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ScienceDirect
Surface & Coatings Technology 202 (2007) 331–335
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

Microstructure properties of pulse plated Ni–Co alloy

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Received 19 July 2006; accepted in revised form 18 May 2007
Available online 24 May 2007

Abstract

Ni–Co alloys were pulse plated in three different baths, namely sulfamate, Watts and chloride baths, in order to investigate the cross-section homogeneity and microstructure by means of GDOES and TEM. Furthermore, microhardness measurements were carried out to find the link between the mechanical properties and the cross-section characteristics of the alloy coatings. According to this work, the Ni–Co alloy layers deposited from sulfamate and Watts baths were homogeneous in the whole cross section and showed significantly lower microhardness than those of, grown from chloride containing bath.

Keywords: Nickel–cobalt; Passivity; Pulse plating; TEM; GDOES; Hardness

1. Introduction

Pulse-electrodeposition process has an advantage over the continuous process, i.e. pulse current electrodeposition induces a higher rate of grain nucleation and results in a more refined grain structure, which benefits the deposit properties of coatings [1].

In pulse electrochemical deposition, ions cross the electrified interface where the charge transfer occurs then they incorporate into crystal lattice of the cathode material. However, the adatoms usually adsorb far from growth steps so the incorporation into a crystal lattice needs surface diffusion [1]. On the other hand, during surface diffusion, surface segregation of adatoms can occur, that may affect the structure as well as the physical and the chemical properties of the nanostructured thin films [2].

Generally, a lot of works have been carried out on the effects of plating parameters on the composition and morphology of Ni–Co alloys [3,4,5,6,7,8,9,10,11] as well as their catalytic [12,13] and magnetic properties [14,15]. Investigations on Ni–Co alloys with different composition and microstructure show that physical and electrochemical properties strongly depend on the Co-content of the alloy. Myung at al [5] showed the coexistence of hcp and fcp phases between 70–80 at.% of Co content. In this region, the grain size is smaller and the corrosion resistance decreased. Wang et al. [16] observed the maximum microhardness of Ni–Co alloy at a Co-content of 49 at.% in the alloy. Applying different plating techniques, but obtaining a constant Co content, the hardness of Ni–Co alloy is increased by 20% in the case of pulse current and by 70% in the case of pulse reverse electrodeposition [17]. Similar trend was observed by Wattson [21].

Out of these reports, however, a few focused on the mechanical properties of the alloy, none of these investigated the link between the cross-section homogeneity and the mechanical property of the alloy coatings. Therefore, in this paper, the cross-section microstructure of pulse plated Ni–Co alloys deposited form different baths were studied and compared to their composition and microhardness.

2. Experiment

For the deposition experiments, steel discs, with an area of 1 cm^2 were used as substrates. Before each experiment, the substrate surfaces were polished with emery paper and washed with isopropyl alcohol. Ni–Co samples were deposited from three different types of bathes, namely from chloride, Watts and sulfamate baths using a computer controlled pulse current generator applying peak current density of 0.05 A cm^{-2}. The compositions of the electrolytes are listed in Table 1. Since the

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doi:10.1016/j.surfcoat.2007.05.057

Table 1
Composition of the different baths, used for the deposition.

Bath type	Chemicals	Composition
Sulfamate bath	Ni-sulfamate	1.65 M
	Ni-bromid	0.2 M
	$CoCl_26H_2O$	0.06 M
	H_3BO_3	0.6 M
	$C_{10}H_5(NaSO_3)_3H_2O$	0.01 M
Chloride bath	$NiCl_2$ $6H_2O$	0.6 M
	$CoCl_2$ $6H_2O$	0.06 M
	NH_4Cl	0.7 M
	H_3BO_3	0.6 M
	$C_{10}H_5(NaSO_3)_3$ H_2O	0.01 M
Watts type bath	$NiSO_4$ $6H_2O$	0.17 M
	$NiCl_2$ $6H_2O$	1.25 M
	$CoCl_2$ $6H_2O$	0.06 M
	H_3BO_3	0.65 M
	$C_{10}H_5(NaSO_3)_3$ H_2O	0.01 M

anomalous deposition of Ni–Co is well known, the quantity of Co was kept low, so its kinetic deposition mechanism was mass transport controlled [25]. The composition of the different baths was chosen as those of, which are used for the industrial deposition of Ni–Co. [19]. Sometimes, the electrode behaves as a capacitor that needs charge to raise its potential to the value required for metal deposition at the rate corresponding to the applied pulse current. So the charging time should be shorter then the pulse duration, otherwise the current pulse is strongly distorted [1]. Therefore, both the on-time (t_{on}) and the off-time (t_{off}) were kept constant at a value of 5 ms in each experiment. Pt acted as a counter electrode.

Depth profile analysis of the electrodeposited alloys was performed by Glow Discharge Optical Emission Spectrometry (GDOES) using JY Quantum 2000 RF glow discharge spectrometer equipped with a 4 mm diameter anode and operated at 15 W in an argon atmosphere. The compositions of the deposited Ni–Co alloys were determined by Inductively Coupled Plasma Atomic Emission system (ICP-AES).

The surface morphology and microstructure of the alloy deposits were investigated by Transmission Electron Microscopy using a Philips CM20 electron microscope, operated at 200 kV and equipped with a NORAN Ge detector EDS spectrometer. The cross sections of samples for TEM were made by Ar^+ ion-milling using the Technoorg Linda made ion millers at 10 keV ion energy [22].

Microhardness of the deposit was measured using a Zeiss Durimet Vicker's microhardnes indenter using a load of 50 g for 20 s. Indentions were made on approximately 15 μm thick deposits.

3. Results and discussion

3.1. Glow Discharge Optical Emission Spectroscopy (GDOES)

Jayaganthan reported an enrichment of Ni atoms at the initial stage of deposit formation in different Ni–Me bimetallic alloy depositions when the grain size decreased [2]. In our experiments, the GDOES depth profiles shown in Fig. 1. indicate that electrodeposited Ni–Co alloys on steel substrate have uniform composition through the whole cross-section of the coating from different baths. The bath type did not play a determining role regarding the compositional properties in the initial stage of deposit formation. It has to be added that the transition between the substrate and the layer is not staged due to the minor roughness of the substrate surface. The composition values of the layers are given in Table 2.

3.2. Morphology and phase structure of Ni–Co alloys

Typical cross-sections of Ni–Co alloys deposited from sulfamate, Watts and chloride baths are shown in Fig. 2a–c,

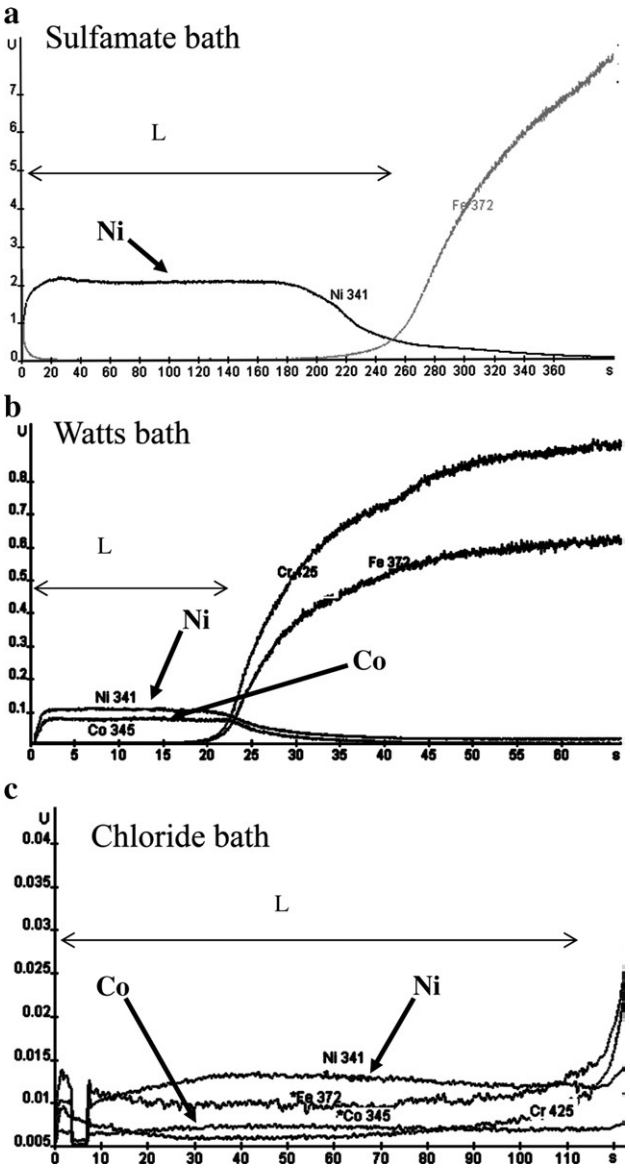

Fig. 1. Depth profile analysis of Ni–Co alloys deposited from a, Sulfamate (only Ni and Fe signals were recorded due to instrument error), b,Watts, c, chloride bath. Ordinates: intensity signal in a. u. vs. sputtering time (s) deposition parameters: $t_{on}=t_{off}=5$ ms, $j=0.05$ A cm^{-2}. L: deposited layer.