

Effect of Nanocomposite Coatings on the Basis of Fe-Cr-Ni Nitrides on Tribotechnical Properties of Metal-Polymeric of Friction Pair " Steel 38XH3MΦA – Polyamide ΠA-66 "

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Abstract – The effect of nanocomposite coatings on the basis of Fe-Cr-Ni-N and Fe-Cr-Ni, produced on samples from steel 38XH3MΦA using magnetron deposition with heating of a substrate to 300 °C at ionic bombardment and without it on nanohardness and wear resistance of metallic components is studied in a friction pair with a rider from polyamide – ΠA-66. The nature of tribomechanical behaviour is established depending on epy regime and coating deposition condition. The correlation between The structure-phase state (the phase structure, lattice parameter, medium-sized of grains and internal elastic stresses) and the properties of coatings is discussed.

1. Introduction

Broadening the field of application in engineering of metal-polymeric friction pairs makes an actual problem of increasing there wear resistance. One of the ways of solution of this problem is improvement of properties of polymers in the development of new composite materials. Another, rather new and promising method is modification of the surface layer of conjugate metal parts [1–3], which play an important role in the operation of a friction pair. They stiffen a unit of friction, remove heat, support given a geometry of the friction surface. Depending on the working conditions the metallic parts usually wear according to the mechanism of hydrogenous wearing [4, 5]. To increase the service life of a metal-polymeric friction pair used as seals in petrochemical and food-processing industries, high-performance high-strength steels and hard alloys are used. The characteristics of these friction pairs depend not only on the physical-mechanical properties of these materials, but also on the morphology and the structural – phase condition of the surface layer [2, 6].

The purpose of the present work is the research of the effect of nanocomposite coatings on the basis of Fe-Cr-Ni-N and Fe-Cr-Ni produced on the working surface of metallic components from the steel 38XH3MΦA by the vacuum magnetron method in

different structural – phase conditions on tribotechnical and mechanical properties in a friction pair with a polyamide ΠA-66 in conditions of hydrogenous wearing.

2. Experimental

Deposition of coatings carried out on vacuum set up such as "Quantum" [7] using a magnetron of a direct current with the target diameter of 120 mm made from a stainless steel 12X18H9. The power of the magnetron discharge was 2,5 kW. An argon or an argon and nitrogen mix was used as a working gas in the deposition of nitride coatings. The total pressure p_0 of the working gas was equal to 0,3 Pa. Before the deposition a vacuum chamber was evacuated up to the pressure of residual gas $2 \cdot 10^{-3}$ Pa. A molybdenum heater was used for heating samples deposition. Temperature was measured using a chromel-alumel thermocouple an accuracy of ± 5 °C. The coating formed on samples 6×6×15 mm in size from steel 38XH3MΦA, which was exposed to oil quenching and tempering from temperature the 850 °C and letting down on air at 500 °C. The faces of the samples, intended for deposition of coatings, were ground and polished up to $R_r=0,08$ μm. Before the deposition in an evacuated chamber the samples were degreased by organic solvents, rinsed by alcohol and drying. Coatings were produced on substrate heated up to 300 °C, which were arranged in parallel to the targets of the magnetron at a distance of 50 mm. Part of the coatings was formed at ionic bombardment with the bias $U_s=-100$ V. The thickness of deposited coatings was 15 ± 5 μm. For comparison the crew of samples (H0) without coatings was investigated.

Friction and wearing tests were carried out using a machine under the scheme "the rotated disk – fixed a contact". Samples with the coating were used as contact. The rider is a disc with a thickness of 10 mm and a diameter of 50 mm from ΠA-66 polyamide. Wear was carried out in the air in the condit-

ions of dry slip rotated cylindrical rider with at a speed of 100 rpm relative to a fixed sample at a load of 300 N, applied normal to the coating surface. Wear resistance of the coatings was determined as the relation of wear time to the loss of weight of the coating. Coating thickness was calculated using the weighing data before and after the deposition and also controlled using an optical microscope BMG-160.

X-ray analysis carried out using a diffractometer DRON-3 in the interval of angles ~ 20 – 140 degrees at FeK_α radiation. To determine the crystalline lattice parameter (a), size of area of coherent scattering (d), microstresses (σ_i) and the texture of coatings, the main characteristic of diffraction peaks were used [8].

3. Results and discussion

Using X-ray analysis it is shown that there are two main phases of the α -Fe(Cr,Ni) having bcc lattice and γ -Fe(Cr,Ni) with fcc structures in the ratio 3:2 in the coatings produced on the basis of stainless steel 12X18H9 using magnetron method. The addition of nitride ($p_{\text{N}_2}=0,03$ Pa) to the working gas mixture results in the change of the phase structure of a coating. The volume fraction of the γ -Fe(Cr, Ni) increases up to 93 %, the α -Fe(Cr, Ni) disappears absolutely. Nitrides (Fe, Cr, Ni)₃N (ε -phase) with a close-packed hexagonal lattice and (Fe, Cr, Ni)₄N (γ' -phase) with a cubic lattice B1 (type NaCl) appeared in the quantity of 5 % and 2%, accordingly. The γ -phase completely transforms in to cubical nitride (Fe, Cr, Ni)₄N also, in large quantities about 95–97 % in the coating, whereas the hexagonal nitride (Fe, Cr, Ni)₃N remains at the same level of 3–5 % if p_{N_2} increase up to 0,06 Pa. With a further increase in the partial pressure of nitride up to 0,15 Pa, the volume fraction of γ' -phase decreases down to 30 %, ε -phases increases up to 34 %. The ζ -phase (Fe, Cr, Ni)₂N appears with an orthorhombic lattice in the quantity of 36 %. The notation of the phases is used according to the equilibrium diagram [9].

It is should be noted, that the superstructure line (100) of the Fe_4N phase occurs already at a minimal pressure of p_{N_2} . The appearance of this line means the presence of the ordered γ' -phase with an ordered atom arrangement of nitride atoms in crystal lattice of γ -phase. The observed transformation of the phase structure in the coatings under study corresponds to the equilibrium diagram of iron – nitride [9].

There is a preferential crystallographic orientation (211) in the α phase and (220) in γ -phase coatings on the basis of the Fe-Cr-Ni. The deposition of coatings in the gas mixture of argon with nitride changes the preferential crystallographic orientation of the γ -phase and becomes (200). When partial pressure of nitrides increases, the orientation (200) becomes main and for the γ' -phase. An average value of area of coherent scattering (D), which can be close to the average grain size of the main phase [5]

in a metallic coating is 20–25 nm, while in nitride coatings D decreases down to 8–15 nm.

One can see that an average value of the lattice parameter of the main phases α -Fe (Cr, Ni) and γ -Fe (Cr, Ni) in the coating (H1) is equal to 0,287 nm and 0,359 nm, which are known in the literature [9]. Coatings (H2) produced in the atmosphere of argon with nitride at $p_{\text{N}_2}=0,03$ Pa have the larger lattice parameter γ -phase and it is equal to 0,363 nm. It is related to an increase in nitride concentration. According to [9] it can take place at $c_{\text{N}}=2,1$ %. The average value of lattice parameter of the γ -phases is 0,377 nm, which is lower than the tabular information equal to 0,380 nm [9].

Table I. Phase and structural characteristics of initial samples and also samples with coatings (a – lattice parameters, D – grain size, $\Delta d/d$ – area of coherent scattering, V – volume ratio of phases, I – internal stresses)

Sample party	Phase compound	Phase symbol	a , nm	D , nm	σ , MPa	$\Delta d/d \times 10^{-3}$	V , %
H0	Fe	α	0,287 \pm 0,001	–	–	–	100
H1	Fe(Cr,Ni)	α	0,287 \pm 0,001	25 \pm 3	800	4 \pm 0,1	60
	Fe(Cr,Ni)	γ	0,359 \pm 0,001	25 \pm 3	800	4 \pm 0,1	40
H2	Fe(Cr,Ni) ₃ N	γ	0,363 \pm 0,001	8,3 \div 12,5	240 \div 740	1,25 \div 3,7	93
	(Fe, Cr, Ni) ₃ N	ε	–	–	–	–	5
	(Fe, Cr, Ni) ₄ N	γ'	0,377 \pm 0,001	–	–	–	2
H3	(Fe, Cr, Ni) ₃ N	ε	–	–	–	–	3
	(Fe, Cr, Ni) ₄ N	γ'	0,375 \pm 0,001	10 \div 14	880 \div 2000	4,4 \div 10	97
H4	(Fe, Cr, Ni) ₃ N	ε	–	–	–	–	5
	(Fe, Cr, Ni) ₄ N	γ'	0,384 \pm 0,002	16 \div 23	300	1,5 \pm 4 \div 0,1	95
H5	(Fe, Cr, Ni) ₂ N	ζ	–	17	900	4,5 \pm 0,1	36
	(Fe, Cr, Ni) ₃ N	ε	–	–	–	–	34
	(Fe, Cr, Ni) ₄ N	γ'	0,378 \pm 0,001	17	1140	5,7 \pm 0,1	30

This value of the lattice parameter is characteristic of γ -phases alloyed by nickel since the nickel nuclear radius is less than that for iron and so and it is enter the lattice by the substitution type [10]. The same values of the lattice parameter of the γ -phase take place in the coatings (H3) and (H5). However, the coating (H4), produced in the conditions of ionic bombardment has of the lattice parameter of 0,384 nm exceeding in the literature. It can be the result of increase in the nitride concentration in the γ -phase above the equilibrium 6.14 % due to implantation of accelerated nitride ions.

It is known [10] that additional nickel atoms in Fe_4N lead to ordering in the Fe sublattice. Nickel atoms are located predominantly in the center of the atomic cell. This ordering in the substitution type of the Fe_4N phase is combined with ordering as the interstitial type. As result, the phase Fe_4N is ordered well. It is known that the long-range order decreases the hydrogen penetrability. As results, the working properties of the coating improve [11, 12]. Phase characteristics affecting the hydrogen penetrability and

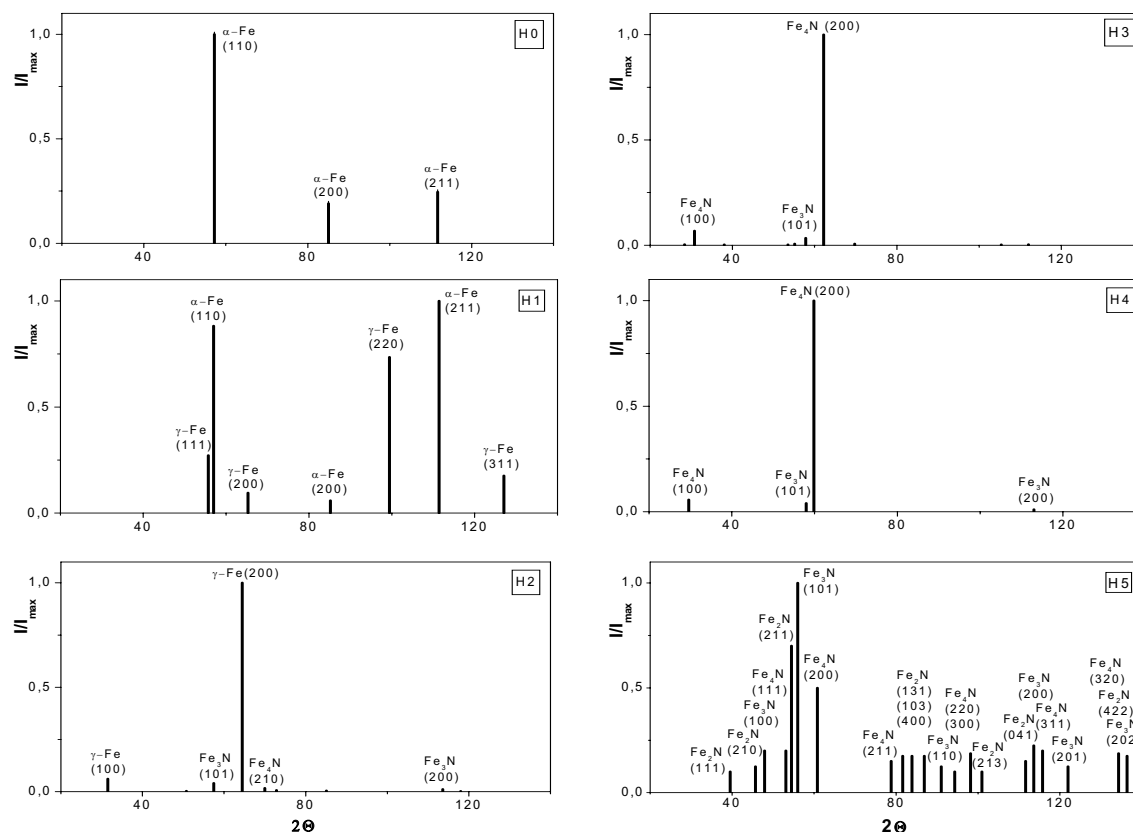


Fig. 1. X-ray pattern of initial samples of 38XH3MΦA (H0) and coating on the basis of Fe-Cr-Ni (H1) and Fe-Cr-Ni-N (H2–H5)

hydrogenous wearing, are listed in the Table. The high internal stresses have, in the mainly, a compressing nature, which, in turn, reduces the hydrogen penetrability.

The adhesive interaction of a polymer with a the metallic surface of a metal-polymeric friction pair results in the formation of a thin polymer film with a constant thickness, inside which molecular chains are oriented in the direction of the slip [3], and serves as lubricant. However, during the slip there is a gradual degradation of the film. As a result of its decomposition, hydrogen diffusion in the surface layer of the metallic component of the friction pairs, and the carbon products of wear will be formed. The hydrogen accumulates in the metal and gradually breaks the surface metallic layer and is removed with the products of the polymer wear [4]. Instead of the worn a new one, polymer film will be formed.

Change of the structural – phase condition leads to change of the tribomechanical properties of coatings. One can see that the wear resistance of coatings increases when the lattice parameter γ and γ' -phases increases. The main cause of this fact is the increase in the nitride concentration in the coating. High wear resistance is related to filling the interstitial site by nitride atoms, which results in decreasing the penetrating power of hydrogen through the coating [13, 14, 15]. Nitrides atoms in the ordered

γ' -phase the occupying the places in the centers of the elementary cubes of the lattice reduce the number of places, which one can be occupied by hydrogen atoms in the crystal lattice.

Thus, a protective action of the investigated coatings at hydrogenous wear of the samples of high-strength steels 38XH3MΦA in the coatings of the γ and γ' -phases take place due to a complex effect. At first, there is an increase in the hardness of the surface layer of the samples. Secondly, there is a nanocrystalline structure of the coatings having a large number of traps for hydrogen atoms [15]. Third, the value of wear resistance is higher owing to the presence of a more solid γ' -phase, a smaller grain size, higher internal elastic stresses [5,9]. The lattice parameter of the γ and γ' -phases depends on the nitride contents in the solid solution. It means that the hardness of the coating increases with an increase in the nitride concentration.

Hydrogen penetrability in steels occurs due to diffusion of hydrogen predominantly on the interstitial site, and also on the defects of a crystalline lattice. It is known that [15, 16, 17] the diffusion rate of hydrogen in steel decreases when the following parameters change:

1. transformation of α -phase in γ' -phase;
2. concentration of carbon and a nitride increase in the solid solution;

3. carbon transform from graphite in to carbides;
4. long-range order parameter (η) increases in the γ' -phase;
5. the density of crystalline lattice defects decreases. Saturation of steel by nitride leads to the the above change in its structure. Therefore, nitriding is an effective method of decreasing of hydrogenous wear.

4. Conclusions

1. The protective nanocomposite coating is produced using magnetron deposition combined with heating of a substrate up to 3000C in conditions of ionic bombardment and without it. It has a thickness about 15 m with advanced resistance to hydrogen wear.
2. The phase compounds of the coatings changes from a mixture of anazotic α and γ -phases, through a nitrous γ -phase, further γ' -, ε and ζ -phases when the nitride concentration increases.
3. The highest values of the wear resistance and hardness demonstrate nanocomposite coatings retaining in the main γ' -phase, with the greatest lattice parameter having a maximal lattice parameter and the greatest internal elastic stresses.

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