LLNL-TR-738593

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Electroplating Gold-Silver Alloys for Spherical Capsules for NIF Double-Shell Targets

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September 18, 2017

Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Contents

Abstract

For Inertial Confinement Fusion (ICF) implosions, a design based on gradients of high and mid Z materials could potentially be more robust than single element capsule systems. To that end, gold and silver alloys were electroplated on 2.0 mm diameter surrogate brass spheres using a new flow–based pulsed plating method specifically designed to minimize surface roughness without reducing plating rates. The coatings were analyzed by scanning electron microscope (SEM) and white light interferometry for surface topography, and by energy dispersive x-ray spectroscopy (EDX) to determine near-surface gold and silver compositions. The alloy range attainable was 15 to 85 weight percent gold using 1:1 and 1:3 silver to gold ratio plating baths at applied potentials of -0.7 volts to -1.8 volts. This range was bounded by the open circuit potential of the system and hydrogen evolution, and in theory could be extended by using ionic liquids or aprotic solutions. Preliminary gradient trials proved constant composition alloy data could be translated to smooth gradient plating, albeit at higher gold compositions.

I. MOTIVATION

The National Ignition Facility (NIF) at Lawrence Livermore National Laboratory (LLNL) is a system that focuses 192 high powered laser beams onto a single target capsule approximately two millimeters in diameter to initiate a nuclear fusion reaction. The implications of this project extend from nuclear stockpile stewardship to basic research in fields ranging from Inertial Confinement Fusion (ICF) to interstellar science. Current ignition targets use plastic, Be, or High-Density Carbon (HDC) ablators with deuterium-tritium ice layers as a fuel source.

Other platforms for achieving Inertial Confinement Fusion include more involved capsule designs, such as graded density shells. The production of such shells calls for the development of a new fabrication process. Metal shells are commonly produced by machining halves and attaching them, but while this method may be the quickest and simplest, machined shells are unable to provide a concentration gradient within the alloy. Alternatively, shells produced by physical vapor deposition methods, such as sputter coating, could provide the desired density gradient but are often slow and have the risk of providing uneven surface coatings. Therefore, a specialized electroplating method was explored for the creation of these shells.

II. MATERIALS AND METHODS

While conventional electroplating is a relatively simple process that is commercially used in both the jewelry and electronic components industries, configuring it to provide the necessary smooth and even coating on millimeter scale spheres is a much more challenging process that required a new approach.

This custom technique involved plating spheres in a Teflon and copper wire cage, as shown in Figure 1. The design in effect allowed for a pulsed plating which was accomplished by rapidly moving the sphere between the top and bottom wire cathodes in the cage, thus plating only when the sphere was in contact with the wire. The silver/silver-chloride reference electrode was chosen for its relative stability with the plating solution, and the platinum counter electrode was selected for its high exchange current density and lack of reactivity/dissolution in the plating solution. The entire plating bath was sonicated at 35 kHz to prevent the sphere from sticking to the cathode wires and to reduce mass transfer limitations by mixing the solution.

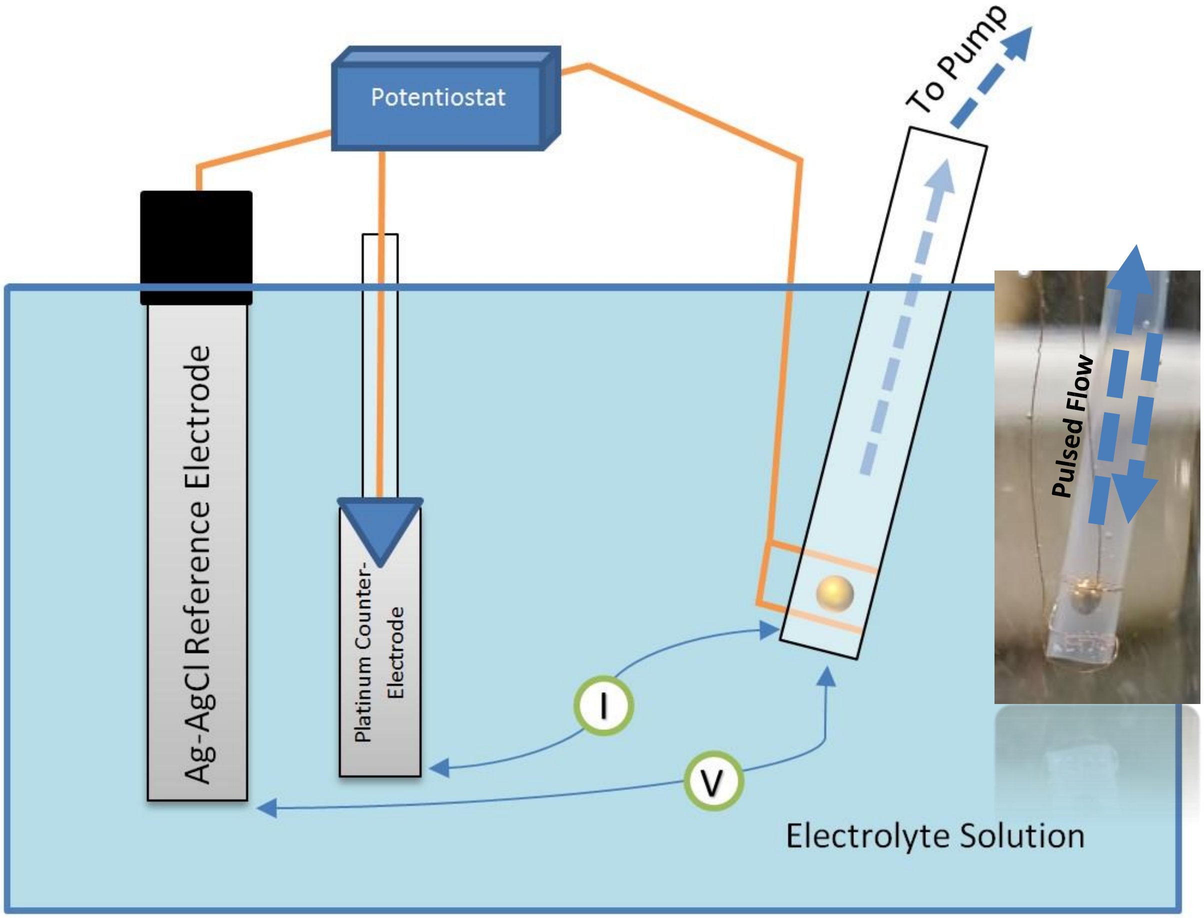

FIG. 1. *A simplified schematic of the plating process that shows the current across the platinum counter electrode and working electrode, and the voltage across the silver-silver chloride reference electrode and working electrode; pulsed flow through the PTFE tubing caused a pulsed plating effect between the sphere and cathode wires.*

The experiments for this study were performed with two-millimeter diameter surrogate brass spheres to understand the fundamentals and effects of changing parameters, with the intent to ultimately scale down to ~600-micron spheres for final production. These smaller mandrels would be made from poly(alpha-methyl styrene) (PaMS), and coated with an initial gold strike layer (on the order of 10 to 100 nanometers) via sputter coating or electroless deposition prior to electroplating.

All experiments were performed in one of three stock solutions, described in Table 1. A selection of parameters were each individually varied, as described in Table 2 and Section 3.

Table 1. *The first plating bath was comprised of gold and silver and cyanide complexes in a 1:1 ratio*

(all aqueous); the second was comprised of gold and silver in a 1:3 ratio; the third solution was identical to the second except the molarity of potassium cyanide was increased to 0.5167M KCN. These solutions will, from here on, be referred to as 1:1, 1:3 low CN, and 1:3 high CN solutions.

	1:1 SOLUTION	**1:3 LOW CN SOLUTION**	**1:3 HIGH CN SOLUTION**
$KAG(CN)_2$	0.05M	0.0167M	0.0167M
$KAU(CN)_2$	0.05M	0.05M	0.05M
KCN	0.25M	0.1167M	0.5167M
KOH	0.5M	0.5M	0.5M

Table 2. *Standard plating values shown in 'Default' row. A series of six (A-F) different parameters were tested individually (with all other variables held constant) in the 1:1 bath. Additional tests varying only voltage were performed in the 1:3 baths (refer to Table 1).*

PARAMETER CAGE SIZE FLOW TEMP TIME SONIC POTENTIAL CONCENTRATION TESTED (MM) (ML/MIN) (°C) (MIN) (ML) (VOLTS) (MOLARITY)

DEFAULT	3.00	230	50	20	80	-1.3	1:1
A – CAGE SIZE	**3.00 to 7.00**	230	50	20	80	-1.3	1:1
B – FLOW	3.00	**80 to 435**	50	20	80	-1.3	1:1
C – TEMP	3.00	230	**50 to 60**	20	80	-1.3	1:1
D – TIME	3.00	230	50	**2 to 60**	80	-1.3	1:1
E – SONIC AGITATION	3.00	*230 & 435*	50	20	**80 & 400**	-1.3	1:1
F –POTENTIAL	3.00	230	50	20	80	**-0.7 to -2.15**	1:1

G - CONCENTRATION	3.00	230	50	20	80	*-0.85 to -1.8*	**1:3 high & low CN**

III. PLATING GOLD-SILVER ALLOY SHELLS

A. Cage Size – 5 trials

One of the novel attributes of this approach was the use of a plating wire-cage whereby the pulsing was effectively created by intermittent contact with the cathode wires (on) and travel time in the PTFE tubing (off) forced by motion from the pump, rather than by the conventional method of pulsing via the potentiostat. However, this also meant that the wires in the cage were always being plated as they had a constant voltage applied to them, while the coating on sphere would be thinner depending of the dutycycle of the pulsing. To test how the spacing of the wires, and therefore the amount of time the sphere spent travelling between wires, impacted the quality and composition of the plating, cages were built at 4.00 mm, 5.00 mm, 6.00 mm, and 7.00 mm. Results were then compared to the baseline 3.00 mm cage. As expected, the plating rate decreased as the travel distance between the wires increased since there was a longer period for which the spheres were not in contact with the wires. It should be noted that in all designs, the pump flow was sufficient to cause the sphere to touch and bounce (due to sonication) against the wire within a fraction of the pump cycle, i.e., the travel time between wires was not as long as the pump cycle. The EDX measured gold compositions and SEM images yielded no noticeable differences beyond the normal drift, suggesting that the cage size did not impact anything other than the plating rate.

B. Flow – 11 trials

In the same vein, the flow rate was varied from 80 mL to 740 mL per minute. At low rates, the flow was just barely enough to cause the sphere to travel upward against gravity. This caused sticking at the bottom of the cage, as the plating process essentially welded the sphere to the wire, leading to nonuniform plating around the sphere. At extremely high flow rates the surface quality was also poor for reasons still unknown.

C. Temperature – 5 trials

The plating was done in beaker which was placed inside a heated sonication bath. Operating limitations for this bath only allowed for a temperature range from 50°C to 60°C. While increasing the temperature slightly above the 50°C minimum appeared to have no effect (negative or positive), going closer to the 60°C range appeared to yield poor surface quality with increased roughness, and so no further investigations of this parameter were performed.

D. Time – 10 trials

To prove that the coating had a uniform composition throughout the sphere independent of plating duration, a proxy test was performed by subjecting several brass spheres to the same voltage but for times varying from 2 minutes to 60 minutes. There were no appreciable differences in the compositions for all these spheres, suggesting that the composition plated should be uniform throughout the shell.

E. Sonic Agitation – 5 trials

The standard size of the plating bath involved 80 mL of solution in a 100-mL beaker. To test the effects of sonication, 400 mL of solution were placed into a 500-mL beaker. While intuitively this should have had no effect on the plating quality, the surface roughness was in fact much worse. The pump flow rate was varied between 120 mL/min and 330 mL/min in an attempt to compensate, but to no avail. Sonication is in integral part of the plating process (completely unsonicated spheres have surfaces so rough and dendritic that they are unusable). So, it was theorized that the larger volume beaker prohibited the sonic energy from reaching the active section of the plating cell.

F. Applied Potential – 28 trials

The above tests were performed as optimization steps. The applied potential, however, was a key parameter chosen to intentionally change the gold composition, as varying potential over time was chosen to be the best way to create a gradient, based on the principles described below and shown in Figure 2.

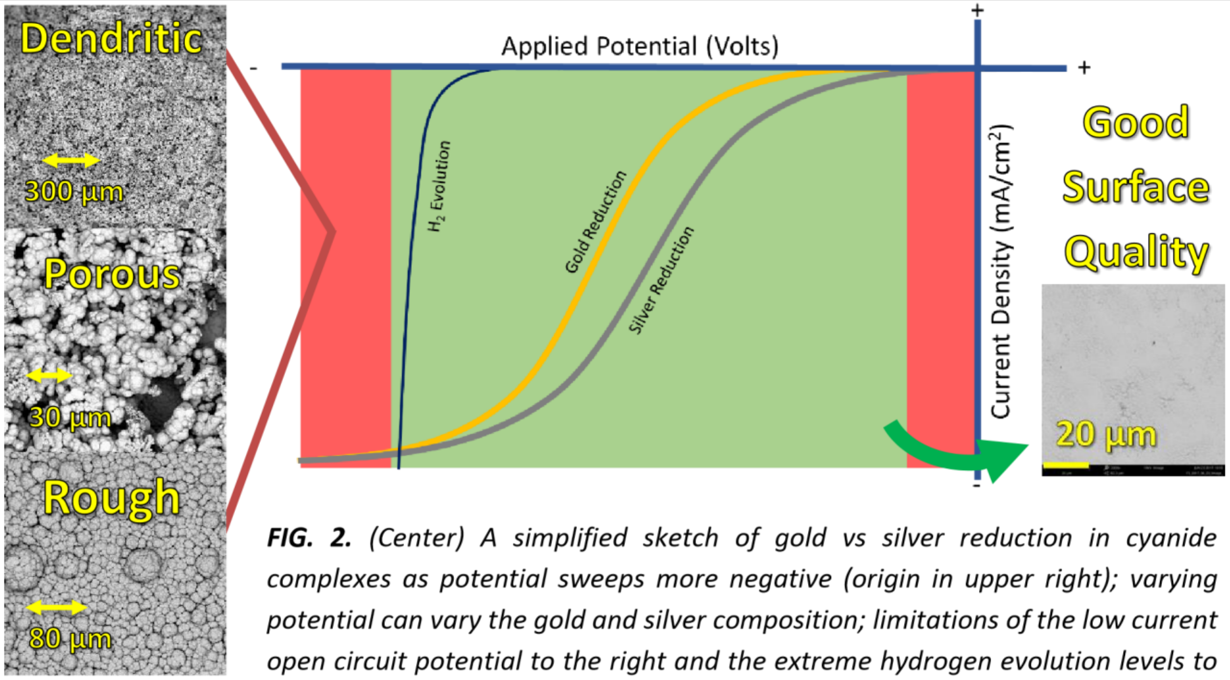

FIG. 2. *(Center) A simplified sketch of gold vs silver reduction in cyanide complexes as potential sweeps more negative (origin in upper right); varying potential can vary the gold and silver composition; limitations of the low current open circuit potential to the right and the extreme hydrogen evolution levels to the left are shown in red. SEM images to the left indicate undesirable results in this regime; desirable surface quality example to the right.*

To create alloys, the voltage was set at a desired value between the open circuit potential and severe hydrogen evolution zone (i.e. set in the green section of Figure 2). Upon changing potentials, a range of gold-silver ratios could be achieved. The data collected can be seen in Figure 3 as the red diamonds. It should be noted that additional trials were performed at voltages deep in the hydrogen evolution range (-2.15 to -1.75 volts, spaced every 0.5 volts and in duplicate), but these results showed such poor surface qualities that they were excluded from the Figure. Additionally, the gold composition had plateaued at around negative 1.6 volts, and so there was no major benefit to plating in this range. This series of tests provided a plating range (in the 1:1 solution) of 15 to about 60 weight percent gold (with acceptable or slightly subpar surfaces).

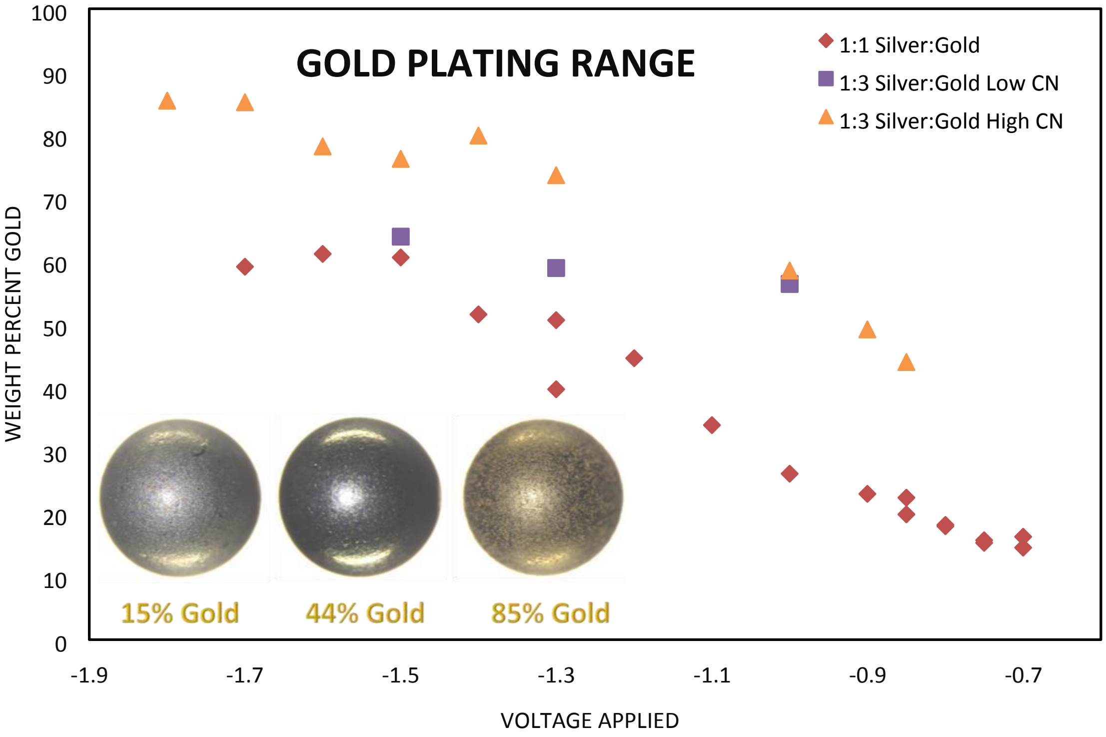

FIG. 3. *Gold weight percent composition as determined by EDX for shells plated at potentials ranging from -0.7 to -1.8; gold composition ranged from 15 to 85 wt% in trials across the three plating baths (optical images in bottom left show examples of these shells).*

G. Changing Concentration – 13 trials

In an attempt to extend the range of metal compositions to include more gold-rich alloys, the new 1:3 silver-gold solution was prepared, starting initially with 0.25 molar CN^-. The gold composition range attainable from this solution was probed (Figure 3, purple squares), but early tests suggested a lackluster gain in gold content. Therefore, the cyanide concentration was increased to 0.65 molar CN^-. The result was that the plated gold composition observed was much higher (up to 85 wt% gold – Figure 3, orange triangles). However, it was not clear if whether the changes were due to drift in the gold-cyanide complex equilibrium, drift in pH of the buffer, or if the cyanide was acting like a brightener in solution. Note that, compared to the 1:1 solution, the open circuit and hydrogen evolution drop-off potentials of the 1:3 solution were shifted slightly into the more negative range at about -0.84 volts and -1.8 volts, respectively.

IV. GRADIENTS

A. Gradient Shells

The next logical step in the process was to begin creating graded alloy shells with the highest gold concentrations towards the center and increasingly more silver going radially outward. By combining the plating rate and composition data at a variety of different voltages, a program was created to produce an expected 60 to 15 wt% gold graded concentration shell using the 1:1 solution. This program was input into the potentiostat controller, and tested across three replicate trials. Initial results seemed promising, with slightly rough but still acceptable surfaces.

Approximately ¼ to ¾ of the sphere was polished off to create a flat cross section, where the edge was observed via EDX. Stitched SEM images of the three preliminary gradient concentration shells can be seen below in Figure 4. Corresponding potential and current graphs when plating, along with calibrated EDX results across the gradients are shown in Figures 5,6.

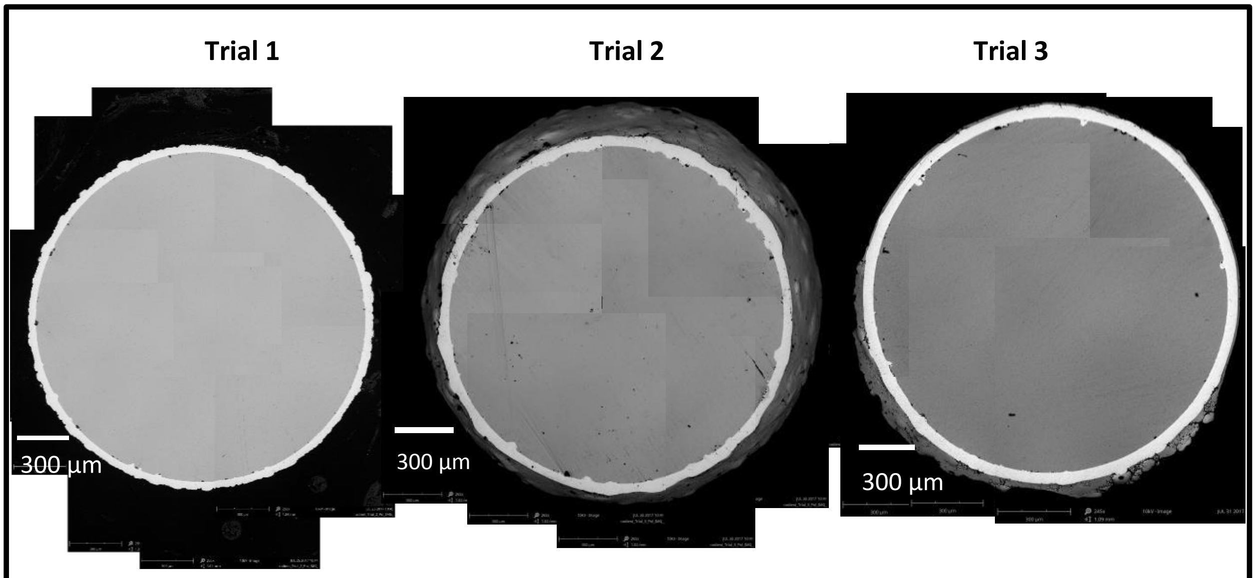

FIG. 4. (Left to Right) Stitched SEM images of Trials 1, 2 and 3 (10 kV, 'Image' intensity).

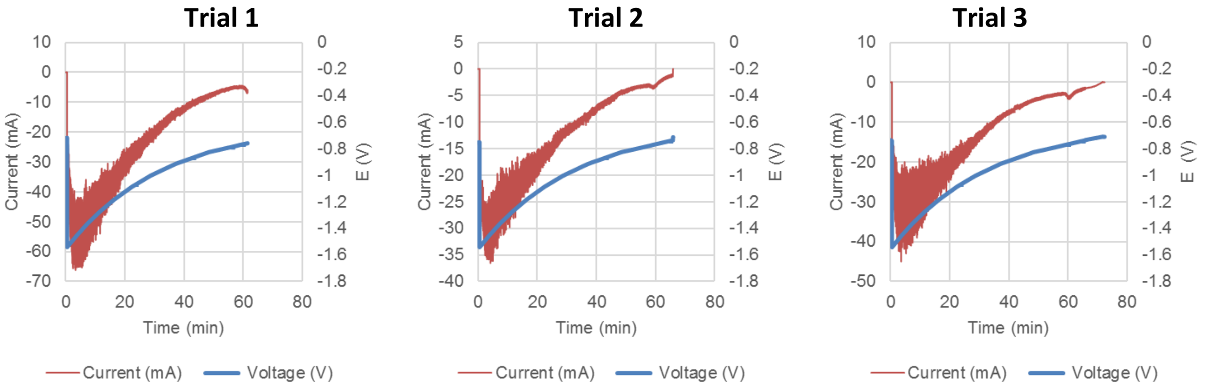

FIG. 5. Corresponding current and voltage graphs obtained by potentiostat when plating. Voltage over time was the user defined parameter; current applied to maintain said voltages was measured.

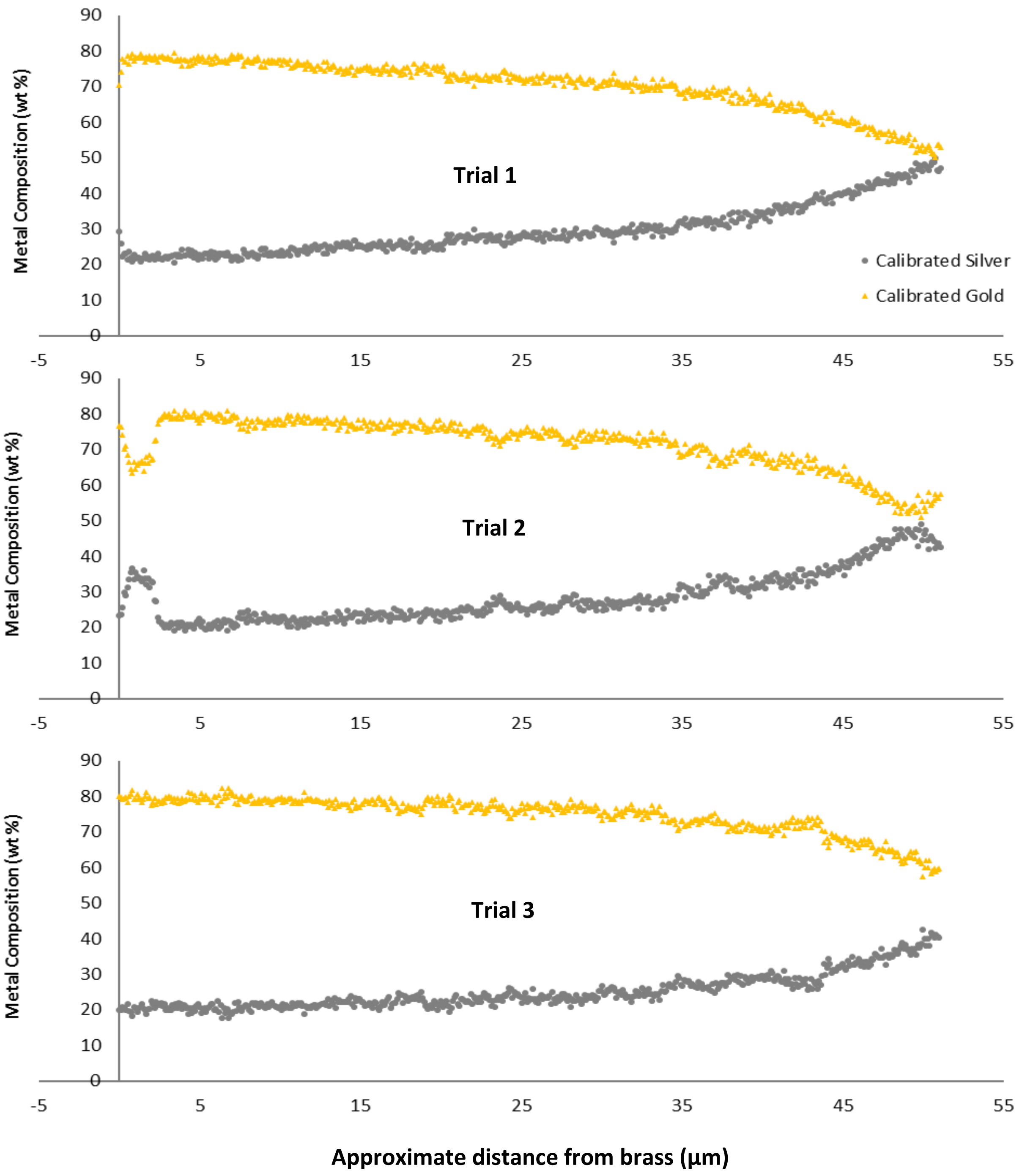

FIG. 6. Calibrated weight percent gold and silver across graded shells (top to bottom, trials 1-3).

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[1] Refer to section IV.C regarding calibrations.

Although the compositions did deviate from the predicted values, the gradient profile itself was very smooth, with no noticeable bands or jumps in concentration. The original plan involved creating a linear gradient. However, since the sphere was not polished to exactly the halfway point (an artifact of equipment limitations), the nonlinearity observed in Figure 6 may have been caused by measuring the gradient at an angle, as opposed to straight on. As such, the actual plating thickness might vary as well.

B. Effects of Polishing

The spheres were each individually polished using fixed alumina abrasive sandpaper starting with 400grit, subsequently followed by 12, 9, 3, and 1 µm grit. At each side of the brass to gold-silver alloy boundary, EDX scans were performed to check if smearing had occurred deep enough to affect the observation volume of the EDX. No gold or silver were found on the brass side of the interface, and similarly no copper or zinc were found on the coating side. White light interferometry scans were performed with using Veeco Wyko and the surface roughness was found to only be approximately ±1 micron (Figure 7).

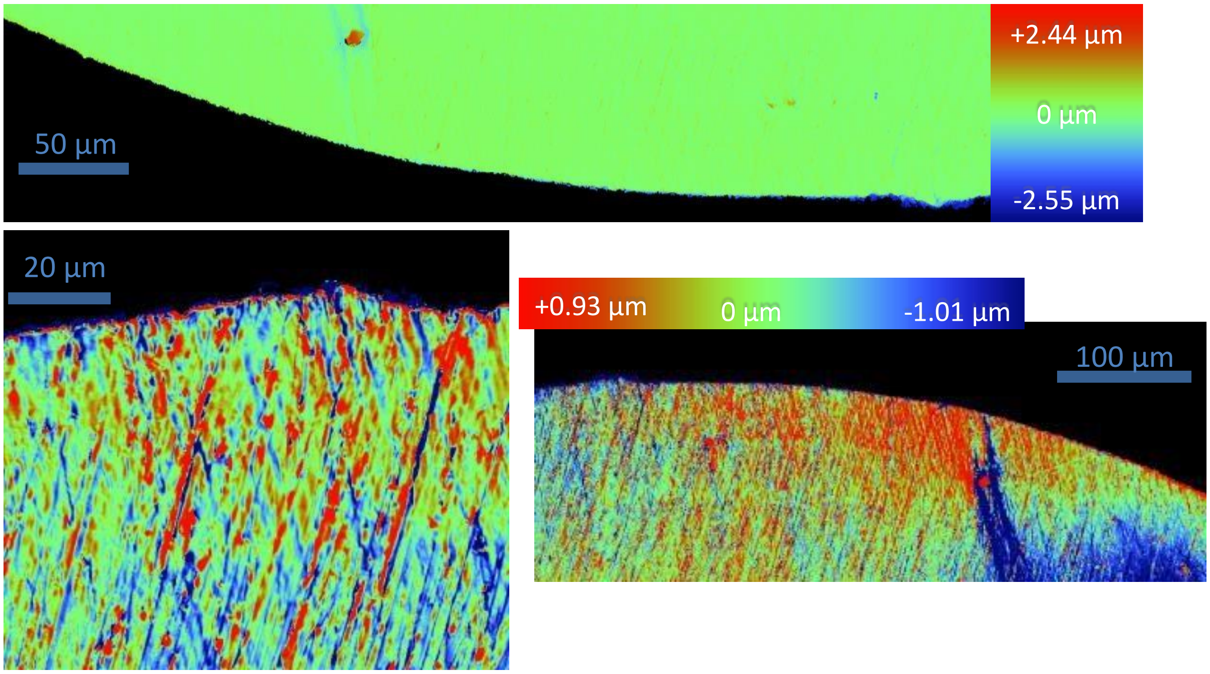

FIG. 7. White light interferometry results of polished gradient shell edge. The bottom left image is a magnified portion of the bottom right image, and has the same corresponding depth scale.

C. EDX Gradient Data Skew

The initial intent of the gradient program was to create a linear alloy gradient that ranged from approximately 60 to 15 wt% gold across a ~60 µm thick shell. With values substantially higher than those predicted, the validity of the method of analysis was investigated. It was found that the values provided by the EDX linescan did not match those obtained from an area map or a point scan when checked against

NIST standards. Therefore, point scans were re-done on the same section of a sample (Figure 8). These data findings suggested that the range plated was actually closer to 70 to 40 wt% gold (60% shown in Figure; as low as 40% at actual shell edge).

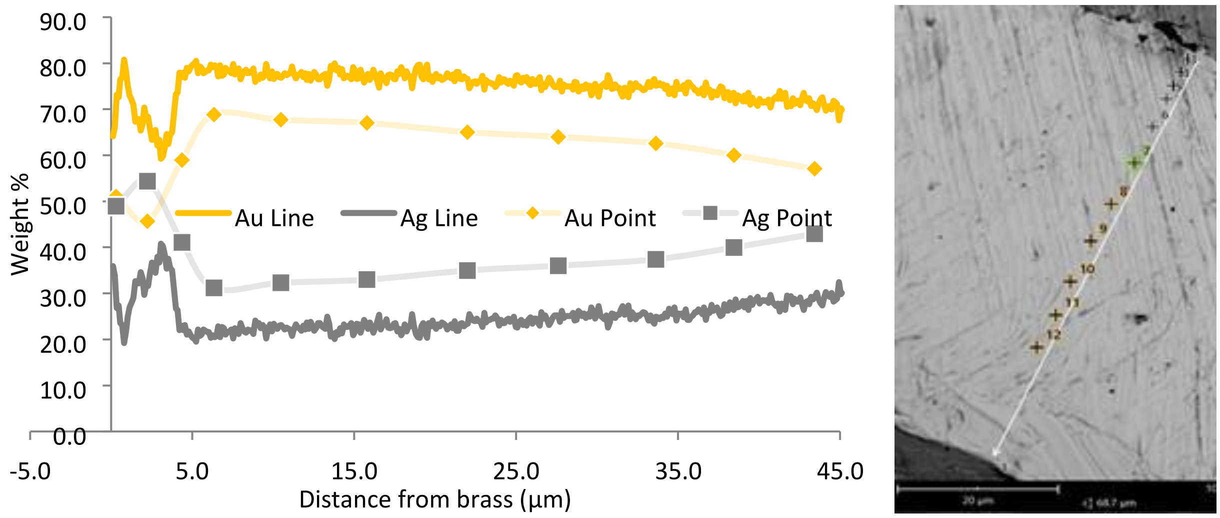

FIG. 8. Comparing the linescan (*Line*) results to point scan (*Point*) results at the same location; point results match calibrated predictions from NIST standards, linescans do not.

V. CONCLUSIONS AND FUTURE ENDEAVORS

We performed a comprehensive study of the parameter space for a custom electroplating method for making graded concentration Au-Ag alloy shells. Conditions that led to coatings that were highly porous or had dendritic surfaces due to hydrogen evolution were noted and marked as unacceptable. Experiments involving time, cage size, temperature, and flow yielded no noticeable trends regarding gold concentration, although it should be noted that at high temperatures (60+°C) and high flow rates (progressively worse past ~400

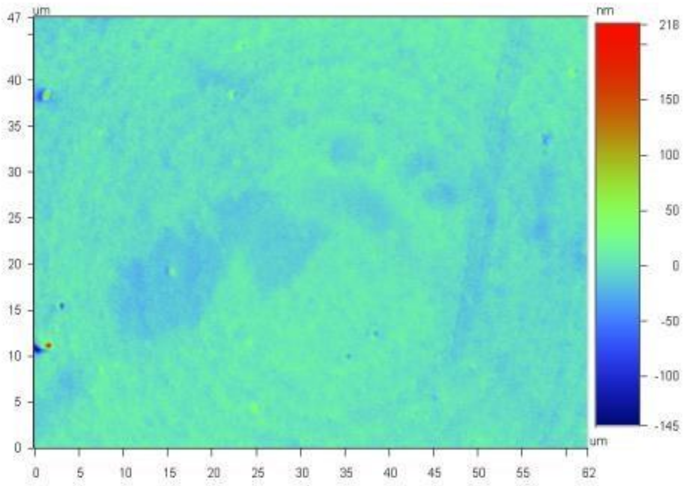

FIG. 9. Surface quality of gold -coated PaMS mandrel (via sputter coating); roughness in order of ±200 nm compared to the order of ±20 µm for brass

mL/min), the surface quality became more pitted and dendritic.

For the 1:1 solution, the acceptable plating voltages ranged from the open circuit potential of -0.67 volts to -1.5 volts. Within this regime, alloys ranging from 15 to 60 wt% gold were attainable. Using the 1:3 high CN solution, the maximum of this range was elevated to nearly 85% gold, with usable potentials ranging from -0.85 volts to -1.8 volts.

Future work in this field will involve trials to narrow the spread of results and increase repeatability. The next step will be to move away from the surrogate brass spheres and instead plate a polymer based mandrel such as PaMS (Figure 9) or GDP coated with a gold strike (a thin coating applied via conventional PVD methods), and to chemically etch away the interior leaving behind just the plated metal shell. Beyond this, the design would need to be scaled down to by a factor of 4 to be practical for NIF targets.

VI. ACKNOWLEDGMENTS

The authors would like to acknowledge Ed Lindsey, Abbas Nikroo, and Morris Wang for their support and guidance in this summer internship project.

This work performed under the auspices of the U.S. Department of Energy and an appointment to the Office of Science, Science Undergraduate Laboratory Internship (SULI) Program at the Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.