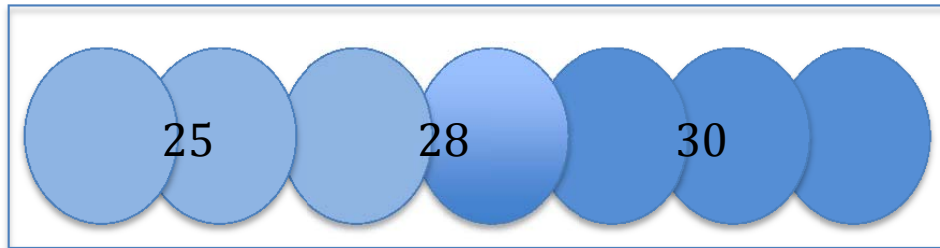


Fig. 3. The Zr coating thickness (in μm) on a SS substrate measured by XRF. The XRF spot size is 10 mm diameter.

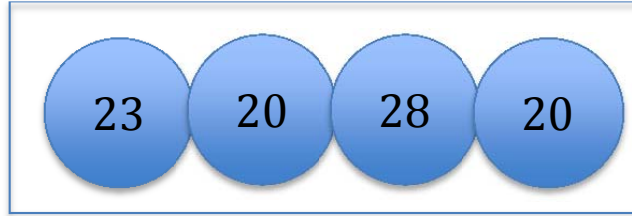


Fig. 4. The Zr coating thickness (in μm) on a U-Mo substrate measured by XRF. The XRF spot size is 10 mm diameter.

integration times chosen is 2 μm . The Zr thickness variation on the SS foil was 5 μm over the length of 70 mm. The variation was monotonic perhaps indicating a systematic variation in thickness with location on the foil. The Zr thickness on the U-Mo foil showed 8 μm variation over the length of 40 mm. The thickness variation was more random on the U-Mo foil.

3.2 Molybdenum Coatings

Due to the high melting temperature of Mo ($T_m = 2623^\circ\text{C}$) compared to that of Zr ($T_m = 1855^\circ\text{C}$) and the temperature limitations of the U-10Mo ($T_m \approx 1200^\circ\text{C}$ [4]), the thermal processing conditions that produced a dense, recrystallized microstructure in Zr were not possible for Mo. The Mo coating cross section on U-Mo is shown in the SEM image in Fig. 5. The average thickness of the coating is 57 μm with a maximum thickness of 90 μm and a minimum thickness of 41 μm . The porosity in the coating was measured with image analysis to be 4.5% for the top side coating in Fig. 5 and 6.1% for the bottom side coating. The interface between the U-Mo substrate and the Mo coating is shown in Fig. 6. The contact between the coating and substrate is intimate with the coating closely following the contour of the substrate.

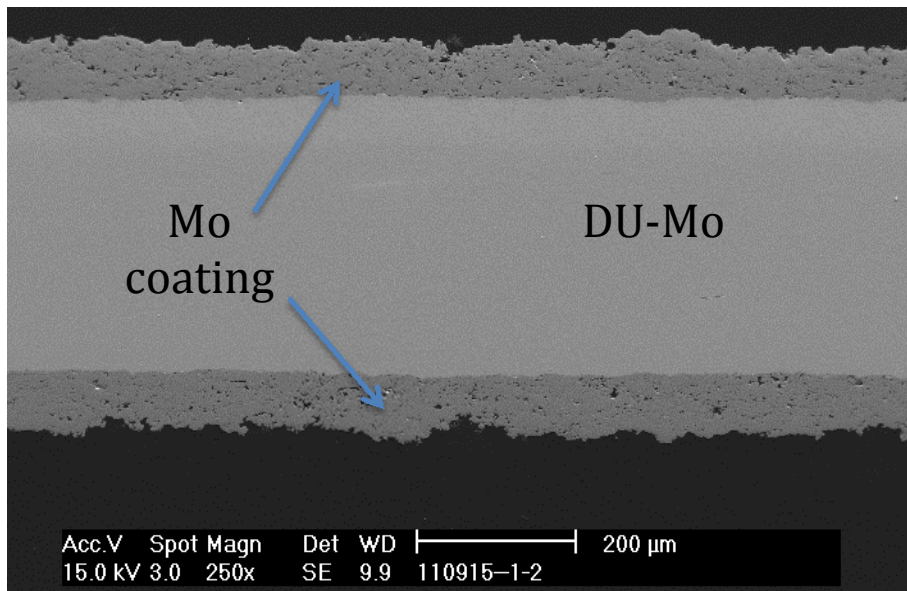


Fig. 5 Mo plasma sprayed coating on U-Mo substrate.

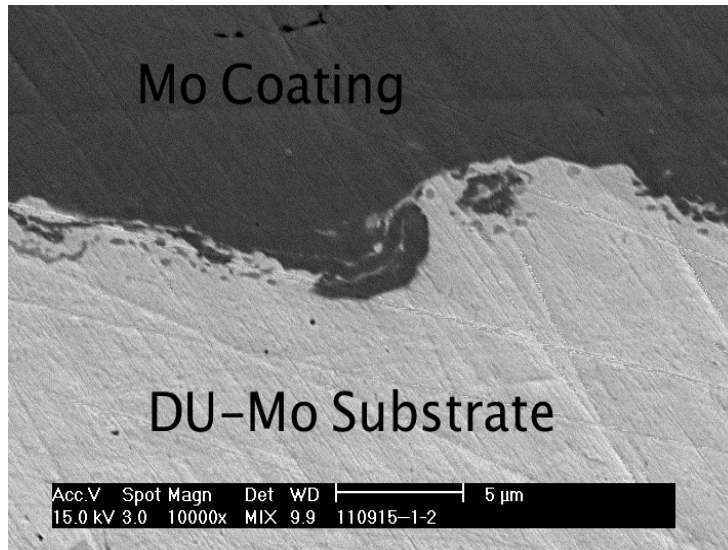


Fig. 6 The interface between the Mo coating and the U-Mo substrate shown in a mixed back-scatter/secondary electron SEM image.

An important consideration for material recycle is the impurity content of the coating. If large quantities of impurities are found in the coating, its suitability for recycle is diminished. Chemical composition analytical testing of the Mo starting powder and a Mo coating sprayed under high power and lower power conditions was conducted to determine chemistry changes during plasma spraying. Fig. 7 shows the chemistry results. Results for the Al, Cu, Hf, Mg, Mn, N, Na, P, S, Si, Ta and Zn are below the levels shown in Fig. 7. There was a slight decrease in Fe in the coatings compared to the powder and a significant decrease in the O and Ni. Since contamination pick up is minimal and there is some reduction in impurities, recycle of the Mo coating is expected to be feasible.

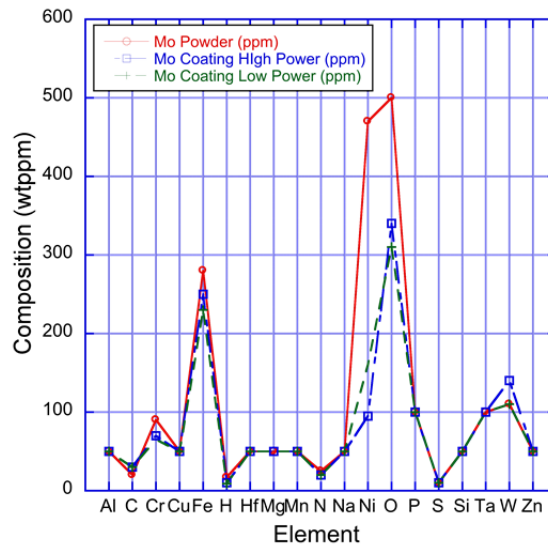


Fig. 7. Chemical composition of the Mo powder and Mo coatings deposited at high and low power.

Measurements of the surface profile of various Mo coatings was performed using the 2-D laser displacement sensor. The surface location at 800 points across the laser line was recorded for each location on the coated foils. The mean height value was calculated and the average absolute deviation from the mean (R_a) was calculated and is shown in Fig. 8. These values were calculated from 23 separate sprayed samples with 10-12 locations measured on each sample. R_a values range from 0.003 mm to 0.007 mm. Values for R_v (maximum valley depth below the mean) and R_p (maximum peak height above the mean) are shown in Fig. 9 and 10 for the same

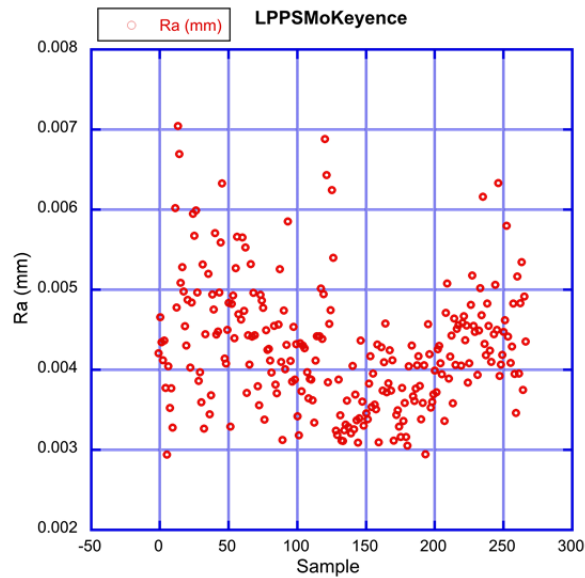


Fig. 8. Roughness values (R_a) for 23 Mo coatings.

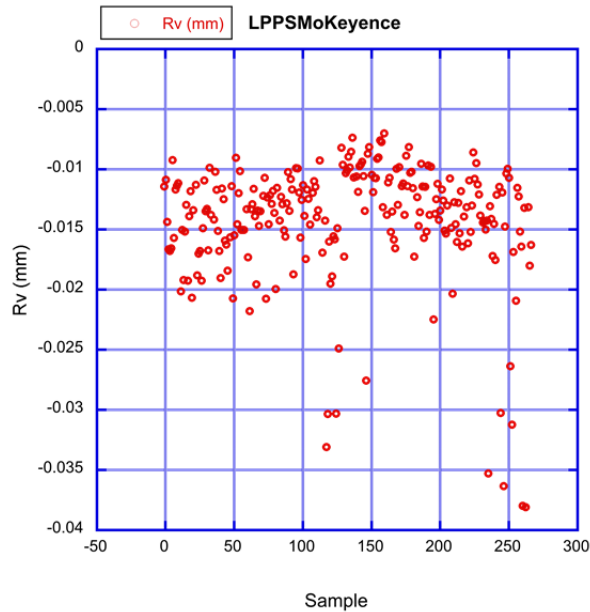


Fig. 9. Maximum valley depth (R_v) values for 23 Mo coatings.

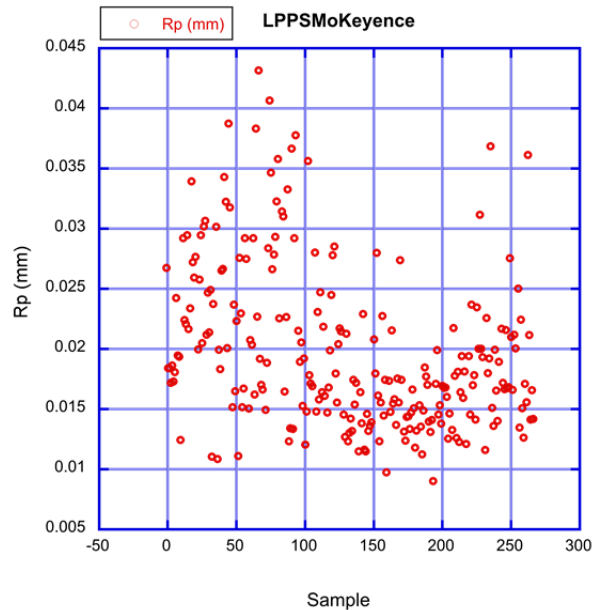


Fig. 10. Maximum peak height (R_p) values for 23 Mo coatings.

samples as Fig. 8. The average value for R_v is 0.0147 mm below the mean coating height and the average value for R_p is 0.0198 mm above the mean coating height. The average R_v value suggest that the coating should be thicker than 0.015 mm in order to ensure that the average fuel foil has complete coverage.

3.3 Scale Up

In order to demonstrate plasma spraying on foils the same size as the high neutron flux test reactor fuel, scale up experiments using large 610 mm x 102 mm x 0.33 mm SS foils as substrates. Due to constraints on the plasma spray torch manipulator, the foils were coated in two runs each coating the full width and half the length of the foil. A large foil coated with Mo is shown in Fig. 11. Due to the size of the foil, the plasma torch trajectory over the foil was modified. This modified trajectory caused localized heating and warping of the foil. Experiments are ongoing to modify the heating pattern to even the temperature distribution during deposition.

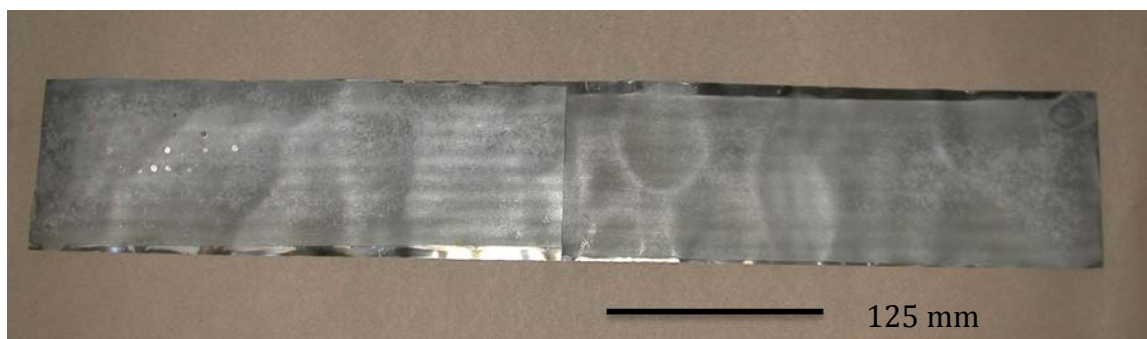


Fig. 11. Large SS foil coated with Mo.

4. Conclusions

The research reported in this paper has resulted in the following conclusions.

- Zr and Mo plasma sprayed coatings form a continuous barrier on the top and bottom of coated foils and possess a roughness inherent in the spraying process.
- Zr coatings can be deposited with very little porosity (<0.5%) possessing a re-crystallized, equiaxed grain structure of average grain diameter 6.5 μm and having elemental interdiffusion across the substrate/coating interface.
- Zr coating thickness variations measured by XRF and averaged over a 10 mm diameter spot size were found to be 5 μm and 8 μm on the samples investigated.
- Mo plasma sprayed coatings had higher porosity (5-6%) but have intimate contact with the substrate.
- The Mo coatings have chemical compositions similar to the starting powder with the exceptions that the Ni and O are lower in the coatings.
- Scale-up of the plasma sprayed samples to reactor fuel foil size require uniform heating in order to decrease the distortion effect of localized hot spots.

5. Acknowledgements

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6. References

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