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Catalytic nitriding of steel components operating in difficult conditions of hydro-abrasive wear

Larisa Petrova[1,a *], Alexander Malakhov[1,b] , Peter Demin[1,c] , Khushnuda Sharifhodgaeva[2,d], Nodirjon Tursunov[2,e]
[1]Moscow Automobile and Road Construction State Technical University (MADI), 64, Leningradsky prospect, 126319, Moscow, RF
[2]Tashkent State Transport University, 100167 Tashkent Temeryurchilar 1, Uzbekistan
[a]petrova_madi@mail.ru, [b]malahov-alex@yandex.ru, [c]petr-demin@yandex.ru, [d]abdulhabib@mail.ru, [e]u_nadir@mail.ru

Abstract. In the paper, the catalytic effect of previously deposited copper oxide film on nitriding process is described. Mechanisms of iron nitriding intensification are discussed: ammonia dissociation, nitrogen ions adsorption at metal surface, and nitrides formation acceleration. Microstructure of nitrided layers in Armco-iron and in high-chromium steel is examined. It was shown the increase of abrasive wear resistance of nitrided 20Cr13 steel.

Keywords: Nitriding, chromium steel, catalytic effect, nitrided layer, wear resistance.

Introduction

Many parts of equipment for gas and oil production (drilling rigs, pumps, sprayers, etc.) operate in a hydraulic flow containing solid abrasive particles [1]. Exposure of components in corrosive liquids under high pressure aggravates extremely hard conditions of waterjet wear.

Thus, elements of a submersible module for logging oil and gas wells work under hydrostatic pressure from 0.1 to 150 MPa at temperatures from -45 to + 450°C [2]. During operation, the module parts contact directly with the borehole wall and drilling fluid containing water, oil, solutions of salts, acids and alkalis, and gases (methane, hydrogen sulfide). Taking into account these conditions, some components of submersible modules (axles, screws, nuts, pins, forks, sleeves, clamps) are made of high-chromium steels (13-18%Cr) [3].

Wear of a metal surface by abrasive particles is one of the main reasons for reducing the service life of such machines. Abrasive wear of the surface is the result of micro scratching of the metal with hard particles, so the wear degree depends on the ratio of the hardness of the metal and the abrasive particles. Waterjet wear can be considered as a special case of abrasive wear. However, when the abrasive particles move in a stream of liquid, some additional factors contribute to the destruction of a steel surface. At high flow rates, fluid local impacts may behave like solid particles that cause cavitation destruction of the metal [4]. A hydroflow, combined with the action of abrasive particles, removes protective oxide films from the steel surface, which accelerates electrochemical corrosion.

Since the main extreme influences are perceived by the surface of the parts, then methods of chemical thermal treatment (CTT) are effective to improve their reliability. Comparing to the coatings deposition methods, CTT processes have significant preferences due to the diffusion penetration of saturating atoms into the metal’s crystal lattice: high adhesion of the layer with the steel substrate, and fluently decreased depth concentration profile of an element that provides gradual properties changes.

Nitriding is one of the most effective methods of thermo-chemical treatment for steel parts and tools as it ensures significant increase of their wear resistance, corrosion resistance, and fatigue strength at relatively low process temperatures. Nitriding process is successfully used for increase of wear resistance of ferritic steels [5]. Formation of nitrides at the nitrided surface of chromium-containing steels contributes to the resistance against a hydraulic flow with abrasive particles. The volume changes in the surface layer lead to the appearance of favorable residual compressive stresses in the hardened zone, which reduces the sensitivity of steel to stress concentrators arising in the process of micro-shocks action.

There are several obstacles for effective application of nitriding for surface strengthening of chromium steels. Firstly, the procedure of previous de-passivation is necessary for removing of oxide films from the surface. Besides, the problem of corrosion resistance loss appears because of possible chromium nitrides formation [6, 7]. Some of these problems may be overcome during nitriding techniques with preliminary oxidation [8].

The important limitation in nitriding of high-alloyed steels consists in the low rate of a diffusion layer growth that is the result of very slow diffusion of nitrogen. For example, for forming of a nitrided layer in 13%Cr steel of 0.2…0.3 mm thickness, the duration of the classic gas nitriding should be not less than 30 hours [9]. Thus, the problem of nitriding intensification is the most important for processes further development.

The process temperature is considered the main physical factor for nitriding intensification because the diffusion coefficient of nitrogen is the exponential function of the temperature. Thus, high temperature nitriding seems to be the only way for forming of extended diffusion layers in ferritic and austenitic steels, as well as in nickel-based alloys [5, 10]. For many steels, the nitriding temperature is limited by some factors critical for keeping their properties.

Temperature increase is not only mode of process acceleration. Activation of steel saturation with nitrogen may be achieved by application of high-energy sources: electric discharge, laser, plasma, ultrasonic effects. For nitriding intensification of alloyed steels, controlled atmospheres are used as well as gas-cyclic and staged processes [11].

It was shown that catalytic properties of metal oxides may be used for nitriding intensification. For example, copper oxide film at the steel surface accelerates the nitriding layer growth in carbon steels [12]. The purpose of the study consists in the investigation of catalytic effect of copper oxide films on nitriding of chromium steels and in the examination of hydro-abrasive wear resistance of nitride steels for oil and gas production components.

Methods of study

Experimental study of catalytic nitriding was carried out on specimens made of Armco-iron (model material) and of chromium steel 20Cr13 (AISI 420). CTT of the model material included stages of oxidation and nitriding. Before nitriding specimens were covered by thin copper film deposited from 1% solution of blue vitriol. Exposure in the air atmosphere at 585ºC during 1-3 minutes results in the formation of the copper oxide coating. Nitriding of samples with CuO coating was carried out in ammonia at the same temperature (585ºC) during 3 hours.

Specimens of chromium steel covered with copper film were subjected to gas-cyclic processes at 585ºC with alternating stages of oxidation and nitriding. At each oxidation stage in the air atmosphere, formation of CuO layer occurs; at the next stages in ammonia, nitriding of steel under the CuO film proceeds together with the reduction of copper oxide by hydrogen. Oxidation stages duration was determined depending on necessary thickness of the oxide layer; and nitriding stages duration was selected upon the time of its total dissolution. Stages are repeated for forming of necessary thickness of nitrided layer. Then cooling was carried out in the ammonia atmosphere.

Microstructure of the samples was examined in optical microscope AXIOVERT 25CA and in scanning electron microscope JEOL JSM-6480LV. Elements' concentrations in different points of the layers were determined by EDS spectrometer. Phase composition of the nitrided surface was examined by X-ray diffraction. Phases distribution throw the depth of the layers was estimated by correlation of local nitriding concentrations according to the Fe-N phase diagram.

For microhardness measurement, PMT-3 device was used. Abrasive wear tests were conducted in in a loose mass of corundum sand abrasive particles moving between the test specimen and the rubber roller. Were resistance was measured by weight loss of tested specimens.

Results and discussion

Mechanisms of nitriding intensification of iron with surface oxide film. Nitriding intensification boils down to the search of factors that can accelerate the dynamics of the main elementary physics-chemical processes: 1) ionization of a saturating gas environment; 2) activation of a treated metal surface for better adsorption; 3) stimulation of diffusion processes in a metal substrate. One of the solutions for increase of adsorption of saturating element's atoms/ions at the metal surface consists in the usage of specific properties of active oxide films formed at a steel substrate: presence of oxides increases the number of active centers for adsorption.

Oxides of metals act as the sources of high energy electrons that can easily emit from the surface film; this contributes to the active ionization of ammonia atmosphere during nitriding and to the acceleration of nitrogen ions movement to the metal surface. If an oxide film is thin enough than it may be penetrable for ions with sufficient kinetic energy. In this case, forming of a nitrided layer under the film is possible. This creates preconditions for regulation of phase composition and thickness of the nitrided layer. In particularly, a diffusion layer based on solid solution may be formed.

Active oxide films may be formed both as the consequence of spontaneous oxidation of the substrate metal or some of the alloying elements and as the result of a special preliminary surface treatment. One of the approaches consists in the deposition of a metal precursor at the steel substrate with the following oxidation.

As it was already mentioned, copper is one of the effective precursors for forming of catalytic oxide film for nitriding intensification. Copper film is formed at the surface of iron specimen according to the reduction reaction from copper sulfate solution:

$$CuSO_4 + Fe \rightarrow Cu \downarrow + FeSO_4 \qquad (1)$$

During the contact of iron specimen with CuSO4, Cu^{2+} ions move into the solution (Fig. 1 a); thus the surface becomes charged negatively. At the same time Cu^{2+} ions deposit from the solution at the iron surface. In the conditions of dynamic equilibrium, the quantity of Fe^{2+} ions in the solution is equal to the quantity of Cu^{2+} ions deposited at the substrate. This state corresponds to the maximum thickness of the copper precursor.

Heating of covered samples in the air atmosphere provides the oxidation of copper precursor. The process of oxygen dissociation occurs; oxygen ions are adsorbed by the surface, and then diffuse into the copper film (Fig.1 b). At the initial stage of oxidation, Cu_2O oxide is formed, which transfers then to CuO oxide. The completeness of the oxidation depends on the thickness of the copper precursor. CuO interacts with ammonia according to the reaction of copper reduction:

$$2NH_3 + 3CuO \rightarrow N_2 + 3Cu + 3H_2O \qquad (2)$$

Intensification of ammonia dissociation is accompanied by active nitrogen ions formation. Well-developed surface of the oxide film creates a number of adsorption centers that contributes to the increase of nitrogen ions number at the surface (Fig. 1c).

Nitrogen ions penetrate through the thin oxide film in the iron substrate. Diffusion of nitrogen ions into the depth leads to the nitrided layer formation under the copper oxide film with the structure corresponding to the phase transformations in the Fe-N system.

Influence of copper oxide film on the kinetics of nitrided layer growth. Experiments confirmed the suggested schemes and discussed mechanisms of elementary processes during nitriding under copper oxide film. Metallographic examinations and evaluation of nitrogen concentration at different depth from the surface discovered the penetration of nitrogen under the copper oxide film and formation of nitrided layer in iron specimens (Fig. 2).

Elements' spectrum from the surface shows that during the nitriding process, copper oxide is resolved, and copper is reduced from the oxide (Fig. 3). Copper atoms diffusion into the iron substrate occurs to the depth of 90 µm (Fig. 2).

X-ray diffraction examination identifies ε-phase $Fe_{2\text{-}3}N$ directly at the surface with nitrogen concentration about 11 wt.%. Examination of nitrogen concentration profiles and micrographs of the layer gives the reason to evaluate the thickness of ε-phase zone as about 70 µm (Fig. 2). According to the nitrogen concentration decrease with the depth, we can suppose forming of ε+γ' compound layer under the ε-phase zone. At the depth more than 100 µm, an internal nitriding zone $Fe_{\alpha}(N)+\gamma'$ is formed; the total thickness of the nitrided layer is up to 200 µm.

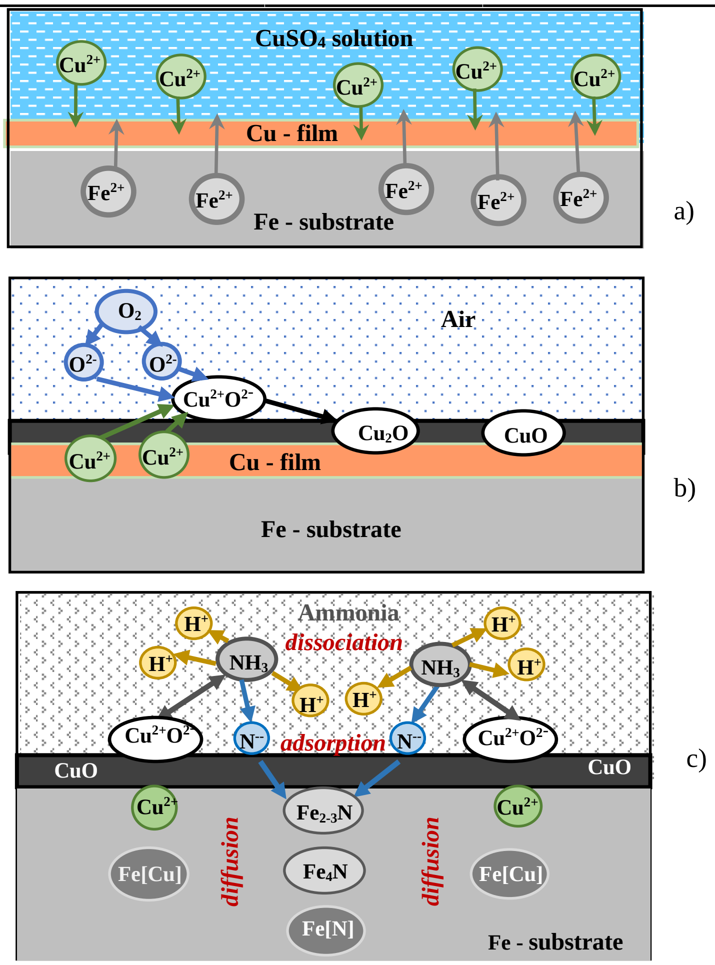


Fig. 1. Schemes of elementary processers during catalytic nitriding: a) Cu-film formation at Fe-substrate; b) Cu-film oxidation; c) nitrided layer formation under CuO film

Catalytic nitriding of chromium steel with previously formed copper oxide film. Analysis of kinetics of nitrided layer growth in chromium steel has shown the catalytic effect of copper oxide film. For example, the process duration of 1.5 hour is enough for forming of 150-μm nitrided layer in 20Cr13 steel during gas-cyclic process with previous deposition of copper oxide. Whereas the time of 15-20 hours is required for such layer thickness achievement during classical gas nitriding in ammonia. Catalytic nitriding duration is 5 times less comparing to the time of traditional oxi-nitriding necessary for the same layer formation.

Some differences in the diffusion layer structure were discovered in chromium steel comparing to the structure of Armco-iron model material. ε-phase formation is not observed, whereas powder-like sintered composite layer of γ'-Fe_4N nanoparticles is formed at the surface (Fig. 4 a). This may be the result of counter iron diffusion from the substrate throw the copper oxide nano-film. Alternation of ammonia-air saturation atmospheres activates the interaction between iron ions and adsorbed nitrogen ions at the surface. In the internal nitriding zone, nano-particles of chromium nitrides CrN are observed in ferrite matrix (Fig. 4 b) that is the precondition of precipitation hardening.

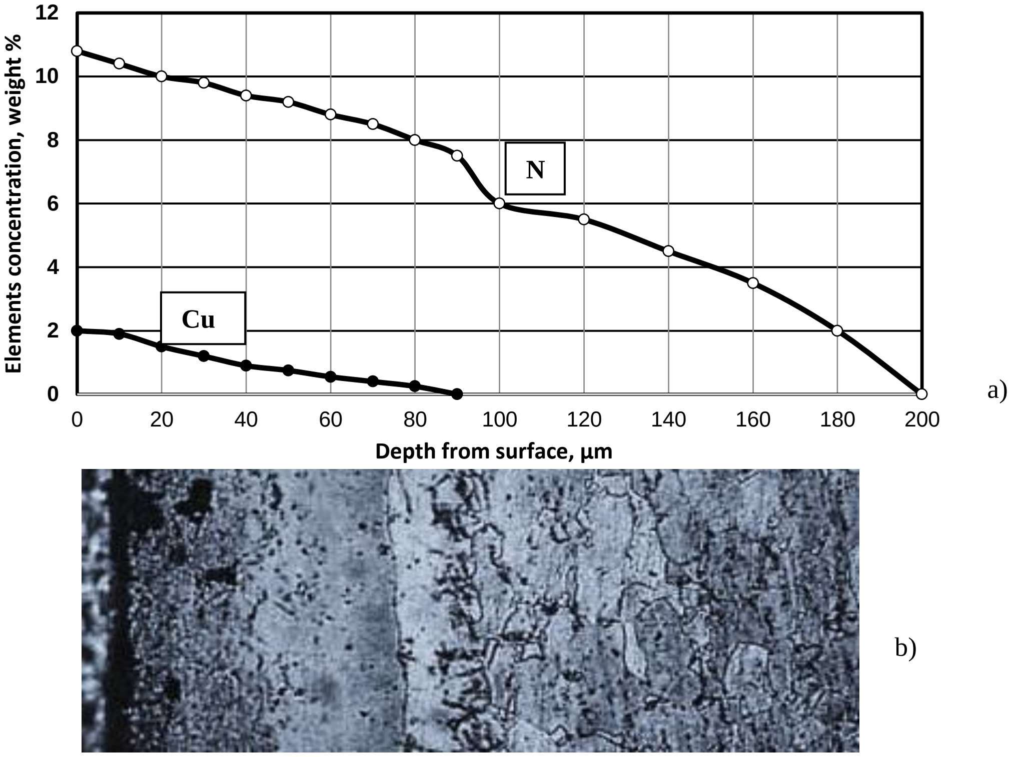
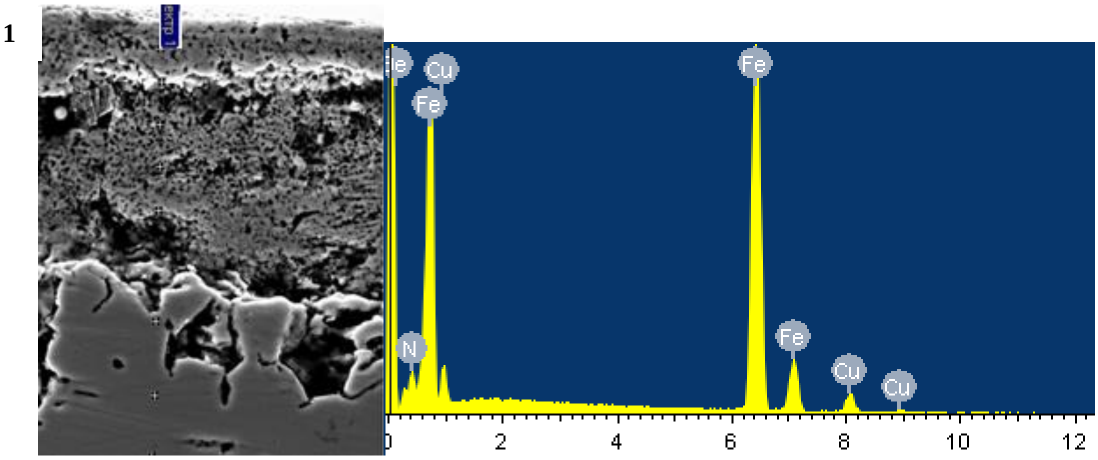


Fig. 2. Nitrogen and copper concentration profiles in Armco-iron (a) and microstructure of nitrided layer formed under CuO film (b)



a)

b)

Fig. 3. SEM image of surface compound layer in nitrided Armco-iron (as) and elements' spectrum in the point "1" (b)

It was shown that catalytic nitriding with CuO film significantly increase abrasive wear resistance of 20Cr13 steel (Fig. 5). Weight loss parameter halved as at the workability stage and at the stage of steady wear.

Both parts of the nitrided layer in chromium steel play their role during machine components operation in hydro-abrasive wear conditions. Relatively soft surface coating of powder-like ferrous nitrides provides workability of the surface at the initial period of friction. The extended internal nitriding zone strengthened by dispersed CrN particles contributes to the wear resistance due to the so-called Charpy structure. Untreated core of the specimen keeps the monophasic structure of alloyed ferrite which is resistible to impact loads.

On-location tests of logging equipment with components treated according to the described nitriding method have shown that their service life under the impact and friction loads increased from 3 to 7.5 times.

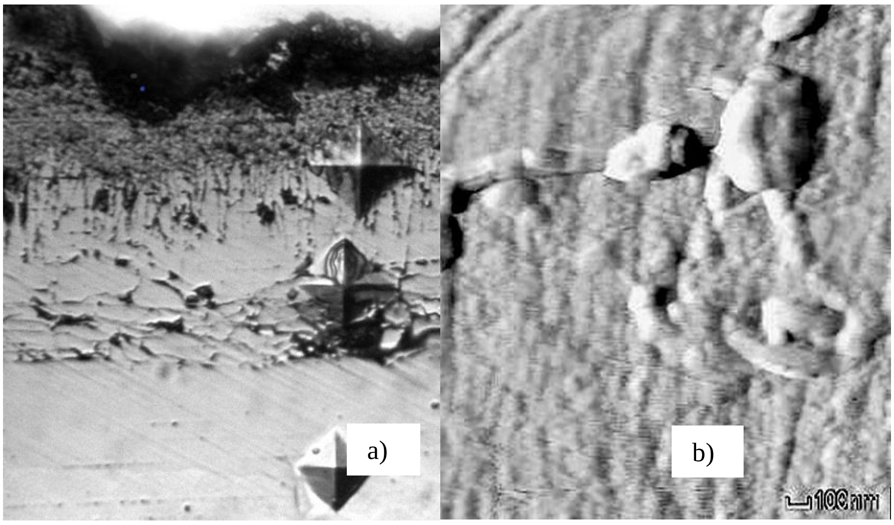


Fig. 4. Microstructure of 20Cr13 nitrided steel: a) – surface composite layer; b) – chromium nitrides in the internal nitriding zone (SEM)

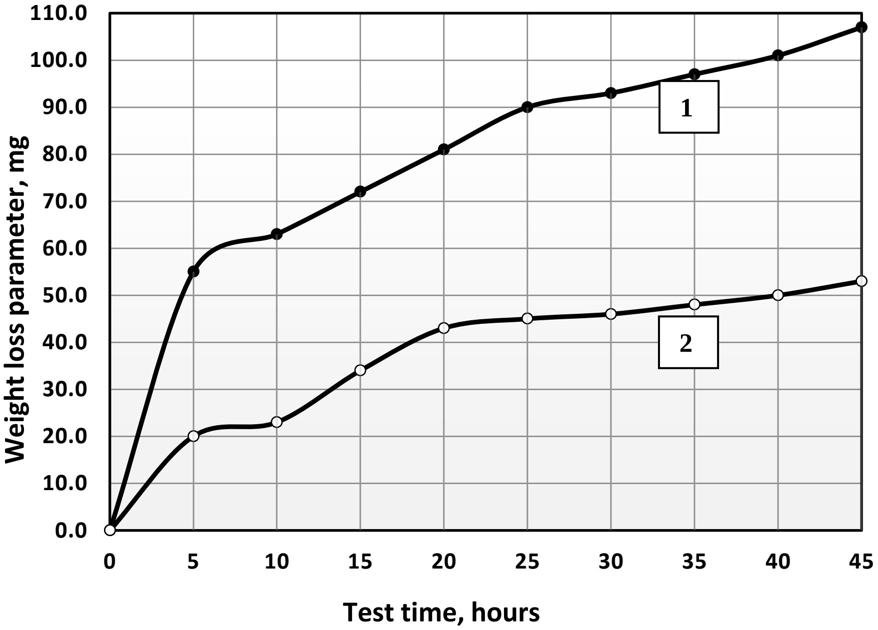


Fig. 5. Abrasive wear resistance of 20Cr13 steel without surface treatment (1) and after catalytic nitriding with copper oxide film (2)

Conclusion

Catalytic effect of copper oxide film on nitriding process is confirmed for both Armco-iron and high-chromium steel due to the mechanisms of acceleration of ammonia dissociation, activation of nitrogen ions adsorption at metal substrate, and intensification of nitrides formation at the surface. The structure of nitrided layer in 20Cr13 steel after catalytic gas-cyclic nitriding provides high wear resistance and contributes to the multiple increase of the service life of machine parts operating in hydro-abrasive wear conditions.

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