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Prognosis performance properties of metallic coatings

The paper considers various properties of nanocrystalline coatings. The methods of determining the surface tension of the deposited coating on the basis of the size dependence of their physical properties. It is shown that predict the mechanical properties of the coatings, their melting point, heat resistance, wear resistance, corrosion resistance, etc. It can be based on a theoretical evaluation of the surface tension. Currently there is no quantitative theory that allows to predict the desired properties of the coating, depending on the technological conditions, the materials used and the target cathodes, etc. Therefore, even high quality models proposed in this paper can help prevent a large volume of routine, but expensive works.

Key words: coating, nanostructure, surface tension, heat resistance, corrosion resistance, wear resistance.

Introduction

In the literature reviewed various methods of depositing nanostructured films [1]. However, most of the work is devoted to the traditional methods of film deposition: vapor deposition and plasma. The most promising for nanostructured coatings are vacuum ion-plasma methods: magnetron sputtering, ion and vacuum arc deposition. This is due to the fact that in addition to thermal factors there are other — high degree of ionization and the energy flux density of the particles.

In recent years, the concept has evolved high-entropy or multi-element alloys and coatings based on them [2–6].

The stability of the structure and composition, as well as high performance systems high-entropy create very attractive possibility of the formation based on these coatings in order to improve the surface characteristics or use them as protective films that prevent harmful impurities in the surface layers.

In the present work shows the possibility of predicting certain important properties of nanostructured coatings multielement.

The surface tension of the deposited coatings.

In [7, 8], we have demonstrated the possibility of experimental determination of the surface tension of coatings deposited by the size dependence of their properties.

We used the method of measuring the surface tension by determining the dependence of the microhardness on the thickness of the deposited coating. The dependence of the microhardness of the deposited coating on its thickness is described by the formula [7]:

$$\mu = \mu_0 \cdot \left(1 - \frac{d}{h}\right), \tag{1}$$

where μ — micro hardness of deposited coatings; μ_0 — micro hardness «fat» sample; h — thickness of the deposited coating.

The parameter d is associated with a surface tension σ formula [7]:

$$d = \frac{2\sigma\upsilon}{RT}. \tag{2}$$

Here σ — the surface tension of the bulk sample; υ — volume of one mole; R — gas constant; T — temperature.

The coordinates $\mu \sim 1/h$ ($1/h$ — reverse deposited coating thickness) obtained straight line the slope of which determines the d, and formula (2) is calculated as the surface tension of the deposited coating (σ).

One can use any size dependence of the properties of $A(r)$ coatings (electrical conductivity, magnetic susceptibility, etc.), which are described by the equation:

$$A(r) = A_0 \cdot \left(1 - \frac{d}{h}\right). \tag{3}$$

In [9] defined by the surface tension of the pure metals. The results are shown in Table 1.

Table 1

Surface tension of pure metals (M) at a temperature of 300 K [9]

M	σ, J/m^2	M	σ, J/m^2	M	σ, J/m^2	M	σ, J/m^2	M	σ, J/m^2	M	σ, J/m^2	M	σ, J/m^2
Li	0,152	Sr	0,730	Sn	0,205	Cd	0,294	Fe	1,508	Gd	1,285	Ac	1,023
Na	0,071	Ba	0,683	Pb	0,300	Hg	0,07	Co	1,463	Tb	1,331	Th	1,723
K	0,037	Al	0,633	Se	0,193	Cr	1,873	Ni	1,426	Dy	1,380	U	1,105
Rb	0,012	Ga	0,003	Te	0,425	Mo	2,573	Ce	0,777	Ho	1,434	Np	0,613
Cs	0,002	In	0,129	Cu	1,056	W	3,373	Pr	0,908	Er	1,470	Pu	0,610
Be	1,258	Tl	0,276	Ag	0,934	Mn	1,217	Nd	0,998	Tm	1,518	Am	0,973
Mg	0,623	Si	1,386	Au	1,036	Tc	2,173	Sm	1,025	Yb	0,797	Bk	0,998
Ca	0,818	Ge	0,931	Zn	0,399	Re	3,123	Eu	0,875	Lu	1,625	–	–

The surface tension of the coating Zn–Cu–Al was determined by the method described above. A quantitative analysis of the elemental composition of the composite coating was carried out on JEOL JSM-5910 electron microscope. Results stoichiometry calculation gave the following result: $Zn_{0,59}Cu_{0,01}Al_{0,40}$. The mean value of the surface tension is equal to: $\sigma_{Zn-Cu-Al} = 0{,}351$ J/m^2. The surface properties of coatings in most cases correspond to the principle of additivity. Then, the condition:

$$\sigma_{Zn_{0,59}Cu_{0,01}Al_{0,40}} = 0{,}59\sigma_{Zn} + 0{,}01\sigma_{Cu} + 0{,}40\sigma_{Al}. \tag{4}$$

Using the data in Table 1 for σ_{Zn}, σ_{Cu} and σ_{Al}, obtain $\sigma_{Zn-Cu-Al} = 0{,}\ 412$ J/m^2. Experimental and theoretical values for the coating Zn–Cu–Al were close to each other: ($\sigma_{Zn\text{-}Cu\text{-}Al} \approx 0{,}4$ J/m^2). Similar measurements were carried out for a number of multi-coatings. The equation of the type (4) turned out to be true for all investigated coatings.

This result leads to the following important conclusion: using the additive property of the surface tension, it is possible to select components of the coating so as to increase or decrease the surface tension of the coating compared to pure metals.

Forward and reverse Hall-Petch effect

Experimental study of mechanical properties of nanomaterials and nanostructured coatings showed that the tensile strength, hardness, many metals (Pd, Cu, Ag, Ni et al.) is significantly higher than the corresponding bulk analogs [9, 10]. Increased strength and hardness with decreasing grain size up to a certain critical size is typical for virtually all crystals. This follows from the known Hall-Petch equation that yield strength σ_T depends inversely on the average grain size d [10]:

$$\sigma_T = \sigma_M + kd^{-1/2}, \tag{5}$$

where σ_M — the limit strength of the single crystal; *k* — coefficient of some dimension.

Typically, Hall-Petch relationship (5) is performed for a large part of the nanomaterials studied only up to a certain grain size, while at lower values it is bucking the effects of hardness (strength) decreases with decreasing grain size.

Despite the large number of studies on the influence of the size factor on the mechanical properties of nanostructures, the physical mechanisms of this effect remain the subject of ongoing discussions. A comprehensive review of the problem is given in [11]. In [12], an equation for the yield point:

$$\sigma_T = \sigma_M + C\sigma d^{-1/2}. \tag{6}$$

Equation (6) coincides in shape with the Hall-Petch equation (5). However, the coefficients of proportionality differ in both formulas. In the case of the equation (6) the behavior of the yield strength of small particles is also determined by the size of their surface tension σ.

For small *d* Rusanov got asymptotic linear relationship [13]:

$$\sigma = Kd. \tag{7}$$

Here *K* — coefficient of proportionality.

Formula (7) is obtained on the basis of thermodynamic consideration and should be applicable to small objects of various nature. In this case, the equation (6) takes the form:

$$\sigma_T = \sigma_M + CKd^{1/2}. \tag{8}$$

Equation (8) represents the opposite effect Hall-Petch.

From equation (6) that the Hall-Petch equation begins to be violated from the moment when it begins to appear the size dependence of the surface tension. Calculated in [12] the critical radius values for most metals are shown in Table 2. Table 2 shows that the critical radius of pure metals is not more than 10 nm. For example, for tungsten critical radius is 8.4 nm, i.e. within experimental error, it coincides with the experimental value given in [11].

Thus, the results presented in Table 2 can be used to estimate the size of nanostructured metal coatings (especially multilayer) when replaced on the reinforcing properties of softening.

Table 2

Critical radius of pure metal particles (M)

M	r_k, *nm*	M	r_k, *nm*	M	r_k, *nm*	M	r_k, *nm*	M	r_k, *nm*	M	r_k, *nm*	M	r_k, *nm*
Li	1,4	Sr	8,3	Sn	2,0	Cd	1,9	Fe	3,1	Gd	7,6	Ac	7,1
Na	2,1	Ba	8,9	Pb	2,6	Hg	0,8	Co	2,8	Tb	7,5	Th	9,6
K	3,7	Al	2,2	Se	1,9	Cr	3,8	Ni	2,7	Dy	7,6	U	4,2
Rb	4,2	Ga	0,9	Te	3,5	Mo	6,5	Ce	5,4	Ho	7,8	Np	2,6
Cs	5,2	In	1,6	Cu	2,3	W	8,4	Pr	6,0	Er	7,8	Pu	2,7
Be	1,8	Tl	2,4	Ag	3,1	Mn	2,8	Nd	6,4	Tm	7,4	Am	6,4
Mg	3,1	Si	4,9	Au	3,3	Tc	5,1	Sm	6,3	Yb	6,5	Bk	5,2
Ca	7,0	Ge	4,0	Zn	1,5	Re	7,1	Eu	8,3	Lu	8,2	–	–

Evaluation melting temperature nanocrystalline coatings

In [14] it is shown that for pure metals with high accuracy, the relation:

$$\sigma = 0,7 \cdot 10^{-3} \cdot T_m, \qquad (9)$$

where T_m — melting point metal.

Taking into account the additive coating the surface tension, the equation (9) can be rewritten as:

$$T_m = 1,4 \cdot 10^3 \cdot \sigma \; (K). \qquad (10)$$

As an example, Table 3 shows the melting temperature multielement coatings obtained while spraying us various cathodes.

Table 3

Melting point multielement coatings obtained in argon

Coating	T_m, K	Coating	T_m, K
12Cr18Ni10Ti + Zr	1358	12Cr18Ni10Ti + Zn–Al	1537
12Cr18Ni10Ti + Zn–Cu–Al	1530	12Cr18Ni10Ti + Al	1602
112Cr18Ni10Ti + Fe–Al	1809	12Cr18Ni10Ti + Cu	2023

Steel melting temperature depends on their chemical composition, but is in the range (1450–1520) K. As seen from Table 3 the coating 12Cr18Ni10Ti + Al, 12Cr18Ni10Ti + Fe–Al and 12Cr18Ni10Ti + Cu on the melting temperature significantly superior to many steel.

Evaluation of heat resistance of nanocrystalline coatings

Currently refractory coating deposition is carried out mainly by arc or magnetron vacuum methods [15, 16]. Thus, various target compounds comprising metals such as chromium, titanium, zirconium in combination with non-ferrous metals. We investigated the coating deposited by ion-plasma method while spraying steel cathode 12Cr18Ni10Ti and composite cathodes. Method for determination of heat resistance is based on GOST 6130–71. The experimental results are presented in the table. 4.

From a comparison of the results of Tables 4 and 1, the conclusion: the greater the surface tension of the coating, the greater its heat resistance. If the heat resistance mark — ζ, then said mathematically can be expressed as a functional relationship:

$$\varsigma = f(\sigma) = C \cdot \sigma, \qquad (11)$$

where C — a constant.

Table 4

Loss of coating weight, resulting in an argon atmosphere, after heat treatment at 600 ºC for 100 hours

Coating	Weight oxidized coating, mg
A sample of uncoated, steel 45	56,8
12Cr18Ni10Ti + Zr	24,4
12Cr18Ni10Ti + Zn–Cu–Al	14,4
12Cr18Ni10Ti + Fe–Al	5,6
12Cr18Ni10Ti + Zn–Al	14,2
12Cr18Ni10Ti + Al	4,8
12Cr18Ni10Ti + Cu	2,7

Evaluation of corrosion resistance of nanocrystalline coatings

Anti-corrosion coatings obtained by magnetron method considered in [17–20]. In cases where the corrosion process proceeds as general corrosion, a change in the amount of metal can be used for evaluating corrosion rates in a process changing the amount of the reaction agent (oxidant), or one of the products of corrosion over time. Since the corrosion process is heterogeneous, the appropriate quantitative characteristics should be attributed to the surface of the unit.

Table 5 shows the corrosion rate at 600 ºC studied coatings, which was determined by the formula:

$$v_к = \Delta m / S \cdot t, \qquad (12)$$

where Δm — decrease (increase) in weight; S — area of the sample; t — time.

Table 5

The corrosion rate at 600 ºC the coating obtained in argon

Coating	The corrosion rate in g/m^2 h
A sample of uncoated, steel 45	2,84
12Cr18Ni10Ti + Zr	1,22
12Cr18Ni10Ti + Zn–Cu–Al	0,72
12Cr18Ni10Ti + Fe–Al	0,28
12Cr18Ni10Ti + Zn–Al	0,71
12Cr18Ni10Ti + Al	0,24
12Cr18Ni10Ti + Cu	0,13

From the comparison results tables 5 and 1, the conclusion: the greater the surface tension of the coating, the greater the corrosion resistance. If corrosion resistance mark — χ, then said mathematically be written as:

$$\chi = f(\sigma) = C_1 \cdot \sigma, \qquad (13)$$

where C_1 — a constant.

Evaluation of wear resistance of nanocrystalline coatings

The wear resistance of the coating is determined by the work of her destruction, which is equal to:

$$A = \sigma \cdot S, \qquad (14)$$

where S — area of the sample surface.

As an example, in Table 6 shows the results of calculation of the fracture coating (S = 1 m^2) from the experimental value of the surface tension σ.

Table 6

Job destruction of some multi-element coatings

Coating	Energy destruction coating, J
Zn–Cu–Al	2,43
Cr–Mn–Si–Cu–Fe–Al	7,11
Mn–Fe–Cu–Al	3,67

Conclusion

It follows from the above results that the majority of properties of the coatings is determined by their surface tension (surface energy). Using Table 1 and obtained in the ratio, it is possible to predict the performance properties of coatings based on their functionality.

Currently there is no quantitative theory that allows to predict the desired properties of the coating, depending on the technological conditions, the materials used and the target cathodes, etc. Therefore, even high quality models proposed in this paper can help prevent a large volume of routine, but expensive works.

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Металл жабындардың пайдалану қасиеттерін болжау

Мақалада нанокристалл жабындардың әр түрлі қасиеттері қарастырылды. Физикалық қасиеттерінің өлшемдік тәуелділігіне негізделген тұндырылған жабындардың беттік керілуін анықтайтын тәсілдер ұсынылған. Жабындардың механикалық қасиеттерін, балқу температурасын, қызуға, тозуға және коррозияға төзімділігін олардың беттік керілуін теориялық бағалау негізінде болжауға болатындығы көрсетілді. Қазіргі уақытта оларды алудың технологиялық шарттарына, катодтар мен нысаналардың және т.б материалдарына тәуелді болатын жабындардың қалаған қасиеттерін болжай алатын сандық теория жоқ. Авторлардың ойынша, мақалада ұсынылған сапалық модельдерде көп көлемді, жалықтыратын, бірақ қымбат жұмыстардан құтылуға септігін тигізуі мүмкін.

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Прогнозирование эксплуатационных свойств металлических покрытий

В работе рассмотрены различные свойства нанокристаллических покрытий. Предложены способы определения поверхностного натяжения осаждаемых покрытий на основе размерной зависимости их физических свойств. Показано, что прогнозировать механические свойства покрытий, их температуру плавления, жаростойкость, износостойкость, коррозионную стойкость и т.д. можно на основе теоретической оценки их поверхностного натяжения. В настоящее время, отмечено в статье, нет количественной теории, позволяющей прогнозировать желаемые свойства покрытий в зависимости от технологических условий их получения, используемых материалов катодов и мишеней и т.д. Поэтому, подчеркнуто авторами, даже качественные модели, предложенные в настоящей работе, могут помочь избежать большого объема рутинных, но дорогих работ.