EVOLUTION OF THE INCLUDED HYDROGEN, INTERNAL STRESS, MICROHARDNESS AND MICROSTRUCTURE OF ELECTRODEPOSITED COBALT

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Abstract—An interrupted electrolysis with different duration of the pause (zero current)- τ_{off} for the plating of cobalt layers is applied. The alteration of their internal stress (IS), microhardness and microstructure with variable τ_{off} within the range 0–900 s and constant plating period $\tau_{on} = 120$ s is investigated. The amounts of hydrogen leaving the coating both after the deposition is over, v_{H} , and during the pauses, v_{H}^{off} , are determined. A permanence of the structure (phase composition, crystalline orientation and coherent scattering domain size) of cobalt coatings, deposited both by conventional and interrupted electrolysis regardless of the pause duration is established. The increasing total amount of desorbed hydrogen, $v_{H}^{aff} = (v_{H}^{off} + v_{H})$, as τ_{off} becomes longer is the cause of the observed augmentation of the IS, microdeformation and decrease of microhardness. It is shown that the hydrogen desorption can occur not only when the electrodeposition is over, but also during the plating process.

INTRODUCTION

Several authors have established an increase of the IS after switching off the electrodeposition current when plating nickel [1-3], cobalt [3, 4], palladium [5-7] and palladium-nickel alloy[8]. This effect has been related to the desorption of hydrogen, included in the coating during the deposition[3-8]. The essence of this phenomenon is the appearance after the hydrogen evolution of a free volume within the coating, which tends to decrease the size and is equivalent to a preliminary stretching. The monitoring of the kinetics of post electrolysis increase of the IS, checked by dilatometric method, offers a possibility to determine the effective diffusion coefficient of hydrogen. Besides, the difference between the deformations at the moment when the deposition current is switched off and after the hydrogen evolution process is over can be used for the independent evaluation of its amount which left the coating[9, 10].

It appeared interesting to determine to what extent the change in the conditions for the hydrogen evolution can affect the IS and microstructure of cobalt coatings. The present paper is in fact aimed at tracing alterations of the IS, the microhardness and microstructure of cobalt layers, deposited by interrupted electrolysis (Fig. 1) with variable duration of the pauses (zero current), τ_{off} , within the range 0–900 s and constant plating period, $\tau_{on} = 120$ s, as well as the amounts of hydrogen leaving the coating both after the deposition $v_{\rm H}$ and during the pauses $v_{\rm H}^{\rm off}$.

The selection of the τ_{on} and τ_{off} periods of the interrupted electrolysis, were considerably longer than those used during pulsed electrodeposition[11, 12], is made in order to meet the requirement that the plating regime should not alter substantially the structure of the coating and affects the hydrogen evolution conditions only.

EXPERIMENTAL

Plating conditions

The cobalt coatings were deposited from electrolyte containing: 0.89 CoSO₄ \cdot 7H₂O; 0.32 H₃BO₃ mol dm⁻³, at cathodic c.d. 4 A dm⁻², T=303 K and pH 3.0. The deposition period (τ_{on}) was kept constant (120 s) while the duration of the pauses was altered ($\tau_{off}=0$; 120; 240; 360; 600; 900 s) (Fig. 1). The electro-deposition was carried out in a double chamber electrolytical cell with a volume of 700 cm³, kept under continuous circulation of the electrolyte.

Determination of the internal stress

The IS is determined by the dilatometric method using an instrument improved by us and described in [3]. The value of average stress during electrodeposition $(\bar{\sigma})$ was determined:

$$\bar{\sigma} = \frac{\bar{E}_o d}{2t} \frac{\lambda}{l_o},\tag{1}$$

where $\bar{E}_o = E_o/(1 - v_o)$ is the reduced elasticity modulus of the platinum substrate (v_o = the Poisson coefficient), d = the thickness of the substrate (0.2 mm), l_o = its initial length (85 mm), t = thickness of the coating (16.5 μ m) and λ = the length change of the cathode at the moment when the plating current is switched off.

Under interrupted electrolysis conditions $\lambda = \Sigma \lambda_i^{on} + \Sigma \lambda_i^{off}$ (Fig. 2). The length change of the system substrate-coating as time elapses during the periods $\tau_{on} (\Sigma \lambda_i^{on})$ is related to the IS, created as a result of the electrodeposition, $\bar{\sigma}_{on}$. During the τ_{off} periods, $\Sigma \lambda_i^{off}$ is connected with the IS caused by the diffusion of hydrogen only, $\bar{\sigma}_{off}$. It can be noted in Fig. 2 that when the pauses are relatively shorter, the processes which occur during this period (τ_{off}) cannot be completely



Fig. 1. Interrupted electrodeposition.

accomplished and the steps gradually become less distinct. The average stress occurring during interrupted electrolysis is: $\bar{\sigma} = \bar{\sigma}_{on} + \bar{\sigma}_{off}$. The stationary average stress $(\bar{\sigma}^*)[13]$ was determined using Equation (1) and inserting λ^* —the length change of the cathode after the stationary state of the post-electrolysis processes has been reached $(\lambda^* = \lambda + \lambda_{\infty})$; λ_{∞} is the post electrolysis length change of the system substrate-coating.

Determination of the amounts of desorbed hydrogen

The hydrogen desorption causes dilatometric alterations, which are used for hydrogen concentration evaluation[9]:

$$C_{\rm H} = \frac{3}{\Delta v / \Omega} \left(1 + \frac{\tilde{E}_{\rm o} d}{\tilde{E} 2t} \right) \frac{\lambda_{\infty}}{l_{\rm o}}, \tag{2}$$

where $C_{\rm H}$ is the atomic hydrogen concentration, Ω is the atomic volume of cobalt, Δv is the change in the atomic volume due to the addition of a hydrogen atom ($\Delta v/\Omega = 0.28$ in the case of Ni [14] and since no literature data for cobalt are available, we used with a certain approximation the same value), $\tilde{E} = E/(1 - v)$, the reduced elasticity modulus of the coating, while v is the corresponding Poisson coefficient.

From $C_{\rm H}$ it is not difficult to evaluate $v_{\rm H}$ (cm³ g⁻¹ Co)[15]. The cathode length $(l_{\rm o})$ and width (b) as well as the thicknesses of the coatings deposited

at different τ_{off} are identical, their volumes are similar and $v_{\rm H}$ quantity is proportional to the hydrogen amount evolved from the entire coating after the current is switched off: $V_{\rm H} = v_{\rm H} 2l_o tb\rho$ (ρ is the density of Co). Thus the dependences of $V_{\rm H}$ and $v_{\rm H}$ on τ_{off} are identical and we can talk about hydrogen quantities showing $v_{\rm H}$ variation. In order to evaluate the amount of hydrogen evolved during the pauses ($v_{\rm H}^{off}$), instead of λ_{∞} [Equation (2)] we used the overall change in the length of the cathode together with the coating, within the $\tau_{off} - \Sigma \lambda_i^{off}$ (Fig. 2). For the entire deposit $V_{\rm H}^{off} = v_{\rm H}^{off} 2l_o tb\rho$.

Determination of the microhardness and structure investigations

To carry out these investigations, electrodeposition was performed onto copper substrates $(20 \times 10 \text{ mm})$ with copper frameworks. The thickness of the cobalt coatings deposited onto these substrates was approximately 30 μ m. The Vickers microhardness was measured with a "Leitz Wetzlar" unit using a 0.050 kg load. The magnetic characteristics (coercivity and B-H loop squareness ratio) were determined by using an apparatus described in[16]. The preferred crystalline orientation of the cobalt samples was checked by analysing the pole chart, traced by the Schulz method[17], using the $\{10\overline{1}1\}$ lines for the hcp-phase and $\{200\}$ for the fcc-phase. The quantitative phase analysis was carried out by comparing the integral intensity of the pole charts of the samples, to those of standard specimens[18, 19].

The determination of the size of coherent scattering domains (CSD) and the microdeformations was carried out by analysing the broadening of the X-ray diffraction lines, traced with a Philips diffractometer under conditions shown in Table 1. A version of the approximation method was used, where the profile of the diffraction line is described by a Voigt function, representing a convolution of the Cauchy and Gauss functions[20, 21]. The so-called form factor was intro-



Fig. 2. Experimental curves of the cathode length change (λ) vs time (τ) during interrupted electrodeposition of cobalt coatings. $\lambda < 0$ due to the presence of tensile stress.

	Co samples	Ni standard			
Diffraction line	(1120)	(220)			
Scanning speed/deg min ⁻¹	1/2	1/4			
Time (background)/s	1000	1000			
Time (peak)/s	20	40			
20 interval/deg	78.5-83.5	79.5-83.66			
and time/s	600	1000			
for the measurement of the	integral intensit	y			

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duced as an experimental parameter: $\Phi = 2W/\beta$, where 2W is the half-width (the total width of the diffraction line at a level equal to 1/2 of its maximum height), while β is the integral width (the area under the diffraction line, divided by its maximum height).

The Voigt analysis is based on the separation of the Cauchy and Gauss components of the widths of the observed (β_G^h and β_G^h) and instrumental (β_G^g and β_G^g) profiles and then calculating the respective components of the physical profile (β_G^f and β_G^f):

$$\beta_{\rm C}^{\rm f} = \beta_{\rm C}^{\rm h} - \beta_{\rm C}^{\rm g},\tag{3}$$

$$(\beta_{\rm G}^{\rm f})^2 = (\beta_{\rm G}^{\rm h})^2 - (\beta_{\rm G}^{\rm g})^2,$$
 (4)

where β_{C}^{h} , β_{G}^{g} , β_{G}^{h} and β_{G}^{g} are determined by empirical equations[20], in which the form-factor participates as a parameter.

It is well known that the physical profile reflects the effects of the small size of the CSD and the microdeformations. Their separation is carried out on the basis of a single line[21] only, under the presumption that the broadening due to the small sized CSD is according to the Cauchy-type only, while that due to the microdeformations is of the Gaussian-type:

$$D = \alpha / \beta_{\rm C}^{\rm f} \cos \theta, \tag{5}$$

$$\tilde{e} = \beta_{\rm G}^{\rm f} / 4 {\rm tg} \theta, \qquad (6)$$

where α is the wave length of the radiation used and θ is the Bragg angle.

RESULTS AND DISCUSSION

Structure

As it can be expected, the structure of cobalt coatings, deposited under conventional electrodeposition conditions and those plated at various durations of the pauses (interrupted electrolysis) do not display a detectable difference in the phase composition, texture and size of the CSD. All samples contained approximately 80% hcp-phase with a distinct axis of preferred orientation $\langle 11\overline{2}0 \rangle$ with a constant degree of perfection and a fcc-phase with a rather slight texture along the (110) axis. This is in agreement with previous data[22]. The results of the Voigt analysis and the measurement of the magnetic characteristics are presented in Table 3. Ot. the basis of the experimental parameters shown in Table 2 and Equations (3) and (4), the Cauchy and Gauss components of the physical profile were determined and used for the evaluation of the CSD size and the microdeformations by applying Equations (5) and (6). The microdeformation value of samples deposited under conventional plating conditions ($\tilde{e} = 1.3 \times 10^{-3}$) is in agreement with data published by Zhichareva and Zhicharev[23] using a Fourier analysis for the investigation of the profile of diffraction lines.

The coercivity is a structure-sensitive property. Its value for samples deposited at different durations of τ_{off} provides independent evidence for the extent of similarity of the respective structural parameters (Table 3). At the given phase composition (approx. 80% hcp) which remains constant, the coercivity should depend above all on the CSD size[18, 24], since the effect of the energy of magnetocrystalline anisotropy prevails over the magnetoelastic energy.

Internal stress, microhardness and hydrogen evolved

The amount of hydrogen evolved after the electrodeposition is over (v_H) decreases as the duration of the pauses is increased (Fig. 3c), since its chances for desorption are enhanced early before the formation of the coating is completed. Still due to this reason, as τ_{off}

ф $I_{o}/\text{imp}\,\text{s}^{-1}$ $2w \times 10^3$ /rad $\beta \times 10^3$ /rad $(2w/\beta)$ $\beta_{\rm c} \times 10^3$ /rad $\beta_{\rm G} \times 10^3/{\rm rad}$ τ_{off}/s Ni-stand. 578±3 $2.61 \pm .08$ $3.72 \pm .03$ $.70 \pm .01$ $2.9 \pm .1$ $1.4 \pm .1$ $.77 \pm .02$ 4.9±.5 0 1756 ± 9 $6.5 \pm .2$ $8.46 \pm .05$ $4.9 \pm .7$ 0 1869 ± 9 6.5<u>±</u>.2 $8.52 \pm .05$ $.76 \pm .01$ $5.1 \pm .3$ 4.8<u>+</u>.3 120 7.4±.2 1709 ± 9 $9.46 \pm .06$.78 ± .02 $5.2 \pm .7$ $5.7 \pm .5$ 120 1661 ± 9 7.4±.2 $9.17 \pm .06$ $.80 \pm .02$ $4.3 \pm .7$ $6.1 \pm .5$ 240 1487 ± 8 7.4±.2 $9.45 \pm .06$.78 ± .02 $5.2 \pm .7$ 5.7 + .5240 $7.4 \pm .2$ 1724 ± 9 $9.36 \pm .06$ $.79 \pm .02$ $4.9 \pm .7$ 5.8±.5 $8.7 \pm .2$ 5.3±.7 360 1206 ± 7 10.86 + .08.80 + .02 $7.1 \pm .5$ 360 $7.8 \pm .2$ 1663 ± 9 $9.64 \pm .06$.81±.02 4.3±.7 6.6<u>+</u>.5 600 1335 + 88.2±.2 $10.31 \pm .07$ $.80 \pm .02$ 5.0±.7 $6.7 \pm .5$ 600 1443 ± 8 8.3<u>+</u>.2 $10.31 \pm .07$ $.80 \pm .02$ $5.0 \pm .7$ 6.8±.5 7.8±.2 900 1800 ± 9 $9.84 \pm .06$.79 ± .02 4.9±.7 $6.3 \pm .5$ 900 1913±9 $8.2 \pm .1$ $.84 \pm .02$ $9.86 \pm .06$ $3.5 \pm .4$ $7.4 \pm .3$

Table 2. Parameters of the X-ray lines profile. B_o (Ni standard) = 7.45 ± .08 imp s⁻¹; B_o (Co samples) = 40.0 ± .2 imp s⁻¹ I_o = peak intensity, corrected for the background; B_o = background.



Fig. 3. Relationships of: (a) average stress during electrodeposition, $\bar{\sigma}$ (Φ) and $\bar{\sigma}_{on}$ (∇), stationary average stress, $\bar{\sigma}^*$ (Δ) and microdeformations, \tilde{e} ; (b) total amount of hydrogen evolved, $v_{\rm H}^*$ and microhardness, HV; (c) amount of hydrogen evolved after electrodeposition is over, $v_{\rm H} v_{\rm S}$ the duration of pauses, $\tau_{\rm off}$, during the interrupted electrodeposition of cobalt coatings.

becomes longer, the total amount of evolved hydrogen $(v_{H}^{*} = v_{H}^{off} + v_{H})$ is increased. In fact this is the reason for the increase of the IS— $\bar{\sigma}$ and $\bar{\sigma}^{*}$ observed in Fig. 3a. It can be noted that the differences between them $(\Delta \bar{\sigma}^{*} = \bar{\sigma}^{*} - \bar{\sigma})$, *ie* the post-electrolysis alterations of IS, decrease slightly due to the decrease of v_{H} . As τ_{off} becomes longer, the $\bar{\sigma}_{on}$ stress also decreases. When $\tau_{off} = 900$ s, the value of $\bar{\sigma}_{on}$ is approximately 1/3 of the $\bar{\sigma}$ value (the remaining 2/3 are a result of hydrogen desorption) and represent about 50% of the figures of the average stress in samples deposited under conventional electrolysis conditions ($\tau_{off} = 0$). Taking into consideration the already mentioned constant structure, this fact provides clear-cut evidence that hydrogen evolution is possible not only when the electrolysis is over, but during the deposition process as well. This is the reason for the decrease of $\bar{\sigma}_{on}$ with the increase of τ_{off} instead of to be independent on the pause duration.

The alteration of microdeformations (\tilde{e}) proceeds simultaneously with the change of IS. Under the deposition conditions selected for our experiments, the reason for the shape of the two relationships (IS and microdeformations) is one and the same: the increase of the amount of desorbed hydrogen early before the coating formation is completed, as the duration of the pauses becomes longer. This is the only reason which provides an explanation of the observed decrease of microhardness as τ_{off} becomes longer. Data obtained by us show that the highest microhardness value of the coatings is reached in samples which have been electrodeposited under conventional

τ_{off}/s	$\beta_{\rm c}^{\rm f} \times 10^3/{\rm rad}$	$\beta_{\rm G}^{\rm f} \times 10^3/{\rm rad}$	D/nm	$\tilde{e} \times 10^3$	H _c /Oe	γ
0	$1.9 \pm .7$	$4.7 \pm .6$	108 ± 41	$1.3 \pm .1$	58 <u>+</u> 1	0.43
120	$2.1 \pm .4$ $2.2 \pm .7$	$4.0 \pm .5$ 5.5 ± .5	98 ± 19 95 ± 32	1.3±.1 1.6±.1	61 ± 1	0.45
120	1.3 <u>+</u> .7	5.9±.3	162 <u>+</u> 95°	1.7±.1		
240	$2.2\pm.7$	5.6 <u>+</u> .5	97±33	1.6±.1	61±2	0.46
240	1.9 <u>+</u> .7	5.7 <u>+</u> .5	111 ± 44	1.6 <u>+</u> .1		
360	$2.3 \pm .7$	$6.9 \pm .5$	92±31	$2.0 \pm .1$	62 ± 1	0.46
360	1.3±.7	$6.4 \pm .5$	156 ± 89	1.8±.1		
600	2.0 ±.7	6.6±.5	106 <u>+</u> 41	1.9 <u>±</u> .1	62±1	0.46
600	$2.0 \pm .7$	$6.6 \pm .5$	106 ± 41	1.9±.1		
900	1.9±.7	$6.1\pm.5$	107 ± 41	$1.8 \pm .1$	62+1	0.46
900	0.5±.4	7.6±.5	> 200	2.1 ±.1	~= <u>+</u> ·	0.10

Table 3. Size of the coherent scattering domains, microdeformations, and magnetic characteristics of cobalt samples, deposited at various τ_{off} .

electrolysis conditions ($\tau_{off} = 0$), where the overall amount of desorbed hydrogen is the lowest (0.55 cm³ g⁻¹ Co).

It is well known that microhardness is very sensitive to hydrogen included in the coating. It has been established[25] that as the amount of hydrogen codeposited with the coatings decreases, microhardness is lowered. Janko and Szummer[26] have observed an abrupt increase of microhardness in hydrogenated nickel single crystals. After hydrogenation was over, the microhardness decreased due to the desorption of hydrogen, but nevertheless the pre-hydrogenation level is never reached, even after a month long ageing of the single crystals.

As already mentioned, in our case also, (Fig. 3a) the desorption of hydrogen is accompanied by an enhancement of the microdeformations. By comparing their alterations with the change of the microhardness when τ_{off} increases, it can be presumed that the decrease of microhardness would have been more enhanced if microdeformations were not changed. In other words, the increase of microdeformations affects reversely the microhardness and this effect is subtracted from the stronger influence which the desorbing hydrogen exerts upon the microhardness.

CONCLUSION

By changing the duration of the pauses in the interrupted electrodeposition of cobalt coatings, conditions have been established for plating in order to ensure an increase of the IS without a considerable alteration of the structure of the deposits (phase composition, texture and CSD size). It has been proved that the reason for the change of the stress is the desorption of hydrogen, co-deposited in the coatings, which may proceed not only after the electrolysis is over, but also during the electrodeposition. This phenomenon is responsible to a considerable extent for the relatively high tensile stress in similar coatings.

REFERENCES

- A. T. Vagramyan and Yu. S. Petrova, Mechanical Properties of Electrolytic Deposits, Consultants Bureau, New York (1962).
- 2. J. B. Kushner, Metal Finish. 56, 52 (1958).
- 3. S. Armyanov and G. Sotirova, Surf. Tech. 17, 329 (1982).
- 4. S. Armyanov and R. Weil, Plat. Surf. Finish. 63, 49 (1976).
- 5. H. D. Hedrich and Ch. J. Raub, Metalloberfläche 31, 11,512 (1977).
- 6. H. D. Hedrich and Ch. J. Raub, Surf. Tech. 8, 347 (1979).
- 7. H. D. Hedrich and Ch. J. Raub, Metalloberfläche 33, 8,308 (1979).
- 8. M. Butz, F. Friedrich and Ch. J. Rauh, Metalloberfläche 37, 3, 89 (1983).
- 9. S. Armyanov and G. Sotirova, Surf. Coat. Tech. 34, 441 (1988).
- S. Armyanov and G. Sotirova, 37th Meeting ISE, Vilnius, U.S.S.R. Ext. Abstr. Vol. II, p. 16, (1986).
- 11. V. A. Sabludovskii, Electrokhimiya 21, 874 (1985).
- 12. E. S. Chen and F. K. Sautter, Plat. Surf. Finish. 63, 28 (1976).
- 13. S. Armyanov and G. Sotirova, Surf. Tech. 17, 321 (1982).
- 14. H. Peisl, in *Hydrogen in Metals* 1, *Basic Properties* (Edited by G. Alefeld and J. Völkl), Springer, Berlin (1978).
- 15. S. Dushman, Scientific Foundations of Vacuum Technique, Wiley, New York, (1962).
- 16. S. Armyanov, Dissertation, Sofia (1974).
- 17. G. L. Schulz, J. appl. Phys., 20, 1030 (1949).
- 18. S. Armyanov and S. Vitkova, Surf. Tech. 7, 319 (1978).
- 19. S. Vitkova, S. Armyanov and N. Pangarov, Comm. Dept Chem. Bulg. Acad. Sci. 7, 685 (1974).
- 20. J. I. Langford, J. appl. Cryst. 11, 10 (1978).
- T. H. de Keijser, J. I. Langford, E. J. Mittemeijer and A. B. P. Vogels, J. appl. Cryst. 15, 308 (1982).

- G. Sotirova, I. Petrova and S. Armyanov, Proceedings of the 7th Symposium on Electroplating, Scientific Society of Mechanical Engineers, Omikk-Technoinform, p. 332, Budapest (1985).
- 23. I. G. Zhichareva and A. I. Zhicharev, Electrokhimiya, 18, 1095 (1982).
- 24. S. Armyanov and S. Vitkova, Phys. St. Solid 26, 553 (1974).
- E. M. Levy, R. D. MacInnis and T. P. Copps, *Plating* 56, 533 (1969).
- 26. A. Janko and A. Szummer, Bull. Acad. Pol. Sci. 14, 11-12 885 (1966).