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Elastic measurements of plasma spray refractory metal coatings using thermal cycling of bi-layered beams

Andrew Vackel[1], Emma Peleg[1,2], Jack Varga[1], Mia Blea[1], Carl Schmidt[2], Edward Gildersleeve[2]
[1] Sandia National Laboratories, Albuquerque, NM, USA [2] Stony Brook University, Stony Brook, NY, USA

Abstract
This paper presents the results of two metals coatings, molybdenum and tantalum, prepared by Controlled Atmosphere Plasma Spray (CAPS) onto Al 6061 substrates that were thermal cycled to calculate the effective coating modulus. Traditional uniaxial tensile testing samples were prepared from thicker duplicate coatings for comparison, as well as to measure thermal expansion properties and oxygen and nitrogen content. The molybdenum samples cut from thicker coatings were un-able to be tensile tested due to their fragility. Thermal cycle testing of molybdenum on an Al 6061 substrate was found to have a modulus approximately 18 to 19% of literature values for bulk molybdenum using the bi-layer beam thermal cycling method. Additionally, non-linear modulus behaviour was observed in the molybdenum sample when enough thermal strain was induced to shift the coating from a compressive to tensile stress state. The tantalum coating was found to have a modulus approximately 42 to 46% of literature values for bulk tantalum using the bi-layer thermal cycling method. Traditional tensile testing measured a modulus approximately 44 to 46% of bulk, which shows good agreement between the two methods and supports that the bi-layer thermal cycling method is valid for plasma sprayed refractory metal coatings.

1 Introduction

The mechanical properties of thermal spray coatings are important properties that are needed to properly predict mechanical response of a coated structure. While it is not expected that the atom-to-atom elastic modulus of a material phase should be greatly altered by thermal spray processing (i.e., within crystallized grains of individual splats of material), the porous microstructure of a thermal spray coating can be expected to have a different “effective” elastic modulus (herein referred to as simply as “modulus” or “moduli”). Measuring thermal spray coating moduli remains a challenging task due to the brittle nature of the relatively thin deposits that are mated to a substrate. Thermal cycling of bi-layered coating-substrate beams provides a method to measure the elastic behavior of the coating by simultaneously measuring changes in beam curvature as thermal strain is induced by the thermal expansion mismatch of the coating and substrate, given by the relationship in Equation 1 [1].

$$\frac{\Delta K}{\Delta T} = \Delta\alpha \frac{6E'_s E'_c ht(h+t)}{E'^2_s h^4 + E'^2_c t^4 + 2E'_s E'_c ht(2h^2 + 3ht + 2t^2)}$$

Equation 1. Relationship between change in curvature per change in temperature (ΔK/ΔT) of a bi-layered beam and the difference in linear thermal expansion between the coating and substrate (Δα), in-plane modulus (modulus/(1-Poisson ratio)) of the substrate and coating (E'_s, E'_c, respectively), and the thickness of the substrate and coating (h, t, respectively).

This technique requires accurate knowledge of the coefficient of thermal expansion (CTE) behavior of the coating and has been successfully performed for ceramic coatings [1-4]. However, use of this technique for metal coatings is complicated due to material oxidation occurring when coating deposition is performed in ambient environments, which results in uncertainty of the coating’s CTE behavior (coating CTE could be measured by dilatometry, but would still require a thick coating and machining for testing). This complication is minimized for metal materials sprayed in a controlled inert atmosphere, thus greater certainty in the elastic measurements of coatings using thermal cycling of bi-layered beams is achieved. This measurement method may be more conducive to typical thermal spray applications by allowing the measurement of a larger deposit area with a thin coating mated to a substrate as opposed to machining free-standing coatings out of thicker samples for traditional tensile testing. By eliminating the need for machining and thick deposits, measurement of coating moduli can be performed more rapidly for coating development efforts. Furthermore, unique observations such as non-linear moduli in the ceramic coatings reported in [1-4] provides further insight into coating behavior, which may not even be observable in traditional tensile testing should it exist in metallic coatings.

2 Experimental Methods

2.1 Sample Preparation

All samples were produced using the Controlled Atmosphere Plasma Spray (CAPS) system at Sandia National Labs. The CAPS system consists of an SG-100 plasma spray torch housed with a vacuum plasma spray chamber that can be evacuated and backfilled with either nitrogen or argon. Prior to performing all spray operations, the

CAPS chamber was evacuated to a pressure of <150mTorr, followed by backfilling with ultra-high purity argon to a pressure of 640 Torr[1]. Chamber pressure was maintained by a butterfly valve with feedback control during spraying. Argon was used as the primary gas and powder carrier gas. Helium was used as the secondary gas. Torch parameters for spraying are given in Table 1. The same torch parameters were used for both materials that were sprayed. The molybdenum and tantalum powders used for spraying were Metco 63NS and Amperit 150.074, respectively.

Table 1. SG-100 Plasma torch settings used for coating deposition.

Parameter	Setting
Anode/cathode/gas ring	730/720/112
Argon [slpm]	50
Helium [slpm]	12
Current [A]	540
Powder Carrier Gas [slpm]	3.0, internal injection
Spray Distance [mm]	100

Two sets of samples were generated for each material. The first set was sprayed to thicknesses >1mm. Coating material was cut by wire electro-discharge machining (performed in de-ionized water) to extract samples of appropriate dimensions for measurement of linear CTE, oxygen and nitrogen content, and tensile properties. Cut samples were lightly cleaned using sandpaper to remove re-cast residue from the cutting process. The second set of samples was sprayed to target a thickness of ~250µm and was deposited onto grit blasted Al-6061 beams with nominal dimensions of 25.4 x 229mm and were used for bi-layer beam thermal-cycling to determine the coating elastic modulus. Substrate curvature before and after spraying was measured using a Keyence VHX 7000. Thickness and mass of the thermal-cycling samples were measured by ball-micrometer and balance, respectively, before and after coating deposition.

2.2 Material Analysis

The CTE of the >1mm samples was measured using a DIL 402 Expedis with a SiC-element furnace and Al_2O_3 double sample carrier manufactured by Netzsch. A 3°C/min ramp rate under flowing argon at 20 mL/min was used. Thermal strain was measured as a function of temperature along the longest dimension (in-plane) of the test specimen (5 mm x 4 mm x ~1 mm). The linear CTE was determined from the change of thermal strain with respect to the temperature. Data collected in the third cycle between 25°C are 475°C are reported within this manuscript.

Elemental analysis of oxygen and nitrogen was performed on the tantalum and molybdenum powders and the >1mm deposits using an ONH 836 Interstitial analyzer. Prior to analysis the rectangular samples were cut into three equal pieces for triplicate analysis. The pieces were then rinsed with deionized water (3 x 2 mL) and acetone (3 x 2 mL) to remove any residue from the sanding and cutting process. The samples were then dried before analysis. All samples were placed in nickel capsules to aid in melting, then placed in a graphite crucible with graphite powder to convert any oxygen to carbon monoxide or carbon dioxide for analysis. Different quality control (QC) samples were measured to verify the analyzers were calibrated correctly. The QC's were run after the calibration, during the run, and after the run. All the QC's are well within the allowed range of the given value.

Tensile testing was performed on dog bone specimens cut from the >1mm deposits with a gauge length of 0.164 in {4.17mm} in uniaxial tension using an MTS Actuator LVDT load frame (S/N212) equipped with a 100 lbf load cell. For each test, strain data was collected using output from Digital Image Correlation (DIC) extensometers which met the length requirement of four times the specimen width. The DIC software used was Vic2d with subset size of 90x90 pixels. Specimens were loaded in tension at a displacement rate of 0.00082 in/s {0.021mm/s} until failure corresponding to a strain rate of 0.005 s^{-1} for the 0.164 in {4.17mm} gauge length. In addition to ductility, measurements of the ultimate tensile strength, yield stress and strain, elastic modulus, toughness, and uniform elongation were made for each sample.

Thermal-cycling and simultaneous curvature measurements of the bi-layer beam samples (with ~250 µm coating thickness) were performed using an Ex-situ Coating Property (ECP) sensor made by ReliaCoat Technologies. Samples were repeatedly thermal cycled between furnace temperatures of 25°C to ~250°C. Temperature was monitored by a thermocouple attached to the substrate. Curvature-temperature measurements of the bi-layered beams were used to calculate coating moduli using the previously measured substrate and substrate + coating

[1] Atmospheric pressure in Albuquerque, NM, USA is ~630 Torr, making the 640 Torr chamber pressure slightly positive relevant to ambient to prevent air leakage into the chamber during spraying.

thickness measurements and the properties given in Table 2 using Equation 1. Inverse analysis using the methods described in [1,2] was also performed to convert the measured data into stress-strain and to determine the degree of non-linearity of the coating moduli. Residual coating stress was also calculated for the as deposited samples using the Stoney formula [5], given in Equation 2.

Table 2. Properties used for analysis of bi-layered beam thermal cycling for coating modulus calculations.

Al-6061	
E_s	68.9 x10^9 Pa
v	0.33
α	23.6 x10^{-6}/°C
Molybdenum	
α	5.96 x 10^{-6}/°C
Tantalum	
α	6.69 x 10^{-6}/°C

$$\sigma_{residual} = \frac{E'_s h^2 \Delta K}{6t}$$

Equation 2. Stoney formula for calculating coating residual stress using the in-plane modulus (modulus/(1-Poisson ratio) of the substrate (E'_s), the change in in substrate curvature before and after coating deposition (ΔK), and the thickness of the substrate and coating (h, t, respectively).

Metallographic cross sections were prepared from three sections within each bi-layer sample after thermal cycling and examined by Scanning Electron Microscopy in Backscatter Electron mode (SEM-BSE). Image analysis was performed using a custom Python script and the multi-Otsu method [6] to determine sample porosity at a magnification of 500x.

3 Results

3.1 Coefficient of Thermal Expansion (CTE)

Measured linear CTE of the samples cut from the >1mm thick coatings were 5.71 x 10^{-6}/°C for molybdenum and 6.97 x 10^{-6}/°C for tantalum for 25°C to 475°C. Measured results were generally within ±10% of reported bulk values (Table 2), minimizing the expected error expected when analysing the results of bi-layer beam thermal cycling (demonstrated in Section 4).

3.2 Chemical Analysis

Measured oxygen and nitrogen content of the coatings (>1mm thick) of the two materials are given in Table 3. The difference between the measurements in the coatings and powders are given as well. Modest increases in oxygen and nitrogen levels were measured for both materials except for oxygen in molybdenum.

Table 3. Oxygen and nitrogen content of feedstock powders and >1mm coatings

	Mo	Ta
Powder Oxygen wt. %	0.1361 ± 0.0013	0.0439 ± 0.0072
Coating Oxygen wt. %	0.1200 ± 0.0112	0.0916 ± 0.0095
Powder Nitrogen wt. %	0.0114 ± 0.0009	0.0696 ± 0.0207
Coating Nitrogen wt. %	0.0802 ± 0.0003	0.0942 ± 0.0395

3.3 Tensile Testing

Tensile testing was performed only on samples cut from the >1mm tantalum coatings. The molybdenum samples were too fragile and brittle to cut and perform tensile testing. The stress-strain data for the three tantalum samples are given in Figure 1. Ultimate tensile strength, ductility, and the elastic modulus were calculated for the three samples. Averages and standard deviations (as ±) were 114 ± 54 MPa for the ultimate tensile strength, 0.15 ± 0.06% ductility, and 82 ± 4 GPa for the elastic modulus.

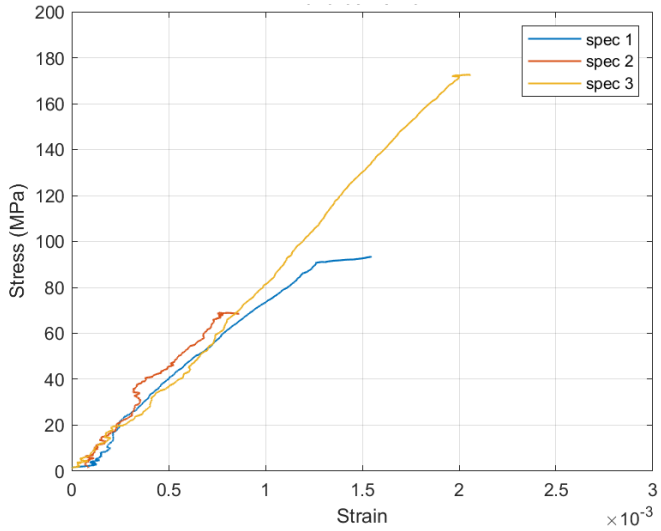

Figure 1. Stress-strain data for tensile samples cut from >1mm thick tantalum coatings.

3.4 Bi-layer Thermal Cycling

Thickness and curvature measurements of the molybdenum and tantalum samples prepared for bi-layer thermal cycling are given in Table 4 as well as calculations of the coating density made by dividing the coating mass by coating thickness and sample surface area. Comparison to bulk densities were calculated and are reported. Calculation of the coating residual stress using the Stoney formula in Equation 2 are also reported in Table 4 (note: the ± uncertainty calculations for residual stress did not include a curvature uncertainty component).

Table 4. Thickness and curvature measurements of the bi-layered beams used for thermal cycling. Measurements were used to calculate coating density, percent of theoretical density, and coating residual stress

Sample	Mo on Al 6061	Ta on Al 6061
Substrate Thickness [mm]	2.230 ± 0.001	2.221 ± 0.001
Coating Thickness [mm]	252 ± 2	229 ± 3
Pre-Spray Curvature [m^{-1}]	0.090	0.074
Post-Spray Curvature [m^{-1}]	0.289	0.363
Coating Density [g/cm^3]	8.4 ± 0.1	14.8 ± 0.6
% of theoretical density	~82	~89
Coating Residual Stress [MPa]	-67.2 ± 0.9	-106.5 ± 1.5

Curvature vs. temperature data from two thermal cycles of the bi-layered beams are given in Figure 2 (Note that the initial curvature data is tared to 0 m^{-1}). The approximate temperature at which the coatings should transition from a compressive to a tensile stress state based on the pre-test curvature and curvature-temperature relationship is indicated by the dotted line on the plots (both coatings were calculated to be in a compressive residual stress state at room temperature, as reported in Table 4). The heating and cooling portion of the thermal cycle is indicated on the molybdenum on Al 6061 sample but is less distinguishable for the tantalum on Al 6061 sample.

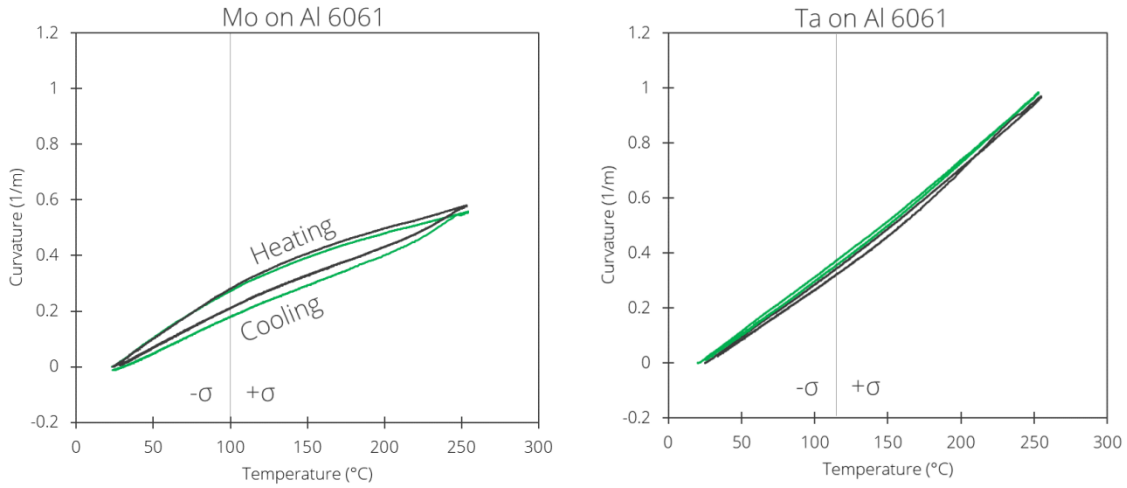

Figure 2. Curvature-temperature data for bi-layered thermal cycled samples. Heating and cooling portions of the thermal cycle is indicated on the Mo on Al 6061 sample. The temperature at which the coating is expected to transition from a compressive to tensile state is indicated by the dotted line.

3.5 Microstructure

SEM-BSE micrographs of the molybdenum and tantalum coatings cut from the bi-layer thermal cycling samples are shown in Figure 3. Image analysis on the coatings measure a porosity content of 10.9 ± 1.1% for the molybdenum coating and 5.7 ± 0.5% for the tantalum coating.

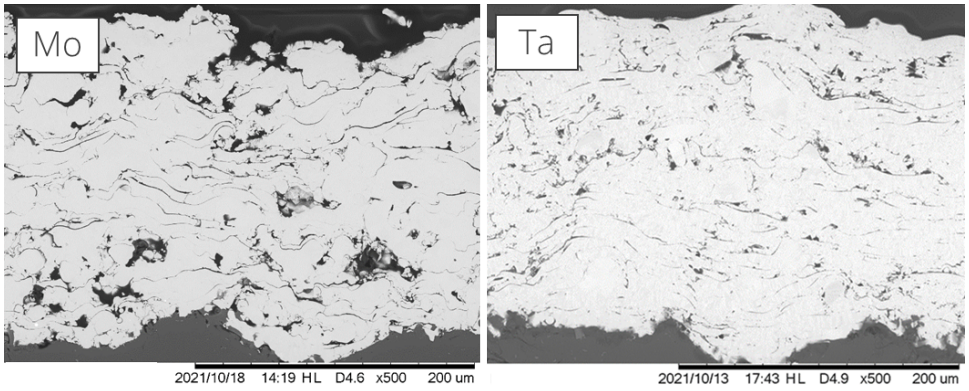

Figure 3. SEM-BSE micrographs of molybdenum and tantalum coatings cut from the bi-layer thermal cycling samples

4 Discussion

As seen in Equation 1 and discussed in the introduction, using bi-layer beam thermal cycling to calculate coating moduli requires that the CTE of both the substrate and coating is known. It can be reasonably expected that the Al 6061 substrates have the same CTE properties as those reported in literature though the same cannot be expected of thermal sprayed metals due to processing induced phases changes or reactions, particularly oxidation. The argon spraying atmosphere and inert processing gases (i.e., argon, helium) of CAPS was used to minimize oxidation (or nitriding), thus minimizing deviations for the coating's CTE from those of bulk materials. CTE measurements for the two coatings were within ±10% of bulk reported values. The low CTE of refractory metals and the high CTE of Al 6061 is expected to amplify curvature vs. temperature response as seen in Equation 1 and a difference of ≤10% for the coating CTE leads to a difference of ~5% or less in the $\Delta\alpha$ term with these coating-substrate pairings. Thus, the approach of using reported bulk CTE values for the coating materials for modulus analysis is justified. The effect on coating modulus calculations from these assumptions are discussed below.

The tensile testing performed on the tantalum samples that were cut from the >1mm thick coating highlight the brittle nature of the coating, with little to no ductility observed. While it is known that oxygen embrittles tantalum, Klop et al. [8] report ductility on the order of ~5% for room temperature tensile properties of bulk tantalum with oxygen content up to ~0.17 wt.% as opposed to the ~0.15% ductility measure for ~0.1wt. % oxygen in the CAPS tantalum coatings. Nitrogen also embrittles tantalum but it is likely that the porosity within the coating microstructure contributes to the tantalum coating's very low ductility. The porosity within the microstructure is also likely to be the principal cause of the highly variable ultimate tensile strength of the tantalum coatings, where the stochastic position, orientation, and size of pores and inter-particle gaps act as defects and failure initiation sites. The modulus of the coatings measured by the tensile testing were reasonably repeatable with an average value of 82 ± 4 GPa and correspond to a range roughly 42 to 46% of bulk tantalum. Kopp et al [8] also report an ~8% increase in the modulus of tantalum with oxygen content ~0.17wt. %, which would correspond to the tensile testing results having a range roughly 39 to 43% of tantalum with ~0.17 wt. % oxygen content (which is close to the combined amount of oxygen and nitrogen measured in the coatings, assuming they embrittle tantalum similarly).

Comparison of the density and porosity measurements using the mass per volume technique and cross section image analysis, respectively, for the bi-layer beam samples leads to some disagreement between the two methods though both qualitatively indicate the molybdenum coating to be less dense/more porous than the tantalum coating. The mass per volume technique resulted in consistently higher coating porosity (~18% for molybdenum, ~11% for tantalum) compared to the image analysis technique (~11% for molybdenum, ~6% for tantalum). Though the metallographic cross sections were prepared from the samples after thermal cycling, it is highly un-likely that the coating densified from thermal cycling based on the low homologous temperatures experience by the coatings (~0.10 for molybdenum, 0.08 for tantalum). Potential reasons for the difference in measured porosity between

these two techniques may be due to systematic error in coating thickness (e.g., coating roughness) or inaccurate area measurement for the mass per volume technique or un-optimized metallographic sample preparation that obscures porosity in the image analysis technique. Greater certainty in porosity/density measurements will be necessary should a correlation between coating porosity and modulus be made in future studies.

Residual stress calculations of the two coatings made using the Stoney formula (Equation 2) indicate both coatings are in compression. Coating formation during plasma spray typically results in a tensile stress in the coating material as molten droplets under-go constrained shrinking as the adhered material cools and solidifies (with several forms of strain relaxation possible) [9]. However, elevated substrate temperatures and the smaller CTE of the coatings would induce compressive residual stress as the coating-substrate system cools back to room temperature.

Examining the curvature-temperature data of the bi-layer beams during thermal cycling (Figure 2), a hysteresis between the heating and cooling cycle on the curvature-temperature for the molybdenum sample is easily observable. Furthermore, the slope of the curvature-temperature data for the molybdenum sample is visibly lower at temperatures higher than the expected compressive to tensile coating stress transition. Preliminary inverse analysis [1,2] of the molybdenum's curvature-temperature data calculated an elastic modulus of ~61 GPa (~18 to 19% of bulk [7]) and a non-linearity degree of 2.3, which corresponds to the ratio between the former modulus and the one calculated as the secant modulus after 0.1% strain from the transition temperature. Similar behaviour has been reported by studies of ceramics using the same technique [1-4] and was attributed to the opening of pores and the coinciding reduction of frictional forces between the deposited droplets as the coating was put into tension. A similar mechanism may be at play for the molybdenum but would require further investigation to confirm.

The curvature-temperature data of the tantalum sample is more linear (even when the coating is in a tensile stress state) and a simple solving of Equation 1 by using selected temperature ranges of the thermal cycling data, thickness measurements in Table 4, and reported values in Table 2 is shown in Figure 4. Additionally, calculated modulus values using ± 5% of the measured tantalum thickness or ± 10% of the CTE used in Table 2 are also shown to demonstrate the relative insensitivity of the calculated modulus that bracket the uncertainties of those inputs to Equation 1 (though coating thickness was closer to ± 1% uncertainty).

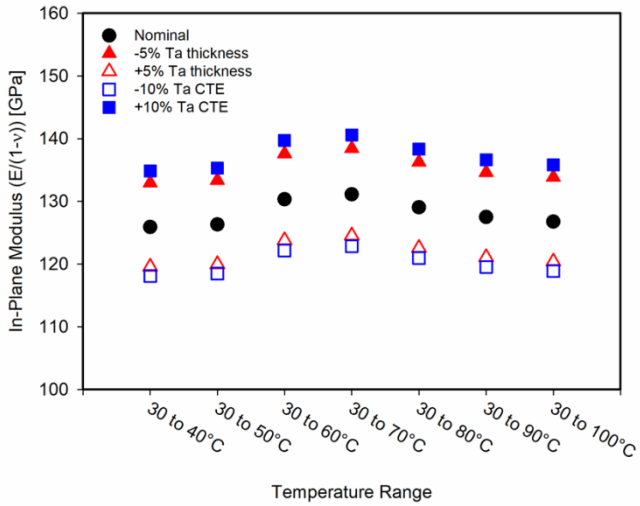

Figure 4. Tantalum coating modulus calculated over varying temperature ranges using Equation 1 as well as variation in coating thickness and CTE.

Figure 4 reports an in-plane modulus (modulus/ (1-Poisson ratio)) as calculated by Equation 1 and ranges from 125 to 131 GPa, which relates to approximately 44 to 46% of the in-plane modulus value of bulk tantalum (186 GPa/ (1-0.35) [7]) when using the nominal input to Equation 1. The ±5% in coating thickness leads to ~±5 to 6% difference in modulus calculation (coating thickness for these samples were on the order of ±1%). A ± 10% in coating CTE leads to ~±6 to 7% difference in coating modulus calculation (coating CTE was measured to within ±10% of bulk values). Thus, the robustness of the bi-layer beam thermal cycling method for modulus calculation in this scenario (i.e., substrate-coating pairing, their respective thicknesses, and coating purity) is demonstrated.

In terms of percentage of coating modulus to bulk material in the case of tantalum, the bi-layer beam thermal cycling method (44 to 46% of bulk) agrees very well with the tensile testing method (42 to 46% of bulk). The in-ability to tensile test the molybdenum samples does not allow a similar comparison for the molybdenum. However, the lower percent-of-bulk modulus for the molybdenum coating (~18 to 19%) and further reduction in modulus in a

tensile state observed by analysing the curvature-temperature data does corroborate the fragility of the molybdenum samples and their inability to be tested without pre-mature failure.

5 Conclusion

Calculations of the modulus via bi-layer beam thermal cycling for molybdenum and tantalum CAPS coatings were performed and compared to traditional testing. Chemical analysis and CTE measurements were performed to inform coating properties and the validity of using the thermal straining method. The tantalum coating was found to have a modulus approximately 42 to 46% of the literature values for bulk tantalum using bi-layer beam thermal cycling, while tensile testing measured approximately 44 to 46% of bulk. The molybdenum samples were un-able to be tensile tested due to their fragility, but the coating was found to have a modulus approximately 18 to 19% of bulk molybdenum by the bi-layer beam thermal cycling method. Additionally, non-linear modulus behaviour was observed in the molybdenum sample when enough thermal strain was induced to shift the coating from a compressive to tensile stress state. Similar behavior has been observed in ceramic samples subjected to similar testing [1-4] but further microstructural analysis would be necessary to determine the mechanism for the behavior in CAPS molybdenum. The results presented here demonstrate the utility of using bi-layered thermal straining to characterize the modulus of plasma spray refractory metal coatings which can reduce testing times and potentially be used to explore modulus sensitivity to processing techniques.

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7 References

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