Technical Article

Direct & Pulse Current Electrodeposition Of Iron Group Thin Film Alloys Containing Vanadium by M. Schwartz, C. Arcos & K. Nobe

Direct current (DC) and pulse current (PC) electrodeposition of binary and ternary alloys of the iron group (IG) metals and vanadium are discussed. 90 Co/10 Fe alloy compositions with substitutional additions of desirable small amounts of V (~2%) were obtained; Co-Ni-V and Ni-Fe-V alloys were also deposited. The effects of complexer, pH and current density on deposit composition and cathode current efficiency (CCE) are discussed and compared to deposition of binary alloys of the iron group only. Impedance measurements indicate greater corrosion resistance for ternary Co-Fe-V alloys than for binary Co-Fe alloys. Crude magnetic measurements show approximately two times greater "relative magnetic moments" for Co-Fe-V deposits than for deposits from typical Ni-Fe (Permalloy) solutions.

Electroplating of metals and alloys plays an important role in the manufacture of magnetic data storage devices. Preparation of these metallic thin films by electrodeposition processes is much more suitable for mass production and much less costly than by vacuum deposition processes.¹ Electrodeposition processes are essentially continuous while vacuum deposition processes require significant down time. Furthermore, energy requirements are substantially less for electrochemical processes compared to vacuum processes.² Therefore, if magnetic thin films of superior magnetic properties can be produced by electrodeposition, substantial energy savings (over an order of magnitude compared to vacuum technologies) can be achieved, contributing to further decline in manufacturing costs for data storage units.

The recording head cores of magnetic storage devices are fabricated from materials which have soft magnetic properties and are characterized by high magnetic satura-

Nuts & Bolts: What This Paper Means to You

Plated coatings are very important in the manufacture of magnetic storage devices. Direct and pulse current plating of alloys of the iron group metals (iron, nickel and cobalt) with vanadium are studied here. The addition of vanadium in the alloy coating gives us films that allow higher recording capacities and memory chips that retain information, even with the power turned off. The results of an extensive study of the deposition of these alloys... how the operating factors alter the composition and properties... are given. In addition to the magnetic effects, they show improved corrosion resistance.

tion (B_a), low coercivity (H_a), near zero magnetostriction (λ) and high permeability (μ).³

Electrodeposited Permalloy (80 Ni/20 Fe) films have such desirable magnetic properties and have been used exclusively as pole material in thin film heads for digital recording.4 However, projections of higher storage density and output performance for recording applications show that soft magnetic materials superior to Permalloy are required.² Thus, considerable effort has been directed to the development of materials similar to Permalloy but with higher magnetic saturation, higher permeability and higher resistivity.5,6

Since the discovery of the giant magnetoresistance (GMR) effect in 1988, *i.e.*, the change in electrical resistance in response to an applied magnetic field, it has attracted considerable attention.7 GMR reading heads significantly increase the capability to read high areal density computer disks. GMR films in non-volatile memory chips can provide information retention even with the power off. Sensors based on GMR materials can be applied to automotive components, such as anti-lock brakes and the regulation of crank-shaft speeds, raising fuel economy and lowering exhaust emissions.8 As indicated above, electrodeposition offers many advantages over physical vapor deposition (PVD) technologies. Ross9 and Schwarzacher and Lashmore¹⁰ reviewed the feasibility and advances in the fabrication of electrodeposited GMR materials and films (IG metals and alloys sandwiched with non-magnetic metals, e.g., Cu or Ag) with properties equivalent to PVD films.

Liao obtained 90 Co/10 Fe thin film electrodeposits having zero magnetostriction and a B_a twice that of Permalloy (80 Ni/20 Fe), making it a promising thin film head material for use with future higher coercivity recording digital disks.⁵ In spite of these properties, the 90 Co/10 Fe alloys do not satisfy all the mechanical and physical requirements for thin film heads because of poor corrosion resistance, brittleness and low resistivity. Because these shortcomings need to be overcome before Co-Fe alloys can be used as thin film heads, considerable industrial research has been devoted to this problem.^{11,12}

It has been reported that the addition of 2% vanadium to bulk equiatomic Co-Fe alloys has little effect on their

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magnetic properties, but substantially increases electrical resistivity.¹³ On the other hand, bulk Co-Fe alloys with 4 to 15% vanadium produce alloys with high coercivity. These permanent magnetic materials are known as Vicalloys.¹⁴

Development and applications of Permendur (50 Co/50 Fe), V-Permendur (49 Co/49 Fe/2 V) and Supermendur (high purity 49 Co/49 Fe/2 V) prepared by metallurgical methods date back to over 50 years ago. The technological importance of these Co-Fe alloys was based on their high magnetic saturation (B_s), high permeability (μ), low magnetocrystalline anisotropy and low coercivity (H_c), which made these alloys attractive as soft magnetic materials.¹⁵ Supermendur has superior properties because of its high purity; at room temperature it has the highest known B_s (2.4 T) and a low H_c (0.2 Oe).

Bulk Supermendur's high temperature properties and high magnetic saturation values enable substantial weight and size reductions and make it suitable for applications such as in high speed aircraft electric generators and high temperature magnetic components. The addition of about 4% Ni to bulk Co-Fe-V ternary alloys restricts grain growth and enhances ductility and strength with heat treatment over a wide temperature range.¹⁶ Also, corrosion resistance will be increased. Furthermore, thin films of this alloy show promise for use in components of micromotors.

In addition to these properties, the incorporation of small quantities of vanadium to Co-Fe alloys has three important potential effects. The resistivity of the alloys will be increased, brittleness minimized, and mechanical strength increased considerably.^{15,16} Also, the Curie temperature (T_c) approaches 1000°C (1832°F).¹⁵

Magnetic properties which are sensitive to the microstructure of the film are affected by preparation methods.¹⁷ Although Co-Fe-V films prepared by vacuum sputtering have poor soft magnetic properties (*e.g.*, high coercivity) making them unsuitable for thin film heads,¹⁸ electroplated films often have better magnetic properties than sputtered ones.¹⁹ This has been observed for Permalloy thin film heads where the output voltage of electroplated heads is 20% greater than that of sputtered thin film heads.²⁰

Israel and Meites, citing various investigators, report that attempts to electrodeposit metallic vanadium from aqueous solutions on solid cathodes have not been successful.²¹ They suggested that one of the contributing factors was the comparative low hydrogen overvoltage of vanadium. Russian investigators, however, reported codeposition of various V-binary alloys with Fe, Co, Zn and Cr, for which they provided solution formulations, operating conditions and resulting claimed deposit contents, with references.^{22.24}

Kunaev reported electrodeposition of Fe-V alloys (5–12% V) from FeCl₂, NH₄VO₃, NaCl solutions containing 90 g/L Fe and 30 g/L V.²² A graphite anode and stainless steel cathode in a diaphragm cell were used. Current density ranged from 5 to 12.5 A/dm² (46.4 to 116.1 A/ft²) and the pH was held between 1.0 and 2.0.

Vyacheslavov, *et al.* deposited Co-V alloys from CoCl₂-NH₄VO₃ solutions containing 15 g/L (Co+V) with and without NaKTartrate at pH \leq 1.0, current density 5.0 to 7.0 A/dm² (46.4 to 65.0 A/ft²) and temperature 20°C (68°).²³ The vanadium content in the deposit ranged from 2.0 to >25%, increasing as the solution V/Co ratio increased from 0.2 to 2.0, and the solution pH decreased from 2.0 to 0.4.

Zosimovich and Kublanovskii, however, reported that no vanadium was detected in deposits from Co solutions containing NH_4VO_3 ,²⁴ Gray, brown-tinted deposits were obtained from solutions containing $CoSO_4$, $VOSO_4$, and H_3BO_3 at pH 3.0, current density 5.0 A/dm² (65.0 A/ft²) at room temperature. Unexpectedly, the deposits contained up to approximately 6% boron. Probable inclusion because of increased pH in the cathode boundary layer was assumed. They surmised that the vanadium was present as VO in the deposit, *i.e.*, V(IV) was reduced to divalent vanadium from a

Table 1 Effect of pH & Current Density on Co-Fe-V & Co-Fe Alloy Compositions

A. Co-Fe-V Alloys

рН	CD A/dm ²	CD A/ft ²	Co at%	Fe at%	V at%	CCE %
	0.53	4.92	85.8	14.0	0.2	75.6
5.5	1.02	9.48	89.0	10.7	0.3	76.4
6.5	0.55	5.11	87.4	11.4	1.3	67.6
	1.08	10.03	89.0	10.2	0.8	76.4
7.0	0.55	5.11	89.9	8.2	1.8	59.8
7.0	1.03	9.57	90.8	7.2	2.0	55.8
7.5	0.53	4.92	92.6	5.1	2.4	55.8
	1.02	9.48	92.4	5.1	2.4	63.9

NOTES: CCE = Cathode current efficiency.

Solution composition: 0.3M $CoCL_{2}$, 0.033M $FeSO_{4}$, 0.17M $VOSO_{4}$, 0.25M $Na_{3}C_{6}H_{5}O_{7}$, 0.1M $H_{3}BO_{3}$, 1.0M $NH_{4}Cl$, pH adjusted with $NH_{4}OH$, room temperature.

B. Co-Fe Alloys

pН	CD A/dm ²	CD A/ft ²	Co at%	Fe at%	CCE %
5.5	0.55	5.11	88.8	11.2	88.5
	1.05	9.75	90.2	9.8	90.3
7.5	0.53	4.92	90.9	9.1	78.7
1.5	1.02	9.48	91.6	8.4	71.0

NOTES: Solution composition: 0.3M CoCl₂, 0.033M FeSO₄, 0.17M $Na_3C_6H_5O_7$, 0.1M H_3BO_3 , 1.0M NH_4Cl , pH adjusted with NH_4OH , room temperature.

 $[VO(H_2O)_3]^{+2}$ complex. The vanadium content reached a maximum (30%) as the $CoSO_4/VOSO_4$ solution ratios, prepared by mixing 0.5M solutions containing 30 g/L H_3BO_3 , increased to 14/6 and decreased as the ratio increased further. At a 1:1 ratio, the deposit contained 51.7% Co, 24% V and 5.6% B.

We have been conducting studies in our laboratory to assess the efficacy of pulse plating iron group alloys²⁵⁻²⁷ and incorporating small amounts of vanadium to iron group metals to produce binary and ternary magnetic thin film alloys.²⁸⁻²⁹

Experimental

A power supply^{**} was used to provide direct current (DC) and pulse current (PC) waveforms. A total of 60 coulombs was passed per run to produce deposits 1 to 2 μ m (39 to 79 μ -in.) thick. The shape of the PC waveforms was monitored with an oscilloscope. Electrodeposition in quiescent solutions was performed at room temperature with a constant external magnetic field (1.5 kG).

Stock solutions (pH 3) were prepared and diluted with deionized water. Unless otherwise noted, the plating solutions contained $0.3M \operatorname{CoCl}_2$, $0.033M \operatorname{FeSO}_4$ or $0.05M \operatorname{NiSO}_4$, $0.17M \operatorname{VOSO}_4$, $1.0M \operatorname{NH}_4\operatorname{Cl}$ and $0.1M \operatorname{H}_3\operatorname{BO}_3$. Sodium citrate, $\operatorname{Na}_3\operatorname{C}_6\operatorname{H}_5\operatorname{O}_7$, (usually 0.25M) was the complexing ligand, providing a total metal/L ratio of 2.0. Binary iron group (IG) deposits were electrodeposited from similar solutions without VOSO_4 . Initially, NaCl , KCl or $(\operatorname{NH}_4)_2\operatorname{SO}_4$ were present as supporting electrolyte. No significant effect was observed, however, and they were eliminated. The solution pH was raised with NH_3 (aq) and lowered with $\operatorname{H}_2\operatorname{SO}_4$ or HCl. About 120 mL (4.07 fl. oz., US) of solution was used during electrodeposition. Each solution was used at room temperature and without agitation

^{**} Kraft Dynatronix Model DPR 20-5-10, Dynatronix, Inc., Amery, WI 54001 USA.

Table 2 Effect of pH & Current Density on Co-Ni-V & Co-Ni Alloy Compositions

A. Co-Ni-V Alloys

pН	CD	CD	Со	Ni	V	CCE
-	A/dm ²	A/ft ²	at%	at%	at%	%
5 5	0.56	5.20	98.1	1.9	0.0	78.7
5.5	1.06	9.84	96.9	3.1	0.0	79.1
(5	0.51	4.73	96.2	3.0	0.8	79.2
0.5	0.99	9.19	95.6	3.9	0.5	76.1
7.0	0.56	5.20	95.4	2.6	2.1	46.7
7.0	1.05	9.75	93.9	4.9	1.2	59.8
75	0.51	4.73	95.2	2.1	2.7	36.9
1.5	0.98	9.10	95.3	3.2	1.5	47.2

NOTES: CCE = Cathode current efficiency. **Solution composition:** 0.3M CoCl₂, 0.05M NiSO₄, 0.15M VOSO₄, 0.25M $Na_3C_6H_5O_7$, 0.1M H_3BO_3 , 1.0M NH_4Cl , pH adjusted with NH_4OH , room temperature.

B. Co-Ni Alloys

рН	CD A/dm ²	CD A/ft ²	Co at%	Ni at%	CCE %
5.5	0.52	4.83	96.8	3.2	91.8
	1.02	9.48	95.2	4.8	88.0
7.1	0.56	5.20	95.6	4.4	95.0
	1.07	9.94	87.8	12.2	91.8
7.5	0.54	5.02	97.7	2.3	91.3
	1.04	9.66	89.6	10.4	87.9
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NOTES: Solution composition: 0.3M $CoCl_2$, 0.05M $NiSO_4$, 0.17M $Na_3C_6H_5O_7$, 0.1M H_3BO_3 , 1.0M NH_4Cl , pH adjusted with NH_4OH , room temperature.

for a maximum of five or six deposition runs in order to minimize concentration effects. Deposition conditions (pH, current density and cathode current efficiency) are listed in the various tables.

Brass panels (10 cm²; 1.55 in².) served as cathodes. Surfaces were prepared by a procedure involving mechanical and chemical treatments. First, the panels were soaked in a saturated alkaline cleaning solution^{***} for 10 min, rinsed with deionized water, then immersed in 25 vol% sulfuric acid for 30 sec and finally rinsed with deionized water. Surfaces were activated just before electro-deposition by immersion in 15 vol% HCl for 30 sec. Soluble Co, Fe, or Ni anodes were used, depending on the solution.

After visual observation under an optical microscope, the deposits were dissolved in 25 or 33 vol% nitric acid and analyzed by atomic absorption spectrophotometry (AAS). Deposits containing nickel as the major component were dissolved in the more concentrated nitric acid. Although not included here, some SEM-EDX measurements on deposits were also performed. Deposit compositions are reported as atomic percent.

The corrosion resistance of the deposits in sodium chloride (0.5M) solutions of pH 5.8 was determined by impedance measurements. The latter was performed with an impedance gain/ phase-analyzer**** and a potentiostat[†].

A preliminary, qualitative attempt to estimate the "magnetic moment" of the deposits involved adapting a single-pan analytical balance to measure the vertical force (displacement) of the deposited specimen from attraction by a permanent bar magnet located at a fixed, constant distance below the balance pan (0.35 kG, 1.25 cm). The specimens were weighed in the absence and presence of the magnetic field. The resulting displacement was normalized (per unit deposit mass) to provide comparative magnetic values.

Results & Discussion

Preliminary experiments beginning in 1993 to develop 1:1 Co-Fe alloy deposits containing small amounts of V were performed using solutions containing equimolar concentrations of the three metals. Solutions containing 0.5M of each and 0.1M Na₃C₆H₅O₇ resulted in vanadium contents that were highly dependent on solution pH, and current densities ranging from 1.0 to 2.0 A/dm² (9.3 to 18.6 A/ft²). Solutions containing lower equimolar metal ion concentrations (0.33M) but with increased Na₃C₆H₅ O₇ concentration (0.33M) resulted in deposits containing $\leq 1\%$ V at pH 4.3. Increasing the citrate concentration to 0.5M further decreased the vanadium content to $\leq 0.2\%$. It appeared that an optimum ratio of complexing agent to vanadium and/or the iron group constituents was required for higher vanadium contents. Vanadyl sulfate (VOSO₄) was the preferred source of V because higher deposit V contents were obtained than from solutions containing NH₄VO₃.

Because of the attractive magnetic properties of 90 Co/ 10 Fe binary alloys^{11,12} and those of ternary Co-Fe-V alloys (Supermendur), our study then concentrated on developing ternary deposits of nominal 9/1 iron group metals containing approximately 2% V. These were compared to binary alloys, *i.e.*, from equivalent solution compositions without vanadium. Solution compositions and deposition conditions are given here in various tables.

Table 1A shows the effects of pH and current density on Co-Fe-V ternary deposits. Increased pH and current density resulted in increased Co and V contents. At pH 5.5, only 0.2-0.3% V deposited. The vanadium content increased while the iron content decreased significantly with pH \ge 7. At pH 7.5, current density had little effect on the deposit composition (92.5 Co/5.1 Fe/2.4 V). With increased pH, the cathode current efficiency decreased from ~75% to ~56 % at the lower current density. The change was less at the higher current density.

Generally, increased vanadium appears to be associated with decreased cathode current efficiency, *i.e.*, increased rate of the hydrogen discharge reaction. This suggests, possibly, the codeposition of V and iron group metals from adsorbed hetero-dinuclear biscitrate complexes by a mechanism involving step-wise reduction by adsorbed H atoms and/or direct electron transfer:

$$\begin{split} \mathbf{M}^{+2} + \mathbf{VO}^{+2} + 2\mathbf{L}^{-3} &\rightarrow [\mathbf{M}^{II} \ \mathbf{V}^{IV}\mathbf{O} \ \mathbf{L}_2]^{-2} \rightarrow \\ [\mathbf{M}^{II} \ \mathbf{V}^{II} \ \mathbf{L}_2]^{-2} &\rightarrow \mathbf{MV} + 2\mathbf{L}^{-3}. \end{split}$$

This mechanism may also be extended to hetero-trinuclear (*e.g.*, CoFeV) biscitrate complexes. The iron group metal citrate complexes, which had been proposed by Bobtelsky and Jordan^{30,31} have been envisioned by Holt and co-workers in IG-W and IG-Mo codeposition from citrate baths.^{32,33} Podlaha and Landolt suggested adsorbed citrate complex were involved in the codeposition of IG-Mo alloys.³⁴ Younes and Gileadi suggested an intermediate citrate complex as a precursor for electrodeposition of Ni-W alloys.³⁵ Sal'nikov and coworkers proposed hetero-dinuclear biscitrate complexes of V³⁶ and IG metals.³⁷ The role of metal ion complexes in the mechanism of electrodeposition of metals has been critically examined by Lyons.³⁸ It is clear that the coordination chemistry of metal ions and additives in plating baths is a crucial consideration in the electrodeposition of metals and alloys.

With increasing solution pH, the deposit Co and V contents increased and the Fe content decreased. It appears that codeposition of V either enhanced deposition of Co or inhibited that of Fe.

^{***} Alconox, Alconox, Inc., White Plains, NY 10603 USA.

^{****} Solartron Model 1260, Solartron Analytical, Farnborough, Hampshire GU14 0NR UK.

[†] PAR Model 273, Princeton Applied Research, Oak Ridge, TN 37830 USA.

Although the ratio, total metals/ligand (R=2.0), was equivalent for both the ternary and binary solutions, it is suggested that including V(IV) into the complex affected the relative "complex strengths" with respect to Co, Fe and V as a function of pH and the resulting deposit compositions. Similar, although less significant, trends were observed with Co-Fe binary deposits. Deposit Co content increased with increased pH and current density. Cathode current efficiency decreased with higher pH (Table 1B).

Attempts to deposit ternary alloys containing a 90 Co/10 Ni nominal deposit content from similar solution compositions resulted in low deposit Ni contents (~2 to 5%) at the pH values and current densities investigated, being higher at the higher current densities (Table 2A). Previous studies have shown that codeposition of Co-Ni was considerably more anomalous than Co-Fe and Ni-Fe.39 No vanadium was codeposited until the solution pH reached 6.5, and the vanadium increased with increased pH (pH 7.5). At pH 7 and 7.5 and the lower current density (0.5 A/dm²; 4.6 A/ft²), the deposit V content was 2% and 2.7%, respectively. With increased pH, the cathode current efficiency showed a similar but larger decrease than in the Co-Fe-V solutions. The trends in the deposit compositions are similar to Co-Fe-V deposits. There appears to be a relationship of increased deposit V content and decreased Ni content associated with decreased cathode current efficiency.

Binary Co-Ni deposits from equivalent solutions also contained low Ni contents (~2 to 5%) at current densities of from 0.55 to 1.0 A/dm² (5.1 to 9.3 A/ft²). At the higher pH values (7 and 7.5) and current densities (~1.0 A/dm²; ~9.3 A/ft²), the deposit Ni contents were 12.2 and 10.4%, respectively (Table 2B). The cathode current efficiency ranged from 95% to 88%, being slightly lower with increased current density.

The effects of pH and current density on the deposition of Ni-Fe-V alloys are shown in Table 3A. No vanadium was codeposited from solutions containing Ni/Fe ratios of 10/1 and 30/1 until the solution pH was increased to 7.5, the resulting deposits containing 0.2 to 0.3% and 0.6 to 1.4% V, respectively. At the 10/1 ratio,

the iron content decreased by almost one-half at the higher current density at all pH values. The cathode current efficiency also decreased. At the 30/1 ratio, the iron contents were 10% or less, decreasing with increased pH and at the higher current density. The cathode current efficiency decreased from 50 to 60% at pH 5.5 to 25 to 29% at pH 7.1, with a concomitant increased vanadium content.

For binary Ni-Fe deposits (solution ratio 10/1), the iron content decreased tenfold (from \sim 33% to 25%, to \sim 2.5 to 3%) as the pH increased from 5.5 to 7.5 with the higher percentages at the lower current density (0.52 A/dm²; 4.83 A/ft²). The cathode current efficiency increased (Table 3B). Although the M/L ratio (2.0) is similar to the Co-Ni and Co-Fe ratios, the iron contents were sharply reduced at solution pH 7.5.

Table 4 summarizes the effects of pH and current density on deposit composition of binary iron group + V alloys. At pH 5.6, only Co or Ni deposited at all applied current densities (0.57, 1.08 and 4.0 A/dm²; 5.3, 10.0 and 37.4 A/ft²). The Fe-V deposit contained ~1.0% V. At pH 7.0, all deposits contained V: Fe > Ni > Co. The vanadium contents decreased with increased current density for all binary alloys and were approximately two to three times lower when deposited at 4.0 A/dm² (37.4 A/ft²) than at 0.5 A/dm² (4.6 A/ft²). The

Table 3 Effect of pH & Current Density on Ni-Fe-V & Ni-Fe Alloy Compositions

A. Ni-Fe-V Alloys

Ratio Ni/Fe	рН	CD A/dm ²	CD A/ft ²	Ni at%	Fe at%	V at%	CCE %
	5.6	0.50	4.64	69.3	30.7	0.0	54.4
	3.0	1.01	9.38	81.1	18.9	0.0	59.1
	6.5	0.50	4.64	72.0	28.0	0.0	64.8
10/1	0.3	0.99	9.19	84.3	15.7	0.0	64.2
10/1 -	7.0	0.52	4.83	74.1	25.8	0.0	57.7
	7.0	1.02	9.48	84.6	15.4	0.0	61.6
	7.0	0.52	4.83	76.8	23.1	0.2	47.3
	/.0	1.01	9.38	86.1	13.6	0.3	42.0
30/1 -	5 5	5.5	5.11	89.9	10.1	0.0	50.3
	3.3	1.05	9.75	94.7	5.3	0.0	60.5
	7 1	5.4	5.02	90.6	8.8	0.6	28.5
	/.1	1.05	9.75	92.5	6.1	1.4	24.7

NOTES: CCE = Cathode current efficiency.

Solution composition: Ni/Fe R=10: 0.3M NiCl₂, 0.03M FeSO₄, 0.17M VOSO₄, 0.25M Na₃C₄Q₇, 0.1M H₃BO₃, 1.0M NH₄Cl, pH adjusted with NH₄OH, room temperature. Ni/Fe R=30: 0.3M NiCl₂, 0.01M FeSO₄, 0.19M VOSO₄, 0.25M Na₃C₆H₃O₇, 0.1M H₃BO₃, 1.0M NH₄Cl, pH adjusted with NH₄OH, room temperature.

B. Ni-Fe Alloys

Ratio Ni/Fe	рН	CD A/dm ²	CD A/ft ²	Ni at%	Fe at%	CCE %
	5 5	0.52	4.83	67.3	32.7	65.0
10/1	3.3	1.03	9.57	75.2	24.8	62.5
	7.5	0.52	4.83	97.0	3.0	82.8
		1.03	9.57	97.5	2.5	77.3

NOTES: Solution composition: 0.3M NiCl₂, 0.03M FeSO₄, 0.17M Na₃C₆H₅O₇, 0.1M H₃BO₃, 1.0M NH₄Cl, pH adjusted with NH₄OH.

Table 4 Effect of pH & Current Density on Fe-V, Co-V & Ni-V Alloy Compositions

	CD	CD	Fe	Со	Ni	\mathbf{V}	CCE
рн	A/dm ²	A/ft ²	at%	at%	at%	at%	%
			99.0			1.0	38.8
	0.57 ± 0.01	5.30±0.09		100.0			80.9
					100.0		58.6
			98.5			1.5	45.8
5.6±0.1	1.08 ± 0.01	10.00 ± 0.09		100.0			82.2
					100.0		65.8
			99.4			0.6	44.3
	4.03±0.02	37.44±0.18		100.0			61.0
					100.0		56.4
			98.1			1.9	35.8
	0.57 ± 0.03	5.30±0.28		98.9		1.1	65.3
					98.9	1.1	32.7
			98.8			1.2	39.3
7.0 ± 0.0	1.08 ± 0.02	10.00 ± 0.18		99.4		0.6	55.5
					99.1	0.9	30.4
			99.4			0.6	29.1
	4.03±0.02	37.44±0.18		99.5		0.5	47.4
					99.6	0.4	30.1

NOTES: Solution composition: 0.3M ferrous metals as chlorides, 0.2M VOSO₄, 0.25M Na₃C₆H₃O₇, 0.1M H₃BO₃, 1.0M NH₄Cl, pH adjusted with NH₄OH, room temperature.

Table 5 Estimate of "Magnetic Moments" & Corrosion Resistance of Co-Fe-V Versus Co-Fe & Ni-Fe Deposits

	Co at %	Fe at%	V at%	Ni at%	CCE	Relative magnetic moment	R_p Ω/cm^2
$\overline{\mathbf{DC}^*}$		18.7		81.3	98.5	1.00	2308
DC**	91.6	8.4		01.5	91.2	1.11	793
DC	93.0	6.6	0.4		73.2	1.83	649
PC-1	92.5	7.0	0.5		68.7	1.99	878
PC-2	92.5	6.9	0.6		69.4	2.00	1209
PC-3	92.2	7.1	0.8		73.2	2.02	1760

NOTES: Solution composition: 0.3M CoCl₂, 0.033M FeSO₄, 0.17M VOSO₄, 0.25M $Na_3C_6H_5O_7$, 0.1M $H_3BO_{3^*}$ 1.0M NH_4Cl , pH 7.1 adjusted with NH_4OH , room temperature, average current density = 1.0 ± 0.1 A/dm² (9.29 ± 0.9 A/ft²).

PC duty cycles: $\gamma = 0.5$ (PC-1); 0.167 (PC-2); 0.10 (PC-3); $T_{on} = 5$ msec.

Solution composition: Binary NiFe alloy (approx. Permalloy):⁴⁰ 0.2M NiCl₂: 0.005M FeCl₂, 0.7M NaCl, 0.4M H₃BO₃, 0.0075M saccharin, pH 3.0, current density = 0.5 A/dm² (4.6 A/ft²).

** Solution composition: Binary CoFe alloy, same as above for PC without VOSO4.

Table 6 Estimate of "Magnetic Moments" Of Co-Fe Deposits: Effect of DC Versus PC Waveforms

	Со	Fe	CCE	Relative
	at%	at%	%	Magnetic Moment
DC	91.6	8.4	91.2	1.11
PC-1	91.3	8.7	90.1	1.27
PC-2	91.2	8.8	89.9	1.56
PC-3	91.1	8.9	88.2	1.93

NOTES: Solution composition: $0.3M \operatorname{CoCl}_2$, $0.033M \operatorname{FeSO}_4$, 0.17M $\operatorname{Na}_3C_H_5O_7$, 0.05M H_3BO_3 , 1.0M NH_4Cl , pH 7.1 adjusted with NH_4OH , room temperature, average current density = 1.0 ± 0.1 A/dm^2 (9.29 ± 0.9 A/ff^2).

cathode current efficiencies of the binary alloys deposited from pH 7.0 solutions were: $Co-V > Fe-V \ge Ni-V$, at all current densities.

The effects of DC and PC waveforms on Co-Fe-V deposit compositions and magnetic properties, compared to binary Co-Fe and Ni-Fe (Permalloy) deposits, are shown in Tables 5 and 6. Pulsed-current square waveforms with 1.0 A/dm² (9.29 A/ft²) average current density and duty cycles (γ = Time on/Time on + Time off): 0.5 (PC-1), 0.165 (PC-2) and 0.1 (PC-3), with time on = 5 msec, were used. Peak current densities ($I_{pc} = I_{ave} / \gamma$) were 2.0, 6.0 and 10.0 A/dm² (18.6, 55.7 and 92.9 A/ft²) with off times of 5.0, 25.3 and 45 msec, respectively. Pulsed current did not significantly affect the Co and Fe contents but the vanadium content increased with increased peak current density and off time (DC < PC-1 < PC-2 < PC-3). The iron content of the binary Co-Fe alloys was higher for the pulsed-current deposits, increasing with increased off times.

Using the crude "magnetic moment" calculations based on the magnetic displacement force/gm deposit described above, the "magnetic moments" of Co-Fe-V deposits were greater with pulsed-current deposition than with DC and increased with increased peak current density and off time: DC < PC-1 <PC-2 < PC-3 (Table 5). This may also be a result of the increased vanadium content. The "magnetic moments" increased similarly with the binary Co-Fe deposits (Table 6).

Table 5 also compares the magnetic moment measurements of Co-Fe-V vs. Co-Fe and Ni-Fe (approximate Permalloy composi-

tion) deposits. The relative magnitude of these magnetic values increased in the following order: Ni-Fe (DC) < Co-Fe (DC) < Co-Fe-V (DC) < Co-Fe-V (PC-1) < Co-Fe-V (PC-2) < Co-Fe-V (PC-3). Pulsed-current Co-Fe-V deposits exhibited twice the values obtained for the Ni-Fe deposit, with the DC Co-Fe-V deposit only slightly lower (1.8X). Liao reported magnetic saturation values of 90 Co/10 Fe deposits double that of Permalloy.⁵ "Magnetic moment" values for DC Co-Fe deposits obtained in this study were only about 10% higher than those of DC Ni-Fe deposits.

In this work, NH₄OH was simply added to adjust solution pH without regard to its concentration. More recent studies in our laboratory⁴¹ have indicated that control of solution NH₃ concentration is an important variable influencing the vanadium content, rather than being added simply for pH adjustment. Therefore, the uncontrolled additions of NH₃ (aq) may have accounted for the apparent discrepancies with respect to Co-Fe-V deposit compositions in Tables 1 and 5.

Impedance measurements to determine the corrosion (polarization) resistance (R_p) of the binary and ternary alloy deposit compositions are also included in Table 5. The corrosion resistance decreased in the following order: Ni-Fe (DC) > Co-Fe-V (PC) > Co-Fe-V (DC) > Co-Fe (DC). For

Co-Fe-V deposits obtained by pulsed current, the corrosion resistance increased as the duty cycle (γ) decreased from 0.5 to 0.1. For Co-Fe-V deposits obtained with a duty cycle of 0.1, the corrosion resistance was about 75% that of Permalloy.

Summary & Conclusions

Electrodeposition of ternary iron group alloys containing small amounts of vanadium was investigated and compared to equivalent iron group binary alloys. The previously observed anomalous codeposition of iron group binary alloys³⁹ also occurred with electrodeposition of these ternary alloys.

There appears to be an optimum ratio of complexer (citrate) to the total metal ion concentration for electrodeposition of V-containing alloys at pH \geq 5.5. Generally, the vanadium content increased with increased pH in the range 5.5 to 7.5, and current densities from 0.5 to 1.0 A/dm² (4.6 to 9.3 A/ft²). Vanadyl sulfate (VOSO₄) was the preferred source of vanadium because higher vanadium contents were obtained than from solutions containing NH₄VO₃.

For Co-Fe-V alloys, the Co and V contents increased and Fe decreased significantly as a result of increased solution pH. The deposit composition did not change appreciably at $pH \ge 7.0$ with 2.4% V content at pH 7.5. The binary Co-Fe deposits showed similar but less significant trends.

No vanadium was found in deposits from ternary Co-Ni-V solutions at pH \leq 6.5. The vanadium content was 2.1% and 2.7% at solution pH values of 7.0 and 7.5, respectively, at about 0.5 A/dm² (4.6 A/ft²). The nickel content was less than 5% under all deposition conditions. Binary Co-Ni deposits also contained less than 5% Ni, except at the higher current density of 1.0 A/dm² (9.3 A/ft²).

Deposition of vanadium was inhibited from ternary Ni-Fe-V containing solutions, except at pH > 7.0. The vanadium content was 1.4 % from a 30:1 Ni:Fe solution ratio at the higher current density.

Attempts to deposit binary Co-V or Ni-V alloys from solutions at pH 5.5 were unsuccessful at current densities ranging from 0.5 to 4.0 A/dm² (4.6 to 37.2 A/ft²). Only Fe-V alloys were obtained with a maximum 1.5 % V at the intermediate 1.0 A/dm² (9.3 A/ft²). However, with increased pH (7.0), all deposits contained V: Fe > Ni > Co. The vanadium content decreased with increased current density, being approximately two to three times lower at 4.0 A/dm² (37.2 A/ft²) than at 0.5 A/dm² (4.6 A/ft²).

Generally, for the ternary alloy solutions, the cathode current efficiency decreased with increased vanadium content and solution pH. This increase in vanadium content, accompanied by decreased cathode current efficiency (increased rate of the hydrogen discharge reaction) suggests a cathodic reduction mechanism of V(IV) involving adsorbed H atoms.

Pulsed current modification resulted in increased vanadium content, the longer off times (t_{off}) being more effective. Increased solution agitation had the same effect. Convective mass transport appears to affect the electrodeposition of vanadium.

Pulsed current increased the "relative magnetic moments" of Co-Fe-V deposits as compared to DC. The ternary alloys exhibited higher "magnetic moments" compared to binary Co-Fe deposits. Compared to DC, the effect of pulsed current electrodeposition of binary Co-Fe alloys was significantly greater, with increased off time resulting in substantially increased "magnetic moments" without significantly affecting deposit composition or cathode current efficiency.

Co-Fe-V deposits exhibited increased (~2X) "magnetic moments" over Ni-Fe (Permalloy type alloys) deposits, regardless of DC or PC waveforms. The corrosion resistance of the deposits decreased in the following order: Ni-Fe (DC) > Co-Fe-V (PC) > Co-Fe-V (DC) > Co-Fe (DC). For Co-Fe-V deposits obtained with a PC duty cycle (γ) of 0.1, corrosion resistance was about 75% that of Permalloy deposits.

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