Influence of hydrogen content in working gas on growth kinetics of hardened layer at ion nitriding of steels

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Abstract. The paper studies the influence of hydrogen content of 10 to 30 % in the working gas on the growth kinetics and the structure of the hardened layer at ion nitriding of martensitic, austenitic and perlitic steels. It has been found for martensitic (quenching from 930°C and tempering at 600°C) and austenitic steels that the presence of H₂ in the amount exceeding 20% in a working chamber provokes hydrogen embrittlement of the hardened layer, which can lead to further destruction of the surface of the nitrided layer. The paper further presents some recommended values of H₂ content in a working chamber for ion nitriding of these steels. It has been proven that the change in the hydrogen content within 10-30% of the working gas at ion nitriding has insignificant effect on the surface hardness and thickness of the diffusion layer in martensitic steels (quenching from 1050°C and annealing at 800°C) and perlitic steels.

1. Introduction

There is a great demand for increased reliability and durability of modern machines and mechanisms in the current economic conditions. Practice shows that the most common reason of machine failure is wear of its individual parts. Nitriding in glow discharge is an efficient method to increase resistance to wear and contact fatigue failure of the surface of machine parts [1]. The possibility to control phase composition and structure of the diffusion layers over a wide range makes this method of surface hardening of great interest. However, long duration of this process (20...30 hours) is its main drawback.

Studies [2, 3] show that working gas composition greatly influences the structural and phase composition, mechanical and operational properties of the hardened layer at nitriding in glow discharge. It is known [4] that the use of up to 5% of hydrogen in a working gas makes it possible to increase the rate of diffusion saturation of steel surfaces with nitrogen. Being an efficient reducing agent, hydrogen prevents the formation of iron oxides on the surface of a workpiece, which hinders the nitriding [5]. High content of hydrogen triggers undesirable changes in the mechanical properties of metals, i.e. hydrogen embrittlement due to large diffusion mobility and penetration into the metal at high thicknesses. The presence of argon in the working gas also contributes to the acceleration of nitrogen diffusion into the metal due to numerous microdefects to the surface of the material produced during bombardment [6, 7]. At present, national and international communities lack literature data on the influence of multicomponent gas saturating media on the rate of diffusion growth of a hardened
layer at ion nitriding. Therefore, regulation of working gas composition with the view to increase the efficiency of ion nitriding is an urgent task.

2. Experiment
Martensitic steels [0.13-0.19 C; 2.78 Cr; 1.26 Ni; 0.46 Mo; 0.45 V; 1.22 W; 0.18 Nb] after quenching from 930°C and tempering at 600°C and [0.10-0.16 C; 10.5-12.0 Cr; 1.5-1.8 Ni; 0.18-0.30 V; 0.35-0.50 Mo; 1.60-2.0 W] after quenching from1050°C and tempering at 800°C, austenitic steel AISI 321 [0.12 C; 17-19 Cr; 9-11 Ni; 0.8 Ti] after quenching from 1050°C and perlitic steel [0.35-0.42 C; 0.3-0.6 Mn; 0.2-0.45 Si; 1.35-1.65 Cr; 0.15-0.25 Mo; 0.7-1.1 Al] after quenching from 930°C and tempering at 600°C were subjected to ion nitriding.

The experiment was carried out using a modernized ELU-5 installation that was intended for vacuum heat and chemical heat processing (figure 1). The samples were ion-purged during 10 min at \( P=10 \text{ Pa} \) in Ar before nitriding; at this the surface temperature did not exceed \( T=250°C \). The diffusion saturation was carried out in a working mixture of \( \text{N}_2, \text{Ar} \) and \( \text{H}_2 \). The composition of the working gas and the parameters of ion nitriding are given in table 1.

![Figure 1. Schematic diagram of ion nitriding using the ELU-5 installation.](image)

| No. of processing mode | Composition of working gas, % | Temperature, °C | Pressure, Pa | Duration, h |
|------------------------|-------------------------------|-----------------|--------------|-------------|
| 1                      | Ar 60; \text{N}_2 30; \text{H}_2 10 |                  |              |             |
| 2                      | Ar 55; \text{N}_2 30; \text{H}_2 15 |                  |              |             |
| 3                      | Ar 50; \text{N}_2 30; \text{H}_2 20 | 550             | 150          | 6           |
| 4                      | Ar 45; \text{N}_2 30; \text{H}_2 25 |                  |              |             |
| 5                      | Ar 40; \text{N}_2 30; \text{H}_2 30 |                  |              |             |

Surface microhardness was measure using a Struers Duramin-1 microhardness tester. The static load applied to the diamond indenter during 10 seconds was 980.7 [mN] (100 g).

An Olympus GX-51 optic microscope was used to investigate the sample microstructure.
3. Results and discussion
Figure 2 shows optical photographs of the microstructure of the hardened layer of martensitic steel samples (quenching from 930°C and tempering at 600°C) after ion nitriding at different hydrogen contents in the working gas.

Microstructure analysis of the samples showed that the thickness of the modified layer varied from 10 to 130 μm relative to the increase in the H₂ content in the working gas mixture from 10 to 30%. The zone of internal nitriding in steels presumably is a solid solution of nitrogen in α-Fe [8-10]. Three zones can be seen in the pictures: I – embrittled layer, II – diffusion zone, III – basic material (matrix). For the samples subjected to ion nitriding in the working gas where the hydrogen content was 10 and 15%, the embrittled layer (I) is absent, the transition between the matrix (III) and the diffusion zone (II) is smooth. The thickness of the hardened layer makes h~10 μm and 45 μm.

When H₂ content in the working medium exceeds 20 %, the structure of the nitrided layer demonstrates microcracks that are directed along the boundaries of the former α-phase grains. When H₂ content in the working medium exceeds 25 %, the size of microcracks grows, there are small chips in the near-surface areas. The cracking is identified as intergranular, since a grid of cracks is formed over the former boundaries of α-phase grains. There is an interface between the embrittled layer (I) and the diffusion zone (II), which indicates the peeling of the embrittled layer (I) from the matrix (III).

Figure 3 shows optical photographs of the microstructure of the hardened layer of martensitic steel samples (quenching from 1050°C and tempering at 800°C) after ion nitriding at different hydrogen contents in the working gas. Microstructure analysis of the samples showed that 10-30 % of H₂ content in the working gas had no significant influence on ion nitriding intensity. The microstructure of all samples has three zones: I – nitride zone, II – diffusion zone, III – matrix. The transition between the diffusion zone (II) and the matrix (III) is smooth. Nitride zone (I) presumably consists of iron nitrides and alloying elements. Diffusion layer is a solid solution of nitrogen in α-Fe. The thickness of the diffusion layer makes h~200 μm. All samples demonstrated absence of hydrogen embrittlement defects in the form of microcrack grids and surface chips.

![Figure 2](image-url)

Figure 2. Microstructure of the hardened layer of martensitic steel samples after ion nitriding at different hydrogen contents in the working gas: a – 10%H₂; b – 15%H₂; c – 20%H₂; d – 25%H₂; e – 30%H₂.
Figure 3. Microstructure of the hardened layer of martensitic steel samples after ion nitriding at different hydrogen contents in the working gas: a – 10%H$_2$; b – 15%H$_2$; c – 20%H$_2$; d – 25%H$_2$; e – 30%H$_2$.

Figure 4 shows optical photographs of the microstructure of the hardened layer of perlitic steel samples after ion nitriding at different hydrogen contents in the working gas.

Figure 4. Microstructure of the hardened layer of perlitic steel samples after ion nitriding at different hydrogen contents in the working gas: a – 10%H$_2$; b – 15%H$_2$; c – 20%H$_2$; d – 25%H$_2$; e – 30%H$_2$.

Microstructure analysis of the perlitic steel samples showed that 10-30 % of H$_2$ content in the working gas had no significant influence on ion nitriding intensity. The thickness of the diffusion layer
made \( h \approx 195-250 \mu m \). All samples demonstrated the absence of hydrogen embrittlement defects in the form of microcrack grids and surface chips.

Figure 5 shows optical photographs of the microstructure of the hardened layer of austenitic steel samples after ion nitriding at different hydrogen contents in the working gas.

![Figure 5](image)

**Figure 5.** Microstructure of the hardened layer of austenitic steel samples after ion nitriding at different hydrogen contents in the working gas: a – 10%H\(_2\); b – 15%H\(_2\); c – 20%H\(_2\); d – 25%H\(_2\); e – 30%H\(_2\).

Microstructure analysis of the austenitic steel samples showed that the thickness of the modified layer varied from 5 to 70 \( \mu m \) relative to the increase in the H\(_2\) content in the working gas mixture from 10 to 30\%. Three zone can again be seen in the pictures. For the samples subjected to ion nitriding in the working gas where the hydrogen content was 10 and 15\%, the embrittled layer (I) is absent, the transition between the matrix (III) and the diffusion zone (II) is smooth. The thickness of the hardened layer makes \( h \approx 5 \mu m \) and 40 \( \mu m \).

When H\(_2\) content in the working medium exceeds 20 \%, the structure of the nitrided layer demonstrates microcracks that are directed along the boundaries of the former \( \alpha \)-phase grains. When H\(_2\) content in the working medium exceeds 25 \%, the size of microcracks grows, there are small chips in the near-surface areas. The cracking is identified as intergranular, since a grid of cracks is formed over the former boundaries of \( \alpha \)-phase grains. An increase in the H\(_2\) content from 20 to 30\% does not increase the thickness of the diffusion layer, which is \( \approx 70 \mu m \).

Microhardness analysis of the martensitic steel (quenching from 930 °C and tempering at 600 °C) and austenitic steel (figure 6a, b) showed that when hydrogen content in the working gas increased from 10\% to 20\%, a noticeable increase in surface microhardness was observed. Increased thickness of the hardened layer is due to high diffusion mobility of H\(_2\) and its penetration into the metal at high thicknesses. When hydrogen content further increases up to 30 \%, microhardness and thickness of the hardened layer improve slightly.

A change in the hydrogen content within 10-30\% of the working gas at ion nitriding has insignificant effect on the surface hardness and thickness of the diffusion layer in martensitic steels (quenching from 1050 °C and annealing at 800 °C) and perlitic steels.
Figure 6. Dependence of microhardness distribution over the thickness of the diffusion layer after ion nitriding at different hydrogen content in the working gas composition: martensitic steel (quenching from 930 °C and tempering at 600 °C) (a), austenitic steel (b), martensitic steel (quenching from 1050 °C and annealing at 800 °C) (c), perlitic steel (d).

4. Conclusion
The study of the influence of hydrogen content in a working gas on the structure and mechanical properties of martensitic, austenitic and perlite steels at ion nitriding has established that:

1. The presence of over 20% H$_2$ in a working chamber provokes hydrogen embrittlement of the hardened layer in martensitic (quenching from 930°C and tempering at 600°C) and austenitic steels. As a result, embrittlement and further destruction occurs in the near-surface regions of the nitrided layer. Ion nitriding of steels is recommended at over 20% of H$_2$ content in a working chamber.

2. A change in the hydrogen content within 10-30% of the working gas at ion nitriding has insignificant effect on the surface hardness and thickness of the diffusion layer in martensitic steels (quenching from 1050°C and annealing at 800°C) and perlite steels.

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