Influence of electrolyte-plasma surface hardening on the structure and properties of steel 40KhN

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Abstract. The optimal electrolyte composition for electrolyte-plasma surface hardening of 40XH steel, which does not lead to the surface layer to erosion, oxidation and decarburization are determined in this work. It is shown that after electrolytic-plasma surface hardening a modified layer with a thickness of 1–1.2 mm is formed with high hardness and wear resistance which consisting of a hardened layer of fine-grained martensite, an intermediate layer of perlite and martensite.

1. Introduction
In the last time, the technology of electrolytic-plasma hardening ha a particular interest due to which one can achieve sufficiently high performance properties. Electrolyte-plasma hardening (EPH) is one of the methods of high-speed heating where the workpiece is a cathode or anode relative to an aqueous electrolyte. It is possible to produce hardening, chemical-thermal and thermocyclic processing of materials which are depending on the heating mode, electrolyte composition, design parameters of the equipment, [1, 3]. Under this situation the electrolytic-plasma hardening is the most economical and productive method. It is characterized by less energy consumption, simplicity of technological equipment and large size of the hardened zone. The advantages of the method are a sufficiently large process performance and the ability to strengthen the details of a large mass and complex profile [3]. Based on the above, it is relevant to study the effect of electrolytic-plasma hardening regimes on the structural properties of alloyed structural steels.

2. Materials and methods of research
Electrolyte-plasma surface hardening of the samples was carried out in a laboratory installation which developed and manufactured at the “Surface Engineering and Tribology” Research Center at S. Amanzholov East Kazakhstan State University.

Steel 40KhN was chosen as the object of study. The choice of research materials is justified by the fact that this steel is widely used in the manufacture of parts for mechanisms operating under constant load conditions, when the mechanisms operate at high sliding speeds and high vibrations. Such as: connecting tubes and couplings for mechanisms in the oil industry, piston rods, axles, and shafts, gears, hydraulic cylinder rods and similar parts, as it provides high quality of the final product. The chemical composition of steel 40KhN is presented in table 1.
Table 1. Chemical composition of steel 40KhN (GOST 4543-71).

| C    | Si    | Mn    | Ni    | S    | P    | Cr    | Cu    |
|------|-------|-------|-------|------|------|-------|-------|
| 0.36–0.44 | 0.17–0.37 | 0.5–0.8 | 1–1.4 | till 0.035 | till 0.035 | 0.45–0.75 | till 0.3 |

We set ourselves the task of identifying the features of structure formation in steel 40KhN under electrolytic-plasma surface hardening.

Tribological tests on sliding friction were carried out on a THT-S-BE-0000 high-temperature tribometer at the Tomsk Materials Sharing Center of Tomsk State University using the standard “ball-disc” method (international standards ASTM G 133-95 and ASTM G 99) [4]. The wear tracks were researched using the contactless 3D profilometer of MICROMEASURE 3D station.

The elemental composition of the sample treated in electrolyte plasma was tested on scanning electron microscope JSM-6390LV of JEOL company (Japan), with the addition of an energy dispersive microanalyzer INCA Energy of OXFORD Instruments company. Microhardness measurements were carried out on the device PMT-3 in accordance with GOST 9450-76. Samples of size 10×10×20 mm³ were cut out from the shaft with a diamond disc 1 mm thick, which was immersed in a coolant. The sample does not experience deformation and thermal effects at low cutting speeds (n = 350 rpm) and low load (m = 250 g). For metallographic microanalysis, thin sections after polishing using chromium dioxide paste were etched with a 5% alcohol solution of nitric acid.

3. The results of research and their discussion

The formation of a stable continuous gas-vapor shell around the active electrode is a prerequisite for the implementation of electrolyte-plasma hardening. The formation of a stable continuous vapor-gas shell is influenced not only by the electrical circuit parameters, but also by the molecular properties of the fluid, which depend on the composition of the electrolyte and its concentration [5, 6]. Besides of it, the main indicators of quality electrolyte-plasma processing, which include hardness, the thickness of the modified layer and wear resistance depend on several factors: the composition of the electrolyte, current density, voltage, electrolyte temperature, processing time. Among these factors, the most important role belongs to the composition of the electrolyte.

Aqueous solutions of sodium carbonate are most widely used for surface hardening of steels [7]. As it is known [8, 9], sodium carbonate is the most optimal component providing a stable discharge for the cathode process. In this regard, an electrolyte based on sodium carbonate was chosen for surface hardening. In order to prevent the decarburization process to the electrolyte composition was added the urea. The choice of carbamide is due to the fact that this substance is a source of carbon, as well as characterized by low cost and environmental safety. It is also important to note that urea is highly soluble in water: at 20°C, the solubility of urea is 51.83% (mass) [10]. In addition, sodium carbonate interacts well with urea. In this regard, sodium carbonate was chosen as the component providing the optimal electrolyte conductivity, and urea was chosen to prevent the decarburization of the surface.

We selected the following electrolytes containing urea and sodium carbonate with various concentrations for EPH (table 2).

High hardness is observed in samples treated in electrolytes containing 15 and 20 % carbamide. The samples treated in electrolytes containing 10 % carbamide and 15–20 % sodium carbonate showed the lowest hardness. This is probably due to the decarburization of the surface layer. Thus, carbamide contains carbon and nitrogen in greater quantities than sodium carbonate, which allows the surface to be modified and prevents surface decarburization. At the same time, a change in the concentration of sodium carbonate does not lead to a significant change in the surface hardness.
Table 2. Solution composition.

| Electrolyte number | Amount of concentrate and water % |
|--------------------|-----------------------------------|
|                    | Sodium carbonate, Na₂CO₃          | Carbamide, (NH₂)₂CO | Water, H₂O |
| No.1               | 10                                | 15                  | 75         |
| No.2               | 15                                | 15                  | 70         |
| No.3               | 10                                | 20                  | 70         |
| No.4               | 15                                | 10                  | 75         |
| No.5               | 20                                | 10                  | 70         |

Figure 1 shows the dependence of the microhardness of steel 40KhN on the composition of the electrolyte. EPH (Electro Plasma Hardening) was carried out by exposure to electrolytic plasma for 3 seconds, followed by cooling in a flow-through electrolyte. The electrolyte temperature was ≈ 40°C. It can be seen that the microhardness of the samples increases with an increase in the concentration of urea in the electrolyte and reaches 4420 MPa.

Thus, we have obtained the most optimal electrolyte composition for electrolyte-plasma surface hardening of steels, which does not cause the surface layer to erosion, oxidation and decarburization. Such an electrolyte is an electrolyte containing up to 15% sodium carbonate and 15% carbamide. Besides of it, using this electrolyte produces a stable steady discharge.

Table 3 shows the wear rate of steel samples 40KhN before and after EPH. Tests conducted by the scheme "ball-disk". It can be seen that the treated sample shows a significant decrease in wear rate in comparison with the original sample, which indicates a significant increase in wear resistance of steels. The results of testing samples for abrasive wear were characterized by the amount of wear of the samples after the test. Table 2 shows the amount of wear of the sample steel 40KhN before and after hardening of the EPH. It is seen that the amount of wear of the hardened sample is less than that of the non-hardened sample, which indicates an increase in the resistance to abrasive wear of 40KhN.
after surface hardening. Changes in the microhardness of the surface layer of 40KhN steel were studied after EPH.

Table 3 provides the dependences of the microhardness of steel 40KhN on the duration of exposure to electrolytic plasma. It is seen that the microhardness of steel 40KhN after EPH increases by 2 times in depending on the initial state.

| Sample name         | Microhardness, (MPa) | Wear rate, (mm³·H⁻¹·m⁻¹) | The amount of wear, (μm³) |
|---------------------|----------------------|---------------------------|--------------------------|
| 40KhN initial       | 2030                 | 8.9                       | 11.03                    |
| 40KhN after EPH, 3 s| 4407                 | 0.28                      | 0.07                     |

Photos with the help of a profilometer were taken of the zone of contact of the samples for various durations of heating of the EPH (figure 2). Assessing the wear resistance of samples based on the geometrical parameters of the wear tracks, it can be said that the depth of the sample track after EPH is much smaller compared to the untreated sample. The shape of the irregularities in general proves once again the improvement in the tribological characteristics of the test sample. It was found that EPH reduces surface roughness in addition to increasing the hardness of the surface layer which leads to a decrease in friction during operation, and therefore increase its durability.

![Figure 2](image.png)

The microstructure of the cross-section of 40KhN steel after electrolytic-plasma surface hardening is shown in figure 3. It can be seen in figure 3 that the structure of the cross-section of steel is conventionally divided into 3 zones: zone 1 on the surface – hardened layer; zone 2 – heat-affected layer; zone 3 is the matrix. The hardened layer is a homogeneous fine-grained martensitic structure. As the depth increases, a non-uniform structure is formed – a heat-affected zone, which is martensite and perlite. Then this zone turns into a pearlite-ferritic structure, i.e. in the structure of the matrix. The thickness of the modified layer is 1–1.2 mm.
Figure 3. Microstructure of the cross-section of steel 40KhN after EPH with a heating time of 3 s.

Figure 4 shows SEM images of the surface of steel 40KhN before and after EPH.

Figure 4. Steel 40KhN microstructure: a – before, b – after an EPH with a heating time of 3 s.

The energy-dispersive analysis of the surface of steel samples 40KhN was carried out before and after EPH with the aim of identifying the changes in the elemental composition of the surface. Figure 5 shows the results of energy dispersive analysis. No significant changes in the elemental composition of the steel 40KhN surface are observed after EPH.
Figure 5. Results of X-ray microanalysis of the steel surface 40KhN.

Figure 6 presents the X-ray diffraction patterns of 40XH steel in the initial state (figure 6a) and after electrolytic-plasma hardening for a duration of 3 s. X-ray diffraction analysis revealed the presence of an α-phase on the bases of Fe in the initial sample, and Fe₃C lines appeared in the modified layer after electrolytic-plasma hardening.

Figure 6. Diffractogram of 40KhN steel before and after EPH.

Thus, the main advantage of EPH is the possibility of obtaining a modified layer on the surface of steels consisting of martensite with carbide particles, as evidenced by the increase in microhardness and wear resistance. X-ray structural analysis did not reveal the presence of carbide particles, possibly due to their fine dispersion. In this case, the basis of the material does not change, it consists of a
ferritic-pearlitic structure, i.e. the part retains its viscous core. The formation of a modified layer of fine-grained martensite with carbide particles in the surface layers will positively affect the performance properties of the parts, since small carbides keep the matrix from abrasion.

4. Summary
Analyzing the experimental results obtained in the work, we can draw the following conclusions:

- It was determined that the most optimal electrolyte composition for electrolyte-plasma surface quenching of steels that does not lead to erosion, oxidation and decarburization of the surface layer are electrolytes containing up to 15% sodium carbonate and 15% carbamide. It is established that an increase in the concentration of sodium carbonate in the electrolyte leads to an increase in the surface roughness parameter.
- It was established that after EPH a modified layer with a thickness of 1–1.2 mm with high hardness and wear resistance, consisting of a hardened layer of fine-grained martensite, an intermediate layer of perlite and martensite, is formed.
- It was established that the microhardness and wear resistance of steel 40KhN increases after EPH, depending on the processing mode. After EPH with a heating time of 3 s, the microhardness increases up to 2 times, the wear resistance increases up to 30 times. High wear resistance of steels after EPH is associated with the formation of fragmented martensite with dispersed carbides.

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