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# High-temperature strength and corrosion resistance of alloy steel coatings

The investigated coatings were deposited by ion-plasma method while spraying cathode 12X18H10T steel and composite cathodes. It is shown that the larger the surface tension of the coating, the greater the heat resistance. Since the surface tension of the metal is proportional to its melting temperature, it follows that the high-temperature strength primarily depends on the melting point of the metal. The higher melting temperature metal, the higher the recrystallization temperature. As shown experimentally, that the greater the surface tension of the coating, the greater the corrosion resistance.

*Key words:* coating, heat resistance, corrosion resistance, surface tension, melting point, recrystallization.

## *Introduction*

Under high-temperature strength refers to the ability of the material to resist mechanical failure at high temperatures. Already in the 80s of the last century it became clear that you must not go towards the creation of special heat-resistant alloys and application technology to create a variety of heat-resistant coatings to parts of machines and mechanisms operating in extreme conditions. In subsequent years, the interest in heat-resistant materials and coatings continued to grow with the development of rocket and space technology, energy, etc.

If the product is working in an oxidizing atmosphere at a temperature (500..550) $^{o}$C without large loads, it is sufficient that they were only heat-resistant (for example, parts of heating furnaces).

To improve the heat resistance of the steel elements are introduced, which form oxides with oxygen dense lattice structure (chromium, silicon, aluminum). High heat resistance have silhromy, nickel-based alloys — nichrome, steel 08X17T, 36X18H25C2, 15X6CЮ.

Heat resistance — the ability of a metal to resist plastic deformation and fracture at high temperatures. Heat-resistant materials are used for the manufacture of parts operating at high temperatures when there is a phenomenon of creep.

In both cases there is a failure of metals, alloys and coatings. The destruction of the metals in supply of thermal energy is accompanied by accumulation of thermal stress, leading to an increase in the density of dislocations, various defects [1–3].

A special place in the complex of measures to ensure the smooth operation of the equipment is given the reliable protection against corrosion and wear.

Corrosion protection is for many years one of the topical issues that are of great importance for the industry and the national economy [4–8].

The need for measures to protect against corrosion is dictated by the fact that the losses from corrosion bring very big damage. According to reports, about 10% of the annual production of the metal used to cover irrecoverable losses due to corrosion and subsequent spraying. The main damage caused by the corrosion of the metal is associated not only with the loss of large amounts of metal but with the damage or failure of themselves metal structures and mechanisms, as a result of corrosion of various parts and components necessary to lose strength, ductility, impermeability, thermal and electrical conductivity, reflectivity ability and other necessary qualities.

To reduce the cost of metal, increasing the reliability and durability of machine parts and equipment, there are only two ways:

• the use of special steels and alloys;

• coating of articles during manufacture or repair.

Since the production of special steels and alloys due to the consumption of scarce and costly special materials and components, in all industrialized countries is not increasing production of special steels and alloys, using the most advanced technology for coating and hardening of parts.

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*Heat-resistant coating*

Currently applying refractory coatings made substantially vacuum arc or magnetron sputtering [9–21]. Thus, various formulations targets include metals such as chromium, titanium, and zirconium in combination with non-ferrous metals. [18] investigated the spray coating of chromium and aluminum in a nitrogen atmosphere. Fig. 1 and 2 show electron microscopic images and XPS and CrN coatings CrAlN.

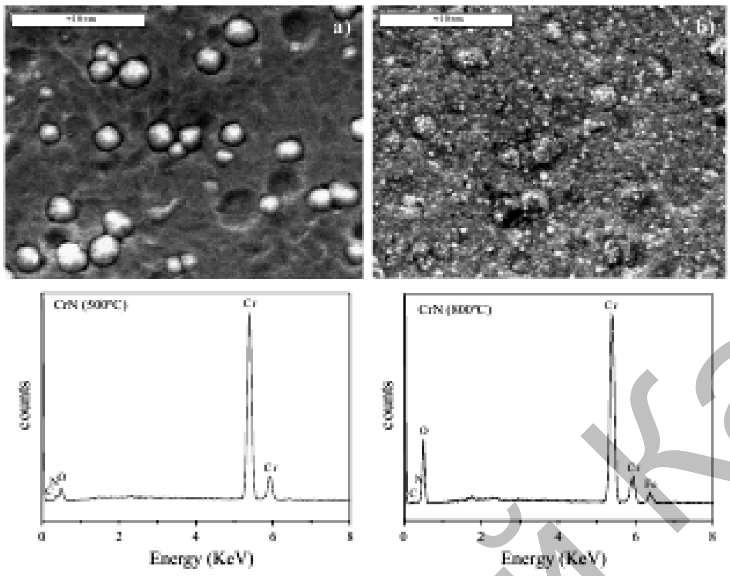


Figure 1. The electron microscopic image and XPS CrN coating
at 550 °C (a) and at 800 °C (b) [18]

Aluminum content of 15 at.%. This hydride phase underwent fragmentation (fig. 1 and fig. 2), which affects the mechanical and tribological properties of the coating. For the coating of CrN microhardness is 35.8 GPa and CrAlN coating — 34,8 GPa, i.e. hardness change slightly. The coefficient of friction decreases from 0.56 to 0.42 to the coating CrN coating CrAlN. However, CrAlN coatings have a high thermal stability (heat resistance) than CrN coating.

Industrial tests of coatings CrAlN, described in [18], showed improved performance tool steel AISI M2, in comparison with the coating CrN. This coating was even better than traditional titanium nitride coatings.

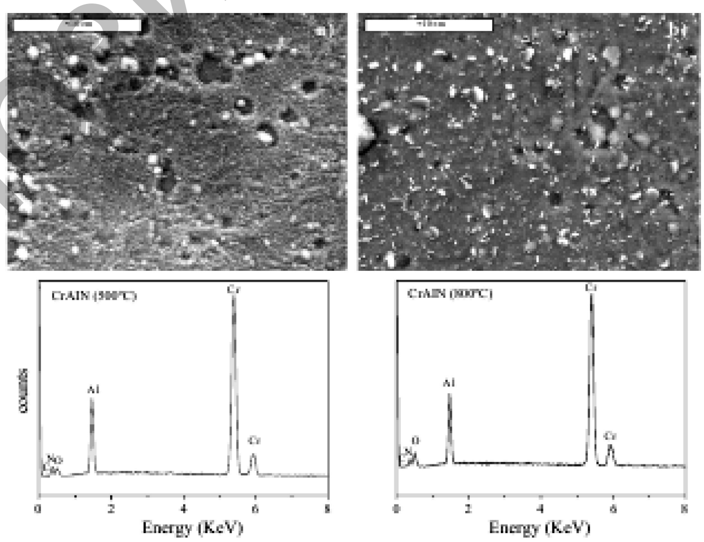


Figure 2. The electron microscope image and XPS CrAiN coating
at 550 °C (a) and at 800 °C (b) [18]

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*Anti-corrosion coatings*

Consider some of the anti-corrosion coatings obtained by magnetron sputtering [22–29]. [22] studied the erosion and corrosion of austenitic steel AISI 304L with the content of nitrogen in the coating to 0.55 wt.%. Corrosion of steel was estimated by weight loss by oxidation, and erosion of — Analysis damage steel reactor containing the suspension of 3,5% NaCl and quartz particles. The results of this work are shown in fig. 3.

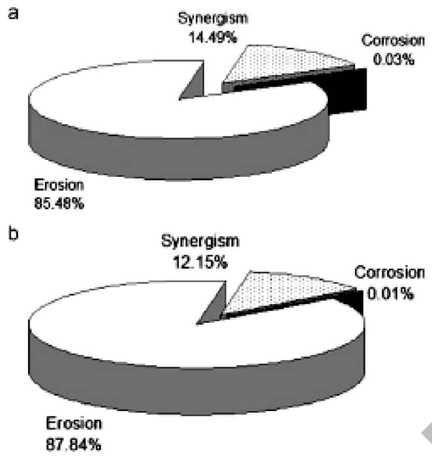


Figure 3. Synergism between corrosion and erosion of the steel AISI 304L without nitriding (a) and after nitriding (b) [22]

Suitable authors noteworthy because, in general, the synergy — is a property of the system, consisting in the fact that the joint cooperation ce elements (subsystems) provided an increase in their total effect to a value greater than the sum of the effects of these elements (subsystems) acting independently from each other. Hence, it enhances communication elements (subsystems), provided their coordinated functioning in the system.

Currently, treatment synergism devoted a huge amount of work: developed its own methodology, formulated the basic laws. However, this theory is based on general systems theory, which is so common, that does not give a quantitative description of the observed effects. Therefore, we will not refer to the synergies that the interpretation of experimental data.

In [24] showed that the corrosion resistance of aluminum alloy is anisotropic. This imposes certain constraints on its surface treatment, in particular on its polishing, which creates a certain dislocation density in the surface layer of the alloy.

Interesting is the work of [28], which investigated the corrosion resistance of the coatings FeCrVN on tool steel. It set a goal — to link the mechanical properties of the coatings at the nanoscale and their distribution over the area of the sample with corrosion-resistant coatings. Using this approach, one can predict the emergence of corrosion spots at an early stage and eventually predict early «corrosive breakdown» alloy.

In [29] studied magnetron coating niobium — niobium oxide. The coating showed very high resistance to corrosion, even in the enriched (heavy) water, obtained by proton irradiation. The mechanism of occurrence of corrosion resistance shown in fig. 4.

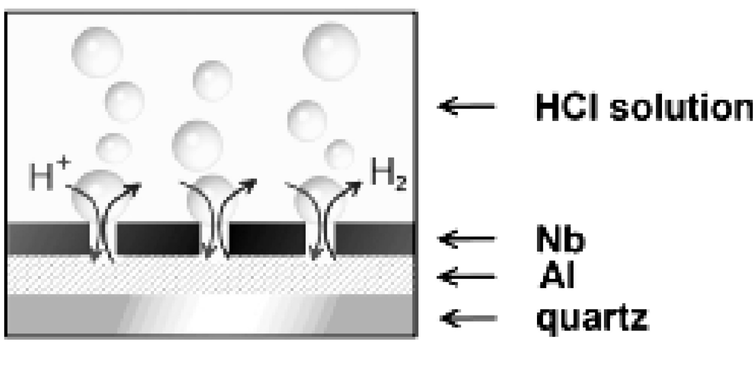


Figure 4. Schematic diagram of the formation of the diffusion barrier [29]

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Although niobium is chemically inert, but it has a coating of a columnar structure characteristic of single-phase films. Therefore, acid or enriched with honey water diffuses these «pillars». With simultaneous sputtering of niobium and niobium oxide, the latter being an amorphous structure, fills the space between the pillars and dramatically increases the value of the diffusion barrier.

*Heat resistance steel alloy coatings*

We investigated coatings were deposited by ion-plasma method while spraying cathode 12X18H10T steel and composite cathodes. Method for determination of heat resistance is based on GOST 6130-71 «Metals. Methods for determination of heat resistance» and coatings the determination of heat resistance of thermal spray coatings. Heat resistance is determined by exposing the coated specimens (and uncoated control) in an air oven for a predetermined time at a constant temperature, followed by weighing, examination, metallographic examination. Accelerated cyclic tests carried out by switching off the oven (10–50) hours. The results of the experiment are shown in table 1 and 2.

Table 1

**The weight loss of the coating produced in argon, after heat treatment at 600 °C for 100 hours**

| The coating | Mass of oxides of coating, mg |
|---|---|
| A sample of uncoated, steel 45 | 56,8 |
| 12X18H10T+Zr | 24,4 |
| 12X18H10T+Zn-Cu-Al | 14,4 |
| 12X18H10T+Fe-Al | 5,6 |
| 12X18H10T+Zn-Al | 14,2 |
| 12X18H10T+Al | 4,8 |
| 12X18H10T+Cu | 2,7 |

Table 2

**The weight loss of the coating produced in a nitrogen atmosphere after heat treatment at 600 °C for 100 hours**

| The coating | Mass of oxides of coating, mg |
|---|---|
| A sample of uncoated, steel 45 | 56,8 |
| 12X18H10T+Zr | 35,1 |
| 12X18H10T+Zn-Cu-Al | 20,7 |
| 12X18H10T+Fe-Al | 8,1 |
| 12X18H10T+Zn-Al | 20,4 |
| 12X18H10T+Al | 6,9 |
| 12X18H10T+Cu | 3,9 |

Comparison of the results in Tables 1 and 2 with the results of [30] follows the conclusion: the greater the surface tension of the coating, the greater the heat resistance. If the heat resistance mark — ζ, say something mathematically can be expressed as a functional relationship:

$$\varsigma = f(\sigma) = C \cdot \sigma, \qquad (1)$$

where C — a constant.

Since the surface tension of the metal is proportional to its melting temperature, it follows that the high-temperature strength primarily depends on the melting point of the metal.

*Corrosion resistance of alloy steel coating*

In cases where the corrosion process proceeds as general corrosion, to evaluate the corrosion rate can change the amount of metal used 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 referred to the unit surface.

Tables 3 and 4 shows the corrosion rate at 600 °C investigated coatings is determined by the formula:

$$v_к = \Delta m / S \cdot t, \qquad (2)$$

where $\Delta m$ — decrease (increase) in weight; $S$ — area of the sample; $t$ — time.

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Comparison of the results of Tables 3 and 4, with the results of [30] follows the conclusion: the greater the surface tension of the coating, the greater the corrosion resistance. If corrosion resistance mark — $\chi$, say something mathematically can be expressed as a functional relationship:

$$\chi = f(\sigma) = C_1 \cdot \sigma, \tag{3}$$

where $C_1$ – *a* constant.

Formulas 1 and 3 are mathematically equivalent. The only difference in the constants $C$ and $C_1$.

Table 3

**Corrosion Rates at 600 °C the coating obtained in argon**

| The coating | Corrosion Rates, $g/m^2 \cdot h$ |
|---|---|
| A sample of uncoated, steel 45 | 2,84 |
| 12X18H10T+Zr | 1,22 |
| 12X18H10T+Zn-Cu-Al | 0,72 |
| 12X18H10T+Fe-Al | 0,28 |
| 12X18H10T+Zn-Al | 0,71 |
| 12X18H10T+Al | 0,24 |
| 12X18H10T+Cu | 0,13 |

Table 4

**The corrosion rate at 600 °C the coating produced in nitrogen**

| The coating | Corrosion Rates, $g/m^2 \cdot h$ |
|---|---|
| A sample of uncoated, steel 45 | 2,84 |
| 12X18H10T+Zr | 1,76 |
| 12X18H10T+Zn-Cu-Al | 1,03 |
| 12X18H10T+Fe-Al | 0,40 |
| 12X18H10T+Zn-Al | 1,02 |
| 12X18H10T+Al | 0,34 |
| 12X18H10T+Cu | 0,19 |

We compare the results obtained with the corrosion rate of certain corrosion-resistant stainless steel (table 5).

Table 5

**The rate of corrosion of the most corrosion-resistant steels**

| Steel grade | Corrosion Rates, $g/m^2 \cdot h$ |
|---|---|
| Х23Н28М3Д3Т | 0,21 |
| Х23Н27М3Т | 0,26 |
| Х18Н12М3Т | 0,80 |

Comparison of the results of Tables 3 and 4 with Table 5 follows the conclusion: the greater the corrosion resistance of the coatings tested is not inferior to the most corrosion-resistant steel.

Moreover, any of the surfaces of tables 3 and 4 are significantly superior corrosion resistance of steel 45, which is widely used as a structural steel in the manufacture of: pinion shafts, crankshafts and camshafts, gears, spindles, tires, cylinders, cams and other normalized, improves, and subjected to heat treatment of superficial parts, which are required increased strength.

*Estimation of melting and crystallization of alloyed steel coatings*

Melting and solidification of the steel depends on its composition. Usually when calculating the $T_L$ and $T_S$ to make assumptions about the additive effect of dopants on these values.

Using the results of experimental determination of the surface tension of the multi-element surfaces, and results of the calculation of this value on the basis of elemental analysis can show that the average value of the surface tension is the value of the additive. In this case, the melting point of the coating can be estimated by the formula:

$$T_L = 1,4 \cdot 10^3 \cdot \sigma \ (K). \tag{4}$$

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The corresponding estimates are shown in Tables 6 and 7.

Table 6

**Melting point multielement coatings obtained in argon**

| The coating | $T_L$, *K* | The coating | $T_L$, *K* |
|---|---|---|---|
| 12X18H10T+Zr | 1358 | 12X18H10T+Zn-Al | 1537 |
| 12X18H10T+ Zn-Cu-Al | 1530 | 12X18H10T+Al | 1602 |
| 12X18H10T+Fe-Al | 1809 | 12X18H10T+Cu | 2023 |

Table 7

**Melting point multielement coatings obtained in a nitrogen atmosphere**

| The coating | $T_L$, *K* | The coating | $T_L$, *K* |
|---|---|---|---|
| 12X18H10T+Zr | 1259 | 12X18H10T+Zn-Al | 1098 |
| 12X18H10T+ Zn-Cu-Al | 1042 | 12X18H10T+Al | 1121 |
| 12X18H10T+Fe-Al | 1448 | 12X18H10T+Cu | 1445 |

As shown in tables 6 and 7, the melting point of the coatings obtained in argon lower than coatings obtained in a nitrogen atmosphere. Especially the big difference is observed for the coatings doped zirconium.

Melting steels depends on their chemical composition, but is in the range (1450–1520) K. As shown in tables 6 and 7 coating 12X18H10T+Al, 12X18H10T+Fe-Al and 12X18H10T+Cu, prepared under argon, at a temperature of the melting far superior to all steel.

## *Conclusion*

In this paper was not intended to produce heat-resistant and corrosion-resistant coatings. Using multielement coverage, we wanted to show the connection between the properties of the coating and the surface energy of the coating, as well as provide a methodology for evaluating the heat resistance and corrosion resistance of coated materials.

## References

1 *Davis J.R.* Heat Resistant Materials. — ASM International, 1997. — 591 p.

2 *Gao W., Li Zh. (Ed.)* Developments in High Temperature Corrosion and Protection of Materials. — Woodhead Publishing Ltd, 2008. — 658 p.

3 *Madhusudana Chakravarti V.* Thermal Contact Conductance. — Springer International Publishing Switzerland, 2014. — XVIII. — 260 p.

4 *Strutt I.E., Nicholls and Barbier B.* The prediction of corrosion by statistical analysis of corrosion profiles // Corrosion science. — 1985. — Vol 25. — No. 5. — P. 305–3l6.

5 *Provan J.W., Rodriguez E.S.* Development of a Markov description of pitting corrosion. — Corrosion (USA), 1989. — Vol. 45. — No. 3. — P. 178–192.

6 *Baroux B.* The kinetics of pit generation on stainless steel // Corrosion science. — 1988. — Vol. 28. — No. 10. — P. 969–986.

7 *Kondo J.* Prediction of fatigue crack initiation life based on pit growth // Corrosion science. — l989. — Vol. 45. — No. 1. — P. 7–11.

8 *Gao W., Li Zh. (Eds.)* Developments in High Temperature Corrosion and Protection of Materials. — Woodhead Publishing Ltd, 2008. — 658 p.

9 *Rea M.D., Gouttebaron R., Dauchot J.-P. et al.* Study of ZrN layers deposited by reactive magnetron sputtering // Surface and Coatings Technology. — 2003. — Vol. 174, 175. — P. 240–245.

10 *Zeman P., Cerstvry R., Mayrhofer P.H. et al.* Structure and properties of hard and superhard Zr–Cu–N nanocomposite coatings // Materials Science and Engineering, 2000. — A 289. — P. 189–197.

11 *Sheng S.H., Zhang R.F., Veprek S.* Phase stabilities and thermal decomposition in the $Zr_{1-x}Al_xN$ system studied by ab initio calculation and thermodynamic modeling // Acta Materialia. — 2008. — Vol. 56. — P. 968–976.

12 *Musila J. Karvankova P. Kasl J.* Hard and superhard Zr-Ni-N nanocomposite films // Surface and Coatings Technology. — 2001. — Vol. 139. — P. 101–109.

13 *Suna J., Musil J., Ondok V., Han J.G.* Enhanced hardness in sputtered Zr–Ni–N films // Surface and Coatings Technology. — 2006. — Vol. 200. — P. 6293–6297.

14 *Musil J., Danie R.* Structure and mechanical properties of magnetron sputtered Zr–Ti–Cu–N films // Surface and Coatings Technology. — 2003. — Vol. 166. — P. 243–253.

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15 *Musil J., Polakova H.* Hard nanocomposite Zr-Y-N coatings, correlation between hardness and structure // Surface and Coatings Technology, 2000. — Vol. 127. — P. 99–106.

16 *Daniel R., Musil J., Zeman P., Mitterer C.* Thermal stability of magnetron sputtered Zr–Si–N films // Surface and Coatings Technology. — 2006. — Vol. 201. — P. 3368–3376.

17 *Xueliang Q., Yanhong H., Yiping W., Jianguo Ch.* Study on functionally gradient coatings of Ti-Al-N // Surface and Coatings Technology. — 2000. — Vol. 131. — P. 462–464.

18 *Scheerer H., Hoche H., Broszeit E. et al.* Effects of the chromium to aluminum content on the tribology in dry machining using (Cr, Al)N coated tools // Surface and Coatings Technology. — 2005. — Vol. 200. — P. 203–207.

19 *Brizuela M., Garcia-Luisa A., Braceras I. et al*. Magnetron sputtering of Cr(Al)N coatings: Mechanical and tribological study // Surface and Coatings Technology. — 2005. — Vol. 200. — P. 192–197.

20 *Monclus M.A., Baker M.A., Tsotsos C. et al*. Investigation of the nanostructure and post-coat thermal treatment of wear-resistant PVD (Cr-Ti-Cu-B)N coatings // Surface and Coatings Technology. — 2005. — Vol. 200. — P. 310–314.

21 *Wang L., Niea X., Housden J. et al*. Material transfer phenomena and failure mechanisms of a nanostructured Cr-Al-Ncoating in laboratory wear tests and an industrial punch tool application // Surface and Coatings Technology. — 2008. — Vol. 203. — P. 816–821.

22 *Lotpez D., Alonso Falleiros N., Tschiptschin A.P.* Effect of nitrogen on the corrosion–erosion synergism in an austenitic stainless stee // Tribology International. — 2011. — Vol. 44. — P. 610–616.

23 *Liu R., Li X., Hu X., Dong H.* Surface modification of a medical grade Co-Cr-Mo alloy by low-temperature plasma surface alloying with nitrogen and carbon // Surface and Coatings Technology. — 2013. — Vol. 232. — P. 906–911.

24 *Lv Jinlong, Luo Hongyun.* Effect of surface burnishing on texture and corrosion behavior of 2024 aluminum alloy // Surface and Coatings Technology. — 2013. — Vol. 235. — P. 513–520.

25 *Lee Y.J., Lee T.H., Kim D.Y. et al.* Microstructural and corrosion characteristics of tantalum coatings prepared by molten salt electrodeposition // Surface and Coatings Technology. — 2013. — Vol. 235. — P. 819–826.

26 *Castillejo F.E., Marulanda D.M.,.Olaya J.J, Alfonso J.E.* Wear and corrosion resistance of niobium–chromium carbide coatings on AISI D2 produced through TRD // Surface and Coatings Technology. — 2014. — Vol. 254. — P. 104–111.

27 *Klemm J., Klemm S.O., Duarte M.J. et al.* Multi-element-resolved electrochemical corrosion analysis. Part I. Dissolution behavior and passivity of amorphous Fe50Cr15Mo14C15B6 // Corrosion Science. — 2014. — Vol. 89. — P. 59–68.

28 *Alvarez-Asencio R., Sababi M., Pan J. et al.* Role of microstructure on corrosion initiation of an experimental tool alloy: A Quantitative Nanomechanical Property Mapping study // Corrosion Science. — 2014. — Vol. 89. — P. 236–241.

29 *Skliarova H., Renzelli M., Azzolini O. et al.* Niobium–niobium oxide multilayered coatings for corrosion protection of proton-irradiated liquid water targets for [$^{18}$F] production // Thin Solid Films. — 2015. — Vol. 591. — P. 316–322.

30 *Yurov V.M., Laurynas V.Ch., Guchenko S.A., Zavatskaya O.N.* The surface tension of hardening coatings // Strengthening technology and coatings. — 2014. — № 1. — P. 33–36.

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## Қоспалы болат қабыршақтарының тотығу тұрақтылығы және қызуға төзімділігі

Мақалада композициялық катодтар мен 12Х18Н10Т болаттан катодты бірқалыпты ыдырату кезінде зерттелген жабындыларға ионды-плазмалық әдіспен енгізілгендігі туралы айтылған. Неғұрлым беттік керілудің жабындысы көп болса, соғұрлым оның қызуға төзімділігі жоғары болатындығы көрсетілген. Сондай-ақ металдың беттік керілуі балқудың қызуына пропорционал, осыдан қызуға төзімділік, біріншіден, металдың балқуы қызуына тәуелді. Металдың балқу температурасы неғұрлым жоғары болған сайын, соғұрлым оның рекристалдану температурасы да жоғары. Экспериментте көрсетілгендей, неғұрлым беттік керілуі жоғары болса, соғұрлым оның тотығуға төзімділігі тұрақты.

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## Жаропрочность и коррозионная стойкость легированной стальных покрытий

В статье отмечено, что исследованные покрытия наносились ионно-плазменным методом при одновременном распылении катода из стали 12Х18Н10Т и композиционных катодов. Определено, что чем больше поверхностное натяжение покрытия, тем больше его жаропрочность. Поскольку поверхностное натяжение металла пропорционально его температуре плавления, то отсюда следует, что жаропрочность, в первую очередь, зависит от температуры плавления металла. Чем выше температура плавления металла, тем выше его температура рекристаллизации. В работе экспериментально показано, что чем больше поверхностное натяжение покрытия, тем больше его коррозионная стойкость.

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