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A Comparison of DC and Pulsed Fe-Ni Alloy Deposits

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ABSTRACT

The effect of hydrodynamics and temperature on the electrodeposition of Fe-Ni alloys has been investigated with dc, pulse, and pulse-reverse electrodeposition techniques. Strong mass-transfer effects in the co-deposition of Fe on rotating cylindrical cathodes were indicated at high current densities. Many features of the present deposition process are shown to be consistent with the Hessami and Tobias model. A comparison of the polarization behavior of single-metal and alloy deposition clearly demonstrate the lower rate of Ni co-deposition in accord with previous reports of anomalous co-deposition of Fe-Ni alloys. X-ray diffraction studies indicate that the crystalline phases (fcc, bcc, and mixed fcc + bcc) in the electrodeposited alloys depend on alloy composition and deposition conditions. Thermal expansion coefficients of electro-formed cylinders of near-Invar compositions ranged from 7.7-10.9 \times 10⁻⁶/°C for unannealed alloys to 4-5 \times 10⁻⁶/°C for alloys annealed at 680°C. Average internal stress of deposits increased with increasing Fe content.

Iron-nickel alloys have found increased use due to their magnetic properties and dimensional stability. In this regard two of the most important Fe-Ni alloys are Permalloy and Invar. Thin films of Permalloy, a Ni-rich alloy (80 weight percent (w/o) Ni, 20 w/o Fe), are currently used in computer memory devices. Invar, an Fe-rich alloy (64 w/o Fe, 36 w/o Ni), is important because of its extremely low thermal expansion coefficient; commercial Invar alloys range from 0.2 to 2×10^{-6} /°C around room temperature compared to other commercial ferrous alloys (steels, cast iron), typically from 1 to 2×10^{-5} /°C. Fe-rich alloys also have some unusual magnetic properties such as a low Curie temperature (232°C) compared to iron (770°C) and nickel (358°C). Also, the magnetic moment of fcc Fe-Ni alloys is a maximum for Invar (1.8 Bohr magnetons). This combination of low Curie temperature combined with a high magnetic moment has been observed for all low thermal expansion metallic materials. Thermal expansion of ferromagnetic materials is the result of two opposing effects: lattice vibrations and magnetics. For most materials the spontaneous volume magnetostriction is small, but Invar's large spontaneous volume magnetostriction compensates for the normal thermal expansion due to lattice vibrations, resulting in a dimensionally stable material.

Electrodeposition of Fe-Ni alloys is of fundamental interest because of the anomalous co-deposition phenomenon. Based on single-metal deposition rates, Ni would be expected to deposit more rapidly than Fe during co-deposition.² However, the reverse occurs because the co-deposition rate of Fe is greater than Ni. This phenomenon, which has been observed by a number of investigators utilizing many different electrolyte systems, is called "anomalous co-deposition." ³ In addition to Fe-Ni alloys, anomalous deposition has been observed for Co-Fe, Ni-Co, Zn-Ni, Zn-Fe, Zn-Co, and Cu-Pb alloy systems.

We have recently reported on an investigation of how the anomalous nature of the co-deposition process is influenced by different current waveforms.⁴ The purpose of the present study is to examine how dc, pulse, and pulse-reverse electrodeposition affect the composition, structure, and properties of the Fe-Ni alloy deposits. The structure and preferred orientation of deposits were determined by x-ray diffraction. Properties of the Fe-Ni alloy deposits,

such as grain size, internal stress, and thermal expansion, were determined as a function of composition and current density.

Experimental

Plating baths were prepared from reagent grade chemicals and distilled water. A sulfamate/chloride plating bath was selected based on previous work, which compared sulfate, chloride and sulfamate electrolyte systems.⁵ Unless otherwise indicated, the plating baths contained 0.75*M* nickel sulfamate, 0.25*M* ferrous chloride, 0.5*M* boric acid, 0.0017*M* sodium dodecyl sulfate as a surfactant, 0.05*M* ascorbic acid to prevent oxidation of ferrous ions, and 0.011*M* sodium saccharin as a stress reducer. Plating baths were adjusted to pH 2.0 with sulfamic acid. Solution pH was monitored frequently and adjusted when necessary.

Deposition using stationary parallel planar electrodes was carried out with an Invar anode (6 cm wide) and a brass cathode (2 cm wide, 0.305 mm thick). After deposit thicknesses of about 5 μ m were obtained, the cathode was rinsed with distilled water and dried. A center portion of the cathode was cut out for analysis by AA spectrophotometry.⁴

Electrodeposition under controlled hydrodynamic conditions was performed with a rotating cylindrical goldplated cathode (0.8 cm od, 0.8 cm length) connected to a Teflon-coated shaft (0.8 cm diam). Anode bags containing sulfur-dispersed nickel surrounded the cathode. Gold plating of the cylinders was carried out in an acidic plating solution (60° C) at 14 mA for approximately 5 min. Turbulent flow conditions at the rotating cylindrical electrode in a solution volume of 750 ml were achieved at the selected rotation rates of 66, 150, and 930 rpm corresponding to Reynolds numbers of 220, 500, and 3117, respectively. Deposits were between 4-7 μ m thick.

Pulse plating (PP) was performed at a selected duty cycle of 0.25 [$\gamma = t_{on}/(t_{on} + t_{off})$] and a pulse frequency of 125 Hz; it has been shown⁶ that the deposit composition was independent of both duty cycle (0.125 $\leq \gamma \leq 0.75$) and pulse frequency between 0.1 and 2000 Hz. Pulse reverse plating (PR) was performed at a duty cycle of 0.5 with an anodic current density (i_a) of 3 and 10 A/dm² and a frequency of 125 Hz; it has been shown that deposit composition was essentially constant in the frequency range of 70–250 Hz.⁶ For PR, $\gamma = t_c/(t_c + t_a)$, with $t_a = t_c$. The average current density for both PP ($i_{ave} = i_{peak} \times \gamma$) and PR [$i_{ave} = (i_c t_c - i_a t_a)/(t_c + t_a)$] was 2.6 A/dm².

X-ray diffraction patterns were recorded for deposits produced on both stationary planar and rotating cylindrical electrodes. Although deposition conditions were similar to those described above, thicker deposits (20 to 30 μ m) were required. Data were obtained with a computer-controlled Picker diffractometer (Model 3488K) with CoK α radiation.

The average internal stress of electrodeposits was measured by the flexible cathode method.⁷ A brass strip (2 cm wide, 0.305 mm thick) insulated on one side with a thin (0.063 mm) tape, was held rigidly at one end. The free end of the strip was allowed to deflect during electrodeposition. The average internal stress (kg/mm²) was determined by the measured deflection of the free end of the cathode strip. For the stress measurements, electrodeposition was carried out to obtain about 5 μ m thick deposits.

Thermal expansion measurements were performed on Fe-Ni alloys, which were electroformed on disposable cylindrical brass mandrels at 54°C and 930 rpm. Deposits were about 25 μ m thick. The samples were annealed by heating in vacuum (6 × 10⁻⁶ Torr) at 680°C for 4 h, followed by cooling to room temperature under vacuum (~6 h). Linear thermal expansion measurements were carried out at a scan rate of 5°C per minute by Lawrence Livermore National Laboratory (LLNL).

Results and Discussion

Figure 1 compares the deposited Fe content obtained at various average current densities and constant hydrodynamic conditions (150 rpm) by dc, pulse, and pulse reverse electrodeposition. For all three techniques, the Fe content



Fig. 1. Comparison of dc, PP, and PR deposition on rotating cylinders. PP duty cycle = 0.25, 125 Hz; PR: $i_a = 10 \text{ A/dm}^2$, $t_a = t_c$, 125 Hz.

initially increased, reached a maximum and then decreased with increasing average current density in accord with other studies of Fe-Ni co-deposition (*e.g.*, see Andricacos *et al.*,).⁸ This type of behavior is characteristic of systems which exhibit anomalous co-deposition. Although the results in Fig. 1 show similar deposit Fe contents by dc and pulse electrodeposition, significantly less anomalous co-deposition by pulse reverse electrodeposition was observed.

The results of a more detailed examination of anomalous co-deposition are shown in the deposit Fe content, dc current density plots in Fig. 2. In these experiments the dependence of deposit Fe content on current density, hydrodynamic conditions (rotation rates), and temperatures (25 and 54°C) was determined. The characteristic of a sharp increase in deposited Fe content in the initial region, followed by a maximum, and then a decrease with increasing current density was observed for all three rotation rates and the two temperatures. The magnitude of the maxima decreased with an increase in temperature but increased with increase in rotation rate. This maximum deposit Fe content shifted to higher current densities with increase in temperature and rotation rate. In general, any change in electrodeposition conditions (e.g., temperature and hydrodynamics) which increase the mass-transfer effects of Fe⁺² shifted this maximum to higher current densities. Others have made similar observations.^{3,9} At current densities below the maximum, an increase in temperature resulted in a decrease in deposited Fe content, as reported by others,¹⁰⁻¹² while at higher current densities, an increase in temperature had the opposite effect with an increase in temperature resulting in increased deposited Fe content.

Each experiment shown in Fig. 2 was terminated when the quality of the deposit was no longer satisfactory, that is, when the deposits were either rough, powdery, or nonadherent. This current density, above which deposits were of poor quality, will be called the "maximum usable current







Fig. 3. Dependence of maximum usable dc current density on rotation rate.

density." As Fig. 2 shows, this end point increased with increasing rotation rate and temperature. For a rotating cylinder operating in the turbulent flow regime (Re > 200) the dimensionless Sherwood number ($k_{\rm m}d/D_{\rm i}$) follows the empirical relationship^{13,14}

$Sh = 0.0791 Re^{0.7}Sc^{0.356}$

where the dimensionless Reynolds number, $\text{Re} = \omega d^2/2\nu$ and the Schmidt number, $\text{Sc} = \nu/D_i$ (ω angular velocity, d =cylinder diameter, $\nu =$ kinematic viscosity, $D_i =$ diffusion coefficient of species i, and $k_m =$ mass-transfer coefficient). Therefore, the mass-transfer rate (the limiting diffusion current) is proportional to $\omega^{0.7}$. Plots of the "maximum usable current density" $vs. \omega^{0.7}$ at 25 and 54°C are given in Fig. 3. The three rotation rates (rpm) of 66 (Re = 220), 150 (Re = 500), and 930 (Re = 3117) provided linear relationships that did not pass through the origin for both 25 and 54°C indicating strong mass-transfer effects but not masstransfer control at these end points.

Recently, Hessami and Tobias¹⁵ proposed a model for anomalous co-deposition, which describes well the experimental results of Andricacos *et al.*,⁸ who investigated the co-deposition of Ni-rich Fe-Ni alloys on rotating disk electrodes. A key feature of the H-T model, in contrast to the one proposed earlier by Dahms and Croll,¹⁶ is to take into account the thermodynamics and kinetics of Fe and Ni hydroxide ions in the co-deposition of Fe and Ni.

Inasmuch as the H-T model appeared in *This Journal* several months after the experimental part of the present work was completed, some rough approximate calculations were performed to ascertain the applicability of this new model to the present results. Although these calculations are rather crude compared to Hessami and Tobias' more refined numerical computations, nevertheless good qualitative agreement was obtained between calculations and experimental results indicating that the H-T model satisfactorily describes the dependence of the co-deposition be-



Fig. 4. Comparison of experimental dc co-deposition and calculations based on H-T model; 25 and 54°C.

havior of the present Fe-Ni system on current density, hydrodynamic conditions, and temperature. A comparison of the calculated and experimental results for the electrodeposition of the Fe-Ni alloys is given in Fig. 4. Both experiments and calculations show that an increase in temperature lessened anomalous co-deposition. Details of the calculation procedures based on the H-T model and additional comparisons of experiments and calculations are provided elsewhere.⁶

A comparison of the partial current densities of Fe and Ni during co-deposition and the single-metal electrodeposition rates of Fe and Ni as a function of cathodic potentials at 66 and 930 rpm is given in Fig. 5a and b. At both rotation rates, the co-deposition rate of Ni is significantly less than the electrodeposition rate of pure Ni. Conversely, the codeposition rate of Fe is considerably greater than the electrodeposition of pure iron. At both rotation rates, the differences between single-metal deposition and the co-deposition rate for both Fe and Ni decreased as cathodic potentials increased. Also, the "maximum usable current densities" for both single-metal deposition and co-deposition were extended to more cathodic potentials when the rotation rate increased from 66 to 930 rpm.

Figures 6a and b compare the partial current densities of Fe and Ni during co-deposition at 25 and 54°C for 66 and 930 rpm, respectively. The partial current densities of both Fe and Ni were appreciably higher at 54°C than at 25°C. For 54°C, Ni partial current densities were higher than Fe at very low cathodic potentials. On the other hand, Fe partial current densities were higher than Ni in a broad intermediate range of cathodic potentials, returning to higher Ni partial current densities at high cathodic potentials. The latter transition increased substantially to higher cathodic potentials when the rotation rate increased from 66 to 930 rpm. For 25°C, the Ni partial current density approached but did not exceed Fe partial current densities at higher cathodic potentials.



Fig. 5. Comparison of co-deposition and single-metal deposition of Fe and Ni on rotating cylinders; (a, left) 66 rpm, (b, right) 930 rpm.



Fig. 6. Co-deposition of Fe and Ni on rotating cylinders at 25 and 54°C; (a, left) 66 rpm, (b, right) 930 rpm.

Figure 7 compares the partial current densities of Fe and Ni during co-deposition as a function of cathodic potentials for dc, pulse, and pulse reverse electrodeposition at 150 rpm and 25°C. DC co-deposition rates of Fe and Ni were higher than those for either pulse or pulse reverse electrodeposition. For both dc and pulse electrodeposition, Fe partial current densities were always greater than Ni but the differences decreased considerably at higher cathodic potentials. For pulse reverse electrodeposition, except for a small intermediate cathodic potential range where the Fe partial current densities were slightly higher than Ni, Fe and Ni partial current densities were essentially equivalent. It is quite evident that pulse reverse electrodeposition lessened anomalous co-deposition. Good deposits were obtained at much greater cathodic potentials for PP and PR than for dc electrodeposition.

Crystal orientation, grain size, and thermal properties have pronounced effects on many properties of electrodeposits. Therefore, the effects of electrodeposition conditions, including waveforms, on the structure of the deposits were investigated.

X-ray diffraction measurements were performed to examine the structure of electrodeposited Fe-Ni alloys at various deposit compositions using dc, PP, and PR (Fig. 8). Single-metal electrodeposits of Ni and Fe exhibit fcc and bcc phases, respectively, similar to thermally prepared metals. Thermally prepared alloys exhibit fcc phases up to approximately 67% Fe, a mixture of fcc and bcc phases at intermediate compositions, and bcc phases above 72% $\mathbf{F}e^{17-19}$; this is also observed for electrodeposited alloys (Fig. 8). DC deposition on stationary electrodes indicated a mixed phase region between 62 and 68% Fe. PR expanded this region to approximately 70% Fe, while PP extended it to 73%. For cylindrical electrodes rotating at 150 rpm, dc deposition resulted in a marked shift of the mixed phase region to between 50 and 62% Fe, whereas for PR the mixed phase ranged from 58 to 70 weight percent (w/o) Fe. De-



Fig. 7. Comparison of dc, PP, and PR deposition on rotating cylinders at 150 rpm. PP and PR conditions as in Fig. 1.

posits of near-Invar compositions (64 w/o Fe and 36 w/o Ni) were a mixture of fcc and bcc phases.

X-ray diffraction patterns of stationary PP deposits (Fig. 9a) resulted in (111) and (200) preferred orientation, the latter decreasing with increasing Fe content, with presence of (222) and (311) planes for fcc alloys; dc deposits (not shown) produced similar patterns. The bcc deposits showed (110) and (211) preferred orientation planes with the latter increasing markedly with Fe content >90%; dc deposits, on the other hand, exhibited decreasing (211) orientation.

PR fcc deposits showed strong (111) and (200) preferred orientation, the latter decreasing markedly in the 50 to 63% Fe composition range (Fig. 9b). For bcc alloys (\geq 74% Fe) the (110) and (211) crystal planes exhibited preferred orientation, with the latter increasing with increasing Fe content.

As shown in Table I, thermal coefficients of expansion (TCE) of unannealed alloys are less than those of bulk Fe and Ni.²⁰ However, Invar electrodeposits have higher TCEs than thermally prepared Invar because the deposits are a mixture of fcc and bcc phases; low TCE values have only been reported for fcc alloys. A single fcc phase was obtained by annealing the near-Invar deposits above their recrystallization temperature resulting in reduced thermal coefficients of expansion.

Figure 10 compares lattice parameters for Fe-Ni alloys deposited on stationary electrodes (data points) with thermally prepared fcc¹⁸ and bcc¹⁹ alloys (solid lines). For homogeneous fcc alloys, lattice parameters of the electrodeposits were similar to thermally prepared alloys. The linear increase in lattice parameter with deposit composition indicates that the Fe-Ni deposits are true alloys. The decrease in lattice parameter for thermally prepared fcc alloys greater than 60 w/o Fe was not observed for the electro-

·	fcc	•••••	fcc+bcc	♦ bc	c			
Δ	Δ			$\diamond \diamond \diamond$	DC,stat			
Δ	Δ	Δ			PP,stat			
Δ	Δ	ΔΔ			PR,stat			
Δ		ΔΔ	• • • •	$\infty \diamond$	DC,150rpm			
Δ	Δ	ΔΔ	$\triangle \bullet \bullet \bullet$	\diamond	PR,150rpm			
<u> </u>								
0	10 20	30 40	50 60 70	80 90 1	00			
	wt% Fe							

Fig. 8. Crystal lattice type for Fe-Ni deposits on stationary and rotating electrodes ($i_{ave} = 2.6 \text{ A/dm}^2$). PP and PR conditions (2nd and 5th rows, as in Fig. 1; 3rd row, $i_a = 3 \text{ A/dm}^2$, other conditions as in Fig. 1).

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Fig. 9. Diffraction patterns for Fe-Ni alloys deposited on stationary electrodes ($i_{ave} = 2.6 \text{ A/dm}^2$). (a, left) Pulse plating, (b, right) pulse reverse plating. PP conditions as in Fig. 1; PR conditions as in 3rd row, Fig. 8; (*) reflections due to brass substrate.

deposited alloys because of the inhomogeneity (*i.e.*, mixed fcc and bcc) in this composition range. The lattice parameters for homogeneous bcc electrodeposits were not a linear function of composition and, except for alloys with high Fe content, were less than those for thermally prepared alloys.

Figure 11 shows deposit tensile stress increasing with Fe content up to a maximum of about 35 kg/mm² at 74 w/o Fe. Tensile stresses decrease above this composition, probably because of microscopic cracking leading to internal stress relief. Deposits containing 94% Fe exhibited visible stress cracking precluding stress measurements. The internal (residual) stress in the deposits was independent of the current waveform, *i.e.*, stress in dc, PP and PR deposits were essentially the same.

The grain size (GS) was estimated with x-ray diffraction by means of the Scherrer formula

$L=0.9\lambda/B_{\rm GS}\cos\theta_{\rm c}$

where *L* is the diameter of the grain (Å), λ is the wavelength of the x-ray radiation (A), $B_{\rm GS}$ is the half-height width (rad) of the 2 θ -diffraction peak due to GS, and $\theta_{\rm c}$ is the diffraction angle of the peak center. Figure 12 shows the effect of Fe content on the GS of electrodeposits on stationary electrodes. The GS decreased with increasing Fe content for fcc alloys. PP and PR waveforms did not have any significant effect on GS except that PR gave slightly larger GS in 35-45 w/o Fe deposits. In the near-Invar composition range, the GS reached a minimum of 30-40 A. Conversely, in bcc alloys, the GS increased with Fe content.

Table I. Thermal expansion coefficients of electroformed Fe-Ni cylinders.

Weight percent iron	Waveform type	Phase	10 ⁻⁶ /°C
61	dc	fcc + bcc	8.1
64	dc	fec + bee	7.7
68	de	fcc + bcc	8.4
61	\mathbf{PR}	fec + bee	9.0
67	\mathbf{PR}	fcc + bcc	10.9
65 ^a	\mathbf{PR}	\mathbf{fcc}	4.6
69ª	\mathbf{PR}	fee	4.2
Iron [20]		bee	12
Nickel [20]		fee	13

* Annealed.

For dc deposits on rotating cylinders, a minimum GS of 40-50 A was obtained in 45-60 w/o Fe alloys;⁶ current density and rotation rate had little effect on grain size. PP resulted in GS similar to dc. Although PR deposits had larger GS in the low and high Fe composition range, at intermediate alloy compositions GS was similar to dc deposits.⁶



Fig. 10. Comparison of lattice parameter for Fe-Ni deposits on stationary electrodes ($i_{ave} = 2.6 \text{ A/dm}^2$) and for thermally prepared alloys (—). PP and PR conditions as in Fig. 1.





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Fig. 12. Grain size of Fe-Ni deposited on stationary electrodes $(i_{ave} = 2.6 \text{ A/dm}^2)$. PP and PR conditions as in Fig. 11.

Conclusions

Electrodeposition of Fe-Ni alloys with dc, pulse, and pulse reverse current waveforms has been investigated. As reported by others, the Fe content increased to a maximum and then decreased with increasing current density. This behavior is characteristic of anomalous co-deposition. DC and PP were similar, whereas anomalous co-deposition was significantly less with pulse reverse waveforms; the latter produced good quality deposits at higher current densities. For all three waveforms good quality deposits were obtained at higher current densities with increased temperatures and hydrodynamics.

A comparison of the experimental results and calculations based on the Hessami-Tobias model indicates good qualitative agreement in the co-deposition behavior for the electrodeposition conditions studied.

Electrodeposited alloys $\leq 60\%$ Fe exhibited a fcc phase region and \geq 72% Fe a bcc phase region with mixed phases at intermediate compositions, similar to thermally prepared alloys. Deposition on rotating cylindrical cathodes resulted in a shift of the mixed phase region to deposits with lower Fe content. Deposits exhibited preferred orientations of (111) and (200) for fcc alloys, and (110) and (211) for bcc alloys. However, the deposited Fe content and waveform influenced the intensities of preferred orientations.

For homogeneous fcc deposits, lattice parameters increased linearly with Fe content, similar to thermally prepared alloys. On the other hand, the lattice parameters for homogeneous bcc deposits were smaller. Deposit tensile stresses increased with increasing Fe content to a maximum of approximately 35 Kg/mm² (~70% Fe); the observed decrease at higher Fe content is attributed to internal stress relief as a result of microscopic cracking.

Deposit grain size decreased with increasing Fe content for fcc alloys but increased for bcc alloys. Pulse and pulse reverse waveforms did not significantly affect deposit grain size, except for larger GS obtained with the latter in low and high Fe deposits.

Thermal coefficients of expansion of deposits in the Invar composition range were higher than those of thermally prepared alloys and this is attributed to the mixed phase character of the deposits. Homogeneous fcc phases were obtained by annealing the deposits above the recrystallization temperature, reducing the TCE to values slightly above those of thermally prepared alloys.

Acknowledgments

David Grimmett appreciates the support of an IBM Manufacturing Research Graduate Fellowship (1989-1990). He is also grateful for AESF Scholarships (\$1000) in 1988-1989 and 1989-1990 and the assistance of a UCLA Academic Senate grant. Jack Dini (LLNL) kindly provided the Invar anode and arranged for the measurements of the thermal expansion coefficients. Brian K. Nobe assisted with the graphics.

Manuscript submitted Feb. 3, 1992; revised manuscript received Aug. 7, 1992. This was Paper 405 presented at the Phoenix, AZ, Meeting of the Society, Oct. 13-17, 1991.

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