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PLASMA SPRAYED ZIRCONIUM DIFFUSION BARRIER DEVELOPMENT FOR MONOLITHIC U-MO METALLIC FUEL

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ABSTRACT

Development activities for producing a zirconium diffusion barrier between the U-Mo fuel and the 6061 aluminum cladding for monolithic metallic research reactor fuels has been ongoing at Los Alamos National Laboratory. Parameters of plasma spraying including plasma power, gas flow rates, and substrate temperature affect the coating density and bond strength. The surface composition of the U-Mo immediately prior to coating and the interfacial layer that forms between the U-Mo and the zirconium affect coating adhesion and are controllable to some extent by the processing parameters for plasma spraying. There is a clear correlation between increased substrate temperature during spraying and improved bond strength. Microscopic analysis suggests that as deposition temperature increases, thickness of a U-Mo-Zr-O interfacial layer increases; the coating bond strength seems to correlate with interlayer thickness. The information gained during this development program is being used to optimize zirconium diffusion barrier coatings for the production of test samples for the upcoming MP-1 reactor experiment.

1. Introduction

1.1 Program Background

The United States government is committed to further strengthening nuclear security and nonproliferation in order to reduce the threat of terrorists acquiring nuclear material. To meet this important mission, the US Department of Energy/National Nuclear Security Agency's Office of Material Management and Minimization (M^3) Reactor Conversion Program minimizes the use of highly enriched uranium (HEU) in civilian applications by working with governments and facilities around the world to convert research reactors to the use of non-weapons-usable low-enriched uranium (LEU) fuels. Each reactor converted not only eliminates the need for HEU at civilian sites, but also reduces the amount of HEU being manufactured, stored, and transported, where it is at its most vulnerable. In instances where suitable LEU fuels do not exist for particular reactors to convert, the M^3 Reactor Conversion Program contributes to the development of new LEU fuels. Currently, the M^3 Reactor Conversion Program is committed to developing a high-density U-Mo LEU fuel that will be able to convert high performance research reactors while establishing an efficient and economic fabrication capability to make the fuel. To that end, Los Alamos National Laboratory (LANL) has been tasked with developing a method to affix Zirconium fuel diffusion barrier *via* plasma spraying, which will prevent a reaction between the U-Mo fuel and the aluminum cladding.

A successful diffusion barrier requires adequate Zr thickness, uniform coverage, adequate bonding at the Zr/fuel and Zr/cladding interfaces, and maintenance of the original fuel properties (*i.e.* dimensions, crystal phase concentration, alloy composition and dispersion, neutronics, *etc.*). This work outlines Zr plasma spraying techniques [1-4], parameters affecting bond strength [5-6], and characterization of the Zr diffusion barrier [7].

2. Plasma Spray Procedures

2.1 Spraying

Depleted uranium with 10 weight percent molybdenum (DU-10Mo) ingots were cast and ~300 micron thick foils rolled from the castings at LANL. Following rolling, the uranium foil has a black oxide scale, shown in Figure 1A. This oxide layer, as well as other contaminants, is removed using a sequence chemical cleaning. First, the foil is sonicated in Blue Gold ™ detergent at 60°C to remove surface organics, then soaked in a caustic 10% NaOH solution, and then finally transferred to 50% HNO_3 etchant to expose bare uranium foil (Figure 1B). The cleaned foil is rinsed with DI water and dried in a nitrogen atmosphere. To prepare the foil for plasma spraying, the foil is mounted onto a stainless steel support, a square tube allowing four foils to be sprayed at the same time, with screws to secure the edges of the foil, as shown in Figure 1C.

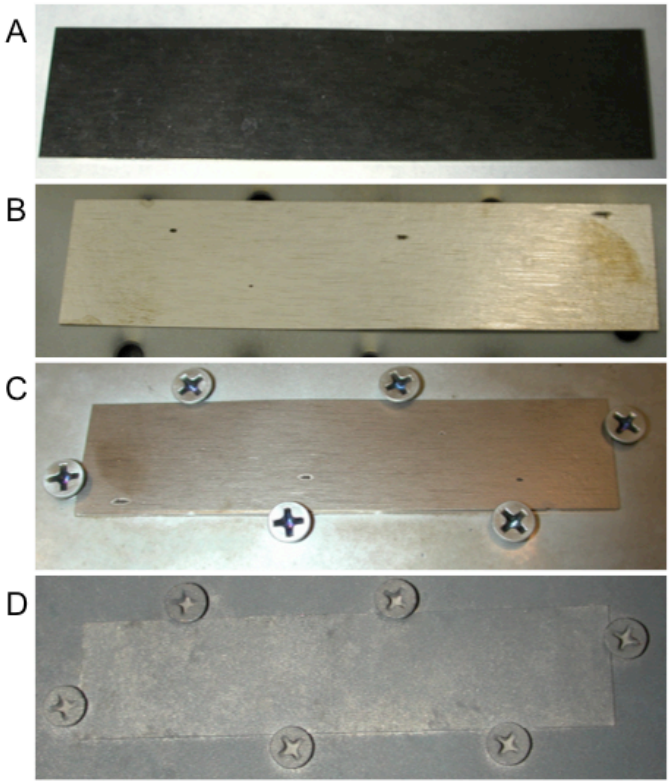

Fig. 1. A) Photograph of rolled DU-10Mo with black oxide surface. B) Bare DU-10Mo foil after chemical cleaning. C) Bare DU-10Mo foil mounted in plasma spray chamber holder. D) DU-10Mo foil following Zr plasma spray coating.

The square sample holder rotates while the plasma gun (SG-100, Praxair/TAFA, Concord, NH, USA) rasters in the over the rotating tube. The vacuum chamber was evacuated then backfilled with argon to 70 Torr, with an oxygen content of less than 100 ppm prior to spraying. 99.2% purity Zr powder (ATI Wah Chang, Albany, OR, USA) with particle size ranging from 5 – 50 microns is used to deposit a ~30 micron Zr coating in an Ar-He plasma. A photograph of a sprayed foil in the mount is shown in Figure 1D. To test the effects of spraying conditions on bond strength, deposition conditions were varied; these parameters are outlined in Table 1. Following the plasma spraying of one side of the foil, the foils are turned over, re-mounted and then sprayed on the second side. The maximum foil temperature (T_{MAX}) during plasma spraying

was determined using an infrared camera. The bond temperature for each sample is the lower of the temperatures reached on the two sides during the two spray runs.

Sample ID	Plasma Current (Amps)	Plasma Gas (LPM)		Bond Temp (°C)
		Argon	Helium	
151007	850	30	25	602
151008	850	30	25	655
151013	950	30	25	726
151014	950	25	30	843
151015	850	25	30	776

Table 1. Summary of Zr Layer Plasma Spray Conditions

3. Fuel and Cladding Characterization

3.1 Bond Strength

A viable high-density U-Mo LEU fuel requires a thin Zr layer with strong adhesion between the Zr and U-10Mo fuel, as well as strong adhesion between the Zr and eventual Al cladding layer. Room temperature, quasi-static tensile strength testing was performed to quantitatively test the adhesion strength of the plasma sprayed Zr coating to the U-10Mo foil. Aluminum mounts were fabricated and attached to each side of the Zr coated foil using commercial grade epoxy. A foil and the testing mounts are shown in Figure 2A. These mounts are then loaded into a tensile testing apparatus, which applies a uniaxial force on the foil mount. The mount fixtures are connected by ball joints to prevent twisting, shearing, etc. during the test (Figure 2B). The tension force is increased steadily until failure; this failure force divided by the area of the foil is determined to be the “strength” of the Zr-U-Mo bonding.

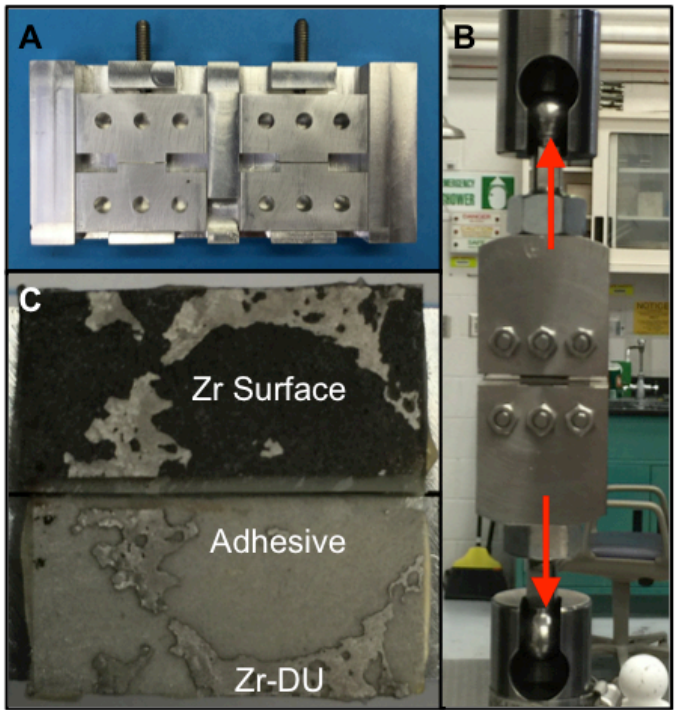

Fig. 2. A) Aluminum tensile testing mounts for determining bond strength of Zr coating on U-10Mo foils. This photo shows two testing mounts, resting side by side in a holder, to ensure proper sample orientation during epoxy curing. B) Tensile testing apparatus, with sample mount loaded and attached by ball joints. Arrows show the direction of force. C) Typical image of fractured foil surfaces, following tensile testing. In this sample, the failure occurred primarily in the mounting adhesive, as indicated by the overall integrity of the Zr coating on one side and adhesive on the other. In some small areas, the failure occurred in a Zr-U interface layer.

Analysis of the fractured surfaces (Figure 2C) following tensile testing helps to determine in what portion of the foil the failure occurred. The results of the tensile bond strength testing are summarized in Table 2. The weakest bond sample (ID# 151007) failed at a load of 6,574 N, which translates to a strength of 36.23 MPa. Visual inspection, together with SEM/EDS analysis, suggests that the bond failure occurred primarily in a Zr-U intermetallic layer, with significant amounts of Zr and U-10Mo remaining on both sides of the fracture surface. A representative backscattered electron SEM image of the fracture surface is shown in Figure 3A. ID# 151008 failed at a similar load as sample 151007, with a strength of 37.60 MPa. Adjustment of plasma spray parameters (primarily affecting substrate temperature) leads to an increase in bond strength, with ID# 151013, 151014, and 151015 showing a tensile strengths of 50.12, 58.88, and 53.66 MPa, respectively. Visual analysis of the stronger samples suggests that the failure occurred primarily in the adhesive epoxy, with a significant amount of the Zr coating on one testing mount and adhesive on the other corresponding mount. A photograph of the two sides of the fracture surface for the strongest sample (ID# 151014) is shown in Figure 2C and a representative backscattered SEM image is shown in Figure 3B. Note that there is significantly less U-10Mo exposed in the stronger bound sample (Figure 3B) than in the weakest sample, Figure 3A. Characterizing the Zr/U10Mo interface will show which factors affect the Zr coating adhesion strength and how that correlates to plasma spray conditions and resulting bond strength.

Sample ID	Failure Load (N)	Strength (MPa/psi)	Failure Point
151007	6,574	36.23 / 5255	Zr-U10Mo Interface
151008	6,823	37.60 / 5453	Zr-U10Mo Interface
151013	9,095	50.12 / 7269	Zr-U10Mo Interface
151014	10,684	58.88 / 8540	Adhesive
151015	9,738	53.66 / 7783	Zr-U10Mo Interface

Table 2. Summary of Bond Strength Testing

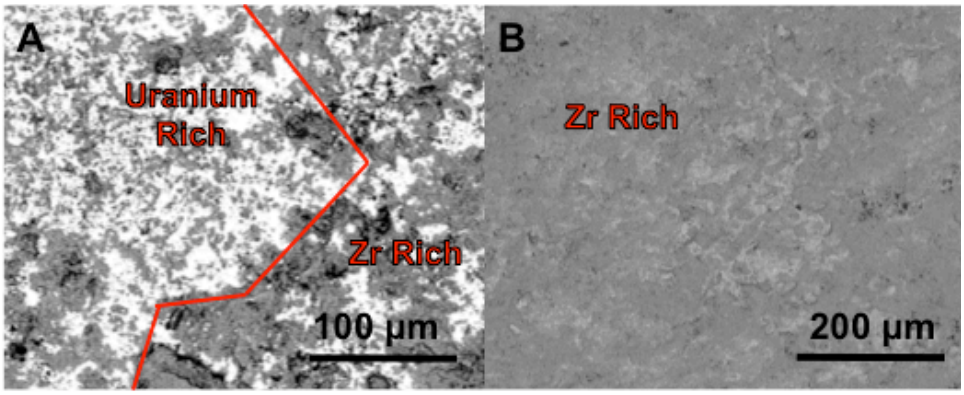

Fig. 3. A) Backscattered electron SEM image of Sample ID# 151007 fracture surface following tensile strength testing (weakest bond). B) Backscattered SEM image of Sample ID# 151014 fracture surface following tensile strength testing (strongest bond). The concentration of uranium is much higher in A) fracture surface, indicative that the fracture occurred at the Zr-U10Mo interface, as compared with the more uniform Zr coating in B) where the fracture occurred in the testing epoxy.

3.2 Zr-U Interfacial Layer Characterization

To characterize the Zr coating and interfacial phenomenon, the coated DU-10Mo foil was cross-sectioned, mounted in epoxy, and polished using standard metallographic techniques. Before imaging with scanning electron microscopy (SEM), the mount was sputtered with a thin layer of carbon to improve conductivity.

The Zr coated DU-10Mo foil with the strongest bond strength (ID# 151014) was SEM imaged using a backscattered electron detector. Backscattered electrons result from elastic scattering of the incident beam with the sample; higher Z (atomic number) elements are more likely to produce elastic collisions and appear “brighter” in a backscattered electron image, allowing for composition analysis of a sample, compared to the topographic information provided by conventional, secondary electron SEM. Backscattered imaging of the coated foil can be seen in Figure 4, along with selected area elemental analysis (using standard-less energy dispersive spectroscopy or EDS) of the Zr coating, DU-10Mo foil, and interfacial layer. The high carbon content in the elemental analysis, and to some extent the oxygen content, result from a combination of the polymer epoxy mount and carbon surface sputtering and should be regarded as background.

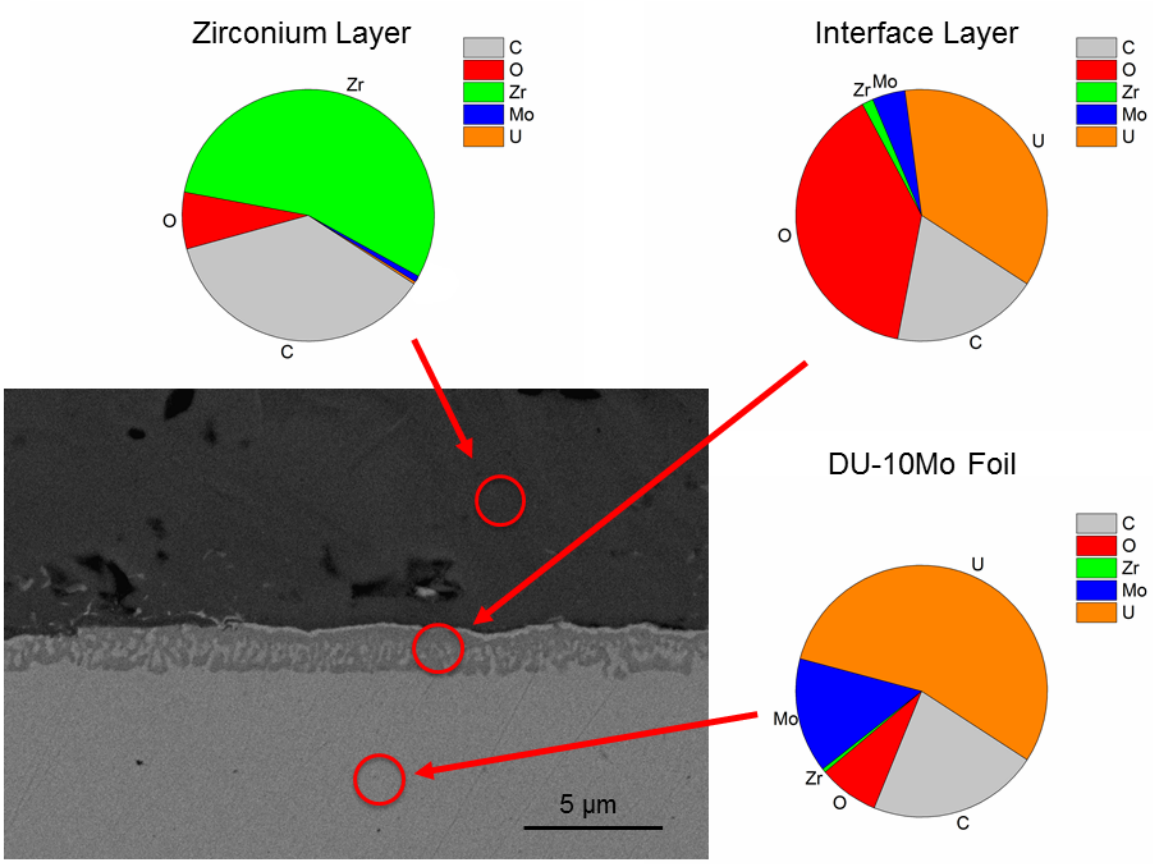

Fig 4. Backscattered SEM imaging of Zr plasma spray coated DU-10Mo foil cross section (ID# 151014), highlighting the Zr-U interface. Pie charts show result of EDS elemental analysis (atomic percentage) of the Zr coating, Zr-U interfacial layer, and bulk U foil, respectively.

EDS Element	Zr Barrier	DU-10Mo	Interface
C	36.52%	21.99%	0.19%
O	7.29%	7.75%	39.15%
Zr	55.06%	0.50%	1.44%
Mo	0.81%	14.76%	4.21%
U	0.32%	55.00%	36.31%

Table 3. EDS Elemental Analysis (atomic %) of Zr coated DU10Mo ID#151014

Backscattered electron imaging of the interfacial layer seems to show an interdiffusion Zr-U layer of ~ 1 micron thickness. This interfacial layer is relatively uniform across the entire length of the coated foil. Table 3 quantifies the selected area elemental analysis. As expected, the Zr coating is almost pure Zr metal, with minimal oxidation; likewise, the bulk DU-10Mo foil is predominantly U and Mo. However, spot analysis of the interfacial layer shows a strong oxidation signal, almost equimolar with uranium. There is also a trace amount of Zr, which indicates diffusion of Zr, but not as significant as would be expected in a Zr-U intermetallic layer. More sensitive characterization is necessary to determine if this interfacial is an existing uranium oxide prior to spraying, or an U-Mo-Zr-O interfacial layer formed during deposition.

Comparison of the approximate interfacial layer thickness, together with plasma spray processing temperatures with the bond strength is shown in Table 4. The effect of interfacial layer thickness and plasma spray temperature on the Zr-DU10Mo bond strength is graphically compared (Figure 5). Clearly, there is a correlation between increased bonding temperature during the plasma spray process and the resulting bond strength, with the highest strength bond (ID# 151014) having the highest processing temperatures. Also, the approximate thickness of the interfacial layer increases with processing temperature, and seems to correlates with bond strength. More in depth and sophisticated characterization of the composition of this interfacial layer and its effects on bond strength must be performed. Also, post processing heat treatments of the Zr coated foils, in order to artificially increase of diffusion of the Zr-DU10Mo system and the thickness of the interfacial layer, will give a much clearer idea of the impact of processing conditions on the resulting bond strength.

Sample ID	Bond Strength (MPa)	Bond Temp (°C)	Interface Layer Thickness (μm)
151007	36.23	602	0.263
151008	37.60	655	0.648
151013	50.12	726	0.868
151014	58.88	843	1.185
151015	53.66	776	0.83

Table 4. Effects of Processing Temperature and Interface on Bond Strength

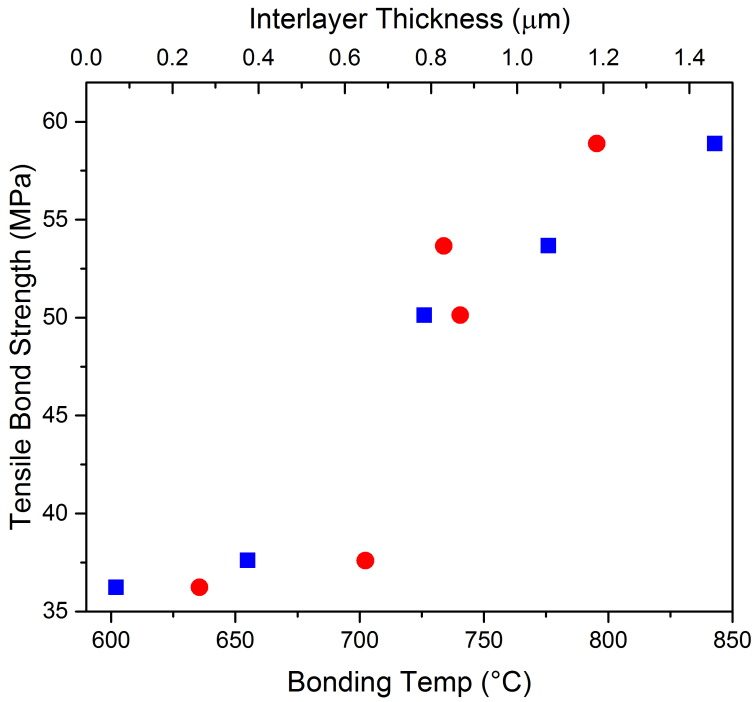

Figure 5. Effect of bonding temperature (blue square – bottom axis) and interfacial layer thickness (red circle – top axis) on the Zr-U10Mo bond strength.

4. Conclusions

In this work, the effects of substrate temperature and corresponding interfacial layer thickness on bond strength of plasma sprayed Zr diffusion barrier coatings on DU-10Mo are investigated. The integrity of the Zr-U bond is quantitatively measured by room temperature quasi-static tensile strength testing. There is a clear correlation between improved bond strength and higher substrate temperature during plasma spraying. There also appears to be a correlation between improved bond strength and thickness of the interfacial layer between the Zr coating and the DU-10Mo surface. Microscopic elemental analysis shows this ~1 μm interfacial layer is composed of U, Mo, Zr, and O. Further characterization will help elucidate the composition of this interface and what role it may play in coating bond strength.

5. Acknowledgments

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6. References

[1] K. J. Hollis, “Diffusion Barrier Coatings for Uranium Fuel used in Nuclear Reactors”, Advanced Materials & Processes, Vol. 168, No. 11 (2010), 57-59.

[2] K. J. Hollis, “Plasma Spraying of Diffusion Barrier Coatings for LEU Monolithic Fuel”, Proc. RERTR 2012 – 34th International Meeting on Reduced Enrichment for Research and Test Reactors, Warsaw, Poland, October, 2012.

[3] K.J. Hollis, R. Leckie, and D.E. Dombrowski, “Plasma Sprayed Zirconium for US HPRR LEU Conversion Fuel Diffusion Barrier, Proc. RERTR 2012 – 35th International Meeting on Reduced Enrichment for Research and Test Reactors, Vienna, Austria, October, 2014.

[4] K.J. Hollis, D.R. Cummins, and D.E. Dombrowski, “Optimization of Zirconium Plasma Spraying for MP-1 Fabrication”, Proc. RERTR 2015 – 36th International Meeting on Reduced Enrichment for Research and Test Reactors, Seoul, South Korea, 2015.

[5] K. Hollis, C. Liu, R. Leckie, M. Lovato, “Bulge Testing and Interface Fracture Characterization of Plasma Sprayed and HIP Bonded Zr Coatings on U-Mo”, Journal of Thermal Spray Technology, Vol. 24 Issue 1 (2015), pp. 271-279.

[6] Hollis, K., N. Mara, R. Field, T. Wynn, J. Crapps, P. Dickerson: Characterization of Plasma Sprayed Zirconium on Uranium Alloy by Microcantilever Testing. Journal of Thermal Spray Technology, 22 (March 2013), Issue 2-3, pp. 233/41.

[7] K.J. Hollis, M.E. Hawley, P.O Dickerson, “Characterization of Thermal Diffusion Related Properties in Plasma Sprayed Zirconium Coatings”, J. Therm. Spray Technol., 21(3-4), June 2012, p 409-15.