D396

Journal of The Electrochemical Society, **157** (7) D396-D405 (2010) 0013-4651/2010/157(7)/D396/10/\$28.00 © The Electrochemical Society



**Electrodeposition of Metastable Au–Ni Alloys** 

E. Rouya,<sup>a,z,\*\*</sup> G. R. Stafford,<sup>b,\*</sup> U. Bertocci,<sup>b</sup> J. J. Mallett,<sup>a,\*\*</sup> R. Schad,<sup>c</sup> M. R. Begley,<sup>a,d</sup> R. G. Kelly,<sup>a,\*\*</sup> M. L. Reed,<sup>e</sup> and G. Zangari<sup>a,\*\*</sup>

<sup>a</sup>Materials Science and Engineering, <sup>d</sup>Mechanical and Aerospace Engineering, and <sup>e</sup>Electrical and Computer Engineering, University of Virginia, Charlottesville, Virginia 22904, USA National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA <sup>c</sup>Physics and Astronomy and Center for Materials for Information Technology, University of Alabama, Tuscaloosa, Alabama 35487, USA

The electrodeposition of Au-Ni alloys from near-neutral, sulfite-based electrolytes derived from a commercial bath for soft gold plating is investigated. Alloy compositions ranging from 0 to 90 atom % Ni were obtained by varying the deposition potential, with Ni content increasing with overpotential. Cathodic efficiency was lower than 50% due to concurrent parasitic reactions, including the reduction of products from the decomposition of sulfites and the hydrogen evolution reaction. As-deposited films form a continuous series of metastable solid solutions and exhibit a nanocrystalline morphology, with grain size decreasing with increasing Ni content and a possible Ni enrichment at the grain boundaries. Thermal annealing at 200°C was sufficient to start the relaxation of the metastable solid solution toward the thermodynamically stable biphasic configuration of pure Au and Ni phases; however, 400 °C was necessary to complete the phase separation process within  $\sim 1$  h. The formation of a metastable structure is interpreted in terms of the limited surface diffusivities of adatoms at the growing interface and atomic volume differences. The excess free energy of the as-deposited alloys with respect to the stable, phase separated configuration is estimated between 6 and 18 kJ/mol, consistent with what can be expected in electrochemical processing. © 2010 The Electrochemical Society. [DOI: 10.1149/1.3421749] All rights reserved.

Manuscript submitted February 1, 2010; revised manuscript received April 5, 2010. Published May 13, 2010.

Electrochemically deposited alloys often develop crystal structures that differ from those predicted by their corresponding metallurgical phase diagrams. Typically, electrodeposited alloys may form supersaturated solid solutions or metastable structures; intermetallic compounds are usually difficult to obtain, but in some cases, ordered phases absent from the equilibrium phase diagram may be formed.<sup>1-5</sup> These patterns of behavior are a direct consequence of the electrochemical deposition (ECD) process occurring out of equilibrium; at high deposition rates, the formation of new atomic layers may take place before adatoms diffusing on the growing surface have sufficient time to reach equilibrium surface sites. Correspondingly, the alloy film would develop a metastable structure, and the alloy free energy would be higher than that calculated by thermodynamic means.

The ability to predict the structure of electrodeposited alloys as a function of alloy composition, electrolyte chemistry, and deposition conditions is an open problem in electrochemical materials science. Although the Hume-Rothery rules<sup>6</sup> provide guidelines to determine the tendency of bulk binary alloys to form solid solutions as a function of the relative molar volume, electronegativity, and valency of the elements involved, research on electrodeposited alloys provides only circumstantial evidence and rule of thumbs to predict the alloy structure; no rigorous general theory is yet available.

Au-Ni alloys are, in this respect, a particularly interesting model system. Bulk Au-Ni in fact exhibits a miscibility gap below  $\sim 1090$  K<sup>7,8</sup> induced by the lattice deformation energy resulting from the difference in molar volume of the two elements, which overcomes the chemical interactions that would otherwise tend to form a solid solution.<sup>9</sup> Bulk solid solution formation is therefore hindered by a steric (volume) effect, which is acknowledged to have limited bearing in ECD processes.<sup>4</sup> However, Au–Ni surface alloys are stable, as a consequence of the higher electron density of Au atoms, which increases the effective coordination number of surface Ni, decreasing the surface energy.<sup>10</sup> Film growth occurs by surface diffusion and attachment of atoms at surface sites; there is therefore a significant possibility that the resulting alloys may form metastable solid solutions. Au–Ni,<sup>11,12</sup> as well as Au–Co,<sup>13,14</sup> films have been electroplated

for use in microelectronics packaging as electrical connectors; these

In this work, we use a sulfite-based Au solution for the ECD of Au-Ni alloys. We investigate the electrodeposition process, the structure and morphology of the resulting Au-Ni alloys, and we study the transformations following thermal annealing. Finally, we interpret the observed alloy structure and morphology in terms of kinetic phenomena and thermodynamic parameters.

#### Experimental

Alloy electrodeposition .- The alloy films were grown from a sulfite-based commercial solution for soft Au electrodeposition (Techni-Au 25-ES RTU<sup>d</sup>)<sup>15</sup> that was diluted 2:1 with ultrapure Milli-Q water produced in house (resistivity 18.2 M $\Omega$  cm) and contained a predetermined amount of NiSO<sub>4</sub>. The final metal ion concentrations in the bath were 0.021 M Au<sup>+</sup> and 0.126 M Ni<sup>2+</sup>. Finally, the pH was adjusted to 6.6 by adding diluted NaOH. The as-prepared electrolyte was stable for  $\sim 1$  week, after which a slight purple tint in the solution becomes noticeable, corresponding to the formation of colloidal Au. This is probably due to the disproportion-ation of Au(I) species, as previously reported.<sup>16,17</sup> Besides the Au sulfite complex  $(Au(SO_3)_2)^{3-}$  (with a stability constant at 298 K of  $\beta = 26.8$ ), the Au bath contains ethylenediamine (EDA,  $C_2H_4(NH_2)_2$ ) to improve the stability of the Au complex at a nearneutral pH;<sup>15</sup> it is thus possible that the added Ni is partly complexed by EDA because the stability constant of this complex is  $\beta = 7.5.$ 

The electrodeposition of Au-Ni alloy films was carried out in a three-electrode, two-compartment prismatic cell. The counter electrode was a Pt mesh, immersed in the same compartment as the

alloys are known as a form of hard gold. In these applications, the transition-metal content is limited to a few atom %, and the formation of metastable solid solutions provides for the necessary hardness and wear resistance. These films are nanocrystalline, with the width of the diffraction peaks increasing with transition-metal content. In particular, the growth of a reportedly amorphous Au-Ni structure at Au  $\sim 20$  atom % has been attributed to a large amount of incorporated carbon when using a cyanide/citrate electrolyte.<sup>12</sup> Inoue et al.<sup>13</sup> and Guan and Podlaha<sup>14</sup> report the formation of nanocrystalline Au-Co alloys when plating from solutions based on Au sulfite

<sup>\*</sup> Electrochemical Society Fellow. \*\* Electrochemical Society Active Member.

<sup>&</sup>lt;sup>z</sup> E-mail: er5v@virginia.edu

<sup>&</sup>lt;sup>d</sup> Certain names are mentioned for experimental information only; in no case does it imply a recommendation or endorsement by NIST.

working electrode. The reference electrode was saturated sulfate ( $V_{SSE} = 0.615 V_{SHE}$ , where SSE is the saturated sulfate electrode and SHE is the standard hydrogen electrode), separated from the working electrode by a Luggin capillary. In this paper, all the potential values are reported with respect to the SSE reference. Cyclic voltammetry and potentiostatic ECD of Au–Ni alloys were performed using a 6310 potentiostat from Princeton Applied Research.

Several substrate materials were used in this investigation. Gold substrates were prepared by sequentially sputtering a Cr adhesion layer (15 nm) and a Au layer (160 nm) onto the native oxide of a Si wafer using a multitarget Kurt J. Lesker sputtering system. The samples were cut into  $1.2 \times 1.2$  cm<sup>2</sup> pieces, which were placed in electrical contact with a  $1.2 \times 10$  cm<sup>2</sup> brass bar and covered with lacquer (XP-2000 lacquer, Tolber MICCRO Products) to expose a  $1 \times 1$  cm<sup>2</sup> area in contact with the electrolyte. Copper electrodes were obtained by electropolishing copper plates (99.9% purity), using a 90 vol % H<sub>3</sub>PO<sub>4</sub>:10 vol % ethanol solution, to an average root-mean-square roughness of 3 nm over  $5\times5~\mu\text{m}^2,$  as determined by atomic force microscopy. Low carbon steel plates were cut to  $1 \times 1$  cm<sup>2</sup> squares and mechanically polished using up to 1200 grit silicon carbide polishing paper. The Au-Ni alloys were electrodeposited under potentiostatic conditions at room temperature (25°C) in a quiescent solution. The thickness of the films ranged from 350 nm up to 1  $\,\mu\text{m}.$ 

*Thermal annealing.*— Au–Ni films on various substrates were annealed with an AXIC, Inc. As-One rapid thermal annealer (RTA) at various temperatures between 200 and 400°C under a vacuum of  $2.6 \times 10^{-5}$  Torr. The temperature ramping rate was 7°C/s and the sample was removed when the temperature reached 55°C. Annealing of films was also performed during in situ X-ray diffraction (XRD) measurements, as described in the next section.

*XRD and in situ annealing.*— Crystal structure was determined by XRD using either a Scintag XDS-2000 X-ray diffractometer for symmetric  $\theta/2\theta$  scans or a Rigaku SmartLab instrument for glancing-angle  $\Omega/2\theta$  scans. In both systems, a Cu K $\alpha$  radiation ( $\lambda = 1.5405$  Å) was used as the X-ray source. In the latter case,  $\Omega$ , the incident beam angle, was fixed at 5°. The slit widths for both the X-ray beam and detector were adjusted to 5 mm to yield an optimal signal-to-noise ratio during data acquisition.

Glancing-angle XRD measurements were also performed in situ during thermal annealing of Au-Ni films electrodeposited on steel substrates using the Rigaku instrument; for this purpose, an Anton Paar domed hot stage with a gas inlet/outlet and an air-cooling system was used; the stage plate was made of a Ni-Cr alloy and was heated by a resistive heater. The temperature was monitored via a thermocouple located beneath the plate and connected to a temperature control unit. Thermal annealing experiments consisted of an initial chamber evacuation down to a pressure of about  $10^{-2}\ {\rm Torr}$ followed by backfilling with Ar/5% H<sub>2</sub> gas to suppress oxide formation on the film and substrate. Continuous gas flow (pressure = 3-5 psi) was maintained during each annealing process. Two sets of measurements were performed; in the first set, the temperature was ramped up to a predetermined value and was then kept constant while several scans in a predefined 20 range were successively collected. In the second set of experiments, a predetermined temperature was reached, then it was kept constant while collecting an XRD scan; the procedure was then repeated at several, successively higher, temperatures.

*Electrochemical quartz crystal microbalance.*— Simultaneous acquisition of the electrodeposition current and the resulting mass increase at the electrode vs time was achieved by using an electrochemical quartz crystal microbalance (EQCM, model RQCM, Maxtek, Inc.).<sup>19</sup> The EQCM experiments were conducted onto polished, AT-cut blank quartz crystals (resonant frequency 5 MHz) coated with a Ti/Au bilayer. The Au–Ni electrolyte was first vigorously deaerated with high purity Argon gas for 30 min before deposition, then the gas flow was decreased during the experiments to avoid

bubbling. The potential was stepped in 25, 50, or 100 mV increments, first in the negative then in the positive direction, while the EQCM response was monitored. The experimental mass increase  $\Delta m_{\rm exp}$  of the electrode was measured at each potential step and was used together with alloy composition data at the corresponding potentials to calculate the cathodic efficiency (CE) using the following formula

$$CE = \frac{\Delta m_{exp}}{\Delta m_{th}}$$
[1]

where  $\Delta m_{\text{th}}$  is the theoretical mass increase per unit area calculated through Faraday's law

$$\Delta m_{\rm th} = \frac{Q(\mathrm{AW})_{\rm alloy}}{z_{\rm alloy}F} = \frac{Q[X_{\rm Au}(\mathrm{AW})_{\rm Au} + X_{\rm Ni}(\mathrm{AW})_{\rm Ni}]}{(1 + X_{\rm Ni})F}$$
[2]

Where  $X_{Au}$  and  $X_{Ni}$  are the atomic fractions of Au and Ni, respectively, in the alloy, AW is the atomic weight, Q is the total charge, and F is Faraday's constant. The number of electrons transferred in an ideal elementary reduction process,  $z_{alloy}$ , is a weighted average of the electrons transferred in the reduction of Au and Ni ions.

The average film growth rate R [Å/s or monolayer (ML)/s] was estimated using Eq. 3a and 3b, which assumes the alloy density and lattice constant to be weighted averages of the corresponding values for the pure metals

$$R = \frac{\Delta m_{\rm exp}}{At(X_{\rm Au}\rho_{\rm Au} + X_{\rm Ni}\rho_{\rm Ni})} \left[\frac{\ddot{\rm A}}{\rm s}\right]$$
[3a]

$$=\frac{\Delta m_{\exp}}{At(X_{Au}\rho_{Au}+X_{Ni}\rho_{Ni})(X_{Au}a_{Au}+X_{Ni}a_{Ni})}\left[\frac{ML}{s}\right]$$
[3b]

where *A* is the area, *t* is the deposition time,  $\rho_{Au}$  and  $\rho_{Ni}$  are the densities of Au and Ni, respectively, and  $a_{Au}$  and  $a_{Ni}$  are the lattice constants of bulk face-centered cubic (fcc) Au and Ni, respectively. *R* [ML/s] strictly represents the growth rate for a (001) oriented film.

*Microscopy and composition analyses.*— The surface morphology of the Au–Ni films was examined by using a JEOL-JSM 6700 field-emission scanning electron microscope with a beam voltage of 5 keV. Chemical analysis was performed by an attached energy-dispersive X-ray spectroscopy (EDX) detector. To ensure excitation of the relevant transitions (the electron transitions used for elemental analysis were K $\alpha_{Ni}$  = 7.477 keV and M $\alpha_{Au}$  = 2.12 keV), a beam voltage of 20 keV was used. Imaging with atomic number contrast was performed using backscattered electrons to confirm phase separation in annealed Au–Ni films. Microstructural characterization of the as-deposited films was carried out by transmission electron microscopy (TEM) using a JEOL 2000FX instrument. Surface elemental analysis and depth profiles were obtained using an Auger electron spectrometer (AES) Perkin-Elmer PHI 660 Scanning Auger Multiprobe (MAIC, University of Florida).

## Results

*Electrochemical characterization.*— Figure 1 shows the linear sweep voltammograms (LSVs) of a Au electrode immersed in the 2:1 diluted Au solution at pH 6.6 and in the Au–Ni solution. The Au solution exhibits an onset potential at -0.9 V and a diffusion-limiting current of 5.5 mA/cm<sup>2</sup>, starting at about -1.11 V. Below -1.25 V, the current increases again due to the hydrogen evolution reaction (HER). The cathodic current onset in the Au–Ni solution is observed at a similar potential; the current values in this electrolyte are initially larger than that for Au, but at higher overpotentials, the alloy current is suppressed with respect to Au. The HER on the Au–Ni alloy deposited during the scan occurs at a lower overpotential than on Au due to the better electrocatalytic behavior of Ni.

Au–Ni films were electrodeposited at potentials between -0.9 and -1.1 V. Figure 2 displays the alloy composition as measured by EDX on Cu substrates as a function of the applied voltage. A wide range of compositions (0–90 atom % Ni) was obtained by varying



**Figure 1.** LSVs obtained for a Au electrode immersed in Au  $^{15}$  and Au–Ni solutions. The vertical dotted lines bracket the potential range used for alloy deposition. Scan rate was 20 mV s<sup>-1</sup>.

the electrode voltage in only a 200 mV range. The Ni content in the alloy film monotonically increases with decreasing potential.

Figure 3 displays an Auger spectrum of a Au–Ni film (Ni 61 atom %) collected at a depth of  $\sim 150$  nm. The spectrum shows the presence of  $\sim 12$  atom % sulfur (S), whereas carbon, nitrogen, or oxygen were present at negligible levels.

Figure 4 shows the current-time transients for Au–Ni films electrodeposited at various potentials onto Au electrodes. At potentials more negative than -1.0 V, after the double-layer charging transient, these curves exhibit a maximum in current followed by a slow approach toward a constant current value lower than the diffusion limiting current measured for pure Au deposition (Fig. 1). These transients do not fit any of the conventional growth models, indicating that other faradaic processes occur in parallel with the reduction of metallic species. The variation in the steady-state current with potential suggests that at low overpotentials, the reduction process is charge-transfer controlled, between -1.03 and -1.05 V is diffusion controlled and, finally, at -1.1 V, additional reduction processes may occur.

The rate of electrode mass increase dm/dt was determined at various deposition potentials with the EQCM; corresponding data are reported in Fig. 5. The applied cathodic potential was initially







Figure 3. Auger spectrum of a Au-Ni 61 atom % film.

stepped from -0.9 down to -1.1 V, covering the entire alloy composition range (Fig. 2). At each potential, the current and dm/dt were monitored until a steady-state value for the latter was reached, indicating a constant growth rate. The growth rate increased with potential down to about -1.0 V, after which it decreased strongly, then increased again, with a lower slope. The decrease in growth rate occurs at around -1.025 V<sub>SSE</sub>, near the inflection point for the current–voltage characteristics of the Au–Ni solution (Fig. 1). The reversible potential for the HER at the solution pH is -0.99 V<sub>SSE</sub>, which suggests that the decrease in overall growth rate may be induced by the adsorption of water-derived species and the HER onset. After the highest overpotential was reached, a ramp-down of the potential was performed, which yielded a corresponding increase then decrease in growth rate.

Alloy composition vs potential and EQCM data were combined to determine the CE as well as the growth rate as a function of potential; these data are plotted in Fig. 6a and b, respectively. In these calculations, the sulfur content was neglected, leading to an error of less than 5%. The efficiency decreases from 47% at -0.9 V (pure Au) to a minimum of ~15% at -1.025 V and eventually increases again at lower potentials. These values indicate that parasitic reactions occur already at potentials more positive than those at which HER occurs. At -0.9 V, the steady-state current is equal to 173  $\mu$ A/cm<sup>2</sup>, which, at an efficiency of 47%, yields a parasitic



Figure 4. (Color online) Current vs time transients upon potentiostatic codeposition of Au–Ni alloys on Au electrodes as a function of applied potential.



**Figure 5.** (Color online) EQCM data showing the deposit mass increase per unit time and unit area at various cathodic potentials applied to a Au electrode immersed in a Au–Ni electrolyte purged with Ar gas. The reversible potential for the HER is also indicated here.

reaction current of  ${\sim}92~\mu A/cm^2$ . The oxygen reduction reaction is only  ${\sim}400~nA/cm^2$  in deaerated solutions and cannot account for this current.

Figure 6b shows the growth rate of the alloy in both Å/s and ML/s units. At potentials more negative than -1 V, the growth rate decreases with increasing overpotential; we hypothesize that under these conditions, hydrogen adsorption may inhibit and slow down growth. Finally, at higher overpotentials, the growth rate increases with overpotential despite the increase in the rate of HER.



**Figure 6.** (Color online) (a) CE vs applied potential. Each data point represents an average value of a time-varying efficiency, from which a standard deviation was calculated and indicated here via error bars. (b) Calculated growth rate (in Å/s and ML/s) vs potential.



Figure 7. (Color online) Partial current densities of Au, Ni, and parasitic reactions. The reversible potential for the HER is indicated by the vertical dotted line.

Using alloy composition and CE data, the partial current densities for Au ( $I_{Au}$ ), Ni ( $I_{Ni}$ ), and parasitic reactions ( $I_{pr}$ ), plotted in Fig. 7, were calculated.  $I_{Au}$  is larger than  $I_{Ni}$  from -0.9 to about -0.97 V, beyond which the  $I_{Ni}$  and  $I_{Au}$  crossover and the latter begins to decrease steadily, indicating inhibition of Au deposition by Ni.  $I_{pr}$  increases rapidly with overpotential until about -1.0 V, after which the rate of increase is lower; this behavior suggests that the onset of HER changes the mechanism and extent of the initial parasitic reaction.

*Morphology of Au–Ni films.*— The as-deposited Au–Ni films appear bright and uniform. The alloy's color shifts gradually from golden to bright gray with increasing Ni content. Representative surfaces are shown in the scanning electron microscopy (SEM) micrographs in Fig. 8; morphologies consist of irregular or approximately spherical grains. The apparent grain size decreases and the overall uniformity is enhanced with increasing overpotential. Furthermore, the apparent grain size of the films is smaller than that of the Au substrate, as evidenced in Fig. 9a, which shows the edge of a Au–Ni film and the underlying Au substrate. This suggests inhibited growth due to the electrolyte chemistry.

Film growth in some cases results in the formation of hemispherical nodules, irrespective of the applied potential (Fig. 9b). The nodules are slightly richer in Au than the underlying film. The size of these nodules ranges from 100 nm to as much as 1  $\mu$ m. The presence of these particles may stem from bath instabilities, as reported by Green and Roy,<sup>16</sup> where disproportionated colloidal gold has the tendency to form both in solution and on the deposit at near-neutral pH.

*Crystal structure.*— XRD data collected in the  $\theta/2\theta$  Bragg– Brentano geometry on films deposited on Au substrates (not shown) display only diffraction peaks from Au; the only feature that can be attributed to the films is a widening of the Au(111) reflection, in-



Figure 8. Surface morphologies of  $\sim$  300 nm thick Au–Ni alloys of various compositions.



**Figure 9.** (a) SEM surface image at the film/substrate boundary. The apparent grain size of a 300 nm thick Au–Ni 70 atom % film (left) is smaller than that of the Au substrate. (b) SEM image showing nodules formed on the surface of a 300 nm thick Au–Ni 50 atom % film; similar nodules were also observed in alloys with different compositions.

dicative of the superposition of diffraction peaks from similar crystal structures but different coherence length. To achieve a better understanding of the structure of Au-Ni films, diffraction data from films deposited on low carbon steel and on Cu plates were also collected.  $\theta/2\theta$  XRD scans acquired from films deposited on steel and Cu substrates are reported in Fig. 10a and b, respectively. Both sets of data show a broad reflection between 36 and 44° that can be assigned to the close-packed plane of an fcc Au-Ni alloy. The position of the main peak is intermediate between those of Au and Ni, suggesting the formation of solid solutions. The width of the main peaks suggests a nanocrystalline morphology; the coherence length was calculated using the Scherrer equation and is reported in Fig. 11a. In this calculation, all other sources of broadening (instrumental, internal stresses, and inhomogeneities) were neglected; this is clearly an approximation, but due to the large peak widths involved, it is believed that these data still provide a useful semiquantitative trend. The coherence length is observed to decrease with increasing Ni content in the alloy, as already noted in electrodeposited Au-Co.<sup>13</sup> The XRD peaks corresponding to Au-Ni films with 77 and 90 atom % Ni were very weak and broad, making a precise line fit difficult to achieve; the calculated coherence lengths of these samples were unrealistic and therefore were omitted. The lattice constant of the fcc phase was determined by fitting the corresponding diffraction peak to a Lorentzian lineshape. The relative data are shown in Fig. 11b, where they are compared with data available from the literature,<sup>20</sup> obtained on alloys produced by splat quenching, and with Vegard's law. A positive deviation, much stronger than that observed in Ref. 20, is observed for the electrodeposited alloys, suggesting the presence of some inhomogeneities in the films. This hypothesis is supported by the microstructure of an as-deposited Au-Ni film, as revealed by TEM imaging (Fig. 12): Darker round grains with 10-20 nm diameter, which in some cases show an internal structure, are observed within a matrix with lighter contrast, suggesting the precipitation at grain boundaries of an alloy with lower average atomic number.

Thermal annealing .- Two sets of thermal annealing experiments were performed; for these experiments, the Au-Ni films were deposited on low carbon steel substrates to minimize interdiffusion at the substrate/film interface. In the first set, the film was brought at a predetermined temperature, 200 or 225°C, and at this temperature, successive glancing-angle XRD scan was collected using a  $2\theta$  range from  $2\theta = 35$  to  $46^{\circ}$  with a scan rate of 1°/min, corresponding to a collection time for each scan of 11 min. The time between successive scans was about 5 min. It should be stressed that these data are not snapshots of the film structure corresponding to definite annealing conditions but instead represent a structure that may be evolving during data collection; we find, however, that changes in film structure during the experiment are limited. Figure 13a shows the structural evolution of an alloy with 47 atom % Ni annealed at 200°C. The as-deposited film shows a peak around 39° corresponding to the Au-Ni alloy and a second one that can be assigned to Fe(110) but may also be due to the Au(200) or Ni(111) reflections. The first peak shifts in the second scan to a lower angle, but it does not shift any



**Figure 10.** (Color online) (a)  $\theta/2\theta$  XRD patterns of Au–Ni 47, 64, and 78 atom % Ni electrodeposited on Fe substrates.(b)  $\theta/2\theta$  XRD patterns obtained from Au–Ni films (10–90 atom % Ni) electrodeposited on Cu substrates. Scan rate is 1°/min.

further in successive scans. The second peak, however, remains unchanged with successive scans, reinforcing the hypothesis that this may be mostly originated by the steel substrate. Figure 13b shows similar data for the same alloy annealed at 225°. In this case, upon successive scans, i.e., upon longer annealing, the Au–Ni(111) peak gradually shifts to lower angles and approaches the Au(111) peak, whereas the second peak slightly increases in intensity. These data suggest Au enrichment in the main Au–Ni phase; this occurs only to a limited extent at 200°C but proceeds gradually over time at 225°C. Even at 225°C, the overall annealing time is insufficient to completely precipitate out the pure Au phase.

To better understand the structural evolution in Au–Ni alloys, in situ XRD was performed during annealing at higher temperatures. In these experiments, temperature is increased to the value of interest between 200 and 400°C at 50°C steps and then maintained at that value while an XRD scan is collected. The temperature profiles during heating between the various temperatures are reported in Fig. 14a. Figure 14b shows the evolution of the XRD patterns of a Ni 47 atom % alloy between room temperature and 400°C. A gradual shift and sharpening of the Au–Ni(111) peak is observed, which eventu-



**Figure 11.** (Color online) Structural data for Au–Ni films: (a) Calculated coherence length vs atom % Ni based on XRD data in Fig. 10. Error bars indicate a standard deviation over several distinct fitting attempts. (b) Lattice constant vs atom % Ni; the data are compared with those from Ref. 20 (solid lines) and Vegard's law prediction (broken lines).

ally results in the precipitation of pure Au, as determined by the position of the main peak. The substrate peak additionally increases



Figure 12. Bright-field TEM image of an as-deposited Au–Ni film (73 atom % Ni).



**Figure 13.** (Color online) (a) A series of five consecutive  $\Omega/2\theta$  ( $\Omega = 5^{\circ}$ ) glancing-angle XRD scans acquired during in situ annealing of a Au–Ni 47 atom % film at 200°C in Ar/5% H<sub>2</sub>. An XRD scan for the as-deposited alloy just before annealing is also shown. (b) A series of consecutive  $\Omega/2\theta$  ( $\Omega = 5^{\circ}$ ) glancing-angle XRD scans acquired during in situ annealing of a Au–Ni 47 atom % film at 225°C in Ar/5% H<sub>2</sub>. An XRD scan for the as-deposited alloy just before annealing is also shown. All scan rates used were 1°/min.

in intensity; its width changes and shifts to lower angles, indicating the possibility of the growth of Au(200)-oriented grains or of a nanocrystalline Ni phase. The evolution of the coherence length  $\langle d \rangle$ in the Au-rich Au-Ni phase is reported in Fig. 14c. The observed microstructure, as displayed in Fig. 12, suggests a difference in composition between the grains and the grain boundaries; any grain coarsening process would therefore occur through the long-range diffusion of the various elements. The mean free path L of Au and Ni atoms during these annealing processes was estimated at various temperatures, assuming bulk diffusion and using the relation L=  $2\sqrt{(D_i t)}$ , where  $D_i = D_{i,0} \exp(-Q_i/RT)$  is the bulk diffusivity of Au (Ni) in Au–Ni and t is the isothermal annealing time. In the expression above, R is the gas constant, T is the temperature, the index *i* refers to an alloy component,  $D_{i,0}$  is the pre-exponential factor, and  $Q_i$  is the activation energy for diffusion.  $D_{i,0}$  and  $Q_i$ values for the diffusion of Au and Ni in Au–Ni alloys were taken from the work of Kurtz<sup>21</sup> and Reynolds.<sup>22</sup> For a Au–Ni alloy with 50 atom % Ni, the diffusivity and diffusion length of Au and Ni are shown in Table I;  $L_{Au}$  is also plotted in Fig. 14c.



Figure 14. (Color online) (a) Temperature vs time profiles resulting from subsequent temperature ramp-up processes during in situ annealing. (b)  $\Omega/2\theta$  ( $\Omega = 5^{\circ}$ ) glancing-angle XRD scans obtained during in situ annealing of an electrodeposited Au–Ni 47 atom % alloy. (c) Comparison between the coherence length  $\langle d \rangle$  and the diffusion length of Au  $L_{Au}$  during successive annealing experiments from 200 to 400°C. (d)  $\Omega/2\theta$  ( $\Omega = 5^{\circ}$ ) glancing-angle XRD scans obtained during in situ annealing of an electrodeposited Au–Ni 64 atom % alloy. All scan rates used were 1°/min.

Au has a larger diffusivity than Ni. The activation of solid-state diffusion for Au therefore determines the extent of grain coarsening upon annealing. Figure 14c shows that upon annealing at  $T \ge 200^{\circ}$ C, a linear increase in  $\langle d \rangle$  occurs when  $L_{Au}$  becomes of the same order of magnitude of  $\langle d \rangle$  starting at  $\sim 250^{\circ}$ C.

The evolution of XRD patterns of alloy films with 64 atom % Ni upon annealing is shown in Fig. 14d. At a low temperature (200°C), no change is observed in the XRD patterns, whereas at higher temperatures, the Au–Ni peak initially sharpens, then shifts to lower angles until it settles in the position corresponding to that of pure Au. Additional peaks, which are attributed to Fe oxides and were formed during annealing, probably as a consequence of the presence of trace oxygen, complicate the detailed interpretation of the scans but do not change the main conclusions. The substrate peak widens slightly and becomes more asymmetric, probably indicating the growth of a Au(200) phase or a Ni phase.

Data supporting grain growth and phase separation in annealed Au–Ni alloys were obtained by SEM imaging combined with spatially resolved elemental analysis. Figure 15a shows an SEM image of an alloy (85 atom % Ni) annealed at 300°C for 5 min. Grains with sizes below 100 nm are apparent on the film surface. Figure

Table I. Tabulated values for  $D_{Au}$ ,  $D_{Ni}$ ,  $L_{Au}$ , and  $L_{Ni}$  at various temperatures based on a 10 min annealing period.

Temperature (°C)	$D_{ m Au} \ ( m cm^2/ m s)$	$D_{ m Ni} \ ( m cm^2/ m s)$	L <sub>Au</sub> (nm)	L <sub>Ni</sub> (nm)
25	$2.09 \times 10^{-33}$	$3.26 \times 10^{-34}$	$2.24 \times 10^{-8}$	$8.85 \times 10^{-9}$
200	$7.80 \times 10^{-22}$	$2.39 \times 10^{-22}$	0.014	0.008
250	$6.47 \times 10^{-20}$	$2.22 \times 10^{-20}$	0.125	0.073
300	$2.48 \times 10^{-18}$	$9.33 \times 10^{-19}$	0.770	0.473
350	$5.29 \times 10^{-17}$	$2.15 \times 10^{-17}$	3.560	2.270
400	$7.17 \times 10^{-16}$	$3.11 \times 10^{-16}$	13.10	8.650

15c shows a magnified image of a small region, where several bright particles are observed. These same particles are also shown in the backscattered electron image of Fig. 15b, where they appear in dark contrast, indicating that these particles have a lower average atomic number than the surroundings. Elemental profiles for Au and Ni (Fig. 15d) were also collected along the line drawn in Fig. 15c, confirming that the large particles are indeed rich in Ni, whereas the smaller particles are richer in Au.

#### Discussion

*Electrodeposition process.*— The standard redox potential for the Au<sup>+</sup>/Au redox couple is  $E^{\circ}(Au^+/Au) = 1.215$  V<sub>SSE</sub> but due to complexation by sulfite, the observed onset potential is shifted to -0.9 V. Gold reduction from the sulfite complex proceeds via the following reaction<sup>16</sup>

$$Au(SO_3)_2^{3-} + e^- = Au + 2SO_3^{2-}$$
 [4]

The total complexation by sulfite can be calculated to result in a redox potential of about +0.5 V, a value much higher than the observed onset potential. This suggests either the presence of additional complexing agents in the commercial solution and/or a strong inhibition to nucleation. The onset potential of Ni reduction can be estimated to be between -0.9 and -1.12 V. These values are calculated assuming lack of and total complexation by EDA, respectively. The observed onset potential for alloy deposition is similar to that of Au, probably due to the formation of an underpotentially deposited layer of Ni on freshly deposited Au.<sup>23</sup>

LSV data together with the variation in alloy composition vs potential show that the electrodeposition system studied is a normal one, according to the Brenner definition, with the more noble metal depositing first and the less noble metal codeposited to a large extent only at a lower potential. LSV data also show that alloy deposition is inhibited with respect to Au<sup>+</sup> reduction; this could be expected based on purely thermodynamic grounds. Using in fact the enthalpy



Figure 15. (Color online) (a) Low magnification SEM compositional image of a Au–Ni 85 atom % film electrodeposited on Ru and annealed in vacuum at 300°C for 5 min using the RTA. (b) High magnification SEM backscattered electron image from the sample in (a). (c) High magnification SEM image corresponding to (b) with annotated EDX line scan across four particles. (d) Elemental profile (Au, Ni) corresponding to the line scan in (c). The EDX peaks labeled 1–4 correspond to each particle in (c).

of mixing of Au–Ni alloys,<sup>7</sup> a maximum (positive) enthalpy of mixing of 7.4 kJ/mol would result in a maximum polarization of about 200 mV. The depolarization observed at a low overpotential may be explained by the formation of an underpotential deposited layer of Ni on Au or by the formation of a surface alloy.<sup>10</sup>

The CE is always lower than 100%. As discussed by Green and Roy,<sup>16</sup> the ECD of Au from sulfite solutions with pH > 9 occurs with approximately 100% efficiency; however, lower pH values may result in instability of the sulfite ion (SO<sub>3</sub><sup>2-</sup>), which is partially converted to bisulfite (HSO<sub>3</sub><sup>-</sup>) (Eq. 5) below pH 7.26.<sup>24</sup> Both sulfite and bisulfite may successively undergo various reduction processes<sup>24</sup> leading to the formation of dithionite (S<sub>2</sub>O<sub>4</sub><sup>2-</sup>) or dithionous acid anions (HS<sub>2</sub>O<sub>4</sub><sup>-</sup>), thus providing for various parasitic reactions that would decrease alloy reduction efficiency

$$SO_3^{2-} + H^+ = HSO_3^-, \quad \beta = 7.26 - pH$$
 [5]

The electrochemical reactivity of sulfur compounds is supported by the significant incorporation of S in the alloys observed by AES. The negligible oxygen in the deposits furthermore suggests that the sulfite anion is decomposed and S is incorporated as a sulfide  $S^{2-}$  or perhaps as an acidic ion. The process of S incorporation during Ni electrodeposition from additive-containing solutions is well known, but this occurs through adsorption and electrochemical reduction of neutral molecules such as thiourea or saccharin.<sup>25,26</sup> in our case instead, the sulfite anion probably interacts with surface Ni in a different manner. It can be safely hypothesized however that S would likely segregate at grain boundaries<sup>27,28</sup> and probably as a metal sulfide<sup>29,30</sup>.

Yamachika et al. attribute the formation of an amorphous Au–Ni structure to the incorporation of carbon during electrodeposition from cyanide/citrate electrolytes.<sup>12</sup> S incorporation, due to its significant fraction and its large volume, may in principle induce a similar effect in Au–Ni alloys. However, the observation of a two-phase structure and the possibility of S being present mainly at the grain boundaries leads to the belief that the formation of an

amorphous/nanocrystalline structure is an intrinsic feature of the Au-Ni alloy, as discussed in more detail in the following section.

Morphology and crystal structure.— Au-Ni films exhibit a gradual variation in lattice constant with composition (Fig. 11), suggesting the formation of a series of metastable solid solutions, and a strong apparent positive deviation from Vegard's law. The latter cannot be explained simply by assuming a nonideal solution or a higher sensitivity of X-rays toward nearest neighbors with a higher atomic number, which may be the origin of the slightly positive deviation reported in Ref. 20 and reproduced in Fig. 11b. We hypothesize instead that the main phase detected by XRD has a much larger Au content than the average composition measured by EDX. This is possible in nanostructured alloys, where the concentration of grain boundaries is very high and grain boundary segregation of Ni would result in a significant difference between the overall alloy composition and the composition in the crystal lattice.<sup>31</sup> Preliminary TEM data (Fig. 12) confirm this type of nanostructure; bright-field images in fact show light contrast at grain boundaries, indicative of a larger Ni (and perhaps S) fraction. Further support to this hypothesis is provided by the fact that grain size is observed to decrease with increasing Ni content. In fact, with a larger overall Ni fraction, maintaining a constant composition at the grain boundaries requires a decrease in grain size, which results in a larger grain boundary area. A similar behavior was observed in Y-Fe alloys.

The coherence length  $\langle d \rangle$  of the films in the perpendicular direction as determined by XRD (Fig. 11a) is much smaller than the grain size visible by TEM and is limited to a few nanometers. Grain boundary segregation of Ni (and perhaps S) would cause a gradient in lattice constant and lead to non-Scherrer broadening, which may be sufficient to explain the grain size observed by TEM. The larger features that are visible in SEM images should therefore be clusters of nanocrystalline grains. The small grain size is the combined result of the limited diffusion length of surface adatoms during deposition and the difference in molar volume of the two types of atoms. Growth occurs in fact by ion reduction and surface diffusion of

Table II. Tabulated values for  $\Delta H_{mix}$ ,  $G_{exc}^{liquid}$ ,  $G_{exc}^{int}$ ,  $G_{exc}^{a}$ , and  $G_{exc}^{nc}$  with respect to Au–Ni composition. Au and Ni surface energies are 1.63 and 2.36 J/m<sup>2</sup>, respectively;<sup>41</sup> atomic radii are 1.44 and 1.24 Å, respectively.

Ni fraction	$\Delta H_{ m mix}$ (kJ/mol)	G <sup>liquid</sup> at 298 K (kJ/mol)	G <sup>int</sup> (kJ/mol)	$G^{ m a}_{ m exc}$ (kJ/mol)	G <sup>nc</sup> <sub>exc</sub> (kJ/mol)
0.10	2.0	4.0	3.5	6.0	5.5
0.28	5.0	3.7	5.0	8.7	10.0
0.36	6.0	3.6	5.7	9.6	11.7
0.49	7.2	3.6	5.9	10.8	13.1
0.63	7.4	4.0	8.0	11.4	15.4
0.77	6.2	4.4	12.1	10.6	18.3

adatoms across the surface until the diffusing atoms find a local minimum in surface potential, where they reside for a time sufficient to be immobilized by film overgrowth. An approximate surface diffusion length  $L_s$  at a solid/electrolyte interface can be determined by the formula  $L_s = 2\sqrt{(D_s t)}$ , where  $D_s$  is the surface diffusion coefficient of the adatom under consideration and the time t would approximately be the time necessary to form an ML. Diffusivities at electrolyte/solid interfaces have been found to be several orders of magnitude higher than at solid/vacuum interfaces, mainly due to the effect of adsorbed anions and the strong electric fields existing at these regions;<sup>33</sup> a value often used for Au (the faster diffusing species) is  $10^{-14}$  cm<sup>2</sup>/s.<sup>34</sup> With the observed film growth rates, this results in a diffusion path of a few nanometers, agreeing with the coherence lengths reported in Fig. 11a. If the mean free path during electrochemical metal growth is so short, why do electrodeposited metals usually exhibit much larger grain sizes than those calculated here? In pure metals, multiple surface sites correspond to stable minima of the free energy and a surface site corresponding to a crystal position is never far away, enabling consequently the formation of relatively large crystals. In Au-Ni, however, adatoms join existing alloy seeds at locations of local energy minima. Due to the difference in the atomic volume of Au and Ni, many of these locations do not form structures with translational symmetry but tend to form instead icosahedral nuclei<sup>35</sup> or may become the seeds for new nuclei. Icosahedral phases have been observed in Al-Mn alloys electrodeposited from molten salts both in the as-deposited state or after annealing initially amorphous alloys.<sup>36</sup> We observed instead, at least for Au-rich films, a local cubic symmetry, suggesting that new nuclei and nanometric sized grains of a metastable Au-Ni alloy are formed.

*Recrystallization.*— As-deposited Au–Ni films form metastable phases that, upon gentle annealing, tend to relax to the equilibrium configuration either directly or through the formation of intermediate phases.

Annealing at 200°C is sufficient to shift and sharpen the observed XRD reflections, indicating local gold enrichment in the main phase and limited grain coarsening. Although Au-rich phases are clearly observed, Ni-rich phases are not seen, supporting the hypothesis that Ni precipitates at grain boundaries. Ni-rich clusters may be present but would be smaller, as a consequence of the lower diffusion coefficient of Ni in Au–Ni alloys.<sup>21,22</sup> XRD data show that annealing at 400°C is necessary to precipitate pure Au within the processing time investigated; only under these conditions some evidence for the formation of Ni clusters is observed.

Solid-state diffusion of Au explains the observed increase in coherence length only up to 350 °C. Above this temperature, the calculated mean free path of Au is larger than the observed coherence length. At these temperatures, however, void formation is observed in the annealed films; this favors Au diffusion at the solid/air interface, which hampers a simple interpretation of the coarsening process.

*Free energy of the metastable structure.*— Based on the discussion above, a possible structural model for electrodeposited Au–Ni is that of a nanocrystalline structure formed by the incoherent coa-

lescence of small nuclei, with Ni preferentially segregated at grain boundaries. The as-deposited structure is not an equilibrium structure, in which case it may be of interest to calculate its excess free energy with respect to the equilibrium configuration, i.e., phaseseparated Au and Ni. The excess free energy can be estimated in a simple manner under two different assumptions: (*i*) The structure is amorphous and (*ii*) the structure is nanocrystalline, composed of fcc Au–Ni nuclei separated by grain boundaries.

The excess free energy of the amorphous solid  $G_{\text{exc}}^{\text{a}}$  can be approximated by the sum of the enthalpy of mixing  $\Delta H_{\text{mix}}$  of the crystalline alloy and the excess free energy of the liquid at the temperature of the solid (T = 298 K), subtracting the enthalpy of melting.<sup>37</sup> Under these assumptions,  $G_{\text{exc}}^{\text{a}}$  is given by Eq. 6

$$G_{\rm exc}^{\rm a} = \frac{\Delta H_{\rm m}T}{T_{\rm m}} \ln \left(\frac{T_{\rm m}}{T}\right) + \Delta H_{\rm mix}$$
 [6]

where  $\Delta H_{\rm m}$  is the enthalpy of melting,<sup>38</sup> and  $T_{\rm m}$  is the melting temperature obtained from the Au–Ni phase diagram.  $G_{\rm exc}^{\rm a}$  was calculated for various compositions using the Thompson and Spaepen approximation;<sup>39</sup> the results are reported in Table II, showing that amorphicity increases the excess free energy  $\Delta H_{\rm mix}$  by an additional 35–65%.

The excess free energy of nanocrystalline structures could be approximated assuming a simple geometry consisting of nanosized grains of an fcc Au–Ni solid solution separated by grain boundaries and with a grain size comparable to that estimated by XRD analysis. This excess free energy  $(G_{exc}^{nc})$  may then be written as follows

$$G_{\rm exc}^{\rm nc} = G^{\rm int} + \Delta H_{\rm mix}$$
<sup>[7]</sup>

The first term in the right-hand side in Eq. 7 refers to the interfacial free energy, which can be approximated<sup>40</sup> by  $G^{\text{int}} \sim \gamma N_0 V_{\text{at}}/d$ , where  $\gamma$  is the interface energy,  $V_{\text{at}}$  is the average atomic volume of the alloy, and *d* is the grain size. Taking for  $\gamma$  the weighted average of the surface energies of Au and Ni<sup>41</sup> and using a grain diameter equal to the composition-dependent coherence length reported in Fig. 11a,  $G_{\text{exc}}^{\text{inc}}$  values are calculated for various Au–Ni compositions and the results are reported in Table II. This estimate is in excess for two reasons: (*i*) The tendency of Ni to segregate at grain boundaries and the possible presence of S at these locations suggest that the actual  $\gamma$  should be well below this value; it is even possible that the interface energy may become negligible;<sup>31</sup> (*ii*) the use of the Scherrer equation for grain size clearly underestimates the actual grain size, resulting in an overestimation of  $G^{\text{int}}$ . A lower estimate for  $G_{\text{exc}}^{\text{nc}}$  would be  $\Delta H_{\text{mix}}$ .

 $G_{\text{exc}}^{\text{a}}$  and  $G_{\text{exc}}^{\text{nc}}$  are plotted in Fig. 16; qualitatively, the amorphous structure becomes increasingly stable with respect to the nanocrystalline one with larger Ni content, as indeed observed in our films. The calculated values for the excess free energy of Au–Ni films are consistent with the estimated limits for the excess free energy that can be retained upon rapid solidification processes (~3 kJ/mol) and an order of magnitude smaller than the expected limits estimated for quenching processes from the vapor (50 kJ/mol).<sup>42</sup>



Figure 16. (Color online) Excess free energy of metastable Au-Ni films vs Ni fraction, assuming either an amorphous or a nanocrystalline structure.

### Conclusion

We investigated the electrodeposition process, morphology, and crystal structure of Au-Ni alloys electrodeposited from near-neutral, sulfite based solutions as well as their phase transformation and grain coarsening processes upon thermal annealing. The ECD process is normal according to Brenner; codeposition of Au and Ni, however, occurs with a strong polarization probably due to thermodynamic effects related to phase formation. The process efficiency is low (<50%) due to the parasitic reduction of sulfite and dithionite anions into elemental sulfur and to hydrogen evolution. Although metallurgical Au-Ni exhibits a miscibility gap across the entire composition range, electrochemical deposition resulted in the formation of nanocrystalline/amorphous Au-Ni phases for all compositions investigated. Grain size of as-deposited films was of the order of a few nanometers, decreasing with increasing Ni content. Limited surface diffusivity during growth and atomic volume differences can explain the observed grain size. Thermal annealing led to transformation of the nanocrystalline phase into a thermodynamically stable twophase mixture. We hypothesize that Au-rich or pure Au grains are formed, with Ni-rich precipitates present at grain boundaries.

The excess free energy of the as-deposited, metastable Au-Ni films was calculated to be between 6 and 18 kJ/mol, roughly consistent with the excess free energy limits estimated for electrochemical processes. The annealing process results in phase separation and in a decrease in the alloy free energy.

# Acknowledgments

This work was funded by the National Science Foundation under grant no. DMI-0507023.

University of Virginia assisted in meeting the publication costs of this article.

### References

- 1. A. Brenner, Electrodeposition of Alloys, Vol. 1, Chap. 7, Academic Press, New York (1963).
- 2 K. M. Gorbunova and Y. M. Polukarov, in Advances in Electrochemistry and Electrochemical Engineering, H. Gerischer and C. W. Tobias, Editors, Vol. 5, p. 249, John Wiley & Sons, New York (1978).
- G. R. Stafford and C. L. Hussey, in Advances in Electrochemical Science and Engineering, R. C. Alkire and D. M. Kolb, Editors, p. 275, Vol. 6, Wiley-VCH, 3. Weinheim (2002).
- N.P. Fedot'ev and P.M. Vyacheslavov, Plating, 1970, 700.
- P. L. Cavallotti, L. Nobili, and A. Vicenzo, *Electrochim. Acta*, **50**, 4557 (2005). W. Hume-Rothery, R. E. Smallman, and C. W. Haworth, *The Structure of Metals* 5 6. and Alloys, The Institute of Metals, London (1969).
- J. Wang, X. G. Lu, B. Sundman, and X. Su, CALPHAD: Comput. Coupling Phase Diagrams Thermochem., 29, 263 (2005).
- 8. J. Wang, L. B. Liu, H. S. Liu, and Z. P. Jin, CALPHAD: Comput. Coupling Phase Diagrams Thermochem., 31, 249 (2007).
- T. B. Wu and J. B. Cohen, Acta Metall., 32, 861 (1984).
- 10. L. Pleth Nielsen, F. Besenbacher, I. Stensgaard, and E. Laegsgaard, Phys. Rev. Lett., 71, 754 (1993).
- A. Dolati, M. Ghorbani, and M. R. Ahmadi, J. Electroanal. Chem., 577, 1 (2005). 11 12. N. Yamachika, Y. Musha, J. Sasano, K. Senda, M. Kato, Y. Okinaka, and T. Osaka, Electrochim. Acta, 53, 4520 (2008).
- K. Inoue, N. Sasaki, T. Sasadaira, T. Watanabe, and T. Nakata, Mater. Trans., 47, 1546 (2006)
- M. Guan and E. J. Podlaha, J. Appl. Electrochem., 37, 549 (2007)
- 15 www.technic.com, last accessed April 29, 2010.
- T. A. Green and S. Roy, J. Electrochem. Soc., 153, C157 (2006). 16.
- T. A. Green, M. J. Liew, and S. Roy, J. Electrochem. Soc., 150, C104 (2003). 18. T. M. Harris, J. L. Wilson, and M. Bleakley, J. Electrochem. Soc., 146, 1461
- (1999)19. O. E. Kongstein, U. Bertocci, and G. R. Stafford, J. Electrochem. Soc., 152, C116
- (2005)20. J. R. Clinton, E. H. Tyler, and H. L. Luo, J. Phys. F: Met. Phys., 4, 1162 (1974).
- 21. A. D. Kurtz, B. L. Averbach, and M. Cohen, Acta Metall., 3, 442 (1955)
  - 22
  - J. E. Reynolds, B. L. Averbach, and M. Cohen, Acta Metall., 5, 29 (1957). 23.
  - A. Vaskevich, F. Sinapi, Z. Mekhalif, J. Delhalle, and I. Rubinstein, J. Electrochem. Soc., 152, C744 (2005). M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd ed.,
  - NACE Engineers and Cebelcor, Cebelcor, Brussels (1974). 25
  - T. Osaka, T. Sawaguchi, F. Mizutani, T. Yokoshima, M. Takai, and Y. Okinaka, J. Electrochem. Soc., **146**, 3295 (1999).
  - 26. J. George, J. Rantschler, B. Sang-Eun, D. Litvinov, and S. Brankovic, J. Electrochem. Soc., 155, D589 (2008)
  - A. Bhandari, S. J. Hearne, B. W. Sheldon, and S. K. Soni, J. Electrochem. Soc., 27. 156, D279 (2009). 28

  - C. L. Briant, Acta Metall., 33, 1241 (1985). I. Tabakovic, S. Riemer, K. Tabakovic, S. Min, and M. Kief, J. Electrochem. Soc., 29. 153. C586 (2006).
  - 30. J. Edwards, Trans. Inst. Met. Finish., 39, 52 (1962)
  - J. Weissmüller, Mater. Sci. Eng., A, 179-180, 102 (1994) 31. J. Weissmüller, W. Krauss, T. Haubold, R. Birringer, and H. Gleiter, Nanostruct. 32 Mater., 1, 439 (1992).
  - M. Giesen, G. Beltramo, S. Dieluweit, J. Muller, H. Ibach, and W. Schmickler, 33. Surf. Sci., 595, 127 (2005).
  - 34 J. Erlebacher, J. Electrochem. Soc., 151, C614 (2004).
  - 35. C. L. Briant and J. J. Burton, Phys. Status Solidi B, 85, 393 (1978).
  - B. Grushko and G. R. Stafford, Metall. Trans. A, 21, 2869 (1990). 36.
  - 37. K. Lu, Phys. Rev. B, 51, 18 (1995).
  - M. Bienzle, T. Oishi, and F. Sommer, J. Alloys Compd., 220, 182 (1995). 38.
  - C. V. Thompson and F. Spaepen, Acta Metall., 27, 1855 (1979). 39 D. A. Porter and K. E. Easterling, *Phase Transformations in Metals and Alloys*, 2nd ed., Chapman & Hall, New York (1992). 40.
  - L. Z. Mezey and J. Giber, Jpn. J. Appl. Phys., Part 1, 21, 1569 (1982). 41.

  - 42. G. M. Janowski and G. R. Stafford, Metall. Trans. A, 23, 2715 (1992).