DIFFUSION LAYERS FORMATION UNDER DEFORMED IRON ALLOYS SURFACE SATURATION BY NITROGEN

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Nitrided α–Fe and Fe-Cr alloys after preliminary plastic deformation (PPD) were investigated by means of metallography, X-ray diffractometry, microhardness test, electron microscopy and Mössbauer spectroscopy. It was established that nitrided layers consisted of nitride ε- i γ'- phases and α– solid solution of nitrogen in Fe and alloys. It was shown that the existence of narrow regions of deformation 3-8 % and 20–30 % in which the considerable (2 times) increase in microhardness of surface diffusion was observed after nitriding. The microhardness correlation of diffusion layer with its structure, phase composition and thickness of nitrided phases layers was found.

Introduction

A special role in the development of up-to-date high technologies belongs to the technologies based on methods of treatment which combine different power, mechanical and chemical influences. As a rule, the purpose of such combined ways of metal surface treatment is creation of non-equilibrium stressed and strained conditions which can impact on processes of chemical-thermal treatment [1–3]. The problems of creation of non-equilibrium stressed and strained state and its influence on the processes occurring under diffusion saturation by interstitials are not completely cleared up yet.

Nitriding is well known to be widely used in industry for the improvement of mechanical properties of surface layers of iron alloys and steel products. One of the methods in this direction concerns application of chemical-thermal treatment in combination with plastic deformation of surface [4-6].

As a structure-dependent process diffusion substantially depends on the presence of crystal structure defects and non-equilibrium stressed and strained state of metal. Reference data [7–9] and our previous experiments [10–12] have shown that crystal structure defects essentially affect diffusion of nitrogen in metals and phase formation processes. Such influence is explained by different character of interaction of interstitials (carbon and nitrogen) with non-mobile and mobile defects of crystal structure.

Iron alloying with different kind of substitutional elements changes the bond energy U_b of dislocations with interstitials (carbon, nitrogen) and the temperature T_c of Cottrell's type atmosphere condensation [13, 14]. The nonnitride-forming elements (such as Ni, Co, Si, Al) reduce U_b and T_c, and nitride-forming elements (such as W, Mo, Cr, Mn), on the contrary, increase U_b and T_c. Purposeful alloying with substitutional elements and creation of non-equilibrium strained-stressed state by means of PPD is one of the ways of clarification of the physical causes of surface diffusion strengthening.

Experimental

Pure iron and Fe-Cr alloys (with 0.5–1.5 wt. % Cr) in homogeneous α-solid solution region melted in induction vacuum furnace were used as materials for investigation. The content of impurities was 0.003 % C;

0.006 % N, 0.02 % S; 0.01 % O; at the most 0.04 % (Si + Mn + Ni + Ti + Al +Cu) (wt.). The diffusion annealing was performed at T = 1473 K for τ = 6 hours in vacuum. The specimens were prepared both as foil of 20–25 μm thickness by successive multiple rolling and annealing in vacuum for electron microscopy and Mössbauer spectroscopy and as bulk of 0.8–1.5 mm thickness by cutting for X-ray diffraction analysis, metallography and microhardness test.

Recrystallization annealing was carried out at T =1273 K during τ = 0.5–1 hours in vacuum (5×10^{-6} Pa). Preliminary plastic deformation (PPD) was realized by rolling with the true relative deformation degree ε =ln $[(d_0-d)/d]$= 3, 5, 8, 10, 15, 20, 25, 30, 35, 40, 50, 60, 70 %, where d_0 and d are the thickness of the specimens before and after PPD, respectively.

To obtain surface nitrided layers on the base of α–Fe-N solid solution the gaseous saturation of undeformed and deformed pure iron and Fe-Cr alloy plates and foils by nitrogen was accomplished in ammonia (NH_3) environment at T = 823–853 K (below $\alpha\leftrightarrow\gamma$-transition) during τ = 0.5, 1, 2 hours for nitriding of plates and during τ = 5 and 15 min for foils. The diffusion layers of iron and Fe-Cr alloys obtained in plates and foils in initial state and after 5–70 % deformation were investigated by means of metallography, electron microscopy, microhardness test, X-ray diffraction analysis and Mössbauer spectroscopy.

Results and discussion

The microstructure of surface diffusion layers formed in bulk Fe and Fe-Cr alloy samples was studied using light optical microscope with magnification up to ×50-600. To reveal the microstructure the etching in 5 % solution of nitric acid in ethyl alcohol was used.

As a result of the preliminary plastic deformation application the grains were oriented along the axis of rolling. The deformation texture and slip bands on the cross-sections were visible after the deformations more than 8 %.

The microstructure analysis of bulk Fe specimens after nitriding at 823-853 K, for 1 and 2 hours has shown that the diffusion layers consisted of two sub-layers of nitride phases near the samples surface and a zone of solid solution (Fig. 1).

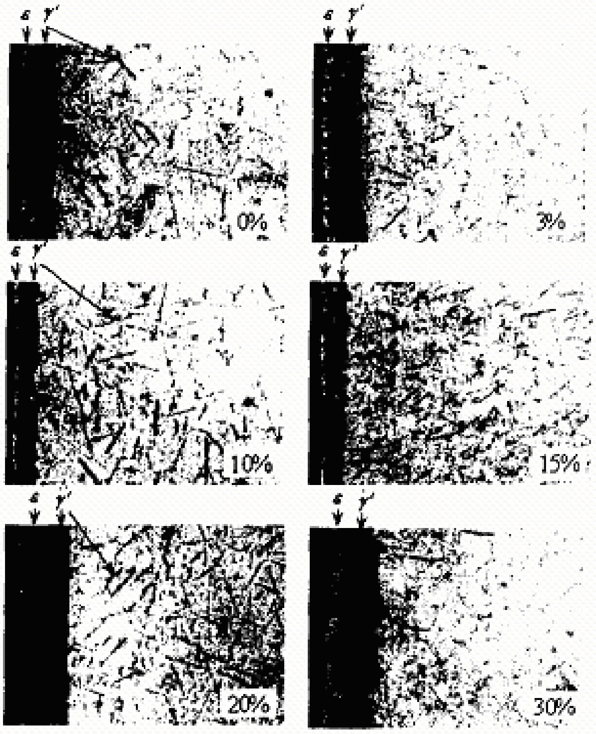

Fig. 1. Microstructures of nitrided layers in Fe after PPD and nitriding at T = 853 K during 1 hour.

Unlike Fe the microstructure of the diffusion layers in the Fe-Cr alloy was solely a zone of solid solution of N in *bcc*-Fe-Cr crystal lattice. The layers with ε- and γ'- nitrides were not formed in Fe-Cr (0.5-1.5 wt.%) alloys.

Two surface nitride layers were clearly seen on all the Fe bulk samples as external light non-etched and dark chemically etched layers (Fig. 1). As X-ray diffraction data have shown the non-etched layer was ε-nitride ($Fe_{2\text{-}3}N$) with *hcp* lattice, and the etched layer belongs to γ'-nitride (Fe_4N) with *fcc* structure. The thickness of these layers is changed non-monotonously. The thickness of the ε-phase layer is 5–35 μm, for γ'-nitride it is 15–35 μm and the total thickness of the layers of these phases varies from 20 up to 60 μm, all these values depending on the degree of deformation (Fig. 2). Two pronounced maximums were observed at the dependence of thickness of the nitride layers on degree of deformation (at 3-5 % and 20-25 %). The thickness of nitride layers achieves up to 29.2 μm for ε-phase, 27.5 μm for γ'-phase with increasing degree of deformation from 3 % to 25 %.

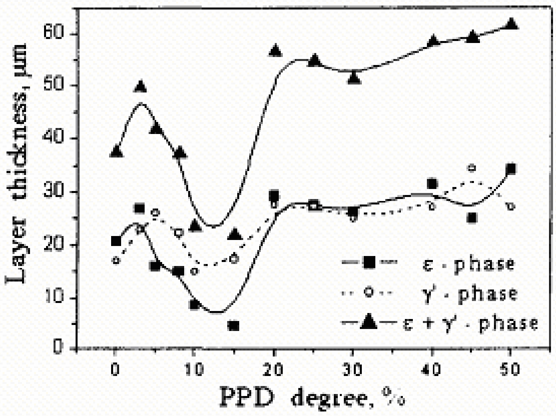

Fig. 2. Thickness of ε- and γ'-nitride layers in Fe after PPD and nitriding at T = 853 K during 1 hour.

The zone with heterophase structure was located under the nitride layers and it was identified as α-solid solution of N in *bcc*-Fe lattice with the numerous precipitations of γ'-phase. The γ'- phase in this zone is revealed in the form of thin needles of length up to 100 μm lying along the shear planes {110} and {112} in the directions of the most close packing of atoms <111> in *bcc* lattice.

Microhardness distribution over the surface layer depth after different deformation degrees and subsequent saturation was analysed.

The application of preliminary plastic deformation up to70 % before saturation led to the increase in microhardness by factor of about 1.5 (from 0.75 to 1.1 GPa for Fe specimens and from 0.9 to 1.5 GPa for Fe-Cr depending on the PPD degree).

After the Fe nitriding (853 K, 1 hour) the maximal value of H_μ was observed for the deformed samples at the degrees of plastic deformation 3-8 % and 20-30 %. Between these two intervals (10-15 %) the microhardness was lower than H_μ for the non-deformed samples (Fig. 3). The 8 % deformation results in almost twice increase of H_μ of Fe at the depth of 10 μm, from 2.3 GPa for the undeformed samples to 4.4 GPa after the deformation. At the further increase of the degree of deformation up to 25–30 % the microhardness at the depth of 10 μm increases more than twice and reaches 4.8 GPa.

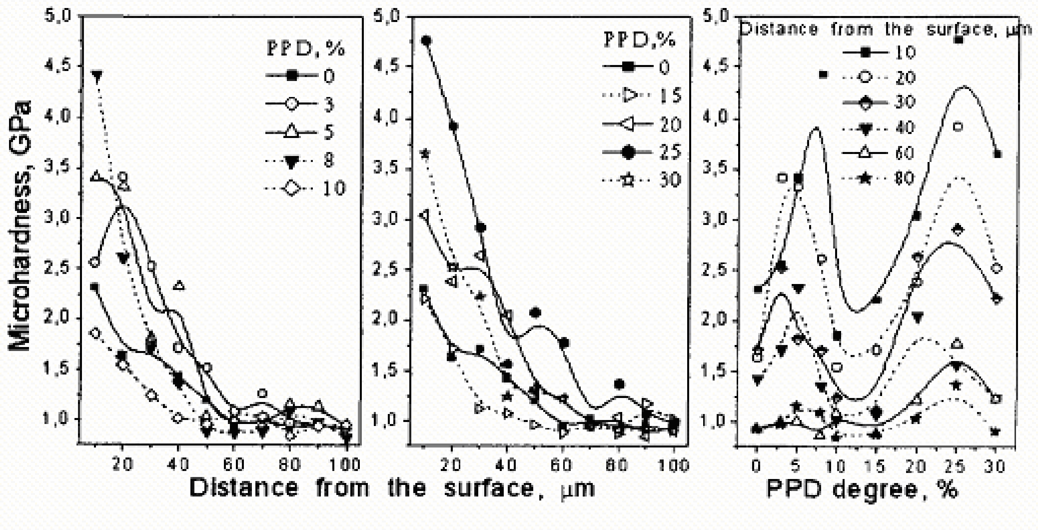

Fig. 3. Microhardness distributions over the depth of the nitrided layers in Fe after different degrees of PPD and nitriding at T = 853 K during 1 hour.

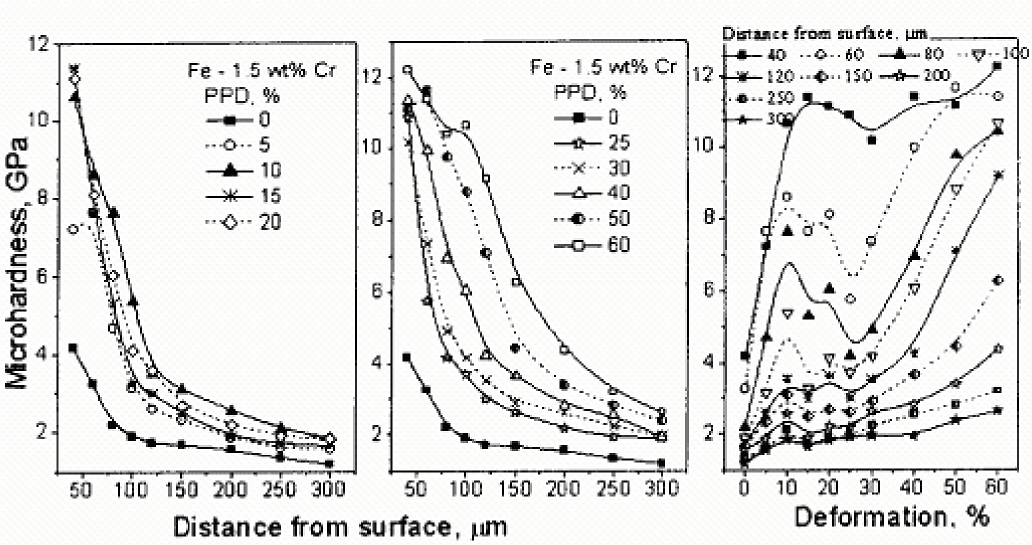

Fig. 4. Microhardness distributions over the depth of the nitrided layers in Fe-1.5 wt. % Cr after different degrees of PPD and nitriding at $T = 823$ K during 2 hours.

In Fe-1.5 wt % Cr alloys after nitriding (823 K, 1 hour), the interval of maximal H_μ = 4.0 GPa at the depth of 40 μm was observed at the 20–25 % degree of deformation what was two times higher than H_μ = 2.1 GPa for the non-deformed samples. After nitriding (823 K 2 hour), H_μ = 11.4 GPa was observed at the same depth (40 μm) at the 10-20 % degree of deformation what was almost 3 times higher as compared to the non-deformed specimen (H_μ = 4.2 GPa) (Fig. 4).

Thus, the non-monotonous dependences of the thickness of the nitrided layers and their microhardness were revealed in the preliminary deformed and following nitrided Fe and Fe-Cr alloys. The similar behaviour of H_μ was observed even at the depth of 60–70 µm.

The investigation of the microstructure of the nitrided foils were performed by means of their "cross sections" using scanning electron microscope SEM (Amray-1830I, +Edax, with magnification up to ×10 000) and transmission electron microscope TEM (JEOL-200 FX+EDS, with magnification ×40 000–150 000). Thinning was carried out using abrasive materials and ion-beam sputtering with Ar^+. Etching in 5 % solution of nitric acid in ethyl alcohol was performed in order to reveal the structural components and to increase the phase contrast under observation with SEM.

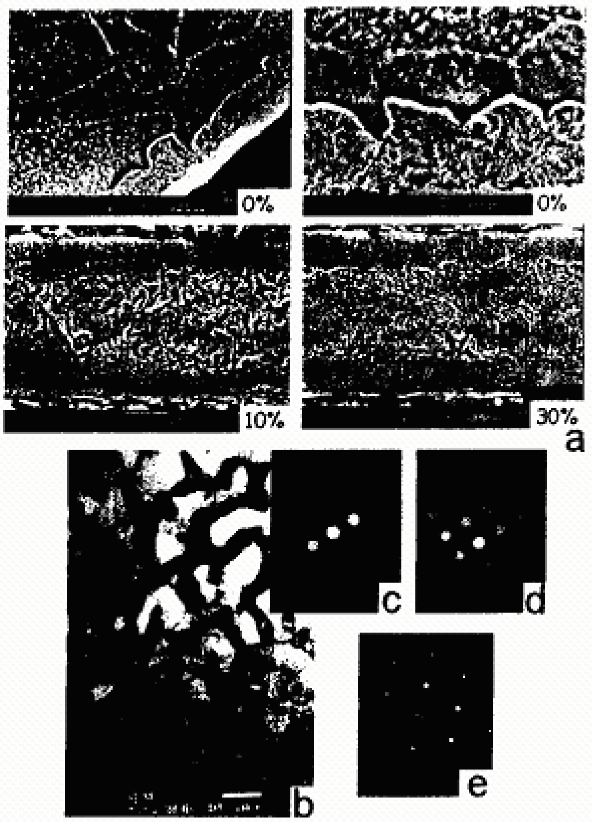

Fig. 5. Electron-microscopic images of microstructure of Fe foils after PPD, the PPD degree being indicated in per cent and nitriding at T = 853 K during 15 min, eutectic (a) of the phases formed in non-deformed foils and their electron-diffraction patterns for γ'-phase (b), ε - phase (c), and α– Fe-N (d).

The obtained results have shown that the diffusion layer in iron (Fig. 5) and Fe-Cr foils is a combination of nitride ε- and γ'-phases and solid solution of nitrogen in α-iron. The diffusion layer in non-deformed iron foils after nitriding consists of the following phases: (i) ε - phase forming a white homogeneous acid-proof layer of ~ 5 μm thickness; (ii) γ' - and ε- or α - phases eutectic as a heterogeneous sub-layer; (iii) α-solid solution of nitrogen in *bcc* iron lattice with disperse ε- or γ'- nitride precipitation representing a non-homogeneous core of foils.

The ε-phase layer has homogeneous thickness over the surface. The γ'- phase is a layer being formed along the former α-phase grain boundaries. Such γ'-phase formation can be explained by accelerated nitrogen diffusion and high solubility along the grain boundaries.

The TEM data (Fig. 5, a-c) show that the dark component of the eutectic (Fig. 5, a) has *fcc* structure with the lattice parameter a = 0.378±0.004 nm (γ'-phase, Fig. 5, b) and the light component has *hcp* structure (ε -*p*hase, Fig. 5,c). The lattice constant of the α-solid solution of N in Fe is a = 0.286 ±0.004 nm (Fig. 5 d) what is consistent with the data from the literature.

A more intense formation of the ε- and γ'- phases was revealed in all deformed iron foils with the degree of deformation 5÷50 % (Fig. 5). The thickness of the ε-phase varied within the range 3÷8 μm and that of the γ'-phase was varied within the interval 15÷50 μm depending on the deformation degree. The porosity in the core of the α- phase after nitriding was revealed and the highest density of pores was observed in the samples after 10÷15 % degree of deformation. The formation of porosity can be caused by the α- phase supersaturation with nitrogen and molecular nitrogen precipitation on the crystal lattice defects resulting from the stress relaxation under heating or cooling in gas environment.

The X-ray diffraction analysis using Co and Fe K_α - radiation (Fig. 6) has confirmed the TEM results and has allowed us to determine the phase composition after different degrees of PPD: (1) a surface layer of the ε–phase; (2) a sub-layer of the γ'-phase; (3) a zone of solid solution of nitrogen in α–Fe.

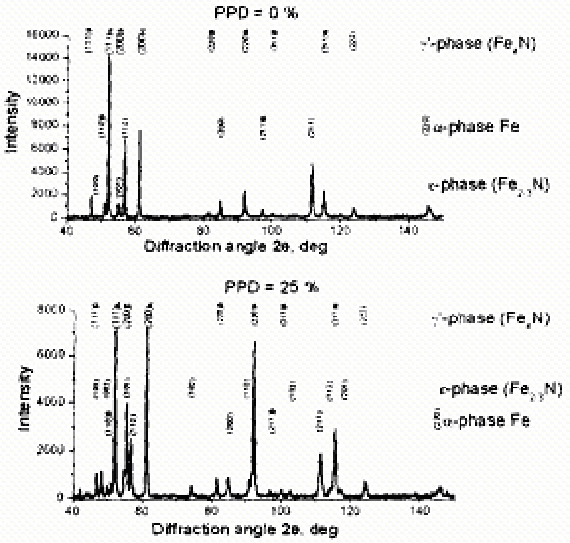

Fig. 6. Diffraction patterns of Fe-foils after PPD and nitriding at T = 853 K during 15 minutes.

The comparison of the microstructural data with the X-ray analysis results points to the fact that the ε-and γ'-nitride layers of the greatest thickness are formed in the samples after 20–30 % PPD. Thus, the PPD affects the volume ratio of the phases in the diffusion zone under nitriding.

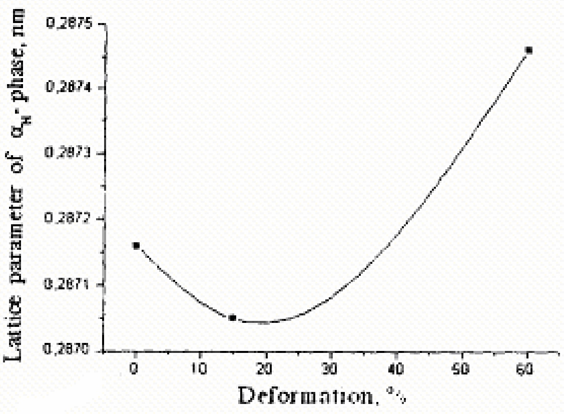

Fig. 7. Lattice parameters of the α - phase of Fe-Cr alloys specimens after deformation and nitriding at T = 823 K during 0.5 hour.

The influence of the deformation on the crystal lattice parameter of the α-phase after nitriding was non-monotonous (Fig. 7). The minimum (a = 0.2870 nm) at the curve corresponds to 15–20 % of deformation. The rise of the deformation degree up to 60 % led to the increase of the α-phase crystal lattice constant up to 0.2875 nm. So, high microhardness of the surface diffusion layer of the deformed specimens (Fig. 4) as compared to the non-deformed ones can be caused by the greater concentration of nitrogen in α-phase. The increase of H_μ at 10–20 % PPD can be caused by dispersion strengthening mechanism as a result of nitrides precipitation on dislocations.

The distribution of nitrogen atoms in the foils of Fe after the deformation and diffusion saturation with nitrogen was studied using Mössbauer spectroscopy. The Mössbauer spectra were obtained at room temperature in transmission geometry. The isotope of ^{57}Co in Cr matrix was used as the source of gamma-quanta.

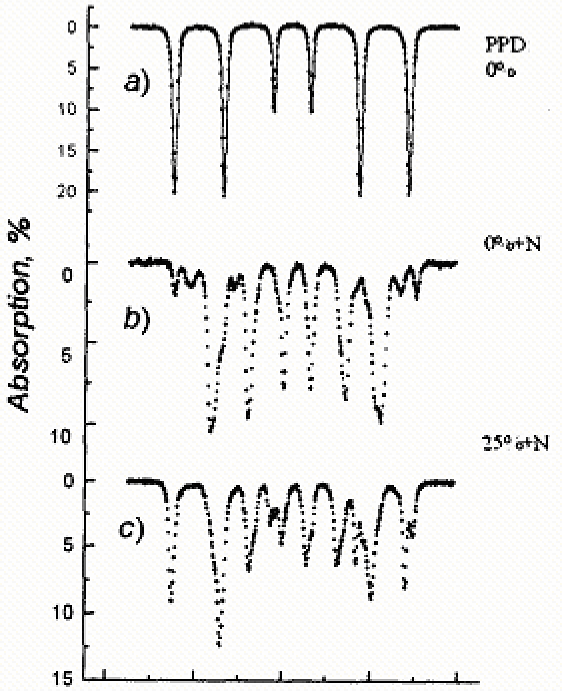

Fig. 8. Mössbauer spectra of (a) α–Fe (PPD = 0 %); (b) α–Fe + N (PPD = 0 %); (c) α–Fe + N (PPD = 25 %), T_m = 300.

The spectra (Fig. 8) obtained from the samples in the initial state after annealing have typical shape for such absorbers and consist of one sextet (Fe) and two sextets (Fe-Cr). The shape of the spectra is not generally changed after plastic deformation of samples. Line broadening results from the high density of dislocations.

The shape of the spectra was considerably changed after nitriding of foils. The analysis of the hyperfine parameters has shown that the NGR spectra consist of several components relating to iron atoms in α-Fe and iron nitrides (ε-phase, γ'-phase).

The obtained Mössbauer results support the metallography and X-ray diffraction data concerning the phase transitions in the deformed samples under the gas nitriding.

Conclusions

PPD considerably affects the phase composition, structure, microhardness and thickness of the layers Fe and Fe-Cr alloys. It was shown that the surface diffusion layers consisted of the ε-, γ'- and α- phases and the layer of the solid solution of N in the α-phase. The high microhardness of the diffusion layers in α-Fe near the surface after PPD and nitriding results from the formation of the ε- and γ'-nitrides containing high concentration of nitrogen and having the crystal structure different from the matrix. The disperse precipitations of the above mentioned nitride phases also strengthen the diffusion layers.

The existence of narrow intervals of deformations of 3-8 % and 20-30 % in which the considerable (almost double) rise of microhardness of the nitrided layers of Fe due to the accelerated formation of nitride phases was found.

The non-monotonous dependence of microhardness of the diffusion layer on PPD results from different mechanisms of nitrogen diffusion in a deformed material. In our point of view, the greatest number of mobile dislocations is formed under the deformation of 3–8 and 20–30 %, which can provide the additional diffusion of nitrogen atoms with Cottrell's atmospheres by the dislocation-dynamic mechanism [15, 16]. Such processes influence on the kinetic of the phase formation what results in the accelerated growth of ε- and γ'- nitrides and in the increase of microhardness of the surface diffusion layers. The slowed-down formation of layers of the ε- and γ'- nitrides under the deformation of 10-15 % results from the reduction of mass transfer of nitrogen in α-Fe probably due to the reduction of the number of mobile dislocations capable to transfer atmospheres of interstitial atoms.

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ФОРМУВАННЯ ДИФУЗІЙНИХ ШАРІВ ПРИ ПОВЕРХНЕВОМУ НАСИЧЕННІ АЗОТОМ ДЕФОРМОВАНИХ СПЛАВІВ ЗАЛІЗА

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Азотовані α–Fe та сплави Fe-Cr після попередньої пластичної деформації (ППД) досліджені за допомогою металографічного, рентгеноструктурного, мікродюрометричного методів аналізу, електронної мікроскопії та месбауерівської спектроскопії. Встановлено, що азотовані шари складаються з нітридних ε- і γ'- фаз та твердого розчину азоту в α–фазі Fe та сплавів. Показано існування вузьких областей деформацій 3-8 % і 20-30 %, у яких після азотування α–Fe спостерігається значне (у 2 рази) підвищення мікротвердості поверхневого дифузійного шару. Знайдено кореляцію мікротвердості дифузійного шару з його структурою, фазовим складом і товщиною шарів нітридних фаз.