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Effects of annealing temperature on morphology and thickness of samarium electrodeposited thin films

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Abstract

Electroplated depositions of Sm were prepared using a vertical well-type electrodeposition unit with an aqueous ammonium acetate electrolyte system, with an average deposition yield just over 87%. The depositions were analyzed for morphology and thickness by scanning electron microscopy (SEM) and chemical composition by energy dispersion X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) before and after firing. The depositions were fired at 125 to 700 °C, while varying the heating rate from 0.5 to 10 °C/min in either an oxidizing or reducing atmosphere. A heating rate of 10 °C/min was slow enough to prevent disruption of the deposition morphology during firing. A gas sweep enhanced the removal of any organic substituents, with an oxidizing environment being more advantageous than a reducing environment.

1. Introductions

Actinide thin-films have gained significant attention over the last several decades for a myriad of applications including accelerator bombardments [1–3], α -spectroscopy [4,5], and fission fragment sources [6–9]. The Californium Rare Isotope Breeder Upgrade (CARIBU) at Argonne

National Laboratory's Argonne Tandem Linear Accelerator System (ATLAS) has generated the need to produce high-activity, thin-film fission fragment sources using ^{252}Cf . The Radiochemical Engineering Development Center (REDC) at the Oak Ridge National Laboratory (ORNL) is one of the few producers of ^{252}Cf in the world and is responsible for every aspect of production, purification, and source fabrication. [10,11] Recently, the largest electrodeposition of ^{252}Cf ever prepared was produced at the REDC, measuring $6.3 \pm 0.4 \text{ GBq}$ ($1.7 \pm 0.1 \text{ Ci}$) ^{252}Cf . [8,9] However, despite the ^{252}Cf material being extensively purified, the source was thicker than desired for the application, reducing the overall fission fragment yield. This is believed to originate from the electrodeposition technique where the organic substituents from the ammonium acetate electrolyte solution are deposited along with the ^{252}Cf .

This work focuses on the effort to better understand the electroplating of lanthanides and actinides by using natural Sm as a representative lanthanide and a surrogate for Cf. The effect of annealing temperature on the deposited film morphology, thickness, and chemical composition will be discussed, with special attention on the differences observed from firing under oxidizing or reducing atmospheres.

2. Experimental

2.1 Materials

Nitric acid (Optima, HNO_3) and ammonium acetate (98.8%, NH_4Ac) were purchased from Thermo Fisher Scientific Inc.; anhydrous samarium chloride (99.9%, ultra-dry SmCl_3) was purchased from Alfa Aesar; ammonium hydroxide (ACS Grade, NH_4OH) was purchased from

Sigma-Aldrich; hydrochloric acid (OmniTrace Ultra, HCl) was purchased from EMD Chemicals Inc.; and distilled deionized (ddi) H₂O was obtained from a Millipore Milli-Q® Academic Ultrapure Water Purification System with a Quantum® EX Ultrapure Organex Cartridge filter operated at 18.2 MΩ cm at 25 °C.

2.2 Electrodeposition

The electrodeposition unit had a well-type configuration and has been described in detail elsewhere. [8] A short description is provided here: The unit comprised a copper cathode that housed an embedded stainless steel (SS) plate as the deposition substrate with a deposition area of 5.6 cm². The solution well was machined out of polyether ether ketone (PEEK). A silicon gasket was used to complete the seal between the well and the substrate. The anode was a platinum plate with slits in it to prevent gas from accumulating between the electrodes. The anode was suspended in the well so that a distance of 1 cm was maintained between the anode and the deposition surface (cathode). The entire unit was designed and fabricated at ORNL. Electrodepositions were carried out using an Agilent E3616A 0-25 V, 0.0-1.7 A DC Power Supply in the constant current mode, allowing the potential to vary.

Prior to each deposition run, the unit was subsequently washed with 1 M HNO₃, ethanol, and ddi H₂O. It was then assembled and leak tested with 0.35 M NH₄Ac for a minimum of 12 h. Upon passing the leak test, the unit was set up for the electrodeposition run. Each run consisted of adding a 200 μL aliquot of 100 mM SmCl₃ 0.05 M HCl (~3.0 mg of Sm³⁺) to the deposition unit, which contained 10.3 mL of 0.35 M NH₄Ac, making the final electrolyte volume 10.5 mL. The anode was then submersed in the electrolyte solution; both electrodes were then connected to the

power source and energized. The current was increased slowly over the first 5 min until it reached the desired setting of 0.700 A, at which point the current was held constant for the duration of deposition, which was 4 h. This current was selected to mimic the current density of 125 mA/cm² used with previous ²⁵²Cf depositions. [8,9] At the end of the deposition, 1 mL of concentrated NH₄OH was added prior to de-energizing the power source to prevent the deposited material from dissolving once the potential was removed. The electrolyte solution was then collected, sampled, and analyzed using neutron activation analysis (NAA). The overall error in deposition yield was calculated by propagating the statistical error from NAA analysis and the systematic error from the experiments using standard methods.

2.3 Deposition Firing

The depositions were heated using a Thermo Scientific Lindberg/Blue M Mini-Mite Tube Furnace TF55035A-1 with a 12 in. heating zone operating from 100–1100 °C, controlled by an Omega Engineering, Inc. digital, multi-segment programmable controller. Several firing patterns were investigated including ambient to 125 °C at 0.5 °C/min, holding for 60 min; and ambient to 700 °C at 0.5 °C/min, holding for 60 min. These firing patterns were conducted under an air atmosphere with no gas sweep and also a 96% He 4% H₂ mixture with a gas sweep of roughly 2 psig in either a quartz or mullite tube. A firing pattern of ambient to 125 °C at 0.5 °C/min, holding for 60 min, and then continuing up to 700 °C at 0.5 °C/min, holding for 60 min, was used under an air atmosphere with no gas sweep. Other firing patterns from ambient to 125 °C, holding for 60 min, and continuing up to 700 °C and holding for 60 min, with heating rates of 2 and 10 °C/min were performed under either an air atmosphere with and without a gas sweep or 96% He 4% H₂ mixture with a gas sweep of roughly 2 psig in an alumina tube.

2.4 Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), and X-ray Photoelectron Spectroscopy (XPS)

Scanning electron microscopy (SEM) along with energy dispersive X-ray spectroscopy (EDS) was performed to study the morphology, thickness, and qualitative chemical analysis using a Hitachi S-3400N Scanning Electron Microscope coupled with a Hitachi EDAX 3400 EDX detector housed at the High Temperature Materials Laboratory (HTML) at ORNL. The SEM electron beam was operated at an accelerating voltage of 10 kV, and the images recorded the back-scattered electron (BSE) detector signal. The EDS data were analyzed for relative chemical composition using the EDAX Genesis software. Images were taken of the deposition substrate with the beam perpendicular to the surface for a top-down view and with the substrate tilted 90° to view the profile of the deposits.

The particle size distributions were determined using ImageJ version 1.50b software. The area of each deposition fragment was obtained, and then a gross estimation of the size of each fragment was approximated by assuming each fragment to be circular and calculating the diameter of each circular fragment. Fragments with an area smaller than 20 μm^2 were removed from the analysis. This simplification allowed for semi-quantitative analysis of the change in size of the fragments before and after firing the depositions.

X-ray photoelectron spectroscopy (XPS) was performed to obtain more detailed analysis of the composition and binding of the depositions using a Thermo Scientific K-Alpha XPS with a double-focusing hemispherical analyzer and a position-sensitive detector with 128 detector

elements. The spectrometer was operated in the constant analyzer energy mode, with a 0.25 m Rowland circle monochromator with a micro-focused X-ray source extraction source window comprised of a water-cooled aluminum-coated anode at an energy of 1486.68 eV and strength of 72 W. The beam size was $400 \times 400 \mu\text{m}$, and the analyzer width was $60 \times 60 \text{ mm}$ operating in a multichannel direct signal mode. The samples were first interrogated with a large survey energy scan to determine the elements present, followed by narrow-region scans to probe the core levels in the elements of interest to better determine type of bonding and oxidation of each element. The samples were then etched using an argon ion beam, and the survey and narrow region scans were repeated. This was performed on a deposition prior to firing and on a deposition fired with the firing pattern starting from ambient to 125 °C, holding for 60 min, and continuing up to 700 °C and holding for 60 min, with heating rates of 2 °C/min under an air atmosphere with a gas sweep of roughly 2 psig, deposition 3.

2.5 Deposition Yield by Neutron Activation Analysis (NAA)

NAA was performed at the High Flux Isotope Reactor (HFIR) in the PT-1 pneumatic tube station to determine the electrodeposition yields. Irradiations were performed on the stock Sm solution and samples of the post-deposition electrolyte solutions for either 20 or 300 s, depending on the expected amount of Sm in each sample. The samples were prepared by taking an aliquot (10 or 100 μL , respectively) to dryness in a high-density polyethylene (HDPE) insert which was sealed and placed into an HDPE pneumatic tube capsule for irradiation. The irradiated samples were analyzed by gamma (γ)-ray spectroscopy using a Canberra N-type high-purity germanium detector (HPGe) with 44% relative efficiency (endcap diameter = 2.5 in.) and a Lynx 32k-channel MCA running Genie 2000 gamma spectroscopy software. The detector has an energy

resolution of approximately 2 keV at 1332 keV. Relevant nuclear data were obtained from Browne and Firestone. [12] The HPGe detector was calibrated using a multi-isotopic standard. The activated ^{153}Sm ($t_{1/2} = 46.284$ h) was tracked by the 103 keV γ -ray. The deposition yields were determined by comparing the [Sm] in the electrolyte solution before and after deposition, taking into account decay time, irradiation time differences, and dilutions.

3. Results and Discussion

The deposition yield from all 16 depositions was very consistent and showed very high deposition efficiency, averaging just over 87% (Table 1). Some variation in yield is not uncommon for electroplated depositions. [13] The results repeated here display higher efficiency and better consistency than previously reported for electrodepositions of Sm from an NH_4Ac electrolyte system. This high efficiency is believed to be a result of a better electrodeposition unit design, which allows for a constant, uniform electric field across the entire surface of the SS deposition substrate by holding the flat anode perpendicular to the surface at a distance of 1 cm.

Table 1
Deposition yield for the sixteen depositions

ID	Deposition Yield (%)	ID	Deposition Yield (%)
1	99.2 $\pm$ 2.2	9	88.2 $\pm$ 1.6
2	87.8 $\pm$ 2.1	10	91.6 $\pm$ 1.5
3	92.6 $\pm$ 2.1	11	70.7 $\pm$ 1.6
4	80.1 $\pm$ 2.1	12	91.7 $\pm$ 1.5
5	85.0 $\pm$ 2.1	13	93.9 $\pm$ 1.6
6	96.3 $\pm$ 1.5	14	94.4 $\pm$ 1.6
7	77.6 $\pm$ 1.6	15	92.4 $\pm$ 1.6
8	91.3 $\pm$ 1.5	16	64.3 $\pm$ 1.5

The depositions, before and after firing, were then analyzed for morphology and thickness with an electron microscope using a BSE detector. Three sets of samples were analyzed: samples fired to 125 °C and held for 60 min (Tables 2 and 3); samples fired to 700 °C and held for 60 min

(Tables 4 and 5); and samples fired to 125 °C, held for 60 min, increased to 700 °C, and held for 60 min (Table 6, 7, and 8). In all three cases, a ramp rate of 0.5 °C/min was used. Additionally, the third case was repeated with alternate ramp rates of 2 °C/min or 10 °C/min. Each firing process was run under either an oxidizing atmosphere (air) or a reducing atmosphere (96% He 4% H₂ mixture). A general description of the unfired depositions will be given followed by the effects of firing the depositions at the various temperatures and ramping rates.

Fig. 1 shows a typical BSE image of the depositions prior to firing. As shown in the figure, the surface is not smooth and has large defects. Severe cracking is seen and is a result of the so-called “mud-caking” effect, which is observed commonly in electroplating techniques with materials assumed to have a “columnar” microstructure. [14,15] The insert in Fig. 1 shows an edge view of a deposition, with a fragment that has pronounced curling of the edges, very much in line with mud-caking. Due to the large cracking of the deposition, a significant portion of the SS substrate is exposed, which can be clearly identified by the parallel grooves, resulting from the machining of the substrate. The surface of the fragments is irregular and can be generally characterized as rough with smooth patches. According to EDS analysis, there is no distinguishable difference in chemical composition of the rough and smooth patches.

Since the surface is not completely covered by the deposition, meaningful results from large-area EDS measurements could not be obtained. Instead, given that the fragments are similar in composition, several spots on different fragments were analyzed, and an average was calculated for the chemical composition of the deposition as a whole. In all cases, a small amount of Pt is observed, indicating slight dissolution and plating of the Pt anode, which is not surprising. There

was a significant amount of carbon in all the depositions, 44-57 atom %. The carbon is believed to originate from the acetate in the electrolyte. It is unclear at this point what the form of the carbon is, but a couple suggestions are offered here. First, the acetate could be coordinating to the surface of the samarium electroplated deposition and terminating the deposited material. Second, the acetate could be incorporated within the deposition. In either case, the acetate serves as a diluent, reducing the overall Sm concentration in the fragments, while increasing the thickness of the fragments. Neither of these effects is desirable for making a thin film of Sm.

Fig. 1. BSE image of a typical prefired deposition with the so-called “mud-caking” features. Insert shows an edge view of a curling fragment.

Depositions 1 and 2 were fired in air, and depositions 3 and 4 were fired in a 96% He 4% H₂ mixture to 125 °C at a ramp rate of 0.5 °C/min (the results of the firings are displayed in Tables 2 and 3, respectively). There appears to be a slight reduction in the C content after firing; however, due to the inherent variability of EDS measurements, especially for light elements such as C, it is difficult to say definitively whether any change had taken place, either chemically or physically. It can be seen in Fig. 2 that the surface characteristics and morphology are very similar to what

was observed prior to firing. This is expected, as at this low temperature, only water will be driven from the deposition. As long as the ramp rate is slow, in this case 0.5 °C/min, the removal of any moisture should be a gentle process and should not cause any violent process to occur and damage the material as it leaves. If only water is being removed, there is expected to be very little reduction in fragment thickness, which is what was observed for the firings in both oxidizing and reducing atmospheres.

Table 2

Deposition thickness, size, and composition before and after firing to 125 °C in air without a gas sweep.

ID		Thickness (μm)	Area (μm^2)	Diameter (μm)		%Sm (atom)	%O (atom)	%C (atom)	%Pt (atom)
				Range	Mean				
1	Unfired	4-8	33-2240	7-53	30 $\pm$ 11	13	31	54	2
	Fired	5-10	32-2256	6-54	27 $\pm$ 14	15	38	46	2
2	Unfired	4-8	26-2505	6-56	26 $\pm$ 14	16	38	44	2
	Fired	4-8	29-4810	6-78	31 $\pm$ 18	15	39	44	2

Table 3

Deposition thickness, size, and composition before and after firing to 125 °C in a 96% He 4% H₂ gas sweep.

ID		Thickness (μm)	Area (μm^2)	Diameter (μm)		%Sm (atom)	%O (atom)	%C (atom)	%Pt (atom)
				Range	Mean				
3	Unfired	3-6	22-5721	5-85	35 $\pm$ 17	15	31	52	2
	Fired	3-9	24-7666	5-99	34 $\pm$ 21	15	38	44	2
4	Unfired	4-9	27-1688	6-46	22 $\pm$ 11	13	32	53	2
	Fired	4-7	21-1052	5-37	19 $\pm$ 9	15	38	45	2

Fig. 2. Deposition after being fired to 125 °C and held for 60 min.

Increasing the firing temperature to 700 °C in both an oxidizing and reducing atmosphere had a significant impact on the depositions. In Fig. 3 it can be seen that substantial shrinkage of the fragments occurred with an average reduction in diameter of 33% in depositions 5–8 (Tables 4 and 5). A much larger fraction of the SS substrate is exposed, with a residue line where it appears the original border of the fragments were prior to shrinking. The fragments are also much brighter relative to the substrate in the BSE image, indicating an increase in electron density, which can be thought of as an increase of average atomic mass of the fragments. In other words, the density of Sm increased. This is clearly shown in the EDS data; the atom % of Sm increased by almost a factor of 2 in the oxidizing atmosphere and 2.6 in the reducing atmosphere, while that of C was cut almost in half in the oxidizing atmosphere and only by 30% in the reducing atmosphere. Once again, the EDS data are not a precise quantitative measurement, especially for light elements like C, but they do indicate a shift in the composition of the material, indicating that the C is being removed from the fragments by the increase in firing temperature. The morphology of the fragments was changed from being mostly rough to mostly smooth. This may

indicate it was the C, presumably in the form of acetate that contributed to the roughness of the surface. Despite there being a considerable difference in size of the diameter of the fragments, the reduction in thickness was not as striking. In fact, it appeared that instead of the deposition becoming thinner with the removal of C, as anticipated, the thickness stayed relatively constant, but the aspect ratio shrunk. That is to say, the change in size, as a result of loss in mass from C, maintained the thickness and reduced the area of the particle.

Fig. 3. Deposition after being fired to 700 °C and held for 60 min.

Table 4
Deposition thickness, size, and composition before and after firing to 700 °C in air without a gas sweep.

ID		Thickness (μm)	Area (μm ²)	Diameter (μm)		%Sm (atom)	%O (atom)	%C (atom)	%Pt (atom)
				Range	Mean				
5	Unfired	4-10	31-2104	6-52	24±12	15	39	44	1
	Fired	3-6	21-3337	5-65	16±11	31	40	24	5
6	Unfired	4-7	21-3262	5-64	24±14	15	39	44	2
	Fired	2-6	21-2547	5-57	17±13	27	42	26	4

Table 5Deposition thickness, size, and composition before and after firing to 700 °C in a 96% He 4% H₂ gas sweep.

ID		Thickness	Area	Diameter (μm)		%Sm	%O	%C	%Pt
		(μm)	(μm ²)	Range	Mean	(atom)	(atom)	(atom)	(atom)
7	Unfired	5-10	21-3379	5-66	21±12	7	36	57	≤1
	Fired	3-7	21-2467	5-56	18±12	18	41	40	2
8	Unfired	4-7	26-4188	6-73	36±19	7	35	57	≤1
	Fired	2-6	21-2007	5-51	17±12	18	41	39	1

A firing program was then investigated where the temperature was held at 125 °C for 60 min before continuing on to 700 °C and holding to identify the effects on morphology and thickness. As shown in Table 6, two heating rates were studied, the 0.5 °C/min as before, depositions 9–10, and 2 °C/min, depositions 11–12. The rate of 0.5 °C/min showed results similar to those of the firing that went straight to 700 °C without holding at 125 °C. The morphology of the two-step firing had no observable differences from the one-step firing when viewed by the electron microscope. It appears any bound water was removed at a moderately slow rate without any violent releases to disrupt the surface of the material. This means that at the rate of 0.5 °C/min there is no benefit to holding the temperature at 125 °C for the purpose of driving off the moisture.

Surprisingly, the faster heating rate of 2 °C/min appeared to increase the relative amount of Sm observed by EDX (Table 6) by slightly reducing the overall C content and significantly reducing the O content compared to the slower heating rate of 0.5 °C/min. For these experiments, the furnace was open on either end of the tube, with no gas sweep. It is believed that at some temperature the heating zone will create a convection current that will not allow air to flow back into the area where the deposition is located, so that the region in the heating zone could become depleted in O₂. If this were to take place, firing at a slower heating rate would spend more time at this depleted atmosphere, and firing at a faster ramp rate would spend less time in this depleted

atmosphere and potentially make it to a higher temperature, driving off more of the organic substituents.

Table 6

Deposition thickness, size, and composition before and after firing to 125 °C, holding, and continuing up to 700 °C and holding in air without a gas sweep.

ID		Ramp Rate (°C/min)	Thickness (μm)	Area (μm ²)	Diameter (μm) Range	Mean	%Sm (atom)	%O (atom)	%C (atom)	%Pt (atom)
9	Unfired	0.5	5-10	22-3976	5-71	26±14	8	36	56	1
	Fired		4-8	21-2362	5-55	14±10	17	41	40	2
10	Unfired	0.5	4-9	21-8047	5-101	26±18	8	36	56	1
	Fired		3-9	21-3015	5-62	18±14	17	41	39	2
11	Unfired	2	4-11	22-8132	5-102	22±14	7	35	57	≤1
	Fired		3-7	20-1971	5-50	16±9	27	32	37	4
12	Unfired	2	5-9	22-2572	5-57	25±12	7	35	57	≤1
	Fired		3-8	20-2022	5-51	15±11	27	33	35	4

To test if the heating zone was becoming depleted, the firing with a heating rate of 2 °C/min was repeated with depositions 1 and 3 in an air atmosphere with a gas sweep to continuously push fresh air over the depositions throughout the firing. At the heating rate of 2 °C/min, the gas sweep made a difference, combusting a larger portion of the carbon and resulting in *ca.* 32 atom % of Sm, an increase of roughly a factor of 2 (Table 7). The morphology of the fragments was comparable with what was discussed earlier, without any evident reduction in fragment size compared to the oxidizing environment. This was then repeated with a faster heating rate of 10 °C/min with depositions 3 and 4, and a very similar result was seen. Again the atom % of Sm was on the order of 32%. This indicates that the heating zone indeed became depleted, leaving a portion of organic substituents uncombusted. By adding an air sweep, the supply of O₂ to the combustion reaction is maintained throughout the entirety of the firing. It was decided that depositions 1–4 could be refired up to the higher temperature of 700 °C as there was no observable change in morphology or definitive change in compositions at the lower temperature of 125 °C.

Table 7

Deposition thickness, size, and composition before and after firing to 125 °C, holding, and continuing up to 700 °C and holding in air gas sweep.

ID		Ramp Rate (°C/min)	Thickness (μm)	Area (μm ²)	Diameter (μm)		%Sm (atom)	%O (atom)	%C (atom)	%Pt (atom)
					Range	Mean				
1	Prefired	2	5-10	32-2256	6-54	27±14	15	38	46	2
	Fired		2-8	20-1523	5-44	14±9	32	35	28	4
3	Prefired	2	3-9	24-7666	5-99	34±21	15	38	44	2
	Fired		2-7	20-1554	5-44	15±10	32	36	28	4
2	Prefired	10	4-8	29-4810	6-78	31±18	15	39	44	2
	Fired		3-8	20-1006	5-36	15±7	32	36	29	4
4	Prefired	10	4-7	21-1052	5-37	19±9	15	38	45	2
	Fired		2-7	20-729	5-30	12±6	32	35	29	4

Changing to a reducing atmosphere, again using a 96% He 4% H₂ gas mixture, and keeping the same firing pattern, at heating rates of 2 and 10 °C/min (Table 8) seems to produce slightly poorer results compared to the oxidizing environment. When compared to the heating rate of 0.5 °C/min up to 700 °C without holding at 125 °C, it can be seen that the faster rates of heating (2 and 10 °C/min) were less effective at increasing the relative amount of Sm and driving off the C, only increasing the Sm atom % by a factor of 1.9.

Table 8

Deposition thickness, size, and composition before and after firing to 125 °C, holding, and continuing up to 700 °C and holding in a 96% He 4% H₂ gas sweep.

ID		Ramp Rate (°C/min)	Thickness (μm)	Area (μm ²)	Diameter (μm)		%Sm (atom)	%O (atom)	%C (atom)	%Pt (atom)
					Range	Mean				
13	Unfired	2	4-10	20-5576	5-84	28±18	18	33	47	2
	Fired		3-8	20-1006	5-59	19±12	32	40	25	3
14	Unfired	2	4-11	20-3031	5-62	15±11	16	34	48	2
	Fired		2-7	20-829	5-32	10±5	31	40	24	5
15	Unfired	10	5-11	20-3207	5-64	29±15	16	30	52	2
	Fired		3-9	21-1132	5-38	20±9	31	35	30	4
16	Unfired	10	4-11	20-5955	5-87	23±18	17	33	49	2
	Fired		3-7	21-1572	5-45	14±9	30	37	29	4

The deposited Sm was studied using XPS to better understand the chemical composition of the Sm before and after firing. Measurements were performed on a plate prior to firing and a plate fired with the same firing pattern as deposition 3. The acquired XPS spectra in the C 1s, O 1s,

and Sm 3d regions for Sm deposition before and after firing are shown in Figs. 4 and 5. The deposits were etched with argon after acquiring initial spectra to determine differences in material as a function of thickness. The XPS spectra in the C 1s region for the unfired plate, Fig. 4, shows a significant amount of carbonate-type carbon, and the O 1s region shows a significant amount of oxygen to carbon bonding, indicating the presence of acetate as a part of the deposition. The presence of electrolyte species has been observed in similar by Vascon *et al.* [16], as well. As summarized in Table 9, the chemical composition was calculated to be $\text{Sm}_2\text{O}_3 \cdot 2.5\text{C}_2\text{H}_3\text{O}_2^-$ on the surface and $\text{Sm}_2\text{O}_3 \cdot 0.5\text{C}_2\text{H}_3\text{O}_2^-$ on the interior of the deposition. The XPS spectra of the fired plate, Fig. 5, show relatively little amount of carbonate-type carbon and oxygen-to-carbon-type bonding. This is especially true beneath the surface of the deposit, as evidenced by looking at the etched spectra of the fired plate. From this, it is assumed that the carbon signal is coming from CO_2 sorbed to the surface of the deposition, resulting in a calculated chemical composition of $\text{Sm}_2\text{O}_3 \cdot 4.5\text{CO}_2$ on the surface and $\text{Sm}_2\text{O}_3 \cdot 0.8\text{CO}_2$ on the interior of the deposition. The excess of O seen in the post-fired etched sample is believed to be due to oxide formation of the SS plate from the firing process. It can be inferred that acetate makes up a large part of the Sm deposition, as indicated by the EDS data, and that the firing process decomposed the deposited acetate, leaving only Sm_2O_3 . It is interesting to note that the atomic percentages calculated using the XPS data show a significant reduction of carbon present. In addition, the carbon appears to be mainly present at the surface, particularly in the case of the fired sample, as seen in comparing the before and after etching analysis.

Fig. 4. XPS spectra of the Sm deposition before firing, collected prior to (red) and post (blue) etching with argon. Regions shown are the C 1s, O 1s, and Sm 3d regions.

Fig. 5. XPS spectra of the Sm deposition after firing, collected prior to (red) and post (blue) etching with argon. Regions shown are the C 1s, O 1s, and Sm 3d regions.

Table 9

Composition of an unfired and fired plate, pre- and post-etching, as observed by XPS.

		Sm (mol)	O (mol)	C (mol)
Unfired	Pre-Etching	2.0	8.2	5.2
	Post-Etching	2.0	3.9	1.0
Fired	Pre-Etching	2.0	11	4.5
	Post-Etching	2.0	6.1	0.8

*mole ratios set so Sm = 2

4. Conclusion

A series of Sm electroplated depositions were performed, with the yields predominately above 80%. Firing to 125 °C in either air or a 96% He 4% H₂ gas mixture did not have a noticeable impact on the fragment size, thickness, morphology, or chemical composition. Increasing the temperature to 700 °C did alter the depositions, reducing the size of the fragments, increasing the relative composition of Sm, and decreasing the relative composition of C. The reducing atmosphere was not as effective at removing the carbon content. Changing to a two-step firing to remove the water at 125 °C and then heating to 700 °C to burn off the organics, while varying the heating rate from 0.5 to 2 to 10 °C/min, showed that 10 °C/min was sufficiently slow to prevent disruption of the deposition morphology during both the drying and combustion stages of the firing. It was shown that a sweep gas is needed to enhance the removal of any organic substituents, and an oxidizing environment to combust the organics is more advantageous than a reducing one. It was also shown that acetate deposits along with the Sm and both decomposed, leaving Sm₂O₃ after the firing process.

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