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Title: Characterization of Thin Walled Mo Tubing produced by FBCVD

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Characterization of Thin Walled Mo Tubing produced by FBCVD

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SUMMARY

The goal of this report is to delineate the results of material characterization performed on Mo tubing produced via the fluidized bed chemical vapor deposition (FBCVD) method. Scanning electron microscopy (SEM) imaging reveals that small randomly oriented grains are achieved in the Mo deposition, but do not persist throughout the entire thickness of the material. Energy dispersive spectroscopy (EDS) reveals the Mo tubes contain residual chlorine and oxygen. EDS measurements on the tube surfaces separated from glass and quartz substrates reveal substrate material adhered to this surface. X-ray diffraction (XRD) revealed the presence of carbon contaminant in the form of Mo_2C and oxygen in the form of MoO_2. Combustion infrared detection (CID) and inert gas fusion (IGF) performed at Luvak Inc. was used to quantify weight percentages of oxygen and carbon in the tubes produced. Hardness value of the FBCVD Mo was found to be comparable to low carbon arc cast molybdenum.

CONTENTS

FIGURES

ACRONYMS

ASTM – American Society for Testing & Materials

C - Carbon

CID – Combustion infrared detection

EDS – Energy dispersive spectrometry

FBCVD – Fluidized bed chemical vapor deposition

IGF – Inert gas fusion

O - Oxygen

SEM – Scanning electron microscope/microscopy

XRD – X-ray Diffraction

1. INTRODUCTION

Previously, we reported on the production of Mo tubing via the fluidized bed chemical vapor deposition (FBCVD) method with the objective of producing tubes with lengths up to 12 inches and wall thicknesses of 250 µm [1]. In conjunction with this objective, it was also important to achieve a microstructure consisting of small randomly oriented grains in order to achieve the desired properties of the resulting Mo clad, namely, radiation tolerance [2], mechanical properties [3], and oxidation resistance [4]. The current deposition rate of 5 µm/hour is significantly slower than a previously reported deposition rate of 100 µm/hour, however the resulting microstructure associated with the higher deposition rates is insufficient for clad applications being highly porous with columnar grain structures [1], [5].

This tradeoff between microstructure and deposition rate is a function of a large number of coupled parameters in the sense that they not only affect residence times and reaction rates of the chemical process, but also the properties of the fluidized bed which play a key role in the resulting microstructure. For example, temperature is directly related to reaction rate as well as the terminal velocity of microspheres in the fluidized bed; gas flow rates must be sufficient to support the fluidized bed while simultaneously maintaining appropriate residence times and reactant quantities necessary for the chemical reaction driving the deposition process. Thus, in order to develop a process for producing tubes that approach the desired microstructure, variations of multiple parameters had to be employed from one deposition to the next.

This work will highlight the physical and chemical characterizations of tubes produced from non-optimized processes that approach the desired microstructure, but vary in multiple production conditions. A variety of analysis techniques were employed to characterize the produced tubes, including scanning tunneling microscopy (SEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD), combustion infrared detection (CID), inert gas fusion (IGF), and micro hardness testing.

2. CHARACTERIZATION METHODS

Samples for characterization were taken from three tubes reported previously as tubes #1 through #3. Briefly, all tubes were fabricated at a furnace temperature of 700°C with tubes #1, #2, and #3 being deposited for 6 hours on a copper substrate, 4 hours on a borosilicate glass substrate, and 17.25 hours on a quartz substrate, respectively. It was observed that the glass and quartz template materials were better suited to adherence of the deposition material having lower roughness than that of the copper. Quartz has been determined to be the optimal template material due to the softening that occurs for borosilicate glass at furnace temperatures of 700°C and higher.

For SEM imaging, samples from tubes #1, #2 and #3 were mounted via carbon tape to stubs such that a cross section of the tube could be imaged revealing the microstructure throughout the tube from the inner to outer surface. The cross sectional samples were produced by simple breaking off a piece of Mo material from the tubes. The outer surfaces of the Mo samples correspond to the interface between the Mo and template material, being deposited on the inner surface of the template tubes. The SEM used to image samples for microstructure is equipped with EDS spectrometer used for elemental analysis of the samples.

For accurate microstructural analysis a cross sectional sample from tube #3 was prepared using standard metallurgical sample preparation techniques: grinding and polishing. The grain size dimensions were analyzed from the inner to the outer tube surfaces. In order to better quantify and identify impurities in the Mo films, samples from all three tubes were sent to Luvak Inc. and tested for oxygen and carbon content via combustion infrared detection (CID) and inert gas fusion (IGF), respectively. These analyses were conducted in accordance with the American Society for Testing and Materials method E-1019 for detecting carbon, sulfur, nickel, and oxygen [6]. Quantitative XRD performed on a sample from tube 3 in

combination with the Luvak results enabled a rough comparison of impurity content from one tube to the next.

Microhardness measurements of tube #3 were carried out using a Buehler Micromet 4 instrument using 100 g load.

3. CHARACTERIZATION RESULTS

SEM images are shown for samples of each tube in Figures 1, 2, and 3. In each case, the microstructure near the Mo substrate interface consists of the desired randomly oriented small grains (bottom edge of Figure 1, top right edge in Figure 2, and bottom edge of Figure 3). The microstructure transitions to larger columnar grains typical of Mo films further from the interface [7]. In an ideal Mo tube for clad applications, the microstructure near the interface would persist throughout the thickness of the entire film. While this is not the case in these tubes, the presence of a desired microstructure near the interface is encouraging.

SEM images obtained from the metallurgically prepared cross sectional surface of tube #3 are shown in Fig. 4. These images revealed a microstructure different from the one shown in Fig. 3. FBCVD Mo shown in Fig. 4 consists of equiaxed fine grains with dimensions of 0.95 ± 0.2 µm at the inner surface and 1.0 ± 0.3 µm at the outer surface. This is exactly the microstructure that we are aiming for to achieve during the FBCVD. The discrepancy with the results shown in Fig. 3 is not clear to us yet. This can be related to the sample preparation technique or the fact that the microstructure might vary along the tube length.

Future optimization of the process could potentially result in the finer grain structure persisting to the entire thickness and length of the tubes. Specifically, in addition to careful optimization of the deposition parameters, use of a higher density bed material for fluidization might serve to more effectively disrupt the formation of columnar grain structures allowing the desired sub-micron scale microstructure to persist.

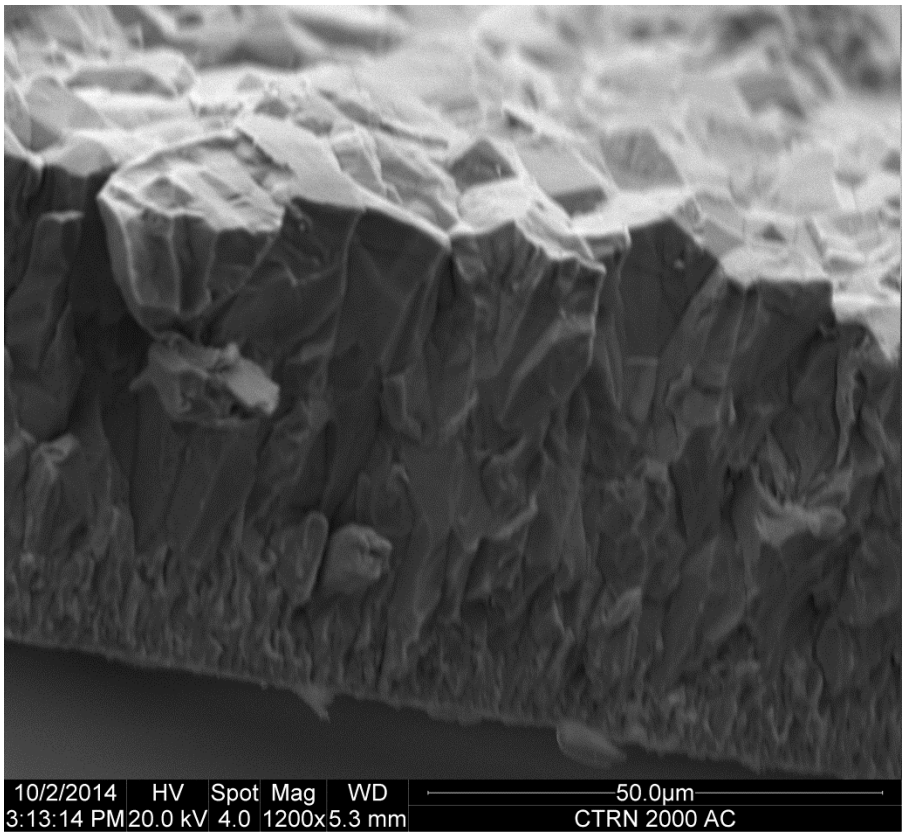

Figure 1. SEM image of Tube 1.

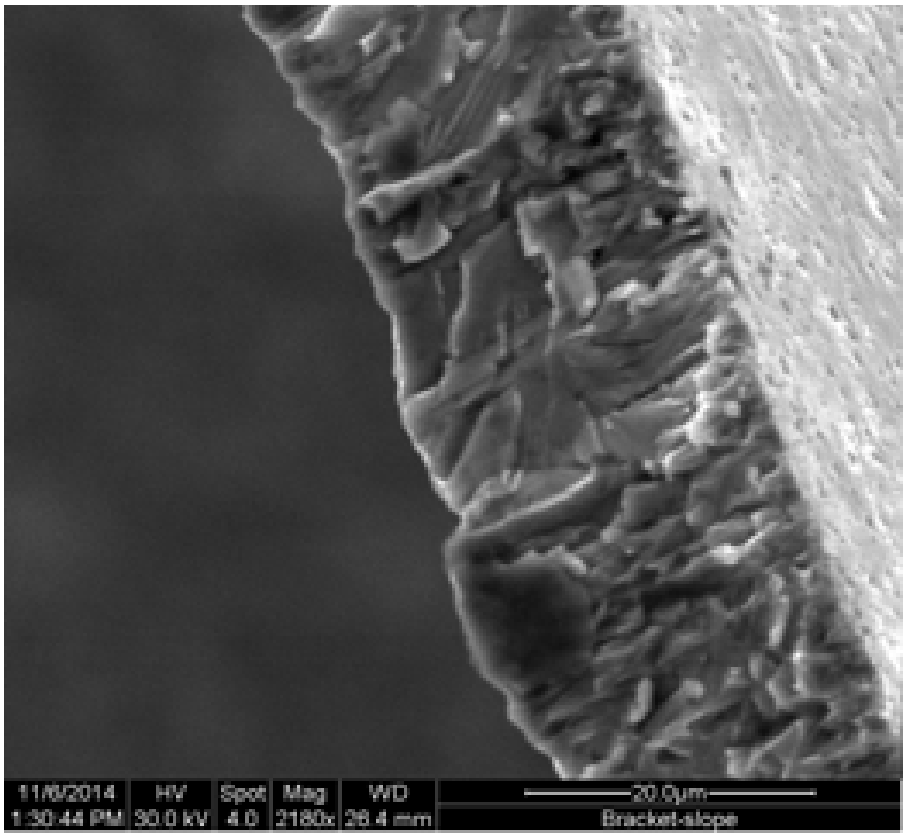

Figure 2. SEM image of Tube 2.

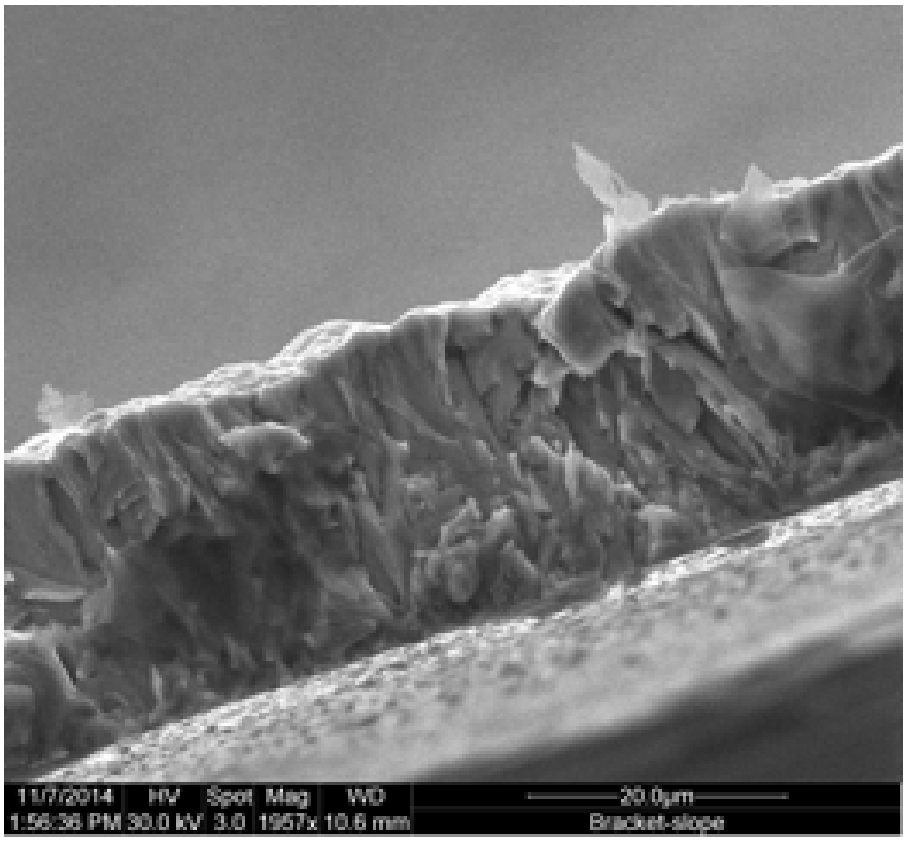

Figure 3. SEM image of Tube 3.

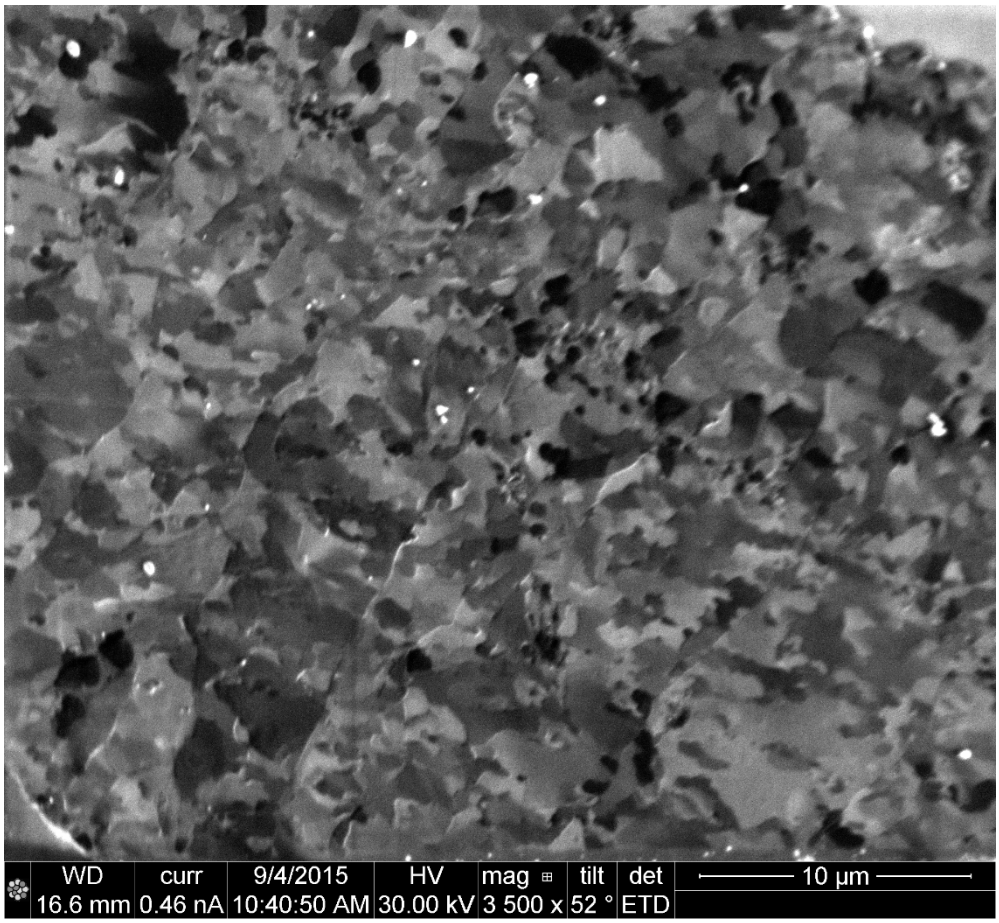

Figure 5. SEM cross sectional image from metallurgically prepared tube #3. The lower left corner corresponds to the inner surface and the top right corner shows the outer surface.

Figure 5 shows a representative EDS spectrum taken of a cross section of the Mo tube, revealing the presence of some oxidation and residual chlorine in the film. An EDS spectrum was also taken for the outer surface of the tube sample, revealing that for the glass and quartz templates, substrate material adheres to the Mo film after separation (Figure 6). This indicates better adhesion of the Mo film to the borosilicate and quartz substrates as compared to the copper substrate.

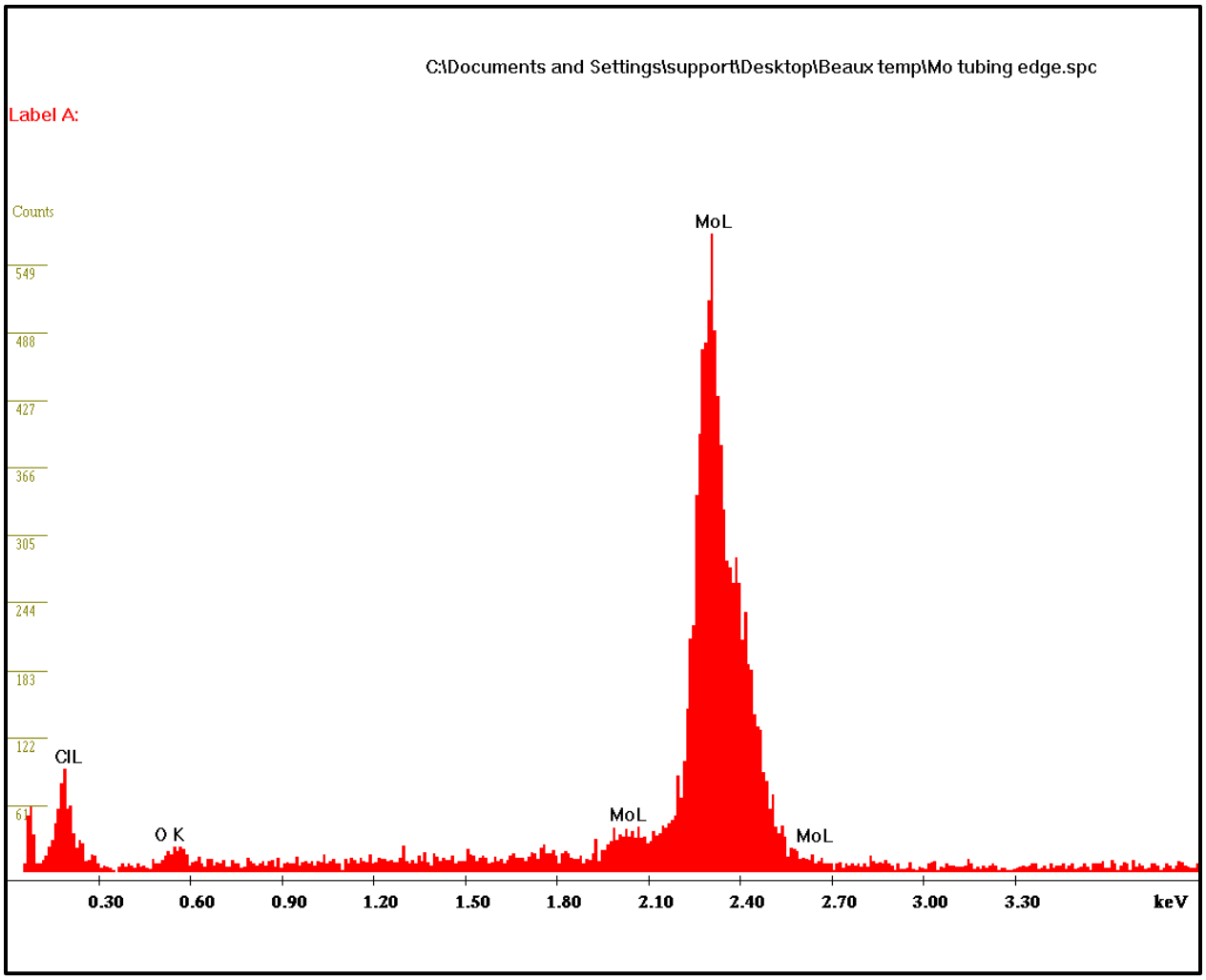

Figure 5. EDS of Tube 1 bulk material.

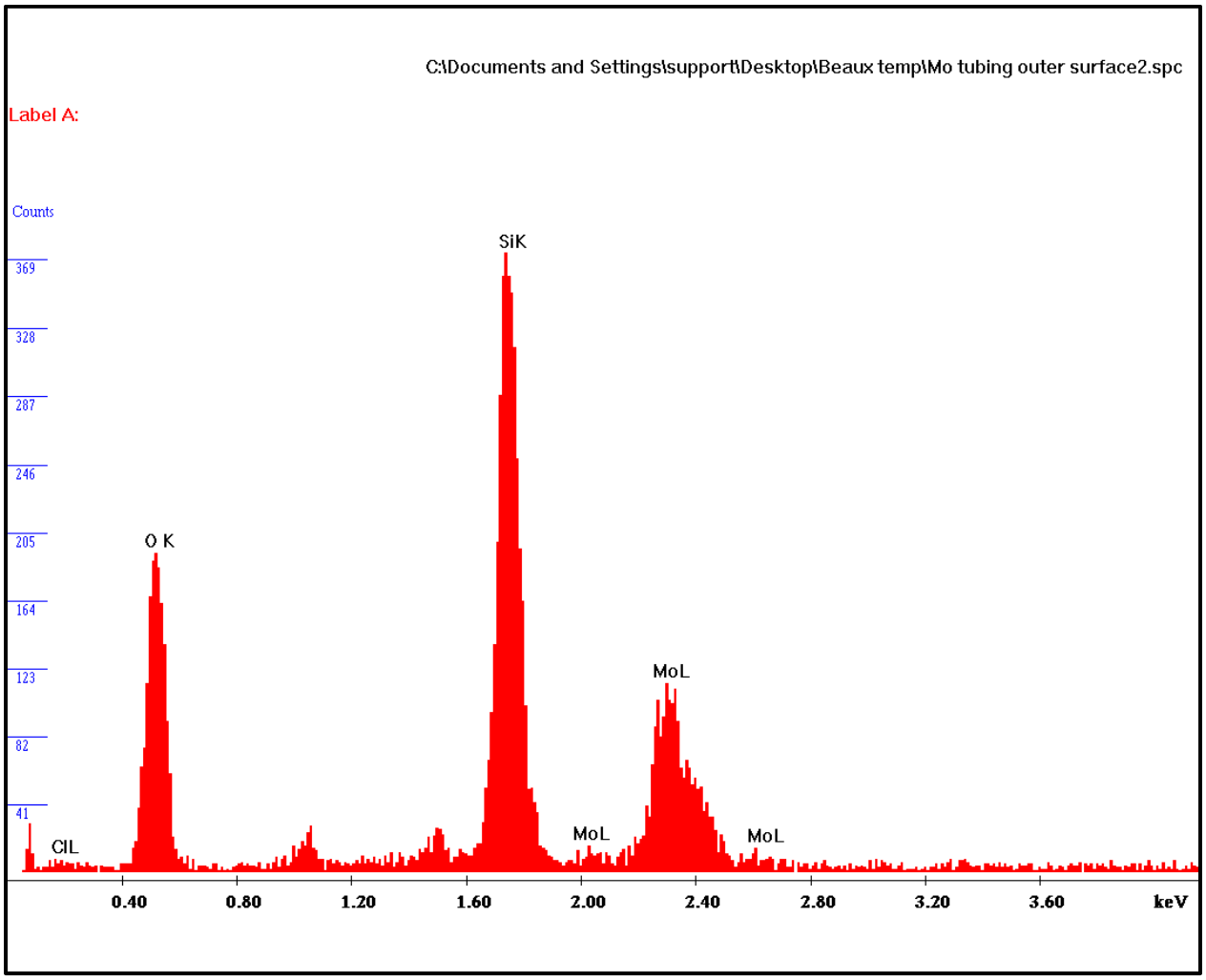

Figure 6. EDS of outer edge of Mo tube sample showing elements associated with substrate material.

XRD results shown in Figure 7 show the presence of Mo_2C when performed on the outer surface and both Mo_2C and MoO_2 when performed on the inner surface of Tube 3. The presence of MoO_2 only on the inner surface of the tube suggests the tube was subjected to surface oxidation prior to separation from its substrate. IGF and CID analysis results from Luvak Inc. also show the presence of both oxygen and carbon in all three tubes (Table 1). The weight percent of carbon from tube to tube is fairly consistent ranging from 0.055 to 0.088 percent. However, the 0.053 weight percent of oxygen in tube 3 is an order of magnitude less than that found in tubes 1 and 2 (0.362 and 0.554 percent, respectively) suggesting a source of oxygen contaminant not present for tube 3.

The presence of carbon in the form of Mo_2C and oxygen in the samples suggests sources of contaminant in the process which could be attributed to the impurities in the ultra-high purity gases used to feed the process, the bed material, the substrate, or combinations thereof. The use of various bed materials as well as inert gas and hydrogen purifiers between the gas cylinders and FBCVD system could serve to reduce contaminants from these potential sources.

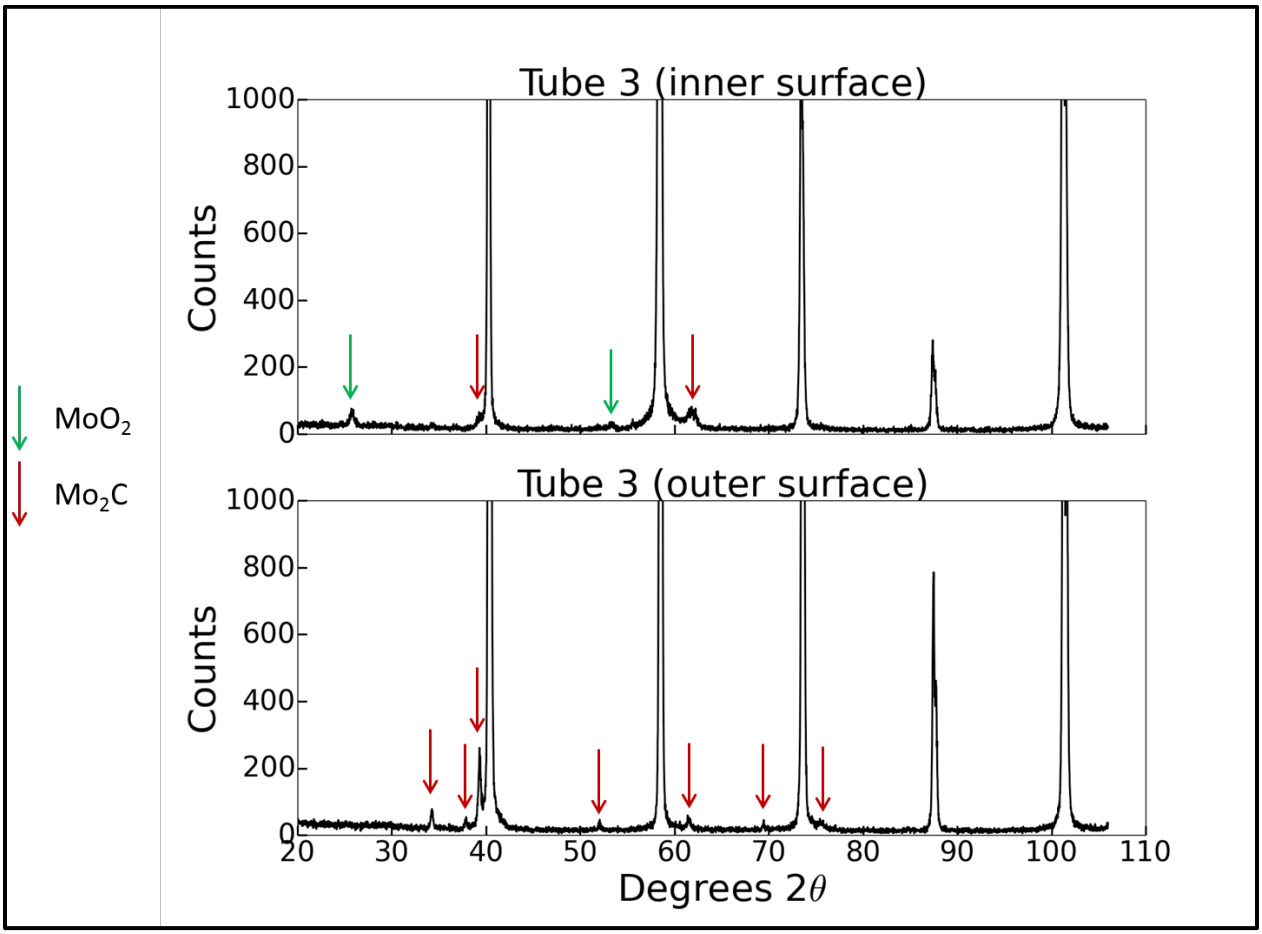

Figure 7. XRD results for the inner and outer surfaces of Tube 3.

Table 1. Weight percentages of O and C as determined by IGF and CID, respectively, at Luvak Inc.

Tube ID	#1	#2	#3
Oxygen [Wt %]	0.362	0.554	0.053
Carbon [Wt %]	0.088	0.055	0.066

Vickers hardness measurements were performed on tube #3 to assess mechanical properties of FBCVD Mo material. Vickers hardness value was found to be 202 ± 20 (Hv) or 1.98 ± 0.2 GPa. The Mo FBCVD material hardness is comparable to arc cast Mo. It resides between ~ 173 GPa reported for Mo with grain size diameter ranging 5-30 µm and 260 GPa for Mo with grain size diameter ranging 1-15 µm [8].

4. CONCLUSIONS

We have succeeded in producing Mo tubes containing the desired small randomly oriented grains; however, this microstructure does not persist throughout the entire thickness of the tubes. Optimization of

the FBCVD process will be conducted in order to produce Mo tubes with a greater persistence of the desired microstructure. Depositions will also be run with varying bed materials and no bed at all to determine the effects on microstructure. Chemical analysis identified chlorine, oxidation, and MoC_2 in the Mo tubes produced.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

[1] I. Usov, “Production of Thin Walled Mo Tubing using FBCVD,” Jun. 2015.
[2] T. S. Byun, M. Li, B. V. Cockeram, and L. L. Snead, “Deformation and fracture properties in neutron irradiated pure Mo and Mo alloys,” *J. Nucl. Mater.*, vol. 376, no. 2, pp. 240–246, May 2008.
[3] G. Liu, G. J. Zhang, F. Jiang, X. D. Ding, Y. J. Sun, J. Sun, and E. Ma, “Nanostructured high-strength molybdenum alloys with unprecedented tensile ductility,” *Nat. Mater.*, vol. 12, no. 4, pp. 344–350, Jan. 2013.
[4] S. Maloy et al., “Molybdenum Cladding Development,” presented at the FCRD AFC Integration Meeting, Idaho Falls, Idaho, United States, 2014.
[5] D. Devlin and I. Usov, “Report on CVD processing of Mo Tubing,” Jul. 2014.
[6] “Standard Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques.” ASTM International.
[7] P. L. Raymond, “Molybdenum Plating Inside of Large Bore Tubes,” *J. Electrochem. Soc.*, vol. 106, no. 5, p. 444, 1959.
[8] B.V. Cockeram, J.L. Hollenbeck, L.L. Snead, " Hardness and electrical resistivity of molybdenum in the post-irradiated and annealed conditions", *J. Nucl. Mater.*, vol. 336 (2005) 299-313