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Anti-corrosion wear-resistant coatings on parts of oil field equipment

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Abstract

The paper reports on the preparation of ion-plasma anti-corrosion and wear-resistant coatings Cr-Mn-Si-Cu-Fe-Al and Cr-Mn-Si-Cu-Fe-Al-Ti. The first coating is prepared using the composite cathode. The second coating is prepared by simultaneous sputtering of composite and titanium cathodes in nitrogen atmosphere. In both cases the cellular microstructure of coatings is observed. The nanohardness of coating Cr-Mn-Si-Cu-Fe-Al, which is 7.4 GPa, is nearly two times as high as the nanohardness of titanium being 4.1 GPa and almost the same as for multilayer film Ti/α-C:H which is 8.0 GPa. The corrosion rate in sulfuric acid (53 wt.%) is about 0.02 mm/year. The nanohardness of coating Cr-Mn-Si-Cu-Fe-Al+Ti, being 14.2 GPa, is nearly equal to the nanohardness of amorphous ribbon Zr-Cu-Ti-Ni, being 14.5 GPa or silicon (100), which is 14.8 GPa. The corrosion rate in sulfuric acid (53 wt.%) is less than 0.01 mm/year. The multilayer film of Ti/α-C:H and amorphous tape Zr-Cu-Ti-Ni are used as abrasives, but their preparation is ten times more expensive than the proposed coatings.

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Keywords: anti-corrosion coating; wear-resistant coating; composite cathode; nanohardness; cellular structure

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1. Introduction

The problem of corrosion and protection of oil and gas field equipment is becoming more urgent and vital. Primarily, this is due to the growth in oil and gas field development and gas condensate development (particularly

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offshore) that contain corrosive components. Besides, intensive methods of oil production, transportation and refining increase wear rate of oil field equipment.

More efficient technologies reducing corrosive wear and increasing lifetime of downhole and other types of oilfield equipment are introduced as long as existing technologies are of low efficiency.

For the time being, all industrial countries are developing modern anti-corrosion coatings for cheaper grades of steel [1-4] instead of developing anticorrosive steel and alloys.

In [7] corrosion resistance of coatings FeCrVN on tool steel is studied. The goal of linking the mechanical properties of coatings at the nanolevel and coating distribution on the sample with corrosion resistance of coatings is set in this work.

Using this approach, the emergence of corrosion spots at early stage can be predictable and, eventually, an early "corrosive breakdown" of an alloy can also be predicted.

Magnetron coatings of niobium - niobium oxide are investigated in [8]. These coatings show a very good resistance to corrosion even in rich (heavy) water obtained by proton irradiation. In recent years, researchers have been interested in high entropy alloys and coatings based on them [5-8]. In this case, the coatings with high performance are obtained.

The findings on the structure and properties of coatings Cr-Mn-Si-Cu-Fe-Al and Cr-Mn-Si-Cu-Fe-Al+Ti are discussed in this paper.

2. Experimental

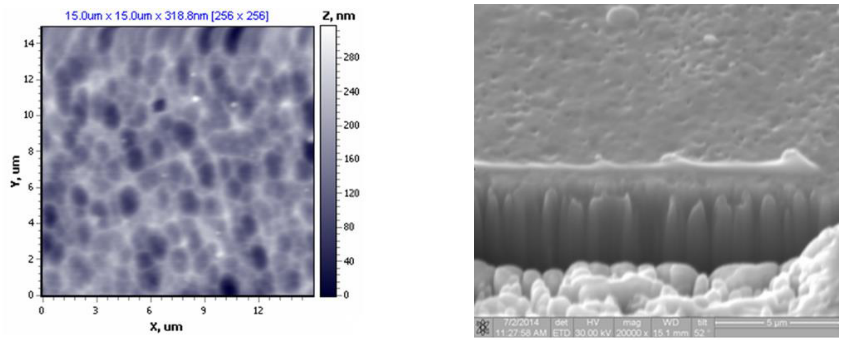
The cathodes composed of Cr-Mn-Si-Cu-Fe-Al were used, these cathodes being received by induction melting method. The coatings were deposited by ion-plasma method in the vacuum unit NNV-6.6I1 on a sample of steel 12Cr18Ni10Ti. Coatings Cr-Mn-Si-Cu-Fe-Al+Ti were obtained by simultaneous sputtering of cathode Cr-Mn-Si-Cu-Fe-Al and a titanium cathode.

The electron-microscopic study was performed on a scanning electron microscope MIRA 3 produced by TESCAN. The research was carried out at an accelerating voltage of 20 kV and a working distance of approximately 15 mm. Four shots at four points on the surface were taken, zooming being of 245-fold, 1060-fold, 4500-fold and 14600-fold for each sample. Besides, an energy-dispersive analysis at 4 points of each sample was conducted.

The thickness of the coatings and their elemental composition was measured using electron microscope 200 Quanta 3D. The phase composition and structural parameters of the samples were performed on diffractometer XRD-6000 X in CuKα-rays. The analysis of the phase composition, the size of coherent scattering regions and the internal elastic stresses ($\Delta d/d$) was carried out using databases PCPDFWIN and PDF4+ as well as program POWDER CELL 2.4. The nanohardness of coatings was determined for the samples by Oliver-Pharr nanoindentation system method and Berkovich indenter with a load of 1g and dwell time of 15 sec. The corrosion resistance of the coatings was determined in accordance with GOST 9.908-85.

3. Results of experiment

The stainless steel substrate was coated with Cr-Mn-Si-Cu-Fe-Al in gaseous nitrogen for 40 min. Fig. 1a shows the image of the coating obtained in an atomic force microscope. Fig. 1b shows a cross section of 1 micron coating produced by a focused ion beam.



a b

Fig. 1. (a) AFM image of Cr-Mn-Si-Cu-Fe-Al coating and (b) its cross section.

Table 1 shows the results of the sample phase composition research.

Table 1. Phase composition of Cr-Mn-Si-Cu-Fe-Al in nitrogen gas environment.

Coating	Phase detection	Phase content, vol.%	The lattice parameters, Å	The size of CSR, nm	Δd/d $*10^{-3}$
Cr-Mn-Si-Cu-Fe-Al	$FeN_{0.0324}$	60.6	a = 3.598	103.4	3.46
	$TiN_{0.31}O_{0.31}$	39.4	a = 4.211	25.6	5.14

The nanohardness of coating Cr-Mn-Si-Cu-Fe-Al in nitrogen gas environment, which is equal to 7.413 GPa was determined and the flow modulus of this coating being equal to 169.5 GPa was determined as well. The fluidity is 0.68%. The coating relaxation is 0.05%. Poisson's number for coating Cr-Mn-Si-Cu-Fe-Al in nitrogen gas environment, being approximately equal to 0.30, was determined for all these parameters to be defined. The corrosion rate in sulfuric acid (53 wt. %) was about 0.02 mm/year. Cr-Mn-Si-Cu-Fe-Al+Ti coating structure obtained by simultaneous sputtering the composite and titanium cathodes is shown in Fig. 2. It is similar to the structure of coating Cr-Mn-Si-Cu-Fe-Al. The nanohardness of coating Cr-Mn-Si-Cu-Fe-Al+Ti is equal to 14.2 GPa. The corrosion rate in sulfuric acid (53 wt. %) was less than 0.01 mm/year.

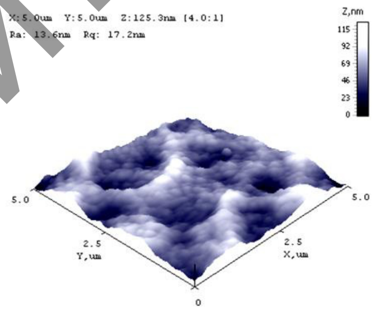


Fig. 2. AFM image of Cr-Mn-Si-Cu-Fe-Al+Ti coating in nitrogen environment.

4. Discussion

Fig. 1b shows that coating Cr-Mn-Si-Cu-Fe-Al is of a columnar structure, which is characteristic of single-phase coatings and described by Thornton model [9]. Single-phase structures were observed in coatings V-Zr-Nb-Hf in

[10]. However, there are two phases in this case (Table 1). This suggests that the mechanism of columnar structure is not described by the model of Thornton. Further, we shall consider different generating mechanisms of these structures. Not without interest is the comparison of the results obtained with the specific data on the nanoindentation of other materials. These data are presented in Table 2.

Table 2. Properties of the materials according to the calculated nanoindentation [11].

Material	H, GPa	E, GPa	R, %
Copper	2.1	121	14
Titanium	4.1	130	19
The multilayer film Ti/α-C:H	8.0	128	34
The amorphous ribbon Zr-Cu-Ti-Ni	11.5	117	42
Silicon (100)	11.8	174	62
Thin film Ti-Si-N	28.4	295	62

The following notations are used in Table 2: *H* is hardness, *E* is Young's modulus, and *R* is an elastic recovery.

We obtained the result of 7.413 GPa. Table 2 shows that the nanohardness of coating Cr-Mn-Si-Cu-Fe-Al is almost 2 times higher than that of titanium and is almost the same as for multilayer film Ti/α-C:H. However, preparation of such film is more difficult than that of coating Cr-Mn-Si-Cu-Fe-Al with a composite cathode. The nanohardness of coating Cr-Mn-Si-Cu-Fe-Al+Ti (14.2 GPa) is nearly equal to the nanohardness of amorphous ribbon Zr-Cu-Ti-Ni (14.5 GPa) or silicon (100) (14.8 GPa).

Thus, the relationship between the coating structure and its hardness is revealed. A coating hardness increases for ordered structures. The relationship between the coating hardness and its structure was discussed in [12].

The cellular substructure is often formed in solidifying due to concentration supercooling (Fig. 3).

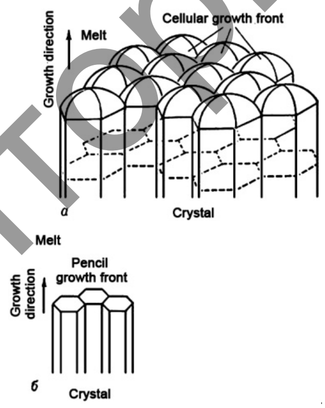


Fig. 3. (a) The cellular structure and (b) pencil (columnar) structure [13].

If a supernatant liquid zone having impurity elements is formed with a cellular structure formation at the solidification front, then the impurity segregation occurrence at the cell boundary arises due to the lateral diffusion impurities flux from the top of the growing projection. The amount of impurity reaching the border of the cell is difficult to measure, this amount depending on the depth of the recess between the cells. The recesses between the cells become deeper as supercooling rises, this being led to the enrichment of cell boundaries with impurity because of impurity diffusion from the top of the cell. The concentration of impurities on the boundary can be several times higher than the concentration in the center of the cell.

The cellular structure consists of a series of parallel elements having the shape of rods and being spaced in the direction of crystallization (Fig. 3). The rods are of a cross sectional shape of regular hexagons and the structure at the solidification front is an aggregate of hexagonal cells. The upper free surface of crystals having such a structure is wavy.

In this case (Fig. 1 and 2) concave cells are observed. A negative gradient of impurity concentration makes it possible.

To address the issue of self-organization of the coating structural units let us consider Bénard cell model. Bénard cells are ordered hexagonally or having a form of cylindrical shafts convection cells in viscous medium with a vertical temperature gradient (Fig. 4).

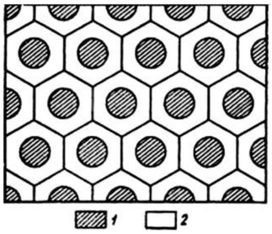


Fig. 4. Scheme of Bénard cells:1 – upward movement, 2 – downward movement.

Bénard cells are one of the three standard examples of self-organization along with the laser and the Belousov-Zhabotinsky reaction. The temperature gradient is the control parameter of self-organization. Heating of an initially homogeneous liquid layer results in diffusion due to density variation.

In overcoming some critical value of the gradient, diffusion does not cause thermal uniformity by volume. Cylindrical shafts rotating in opposite directions (as a clutch gear) originate. The second critical transition originates under gradient temperature increase. In order to accelerate the diffusion, each shaft falls into two smaller shafts. As the control parameter increases the shafts are broken down, the turbulent chaos arises in the region. Analyzing processes in Bénard system the Rayleigh number is selected as a control parameter: $\mathrm{Re} = gL^3 bdT/va,$ where g is a gravity factor, L is a specific size, b is a coefficient of volume expansion, dT is a temperature gradient, v is a kinematic viscosity, and a is a coefficient of thermal environment.

For the formation of Benard cells it is necessary that the number of Re = 10 ... 20. Let us estimate the Rayleigh number in this case: L ≈ 10^{-3} m, b ≈ 11 10^{-6} K^{-1}, dT ≈ 103 K, ν ≈ 10^{-6} Pa m^3 s/kg and ≈ 8 10^{-6} m^2/s, we obtain Re ≈ 14. Thus, the formation of Benard cells in the formation of coatings Cr-Mn-Si-Cu-Fe-Al+Ti is possible.

Let us consider the formation of a cellular structure using the model of YADS-cellular dislocation structure [14]. Plastic deformation of crystals (and coatings) is accompanied by the formation of strain relief on the surface, reflecting the strain localization process in the crystal on the meso, micro and nanoscale level. YADS begins to take shape in a deformed crystal at the end of the second and beginning of the third stage of metals strain hardening curve and finishes at the end of the third stage (see [14] and the references therein). With further deformation of the material a fragmented dislocation structure - FDR is formed (at the fourth and fifth stages of strain hardening curve). YADS is believed to be a process of self-organization of dislocations in a multiple slip. A certain criteria should be satisfied for its occurrence (as is in case of Bénard cells), this criteria linking reproductive factors, immobilization and annihilation of dislocations.

In the process of ion-plasma coating and cooling, strained states are formed in the coating, these states possibly being the sources of dislocations throughout the volume of the deposited coating [15]. A sharp increase in the microhardness of the formed film is the result of dislocation hardening of the coating material.

5. Practical applications

The technique of applying ion-plasma corrosion resistant coatings can be divided into several stages, namely, control, preparation, parts cleaning, corrosion-resistant layer spraying and control stages.

The control step involves checking accompanying papers to verify the material grade and the parts in a lot subjected to anti-corrosion treatment. In addition the absence of mechanical damage to the parts is checked. The hardness of a test specimen is measured. The second step includes preparing the in-process parts and the coating unit chamber. The parts are washed with gasoline, wiped dry, then washed with alcohol and wiped dry again. The chamber from the inside is treated with gasoline and alcohol, and the chamber is pumped to the pressure of (2-5) × 10^{-2} Pa. The parts cleaning is carried out in the chamber by glow discharge first, the voltage of (3-6) kV is applied over a period of 5 or 10 minutes followed by ionic cleaning of the parts. The chamber is evacuated to the pressure of 6×10^{-3} Pa, argon gas is fed to the pressure of $(4\text{-}6)\times10^{-2}$ Pa, and the discharge voltage of (700-800) V is set. The ionic cleaning is carried out over a period of 15-20 min. When the pressure of 6×10^{-3} Pa in the chamber is reached, nitrogen to the pressure of $(6\text{-}9)\times10^{-2}$ Pa is fed into the chamber, the voltage of (900-1000) kV is set and the coating is sputtered. It takes 2 hours to complete the process.

In the procedure described the parts subjected to coating were those of mining equipment. Parts testing had been carried out at the enterprises of JSC "Mittal Steel Temirtau" for 8 months, as well as in the laboratory in excited environment by the method described in GOST 9.008-82 ESZKS (Table. 3).

Table 3 shows that the developed technology of anti-corrosion coatings gives good results of corrosion resistance.

Table 3. Parts characteristics of JSC "Mittal Steel Temirtau" with anticorrosive coatings.

Name of part	Anti-corrosion coating	Service life increase
Stem, Steel 40X	Cr-Mn-Si-Cu-Fe-Al+Ti	5 times
Nipple 12, Steel 35	Cr-Mn-Si-Cu-Fe-Al+Ti	15 times
Clutch 12, Steel 35	Cr-Mn-Si-Cu-Fe-Al+Ti	15 times
RU11.008-01 Coupling, Steel 35	Cr-Mn-Si-Cu-Fe-Al+Ti	15 times
HLG Cork 30, Steel 35	Cr-Mn-Si-Cu-Fe-Al+Ti	15 times
Elbow 10NG12, Steel 35	Cr-Mn-Si-Cu-Fe-Al+Ti	15 times
Cheek right 9.00.00.018 Steel 3	Cr-Mn-Si-Cu-Fe-Al+Ti	15 times

6. Conclusion

Comparing the obtained nanohardness of (7.413 GPa) with the familiar solid materials shows that the nanohardness of coating Cr-Mn-Si-Cu-Fe-Al is almost 2 times higher than the titanium nanohardness and almost the same as for multilayer film Ti/α-C:H. However, preparation of such film is more difficult than that of coating Cr-Mn-Si-Cu-Fe-Al with a composite cathode, which can be easily obtained by induction melting.

The formation of a cellular structure of coating Cr-Mn-Si-Cu-Fe-Al-Ti deposited in the nitrogen environment is not a trivial issue. The formation of the structure fits into these models: concentration supercooling in the presence of the radial gradient of titanium nitride and chromium impurity concentration; Bénard cells, being caused by the presence of the vertical temperature gradient; cellular dislocation structure associated with the presence of plastic strain in the coating.

The results of this work were used in the development of technology and the application of anti-corrosion wear-resistant coatings on parts of mining and oilfield equipment. It is possible to increase the service life of the equipment and give a significant economic effect.

In the long run, it is possible to replace scarce and expensive grades of steel used for manufacturing various parts of mining and oilfield equipment with cheaper steel coatings being proposed.

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