

Phosphorus in iron alloys surface engineering

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Materials

ABSTRACT

Purpose: Purpose consideration of role of phosphorus in iron alloys surface engineering and relations of the iron phosphides layers growth parameters in processes of phosphorising, phosphorcarburising, and phosphonitriding with their structure and properties.

Design/methodology/approach: The layers were generated on a base of Armco iron and 0.4%C, 1.1%Cr steel as a result of annealing in a mixture of argon or carburising, nitriding atmosphere and phosphorus vapours in: temperature $T = 700 - 1170$ K, phosphorus partial pressure $p = 0.1 - 20$ kPa, process duration $t = 3.6 - 21.6$ ks. The diffusion layers were investigated by means of the methods: metallographic, X - ray structural analysis, microanalysis, Vickers and wear dry friction resistance tests.

Findings: Formation of compact layer of phosphides with the adjustable relation of Fe_3P to Fe_2P was described; means of growth and kinetics of iron phosphides layers and phosphocarbured and phosphonitrided were explained, it was found that iron phosphides presence in steel surface increases its hardness and resistance to wear.

Research limitations/implications: Research implications it was found that nucleation Fe_3P crystals starts in areas of surface being found in a certain distance from iron grains boundaries and the growth process of iron phosphide continuous layers is an effect of iron diffusion through phosphide layer from the core towards the surface. In advanced phases of the of iron phosphide layer growth, a gap between the layer and the base is created as a process of degradation of the base layer interface.

Practical implications: Practical implications: it has found that the obtained layers are new kind of composites diffusive layers with iron phosphide particles generated as a result of phosphorising, phosphorcarburising or phosphonitriding with very promising tribobiological properties

Originality/value: An original value of the paper is description of the formation elementary processes, structure and properties of the layers.

Keywords: Metallic alloys; Mechanical properties; Metallography; Materials design; Surface treatment

1. Introduction

For many machine elements operating in different conditions there is requirement of applying of surface with modified structure in order to obtain particular properties of surface [1-5]. The modification widespread diffusive layers e.g. carburized and nitrided ones is possible owing to reinforcing them by some fine ceramic particles e.g. borides, oxides, sulfides and phosphides [6-9]. The

reinforcement in such layers is generated as a result of polyphase diffusion, lattice diffusion and precipitation processes accompanied the process of generating of the base diffusive layer. It is possible in a result of addition of certain chemical elements or compounds to the carburizing or nitriding atmosphere e.g. sulfur, phosphorus or oxygen enabling synthesis of the reinforcement particles. Thus a diffusive layer on a steel play a role of a matrix whereas ceramics precipitation is a reinforcement modifying structure and properties of the layer. That composition

of the layer and the particular reinforcement may be regarding as a composite diffusive layer reinforced by ceramic particles. Structure and properties of such a layer reinforced by iron phosphides are considered in the paper

So far not much attention has been paid to the role of phosphorus as a component of nitriding atmosphere. The beneficial influence of phosphorus on the properties of the surface of steel machine elements, especially on the increase of hardness and resistance in the process of friction is also underestimated. The beneficial influence of phosphorus on surface properties of iron alloy was examined in the [6-9]. There are many possibilities of modifying structure and properties of a surface of iron alloys in function of phosphorus concentration. If the phosphorus concentration in iron is small, a solid solution of phosphorus in iron may be form. Increase of the phosphorus concentration in iron makes a chance of precipitation hardening of the surface. Further increase of the phosphorus concentration in iron allows of forming of the iron phosphites Fe_3P and Fe_2P according to the Fe - P equilibrium system. It was found that the presence of phosphorus in the nitrated layer exerts a substantial influence on its structure and its properties [8, 9]. As the result of phospho - nitriding the precipitates of fine particles of iron phosphides in the nitrated layer as well as continuous zone of iron phosphides may be formed. The presences of iron phosphides in the nitrated layer increases its hardness and wear resistance in the process of dry sliding friction. The essential significance to the course of phospho - nitriding has the notable solubility of phosphorus in ferrite in the temperature of nitriding. The hitherto existing results of research are a convincing justification of searching for technical possibilities of introducing phosphorus to the nitriding layer and to defining the relations between the parameters of the phospho - nitriding and structure as well as properties of diffusive layer.

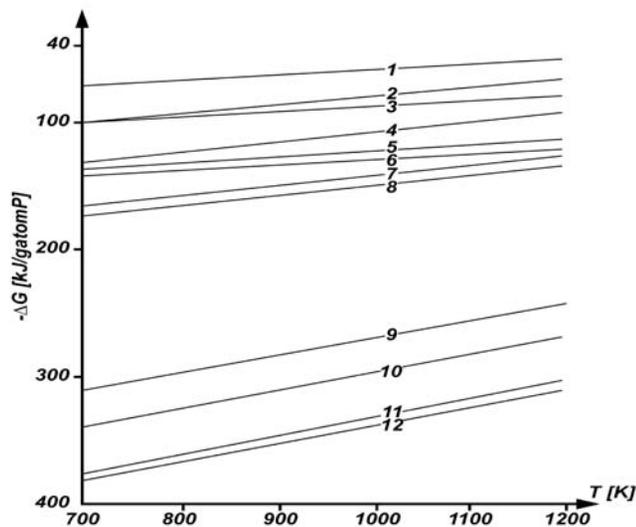


Fig. 1. Dependence of ΔG°_T on T of the reaction: 1 - $2\text{Fe} + \text{P}_4 \leftrightarrow 2\text{FeP}_2$; 2 - $\text{Fe} + \text{P}_2 \leftrightarrow \text{FeP}_2$; 3 - $4\text{Fe} + \text{P}_4 \leftrightarrow 4\text{FeP}$; 4 - $2\text{Fe} + \text{P}_2 \leftrightarrow 2\text{FeP}$; 5 - $8\text{Fe} + \text{P}_4 \leftrightarrow 4\text{Fe}_2\text{P}$; 6 - $4\text{Fe} + \text{P}_2 \leftrightarrow 2\text{Fe}_2\text{P}$; 7 - $12\text{Fe} + \text{P}_4 \leftrightarrow 4\text{Fe}_3\text{P}$; 8 - $6\text{Fe} + \text{P}_2 \leftrightarrow 2\text{Fe}_3\text{P}$; 9 - $2\text{Fe} + 4\text{P} \leftrightarrow 2\text{FeP}_2$; 10 - $\text{Fe} + \text{P} \leftrightarrow \text{FeP}$; 11 - $4\text{Fe} + 2\text{P} \leftrightarrow 2\text{Fe}_2\text{P}$; 12 - $3\text{Fe} + \text{P} \leftrightarrow \text{Fe}_3\text{P}$ [10]

2. Gibbs free energy of reaction in Fe-P system

Reactions of synthesis of iron phosphides: Fe_3P , Fe_2P , FeP in temperature 700÷1200 K have been considered (Fig. 1). For the reaction there have been calculated values of the Gibbs energy (ΔG°_T) related to a molecule of P in function of temperature (T), using standard thermodynamical functions of the reactants [10].

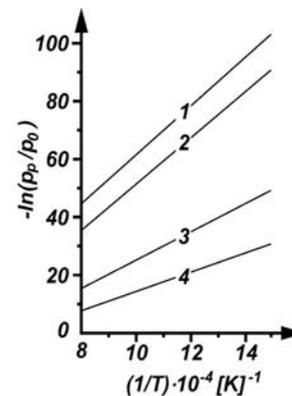


Fig. 2. Values of iron phosphides dissociation pressure of the reactions: 1 - $1 - 4\text{Fe}_3\text{P} \leftrightarrow 12\text{Fe} + \text{P}_4$; 2 - $12\text{Fe}_2\text{P} \leftrightarrow 8\text{Fe}_3\text{P} + \text{P}_4$; 3 - $8\text{FeP} \leftrightarrow 4\text{Fe}_2\text{P} + \text{P}_4$; 4 - $4\text{FeP}_2 \leftrightarrow 4\text{FeP} + \text{P}_4$ [10]

A value of the Gibbs energy of the considered reaction shows that in temperature 700÷1200 K, synthesis of all considered irons phosphides is possible. Reaction of Fe_3P synthesis of iron and atomic phosphorus P has the most profitable value of Gibbs energy ΔG°_T (Fig. 2-4). Calculations results of iron phosphides dissociation pressure p_p according to the considered reaction in temperature of 700 ÷ 1200K under normal pressure are presented on Fig. 2- 4. Iron phosphide Fe_3P has the largest thermodynamical stability of the other iron phosphides. Calculations of P_4 , P_2 and P phosphorus partial pressure (p_{P_4} , p_{P_2} , p_{P_1}) in function of temperature under normal and selected total pressure have been done.

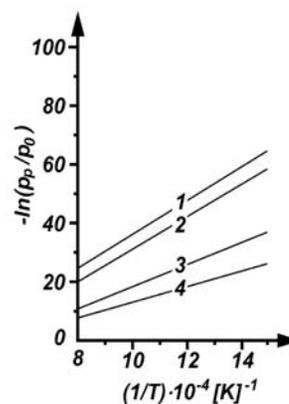


Fig. 3. Values of iron phosphides dissociation pressure of the reactions: 1 - $2\text{Fe}_3\text{P} \leftrightarrow 6\text{Fe} + \text{P}_2$; 2 - $6\text{Fe}_2\text{P} \leftrightarrow 4\text{Fe}_3\text{P} + \text{P}_2$; 3 - $4\text{FeP} \leftrightarrow 2\text{Fe}_2\text{P} + \text{P}_2$; 4 - $2\text{FeP}_2 \leftrightarrow 2\text{FeP} + \text{P}_2$ [10]

A value of the Gibbs energy of the considered reaction show that in temperature 700÷1200 K, synthesis of all considered iron phosphides is possible. Reaction of Fe₃P synthesis of iron and atomic phosphorus P has the most profitable value of Gibbs energy ΔG^o_T (Fig. 2-4).

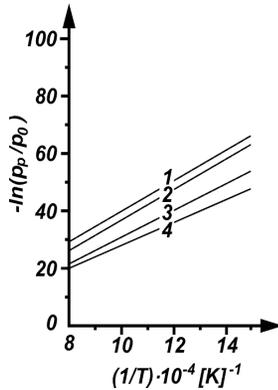


Fig. 4. Values of iron phosphides dissociation pressure of the reactions: 1 - Fe₃P↔3Fe + P; 2 - 3Fe₂P↔2Fe₃P + P; 3 - 2FeP↔Fe₂P + P; 4 - FeP₂↔FeP + P [10]

Table 1.

P₄, P₂ and P phosphorus partial pressure values p_{p4}, p_{p2}, p_{p1} in a state of thermodynamic equilibrium in normal pressure for selected temperatures total phosphorus pressure p = 100 Pa [10]

Temperature [K]	P ₄ , P ₂ and P phosphorus partial pressure		
	p _{p4} [Pa]	p _{p2} [Pa]	p _{p1} [Pa]
1000	99.0	1.00	1.26 · 10 ⁻⁰⁹
1100	96.5	3.50	3.72 · 10 ⁻⁰⁸
1200	90.7	9.30	5.80 · 10 ⁻⁰⁷

Calculations results of iron phosphides dissociation pressure p_p according to the considered reaction in temperature of 700 ÷ 1200K under normal pressure are presented on Fig. 2. Iron phosphide Fe₃P has the largest thermodynamical stability of the other iron phosphides. Calculations of P₄, P₂ and P phosphorus partial pressure (p_{p4}, p_{p2}, p_{p1}) in function of temperature under normal and selected total pressure have been done. Dissociation of phosphorus molecule P₄ can be preceded according to the reactions 1-4

$$P_4 \leftrightarrow 2P, \text{ and } P_2 \leftrightarrow 2P \quad (1)$$

$$K_{1P} = (p_{P2} / p_0)^2 / (p_{P4} / p_0) \quad (2)$$

$$K_{2P} = (p_{P1} / p_0)^2 / (p_{P2} / p_0) \quad (3)$$

$$p_{P4} + p_{P2} + p_{P1} = p_0 \quad (4)$$

Partial pressure values in the state of thermodynamic equilibrium of the phosphorus P₄, P₂ and P have been calculated basing on system of equations 2 – 4. Results of the calculations (Table 1) show, that values of phosphorus P₄, P₂ and P partial pressure p_{p4}, p_{p2}, p_{p1} are more superior, than iron phosphides dissociation pressure p_p values. It provides evidence of possibilities of synthesis iron phosphides in the considered

temperature and pressure first of all as a result of reaction of iron and atomic phosphorus P. As the thermodynamical criteria are considered, iron phosphide Fe₃P synthesises, as a result of reaction of iron with monatomic phosphorus P is privilege.

3. Diffusive iron phosphide layers

Iron phosphides layers were formed on a base of Armco iron and 0.4%C, 1.1%Cr steel in an atmosphere of argon and phosphorus vapour admixture. The following parameters of the process were applied: time t = 0, 6 ÷ 21, 6 ks (3 - 6h), temperature T = 700 ÷ 1223 K (427 - 950°C), partial phosphorus pressure p = 0.1 – 20 kPa. The diffusion layers were investigated by means of the methods: metallographic, X - ray structural analysis, microanalysis, test of Vickers hardness, test of resistance to wear by Amsler A 135 test at load of 1 MPa, way of friction 670 m and a friction speed 21 rad/s. Counter specimen was made from 0.4%C, 1.1% Cr steel (55 HRC) steel.

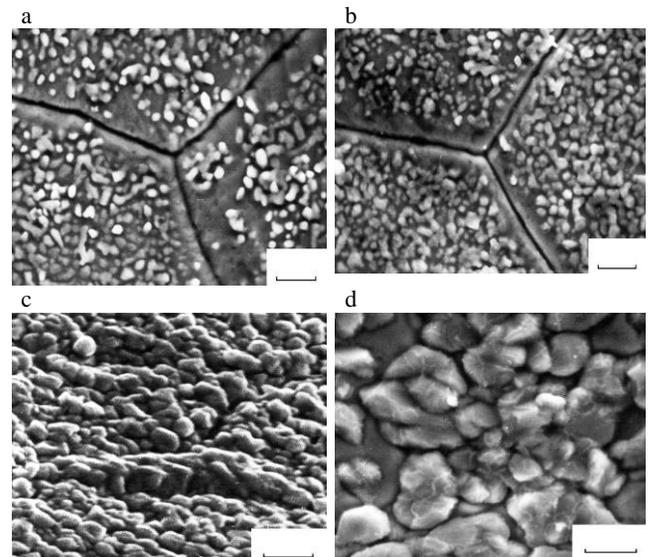


Fig. 5. Scanning image of Armco iron surface after phosphorizing, temperature of process T = 1223 K (950 °C), partial phosphorus pressure p = 100 Pa, time of the process; a - t = 0. 6 ks. (10 min), b - t = 1. 2 ks. (20 min.), c - t = 2.1ks. (35 min.), d - t = 3, 6ks. (60 min.), space bar - 5 μm [11]

As a result of the experiment, layers of silver-grey colour were made. Growth of thin iron phosphides layers begins by Fe₃P crystals nucleation in areas of surface being in a certain distance from iron grains boundaries (Fig. 5-8). Average number of Fe₃P crystals on surface unit increases with time and temperature of the process and phosphorus partial pressure. In further stage of the process Fe₃P crystals join in a continuous layer. Possibilities of iron phosphides synthesis in the considered temperature and pressure as a result of reaction of iron not only with phosphorus P₄, but also with phosphorus P₂ and P has been proved earlier [11]. Concentration of phosphorus on the surface in places, the process of continuous layers growth has begun is 15÷16% P. It

closes to a concentration of phosphorus in Fe_3P phosphide. Concentration of phosphorus on the surface over ferrite grain boundaries is considerably lower ($1\pm 3\%$). Smaller value of phosphorus concentration on surface over ferrite grain boundaries in the first phase of process is an effect of grain boundary diffusion in the core direction, what proves marker position after the phosphorizing process (Fig. 7, 8). In the phosphorizing process advanced stages, concentration of phosphorus in microareas round ferrite grain boundaries increases, and Fe_3P crystals nucleation begins. The phosphide layer produced as a result of the process has multiphase structure. The compact layer consists of zones of iron phosphides Fe_2P , on top of Fe_3P and solid solution of phosphorus in ferrite has been created. Growth of iron phosphide continuous layers is an effect of iron diffusion through phosphide layer from the core towards the surface. This direction of iron diffusion is proved by the indicator position put on the Armco iron surface before the phosphorizing process (Fig. 7). The phosphorus concentration in the layer, determined by X - ray quantitative microanalysis in the compact $\text{Fe}_2\text{P} + \text{Fe}_3\text{P}$ zone does not exceed 15 - 21 Wt.%, in the porous Fe_3P zone - 12 Wt %, and in the phosphorus in ferrite solid solution zone - 1.5 Wt % (Fig. 9-11). After some time of the phosphorizing process dependent on geometry of the sample surface, process temperature and phosphorus partial pressure, gap between the layer and the base was created. The gap creation process is analogous to a dissociation gap creation during high temperature oxidation. After that the gap has been field by secondary forming porous iron phosphide Fe_3P .

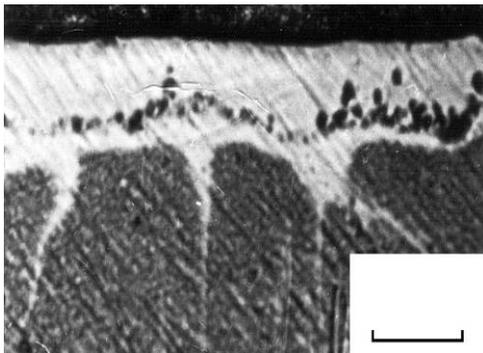


Fig. 6. Microphotography of the phosphide layer on Armco iron produced at the process paramers: $T = 1150 \text{ K}$ ($877 \text{ }^\circ\text{C}$), $p = 2 \text{ kPa}$, $t = 8.1 \text{ ks}$. (135 min.). Under the phosphides zone solid solution of phosphorus in ferrite along ferrite grain boundaries is visible; etched in 0.5 g CuCl_2 ; 0.5 g SnCl_2 ; 30 g FeCl_2 ; 50 ml HCl ; 2000 ml $\text{C}_2\text{H}_5\text{OH}$; 500 ml H_2O , space bar - 30 μm [11]

As a result of the investigations of the phosphorizing process kinetics by gravimetric analysis (Fig. 12-14), unitary increases of product mass m_k [kg/m^2] in process parameters (t , T and p) function, mathematical description of kinetics of process has been done (eq. 5). The equation (5) shows, that the phosphorizing process runs according to the parabolic rule. That means, that the produced layer is compact at least in a part of its thickness, and the slowest phenomena of the process is the phosphorus diffusion. The phosphide layer can be created at temperature above 650 K.

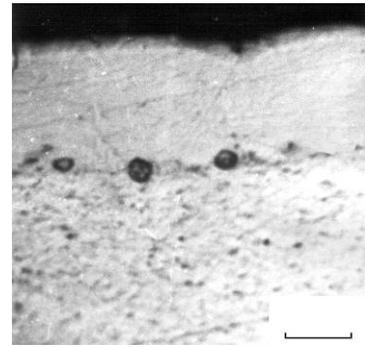


Fig. 7. Indicator position after the phosphorizing, $T = 1050 \text{ K}$ ($777 \text{ }^\circ\text{C}$), $p = 300 \text{ Pa}$, $t = 8, 1 \text{ ks}$ (2, 25 h), space bar - 10 μm [11]

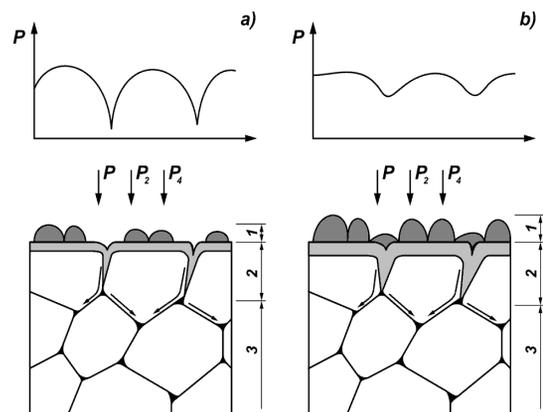


Fig. 8. Phosphorus partial pressure and iron phosphide Fe_3P distribution on Armco iron surface: a - first phase of iron phosphide layer growth, b - further phase of iron phosphide layer growth, 1 - nucleation zone, 2 - zone of grain boundary diffusion in the base, 3 - core zone [11]

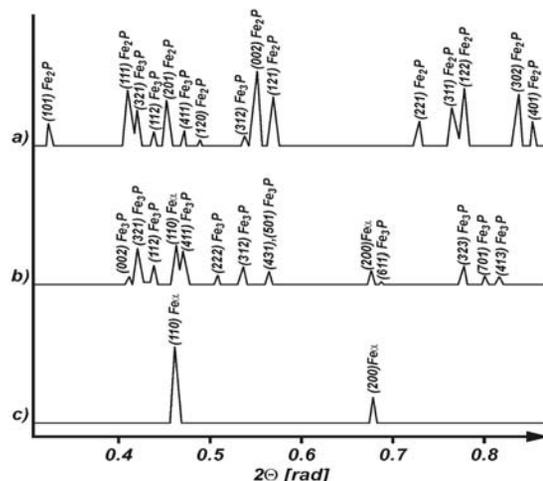


Fig. 9. Diffraction of the phosphide layer on the Armco iron, $T = 950 \text{ K}$ ($677 \text{ }^\circ\text{C}$), $p = 1 \text{ kPa}$, $t = 12.6 \text{ ks}$ (3.5 h). a - surface, b - after removal external zones Fe_2P , c - after removal of zone Fe_2P and Fe_3P [11]

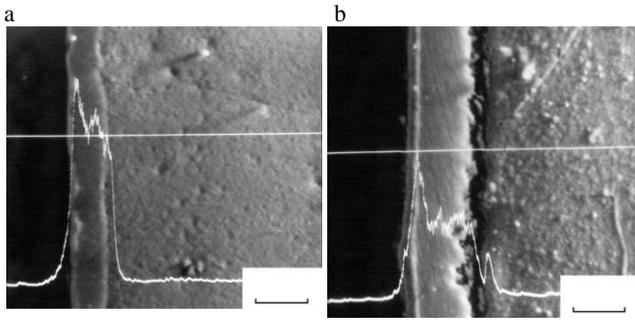


Fig. 10. Phosphide layer on Armco iron basis formed in at the process parameters: $T = 1050 \text{ K}$ ($877 \text{ }^\circ\text{C}$), $p = 1.0 \text{ kPa}$, $t = 11.7 \text{ ks.}$ (3.25 h), a - scanning image, b, c - qualitative phosphorus distribution in the cross section, space bar - $20 \text{ }\mu\text{m}$ [11]

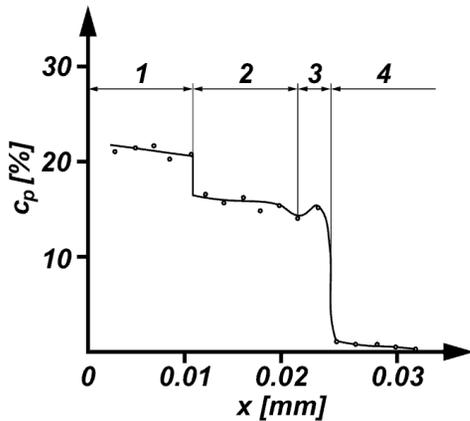


Fig. 11. Phosphorus distribution in the cross section of the phosphide layer produced at the process parameters: $T = 850 \text{ K}$ ($577 \text{ }^\circ\text{C}$), $p = 2.0 \text{ kPa}$, $t = 15.3 \text{ ks.}$ (4.25 h) worked out on the base of results of the quantitative microanalysis [11]

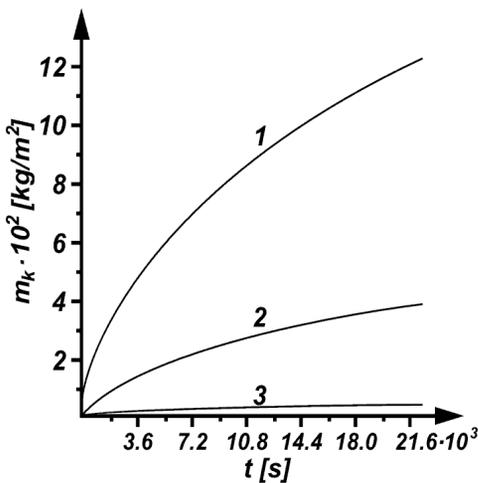


Fig. 12. Dependence of: $m_k = f(t)$ for: 1 - $T = 1150 \text{ K}$ ($877 \text{ }^\circ\text{C}$), $p = 20 \text{ kPa}$; 2 - $T = 950 \text{ K}$ ($677 \text{ }^\circ\text{C}$), $p = 10.15 \text{ kPa}$; 3 - $T = 750 \text{ K}$ ($477 \text{ }^\circ\text{C}$), $p = 0.3 \text{ kPa}$ [11]

Indicator position after the phosphorizing process (Fig. 7) proves, that the phosphide layer is generated as a result of iron diffusion from the core toward the surface. Dependence of unitary increases of product mass m_k of phosphorus partial pressure (p) proves (Fig. 12-14), diffusion of iron from the core towards the surface runs through cation gaps of the phosphide layer.

$$m_k = 5,35 \cdot 10^{-8} \cdot t^{0,5} (T - 650)^{2,17} p^{0,07} \quad (5)$$

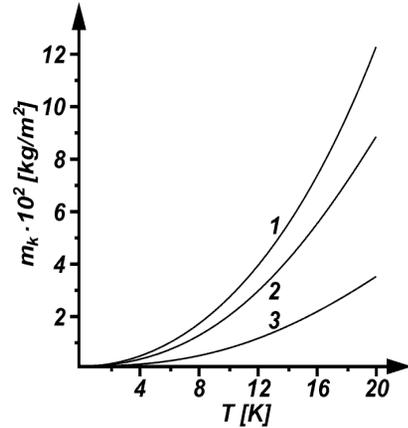


Fig. 13. Dependence of: $m_k = f(T)$ for: 1 - $t = 21.6 \text{ ks.}$, $p = 20 \text{ kPa}$; 2 - $t = 12.6 \text{ ks.}$, $p = 10.15 \text{ kPa}$; 3 - $t = 3.6 \text{ ks.}$, $p = 0.3 \text{ kPa}$ [11]

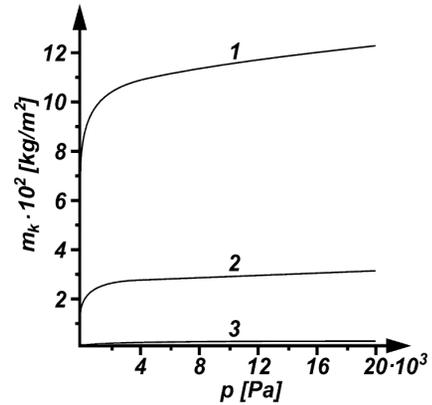


Fig. 14. Dependence of: $m_k = f(p)$ for: 1 - $t = 21.6 \text{ ks.}$, $T = 1150 \text{ K}$ ($877 \text{ }^\circ\text{C}$); 2 - $t = 12.6 \text{ ks.}$, $T = 950 \text{ K}$ ($677 \text{ }^\circ\text{C}$); 3 - $t = 3.6 \text{ ks.}$, $T = 750 \text{ K}$ ($477 \text{ }^\circ\text{C}$) [6]

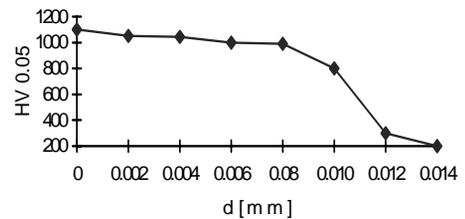


Fig. 15. Hardness $\text{HV } 0.01$ of the diffusive phosphide layer formed at the process parameters: $t = 0.3 \text{ kPa}$, $T = 1150 \text{ K}$ ($877 \text{ }^\circ\text{C}$), $p = 0.3 \text{ kPa}$ [11]

Within the diffusive phosphide layer, there is an outer thin zone of iron phosphide, Fe_2P of a hardness of 1100 HV 0.05, and underneath a phosphide zone, Fe_3P of a hardness of about 1000 HV 0.05, and solid solution of phosphorus in ferrite zone of a hardness of about 250 HV 0.05 (Fig. 15).

Based on the test, the dependence of wear m_t and the coefficient of friction μ on the parameters of the gaseous phosphorizing process is defined by the following equations (6, 7):

$$m_t = 10.15 - 5.89t_1 - 2.61T_1 - 0.17p_1 + 5.22t_1^2 + t_1T_1 + 67t_1p_1 + 4.39T_1^2 + T_1^2p_1^2 + 0.72p_1^2 \quad (6)$$

$$\mu = 0.252 + 0.005t_1 - 0.001T_1 - 0.010p_1 + 0.005t_1^2 + 0.009t_1T_1 + 0.002t_1p_1 + 0.018T_1^2 + 0.007 \quad (7)$$

It results that the specimen wear m_t shows a strong dependence on the parameters of the gaseous phosphorizing treatment, especially on the process time and temperature. Furthermore, the minimum of wear can be observed in intervals: $11000 \text{ s} \leq t \leq 15000 \text{ s}$ and $950 \text{ K} \leq T \leq 1050 \text{ K}$. From the former investigations it results, that the wear decreases together with the increase of the layer thickness, up to the state when the process of gap creation between the layer and the base starts. The layers with the gap show a grid of cracking and extensive spalling after friction tests, which causes the increase of the wear. The best tribological properties of iron phosphide layers have been obtained in the gaseous phosphorizing process parameters shown in Tab. 2.

Table 2.

Optimal parameters of the gaseous phosphorizing process for which the wear and the friction coefficient achieve the minimum in comparison to non-treated iron [11]

Process parameters of phosphide layer creation			Weight of wear m_t [mg]	Coefficient of friction μ
Time	Temperature	Partial pressure of phosphorus		
t [ks]	T [K]	p [kPa]		
3.6	1150	0.25	9.3	0.22
0.4%C, 1.1% Cr steel (55 HRC)			52	0.34

4. Diffusive carburised layers

The diffusive layers have been generated as a result of a gas phosphorcarburising of Armco iron and 0.2%C steel. The phosphorcarburising atmosphere was produced from the suspension of red phosphorus particles in isopropyl alcohol and water mixture instilled directly into the carburising chamber. The process of the diffusive phosphorcarburising was carried out with the following process parameters: temperature $T = 1173 \text{ K}$, phosphorus partial pressure $p = 100 - 300 \text{ Pa}$, process duration $t = 21.6 - 36.0 \text{ ks}$. (6 - 10 hours).

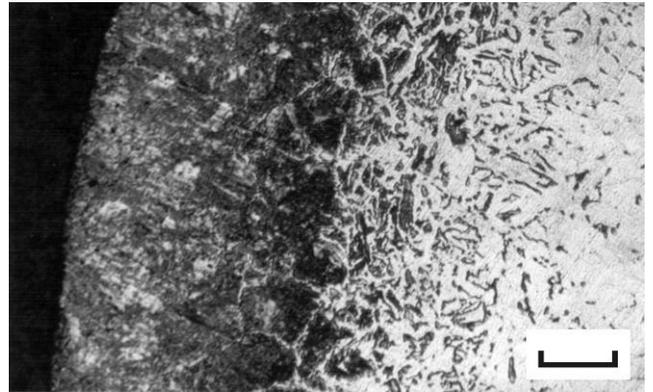


Fig. 16. Microphotography of the carburised ($T = 1173 \text{ K}$, $t = 28.8 \text{ ks}$.) layer on Armco iron; etched in 0.5 g CuCl_2 ; 0.5 g SnCl_2 ; 30 g FeCl_2 ; 50 ml HCl ; 2000 ml $\text{C}_2\text{H}_5\text{OH}$; 500 ml H_2O ; space bar – 0.45 mm [10]

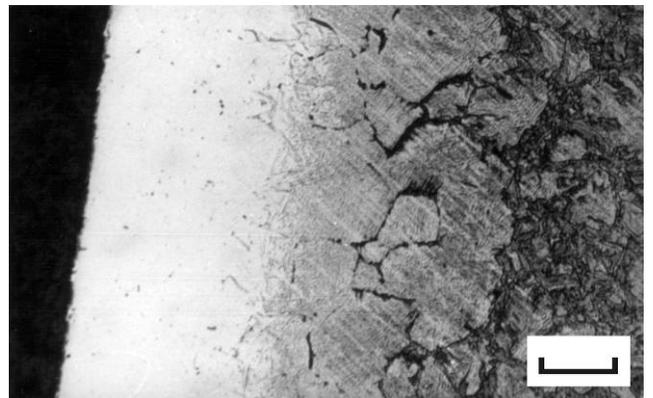


Fig. 17. Microphotography of the phosphorcarburised ($T = 1173 \text{ K}$, $t = 28.8 \text{ ks}$, $p = 10 \text{ Pa}$.) layer on Armco iron; etched in 0.5 g CuCl_2 ; 0.5 g SnCl_2 ; 30 g FeCl_2 ; 50 ml HCl ; 2000 ml $\text{C}_2\text{H}_5\text{OH}$; 500 ml H_2O ; space bar – 0.015 mm [10]

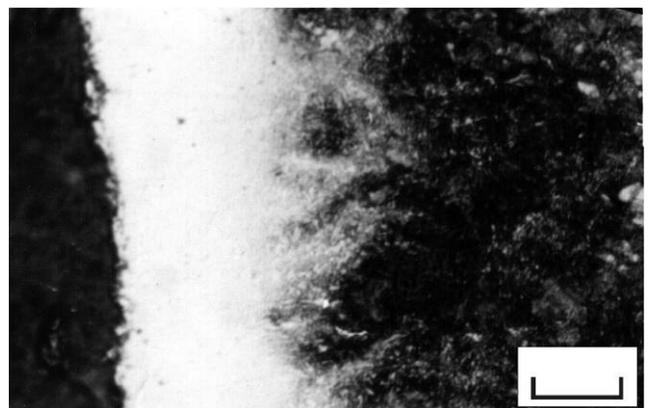


Fig. 18. Microphotography of the outer zone of the phosphorcarburised layer on Armco iron, etched in 0.5 g CuCl_2 ; 0.5 g SnCl_2 ; 30 g FeCl_2 ; 50 ml HCl ; 2000 ml $\text{C}_2\text{H}_5\text{OH}$; 500 ml H_2O ; $T = 1173 \text{ K}$, $t = 28.8 \text{ ks}$, $p = 100 \text{ Pa}$, space bar: 0.010 mm [10]

There have been done investigations of the phosphocarbursed layers by means of complementary methods: metallografy, X - Ray structural analysis, microanalysis, tests of HV 0.05 hardness, and resistance to wear by pin on disk method using the friction parameters: the contact pressure 5.5 MN/m², sliding speed 1 m/s and path of friction 300m, the counter-specimen: high - chromium ledeburitic steel - 62 HRC.

For phosphorus partial pressure $p = 150 - 300$ Pa the phosphocarbursed layer consist of an outer thin zone of iron phosphide, Fe₃P and a zone of phosphorus solution in ferrite over a carburised zone. For phosphorus partial pressure smaller than 150 Pa outer iron phosphide zone does not create (Fig. 16 - 21). The phosphide layers have considerable hardness and wear resistance, and a relatively small friction coefficient (Fig. 22, Tab. 3).



Fig. 19. Microphotography of the outer zone of the phosphor-carburised layer on Armco iron, $T = 1173$ K, $t = 28.8$ ks., $p = 300$ Pa, etched in 0.5 g CuCl₂; 0.5 g SnCl₂; 30 g FeCl₂; 50 ml HCl; 2000 ml C₂H₅OH; 500 ml H₂O; space bar: 0.010 mm [10]

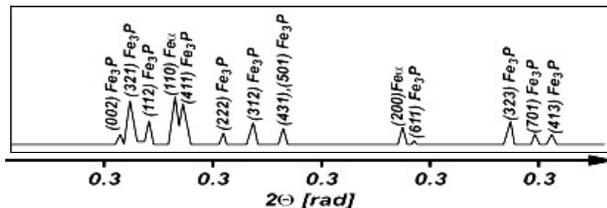


Fig. 20. Diffraction of the phosphocarbursed layer formed on the Armco iron in the process parameters: $T = 1173$ K, $p = 150$ Pa, and $t = 10.8$ ks

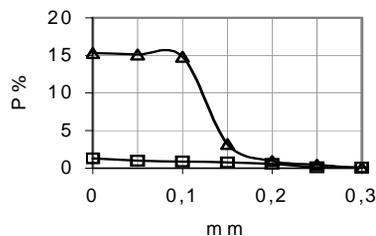


Fig. 21. Phosphorus concentration in the cross section of the phosphocarbursed layer produced at the process parameters: $T = 1173$ K, $t = 28.8$ ks., phosphorus partial pressure \square - $p = 0, 0$ Pa (pure carburising), Δ - 100 Pa [10]

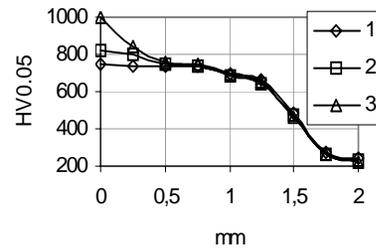


Fig. 22. Hardness HV0.05 distribution in the cross section of the phosphocarbursed layer produced at the process parameters: $T = 1173$ K, $t = 28.8$ ks., phosphorus partial pressure 1 - $p = 0, 0$ Pa (pure carburising), 2 - 100Pa, 3 - 200Pa [10]

5. Diffusive phosphor - nitrated layers

Preparation of the composite nitrated layers with particles of iron phosphides were carried out on a base of the Armco iron, 0.4% C, 1.1% Cr steel and 0.4% C, 1.6% Cr, 1% Al. steel in an atmosphere of the partly dissociated ammonia with an addition of the gashouses phosphorus. Phosphorus vapours were deposited by means of ammonia from an evaporator into the working chamber of the reactor in which the process of generating of the layer was executed. Phosphorus pressure was calculated from the dependence derived from the equation of state of perfect gas [9, 10]. During carrying out the processes through the following parameters were applied: temperature $T = 843 - 893$ K (570 - 620°C), ammonia volume flux $V_a = 5.6 \cdot 10^{-6}$ m³/s, phosphorus partial pressure $p = 10 - 300$ Pa, process duration $t = 10.8 - 21.6$ ks (3 - 6 h). The diffusive layers were investigated by means of the methods: a metallographic one, an X - ray structural analysis, microanalysis, test of Vickers hardness, test of resistance to wear with Falex test at a load of 450 N and a liner velocity of friction 1 m/s.

As a result of the experiments carried out, layers of a silver-grey colour were made on the surface of the specimens. Structure of the layers presented in Fig. 22 and 24. The investigations confirmed that owing to an addition of phosphorus to the nitrating atmosphere, the structure of diffusive layer is subject to the essential change (Fig. 23 - 24).

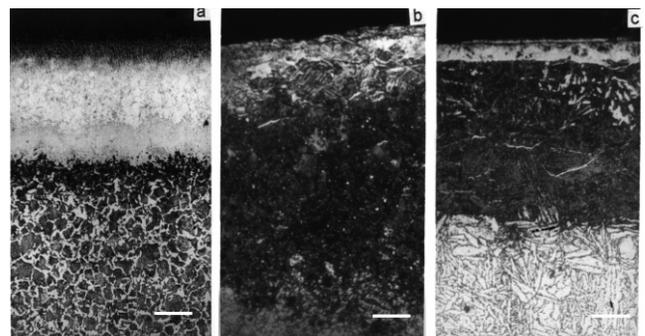


Fig. 23. Microstructure of composite phospho - nitrated layer, process parameters: $T = 843$ K (570 °C), $p = 60$ Pa, $t = 21.6$ ks (6 h), 0.4 % C, 1 % Cr (a); 0.4 % C, 1.4 % Cr, 1 % Al steel (b); 0.4 % C, 5 % Cr, 1.4 % Mo 0.4 % V (c) space bar 0.010 mm [11,12]

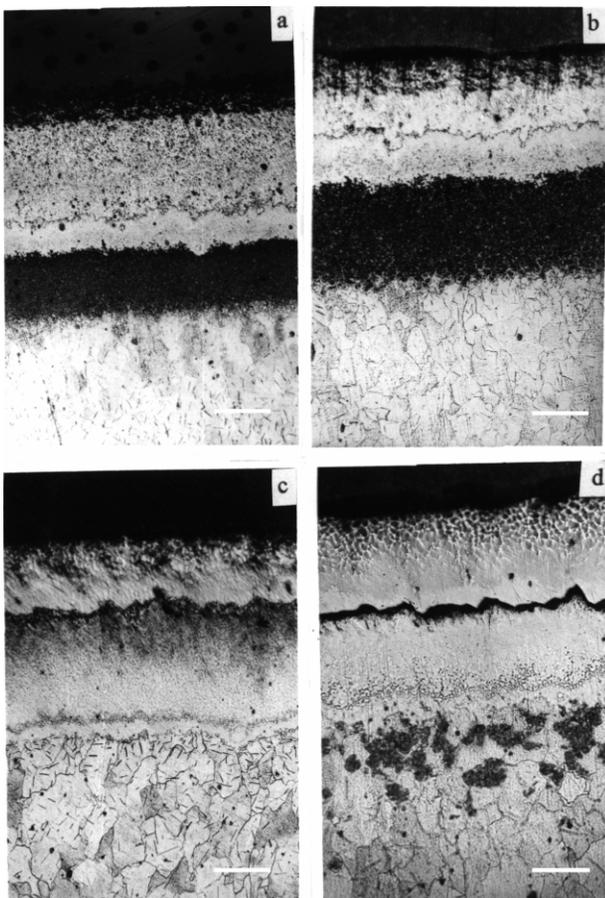


Fig. 24. Microstructure of composite phospho - nitrided layer, process parameters: temperature - $T = 893 \text{ K}$ ($620 \text{ }^\circ\text{C}$), phosphorus partial pressure $p = 60 \text{ Pa}$; process duration - $t = 21.6 \text{ ks}$ (6 h) (a); $T = 893 \text{ K}$ ($620 \text{ }^\circ\text{C}$), $p = 100 \text{ Pa}$, $t = 21.6 \text{ ks}$ (6 h) (b); $T = 843 \text{ K}$ ($570 \text{ }^\circ\text{C}$), $p = 140 \text{ Pa}$, $t = 21.6 \text{ ks}$ (6 h) (c); $T = 863 \text{ K}$ ($590 \text{ }^\circ\text{C}$), $p = 140 \text{ Pa}$, $t = 21.6 \text{ ks}$ (6 h) (d); space bar 0.012 mm [11,12]

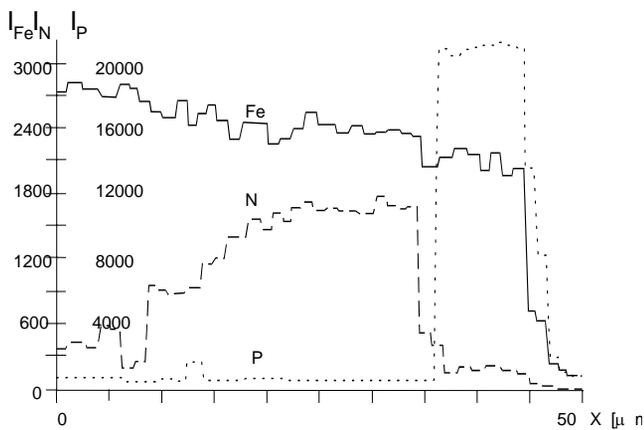


Fig. 25. Concentration of the phosphorus - P, nitrogen - N and iron - Fe in the phospho-nitrided layer; process parameters: $T = 893 \text{ K}$ ($620 \text{ }^\circ\text{C}$), $p = 180 \text{ Pa}$, $t = 21.6 \text{ ks}$ (6 h) [11,12]

Depending on the partial pressure of phosphorus in the nitriding atmosphere it is possible to differentiate two basic types of structure. In the case of low partial pressure of phosphorus i.e. below 120 Pa ., a stripe of iron phosphides Fe_3P precipitates in the zone of nitrides ϵ ($\text{Fe}_{2.3}\text{N}$) and $\epsilon + \gamma$ ($\text{Fe}_{2.3}\text{N}$ and Fe_4N) of the nitrided layer is created as a result of the process (Fig. 25 – 29).

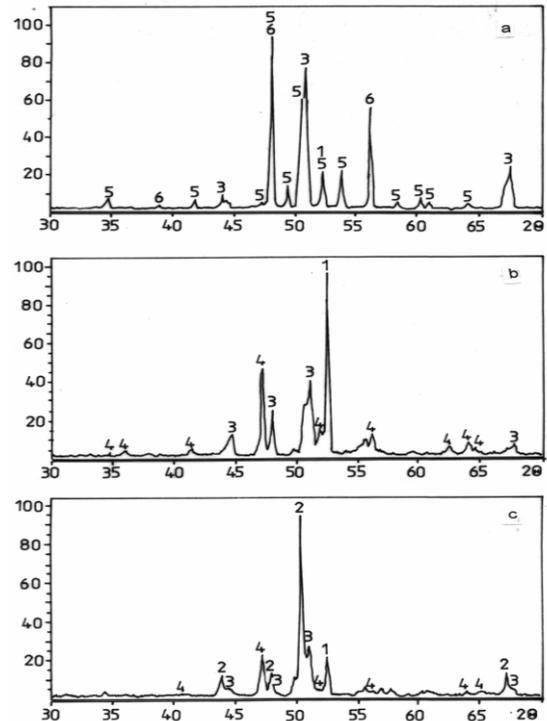


Fig. 26. Diffraction of phospho - nitrided layer formed on the Armco iron in the process parameters: $T = 893 \text{ K}$ ($620 \text{ }^\circ\text{C}$), $p = 150 \text{ Pa}$ $t = 10.8 \text{ ks}$ (3 h) (a); $T = 843 \text{ K}$ ($570 \text{ }^\circ\text{C}$), $t = 10.8 \text{ ks}$ (3 h), $p = 220 \text{ Pa}$ (b); $T = 843 \text{ K}$ ($570 \text{ }^\circ\text{C}$), $t = 10.8 \text{ ks}$ (3 h), $p = 180 \text{ Pa}$ (c); 1 - $\text{Fe}\alpha$, 2- Fe_2N , 3 - Fe_3N , 4 - Fe_2P , 5 - Fe_3P , 6 - Fe_4N

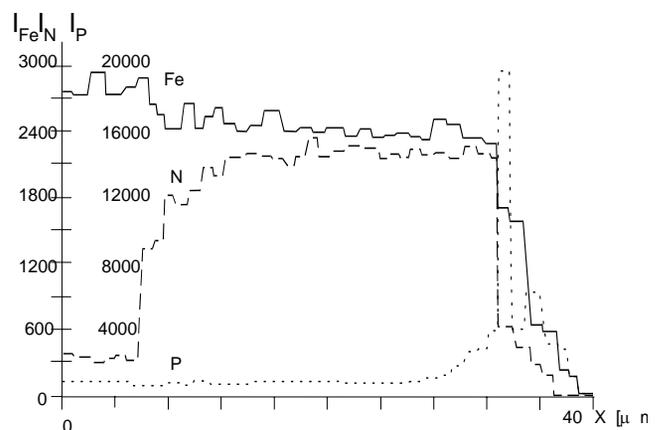


Fig. 27. Concentration of the phosphorus - P, nitrogen - N and iron - Fe in the phospho-nitrided layer; process parameters: $T = 853 \text{ K}$ ($580 \text{ }^\circ\text{C}$), $p = 110 \text{ Pa}$, $t = 21.6 \text{ ks}$ (6 h) [11,12]

Size and concentration of iron phosphides Fe_3P precipitates depend on the parameters of the process and first of all they increase with an increase of phosphorus partial pressure in the nitriding atmosphere.

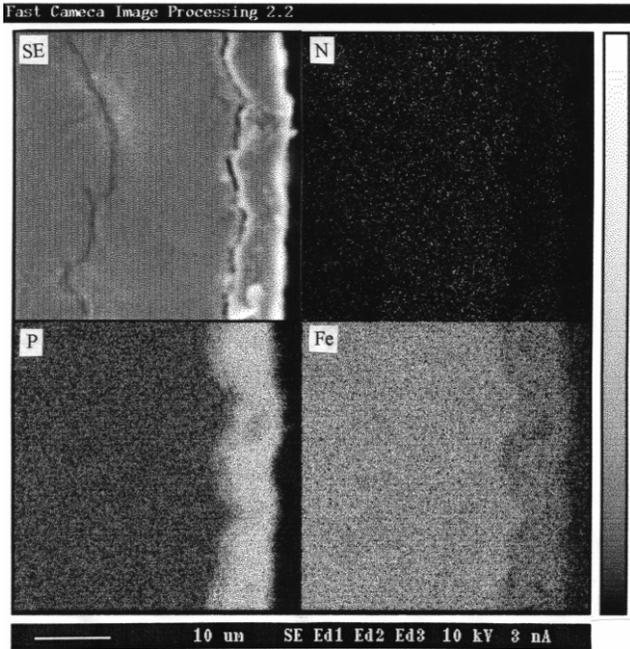


Fig. 28. Distribution of the phosphorus - P, nitrogen - N and iron - Fe in the phospho-nitrided layer, process parameters: $T = 853\text{ K}$ ($580\text{ }^\circ\text{C}$), $P = 190\text{ Pa}$, $t = 10.8\text{ ks}$ (3 h)

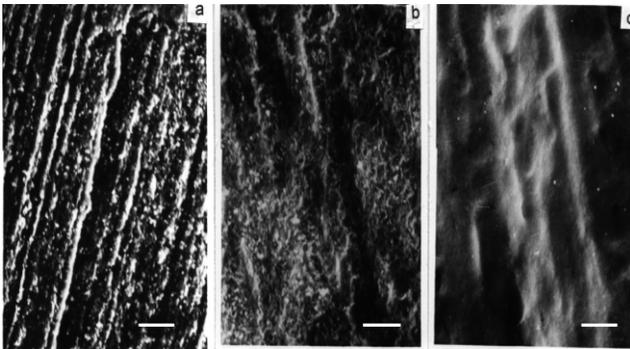


Fig. 29. Scanning image of the phospho - nitrided Armco iron surface, process parameters: $T = 843\text{ K}$ ($570\text{ }^\circ\text{C}$), $t = 10.8\text{ ks}$ (3 h), $P = 10\text{ Pa}$ (a); $P = 80\text{ Pa}$ (b); $p = 140\text{ Pa}$ (c); space bar 0.005 mm

Higher partial pressures of phosphorus in the ammonia atmosphere causes the formation of compact layer of iron phosphides $Fe_3P + Fe_2P$ over the zone of nitrides. The quantity relation of Fe_3P to Fe_2P in the compact layer depends on the partial pressures of phosphorus in the ammonia atmosphere (Fig. 23 - 28). The compact layer of phosphides is continuous only until the thickness of about 0.02 mm . In the case of bigger thickness this zone loses its continuity in the area of boundary with nitrides

zone. As a result of this process a gap in the boundary of the compact layer of phosphide and nitrides zone is created. In the advanced stages of the process of phospho - nitriding the gap is filling by porous Fe_3P . The process of creating the gap and porous Fe_3P is similar to a growth of oxide layers. Qualitative distribution of the phosphorus, nitrogen, and iron in the phospho-nitrided layer is shown in the Figure 27. Phosphorus concentration in the layer, determined by X - ray quantitative microanalysis, is presented in Tab. 4.

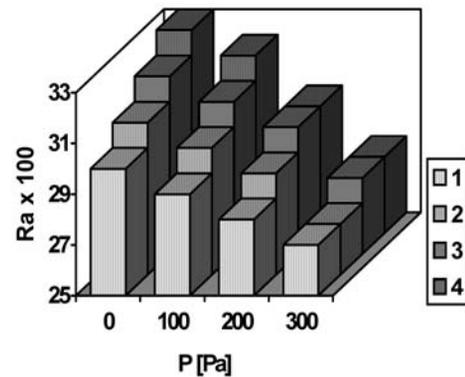


Fig. 30. Influence of phosphorus partial pressure - P on the surface roughness Ra of $0.4\%C$, $1.1\%Cr$ steel after phospho - nitriding in the process parameters: 1 - $T = 843\text{ K}$ ($570\text{ }^\circ\text{C}$), $t = 10.8\text{ ks}$ (3h); 2 - $T = 843\text{ K}$ ($570\text{ }^\circ\text{C}$), $t = 10.8\text{ ks}$ (6h); 3 - $T = 893\text{ K}$ ($620\text{ }^\circ\text{C}$), $t = 10.8\text{ ks}$ (3h); 4 - $T = 893\text{ K}$ ($620\text{ }^\circ\text{C}$), $t = 21.6\text{ ks}$ (6h);

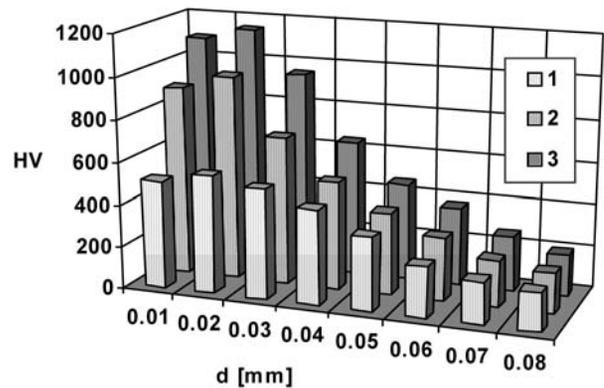


Fig. 31. Hardness HV 0.01 of nitrided layers formed in the process parameters $T = 843\text{ K}$ ($570\text{ }^\circ\text{C}$), $t = 6\text{ h}$, on the distance from the surface d, 1 - Armco iron, 2 - $0.4\%C$, $1.1\%Cr$ steel, 3 - $0.4\%C$, $1.6\%Cr$, $1\%Al$ steel

The admixture of phosphorus to the nitriding atmosphere alters the geometry of the phospho - nitrided surface in a small degree in comparison to the classic nitriding (Fig. 29 -30). A certain increase of the surface smoothness proves of the increasing role of the iron diffusion from the core in the direction of the surface. The presence of iron phosphides in the nitrided layers increases their hardness (Fig 31, 32). This effect is stronger in the lower temperatures of phospho - nitriding. An increase in the layer hardness is especially distinct on Armco iron, in which there are no components forming

hard nitrides. The nitrided layers with iron phosphides show greater resistance to wear in the process of dry friction than layers made in an atmosphere of pure NH_3 (Fig. 33). The increase of the layer hardness and in the resistance to wear is caused by solid solution strengthening and precipitation hardening as a result of the Fe_3P reinforcement presence.

As a result of the DTA/DTG analyses, possibility of oxidation of phosphides and formation of iron phosphates Fe_3PO_4 in the phosphonitrided layers was found. Fe_3PO_4 has been formed, as a result of phosphide oxidation during friction too [13,14].

Table 4.
Limits of phosphorus concentration in the phosphonitrided layer

zone	Phosphorus concentration Wt %
compact $\text{Fe}_2\text{P} + \text{Fe}_3\text{P}$	15 - 21 Wt
porous Fe_3P zone	12 Wt %
Fe_3P precipitates	15 - 21 Wt
$\epsilon + \text{Fe}_3\text{P}$ zone	5 Wt %

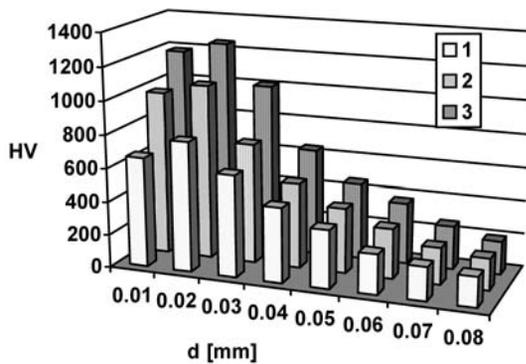


Fig. 32. Hardness HV 0.01 of phospho - nitrided layers formed in the process parameters $T = 843 \text{ K}$ (570°C), $p = 100 \text{ Pa}$, $t = 6 \text{ h.}$, on the distance from the surface d , 1 - Armco iron, 2 - 0.4% C, 1.1% Cr steel, 3 - 0.4% C, 1.6% Cr, 1% Al steel

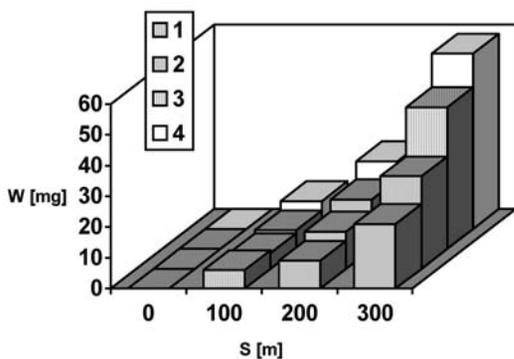


Fig. 33. Dependence of weight wear W on path of friction S of: 1 - phospho - nitrided 0.4% C, 1.6% Cr, 1% Al steel, 2 - phospho - nitrided 0.4% C, 1.1% Cr steel, 3 - nitrided 0.4% C, 1.6% Cr, 1% Al steel, 4 - nitrided 0.4% C, 1.1% Cr steel, in accordance to the Falex test; nitriding parameters as in Fig. 31 and phospho - nitriding parameters as on Fig. 32

6. Conclusions

Consideration of role of phosphorus in iron alloys surface engineering and relations of the iron phosphides layers growth parameters in processes of phosphorising, phosphorcarburising, and phosphonitriding with their structure and properties had been done. Significant influence of phosphorus on iron alloys surface structure and properties had been proved as a result of processes of gaseous phosphorising, phosphorcarburising, and phosphonitriding.

Depending on the partial pressure of phosphorus in an inert atmosphere, the formation of compact layer of phosphides with the adjustable relation of Fe_3P to Fe_2P is possible. Growth of thin iron phosphides layers begins by Fe_3P crystals nucleation in areas of surface being found in a certain distance from iron grains boundaries. Growth of iron phosphide continuous layers is an effect of iron diffusion through phosphide layer from the core towards the surface. In advanced phases of the of iron phosphide layer growth, a gap between the layer and the base is created as a process of degradation of the base layer interface. The gap creation process is analogous to a dissociation gap creation during high temperature oxidation. The gap generated between the layer and the base during the advanced stage of phosphorization causes a decrease in wear resistance.

The presence of phosphorus in iron alloys surface influences its hardness and its tribological properties.

Fe_3P iron phosphide synthesises, as a result of reaction of iron with monatomic phosphorus P is privileged. Possibility of iron phosphide layer and a solid solution of phosphorus in iron on the carburised layers generation have been suggested. For higher partial pressures of phosphorus in the carburising atmosphere, the formation of compact layer of Fe_3P phosphides is possible. Phosphorus increases hardness and decreases friction wear of the carburised layer.

Obtained layers are an example of composites diffusive layers with iron phosphide particles generated as a result of polyphase diffusion, lattice diffusion and precipitation processes accompanied of the phospho - nitriding.

The type, form and the concentration of iron phosphides appearing in the phospho - nitrided layer corresponds, first of all, to the partial pressure of phosphorus in the ammonia atmosphere and then to the remaining parameters of the process. Depending on the partial pressure of phosphorus in the nitriding atmosphere, the formation of compact layer of phosphides with the adjustable relation of Fe_3P to Fe_2P , or of controlled phosphides precipitates concentration in the nitride zone is possible.

Presence of phosphorus in the nitrided layer increases its hardness and its tribological properties owing to the solid solution strengthening and the precipitation hardening as a result of the Fe_3P presence. The best tribological properties have phospho - nitrided layers obtained in the lower than 100 Pa partial pressure of phosphorus in the ammonia atmosphere.

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