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Optimization of Zirconium Plasma Spraying for MP-1 Fabrication

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ABSTRACT

Plasma spraying of zirconium (Zr) in being investigated for the diffusion barrier between the U-Mo fissile material and the aluminum cladding for US HPRR LEU fuel. Interest in plasma spraying is in part due to the application of the Zr to the U-Mo late in the manufacturing process allowing for the more efficient recycle of scrap fuel material which allows higher uranium utilization. Activities involving plasma sprayed Zr for the upcoming MP-1 irradiation tests in the Advanced Test Reactor (ATR) are discussed including U-Mo sample cleanliness measurements, a technique for coating the edges of the samples and comparison of techniques for Zr coating thickness measurement.

1. Introduction

The U.S. Department of Energy National Nuclear Security Administration (DOE/NNSA) Office of Material Management and Minimization (M^3) Reactor Conversion Program aims to reduce or eliminate the use of highly enriched uranium (HEU) dispersion fuels in high-powered research reactors in the United States by replacement with low enriched uranium (LEU) alloy monolithic fuel plates. The upcoming irradiation test for the monolithic fuel developed under this program is called MP-1 and will be irradiated in the ATR reactor at Idaho National Laboratory. The MP-1 test will allow for the evaluation of various fabrication techniques in an effort to down select to the most promising fabrication process. The primary fabrication independent variable in the MP-1 samples is the method used to apply a zirconium (Zr) diffusion barrier between the U-Mo fuel and the aluminum alloy cladding. This barrier prevents the formation of compounds in the U-Al system to minimize the chances of fuel swelling during irradiation.

One of the Zr barrier fabrication techniques is plasma spraying [1,2]. The specifications for the MP-1 samples require complete coverage of the top and bottom sample surfaces with Zr in the thickness range of 25 +/- 12.5 microns [3]. In addition, for the diffusion barrier to be successful, it must remain adhered to both the U-Mo fuel and the Al cladding throughout the irradiation period. Also important in the performance of the Zr barrier is its ability to transfer heat from the fuel to the cladding to avoid overheating the fuel. Both the bonding between the U-Mo and the Zr [4] and the heat transfer across this interface depend on the cleanliness of the U-Mo surface before coating.

In order to quickly assess the surface cleanliness of the U-Mo foils before coating with Zr, the photoelectron emission surface characterization technique was chosen. This technique uses UV photons to cause the emission of photoelectrons from the sample surface. The photoelectron current collected depends on the photoelectron work function of the base sample material as well as those of the surface layers. In general, metal oxides on a metal surface decrease the photoelectron current emitted. Other contaminants can increase or decrease the current compared to the base metal sample. Therefore, the technique does not provide a definitive thickness and composition of surface contaminants but does provide a relative comparison to a known surface condition such as a freshly cleaned surface of a given composition substrate.

A non-destructive measurement of the thickness of a plasma sprayed coating that is in the range of 20 to 80 μm presents a challenge. Energy-dispersive x-ray fluorescence spectrometry (XRF) for measuring Zr coating thickness on was developed at Los Alamos National Laboratory by Thomas Claytor and Deborah Summa [5]. An inexpensive, handheld XRF instrument was chosen for rapid, non-destructive estimation of Zr coating thickness. Although XRF is not usually marketed as a thickness measurement tool, laboratory XRF systems have been used in both absorption and emission modes to assess the thickness of coatings or cladding layers [6-7]. In cases where there is a substrate capable of producing detectable fluorescence emission and where the coating is thin enough for fluorescing x-rays from the base layer to reach the surface (i.e., coating thickness less than the coating material saturation thickness for the substrate material element energy lines), the intensity of the substrate layer signal decreases as the coating thickness increases, with the intensity and thickness being related through the Beer-Lambert law. Similarly, relative intensity of fluorescing elements within the coating itself increases with increasing coating thickness. Provided the coatings are thin enough to permit detection of at least some signal from the substrate and assuming sampling parameters remain fixed, these principles can be used to construct calibration curves for coating thickness. Because XRF is an inherently stochastic process with secondary fluorescence, scattering, transition probabilities, fluorescence yield, etc. all affecting the measured intensities, an empirical calibration procedure is necessary to correlate absolute thickness of the coating with measured XRF signal intensities. Such calibrations are specific to the coating/substrate material combination being investigated.

XRF Zr coating thickness measurements were compared to other more standard techniques. The mass change of the sample after coating was used to estimate the coating thickness with a known coated area and coating density. A contact ball-end micrometer was used to measure the sample thickness before and after coating. A laser profilometer was used to measure sample thickness before and after coating to calculate a coating thickness. Finally, cross sectional optical metallography was used to determine the coating thickness along a single section of the sample. These five techniques were compared on a single sample of Zr coated stainless steel.

2. Experimental Procedure

2.1 Surface Cleanliness

In order to assess the cleanliness of the U-Mo surface, a photoelectron emission instrument was used (SQM 200, Photo Emission Tech., Camarillo, CA, USA). The gain on the detector in the instrument head was set to position 6 and the gain on the instrument controller was set to position 1. The distance between the sample surface and the head measurement end was maintained at 3 mm. Figure 1 shows the instrument setup for this experiment.

A U-10 wt.% Mo foil sample with dimensions 25 mm x 100 mm x 0.350 mm was used for the photoelectron emission measurements. The sample had identification label writing on one side using a “Sharpie” marker pen. The sample was scanned down the center-line at approximately equal spacing on both sides before and after cleaning. The cleaning procedure consisted of a detergent cleaning followed by a caustic cleaning (10% NaOH) followed by an acid cleaning (50% HNO_3) with a final rinse in deionized water.

Fig. 1. Photoelectron measurement instrument with the UV source and electron detector on the left side of the image above the grounded sample holding surface.

2.2 Plasma Spraying

Plasma spraying of Zr onto a stainless steel (SS) substrate (surrogate for U-Mo) was conducted using the parameters shown in Table 1. The SS sample of size 25 mm x 89 mm x 0.25 mm was mounted on a square tube fixture and rotated while the plasma torch traversed over the sample. The sample was held on the edge by tapered head screws as shown in Fig. 2. Prior to spraying, the vacuum chamber was evacuated to 0.02 mbar then back filled with argon to the processing pressure.

Table 1. Plasma spray parameters for Zr coatings.

Parameter	Value
Current (A)	950
Voltage (V)	35
Argon arc gas (SLM)	25
Helium arc gas (SLM)	30
Argon powder gas (SLM)	2.5
Standoff distance (mm)	275
Chamber pressure (mbar)	92
Part rotation speed (RPM)	120

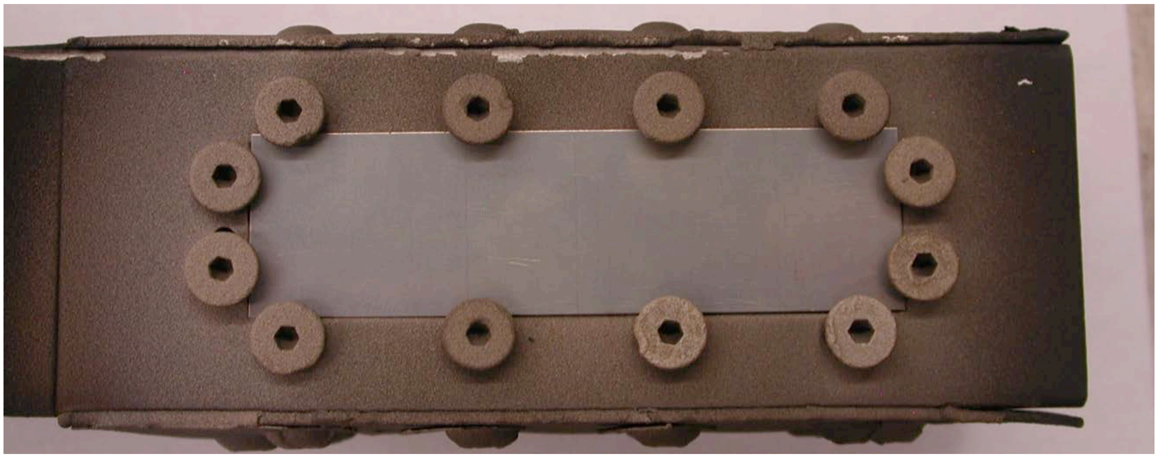

Fig. 2. Sample mounted in square tube using tapered head screws prior to Zr plasma spraying.

2.3 Coating Thickness Measurement

Mass Change Measurement

Each sample was weighed before and after coating. The coated area was measured using a caliper. The average thickness of the coating was estimated using Eq. 1:

$$t = \Delta m / (A \text{ x } \rho \square \qquad \text{Eq.} \quad \square\square$$

where t is the coating average thickness, Δm is the change in sample mass after coating, A is the coated area and ρ is the mass density of the coating.

Metallography

A coating cross section was prepared for light optical metallography (LOM) observation using standard sectioning, mounting and polishing techniques. Measurements of coating thickness were made across the narrower dimension of the substrate at regular distance intervals. A single coating thickness value was calculated by averaging the values taken along the entire coating cross section.

XRF Measurement

The instrument used for handheld XRF measurements was a 50kV, 2W (model Niton XL3t GOLDD+, Thermo Fisher Scientific, Waltham, MA, USA) analyzer with a spot size of 3 mm shown in Fig. 3. Sampling time was 30 seconds per measurement. For calibration purposes, a minimum of 5 measurements per sample configuration (Zr foil thickness) was taken. The analyzer stores each measured spectrum along with count rates at each energy peak. Software routines based on the Method of Fundamental Parameters accounts for the source profile, internal source/detector geometry and inter-element interactions before converting the measured intensities to elemental concentrations.

To calibrate the handheld XRF instrument to the Zr foil thickness, high-purity Zr foils of known thickness were laid over the bare SS plate and a series of five XRF spectra (30 second count time) were taken for each Zr foil thickness. Stacking the Zr foils in various combinations yielded 13 unique thicknesses ranging from no Zr to 0.048 mm. For each spectrum, the built-in software within the XRF analyzer computes a normalized chemistry, reporting all elements detected and the weight percentage of each present in the total. After the data was acquired for each Zr thickness, elemental composition expressed as a percentage of the total was calculated.

Fig. 3. Handheld XRF instrument measuring the Zr thickness of a coated sample.

Laser Profilometer Measurements

A laser profilometer system (Fig. 4) consisting of two opposed measurement heads (LJ-V7060, Keyence Corporation, Osaka, Japan) is used to measure the coating thickness. The signals from each of the heads were combined to give a measurement of the substrate plus coating thickness. Using two heads allows for minimizing the effect of sample curvature on the thickness

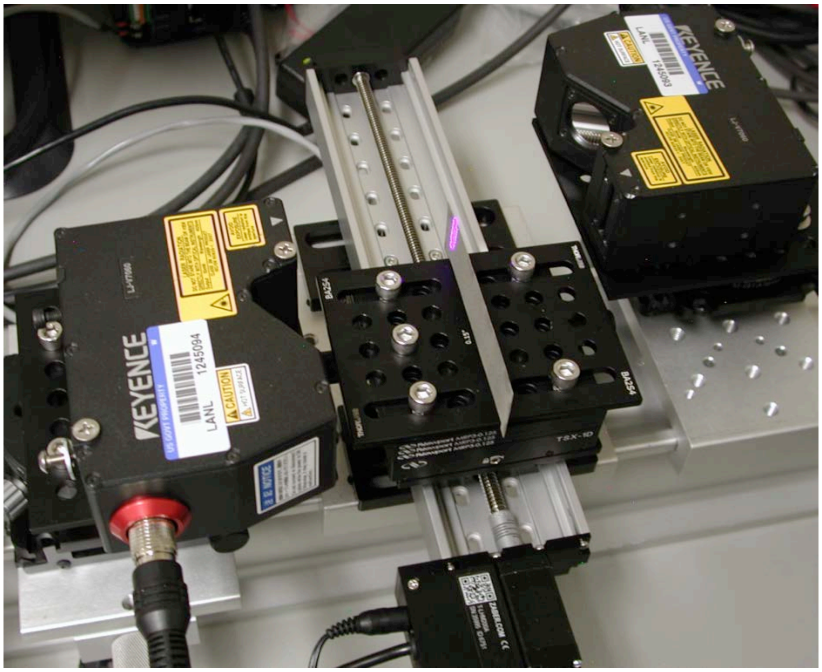

Fig. 4. Laser profilometer system with two heads (left and right) and a sample motion stage in the center.

determination. Each head measures along a line of length 15 mm with 800 data points in that length. The sample is moved while the heads record the thickness along the laser line. The combination of a line measurement with substrate motion allows for a three dimensional reconstruction of the sample thickness.

3. Results and Discussion

3.1 Surface Cleanliness Measurements

The resulting measured photoelectron current values are shown in Fig. 5. Side 1 had sample identification writing and at the location of the writing the current is higher than the surrounding areas without writing. Side 2 did not have writing and the measurements are more uniform and lower than for side 1. After cleaning, both sides had a fairly uniform current that was larger than the areas without writing before cleaning. This indicates that the writing has a high emission current and the oxide has a low emission current. Removing both the oxide and the writing reveals the current characteristic of the clean U-Mo substrate in the post-clean data.

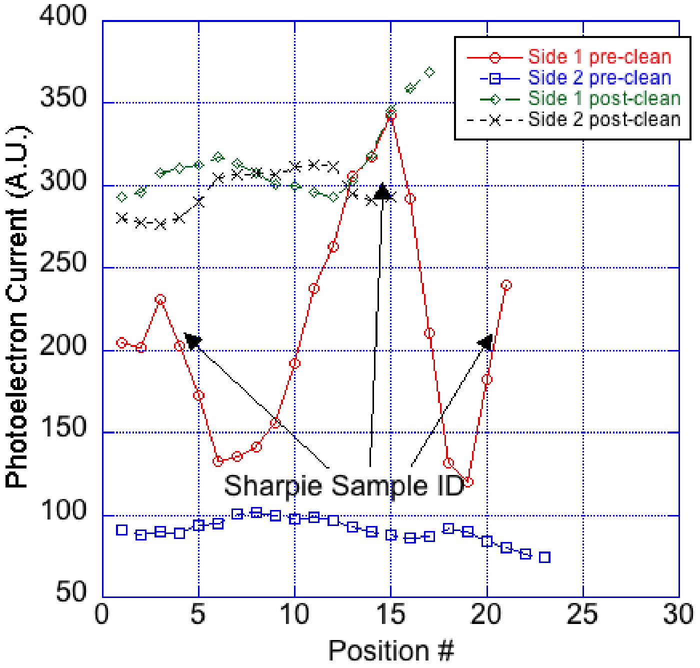

Fig. 5. Photoelectron current from U-Mo sample measured on both sides before and after cleaning.

3.2 Coating Coverage

Figure 6 shows the sample sprayed using the setup shown in Fig. 2. The coating extends to the edge of the sample and also covers the edge as shown in the SEM images in Fig. 7 and 8. This demonstrates the ability of the plasma spray process to coat two surfaces that are perpendicular to each other in a single coating run. This allows additional protection (compared to uncoated edges) against the U-Al reaction on the edges of the sample.

At the location of the hold down screws, there is a small area on the top and bottom of the sample with a thin coating due to the shadowing effect of the screw head. By tilting the sample with respect to the plasma torch, this area can be minimized. Experiments to optimize the coverage under the screw heads are in progress now.

Fig. 6. Surface of Zr coated SS sample sprayed using the tapered head screws.

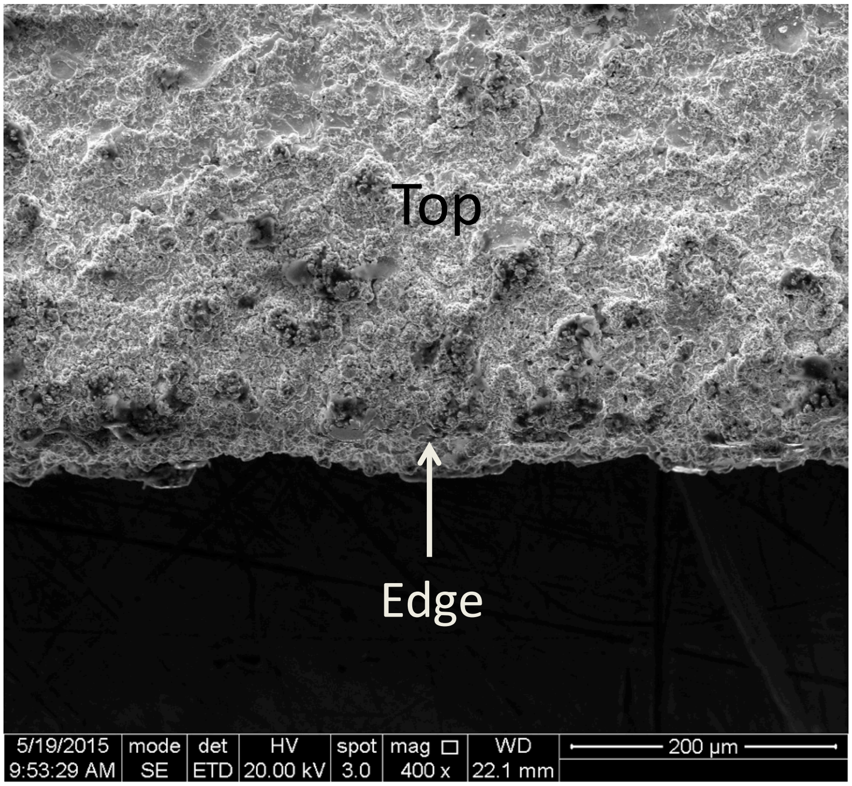

Fig. 7. Zr plasma sprayed coating shown on the top and edge of the SS sample.

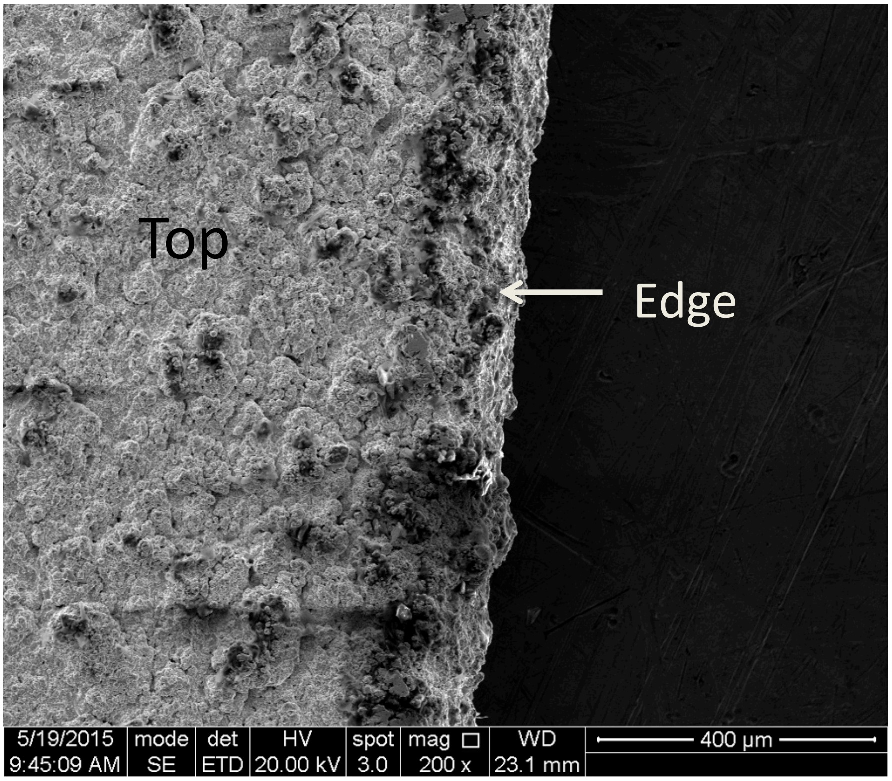

Fig. 8. Zr plasma sprayed coating shown on the top and edge of the SS sample.

3.3 Coating Thickness Measurements

The XRF instrument calibration data is shown in Fig. 9. As the thickness of the Zr foils increases, the Zr signal strength increases and the Fe signal strength decreases as expected. The signal strength varies in a non-linear fashion with the Zr thickness. This causes the XRF instrument to be more sensitive to Zr thickness in the range 0-20 microns and less sensitive in the 20-30 micron range. Beyond 30 microns, there is little sensitivity to Zr thickness.

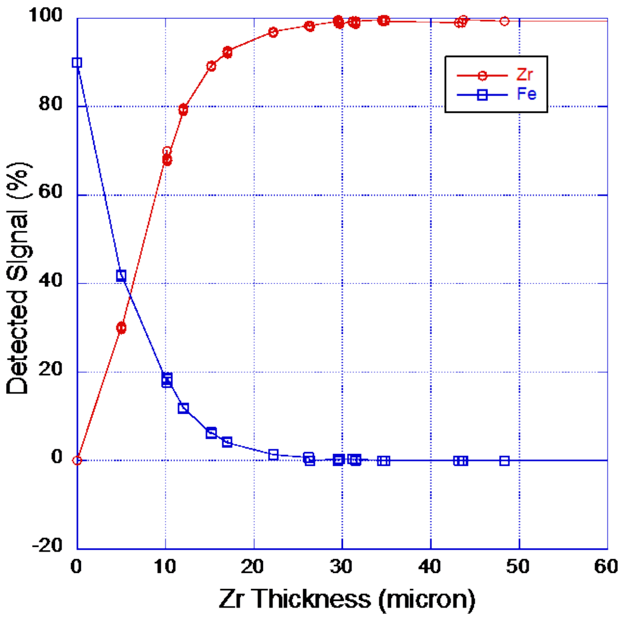

Fig. 9. XRF signal calibration curve for Zr coating on stainless steel.

Zr plasma sprayed coating thickness measurements from five techniques are shown in Fig. 10. The mass gain technique gives only a single equivalent thickness for the entire sample. In Fig. 10, the micrometer gives the greatest average value for thickness. This can be understood since the contact ball of the micrometer touches the features on the coating surface that protrude the most. Therefore, the micrometer would be expected to give a thicker measurement of coating thickness compared to the other techniques. The mass gain equivalent thickness is less than the average thickness values for the micrometer, laser profilometer and microscope techniques and greater than the XRF average thickness value. The mass gain technique is insensitive to spatially varying coating thickness so at any given location, the mass gain equivalent thickness could deviate from the actual thickness significantly. The XRF measurement gives the lowest thickness values of the five techniques for this sample. This is due to the calibration procedure and the non-linear response of the XRF instrument to coating thickness. The effective Zr thickness measurement range is only up to 30 microns on SS. Therefore, any Zr thickness above 30 microns will not be accurately measured but instead will be assigned a value of approximately 30 microns. The flat foils used for calibration and the plasma sprayed coating with peak-to-peak thickness variation of 20-40 microns also causes the XRF thickness measurement to be low. Since any actual thickness more than 30 microns is assigned the value of 30 microns, the coating peaks are effectively clipped off. In addition, the non-linear calibration curve causes the thinner Zr regions to be more heavily weighted in the thickness calculation. These factors combine to cause the XRF Zr thickness to be lower than the actual Zr average thickness. The laser profilometer thickness values closely approximate those of the cross sectional microscope image in both the average value and the height variation. Since the measurements were made on slightly different locations of the sample, exact agreement is not expected.

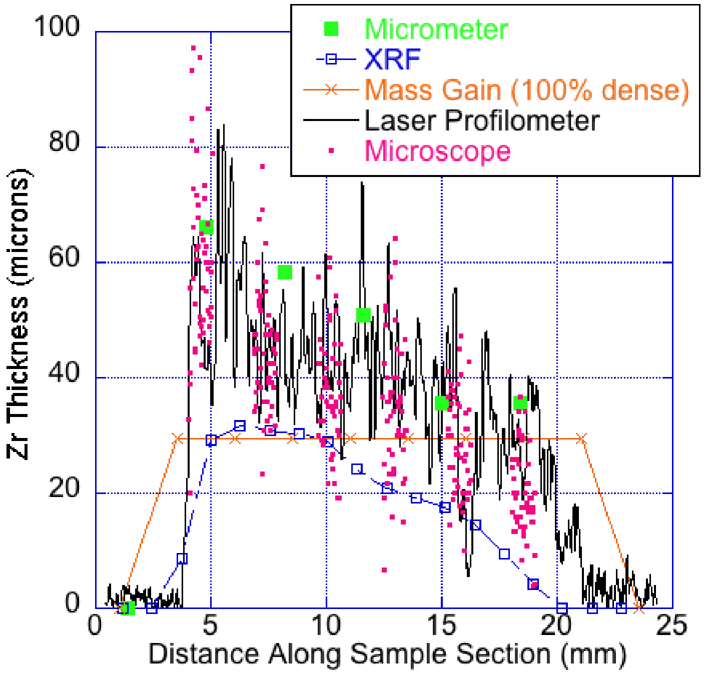

Fig. 10. Comparison of several techniques for measuring Zr thickness.

4. Summary

Recent results for the optimization of Zr plasma sprayed coatings for production of MP-1 reactor test foils have demonstrated the following:

- Photoelectron emission current measurement of U-Mo foils before and after cleaning shows a clear difference with an increase in current for the clean U-Mo surface. In addition, identification markings on the sample were shown to increase photoelectron current compared to the oxidized surface prior to cleaning.
- The use of tapered screws for mounting samples during plasma spraying allows for the coating of the top and bottom surfaces in addition to the edge surfaces. The more complete coating offers more protected surface area to prevent U-Al compound formation.
- Various Zr coating thickness measurement techniques were compared. Micrometer and XRF measurements deviate from the actual thickness for rough coatings. Laser profilometer measurements closely match the destructive analysis results obtained using a microscope to view the sample cross section.

5. Acknowledgements

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