

Cluster Structure Control of Coatings by Electrochemical Coprecipitation of Metals to Obtain Target Technological Properties

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Abstract. The article considers the possibility of controlling the macromolecular structure of ternary alloys in the form of compact coatings, which are obtained by electrochemical means. This method of obtaining metal clusters is more economical than from plasma one. The influence of the cluster structure of the synthesized coatings in the form of a triple alloy of polyligand complex electrolytes on their functional properties is shown. There are presented the results of testing coatings from this ternary alloy of different elemental and cluster composition for microhardness according to Vickers. The highest microhardness was obtained by the coating with the lowest molecular weight of the cluster, which provided a denser packing of atoms.

1 Introduction

The impetuous development of science and technology puts forward a number of requirements for the physical and mechanical properties of structural metals and alloys, as well as the modernization of equipment in the chemical industry, mechanical engineering and instrument making. At the same time, one of the main criteria for creating the latest functional materials is environmental friendliness and resource conservation of technological processes [1].

The performance of materials can be effectively improved by modifying the surface layer by applying electroplating coatings for the intended purpose. Low material consumption, technological simplicity of the process, the possibility of forming coatings of metals and multicomponent alloys, which are difficult to obtain by metallurgical or chemical methods, as well as wide variation in the properties of galvanic sludge depending on the nature of the precipitated components, determine the perspective of use the electrolyte alloys in industries [2, 3].

Electrolytic coatings based on chromium (VI), which are characterized by high hardness and wear resistance are often used to increase the strength of the working surfaces of parts. However, the aggressiveness and carcinogenicity of chromium electrolytes require additional measures to ensure the safety of personnel in the organization of the technological process, as well as special wastewater treatment [4]. Co-precipitation of platinum with Co, Mo, W is used to reduce the cost of platinum catalytic coatings.

2 Main Part

The properties and further target application of the synthesized electroplating coatings directly depend on the type of substance and its structure. Regarding the formation of the properties of the coating, it should be noted that metals are prone to the formation of clusters. Therefore, the question of the formation of the properties of the alloy is a question of the formation of the optimal cluster structure for the formation of the target properties. Electrochemical deposition is a convenient way to target the structure and composition of the cluster.

For solids, we can talk about the existence of a stable supramolecular structure, which is described by the concept of "cluster". The smallest supramolecular formation is a dimer. Nevertheless, the formation of clusters with a large coordination number is also recorded. There is a

method of instantaneous melt freezing to fix metal clusters. The number of atoms in stable forms of metal clusters is often proportional to "magic" numbers. The icosahedral series of clusters involves the grouping of 13, 55, 157 ... 2869 atoms (the shape of a cuboctahedron is also possible). The number 13 represents the shape of a regular icosahedron with triangular faces, where the 13th atom occupies a central position and is internal. The next layer will contain 42 atoms, and 13 others will be internal. However, stable clusters with a different number of atoms are also known. The discreteness of the periodicity of the number of atoms in the cluster is associated with the formation of certain geometric shapes of atomic lattices, which can be volume-centric (VCC), face-centric (FCC), hexagonal densely packed (HDP), etc. The minimum crystal lattice is called the basis. For hexagonal lattices, a number of values of the number of atoms in the cluster 13, 57, 153... are possible, which is characteristic, for example, of Co, but not typical of W and Mo. Although hexagonal packaging has a lower atomic density than face-centric packaging, it is more energy efficient for certain elements. For alkali metals, a number of 8, 18, 20, 34, 40, 58, 68... atoms in the cluster are known (these numbers can also be obtained by combining the number of electrons at the electronic levels). Superclusters can be similarly grouped from nanoclusters.

Regarding the properties of clusters, it is known that the melting temperature of metal dimers is 20–30 K and increases with the growth of basic clusters of matter. A cluster acquires the properties of an entire metal if the number of atoms in the cluster reaches a certain number, for example – 1000 for gold, but this is not always the case. There are probably some dependencies for different types of macromolecules. If we assume the relationship between the molecular weight of the cluster and the melting point of the substance, we can obtain the corresponding dependences in the first approximation (based on the melting point of clusters Au₄ – Au₁₀₀₀, Ag₁₀₀₀ for metals; and on a number of alkanes and melting points of some polymers for organic compounds

Fig. 1 shows that the dependences of the melting temperatures of metals and hydrocarbons are different, which indicates a different structure of the clusters.

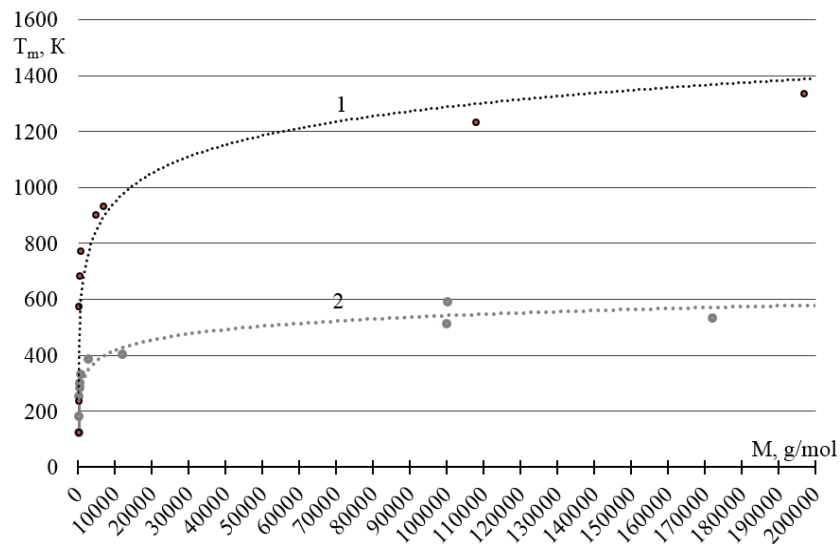


Fig. 1. The nature of changes in the melting temperatures of metals (1) and hydrocarbons (2) depending on the equivalent molecular weight of the cluster

For hydrocarbons, these are usually linear structures based on the dimer principle [5] (it has been observed that the linear structure of the carbon chain is similar to a linear metal cluster stabilized with ligands), for metals – three-dimensional structures based on crystal lattice. The obtained increase in melting temperatures can be described by logarithmic dependences: for metals – $T_m = 147.62 \cdot \ln(M) + 267.78$, for hydrocarbons – $T_m = 54.356 \cdot \ln(M) + 166.28$.

There are corresponding dependencies for other physicochemical properties of the substance, such as hardness. So, it is known that the microhardness of Nickel nanoparticles is several times higher than the hardness of the macro-level substance, and the tensile strength increases 5 times [6].

So, if it were possible to carry out the industrial formation of clusters of a given size and structure, it would be possible to obtain a substance with the desired physicochemical properties.

It is impossible to obtain individual coatings of tungsten and molybdenum from aqueous solutions, but they can be co-deposited in an alloy of complex electrolytes due to complexation with metals of the iron family (Fe, Co, Ni). A significant complication of the process of complexation in the studied system is the fact that tungstate and molybdate ions can act not only as complexing agents, but also as ligands, which leads to the emergence of heteronuclear complexes.

3 Materials and Research Methods

Coatings with cobalt-molybdenum-tungsten alloys were applied to steel substrates St. 3. Preparatory operations for surface treatment of samples were performed according to the generally accepted method in accordance with the nature of the studied material [7]. To eliminate external defects and reduce surface roughness before deposition of coatings was machined with sandpaper (grade 0).

In order to completely remove traces of fatty contaminants of various natures and improve the wetting of the metal with electrolyte, the surface was degreased in a solution of soda ash. Final surface preparation operations included: etching of steel samples, which was carried out in saturated solution of iron chloride (III) for several minutes); rinsing in distilled water and complete removal of residual water with filter paper.

For the preparation of electrolytes in the technology of deposition of alloy coatings cobalt-molybdenum-tungsten and other working solutions used certified brand reagents are chemically pure and pure for analysis

Cobalt-molybdenum-tungsten alloys were coated with citrate diphosphate and ammonium citrate electrolytes (Table 1).

Table 1. Compositions of electrolytes for electrolytic deposition of ternary alloys cobalt - molybdenum – tungsten

Electrolyte components	Concentration of range, [mol/dm ³]	Hydrogen index of solutions, [pH]
citrate-diphosphate		
CoSO ₄ ·7 H ₂ O	0.1–0.2	8.5–10.5
Na ₂ MoO ₄ ·2 H ₂ O	0.04–0.12	
Na ₂ WO ₄ ·2 H ₂ O	0.06–0.16	
Na ₃ C ₆ H ₅ O ₇ ·5,5 H ₂ O	0.2–0.3	
K ₄ P ₂ O ₇	0.3–0.7	
ammonia-citrate		
CoSO ₄ ·7 H ₂ O	0.2	5–8
Na ₂ MoO ₄ ·2 H ₂ O	0.03–0.7	
Na ₂ WO ₄ ·2 H ₂ O	0.06–0.1	
Na ₃ C ₆ H ₅ O ₇ ·5,5 H ₂ O	0.2–0.3	
NH ₄ Cl	0.3	
Na ₂ SO ₄	0.1	
H ₃ BO ₃	0.1	

Preparation of electrolytes was carried out according to the following method. The calculated mass of reagents was separately dissolved with stirring and heating in a small amount of double-distilled water, after which the solutions were mixed in sequence (based on a study of the laws of complexation):

– for citrate-diphosphate electrolyte: 1) sodium citrate solution (Na₃C₆H₅O₇ · 5.5 H₂O) is divided into two parts, to which sodium tungstate (Na₂WO₄ · 2H₂O) and molybdate (Na₂MoO₄ · 2H₂O) are added – first container; 2) to potassium diphosphate (K₄P₂O₇), gradually with constant stirring add

cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) – the second capacity; 3) at the next stage of preparation everything is mixed, but it is necessary to add the second solution to the first to prevent the formation of insoluble precipitates;

– for ammonia-citrate electrolyte: 1) sodium citrate solution is divided into two parts, to which sodium tungstate and molybdate are added – the first capacity; 2) ammonium chloride (NH_4Cl), sodium sulfate (Na_2SO_4) and cobalt sulfate – second capacity. Borate acid (H_3BO_3), the third, is dissolved in hot water ($95\text{ }^\circ\text{C}$); 3) then mix everything and leave the electrolyte to establish equilibrium for the formation of electrode complexes. All electrolyte solutions were adjusted to the required volume with double-distilled water. To establish equilibrium and the formation of complexes, the electrolytes were kept for 8–12 hours. The acidity of the electrolytes was adjusted by adding sodium hydroxide or sulfuric acid. The values of the hydrogen index were monitored with a pH-150 M device with an ECL-6307 glass electrode. The deposition process was carried out with temperature variations from 293 to 353 K.

Macro and microhardness of coatings of cobalt-molybdenum-tungsten alloys, as well as the substrate material (St. 3) was determined by pressing the diamond pyramid on the hardness tester PMT-3 at a load $P = 0.02 \div 0.2\text{ kg}$ and a holding time of 10 s. The experiment was performed after 24 hours of aging coatings at room temperature. H_v values were calculated by the formula:

$$H_v = \frac{1854 \cdot P}{d^2}, \quad (1)$$

d – diagonal of the pyramid indentation, μm .

Measurements were performed at a minimum of 3 points, followed by averaging of data, the confidence interval was ± 10 . The thickness of the alloy coatings for analysis was at least 30 m.

4. Research Results

The authors [8] determined the mechanical and tribological properties of cobalt alloy coatings with molybdenum and tungsten. Experiments of determining the dependence of static microhardness on the current density of electrodeposition of coatings showed that increasing the current density $j = 2\text{--}9\text{ A/dm}^2$ leads to a significant increase in microhardness of coatings in the range of $450\text{--}780\text{ MH/m}^2$. It should be noted that, despite the relatively low concentration of molybdenum in the coating (slightly above 6 wt. %), The quasi-static microhardness is quite high – MH/m^2 (Fig. 2).

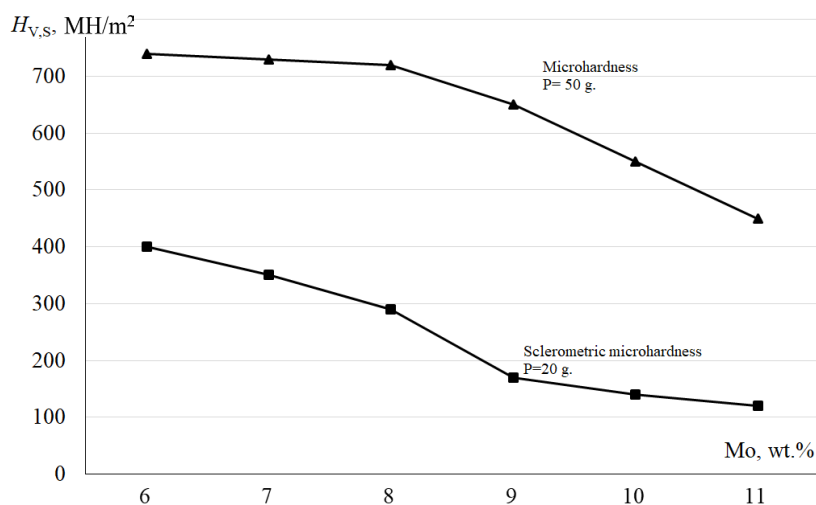


Fig. 2. Influence of molybdenum content in coatings on quasi-static and sclerometric microhardness

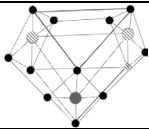


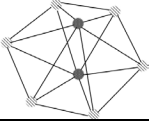

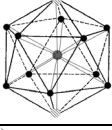
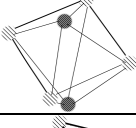
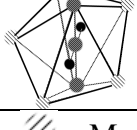
There is a correlation between static and dynamic microhardness, and there is a pronounced relationship between the two types of measured microhardness and the concentration of molybdenum in the coating. It should be emphasized that high values of microhardness are affected

not only by the increase in the concentration of molybdenum in the coating, but also the structure of the coatings, which in the complex leads to high values of microhardness.

We conducted a series of studies on the formation of electrochemical coatings with high physicochemical properties [9]. Coatings of different compositions were obtained. This means that the formation of clusters of different structure was achieved. Usually a cluster of matter is formed on the principle of denser packaging of atoms, as well as energy benefits. This principle is satisfied by an icosahedron with a central atom.

It can be predicted that the densest packing of atoms can be obtained by forming an alloy of metals belonging to different periods. Co-precipitation of Co–Mo–W alloys in different electrochemical regimes was studied, which allowed to obtain different contents of these metals in the alloy. According to the molar ratio, the possible composition of the smallest cluster was estimated by recalculating the molar ratio to numbers close to integers (table 2).

Table 2. Expected structure of clusters of obtained alloys and measured value of microhardness

№	Alloy-forming chemical elements, their atomic masses and molar ratios			Cluster base	H_V , [MH/m ²]
	Co. 59	Mo. 96	W. 184		
<u>1</u>	<u>89.7</u> <u>1.520339</u> 57	<u>5.9</u> <u>0.061458</u> 2	<u>4.9</u> <u>0.02663</u> 1		280
2	88.4 <u>1.498305</u> 52	<u>6.3</u> <u>0.065625</u> 2	<u>5.3</u> <u>0.028804</u> 1		300
3	<u>74.3</u> <u>1.259322</u> 46	<u>10.6</u> <u>0.110417</u> 4	<u>15.1</u> <u>0.082065</u> 3		350
4	<u>70.1</u> <u>1.188136</u> 32	<u>16.1</u> <u>0.167708</u> 6	<u>13.8</u> <u>0.075</u> 2		420
5	<u>68.3</u> <u>1.157627</u> 17	<u>18.8</u> <u>0.195833</u> 3	<u>12.9</u> <u>0.070109</u> 1	 and 5 Co pyramid around W	1100
6	<u>60</u> <u>1.016949</u> 10	<u>22.1</u> <u>0.230208</u> 2	<u>17.9</u> <u>0.097283</u> 1	 full cluster:	1150
7	<u>53.9</u> <u>0.913559</u> 16	<u>24.9</u> <u>0.259375</u> 4	<u>21</u> <u>0.11413</u> 2		1010
8	<u>50.2</u> <u>0.850847</u> 20	<u>26.1</u> <u>0.271875</u> 5	<u>23.7</u> <u>0.128804</u> 3		850

* – the most probable cluster is highlighted in bold; ● – Co, // – Mo, ● – W.

In this way, it was experimentally established that the general trend is an increase in the hardness of coatings in Co–Mo–W alloys with an increase in the total content of refractory components.

The macrohardness of the obtained alloys is $H_\mu = 3000\text{--}3680$ MPa, which is twice as high as in the substrates of St. 3 ($H_\mu = 1500\text{--}1600$ MPa). There is no universal proportionality between the macrohardness H_μ and the microhardness HB, but there is a ratio between them $H_V = (0.5\text{--}0.9) H_\mu$

(depending on the applied load), which allows to evaluate and compare the obtained experimental data.

Vickers microhardness should more accurately reflect the properties of the clusters from which the substance is constructed. So, for Co, Mo, W the parameter H_v (MH/m²) is 130, 150 and 350, respectively; H_v electrolytic coatings of solid chromium, depending on the conditions of production is in the range of 700–850 MH/m². For Co–Mo–W alloys, the microhardness varies from 280 to 1150 MH/m².

The highest strength of the alloy was obtained for the ratio of metals in the alloy Co–60 %, Mo–22.1 %, W–17.9 %, which allowed to form a dense cluster in the form of an icosahedron with a W atom in the center. The microhardness of the coating can be related to the molecular weight of the cluster (Fig. 3). These data show that the strength of clusters increases with decreasing molecular weight.

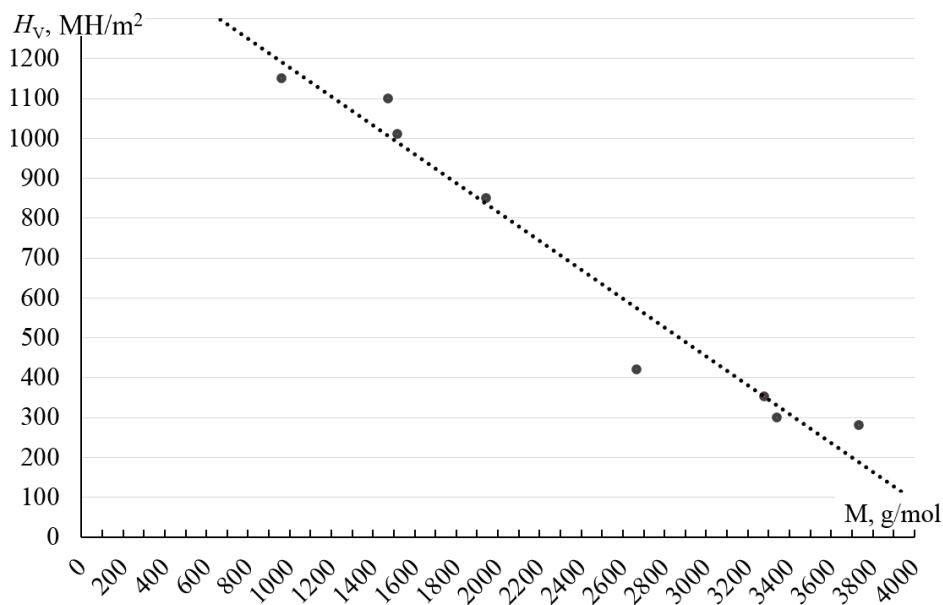


Fig. 3. The nature of the change in the microhardness of the ternary alloy Co–Mo–W from the equivalent molecular weight of the cluster

This dependence is described by the equation: $H_v = -0.3619M + 1539.4$. It turns out that the selection of clusters by electrochemical coprecipitation of different metals allows to obtain a higher packing density of atoms and a higher density of the material [9]. In the resulting compositions, W has the lowest content, and therefore is the base atom for the formation of this cluster structure. It's important to notice, it can form more uniform cluster structure, because the ratio of interatomic distances between the base and prism distance\planes of HDP it's ≈ 1.633 , that's why that is, the ratio is close to ideal (therefore, at elevated temperatures, it is capable of polymorphic transformation of HDP–FCC).

5 Conclusion

This way, it has been proved, that the possibility of controlling the macromolecular structure of ternary alloys in the form of compact coatings, which were obtained by electrochemically way from complex ammonium citrate and citrate diphosphate electrolytes.

For the deposition of high-quality coatings without internal stresses and microcracks, preliminary preparatory operations of the base material, composition and conditions of electrolysis, as well as final washing and drying operations are performed. It has been experimentally established that with increasing the total content of refractory components, the microhardness of alloy coatings, which are applied to a steel base with a thickness of more than 30 μm , increases.

However, the dependence of the microhardness of alloy coatings (according to Vickers) on the molecular weight of the cluster has an extremum, which is explained by the formation of the

optimal cluster structure. The highest strength of the alloy was obtained for the ratio Co–Mo–W (60 %, 22.1 %, 17.9 %, respectively), which allowed to form a cluster in the form of an icosahedron with a W atom in the center. Thus, the strength of clusters increases with decreasing molecular weight.

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