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Electrodeposition of Ru/Co compositionally modulated multilayers

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Operating conditions for the production of thin coatings of ruthenium–cobalt alloys have already been achieved. The present work provides data on the electrodeposition of modulated ruthenium–cobalt alloys using a sulfate–sulfamate electrolyte and a double-current pulse plating technique. Alloy modulation was examined by glow discharge optical spectroscopy. Coulometric measurements during anodic dissolution of cobalt–ruthenium films make it possible to determine exactly the cobalt content and approximate amount of ruthenium in the films.

Keywords: *ruthenium/cobalt deposition, sulfate/sulfamate electrolyte, double-current pulse plating, modulated multilayers*

1. Introduction

Recently, a new class of materials known as compositionally modulated multilayers (artificially structured alloys) have been the subject of research, since these films can exhibit unusual mechanical, electrical and magnetic properties.

There are two ways of obtaining modulated alloys: 'dry' (PVD, CVD) and electrolytic. Electrolytically, such alloys can be obtained by using either a single-bath technique, when deposition is done in a plating solution containing ions of the alloy components [2–8], or a dual-plating bath technique, when the deposition is carried out from separate baths by using a manual transfer of the substrate from one bath to another [9, 10]. A successful application of the single-bath technique is possible when the bath contains noble and less-noble metal ions and the concentration of noble metal ions is considerably lower than that of the less-noble metal. In this case, multilayers are obtained using a double pulse-plating technique. The deposited layer of less-noble metal should not be dissolved during deposition of the more noble metal. The electrodeposition of Cu/Ni multilayers has been investigated most widely [6, 7, 11, 12] while data on electrodeposition of multilayers Co/Pt-metal are fewer [8, 13].

The present work was performed to establish the conditions for electrodeposition of compositionally modulated Co/Ru alloys from a sulfate–sulfamate electrolyte.

2. Experimental data

The electrolyte used for Co/Ru plating was prepared from ruthenium(IV) hydroxychloride and cobalt(II) sulfate-heptahydrate, as in [1]. This standard electrolyte comprised: $0.08\,\mathrm{mol\,dm^{-3}}$ ruthenium(IV), $1.5\,\mathrm{mol\,dm^{-3}}$ cobalt(II), $0.4\,\mathrm{mol\,dm^{-3}}$ sulfamic acid, and about $0.35\,\mathrm{mol\,dm^{-3}}$ sulfuric acid. Potential measurements and alloy deposition were carried out at a temperature of $60 \pm 0.5\,^{\circ}\mathrm{C}$. A platinum electrode, of area $1\,\mathrm{cm^2}$ was used as working electrode. The potentials are given with respect to the normal hydrogen electrode. A platinum plate of area $6\,\mathrm{cm^2}$ served as the counter electrode. When necessary, the working electrode was plated with ruthenium ($1\,\mu$m) from a sulfate–sulfamate bath. A potentiostat (PI–50–1; Byelorussia) and an oscilloscope were used in chronopotentiometric studies and pulse plating.

Depth profiles of the Co/Ru multilayers were defined by glow discharge optical spectroscopy (GDOS). For this purpose the alloy was plated on copper substrates.

3. Results and discussions

It was found possible to obtain ruthenium–cobalt alloys from a sulfate–sulfamate electrolyte and that the composition depends considerably on the current density. This is indicative of the possibility of obtaining modulated coatings of ruthenium–cobalt by pulse plating [1].

The chronopotentiometric studies show that pulse plating using double pulses results in the cathode potential periodically changing between the pre-

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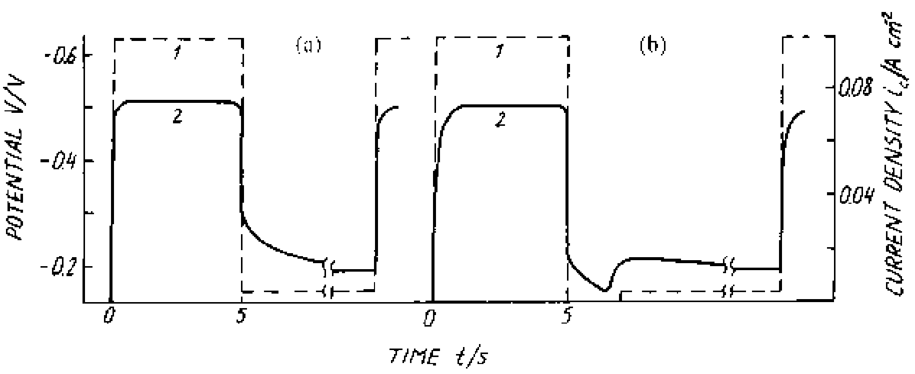

Fig. 1. Current waveforms (1) and chronovoltammograms (2) for deposition of cobalt/ruthenium multilayer using dual-current pulse method (standard electrolyte). Pulse duration: $\tau_1 = 5$ s, $\tau_2 = 300$ s. (a) Uninterrupted plating; (b) with the pause of 2 s after τ_1.

dominant deposition of either cobalt ($E \sim -0.5$ V) at high current densities or ruthenium ($E \sim -0.2$ V) at low current densities (Fig. 1). It should be noted that no transition time for ruthenium(IV) was mentioned by switching on the high density current. When the current is switched to a low current density, the potential value drops rapidly to approximately −0.3 V, and then slowly reaches the stable value of predominant ruthenium deposition. The potential reaches a stable value of approximately −0.2 V much sooner when the current is switched off for a short time after the first pulse (Fig. 1(b)).

In Fig. 2 the depth profile of a bilayered cobalt–ruthenium coating, obtained by dual-pulse plating is shown. It can be concluded from these data that there exists a transition layer between cobalt-rich and ruthenium-rich layers. Taking into account that the thickness of the bilayer was about 800 nm (determined gravimetrically) the thickness of the transition layer is about 80 nm. Note that thin electrodeposited films (i.e., of nanometre thickness) are not compact because the formation of nuclei is the initial stage of the coating growth. Therefore, the GDOS data shows the increased thickness of the transition layer. Also, note that the real area of the electrode is several times greater than the geometrical area: hence, the real thickness of nanolayers is thinner than that calculated.

The depth profiles of cobalt/ruthenium multilayers are shown in Fig. 3. The difference in the amplitude of the components, reflecting the modulation degree, increases with the number of pulse-current periods. The exact alloy composition cannot be calculated from GDOS data because the peak height of the spectrum obtained depends on the content of both elements in the alloy and the nature of the elements themselves.

It has been established that a pause of 2 s after the high current density pulse (Fig. 3(b)) leads to more apparent modulation of the alloy, but the total thickness of the film decreases by about 5% when the thickness of cobalt-rich and ruthenium-rich layers is 100 and 30 nm. The dissolution of cobalt takes place in the pause. When the thickness of both layers is 30 nm, the current pause of 2 s has a negative effect on the modulation degree. The reason for this will be discussed later.

The fact that there is no transition time on the chronovoltammograms in Fig. 1 due to the switching on of the high density current, does not mean that deposition of cobalt alone takes place. In terms of electrochemical regularities, the deposition of the noblest metal, ruthenium, should occur as the earlier process. In accordance with this, when the duration of the high current density pulse (τ_1) is short, the deposition of cobalt should only occur after the

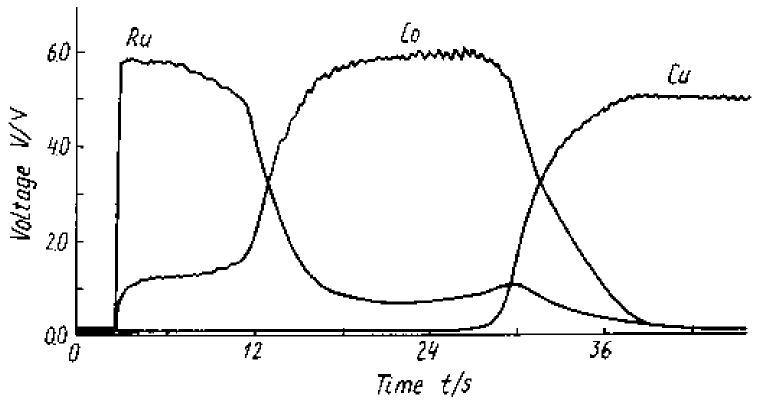

Fig. 2. Depth-profile of cobalt/ruthenium bilayer obtained when: $\tau_1 = 20$ s, $\tau_2 = 600$ s. i_c as for Fig. 1 (standard electrolyte). Thickness of cobalt-rich layer ~600 nm, thickness of ruthenium-rich layer ~200 nm.

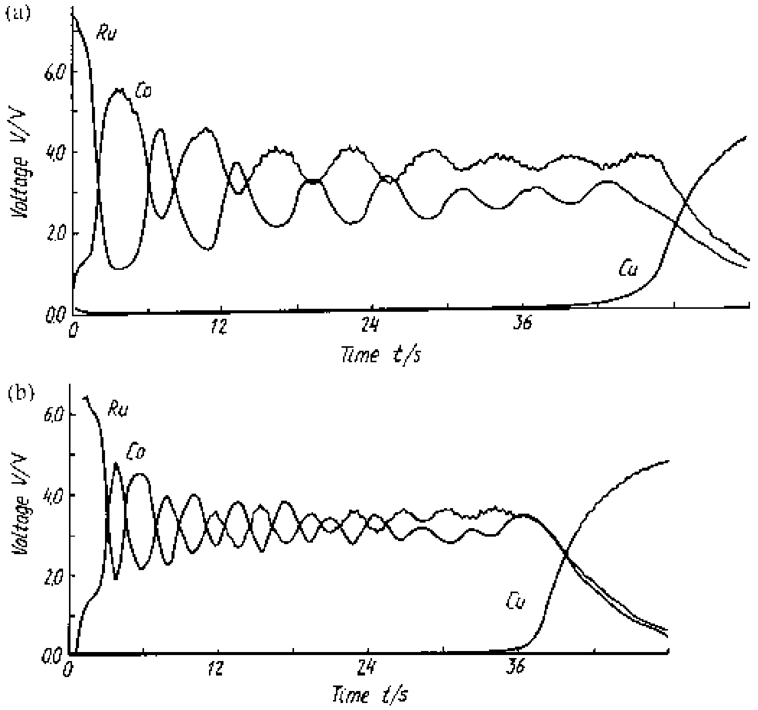

Fig. 3. Depth-profile of cobalt/ruthenium multilayers. (a) $\tau_1 = 5\,\mathrm{s}$ (thickness of cobalt-rich layer ~100 nm), $\tau_2 = 100\,\mathrm{s}$ (thickness of ruthenium-rich layer ~30 nm). Eight cycles. (b) $\tau_1 = 2\,\mathrm{s}$ (thickness of cobalt-rich layer ~30 nm), $\tau_2 = 100\,\mathrm{s}$ (thickness of ruthenium-rich layer 30 nm). 10 cycles. i_c as for Fig. 1 (standard electrolyte).

transition time of ruthenium. Thus, it is necessary to obtain some minimal cathodic charge ($Q_{c,\min}$) below which the deposition of cobalt does not occur. The calculation of transition time (or $Q_{c,\min}$) according to Despic [6, 14] is impossible because of the simultaneous hydrogen evolution and reduction of Ru(IV) to Ru(III) or Ru(II). For this purpose, coulometric measurements of small amounts of cobalt and ruthenium in the deposited films were carried out using anodic stripping analysis.

It was found that in weakly acid sulfate solutions (pH ~3) both ruthenium and cobalt could be anodically dissolved. The dissolution potentials are rather different (Fig. 4). In addition, the current efficiency of cobalt dissolution is 100%. The current efficiency of ruthenium calculated with respect to ruthenium(IV) is only 25–35%. This circumstance makes it difficult to perform highly accurate quantitative analysis of cobalt/ruthenium films by the coulometric method. However, the method is useful to determine the cobalt content exactly and the ruthenium amount more approximately. The anodic charge necessary for complete dissolution of cobalt (Q_a) was found from chronovoltammograms (Fig. 5). The data show that there are three well defined potential regions for cobalt and ruthenium dissolution and also for oxygen evolution on platinum. By comparing curves (4)–(7)

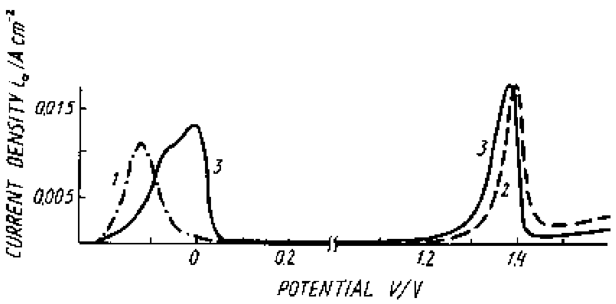

Fig. 4. A LSV for dissolution of: (1) cobalt, (2) ruthenium, and (3) cobalt-ruthenium alloy plated on platinum. Electrolyte: $0.5\,\mathrm{mol\,dm^{-3}}$ sodium sulfate and sulfuric acid added up to pH 3. Sweep rate $1\,\mathrm{mV\,s^{-1}}$.

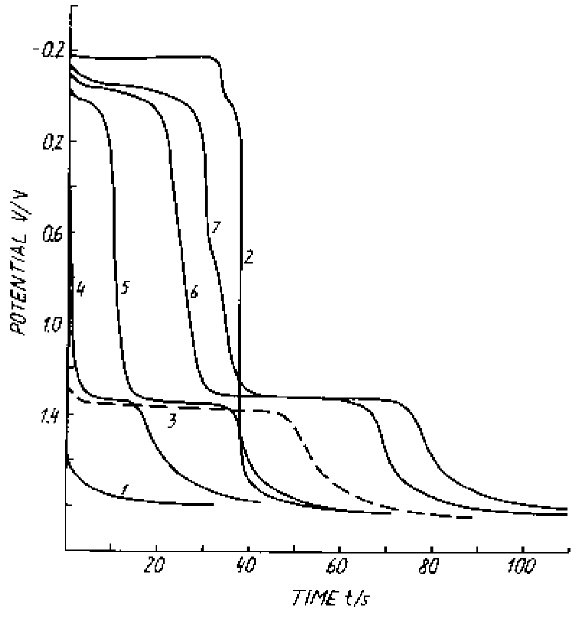

Fig. 5. Chronovoltammograms ($i_a = 0.01\,\mathrm{A\,cm^{-2}}$) for dissolution of: (1) platinum, (2) cobalt, (3) ruthenium, (4–7) alloy cobalt–ruthenium obtained from standard electrolyte when pulse duration (τ_1) was: −1.0 s (4), −2.0 s (5), −4.0 s (6) and 5.0 s (7). (i_c 0.1 A cm^{-2}). Electrolyte: as for Fig. 4.

with (3), it can be seen that cobalt is found in a film when the τ_1 exceeds 1.0 s ($i_c = 0.1\,\mathrm{A\,cm^{-2}}$). It is important that dissolution potentials for pure ruthenium and for ruthenium from its alloy with cobalt are the same (i.e., about 1.35 V). The dependencies Q_a–Q_c obtained from the chronovoltammograms for both metals are plotted in Fig. 6. The value of $Q_{c,\mathrm{min}}$ can be found from these data by extrapolation to $Q_a = 0$. Thus, by switching on the current, the cobalt deposition from standard electrolyte begins only after a Q_c of $0.1\,\mathrm{C\,cm^{-2}}$ (curve 3). This value is valid for the first cycle and is lower for subsequent cycles, because the metal concentration in the diffusion layer decreases. In the case where a high density current is applied after ruthenium deposition at $0.004\,\mathrm{A\,cm^{-2}}$, the $Q_{c,\mathrm{min}}$ is $0.08\,\mathrm{C\,cm^{-2}}$. The value of $Q_{c,\mathrm{min}}$ for ruthenium is about $0.015\,\mathrm{C\ cm^{-2}}$.

The data in Fig. 6 explain the absence of layer modulation when layers are obtained using double pulse-plating of short duration (< 1.0 s) of the high current density pulse. Taking into account that cobalt may dissolve when the electrode is currentless, $Q_{c,\mathrm{min}}$ will increase when plating with a pause after the high current density.

The plots in Fig. 6 enable Q_c to be established to obtain multilayers with the desirable thickness of cobalt-rich layer. The calculation shows a satisfactory coincidence with the GDOS data and also with the measurements of the coercive force of the films, that is, films obtained when Q_c of a high current density pulse is lower than $Q_{c,\mathrm{min}}$, do not contain a cobalt-rich layer and are not ferromagnetic. It was found that the coercive force of cobalt/ruthenium multilayers with layer thickness 30–100 nm range from 300 to 400 oersted ($1\,\mathrm{A\,m^{-1}} \equiv 4\pi \times 10^{-3}$oersted).

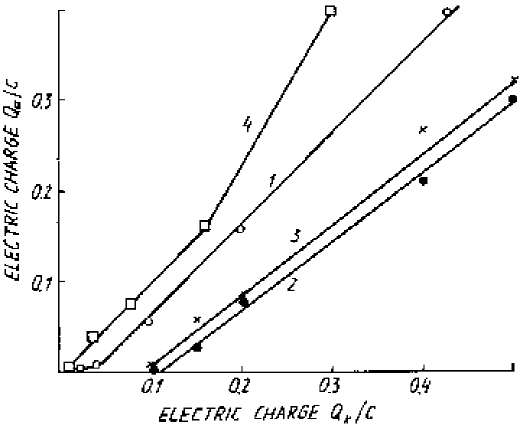

Fig. 6. Relation between Q_a and Q_c for: (1) cobalt (plated on platinum from standard electrolyte not containing ruthenium); (2) cobalt–ruthenium alloy (plated on platinum from standard electrolyte at $i_c = 0.1\,\mathrm{A\,cm^{-2}}$); (3) cobalt–ruthenium alloy (plated from standard electrolyte on platinum coated with 1 μm ruthenium at $i_c = 0.1\,\mathrm{A\,cm^{-2}}$); (4) ruthenium (plated from standard electrolyte at $i_c = 0.004\,\mathrm{A\,cm^{-2}}$).

4. Conclusions

- (i) Compositionally modulated ruthenium/cobalt alloys were obtained from sulfate–sulfamate electrolyte by the dual-current pulse method. The thickness of cobalt-rich and ruthenium-rich layers was in the range 100 to 30 nm. There is no strong boundary between cobalt-rich and ruthenium-rich layers because of the existence of transition layers and of nuclei as the initial stage of film growth. It was found that the electrodeposition of cobalt began only after passing a charge of about $0.1\,\mathrm{C\,cm^{-2}}$.
- (ii) The coulometric measurements during anodic dissolution of cobalt–ruthenium films allow an exact determination of the cobalt content and an approximate determination of the ruthenium in the films.

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