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Effectiveness of Bronze as a Zinc Getter after Being Subjected to Simulated Exposures

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Abstract

Gamma emitting zinc-65 was detected in piping contained in a tritium glovebox after a vacuum thermal process. This contaminate was created during irradiation of components in a nuclear reactor and was borne of natural zinc. The Tritium Extraction Facility prefers to capture the zinc in a high radiation area to minimize potential dose to the worker and to reduce the likelihood of spreading contamination to other areas of the facility. Previous efforts have shown that bronze is an excellent candidate material to act as a zinc getter in the as-fabricated condition. In reality, the extraction process may contain moisture and hydrogen which could cause oxidation or reduction of the surfaces of the zinc getters. A series of experiments was conducted to determine the efficacy of the zinc getters after oxidation and reduction exposures. It was determined that the bronze coupons were moderately effective in most of the oxidized conditions and in all the oxidized and reduced conditions.

Background

Gamma emitting ^{65}Zinc (^{65}Zn) deposits were detected in a glovebox after a vacuum thermal process treating irradiated components to produce tritium; the deposits were analyzed and the results have been reported previously (1). In brief, natural zinc is activated in reactor and removed during the vacuum extraction process and is transported as a metallic vapor and is deposited in the process piping (1). Methods that use specially placed and heated filters to prevent further contamination of the glovebox and piping systems were developed and deployed in the facility (2). Upon completion and implementation of these mitigation strategies, a method and material was identified and selected that could be deployed in a well-protected area of the facility that is better suited to handle the gamma emitting ^{65}Zn (3).

A project was undertaken to develop alternative materials to the commercially available bronze alloys that may be used for zinc vapor capture. While previous research demonstrated the viability of zinc capture using bronze sheets, further consideration of the composition indicated potential issues for the facility (4&5). The commercial bronzes with the desired tin contents (2-10% Sn) typically contain relatively high concentrations of phosphorous that can potentially form phosphoric acid in the presence of beta irradiation, moisture, and hydrogen isotopes (4) or lead that creates a mixed waste, i.e., hazardous material and radioactive, which adds to the disposal costs. Thus, there was interest in developing high purity binary copper-tin alloy as a zinc getter using powder metallurgical approaches (6). The material was shown to be highly effective at capturing zinc vapor over a broad range of compositions in the as fabricated condition. For use in the facility it was determined that characterizing the effectiveness of the getter material after simulated processing conditions would be beneficial.

The processing conditions of the facility include the following sequences: vacuum, moist hydrogen exposure and dry hydrogen exposure. Due to the potential for complex interactions and gas evolution the facility engineers agreed that experiments to simulate the gas evolution and metallurgical reactions should be conducted. A test matrix that used powder metallurgically (PM) bronze samples with compositions that ranged from pure Cu to Cu 5 wt % Sn were prepared, subjected to oxidative and reducing conditions, exposed to zinc vapor and characterized.

Experimental

As described previously [6], a powder metallurgical approach was used to fabricate the zinc getters. High purity copper and tin were used. Figure 1 shows the size and morphology of the starting powders, Figure 1a shows the copper flakes and Figure 1b shows the tin and how it agglomerates. The powders were weighed, to the desired ratio, on a Fischer Scientific Scale with a precision of 0.1 mg, and a the total powder lot size was 10 g. The alloys ranged in composition from 1.25 to 5% Sn, as listed in Table 1. The powder blends were homogenized in a Pulverizer high energy mill with eight to 12 steel balls with diameters of 6 to 10 mm for one hour at 150 RPM in the “forward” direction followed by one hour in the reverse direction.

Approximately 0.5 g quantities of the well mixed powder blends were weighed and placed into a 12-mm diameter steel die, the die was assembled and the powder was compressed at forces between 44 and 51 kN, giving a green density of approximately 80%. Additionally, this pressing condition enabled the as pressed (green) compacts to be handled without crumbling while being inserted into the furnace for sintering.

The green samples were placed on a flat quartz plate in an argon purged tube furnace and sintered using the thermal profile that had been previously developed (6) and is as follows: Argon purge 12 hours at RT, RT to 120°C at 5 °C/min; hold for 1 hour; 120 to 220°C at 5 °C/min; hold for 2 hours; 220°C to diffusion temp at 5°C/min; hold for 2 hours; and furnace cool. The samples were sintered at homologous temperatures ($T/T_{m\text{-}abs}$) between 0.8 and 0.9. Unfortunately, there was a decrease in the sample density after sintering.

Samples were cold rolled in a manual rolling mill to a nominal reduction of 25% to increase the density and surface area. The samples were subsequently surface ground with 800 grit sand paper to remove any oxide film that formed during sintering. Localized areas that were not abraded were dressed using a coarse grinding wheel on a handheld rotating Dremel tool with 120 grit aluminum oxide. The samples were then identified with respect to the composition using a series of dots and individual samples were identified using slits.

The sintering furnace, quartz tube furnace, was modified with a water bubbler and argon flow tube to generate a suitable oxidation environment. A two-hour argon purge at 12 SCFH plus one SCFH flowing through a room temperature water bath proved to be effective to displace the air in the tube furnace. At the end of two-hour purge cycle and for the duration of the oxidation exposure the flow meter of gas through the water bubbler was increased to two SCFH and the dry argon purge was terminated. A total of 12 samples, four of each composition, were oxidized at each temperature; the samples were oxidized at 250, 350 or 450°C for 12 hours.

One sample from each composition, i.e., 0, 1.25, 2.5, and 5.0% Sn, balance Cu, and each oxidation exposure, i.e., 250°, 350°, and 450°C, was subjected to a reduction exposure at each temperature, i.e., 250°, 350°, and 450 °C, in a helium-5% hydrogen gas mixture, as indicated in Table 1. Samples were loaded into a ¾" stainless steel tube with VCR-12 fittings, and the sample tube was connected to the manifold using copper gaskets and a ceramic heater was placed around the sample tube. The system was evacuated and backfilled three times with 99.9% helium prior to heating. The test cell was brought up to temperature under a helium atmosphere and when the temperature stabilized the helium-hydrogen gas mixture flow was started. MKS mass flow controllers were used for the reduction step with a target gas composition of 95% He-5% H_2, which was achieved using a 10% flow for H_2 on a flow controller with a 500 sccm full scale (FS) reading and 47.5% for the He flow controller with a 2000 sccm full scale. Type K thermocouples were used as reference and control thermocouples. The exposures were run for a minimum of 12 hours and were terminated manually. Samples were weighed initially as well as after exposure and visually examined. The condition of all the samples prepared are listed in Table 1.

Oxidized and reduced samples were examined using a Rigaku X-ray Diffraction system using copper K_α radiation. The data were analyzed and compared to the expected compounds for the binary alloy in the presence of oxygen.

Zinc capture effectiveness was characterized for the samples after the treatments using a system described previously (5&6). The zinc deposition apparatus uses ConFlat flanges and four-inch diameter piping for the "zinc pot" and deposition system. These components are connected to an instrumented chamber pumped with a turbomolecular pump backed by a diaphragm pump. The zinc pot and deposition chamber are separately heated using a mantle heater and split tube furnace, respectively. Control, over-temperature and reference thermocouples are applied to the external surface and the internal temperatures are monitored using two ten element thermocouples at a spacing of 31.75 mm. The coupons were placed near the seventh and eighth thermocouple about 230 mm from the bottom of the zinc pot. Nominally five grams of granulated Zn were weighed and placed in the zinc pot, which was an excess amount of zinc to be vaporized under the exposure condition. The system was evacuated for a minimum of 12 hours after sample insertion to ensure that acceptable vacuum levels were achieved. The base vacuum, as measured by a wide range gauge (WRG) located over the turbo molecular pump, was typically in the mid 10^{-7} Torr range prior to initiating an exposure. The heater controllers were programmed automatically to heat to the desired temperature of 350ºC and to hold for the desired exposure time. A stainless steel wool trap was heated to 200°C, conditions determined from Ref. 2, and held for 9 ½ hours, the getter materials were heated to the 350ºC desired set point in 45 minutes and held for 9 hours, and the zinc pot was heated at 8 to 10°C/min to 350°C after a four hour delay for the getter disks to reach the steady state exposure temperature. The temperature and pressure data were recorded at approximately 15 second intervals using a custom LabView data acquisition program. After the system cooled, the apparatus was brought up to atmospheric pressure by venting with helium. The samples were removed and weighed on an Ohaus Discovery analytical scale and photographed using a digital camera.

Selected samples were characterized using an Hitachi TM 3000 tabletop scanning electron microscope with images taken from 500-3000X magnification, at an accelerating voltage of 15 keV, the nominal working distance was 8 mm, and the samples were characterized using a Bruker X-ray energy dispersive spectroscopy at nominally 1000X and 3000X magnifications, and other magnifications were used as needed to show desired features.

Results and Discussion

The appearance of typical samples produced using the powder metallurgy (PM) approach is shown in Figure 2 for disk coupons in the green (as-pressed), sintered, and rolled conditions. The green pellets, Fig. 2a, exhibit surface cracks that varied in density and extent. The as-sintered pellets, Fig. 2b, typically exhibit small bubbles on the surface associated with sub-surface voids and pores, likely caused by the melting of the tin during sintering. They also exhibit a matte surface due to slight oxidation from the impure environment in the sintering furnace, despite a two hour purge at a sufficiently high flow rate to exchange the gas three to five times. The rolled pellets, Fig. 2c, exhibit a smeared surface that is mostly shiny. Excessive rolling causes cracks and splits in the pellets and modified the nominally circular shape to an elliptical one. The samples were subsequently surface ground using a Dremel tool with a resultant surface appearance shown in Fig. 2d. The as-fabricated surface chemistry, SEM EDS, is listed in Table 2.

A sample of each composition, 0, 1.25, 2.5, and 5% Sn was retained in the as-ground condition for exposure. Samples of each composition were oxidized in the argon – moisture gas for 12 hours at 250, 350, and 450°C. The surface appearance of the oxidized samples is shown in Fig. 3. There is a slight discoloration for samples exposed at 250°C and the oxide discoloration gets progressively darker with increased temperature. After the 450°C exposure the pure Cu sample is slightly discolored and the 5%Sn is nearly black. One sample of each composition was retained in the oxidized condition for Zn exposure. The post oxidation treated samples were also examined using SEM/EDS and the compositions are listed in Table 3.

The samples oxidized at the three temperatures were subjected to a reducing atmosphere at 250, 350, or 450°C. To ascertain the efficacy of the reduction treatment, samples that were oxidized at all three temperatures were subjected to each reduction temperature, Table 1, and zinc exposure. In general, the 250°C reduction for 12 hours had very little effect on the surface appearance of the samples, as shown in Figure 4a while samples reduced at 450°C exhibited virtually no surface oxide or discoloration, Figure 4b. The oxygen contents for samples reduced at 250ºC were measured using SEM – EDS with the results listed in Table 4.

The samples oxidized at 450 and as fabricated samples were examined using XRD and the oxides were comprised of stannous oxide, cupric oxide, and cuprous oxide as indicated in Table 5. The predominate oxides detected are tin based for the as-fabricated condition with some copper oxides at the highest oxidation and copper content sample.

Zinc Exposure

Each lot of samples, i.e., as-fabricated, as-oxidized at the three temperatures, and reduced at all three temperatures, was subjected to zinc vapor exposure at 350°C with a zinc source temperature also at 350°C, conditions that were successfully used for previous experimentation (5&6). Due to an over-temperature event or controller malfunction, the samples reduced at 350°C were exposed to two zinc deposition conditions. The first was an aborted zinc exposure that did not produce much weight gain followed by a standard exposure. This may partially explain the increased weights compared to the other conditions. Unfortunately, duplicate tests were not conducted since no additional samples were available. The surface condition of the samples after zinc exposure is shown in Fig. 5. There is visual evidence of zinc capture, the surface coloration changes from a brownish bronze color to a golden brass color, on most of the samples. The exceptions are the as-oxidized samples and several of the 250°C reduced samples. The weight change for each of the samples is indicated in Table 6. These data show that weight gain was achieved for all but the pure copper as fabricated sample. This result is consistent for pure copper samples tested previously (2). The mass changes are shown graphically in Figure 6. There is not a systematic variation of the sample weight gains either with tin content, oxidation condition or reduction condition. This result is encouraging since it appears that slight oxidation products on the surface do not grossly adversely affect the bronze material affinity to capture zinc. The higher than expected mass gain from the 350°C reduction after the dual exposure suggests that an alloy modification that includes zinc may prove beneficial as a zinc getter; this assertion was not borne out upon further testing and the increased effectiveness appears to be a testing anomaly.

This series of experiments combined with the previous experiments for zinc vapor capture indicate that bronze alloys with compositions that range from about 1.2 to 10% Sn provide a zinc active substrate that is active over a temperature range of 250°C to 450°C [5]. These data coupled with the fabrication and preparation methods developed in this project indicate that a prototype zinc and lithium trap should be tested in the TEF. There are still challenges related to the long-term stability of the captured zinc that need to be addressed, however, the simple bronze based alloy is expected to reduce the amount of zinc that is released to the glovebox. Improvements in the fabrication of the zinc getter materials should be considered, such as electroplate Sn and diffusion treatments.

Summary and Conclusion

A series of experiments was conducted on bronze zinc getter coupons that were produced using powder metallurgy/sintering methods. These coupons were exposed to oxidizing and reducing conditions prior to being exposed to zinc vapor at 350°C. The getter coupons were oxidized and reduced successfully in a helium – 5% hydrogen environment. The samples remained active for zinc capture after these treatments.

Samples in the as-oxidized condition also remained active, based on weight change data, but did not visually appear to turn golden in color, which is an excellent visual indicator for zinc capture.

The anomalous zinc capture data for the samples exposed at 350°C with a minor zinc constituent was not repeatable.

Acknowledgements

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Table 1. Conditions used.

Condition	Reduction	100% Cu	98.75% Cu 1.25 % Sn	97.5 % Cu 2.5% Sn	95% Cu 5% Sn
As – Fab	NA	X	X	X	X
250ºC Ox	NA	X	X	X	X
350ºC Ox	NA	X	X	X	X
450ºC Ox	NA	X	X	X	X
250ºC Ox	250ºC	X	X	X	X
350ºC Ox	350ºC	X	X	X	X
450ºC Ox	450ºC	X	X	X	X

Table 2. As fabricated chemistry of the pellets.

As Fabricated	Cu (wt %)	Sn wt (%)	O (Wt %)
Cu	95.89	0.43	3.68
Cu-1.25% Sn	96.84	1.19	1.96
Cu-2.5% Sn	94.07	4.03	1.90
Cu-5% Sn	91.93	4.76	3.31

Table 3. Composition of samples in oxidized condition.

Composition	Oxidation Temp °C	Copper (wt. %)	Oxygen (wt. %)	Tin (wt. %)
0 Sn	250	98.17	1.65	0.19
1.25 Sn	250	97.71	1.17	1.12
2.5 Sn	250	93.70	2.43	3.88
5.0 Sn	250	94.05	1.74	4.21
0 Sn	350	NA	NA	NA
1.25 Sn	350	97.76	1.41	0.83
2.5 Sn	350	92.43	3.32	4.25
5.0 Sn	350	93.78	2.19	4.03
0 Sn	450	97.33	1.71	0.98
1.25 Sn	450	95.96	2.34	1.71
2.5 Sn	450	93.98	2.44	3.58
5.0 Sn	450	93.75	1.53	4.71

Table 4. Surface composition of samples oxidized at 450ºC and reduced at 250ºC in He-5% H2.

Composition	Copper (wt %) as Reduced	Oxygen(wt%) as Reduced	Tin (wt %) as Reduced
0 Sn	98.68	1.32	0.00
1.25 Sn	96.23	1.80	1.97
2.5 Sn	96.64	1.21	2.15
5.0 Sn	91.76	2.7	5.53

Table 5. Oxides present in the as-fabricated and 450°C oxidized condition.

Sample ID	**Oxides**
Cu 0 Sn As Fab	SnO_2
Cu 0 Sn 450 Oxidation	Cu_2 O and CuO
Cu 1.25 Sn As Fab	Cu_2O
Cu 1.25 Sn 450 Oxidation	SnO_2
Cu 2.5 Sn As Fab	SnO_2 and Cu_2O
Cu 2.5 Sn 450 Oxidation	SnO_2
Cu 5.0 Sn As Fab	SnO_2
Cu 5.0 Sn 450 Oxidation	SnO_2 and CuO

Table 6. Weight change (mg) of the samples after the given treatment and zinc exposure.

% Sn	**As Fab**	**Ox 250**	**Ox 350**	**Ox 450**	**Ox 250 Red 250**	**Ox 250 Red 350**	**Ox 450 Red 250**	**Ox 350 Red 250**	**Ox 350 Red 350**	**Ox 450 Red 350**	**Ox 250 Red 450**	**Ox 350 Red 450**	**Ox 450 Red 450**
	0.0	0.5	1.4	0.5	1.2	2.4	0.6	1.3	2.8	3.8	1.5	1.0	0.3
1.25	1.0	0.9	2.3	0.9	1.3	4.2	1.3	1.1	3.5	3.5	1.0	1.2	0.5
2.5	1.1	0.9	1.7	0.9	1.4	3.5	1.1	0.6	3.8	4.3	0.6	1.1	0.6
5	1.5	0.7	1.1	0.7	0.9	3.3	0.4	0.7	2.6	2.4	1.0	1.0	0.6

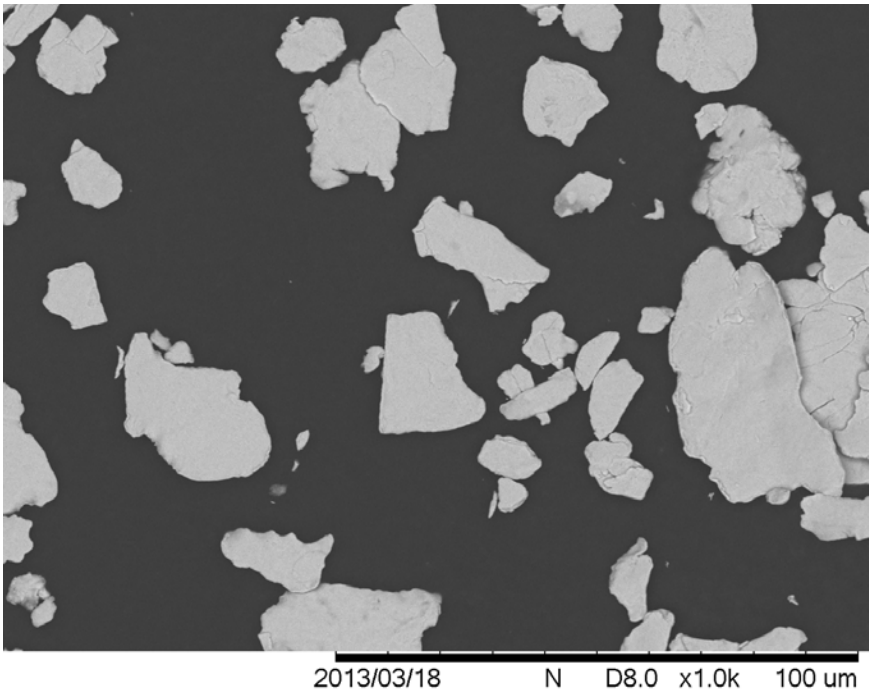

Fig. 1a.

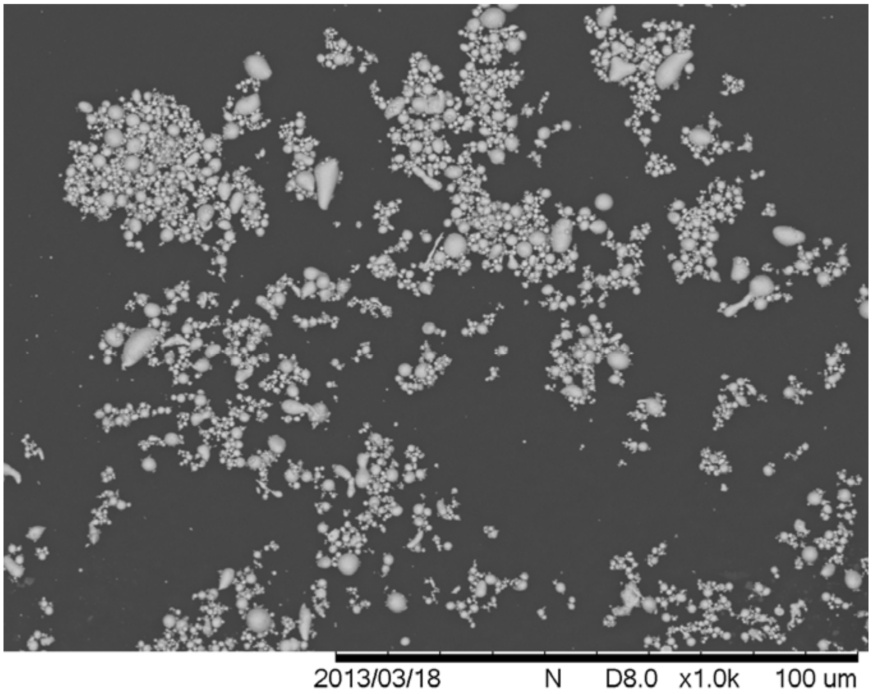

Fig. 1b

Figure 1. Appearance of starting powders used for this experiment (a) copper powder (b) tin powder.

Fig. 2a.

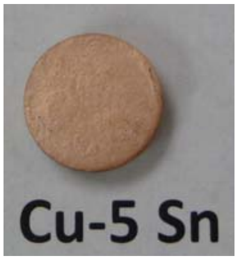

Fig. 2b.

Fig. 2c.

Fig. 2d.

Figure 2. Appearance of pellets used in this experiment (a) green (as pressed pellets) (b) sintered pellets (c) rolled pellets, and (d) surface ground pellets.

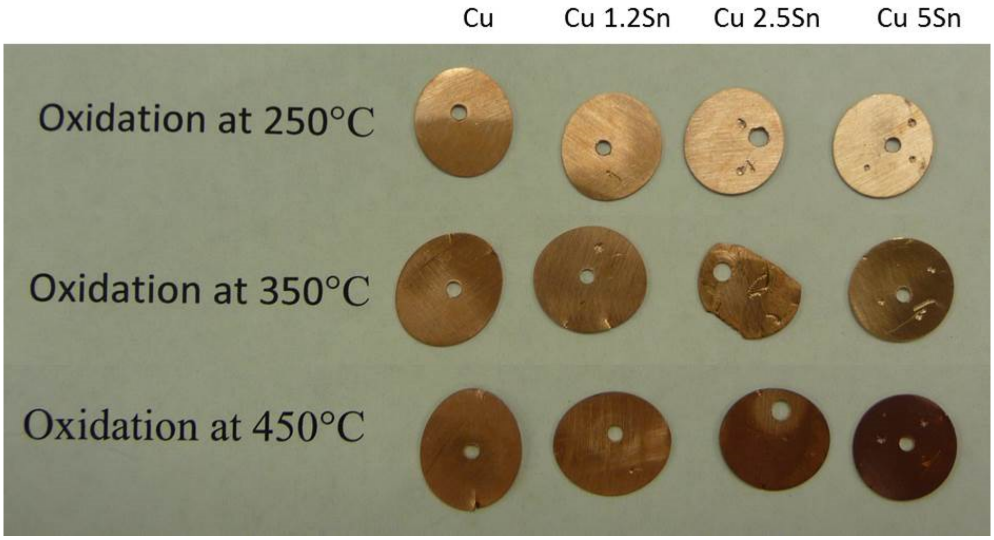

Figure 3. surface appearance of the as-oxidized pellets.

Fig. 4a.

Fig. 4b.

Figure 4. Surface appearance of samples oxidized at 250ºC (first four) 350°C (next four) and 450°C (final four) after being reduced at (a) 250°C and (b) 450°C in He-5% H_2.

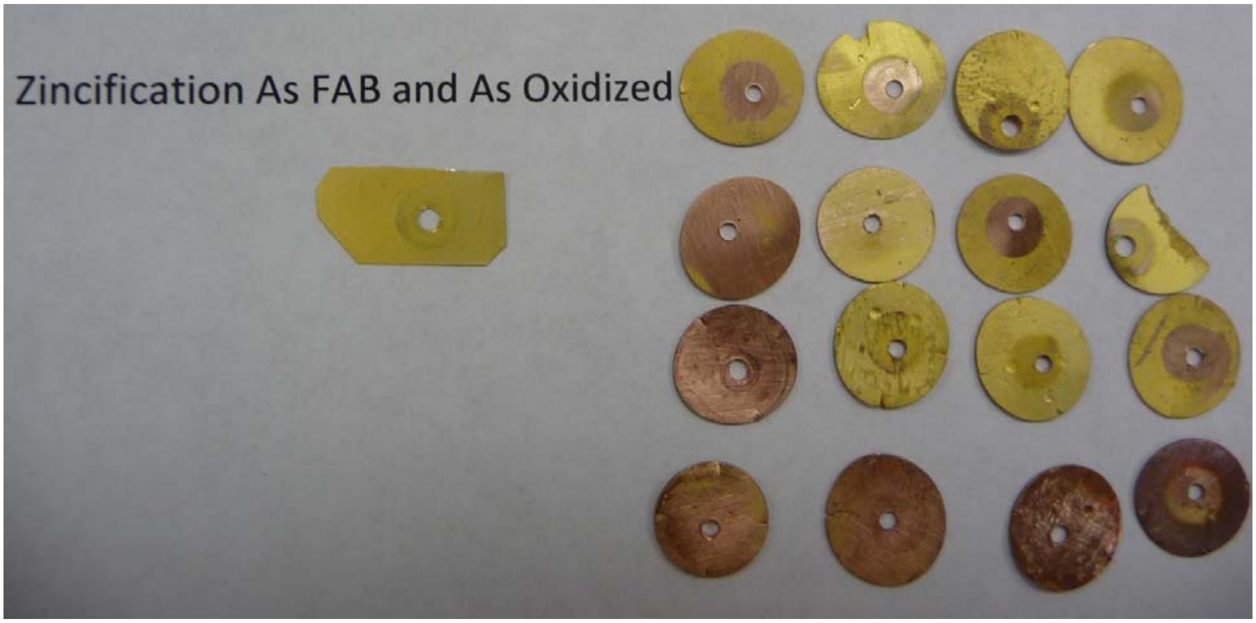

Fig. 5a.

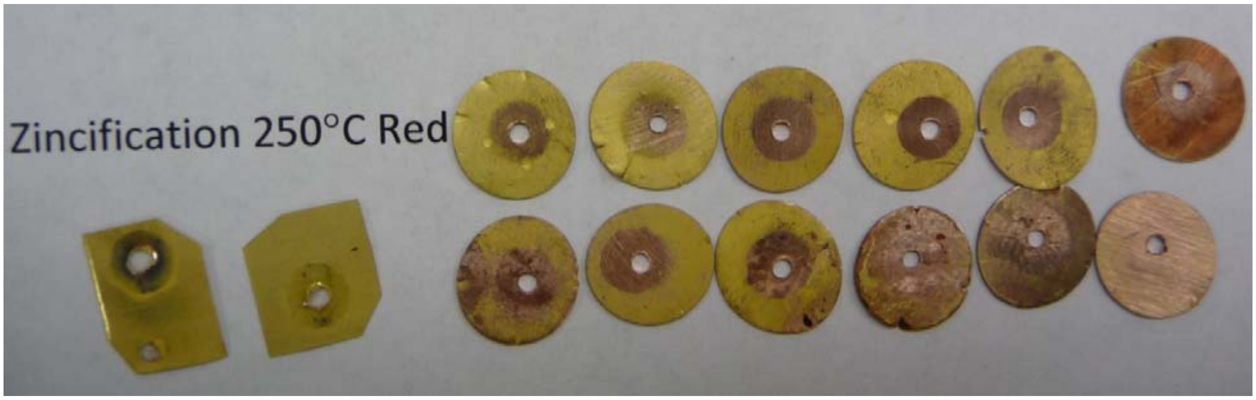

Fig. 5b.

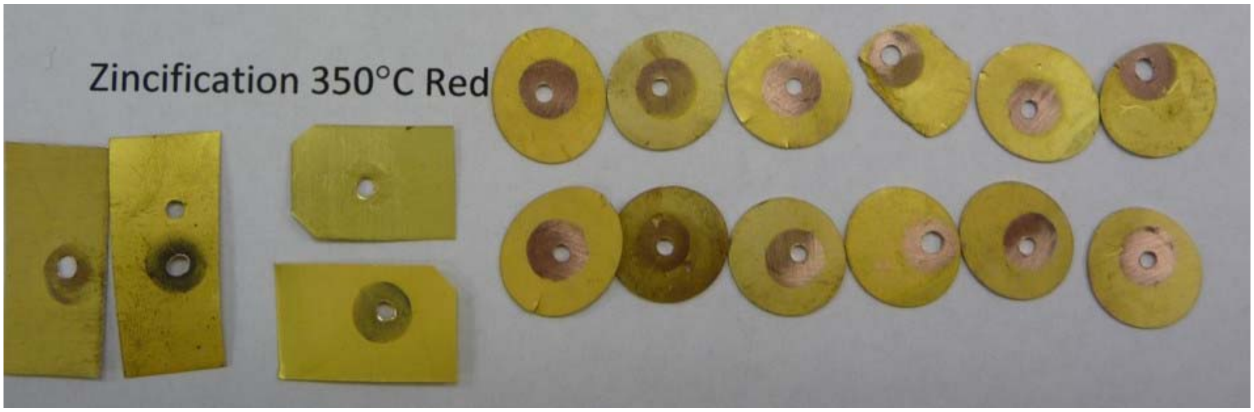

Fig. 5c.

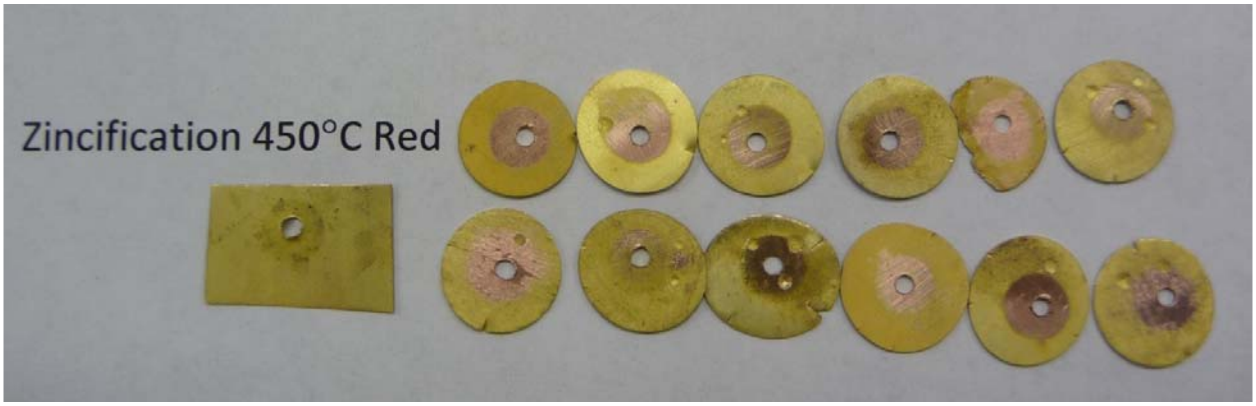

Fig. 5d.

Figure 5. Appearance of the pellets after zinc exposure at a nominal set point of 350°C, (a) in the as fabricated and as oxidized condition, (b) after 250°C reduction (c) after 350°C reduction (d) after 450°C reduction.

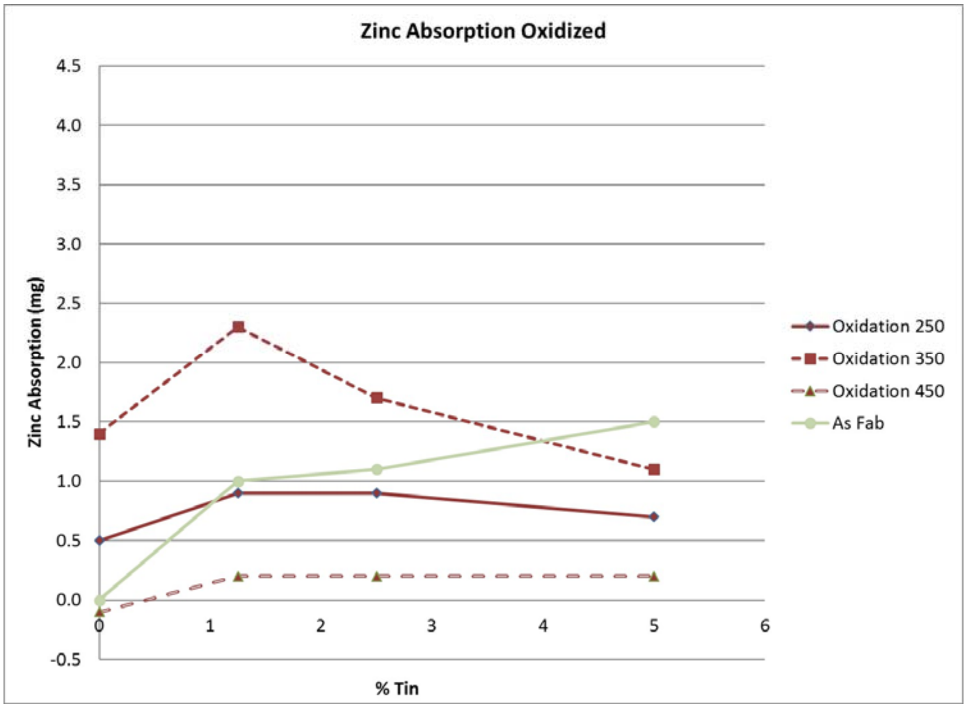
Zinc Absorption Oxidized
Zinc Absorption (mg)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
1
2
3
4
5
6
% Tin
Oxidation 250
Oxidation 350
Oxidation 450
As Fab

Fig. 6a.

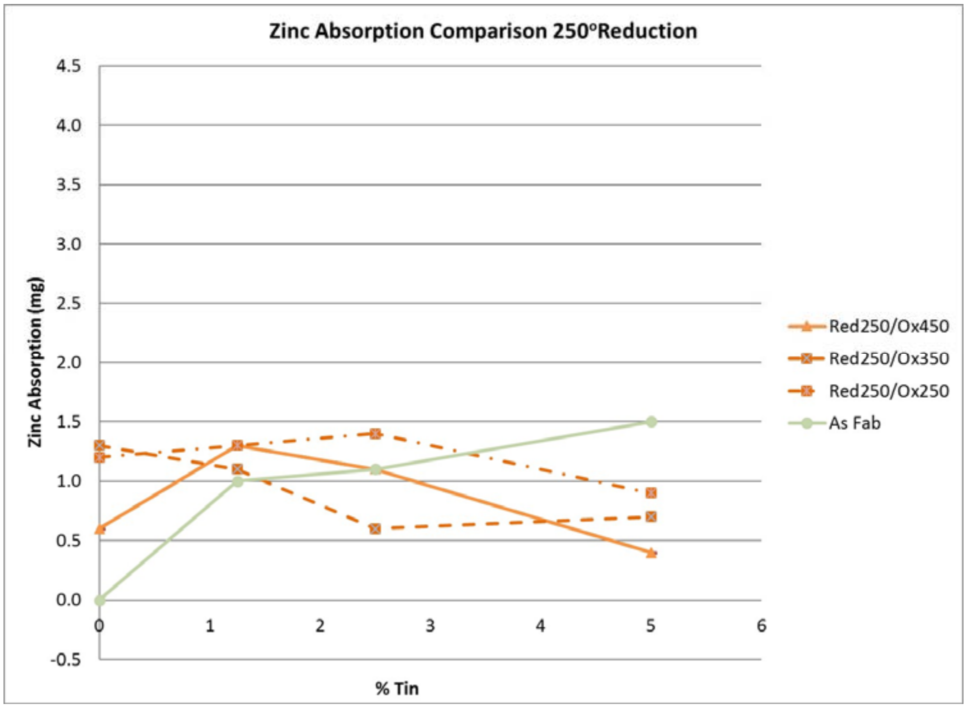
Zinc Absorption Comparison 250°Reduction
Zinc Absorption (mg)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
1
2
3
4
5
6
% Tin
Red250/Ox450
Red250/Ox350
Red250/Ox250
As Fab

Fig. 6b.

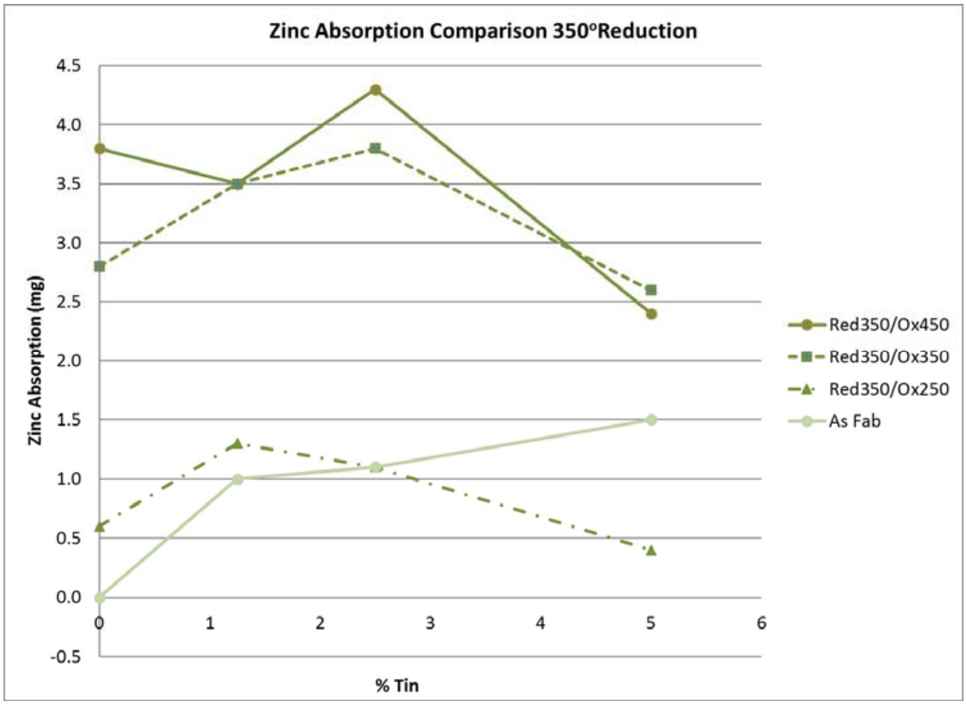

Fig. 6c.

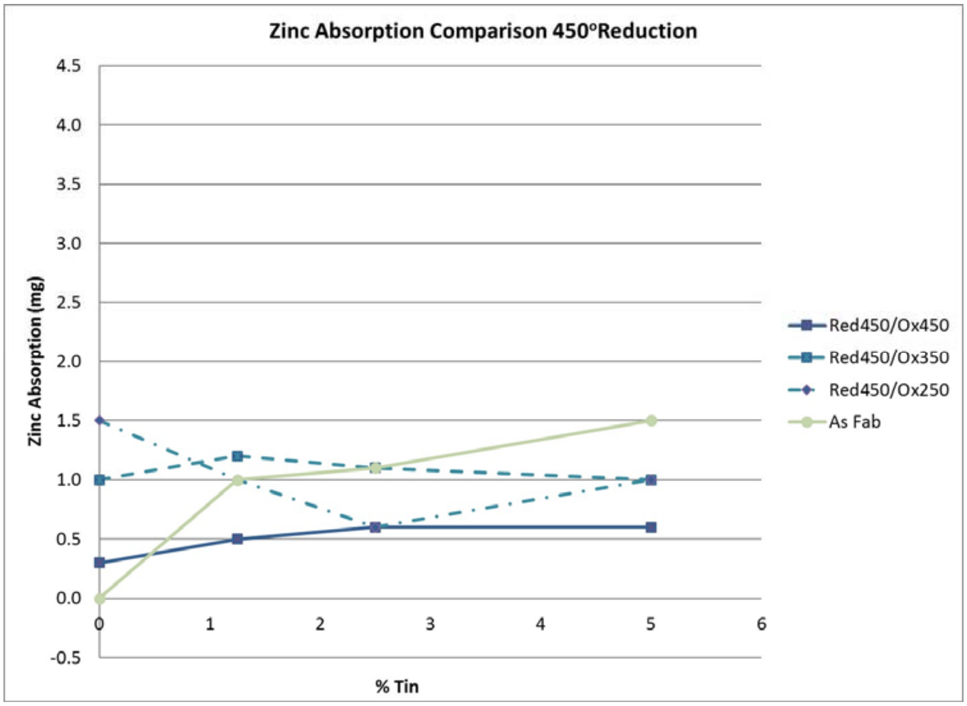

Fig. 6d.

Figure 6. Mass changes associated with zinc exposures for samples in a) the as-fabricated and oxidized condition, b) as fabricated and oxidized at 250, 350, and 450°C and reduced at 250°C, c) as fabricated and oxidized at 250, 350, and 450°C and reduced at 350°C, and d) as fabricated and oxidized at 250, 350, and 450°C and reduced at 450°C.