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Effects of primary dicarboxylic acids on microstructure and mechanical properties of sub-microcrystalline Ni–Co alloys

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ABSTRACT

Nickel–cobalt alloys were deposited from sulfate electrolyte with oxalic, malonic and succinic acids as additives and their microstructure and mechanical properties were studied. The crystal structure, surface morphologies, and chemical composition of coatings were investigated using X-ray diffraction, scanning electron microscope, and energy dispersive spectroscopy. The crystal structure and surface morphology analysis showed that the addition of dicarboxylic acid leads to (2 0 0) crystal face and the surface were more compact and uniform due to the grain refining. Ni_{60}–Co_{40} alloy was achieved when succinic acid is used as additive.

1. Introduction

The electrodepositions of alloys of iron-group metals were intensively investigated for decades because of their particular magnetic and mechanical properties. Due to its low cost compared with cobalt, iron is preferred for the production of Ni-based alloys. However, the presence of cobalt in nickel alloys is known to improve the hardness of the alloy [1,2]. Additives such as saccharin or wetting agents were used for years to reduce internal stress [3]. Organic compounds in small concentrations are added to metal plating baths for a variety of purposes. In the case of nickel–cobalt, addition agents were added to reduce pitting corrosion, to improve corrosion resistance and to impart a mirror-like luster to the surface [4]. Costavaras et al. [5] studied the effect of some acetylenic and aryl–sulfonic compounds and found that the textures of nickel deposits were related to the nature of unsaturation present in the molecule, which also influences the magnitude of the additive activity. Nakamura et al. [6] has reported the influence of saccharin and aliphatic alcohols and their inhibiting effects on the electro-crystallization of nickel from Watt's bath. The introduction of various additives made significant influences on the crystalline structure of Zn, and this is due to the adsorption of additives onto the zinc grain surface, changing the surface morphologies and depressing the growth of certain faces during electroplating [7,8].

We found that little information is available in the literature about the preparation and microhardness study of nanocrystalline Ni–Co alloy electrodeposits [4,9–13]. This paper reports the electrodeposition process in detail and provides information about effects of oxalic acid, malonic acid and succinic acid on the microstructure and micro hardness of the deposits.

2. Experimental

2.1. Materials and reagents

The substrate (cathode) was 25 × 40 × 0.5 mm size mild steel and the 50 × 100 × 10 mm size graphite were used as anode. For the Alloy deposition, 500 ml of electrolyte was prepared from modified Watts-type solutions (Table 1) with 0.4–2 g/l oxalic, malonic and succinic acids as additives. Boric acid was used as a buffer to maintain the bath pH; sodium lauryl sulfate (SLS) was used as a wetting agent to reduce the gas pitting. The pH was adjusted to a constant value of 4.0 ± 0.1 by adding nickel carbonate to raise it or hydrochloric/sulfuric acid to lower it. The electrolyte was prepared by adding the appropriate amounts of analytical grade chemicals to double distilled water.

2.2. Pretreatment of substrates

Before electrodeposition, the substrate was polished with various grade silicon carbide paper (in the following order of grit size 200, 400 and 800), rinsed with deionized water, ultrasonically cleaned with acetone and electrochemically cleaned with alkaline solution containing 70 g/l $H_3PO_4 \cdot 12H_2O$, 50 g/l Na_2CO_3, 10 g/l NaOH, and 0.5 g/l SLS, for a duration of 120 s, and then rinsed with hot and followed by cold deionized water. The mild steel and stainless steel were used as a cathode and an anode respectively.

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Table 1
Bath composition and deposition condition for Ni–Co alloy coatings.

Constituents and parameters	Quantity
$NiSO_4{\cdot}6H_2O$	250 g/l
$NiCl_2{\cdot}6H_2O$	40 g/l
$CoCl_2{\cdot}6H_2O$	30 g/l
H_3BO_3	32 g/l
SLS	0.05 g/l
Current densities	4 A/dm^2
pH	4.0 ± 0.1
Temperature	308 K
Time	30 min
Agitation	Continuous

2.3. Electrodeposition process

Ni–Co alloy coatings were prepared in presence and absence of additive under direct current conditions. The optimized bath compositions and other parameters are given in Table 1. Ni–Co coating without additive was prepared in almost the same solutions mentioned above except the addition of additives under the same electrodeposition conditions. After plating, the deposit was immediately rinsed with running water and dried with hot air. The cathode current efficiency was calculated from the weight gained by the cathode after the electrodeposition.

2.4. Deposit characterization

The surface morphology of the deposit was investigated by scanning electron microscopy (HITACHI Model S-3000H operated at 20 kV) and the content of Co and Ni in the alloy was measured by energy-dispersive X-ray (EDX) spectroscopy attached with the SEM. A (PANalytical, model X' per PRO) X- ray diffractometer with a Cu Kα radiation (λ=1.5418 Å) was used to determine the preferred crystal orientation of deposited Ni–Co alloy by using standard θ–2θ geometry. Crystallites sizes were calculated from the peak broadening of XRD pattern according to the Scherrer equation. Microhardness was measured by an EVERONE microhardness tester [MH-series] using Vicker's indent with a load of 50 g applied for 5 s. Five measurements were performed on the surface of each coating.

3. Results and discussion

3.1. Effect of dicarboxylic acid

3.1.1. On current efficiency

Aqua complexes $[Ni(H_2O)_6]SO_4$, i.e. outer-orbital 4sp^3d^2 octahedral ions, are formed in aqueous solutions of nickel(II) sulfate. The addition of chelating agent such as oxalic acid, malonic acid or succinic acid into the electrolyte decreases the current efficiency and the results are presented in Table 2. The introduction of dicarboxylic acids into a nickel (II) sulfate solution is accompanied by complexation, which is confirmed by absorption spectra [14]. When the concentrations of complex ions are increased, the concentrations of unchelated metal ions decreases and this leads to increase of cathodic over potential and decrease of current efficiency. A similar trend of lowering current efficiency due to a decrease of free Ni^{2+} ions concentration was observed by Appelt and Paszkiewicz [15]. It has been found that the stability of the complexes with respect to a ligand decreases in the following order: $Suc^{2-} > Mal^{2-} > Oxa^{2-}$ [14]. When the stability of complex is increased, the cathodic overpotential will increase and hence the current efficiency is decreased.

Table 3
Elemental composition of electrodeposited Ni–Co alloy from different electrolytes.

Additives	Co content in the alloy in %
Without additive	18
Oxalic acid	25
Malonic acid	27
Succinic acid	40

3.1.2. On alloy composition

The contents of Co, in the Ni–Co alloy deposits produced from solutions containing without dicarboxylic acid and with three different dicarboxylic acids are presented in Table 3. It is clear that the addition of dicarboxylic acid facilitates the deposition of cobalt and hinders that of nickel. When the dicarboxylic is introduced in Ni^{2+} and Co^{2+} containing electrolyte, the Ni^{2+}ion predominantly forms complex because Ni^{2+}–(dicarboxylate) complex is more stable than the Co^{2+} ion according to the Irving-Williams series. This Ni^{2+}–dicarboxylate complex impede the Ni deposition. When comparing three dicarboxylic acids, the cobalt content is very high in presence of succinic acid.

3.2. Structural characterization

Fig. 1 shows surface morphology of Ni–Co electrodeposits in the presence and absence of dicarboxylic acid as additive. The deposit obtained from additive free electrolyte consists of pyramidal-shaped crystallites surrounded by tiny particles. The pyramidal crystallites exhibit a preferential growth in the direction of the electric field [16]. Fig. 1(b–d) shows significant changes in morphology by the addition of different dicarboxylic acid. The alloys obtained

Table 2
Effect of additives on current efficiency, microhardness, crystallite size and crystallographic orientation.

Additives (g/l)	Current efficiency (%)	Micro hardness value	Crystallographic orientation ($h\ k\ l$) Relative peak intensities (I/I_{max}) %				Crystallite size of I_{max} (nm)
			(1 1 1)	(2 0 0)	(2 2 0)	(3 1 1)	
Oxalic acid							
0	98	256	100	28	6	34	78
0.4	97	309	100	65	14	25	57
0.8	96	315	88	100	–		53
1.2	95	348	38	100	–		52
1.6	95	363	32	100	–	–	47
2	93	478	11	100		–	35
Malonic acid							
0.4	97	324	36	100		8	50
0.8	97	340	20	100	5	2	49
1.2	96	380	12	100	46		
1.6	95	289	6	100	–	–	41
2	93	276	5	100	–		32
Succinic acid							
0.4	97	344	28	100	5	4	38
0.8	96	380	21	100	7	1	38
1.2	95	456	17	100	–	–	35
1.6	94	489	15	100	–	–	37
2	92	493	7	100			25