

Influence of the Conditions of Electrode Position and Heat Treatment on the Structure and Properties of Metallic Coatings

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Abstract. Influence of electrodeposition conditions and heat treatment on the structure and properties of metallic coatings has been considered. It has been that at different values of overvoltage, metals crystallize with a cellular, subgrain or monoblock structure. The final formation of the structure occurs during annealing, in the process of which either polygonization or recrystallization develops in the coatings. Varying the conditions of electrodeposition and heat treatment allows obtaining coatings with functional characteristics for specific operating conditions.

Introduction

Electrolytic deposition of metallic coatings is rather widely used for enhancing the protective and strength properties of mechanical parts. However, reserves related to improvement of these properties by means of heat treatment techniques are hardly ever made use of in practice [1-3]. The paper considers formation of the structure in production, aging and subsequent annealing of most common metallic coatings and the influence of structural peculiarities on the properties of electrodeposited layers.

1. Methods and materials

Electrodeposited chromium, nickel, zinc and cadmium were investigated. The coatings were deposited in industrial and laboratory conditions using standard electrolytes. Polarization curves were constructed for a range of conditions of electrolytic coating deposition. The ratio of E / E_{lim} , where E_{lim} is the overvoltage at the cathode, corresponding to the limiting current density (i_{lim}) was used as the integral parameter taking into account the influence of the conditions of electrodeposition. For convenience, the conditions of metal deposition at $E < 0.33 E_{lim}$ were considered mild, at $E > 0.66 E_{lim}$ – hard, and at $E = (0.33-0.66) E_{lim}$ – average.

The obtained samples were annealed in an argon atmosphere, at various time-temperature parameters.

The accelerated corrosion tests were carried out in an environment of 0.1 N sulfuric acid, using the gravimetric method. Before testing, the samples were weighed on an analytical balance with an accuracy of 0.0001g then placed in corrosion cells and kept in this state for 30 days. After that, the



corrosion products were removed, weighing was repeated, the thickness of the corroded layer was determined and the corrosion rate was calculated.

The hardness of the coatings was determined using a PMT-3M microhardness tester, at loads up to 2 N, by the method of the restored print.

Electron microscopy studies of the structure were carried out by transmission electron microscopy of thin foils using an EMV-100L electron microscope.

It was previously shown [4] that depending on the conditions of deposition, the studied metals crystallize with a characteristic type of the structure and can be classified as shown in Table 1.

2. Results and discussion

In metals with relatively high melting temperatures (Cr, Ni), deposited under hard conditions close to the limiting current, a typical cellular structure is formed. The cells are volumes, which are relatively free from dislocations separated from each other by dislocation tangles with a high dislocation density. The boundaries between the cells are often so vague and broad that they are commensurate with the size of the cells. In electron micrographs obtained from the cell boundaries, split reflections are observed and the azimuthal misorientation angle is a few degrees. At cathode overvoltages lower than $(0.7-0.6) E_{lim}$, the boundaries are already flat dislocation walls and, at lowering the cathode polarization, the density of dislocations in the sub-boundaries decreases and the misorientation angle between subgrains decreases to several tens of minutes. Finally, at $E < 0.33 E_{lim}$, the deposition of coatings is characterized by a monoblock structure.

Table 1. The structure of coatings after deposition.

Group	Metals	Conditions of electrodeposition	Type of the structure	Average grain size
I	Cr, Ni	Hard $E > 0.66 E_{lim}$	Cellular	10^{-6}
		Average $E = (0.33 - 0.66) E_{lim}$	Subgrain	10^{-5}
		Mild $E < 0.33 E_{lim}$	Monoblock	10^{-4}
II	Zn, Cd	Hard, Average	Subgrain	10^{-3}
		Mild	Monoblock	10^{-2}

In metals with relatively low melting temperatures (Zn, Cd), under mild conditions of deposition, a monoblock structure is formed with individual dislocations or groups of dislocations, not interconnected within the boundaries. At overvoltages higher than $(0.3-0.4)E_{lim}$, the structure observed is already a subgrain one. It should be noted that to get a cellular structure at electrodeposition of low-melting metals, even at current densities close to the limiting current densities, does not seem possible. The cellular structure is formed only in refractory metals, whose conditions of electrolysis cause significant internal stresses facilitating microplastic deformation at electrocrystallization. It should also be noted, the cellular structure is more easily achieved (i.e., at substantially lower overpotentials) in metals with high values of stacking fault energy.

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 (Table 1).

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.

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 are in good agreement with values of internal stresses, calculated in accordance with the atomic and vacancy model of their formation. Allowing for this correlation, internal stresses can be used as an effective indicator of the development of relaxation processes associated with migration and annihilation of point defects during aging and annealing of electrodeposited metals.

Table-2. Concentration of point defects and magnitude of internal stresses in coatings.

Group	Metal	$i, \text{A/dm}^2$	C_v	C_{ia}	Magnitude (MPa) and sign of internal stresses	
					calculated	experimental
I	Cr	50	10^{-2}	-	+300	+340
		35	$5 \cdot 10^{-3}$	-	+220	+235
		20	10^{-3}	-	+150	+175
	Fe	50	$8 \cdot 10^{-3}$	-	+280	+310
		35	$5 \cdot 10^{-3}$	-	+220	+225
		20	10^{-3}	-	+150	+190
	Ni	10	10^{-3}	-	+200	+230
		6	10^{-4}	-	+150	+175
		3	10^{-6}	-	+100	+115
II	Zn	4	-	10^{-11}	-12	-15
		3	-	10^{-9}	-20	-18
		2	-	$5 \cdot 10^{-4}$	-26	-20
	Pb	4	-	10^{-10}	-15	-10
		3	-	10^{-7}	-22	-25
		2	-	$5 \cdot 10^{-4}$	-38	-35
	Bi	2	-	10^{-10}	-20	-18
		1	-	10^{-7}	-30	-28
		0,5	-	$5 \cdot 10^{-4}$	-44	-40

Earlier [5], experimental dependences of hardness, electrical resistance, lattice parameter and internal stresses on the time of aging were obtained for electrodeposited metals (schematically shown in Figure 1). 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 [6], 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 aging.

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 internal stress 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 annealing. Accordingly, the type of coating structure - cellular or subgrain –does not undergo significant changes during aging either.

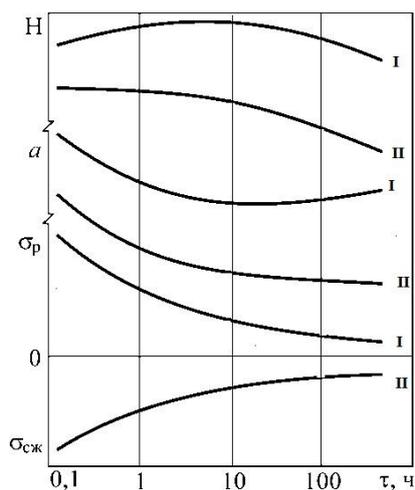


Fig. 1 Nature of the hardness change (H), crystal lattice parameter (a) and internal compression (σ_{com}) and tension (σ_{tens}) stresses of electrodeposited metals of the first (Ni, Fe, Cr), and third (Zn, Pb, Bi) groups in the process of aging

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 second 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 internal stresses. 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 internal stresses 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 [4].

Annealing of coatings leads to transformation of their structure.

If annealing is applied to refractory metals electrodeposited under hard conditions and having, as a consequence, a cellular structure, then at heating the metal, the cells transform into subgrains substantially misoriented relative to each other. In the sequel, the misorientation angles increase and polygonization thus plays the role of the initial stage of recrystallization. Further annealing leads to structural changes associated with enlargement of recrystallized grains and their abnormal growth. It is obvious that such changes are identical to the stages of collective and secondary recrystallization in deformed metals.

A different situation is observed when annealing refractory metals electrodeposited under average conditions and having a subgrain structure. In this case, two variants are possible: at relatively low annealing temperatures, polygonization competes with recrystallization but at heating to a higher temperature, it becomes the initial stage of the latter. By analogy with deformed metals [8], it can be assumed that in the first variant, the dislocations are redistributed by climb and cross-slip, and subgrains have low-mobile boundaries with low angles of misorientation, i.e. a structure is formed which is unfavorable for the formation of recrystallization centers.

In the second variant, due to the increasing role of the conservative slip of dislocations, new subboundaries are not strictly normal to the plane of sliding and have higher misorientation angles and a higher mobility than in the first variant. Migration of these boundaries leads to the fact that some of the formed subgrains transform into recrystallization centers.

In refractory coatings deposited under mild conditions and characterized by a monoblock structure, a classical development of polygonization processes is observed during annealing, when redistribution of dislocations leads to formation of subgrains separated by low-angle boundaries, and then, at recrystallization, new grains are formed with a more perfect structure than the initial grains, surrounded by high angle boundaries.

As for electrodeposited low-melting metals whose homologous return and recrystallization temperatures are below room temperatures, then in them, the structural changes characterizing polygonization and recrystallization take place immediately after electrolysis. Stabilization of the structure of low-melting coatings is in practically acceptable time achieved by annealing at temperatures of 100 - 150°C for 1.0-1.5 hours. Upon annealing, the initial structure of low-melting coatings, under the action of recrystallization changes considerably, regardless of whether it was a subgrain or a monoblock structure. New grains with high angle boundaries are formed. Because of that, after annealing, coatings have higher values of strength properties and increased protective properties compared to the electrodeposited state (Table 3).

Table 3. Changes in the hardness (HV, hPa) and corrosion rate (Vc mm / year) of electrodeposited low-melting metals at annealing.

Metals	Electrodeposition			Annealing, °C					
	Type of the structure	HV	Vc	50		100		150	
				HV	Vc	HV	Vc	HV	Vc
Zn	Subgrain	0.95	0.27	0.68	0.25	0.50	0.20	0.36	0.15
	Monoblock	0.73	0.20	0.52	0.22	0.40	0.20	0.35	0.15
Cd	Subgrain	0.62	0.25	0.41	0.23	0.32	0.20	0.29	0.18
	Monoblock	0.45	0.20	0.35	0.22	0.29	0.23	0.27	0.17

The question of relationship between polygonisation and recrystallization is of great practical interest primarily for refractory metals deposited with formation of a cellular structure or without it [8]. Indeed, the structure formed in the process of electrodeposition determines either the progress of recrystallization at subsequent annealing or its suppression by polygonization with a corresponding change in properties, i.e. polygonization can be used to prevent recrystallization in the cases, where the latter is undesirable. Consider in this context the character of changes in the mechanical and protective properties upon annealing of coatings having a different type of structure after electrocrystallization (Table 4).

Table 4. Changes in the hardness (HV, hPa) and corrosion rate (Vc mm / year) of electrodeposited refractory metals at annealing.

Metals	Electrodeposition			Annealing					
	Type of the structure	HV	Vc	(0.25-0.30)Tm		(0.30-0.35)Tm		(0.35-0.40)Tm	
				HV	Vc	HV	Vc	HV	Vc
Ni	Cellular	5.1	2.1	6.5	2.9	3.5	2.1	2.0	1.8
	Subgrain	4.5	1.8	5.2	2.5	4.5	2.4	3.1	1.5
	Monoblock	4.0	1.6	3.0	2.0	2.2	1.8	2.0	1.4
Cr	Cellular	7.0	1.6	10.5	2.4	6.2	1.7	4.6	1.3
	Subgrain	6.5	1.4	8.3	2.0	7.2	1.8	4.5	1.2
	Monoblock	5.8	1.1	4.8	1.3	4.6	1.1	4.2	1.0

3. Conclusion

The experimental results of determining the mechanical properties show that annealing of coatings with a cellular structure, at the early stages of polygonization, is accompanied by hardening, which is explained by redistribution of mobile dislocations and pinning them in a more stable configuration by atoms of impurity components that form part of the composition of industrial electrolytes [8]. At later stages of polygonization, the hardness decreases and at recrystallization annealing, softening of the coatings takes place.

If annealing is applied to coatings, which, after electrodeposition, have a subgrain structure, then the hardening effect at polygonization is less pronounced than in coatings with a cellular structure, since coatings with a subgrain structure are characterized by a lower density of dislocations compared with the cellular one. However, as mentioned above, due to the fact that in coatings with a subgrain structure, recrystallization is suppressed by polygonization, softening occurs at higher annealing temperatures.

Finally, in coatings with a monoblock structure, in accordance with the classical development of structural transformations at annealing, a decrease in hardness takes place at all stages of polygonization and recrystallization.

Analysis of the changes in protective properties (Table 4) shows that at the stage of pre-recrystallization annealing of coatings, the corrosion rate takes maximum values. The reason for such a behavior is associated with an increase in the number of corrosion centers in the course of polygonisation, first of all, the defects of the crystal structure: after thermal release of hydrogen from the vacancies, point defects are activated and the configuration of the dislocation structure in coatings with cellular and subgrain structures changes; subgrains separated by low-angle boundaries are formed in coatings with a monoblock structure.

Recrystallization annealing leads to formation of new grains separated by high- angle boundaries with a sharply reduced density of point and line defects, so that the protective properties of coatings increase. It should be noted that improvement of corrosion resistance in coatings with a subgrain structure is achieved at higher annealing temperatures than in coatings with a cellular structure. However, in all cases, the temperature of recrystallization annealing is bound by a limit, above which there occurs development of secondary porosity and deterioration of protective and structural properties.

Thus, by forming a different structure in the process of electrodeposition and subsequent heat treatment metal coatings with improved functional characteristics for particular operating conditions can be obtained.

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