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Changes in the Structure and Properties of Electrodeposited Metal Coatings in the Process of Aging

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Abstract: The most commonly used in the industry metal coatings of Cr, Fe, Co, Ni, Cu, Sb, Bi, Pb, Sn were investigated. The influence of electrodeposition conditions on the formation of the structure and properties of coatings has been established, their changes during the aging process were studied and the conditions of heat treatment ensuring the in-service stability of the properties of the coatings have been determined.

Keywords: Electrodeposited, Metal, Coating, Aging, Structure, Properties

1. Introduction

Electrolytic deposition of metallic coatings is widely enough used to enhance structural strength, wear- and corrosion resistance of mechanical parts. However, the physical and mechanical properties of such coatings can change in the course of their operating time, affecting the reliability and durability of the structure as a whole.

The structure of electrodeposited metals is characterized by high concentration of crystalline structure defects exceeding the concentration at thermodynamic equilibrium. Such systems are also characterized by a higher free energy and a tendency to turn into a more stable state after electrolysis. The processes of recovery and recrystallization, occurring at that time, are limited to a decrease in the concentration of defects and their redistribution in the crystal lattice and formation of more equilibrium configurations. Only in low-melting metals (zinc, lead, tin, bismuth, and others.), the mobility of atoms at room temperature (natural aging) is sufficient for active development of processes bringing the deposit into a stable state with a lower free energy. In deposits of metals having higher melting temperatures (copper, silver, nickel, cobalt, iron, chromium, etc.), such a transition is possible only partially. However, in any case, the structure and properties of electrodeposited metals undergo significant changes.

2. Materials and Methods

This article presents the results of aging studies on most common in the industry metallic coatings of Cr, Fe, Co, Ni, Cu, Sb, Zn, Bi, Pb, Sn deposited in simple electrolytes without organic additives (Cr, Fe, Co, Ni, Zn, Sn – from sulfate, Sb, Pb – from trilon-based, Bi – from nitrate). Polarization curves were constructed for a range of conditions of electrolytic coating deposition. The ratio of E/Elim, where Elim is the overvoltage at the cathode, corresponding to the limiting current density (ilim) was used as the integral parameter taking into account the influence of the conditions of electrodeposition. For convenience, the conditions of metal deposition at $E < 0.33$ Elim were considered mild, at $E > 0.66$ Elim – hard, and at $E = (0.33\text{-}0.66)$ Elim - average.

The electrical resistance was measured by the compensation (potentiometric) method using a double bridge R329, with an accuracy of ± 0,01 μΩ. Samples were cut from a coating previously separated from the substrate. Coatings that could not be separated from the substrate were deposited on a pre-annealed wire and then, the electrical resistance was measured. Precise measurement of the lattice parameters was carried out at a DRON-7 diffractometer, in filtered radiation. Assessment of internal stresses was carried out at a special holographic setup for the study of relaxation processes in electrolytic coatings [1]. Annealing of the samples was performed in an atmosphere of argon.

3. Results and Discussion

3.1. Characteristic Peculiarities of the Structure of Electrodeposited Metals

Metallographic studies of coatings [2] have shown that, depending on the deposition conditions, metals of a different nature crystallize with a characteristic type of the structure and can be classified as shown in Table 1.

Metals of the first group (Cr, Fe, Co, Ni), with relatively high melting temperatures, deposited under mild and average conditions, have a subgrain structure. At cathode overvoltages, in the range of (0.6-0.7) Elim, the subgrain structure transforms into the cellular one.

Table 1. *Classification of electrodeposited metals and type of the formed coating structure.*

Group	Metals	Conditions of electrodeposition	Type of the structure
I	Cr, Fe, Co, Ni	Mild, average	Subgrain
		Hard	Cellular
II	Cu, Sb	Mild	Large-block
		Average	Subgrain
		Hard	Cellular
III	Zn, Pb, Bi, Sn	Mild	Large-block
		Average, hard	Subgrain

In metals of the third group (Zn, Pb, Bi, Sn), with relatively low melting temperatures, under mild conditions of deposition a large-block structure is formed. With an increase of the cathode overvoltage to E = (0.3-0.4) E_{lim}, the large-block structure transforms into the subgrain one. It seems impossible to get a cellular structure at electrodeposition of low-melting metals, even at current densities close to the limiting current densities.

Depending on production conditions, metals of the second group (Cu, Sb), whose melting temperatures occupy an intermediate position between metals of the first and the third group, can deposit with structures characteristic of metals of the first and third group. Under mild conditions of deposition, a large- block structure is formed, which during the transition to hard conditions gradually transforms into the subgrain and further into the cellular one.

The structure of coatings of each group of metals is characterized by definite intervals of grain size; the dispersity of the structure is higher in metals with higher melting temperatures, which have been deposited under more hard conditions “Fig. 1”.

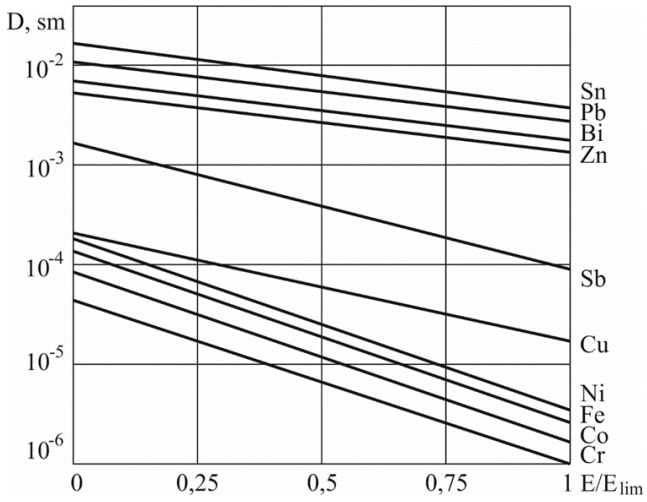

Figure 1. *Dependence of grain size of metals (D) on the conditions of deposition.*

The average size of crystallites of the metals of the first group equals to 10^{-5}-10^{-6} while the size of the third is 10^{-2} cm, i.e. by 3-4 orders of magnitude greater. The different dispersity in different groups of metals can be explained within the framework of the theory of "barriers" [3]. Deposition of the metals of the first group takes place at a high cathode overpotential under release of hydrogen, the percentage of which can be very large at that (up to 85 %). The releasing hydrogen absorbs on the nuclei ("barrier") and prevents their normal growth, causing a fine-crystalline structure of the coatings.

Deposition of the metals of the third group occurs, on the contrary, at a low cathode overpotential and in the absence of hydrogen (no "barriers"), so they have a macrocrystalline structure.

A characteristic feature of deposition of the metals of the second group is the fact that depending on the conditions of electrolysis (current density, composition and pH of the electrolyte), the process can proceed with the release of hydrogen at the cathode or without it. In accordance with this, the dispersity of the coatings varies in a wide range, approaching (in dependence on the conditions of electrolysis) to the dispersity level of metals of the first or third group.

Such a significant difference in grain size determines the peculiarities of formation of point defects of the crystal structure in electrodeposited metals belonging to different groups, in particular. It is known, that in electrodeposited metals with a highly dispersed structure, a dimensional vacancy effect appears, which is manifested in a sharp growth of vacancy concentrations, while in metals having a macrocrystalline structure, there dominates the effect of interstitial atoms [4].

Work [5] presents data on the concentrations of vacancies and interstitials in metals of different groups deposited under different conditions. As it is seen from Table 2, an increase in the deposition potential leads to an increase of point defect concentration in the structure of coatings. Moreover, in all investigated metals, a correlation is observed between the magnitude and sign of internal compression and tension stresses and concentration of interstitials and vacancies,

respectively. In addition to that, the experimentally obtained values of internal stresses (IS) are in good agreement with values of IS, calculated in accordance with the atomic and vacancy model of their formation [6]. Allowing for this correlation, IS can be used as an effective indicator of the development of relaxation processes associated with migration and annihilation of point defects during aging of electrodeposited metals.

Table 2. *Concentration of point defects and magnitude of IS in coatings.*

Group	Metal	Cathode current i_C, A/dm^2	Concentration of vacancies, C_v	Concentration of interstitials, C_{ia}	Magnitude (MPa) and sign of IS	
					Calculated	Experimental
I	Cr	50	10-2	-	+300	+340
		35	5·10-3	-	+220	+235
		20	10-3	-	+150	+175
	Fe	50	8·10-3	-	+280	+310
		35	5·10-3	-	+220	+225
		20	10-3	-	+150	+190
	Co	45	10-3	-	+250	+275
		30	8·10-4	-	+190	+220
		15	5·10-4	-	+125	+140
	Ni	10	10-3	-	+200	+230
		6	10-4	-	+150	+175
		3	10-6	-	+100	+115
II	Cu	5,0	10-3	10-12	+45	+50
		1,2	10-8	10-9	-26	-25
		0,5	10-18	5·10-4	-12	-10
	Sb	5	10-7	10-12	+32	+30
		3	10-12	10-9	-9	-10
		1	10-18	5·10-4	-22	-20
III	Zn	4	-	10-11	-12	-15
		3	-	10-9	-20	-18
		2	-	5·10-4	-26	-20
	Pb	4	-	10-10	-15	-10
		3	-	10-7	-22	-25
		2	-	5·10-4	-38	-35
	Bi	2	-	10-10	-20	-18
		1	-	10-7	-30	-28
		0,5	-	5·10-4	-44	-40
	Sn	8	-	10-10	-25	-20
		5	-	10-6	-35	-31
		2	-	5·10-4	-50	-50

3.2. Stages of Aging of Electrodeposited Metals

Earlier [7], experimental dependences of hardness, electrical resistance, lattice parameter and IS on the time of aging were obtained for electrodeposited metals (schematically shown in Figure 2). On the basis of these data, we'll try to analyze the character of changes in the structure of metals of different groups in the period after electrodeposition.

In metals of the first group, having relatively high melting temperatures, in accordance with the activation energy [8], at room temperature, only those processes are possible which are associated with migration and annihilation of vacancies and hydrogen atoms, whose presence is due to the specifics of the process of electrodeposition of metals belonging to this group. In connection with this, it is possible to distinguish two stages in the aging of coatings.

The first stage, lasting up to 100 hours, is obviously associated with diffusion of the most labile hydrogen. As an interstitial element, hydrogen is located in the interstices of the crystal lattice of coatings and is captured by vacancies - defects having an effective negative charge. In the period after electrolysis, the hydrogen is released from the vacancies and moved from the solid solution to sinks, including pores formed in the process of electrocrystallization, which causes an increase of pressure in them and growth of hardness. Reduction of the crystalline lattice period and electrical resistance at the first stage of aging confirms the dominating role of hydrogen diffusion at the initial stage of operation.

At the second stage, it is the vacancies, less labile than hydrogen atoms that migrate to the sinks. Annihilation of vacancies is indicated by a decrease in IS and an increase in the lattice periods, which, however, remain below the

equilibrium ones even after prolonged aging, indicating a high concentration of excess vacancies in the coatings. Migrating to the pores, vacancies increase the volume of the latter, reducing the pressure of molecular hydrogen in them. This leads to some reduction in the hardness, but does not cause softening, since structure-ordering processes do not develop to the stage of polygonization, which in metals with a relatively high melting temperature may occur at temperatures above 100 ° C, and is possible only at heating. Accordingly, the type of coating structure - cellular or subgrain –does not undergo significant changes during aging either.

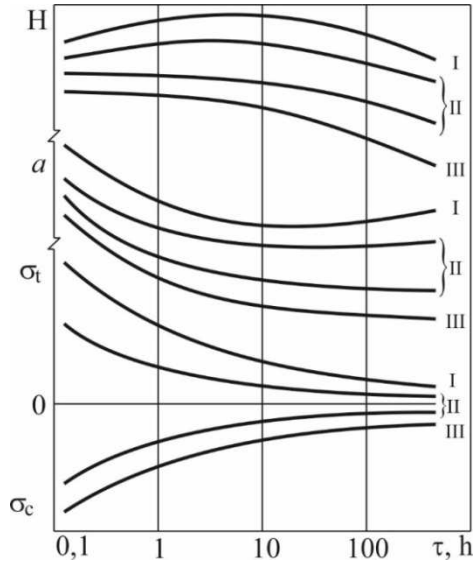

Figure 2. *Nature of the hardness change (H), crystal lattice parameter (a) and internal compression (σcom) and tension (σtens) stresses of electrodeposited metals of the first (Ni, Co, Fe, Cr), second (Cu, Sb) and third (Zn, Pb, Bi, Sn) groups in the process of aging.*

Different conditions of coating deposition result in different quantities of dissolved hydrogen and excess vacancies in Co, Ni, Fe, Cr deposits. However, the nature of coating aging processes does not change/remains the same at that. It can only be noted that 1)the harder the conditions of deposition, the higher the concentration of point defects and 2) it takes a longer period of time for aging processes leading to stabilization of properties and relaxation of stresses to occur.

In contrast to metals with high melting temperatures, in which aging processes are limited to stages of relaxation, in low-melting metals of the third group, a complete development of recovery and recrystallization processes takes place. In these metals, in the course of aging time, the magnitudes of lattice parameters decrease due to migration and annihilation of excess interstitials. The decrease is the most intense at the first stage of aging, within 10-100 hours, correlating with a decrease in the electrical resistance of coatings and the magnitude of IS. It can be noted that, in coatings obtained under hard conditions and characterized by a higher concentration of interstitials, the lattice parameter, electrical resistance and IS reach stable magnitudes for a longer period of time than in coatings obtained under mild conditions. Since in low-melting metals, homologous return temperatures lie below the room temperature, during the second stage of aging, processes of redistribution and annihilation of dislocations take place in them, which are characteristic of the second stage of return - polygonization, resulting in enlargement of structural elements and reduction of the hardness of coatings. After polygonisation, in low-melting metals, at prolonged aging time, recrystallization takes place, which is confirmed by metallographic studies [9].

In metals of the second group, depending on the initial structure formed under different conditions of electrodeposition, the processes of aging and the nature of the change in coating properties will be similar either to those that occur in refractory metals (under hard conditions of Cu and Sb deposition), either to those that take place in low-melting metals (under mild conditions of Cu and Sb deposition).

3.3. Stabilizing Annealing of Electrolytic Coatings

As indicated by the experimental data presented above, the change of the properties in the process of aging is determined by the processes of migration and annihilation of point defects of the crystal structure (vacancies, interstitial and impurity atoms), an excess concentration of which is registered after electrodeposition. These processes require a low energy of activation (0.1-0.5 eV) and occur at low homologous temperatures (~ 0.1 Tm) [8]. However, even a prolonged aging (3000 hours and more) does not lead to stabilization of properties. This primarily refers to IS, which adversely affect the performance properties and lead to cracking, reduction of the protective ability and peeling of the coating from the substrate. Application of annealing accelerates relaxation processes in electrodeposited coatings and provides stabilization of their properties.

Table 3 summarizes the results of studies of the effect of annealing temperature on the character of changes in the internal tension stress in electrodeposited metals of the first and second group.

Table 3. *Effect of annealing temperature on the change in the IS (MPa) in electrodeposited metals.*

Temperature of annealing, Ta/Tm	Cu	Co	Ni	Fe	Cr
0,15	-	150	180	220	400
0,18	60	130	135	150	200
0,21	30	90	100	110	120
0,24	20	30	50	70	80
0,27	10	15	20	50	60
0,30	5	15	20	20	25
0,33	0	5	5	20	25
0,36	0	0	0	5	5

In the electrodeposited metals of the third group, due to their low melting temperatures, stabilization processes take place already at room temperatures. However, the internal compression stress reach minimum values for a substantially long time of natural aging. Relieving of the IS in electrodeposited metals of the third group, in practically acceptable time, is reached, as shown by the experimental results, by annealing at 100 - 150 ° C for 1.5-2 hours, which

activates the relaxation processes (tab. 4).

Table 4. *Change of the properties and structural characteristics in electrodeposited metals at annealing (100 ° C).*

Time	Pb			Zn			
	a, nm	IS, MPa	ΔR/R, %	a, nm	c, nm	IS, MPa	ΔR/R, %
0,25	0,4957	20	100	0,2677	0,487	18	100
0,5	0,4951	5	92	0,2676	0,4856	10	90
0,75	0,4950	1	90	0,2676	0,4855	6	88
1	0,4950	0	89	0,2675	0,4855	2	87
1,25	0,4950	0	89	0,2675	0,4855	0	87
1,5	0,4950	0	88	0,2675	0,4855	0	87

It is significant that here as well, like in metals of the first and second groups, one can observe two stages of internal stress relaxation and corresponding changes in the properties. At the first stage, a reduction of the electrical resistance (10-14%) and the lattice parameters occurs simultaneously with a significant decrease of IS. At the second stage, the electrical resistance reduces insignificantly, the values of the lattice parameters stabilize, the IS reduces to zero.

The sharp reduction of the electrical resistance and the simultaneous reduction of the lattice parameters at the first stage can be explained by the fact that interstitial atoms leave the precipitate lattice. The consequence of this process is a significant relaxation of stresses and improved protective properties of electrodeposited coatings. At the second stage, processes associated with redistribution of dislocations, formation and migration of low-angle boundaries become possible, leading to complete relieving of the IS and stabilization of coating properties.

Although the temperature of annealing provides the necessary activation energy for both migration and annihilation of point defects on the one hand and redistribution of dislocations and boundary migration on the other, the kinetic conditions apparently are such that these processes occur sequentially under these time-temperature parameters of the heat treatment.

The rate of heating and especially cooling at annealing must be moderate to avoid appearance of secondary (thermal) IS, which are highly probable in thin electrodeposited coatings [10].

In order to determine the parameters of annealing, at which the concentration of vacancies and interstitial atoms is reduced to equilibrium values, the diffusion fluxes of point defects in non-equilibrium structures have been calculated [11] and the following equation has been obtained:

$$\tau_{T1}=\tau_{T1}\cdot\exp(-Q/k\cdot(1/T1-1/T2)),$$

where τ_{T1} – is the experimentally determined time, during which at temperature T1, the concentration of point defects is reduced to an equilibrium value; τ_{T2} – is the calculated time, during which at temperature T2, the concentration of point defects is reduced to an equilibrium value; Q – is the point defect activation energy; k = 1,381·10-23, J/K(Boltzmann constant). The results of annealing parameters determination, calculated using the equation, are shown in Table. 5. They are in good agreement with the calculated values (Table. 3 and 4).

Table 5. *The results of calculations of the heat treatment of coatings.*

Material of coating	Electrolyte	Conditions of production			t, °C	τ, h
		t, °C	pH	i_c, A/dm^2		
				50	400	1,0
Cr	Sulphate	40	5,5	35	375	0,75
				20	350	0,5
				50	350	1,0
Fe	Sulphate	40	2,5	35	325	0,75
				20	300	0,5
				45	350	1,0
Co	Sulphate	40	2,5	30	325	0,75
				15	300	0,5
				9	350	1,0
Ni	Sulphate	40	4,5	6	325	0,75
				3	300	0,5
				2	200	0,5
Cu	Sulphate	25	-	1	150	0,5
				0,5	100	1,0
				5	200	0,5
Sb	Trilonate	30	-	3	150	0,5
				1	100	0,5
				5	100	0,5
Zn	Sulphate	25	4	3	75	0,5
				1	50	0,5

The obtained values allow recommending time-temperature conditions of annealing that ensure stabilization of coating properties under operation.

4. Conclusion

1. It has been found that in the process of aging of electrodeposited metals there occurs relaxation of internal stresses caused by migration and annihilation of point defects of the crystal structure.

2. Stabilization of coating properties in practically acceptable time is achieved by annealing at temperatures ~0.3 Tm, when not only the processes of migration and annihilation of point defects but also redistribution of dislocations and migration of low-angle boundaries become possible.

References

[1] I.M. Kovenskiy, V.V. Povetkin. Testing of electrodeposited coatings. M .: Intermet Engineering, 2001. - 136 p. (In Russian)

[2] I.M. Kovenskiy, V.V. Povetkin Electrodeposited alloys: Intermet Engineering, 2003. - 272 p.

[3] I.M. Kovenskiy. Origin of internal stresses in electrolytic coating // Defect structure, morphology and properties of deposit. – USA: Publication of TMS. – 1995. – P. 291-300.

[4] I.M. Kovenskiy. Estimation of the concentration of point defects in electrodeposited metals // Physics of Metals and Metallography. - 1993. - T.75. - №5. - P. 157-158. (in Russian)

[5] I.M. Kovenskiy, A.N. Venediktov, I.A. Venediktova and others. Aging of metal coatings in the process of operation //Proceedings of Institutions of Higher Education. Oil and Gas - 2012. - №2. - P.101 - 106. (in Russian)

[6] I.M. Kovenskiy, A.I. Morgun, N.V. Podbornov. Appearance and relaxation of internal stresses in metal coatings // Proceedings of Institutions of Higher Education. Oil and Gas. - 2002. - №4. - P. 81 - 86. (in Russian)

[7] I.M. Kovenskiy, A.A. Kuksgauzen. Peculiarities of aging of electrodeposited metals // Metals. - 1998. - №5. -P. 74 - 76. (in Russian)

[8] S.S. Gorelik, S.V. Dobatkin, L.M. Kaputkina. Rekristallizatsiya metallov i splavov. M.: MISIS, 2005. – 432 p. (in Russian)

[9] I.M. Kovenskiy, V.V. Povetkin. Metallography of coatings. M .: Intermet Engineering, 1999. - 296 p. (In Russian)

[10] I.I. Novikov. Theory of heat treatment of metals. M .: Metallurgy, 1986. - 480 p. (In Russian)

[11] I.M Kovenskiy, V.N. Kuskov, A.N Venediktov. et al. Technological parameters of stabilizing treatment of electroplatings // Omsk Scientific Bulletin. - 2012. - №2. - P. 72 - 74. (in Russian)