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4. Oxide film thickening during repassivation of nickel/copper alloys containing up to 70% Cu obeys Eq. [13] with A and E_0 values similar to those described for Ni. The high field gradient (and therefore the B value) however, decreases with increase in the copper content of the alloy for both film growth regions (E < and > +18 mV(NHE)).

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Structure Investigations of Electrodeposited Nickel

I. X-Ray Diffraction and Mossbauer Spectroscopic Measurements

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ABSTRACT

Nickel was electrodeposited on copper substrates from sulfamate-sulfite, sulfamate, chloride, and chloride-sulfate electrolytes. The crystalline orientation was determined by x-ray diffraction, the magnetic orientation by Mossbauer spectroscopy of Co-57-doped deposits, and the stress by electrode deflection. The stress level was correlated with the relative intensity of the lines in the Mossbauer emission pattern in the case of deposits with a (100) preferred orientation.

The stress developed in nickel electrodeposits has been of interest for many years because of concern that internal stress may reduce corrosion resistance and also may lead to deformation of the substrate when the substrate is thin. The goal of the studies reported herein was an exploration of techniques based on Mössbauer spectroscopy that might be utilized for qualitative or quantitative measurements of the stress level in nickel electrodeposits. This goal has not yet been totally achieved but partial success has been obtained in the case of deposits with a (100) preferred orientation.

We report in this and the following paper the results of studies of nickel electrodeposits utilizing x-ray diffraction, Mössbauer emission spectroscopy of deposits doped * Electrochemical Society Active Member.

with Co-57, and positron annihilation spectroscopy. For convenience in presenting the results, the first paper deals with the measurements related to stress in the deposits and the second paper deals with measurements related to structural imperfections.

Experimental

The test samples were prepared by electrodeposition of nickel on copper substrates from four different plating solutions: sulfamate-sulfite, sulfamate, chloride-sulfate, and chloride. The copper substrates were 0.2 mm thick and were surfaced prior to electroplating by abrasion with pumice, etching in dilute HNO₃, and washing in distilled water. The experimental conditions for the forma-

		Electro-			
Sample	Composition	concen-	Current		
identifi-	of plating	tration	density		Temp.
cation	baths	(g/l)	(A/dm^2)	рH	(°C)
			~ ,,	F	
1	Sulfamate-sulfite		2.75	4.0	50
	Ni sulfamate	330			
	H_3BO_3	30			
	Na lauryl sulfate	1			
	Na_2SO_3	0.2			
2	Sulfamate		2.75	4.0	50
	Ni sulfamate	330			
	$H_{3}BO_{3}$	30			
	Na lauryl sulfate	1			
3	Chloride-sulfate		5.0	5.6	45
	$NiSO_4 \cdot 7H_2O$	170			
	$NiCl_2 \cdot 6H_2O$	35			
	H_3BO_3	35			
	$Na_2SO_4 \cdot 10H_2O$	70			
4	Chloride		5.0	2.0	60
	$NiCl_2 \cdot 6H_2O$	300			
	H_3BO_3	30			
5	Chloride		5.0	2.0	60
	$NiCl_2 \cdot 6H_2O$	300			
	H_3BO_3	30			
	Na lauryl sulfate	0.5			
6	Chloride		10.0	2.0	60
	$NiCl_2 \cdot 6H_2O$	300			
	H_3BO_3	30			
7	Chloride		10.0	2.0	60
	$NiCl_2 \cdot 6H_2O$	300			
	H_3BO_3	30			
	Na lauryl sulfate	0.5			
8	Chloride		15.0	2.0	60
	$NiCl_2 \cdot 6H_2O$	300			
	H_3BO_3	30			

tion of the deposits are summarized in Table I. Deposits from the choride-sulfate bath were prepared over a temperature range of 20°-60°C. The surface active agent, sodium lauryl sulfate, was added in three cases to minimize pitting. The deposit thickness was 250 μ m in the case of the panels utilized for the x-ray diffraction studies and was 30 μ m in the case of the panels utilized in the Mössbauer studies. In the latter case, a small amount of Co-57 in the form of the chloride was added to the plating bath in order to yield an electrodeposit that was doped with Co-57. The stress in the deposit was measured in four cases using the deflection of the cathode as developed by Hoar and Arrowsmith (1). One side of the cathode was coated with a commercial epoxy-polyamide coating known as "Abdeck" so as to limit the electrodeposit to one side of the cathode. It is not felt that stresses due to water uptake by the coating were significant since the stress measurement was made within 10 min of immersion in the plating bath.

X-ray diffraction data were accumulated using a DRON-3 diffractometer and the K_{α} radiation of molybdenum. The emission Mössbauer spectra were obtained using a spectrometer manufactured by Ranger Electronics. The absorber was K_4 Fe(CN)₆·3H₂O, and all chemical shifts are given relative to this standard. The spectra were fitted by Lorentzian functions.

Results

Stress measurements.—The measured values of the stress are tabulated for four electrodeposits and literature

Table II. Residual stresses in nickel electrodeposits

					(200)	39		
	Residual stress (N/mm²)			8b	(220) (111)	$\frac{42}{100}$	Weak (110)	0.3518
Sample	Our results	Results taken from the literature	Reference	Bolled	(200) (220) (111)	40 37 100	(())) ())	0.0020
		100	(9)		(200)	99		
1		-130	(2)	Nickel	(220)	24		
2	15	17.5	(2)	ASTM	(111)	100		
3	170	260	(3)	Standard	(+==)			
4		410	(4)	Powdered	(200)	42		
5		410	(4)	Nickel	(220)	21		
ĥ	260	490	(4)		()			
ž	280	490	(4)	a and b refer	to parallel r	neasureme	ents of different sa	mples depos-
8		580	(4)	ited from the	same soluti	on.		

ELECTRODEPOSITED Ni

values are cited for deposits prepared under all eight conditions in Table II. It will be noted that our measured values are lower than those taken from the literature.

X-ray diffraction measurements.—The results of the x-ray diffraction measurements are given in Table III. Data are also given for rolled nickel and the values for powdered nickel from the ASTM standard card file are given at the end of the table.

The deposit from the sulfate-chloride bath exhibited very strong (100) preferred orientation as has been reported previously (5, 6). Samples 1 and 2 exhibited a weak (100) preferred orientation and samples 4-8 exhibited a weak (110) preferred orientation.

The x-ray diffraction characteristics of plating bath 3 were also studied as a function of temperature over the range of 20° -60°C. The strong (100) preferred orientation was maintained over the temperature range, 30° -55°C.

Thermal treatment of sample 3 at 500° for 1h in an argon atmosphere did not change the crystalline orientation, and the sample maintained the strong (100) preferred orientation.

Mössbauer spectroscopic measurements.—Mössbauer data for 13 nickel deposits doped with ⁵⁷Co are summarized in Table IV. The isomer shift, the quadrupole splitting, and the effective magnetic field values are those characteristic for ⁵⁷Co atomically dispersed in nickel. The only parameter that exhibited significant differences for deposits formed under different experimental conditions was the relative line intensities, given as R in the table. This parameter is determined by the magnetic orientation

Table III. X-ray diffraction data

	Reflection (Miller			Lattice parameter
Sample	indexes)	I _{rel}	Orientation	a (nm)
1a	(111)	100	Weak (100)	0.3512
	(200)	94	· · ·	
1h	(220)	100	Wook (100)	0 3511
10	(200)	90	Weak (100)	0.0011
	(220)	0.8		
2a	(111)	100	Weak (100)	0.3507
	(200)	74		
9%	(220)	100	$W_{aal} = (100)$	0.9506
20	(111)	100	weak (100)	0.3506
	(200)	15		
3a	(111)	2.1	Strong (100)	0.3524
°u	(200)	100	Succes (100)	0.0001
	(220)	0.2		
3b	(111)	2.4	Strong (100)	0.3518
	(200)	100		
	(220)	0.2		
4a	(111)	100	Weak (110)	0.3513
	(200)	39		
4h	(220)	100	Woolz (110)	0.2515
UF	(200)	35	Weak (110)	0.5515
	(220)	41		
5	(111)	100	Weak (110)	0.3514
	(200)	40		
	(220)	40		
6	(111)	100	Weak (110)	0.3526
	(200)	40		
	(220)	42		0.0510
7	(111)	100	Weak (110)	0.3513
	(200)	31 34		
8a	(111)	100	Weak (110)	0 3517
ou	(200)	39	Weak (110)	0.0011
	(220)	42		
8b	(111)	100	Weak (110)	0.3518
	(200)	40		
	(220)	37		
Rolled	(111)	100		
NT: 1 .1	(200)	99		
ASTM	(220)	24		
Standard	(111)	100		
Powdered	(200)	42		
Nickel	(220)	21		

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Table IV. Mössbauer	parameters	of the 🍯	'Co-doped	Ni-electrodeposits
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Sample	Isomer shift δ* (mms ⁻¹)	Quadrupole splitting ΔE_{Q} (mms ⁻¹)	Effective magnetic field $H_{s/2}$ (Tesla)	Half-width at the half-maximum $\Gamma \text{ (mms}^{-1}\text{)}$	$A_1 + A_6^{**}$	
					$\mathbf{R} = \frac{1}{A_2 + A_5}$	3/R
	$-0.042 \\ -0.033$	-0.003 -0.003	$\begin{array}{c} 26.50 \\ 26.73 \end{array}$	0.320 0.326	3.31*** 3.00	0.90 1.00
2a 2b 2c	$-0.038 \\ -0.037 \\ -0.040$	$-0.003 \\ -0.002 \\ +0.001$	26.84 26.58 26.68	0.300 0.300 0.306	2.33 2.02 2.10	1.28 1.48 1.43
3a 3b	$-0.042 \\ -0.041$	-0.005 -0.007	$\begin{array}{c} 27.00 \\ 26.71 \end{array}$	0.320 0.323	7.50 7.35	0.40 0.41
4	-0.039	+0.013	27.50	0.295	4.06	0.74
5	-0.046	+0.016	26.55	0.296	2.76	1.09
7	-0.045	+0.010	26.05	0.288	2.86	1.05
8a 8b 8c	-0.044 -0.035 -0.042	+0.010 -0.001 +0.011	26.81 26.68 26.67	0.318 0.307 0.319	3.73 3.64 3.67	0.80 0.82 0.82

* Relative to K_4 Fe(CN)₆ · $3H_2O$ absorbent.

** A_i is the area of the *i*th line.

*** An aging for three months at room temperature did not change the results.

(a, b, and c stand for the parallel electrodepositions.)

of the domains in the nickel electrodeposit, and it is affected by the crystalline orientation and by the internal stress (7, 8). Representative spectra are shown in Fig. 1. The ratio of lines 3 to 1 should be unaffected by changes in orientation, and the spectra shown in Fig. 1 do indeed indicate that this ratio is a constant.

Discussion

Previously, it has been predicted (9) that the stress level in nickel electrodeposits can be determined from Mossbauer emission spectra provided that the orientation of the deposit is (100). The reasoning behind this conclusion will be briefly stated, but the original publication should be consulted for a more detailed summary.



Fig. 1. Representative Mössbauer emission spectra from nickel electrodeposits doped with Co-57.

The easy directions of magnetization in a magnetic material are determined by the magnetocrystalline anisotropy and the mechanical stress brought about by magnetostriction. These easy directions are the possible directions for domain magnetization. The relative abundance of the various easy directions is determined by the requirement that the magnetostatic energy should be a minimum. The domain structure, and especially the domain sizes, are related to the necessity for the presence of domain walls where spins out of the easy direction exist. In a magnetic metal, all these effects are coupled and the domain pattern is determined by a local minimum of the sum of the magnetocrystalline, magnetoelastic, elastic, magnetostatic, and domain wall energies.

The magnetic orientation of the sample relative to the spatial orientation of the sample can be determined by measurement of the relative areas of the first and sixth lines in the Mössbauer emission pattern to the second and fifth lines

$$R = \frac{A_1 + A_6}{A_2 + A_5} = \frac{3/4 (1 + \cos^2 \theta)}{\sin^2 \theta}$$
[1]

where A_i is the area of the *i*th line of the Mossbauer spectrum and θ is the angle between the directions of the propagation of the gamma rays and the magnetization (10).

It was suggested that stress in the electrodeposit changes the easy direction of magnetization from the normal (111) direction to the (110) direction in those cases where the (100) plane lies parallel to the metal surface. The magnitude of the stress is assumed to determine the fraction of the domains which have a (110) direction of magnetization. The fraction shows up in the ratio of the line intensities as given in the above equation.

The predicted relationship (9) between the value of 3/R and the stress level in nickel electrodeposits with a (100) preferred orientation is given in Fig. 2. Experimental points determined in this study for samples 1-3, the only ones of the set with a (100) preferred orientation, are also included in the figure. The point for sample 2, in which the stress level was low, falls on the theoretical curve, whereas the points for samples 1 and 3 are seriously off the curve. The zero stress level value is an assumed value taken from the sample heated at 500°C in argon.

A strong (100) orientation is maintained over the temperature range of 30° - 50° C in the case of the panels plated from the sulfate-chloride bath. Mossbauer measurements on similar samples indicated that the 3/R values increased approximately 20% for each 10°C increase in bath temperature. Data given by Brugger (11) and Croly (12), as summarized by Safranek (4), indicate that the stress level in deposits from the sulfate-chloride

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Fig. 2. Comparison between the theoretical curve developed in Ref. (9) and the experimental values for electrodeposits with a (100) preferred orientation. The point at 130 N/mm² represents the literature value for a sample with compressive stress.

bath decreases over the temperature range of interest, namely, 30°-50°C. Thus, these data also support the prediction that deposits with a (100) preferred orientation exhibit a Mössbauer hyperfine split pattern whose character is related to the stress level in the deposit.

One other piece of information supports in a qualitative way the relationship between 3/R and the stress level in (100) oriented nickel electrodeposits. Sample 3 was heated at 500°C in an argon atmosphere for 6h and the 3/Rvalue was determined after slowly cooling the sample to room temperature. The 3/R value increased from its original value of 0.4 to approximately 2, a value characteristic of a very low stress level in the deposit. Concurrently with the change in relative intensity of the lines in the hyperfine split spectrum, the measured effective magnetic field increased to 29.2T from its original value of 26.8. The probable explanation for this increase in the effective magnetic field is the aggregation of cobalt atoms within the nickel matrix.

The measurement of stress, or changes in stress level on thermal treatment by the emission Mössbauer technique, is not practical for routine commercial applications because of the necessity to use the radioactive isotope ⁵⁷Co. However, the method may have application in laboratory studies or in the development of a process. Also, presently the method appears applicable only to deposits with a (100) preferred orientation. This limitation does not seem to be unduly restrictive since deposits made from the sulfate-chloride bath under common conditions of current density and temperature in the absence of organic addition agents ordinarily exhibit a strong (100) preferred orientation.

It does appear that there is a relationship between the ratio of lines 1 and 2 in the Mössbauer spectra and the stress for nickel deposits with a (100) preferred orientation. The chief difficulty is that the line ratio is much less sensitive to stress than the theoretical conclusions in Ref. (9) suggest. Refinements in the theoretical treatment are warranted.

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