COMPARISON OF ELECTRODEPOSITED COPPER-ZINC ALLOYS PREPARED INDIVIDUALLY AND COMBINATORIALLY

S.D. Beattie and J.R. Dahn*
Department of Physics and *Department of Physics and Chemistry
Dalhousie University, Halifax, NS, Canada, B3H 2J3

Email: shane@dahn.phys.dal.ca

ABSTRACT

Combinatorial methods provide a new paradigm for advancing scientific discovery. These methods have captured the attention of the materials industry with the promise of providing new discoveries “faster, better and cheaper”. Thousands of similar, but unique, materials can be created in a single experiment and then tested for a desired property. Typical methods for creating these “libraries” of materials are complex, expensive and slow. Here we describe a simple method for creating a composition-spread library of copper-zinc alloys, where composition varies as a function of position, via electrodeposition. Electrodeposition is a simple, inexpensive and fast deposition method that is easily scaled to industrial proportions. Seven copper-zinc alloys with different compositions were prepared, in bulk, by one-at-a-time electrodeposition methods. The composition and structure of these alloys are compared to alloys prepared by combinatorial methods. It will be shown that copper-zinc alloys prepared using combinatorial methods via electrodeposition are representative of bulk alloys prepared by one-at-a-time methods. Therefore, combinatorial methods via electrodeposition embodies, and even extends, the advantages of combinatorial methods: “faster, better, cheaper, simpler and scalable”.
**Introduction:**

Combinatorial methods are a powerful tool in the rapid discovery of technologically significant materials [1]. Typically, thin-films are deposited in a way such that the composition varies in a controlled manner as a function of position. The film represents a range of similar but unique materials where the composition and structure smoothly vary as a function of position. After the film is characterized a particular composition/structure could be selected by choosing the appropriate position on the film. The composition/structure can effectively be “read” off the film by looking up the appropriate position. For this reason composition-spread films of similar but unique materials are often referred to as composition-spread “libraries” of materials. After characterization the library of materials is tested for suitability in the desired application. For example, a composition-spread library of zinc alloys could be deposited and then exposed to a salt-spray. Presumably, individual alloys would have different corrosion-resistant properties. Since composition varies smoothly with position, the composition with the best corrosion-resistant properties could be readily identified. Further experiments would then focus on a much smaller composition range. Conventional one-at-a-time fabrication and testing methods could not be used in such a way due to the enormous investment of time.

Composition-spread libraries are commonly prepared by thin-film sputter and vapor deposition methods, which are complex, expensive and slow. Electrodeposition, unlike sputter and vapor deposition methods, is inexpensive, fast and simple. We will show how a composition-spread library of binary alloys can be electrodeposited from a single aqueous bath in a single run. We have explored the advantages of composition-
spread libraries of binary alloys prepared via electrodeposition previously [2], using a copper-tin system. The purpose of this study is to compare the composition and structure of binary alloys in the composition-spread library to binary alloys deposited in bulk using one-at-a-time methods. We will show that the composition-spread film is representative of bulk samples prepared by one-at-a-time electrodeposition methods.

**Experimental:**

Electrodeposition was performed in a potassium pyrophosphate bath containing hydrated copper and zinc sulfates: 0.66 M (218 g/L) K₄P₂O₇, 0.013 M (3.2 g/L) CuSO₄•5H₂O, 0.30 M (86.4 g/L) ZnSO₄•7H₂O. This bath was used to deposit both the composition-spread library of copper-zinc alloys and individual bulk alloys prepared by one-at-a-time methods.

Deposition of the composition-spread library of copper-zinc alloys was performed in a homemade, modified Hull cell [3] made from polyvinyl chloride (PVC), as shown in Figure 1. The cell is 7.5 cm wide and 6.9 cm tall. The working electrode (cathode) is inclined at a 51.5° angle with respect to the anode, which is 7.3 cm wide. The closest approach of counter electrode (anode) to working electrode is 1.0 cm, and the furthest separating distance is 9.0 cm. The oblique angled working electrode is 11.0 cm long. The cell has a volume of approximately 250 mL.

Deposition of bulk alloys was performed in a parallel electrode cell measuring 8.2 × 5.0 × 6.7 cm (approximately 250 mL) using pulsed electrodeposition. The working and counter electrodes were separated by 5.0 cm. Pulsed and galvanostatic deposition was performed using a Keithley 236 Source Measure Unit. A Visual Basic program was written to calculate and apply a pulsed waveform from user defined parameters.
Nickel foil was used as the working electrode. The nickel foil, PVC vessel and counter electrode were wiped with acetone, ethanol and then methanol. 3M Plater's tape was used to secure the foil to the PVC backing around the immersed edges to prevent deposition on the back of the foil. Note that the Plater's tape slightly decreased the available area for deposition. In the modified Hull cell the usable area is decreased from 11.0 × 7.3 cm to approximately 10.8 × 7.1 cm. In the parallel electrode cell configuration the usable area is decreased from 8.2 × 6.7 cm to approximately 8.0 cm × 6.5 cm.

Wavelength dispersive spectroscopy (WDS) studies were performed using a JEOL JXA-8200 Superprobe with five wavelength dispersive spectrometers to determine the composition of the electrodeposited films.

X-ray diffraction (XRD) measurements were performed using two separate instruments. XRD scans of the composition-spread film were obtained using an INEL CPS120 curved position sensitive detector coupled to an x-ray generator equipped with a copper target x-ray tube. There is a monochromator in the incident beam path that limits the wavelengths striking the sample to copper Kα. The incident angle of the beam with respect to the sample is about 6°. The detector measures the entire diffraction pattern between scattering angles of 6° and 120° at once. The film sample is placed on a x-y translating stage that allows measurement and move operations to be sequentially programmed. Scans were taken incrementally along the length of the film.

Powder XRD patterns were obtained using a JD2000 diffractometer equipped with a copper-target X-ray tube and a diffracted beam monochromator.

**Electroplating Strategy:**
All deposition runs used a zinc anode as the counter electrode since the solution is predominantly zinc (23:1 molarity zinc:copper). A 75 mA galvanostatic pulse was applied to the Hull cell discussed above for 0.9hrs. Due to the geometry of the Hull cell and poor throwing power of the pyrophosphate bath a current density gradient was established along the length of the oblique angled electrode. The deposition potential was high enough to deposit both copper and zinc. Copper ($Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) = 0.340$ V) has a more positive Standard Hydrogen Electrode (SHE) reduction potential than zinc ($Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) = -0.763$ V), so it will preferentially deposit. However, the zinc concentration is much higher than copper (23:1 zinc:copper). At the low current density end of the film (long, thin arrow in Figure 1), copper ions have ample time to diffuse in from bulk solution and replace the ions being deposited. At the high current density end of the working electrode (short, thick arrow in Figure 1) the molarity difference between copper and zinc becomes more significant. Copper is deposited at its limiting current density but zinc is not. Copper ions slowly diffuse in from the bulk solution while ample zinc ions are available for deposition. Zinc is preferentially deposited simply because there isn’t enough copper around. Alloys deposited at the high-current density end of the film will be rich in zinc while alloys deposited at the low-current density end of the film will be rich in copper, and the area between will show a smooth variation in composition.

This approach has been explored before using a Rotating Cylindrical Hull Cell [4]. Our results are unique because we use a copper-zinc (rather than copper-nickel) system and we compare the structure and stoichiometry of our electrodeposited
composition-spread library of binary alloys to bulk electrodeposited samples prepared by one-at-a-time conventional methods.

Seven different bulk samples were prepared in the parallel electrode cell discussed above using on/off pulsed electrodeposition. The same pulsed waveform was used to deposit each bulk alloy, only the length of the off pulse was varied. A 100 mA pulse was applied for 6.09 s followed by an off pulse, ranging from 0 to 36 s. 2000 cycles were performed corresponding to a theoretical thickness of 20 µm if only zinc is deposited, which is incorrect, but a good approximation. 20 µm thick films are considered bulk compared to the 1-2 µm thick films deposited in the composition-spread library. During the on pulse both copper and zinc are deposited. Copper ions near the working electrode are quickly consumed due to their low concentration. During the off pulse copper ions from the bulk solution diffuse in to replace the copper consumed during the on pulse. Copper ions eventually diffuse onto the surface of the working electrode and ion exchange with deposited zinc. The longer the off pulse the more copper ions will diffuse to the electrode, the more copper will exchange with zinc and the higher the copper content in the deposited film. By varying the length of the off pulse we can control the copper content in bulk deposited films. This is important because we wanted to compare thin-film alloys deposited in the composition-spread library, where copper content varies as a function of position, with alloys prepared by one-at-a-time bulk deposition methods.

**Results:**

Figure 2 is a plot of zinc/copper atomic % vs. position along the substrate prepared by combinatorial electrodeposition. The position is measured from the top (low current
density end) of the film to the bottom (high current density end) of the film. The composition spread is approximately linear for the first five centimeters, then the data becomes more scattered. The increase scatter is attributed to peeling film near the bottom, high current density end of the film. The limiting current density of both copper and zinc ions may have been reached at the high-current density end, resulting in hydrogen evolution, which would also explain why, on average, the composition does not vary significantly.

A second composition-spread library of copper-zinc alloys was deposited for gravimetric analysis. Peeling at the high current density end of the film was still an issue but extra care was taken to ensure the peeling flakes were not lost. Figure 3 shows gravimetric data for seven discs punched from the composition-spread electrodeposited film. 1.32 cm diameter (0.5 inch) discs were sequentially punched along the length of the film and then weighed. Punch position, from the top of the film, is plotted vs. mass of deposited film (total mass minus nickel substrate mass). The average thickness is given on the right ordinate represented by open circles. Thickness was calculated using an average copper-zinc alloy density of 8.1 g/cm³. Thickness variation is almost linear.

Figure 4 consist of three panels with different scattering angle ranges and 12 XRD scans per panel. Each scan was taken sequentially along the length of the composition-spread electrodeposited library of copper-zinc alloys. Three ranges were selected for detailed analysis corresponding to peak positions of known copper-zinc alloys. To the right of the figure are two columns indicating scan number and the approximate zinc content in atomic percent. The approximate zinc content can be inferred from Figure 2 by measuring where each XRD scan was taken relative to the top of the film.
Figure 5 is the copper-zinc phase diagram from reference [5]. A double-headed arrow indicates the area of phase space sampled by the composition-spread electrodeposited film. Short bars indicate the discrete regions of phase space sampled by the seven electrodeposited bulk alloys. Note that all films were deposited at room temperature. The vertical placement of the bars and double-headed arrow does not represent fabrication temperature. The vertical placement is for illustrative purposes only.

Figure 6 shows powder XRD patterns for the seven different copper-zinc alloys prepared by one-at-a-time pulsed electrodeposition methods. The two columns on the right indicate the off-pulse duration and atomic percent zinc. Since a thick film was deposited most of it could be scraped off the nickel substrate. The recovered material was ground in an agate pestle and mortar. Typically, a few milligrams of powdered material could be obtained from each sample, more than enough for powder XRD and electron microprobe analysis. Powder XRD patterns of an electrodeposited film are superior to patterns obtained when the film is attached to the substrate because the film could be highly orientated.

It’s important to establish the role copper plays in the structure of the deposited alloy. The effect of copper content on crystallographic structure of the deposited alloy was explored in two different ways. 1) Compare the crystal structure of electrodeposited films obtained from two different baths with significantly different copper molarities. Figure 7a shows XRD patterns for two films deposited the same way from two different baths where the only difference is the copper molarity, 0.056 M vs. 0.013 M copper sulfate. 2) Compare the crystal structure of electrodeposited films obtained from the
same type of bath but deposited at different current densities. XRD patterns for two films obtained from the same type of bath and deposited at different current densities (3.6 mA/cm² vs. 0.7 mA/cm²) are presented in Figure 7b.

**Discussion:**

Figure 2 shows that a composition-spread library of copper-zinc alloys was successfully electrodeposited from a single bath in a single run where composition varies as a function of position. This method of creating a library of binary alloys is powerful for many reasons: 1) deposition occurred at standard conditions with simple equipment. The most complicated and costly item in the setup is a programmable current source. However, that could be replaced by a “D” cell. If the current source was replaced by a simple D cell the total cost of the experiment would be on the order of a few dollars. 2) The composition-spread alloy library was deposited in less than an hour, and the entire experiment took less than an hour and a half, including preparation time. In that time over a third of the copper-zinc phase diagram was sampled. 3) By changing any number of variables (i.e.: current density, zinc:copper molarity, Hull cell dimensions, temperature, pH, agitation) you can change the region of phase space sampled by the film. 4) All components are inexpensive and readily available. 5) The method can be extended to many other binary systems. 6) The method is simple and 7) It will be shown that the method is scalable. That is, a material deposited in the composition-spread library could be easily made by bulk deposition methods, which are inexpensive and fast.

Figure 2 shows that composition smoothly varies as a function of position in the composition-spread electrodeposited library of alloys. Figure 4 shows that the crystal structure also smoothly varies as a function of position. Scan #1 in panel 4a suggests a
multi-phased structure, since there is a strong peak at 42.0° and a “smear” of peaks between 42.5° and 44.0°. By scan #3 in Figure 4a two peaks near 43.0° and 43.8° are readily identified. The ε-CuZn₅ phase has peaks at 42.2°, 43.4°, 57.6° and 77.8° (Figure 4a, b, c lower scans). These peaks account for four of five peaks observed in Figure 4, scan #3. The alloy in scan #3 is approximately 70 % zinc. From the phase diagram in Figure 5 this corresponds to a region with two co-existing phases: ε-CuZn₅ and γ-Cu₅Zn₈. Unfortunately, γ-Cu₅Zn₈ has only one strong peak, at 43.3°, making it hard to isolate given the two strong peaks of ε-CuZn₅ at 42.2° and 43.4°. Electrodeposited alloys do not necessarily follow the phase diagram since electrodeposition is a non-equilibrium process, this has been observed before [2]. In scan #1, the presence of γ-Cu₅Zn₈ is possible but dubious. Subsequent scans show the intensity of the ε-CuZn₅ peaks diminishing as we move up the film (up Figure 4), in scan #6 the peaks near 57.6° and 77.8° are essentially gone and the peaks at 42.0° and 43.6° are significantly reduced, suggesting the ε-CuZn₅ phase is receding.

Scan #9 shows that the ε-CuZn₅ phase is almost completely gone, replaced with a new phase with a peak near 43.0°, this is no doubt the β′-CuZn phase. Presence of the β′-CuZn phase near the bottom of the film accounts for the fifth peak, near 43.0°, that cannot be attributed to ε-CuZn₅. Scan #9 has a zinc content of approximately 52%, according to the phase diagram β′-CuZn should be the only phase present, as observed. The zinc content is further reduced as we go towards the low-current density end of the film (up Figure 4), and the β′-CuZn phase seems to disappear almost entirely by scan #12. Figure 4 shows how the structure smoothly varies along the length of the film. It is
reasonable to conclude that the structure variation is a consequence of the change in composition, especially since there is some agreement with the phase diagram. However, since the current density varies along the length of the film so does the thickness (Figure 3), we need to determine whether the structural and compositional variation is a function of thickness and not just composition.

Figure 6 shows that the structure of bulk films prepared by one-at-a-time methods is highly dependent on the duration of the off-pulse, supporting the concept of aqueous copper exchanging with deposited zinc. The bottom scan matches well to the $\varepsilon$-CuZn$_5$ phase, as does the zinc content relative to the phase diagram. The middle scan with 45% zinc matches well to $\beta'$-CuZn, which is expected from the phase diagram. With 45 atomic % zinc the phase diagram suggests co-existence of two phases $\beta'$-CuZn and a solid solution of zinc in copper. The top scan represents nano-structured copper. In this region the phase diagram indicates a solid solution of zinc in copper. The XRD patterns were obtained from films of equal thickness, suggesting that the copper content, not the thickness of the film, determines the crystallographic structure. A smooth variation is observed, starting with $\varepsilon$-CuZn$_5$ travelling through the $\beta'$-CuZn phase and ending with nano-structured copper. Note that once again the presence of $\gamma$-Cu$_5$Zn$_8$ cannot be confirmed. The $\gamma$-Cu$_5$Zn$_8$ phase must not be energetically favorable during electrodeposition.

Figures 4 and 6 show that structure has a strong dependence on copper content in the film, which is expected given the number of different phases in the copper-zinc phase diagram. Figure 7 further supports the importance of copper on the structure. By lowering the current density copper ions have more time to diffuse to the electrode and
deposit. Figure 7b shows that the film deposited at 3.6 mA/cm² has a much higher zinc content (70 %) than the one deposited at a lower current density (0.7 mA/cm², 30 % zinc). It's interesting that the 70 % zinc film is much more crystalline than the 30% zinc film, this may be due to the fact that the 30 % zinc film, according to the phase diagram, is a solid solution of zinc in a copper matrix. Figure 7a shows that the film obtained from the high copper molarity (0.056 M) bath has a much higher zinc content (70 %) compared to the film obtained from the lower copper molarity (0.013 M, 30 % zinc) bath. The higher the copper concentration the more quickly copper will diffuse to the working electrode so the more copper will deposit. Figure 7 shows that bulk, nano-structured copper-zinc alloys can be deposited by two different conventional electrodeposition methods (galvanostatic and pulsed). It would be easy to scale the process and deposit kg, rather than mg, of material. Unfortunately the importance of scalability is often overlooked.

**Conclusion:**

A composition-spread library of copper-zinc alloys has been deposited from a single bath in a single run where composition and structure varies smoothly as a function of position. The film was prepared simply, inexpensively and quickly. The composition-spread library follows the copper-zinc phase diagram except the $\gamma$-Cu$_5$Zn$_8$ phase is not observed. The crystal structure and composition of alloys deposited in the composition-spread library is representative of bulk alloys prepared by one-at-a-time methods. This means that a material discovered using the combinatorial electrodeposition method discussed here could be used to find and optimize a material that could then be fabricated using conventional, one-at-a-time bulk deposition methods. Compared to competing
technologies the road from discovery to mass production would be relatively easy. Therefore, we have shown that a combinatorial method via electrodeposition embodies, and even extends, the advantages of combinatorial material science: “faster, better, cheaper, simpler and scalable”.

References:

List of Figures:

Figure 1: Hull Cell drawn approximately to scale.

Figure 2: Atomic percent copper/zinc vs. distance from top of film. The film was deposited galvanostatically in the Hull cell presented in Figure 1.

Figure 3: Deposited mass/thickness vs. distance from top of film. A second composition-spread copper-zinc film was deposited in the Hull cell and punches were then cut from the film and weighed.

Figure 4: Twelve XRD scans taken sequentially along the composition-spread copper-zinc film deposited in the Hull cell. Three scattering ranges are selected for focused study.

Figure 5: The copper-zinc phase diagram. The double headed arrow represents the range of compositions sampled by the film deposited in the Hull cell. Short bars indicate the discrete regions of phase space sampled by bulk films prepared by one-at-a-time methods. Note that all films were deposited at room temperature. The vertical placement of the double-headed arrow and bars is for illustrative purposes only.

Figure 6: XRD patterns of seven individual copper-zinc bulk films prepared by conventional one-at-a-time methods. The rightmost column represents zinc composition in the film determined by WDS. The column to the left of that represents the length of the off pulse used in the pulsed deposition waveform.

Figure 7: XRD patterns of copper-zinc films. Panel a) represents two films deposited from two separate baths where the only difference is the copper
molarity. Panel b) represents two films deposited from the same type of bath but at different current densities.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7