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Evaluation of KorZincAlloy Prepared by Hohman Plating

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PREFACE OR ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

A commercial vendor, Hohman Plating performed contract engineering work to determine the feasibility of producing pin hole free KorZincAlloy bronze material used for zinc gettering. Samples were tested for Sn plating thickness, heat treatability, and chemistry prior to being subjected to a standardized zinc exposure. The samples absorbed zinc and were examined using visual and scanning electron microscopy. Hohman Plating successfully produced KZA that met the target composition, was pin hole free, and was an effective zinc getter.

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LIST OF ABBREVIATIONS

SRNL	Savannah River National Laboratory
KZA	KorZincAlloy
Sn	Tin
Cu	Copper
Zn	Zinc
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
SEM	Scanning Electron Microscopy
EDS	X-ray Energy Dispersion Spectroscopy
TEF	Tritium Extraction Facility
SRTE	Savannah River Tritium Enterprise

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1.0 Introduction

As a precursor step to deploying KorZincAlloy in the TEF process as a zinc-65 (^{65}Zn) getter to be contained in all future process lids, it was determined that a commercial source for the high purity KZA be developed. As background, the initial material that was built into the TEF Process Lid was a combination of SRNL and Hohman Plating collaboration. While Hohman Plating provided the tin plating and outsourced the heat treatment, the process had not been optimized for Sn content and during heat treatment numerous pores had formed. While the pores did not affect performance in lab testing they are aesthetically unappealing and may act as virtual leaks. The optimization study described here was initiated with Hohman Plating in accordance with Appendix A, Statement of Work for Tin Plating and discussed in SRNL-STI-2017-00093.

2.0 Experimental Procedure

Plating was conducted at Hohman Plating using an alkaline tin plating bath. No additional details are available. Samples were vacuum heat treated, cut, and coiled at Hohman plating.

Samples were characterized visually to look for pin holes and other defects. The sample surfaces were characterized using a Hitachi Scanning Electron Microscope (SEM) with an Oxford X-ray Energy Dispersion Spectrometer (EDS). The EDS was used to provide the composition using a semi-quantitative method. The samples were exposed to zinc vapor in a high vacuum system that was purpose built for the zinc gettering project (1).

3.1 Results and Discussion

Hohman Plating plated a 6 inch square sheet of 0.005 inch thick copper from Metals-on-Line using their alkaline tin plating solution. The sheet was plated to a nominal thickness of 0.0001 inch of tin. The sheet was laid out in a grid, as shown in Figure 1, and the thickness was measured at each intersection using X-ray Fluorescence. The data are listed in Table 1, and the thickness results are fairly consistent with some elevated values at the corners. However, all data are within the specified range of 0.00004 to 0.0002.

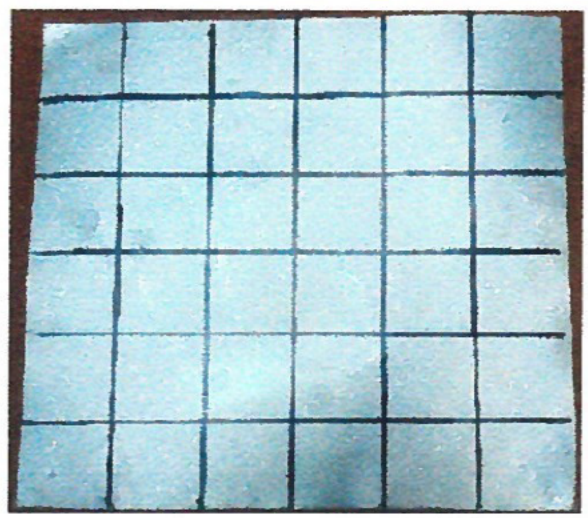

Figure 1. 6” x 6” Sn Plated Copper Sheet as Marked for Thickness Measurement.

The copper sheet was heat treated using the SRNL developed thermal cycle for bronze formation (2). The cycle is:

- Purge with Ar for 2 hours
- Heat to 200 °C to 220 °C at 5 °C/min
- Hold 8 hours in with Ar purge
- Heat to 800 °C at 5 °C/min
- Hold for 1 hour
- Heat to 850 °C at 5 °C/min
- Hold for 1 hour
- Furnace cool under Ar to less than 100 °C

Table 1 Sn Plated Thickness (mils, 0.001 inch)

Front of Panel		X Coordinate				
		1	2	3	4	5
Y Coordinate	1	0.12	0.10	0.1	0.1	0.11
	2	0.1	0.1	0.1	0.1	0.1
	3	0.1	0.09	0.1	0.1	0.1
	4	0.1	0.1	0.1	0.1	0.1
	5	0.1	0.1	0.1	0.1	0.1
Back of panel		X Coordinate				
		1	2	3	4	5
Y Coordinate	1	0.14	0.11	0.1	0.11	0.12
	2	0.12	0.11	0.1	0.1	0.11
	3	0.11	0.1	0.1	0.1	0.12
	4	0.12	0.1	0.11	0.1	0.11
	5	0.12	0.11	0.1	0.1	0.11

Figure 2 Post heat treated bronze sheet exhibiting a shiny golden coloration consistent with bronze.

The heat treatment resulted in the Sn being diffused into the copper and the return of an orange coloration consistent with bronze alloys, Figure 2. There were no indications of melting or pin holes, like those observed previously (3).

The bronze sheet was cut into strips with widths that were between 0.25 and 0.5 inch. These strips were coiled around a 0.5 inch mandrel to form "spring" shapes, as shown in Figure 3. The light orange coloration is consistent with what is expected for bronze. The coils were slightly looser than those that were prepared for the TEF Process Lid that will be tested in the FY16-FY17 extraction.

Figure 3 Coiled bronze after cutting and coiling. This color / tint is more realistic than what is shown in Fig. 2.

The sample coils were further examined at SRNL using scanning electron microscopy (SEM) coupled with X-ray Energy Dispersion Spectroscopy (EDS). These two techniques were used to provide details of the surface topography as well as the chemical makeup, respectively. The copper sheet that was provided has two distinct surface appearances, with one being shiny and smooth and the other being matte and somewhat rough. SEM images from the two sides at low and high magnifications are shown in Figure 4. These images are consistent with previous efforts conducted at SRNL to fabricate the zinc getter material using this starting stock and an SRNL acidic plating bath.

The as fabricated chemistry was determined using SEM – EDS with the results show in Table 3. The composition is very consistent from the analysis of a single coil. These results are not surprising since the plated thickness was consistent. The tin content is lower than expected at nominally 3% but well within the 2 to 10% Sn that has been evaluated over the course of this project (4). The sample composition was

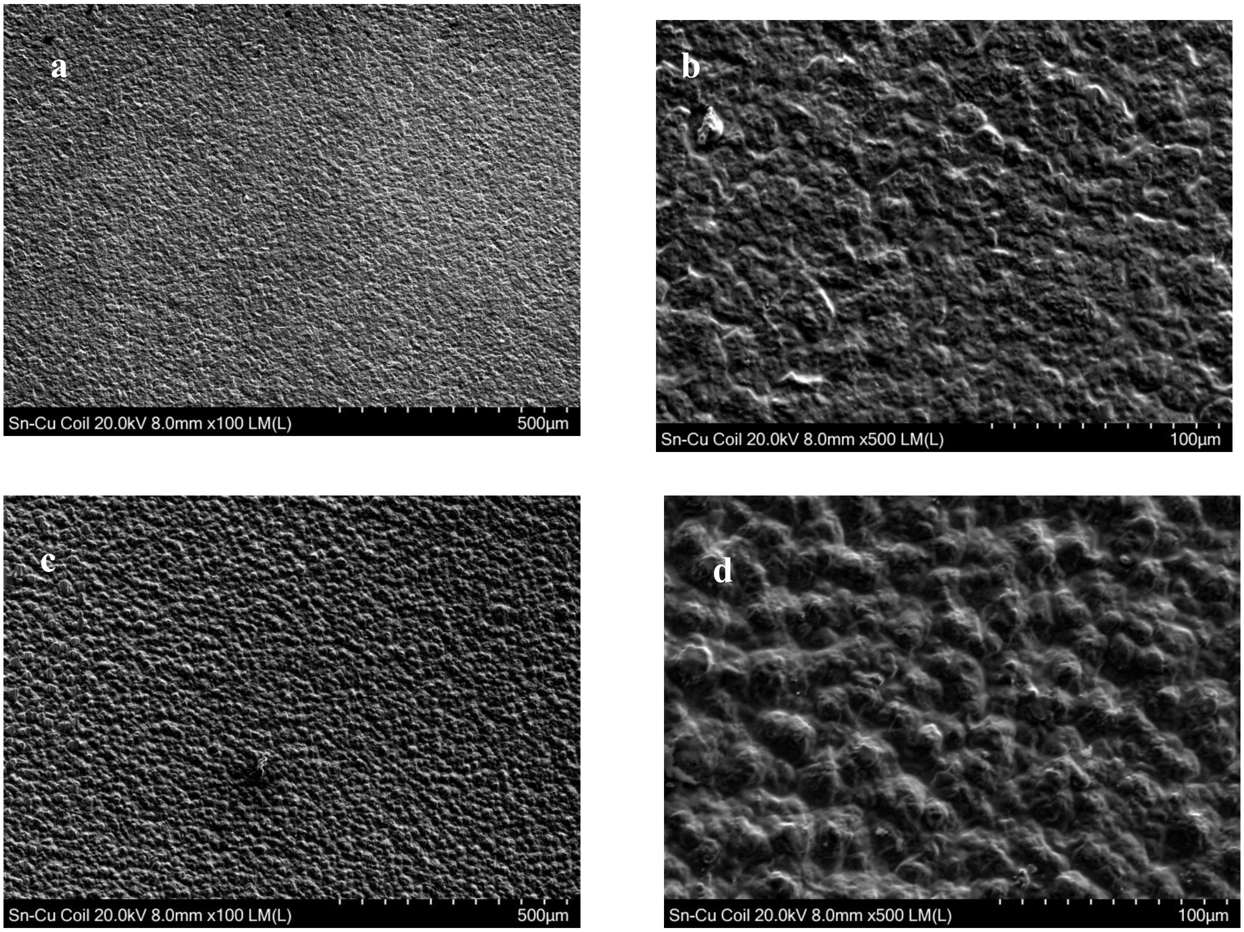

Figure 4 As received condition of the Hohman Plated and diffused bronze; (a and b) are on the smooth side, low and high magnification, respectively and (c and d) are on the rough side, low and high magnification.

also measured using Ion-coupled Plasma Emission Spectroscopy (ICP-ES). A number of sections were cut from two coils to determine the average tin content with variable results, such that they are not reported here. SRTE also has strict chloride content requirements and the chloride content was measured for both surface soluble halides by rinsing the coils and analyzing the effluent and also by dissolution. The halide content was less than 100 ppm which is the detection limit of the method.

A zinc exposure experiment that used similar conditions to the prior zinc getter development testing was conducted (1). These tests use a zinc source temperature and filter temperature of 350 °C, after evacuating the system for twelve hours to achieve a base pressure of 1 x 10^{-6} torr or higher. The filter was heated to temperature four hours before the zinc source to ensure uniform temperature conditions for the getter material. These conditions were selected since there is a large body of data for them and the mass gain due to zinc vaporization is well characterized with the samples turning into a golden color as shown in Figure 5 for the Hohman bronze coils. An as-received coil is shown on the left side of the image to compare the initial and final conditions as well as show the orange to gold transformation. The total mass gain for the coupons is listed in Table 3, as is the nominal specific mass gain, i.e., the mass/surface area. These mass gains are consistent with the amount of zinc vaporized and prior experiments (1).

The zinc exposed coils were subsequently examined via SEM and EDS. Figure 6 shows typical EDS spectra for an as-received and zinc exposed bronze sample and the only elements present above the

Table 3 As fabricated composition of Hohman Bronze as determined via SEM EDS.

Cu-Sn Hohman As Fab					
ID	Cu	Sn	O	Si	C
Inside 100X A	95.8	2.9		1.3	
Inside 100X B	97.1	2.9			
Inside 100X C	97	3			
Inside 500X A	97.1	2.9			
Inside 500X B	96.1	3	0.9		
Inside 500X C	96.9	3.1			
Average	96.7	3.0			
Outside 100X A*	65.7	1.9			32
Outside 100X B	96.9	3.1			
Outside 100X C	96.8	3.2			
Outside 500X A	96.9	3.1			
Outside 500X B	96.9	3.1			
Outside 500X C	96.9	3.1			
Average	96.9	3.1			

High carbon is likely due to sampling error encompassing some carbon tape residue, ignoring the C indicates a 2.8% Sn bronze.

Table 4 Composition of zinc getter material after exposure.

Cu Sn exposed to 4 g zinc vapor			
	Cu	Sn	Zn
Inside 100X A	54.0	1.1	44.9
Inside 100X B	54.1	1.0	44.9
Inside 500X A	54.1	1.0	44.8
Inside 500X B	54.1	0.9	44.9
Average	54.1	1.0	44.9
Outside 100X A	54.8	1.0	44.2
Outside 100X B	54.4	1.0	44.5
Outside 500X A	54.8	1.0	44.2
Outside 500X B	54.7	0.9	44.4
Average	54.7	1.0	44.3

detection limit for EDS are Cu, Sn and Zn. The rough and notionally smooth surfaces in the as received conditions were maintained after the zinc exposure. Low and high magnification images are shown in Figure 7 for both sides of the zinc exposed bronze. The surfaces are uniform with no signs of excessive zinc deposit, which forms geometric shapes with higher purity-more zinc rich deposits. The composition of the bronze getters is shown in Table 4 and it indicates that the zinc getter contains nominally 44% zinc and a consistent composition across the various areas that were examined. The SEM images in Fig. 7 are correlated with the locations indicated in Table 3.

Table 2 Chloride content of coils measured via ICP-ES

Sample Type	Cl	F
Dissolved	<100	<100
Rinsed	<100	<100

Figure 5 Appearance of bronze coil in the as-received and zinc exposed condition. A PM bronze standard sample is also shown.

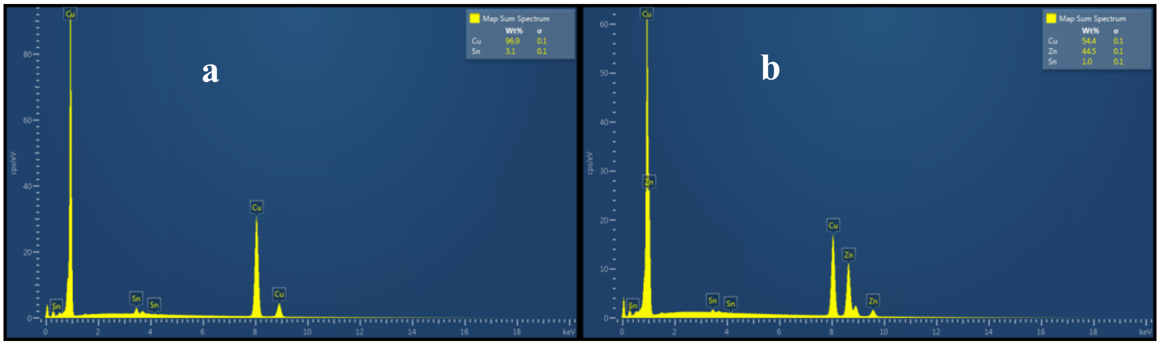

Figure 6 EDS spectra from the (a) As fabricated Hohman bronze and (b) Zinc exposed Hohman bronze

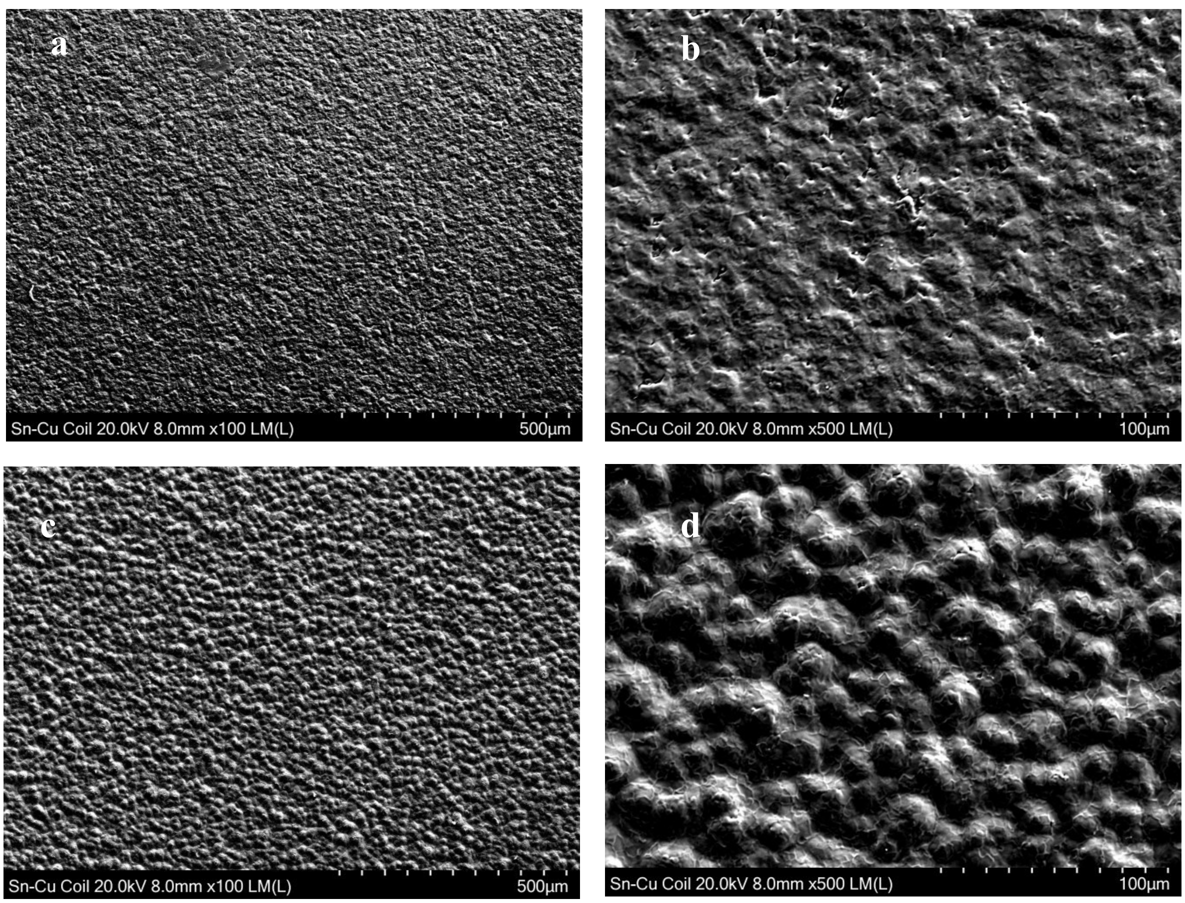

Figure 7 Zinc exposed Hohman bronze after 350 °C zinc exposure; (a and b) are on the smooth side – outside B, low and high magnification, respectively and (c and d) are on the rough side inside B, low and high magnification, respectively.

4.0 Summary and Conclusions

Hohman Plating successfully developed a process to prepare KorZincAlloy by an alkaline electroplating deposition and diffusion process. The plating thickness was uniform over most of the surface with the edges having slightly higher amounts. The diffusion cycle that was used in conjunction with the plated thickness did not produce any pinholes due to melting. The composition of the bronze met the specificated range. The zinc gettering performance was consistent with that of the SRNL produced and the initial Hohman Plating bronze that is installed in the process lid that will be used for and extracted in FY17.

5.0 Recommendations

Hohman plating is a reliable vendor and should be considered as the vendor of choice for future KZA procurements provided KZA acts as it is intended to do so and actively getters the ^{65}Zn that evolves during extraction.

6.0 References

1. P.S. Korinko, Zinc vapor trapping using copper based materials, Journal of Failure Analysis and Prevention, Vol 16, #3, 2016.
2. Email dated 11/08/2016 to Eric Janczak, RE status
3. P.S. Korinko, SRNL-L4410-2015-00012, Thermal Processing of Hohman Plated Sn to Produce Zinc Getter Material, June 2015
4. P.S. Korinko, SRNL-STI-2013-00625, Effect of Thermal Processes on Copper-Tin Alloys for Zinc Gettering, October 2013

Appendix A. Statement of Work for Tin Plating

1.0 SCOPE:

1.1 Description of Work (Services/Repairs to be performed):

Subcontractor shall prepare a methodology for plating copper sheets and obtaining heat treatment of the sheets to produce bronze. The task is a phased activity with initial trial(s) for plating, an optional optimization step, followed by a heat treating phase, with the final phase being a process that will result in electroplating and heat treating of a total of 280 – 300 square inches of copper sheet.

2.0 REFERENCE DOCUMENTS:

None

3.0 WORK REQUIREMENTS:

3.1 Technical Requirement:
All electroplating work shall be performed by the subcontractor at their factory or their subtier suppliers. Heat treatment development / validation / optimization will be conducted by SRNL to existing safe work practices. Phase 4 will be conducted at the supplier or their subtier suppliers.

Phase 1. Scoping Study
The work shall include the following:
Cutting supplied copper to appropriate dimensions
Cleaning surfaces of copper suitably for plating in both acid and alkaline tin baths
Electroplating surface with a target thickness of 0.0001 to 0.0004 inch (1.5 to 6 micrometers)
Examining thickness and providing a report
Providing samples for heat treatment optimization
Phase 2. Optimization (option) in the event that the scoping study did not produce acceptable plating thickness.
This optional phase repeats phase 1 with different, evolutionary process parameters.
Phase 3. Heat treatment development to be conducted by SRNL.
Expose electroplated copper sheet to a thermal profile that will diffuse the tin into the copper sheet to produce bronze with a composition that ranges between 2 to 18% Sn.
Phase 4. Prototype scale up
Vendor shall coat approximately 280 in^2 of bronze with a composition of 2-18% Sn.
Vendor shall provide material in heat treated condition.

3.2 FURNISHED MATERIAL/SERVICES:
SRNL shall provide copper sheet suitable for plating for all the tasks. 5 pieces 12 inches x 12 inches shall be provided for the initial trial, potential optimization, and final phase. Sheets may be cut by the vendor into smaller sizes to facilitate handling, plating, etc. Minimum size piece may be 0.5 x 3 inches.

3.3 Site Conditions:
N/A

3.4 Period of Performance/Schedule Requirements:
Period of Performance shall begin upon receipt of PO and extend for eight weeks.

3.5 Personnel Qualifications/Certification:
N/A

3.6 Deliverables:

Phase 1. Scoping Study

Vendor shall supply a report that summarizes the bath type used and the plating thickness.

Phase 2. Optimization (option) in the event that the scoping study did not produce acceptable plating thickness.

Vendor shall supply a report that summarizes the bath type used and the plating thickness.

Phase 3. Heat treatment development by SRNL.

SRNL shall provide vendor a report containing the thermal profile and chemistry of sheet.

Phase 4. Prototype scale up

Vendor shall supply a report containing the as plated coating thickness, the thermal profile used, chloride content of the sample, and chemistry of sheet, and approximately 280 in^2 of bronze with a composition of 2-18% Sn.

4.0 ACCEPTANCE OF SERVICES:

Subcontractor will provide reports for each phase accomplished, a return to SRS of approximately 280 in^2 of bronze sheets, and all materials not consumed during testing.

5.0 ATTACHMENT:

None

Distribution:

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