Complex beam-plasma surface treatment of high-chromium steel

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Abstract. Here, using scanning and transmission electron microscopy, X-ray diffraction analysis, and tribological test data, we study the surface structure and properties of high-chromium steel 420 exposed to three types of surface modification: intense electron beam irradiation (40 J/cm², 200 µs, 3 pulses), nitriding in low-pressure arc plasma (550 °C, 4 h), and their combination in a single vacuum cycle. The study suggests that all types of treatment enhance the microhardness and the wear resistance of the steel compared to its initial state: their values are increased respectively 1.5 and 3.2 times after irradiation, 2 and more than 800 times after nitriding, and 2.3 and more than 100 times after irradiation and further nitriding in a single vacuum cycle.

1. Introduction
Martensitic stainless steel 420 is widely used to manufacture products operating in low aggressive atmospheres at room or moderate temperature, e.g., ambient air, water solutions of organic acid salts, nitric acid solutions of low and medium concentrations, etc. [1]. The service properties of steels can be improved by forming a submicro- and nanosized multiphase structure in their surface layers [2–5]. Among the promising surface modification technologies is low-energy (≤30 keV) intense pulsed electron beam irradiation [6]. Such treatment is capable of providing nano- and submicrocrystalline multiphase surface layers through very rapid crystallization and quenching (10⁵-10⁸ C/s) to a depth of up to 50 µm for steels and to over 1000 µm for light alloys, and this improves their physicochemical, electrophysical, and strength properties to levels unattainable by conventional surface treatments [2-9].

Here we analyze the surface structure, microhardness, and wear resistance of high-chromium steel 420 exposed to three types of surface modification: intense pulsed electron beam irradiation, nitriding in low-pressure arc plasma, and their combination in a single vacuum cycle.

2. Test material and research technique
The test material was steel 420 (US grade, Russian analogue 20Cr13 steel) containing 0.16-0.25C, 12-14Cr, 0.6Ni, 0.8Si, 0.8Mn, 0.03P, 0.003S, and balance Fe wt% [1]. The steel was exposed to three types of surface modification: (1) intense pulsed electron beam irradiation with surface melting and rapid crystallization, (2) nitriding in low-pressure arc plasma using the PINK generator, and (3) their combination in a single vacuum cycle on the COMPLEX setup [10]. The irradiation and nitriding parameters were constant: irradiation with
three pulses at a beam energy density of 40 J/cm$^2$, pulse duration of 200 µs, repetition frequency of 0.3 Hz, and residual Ar pressure of $\approx 3 \times 10^{-2}$ Pa; and nitriding for 4 h (550°C) at a discharge current of 56 A, bias voltage 400 of V, duty factor of 85 %, frequency of 50 kHz, and P(N$_2$) pressure of 0.6 Pa. The state of the steel surface was examined by X-ray diffraction analysis (XRD 6000 diffractometer), scanning electron microscopy (Philips SEM-515 microscope and EDAX ECON IV microanalyzer), transmission electron microscopy (EM-125 device), and measurements of its hardness (PMT-3 tester, normal indenter load 1 N), friction coefficient, and specific wear rate at room temperature (TRIBOtechnic device). The friction coefficient and the specific wear rate were measured in pin-on-disk tests with a VK8 alloy counterbody shaped as a ball of diameter 3 mm (track diameter 4-6 mm, track length 5-100 m, rotation rate 2.5 cm/s, number of revolutions 3000–8000, load 1-5 N). The wear resistance of the steel surface was assessed after wear track profilometry.

3. Results and discussion

According to optical and electron diffraction microscopy, the initial steel is a polycrystalline aggregate with grains of average size 19 µm, globular M$_{23}$C$_6$ particles ((Fe, Cr)$_{23}$C$_6$) of size 0.15-0.35 µm inside the grains and at their boundaries, and carbide particles in segregated dendrite structures.

When irradiated, the steel assumes a polycrystalline structure with an average grain size of 6.4 µm, which is almost three times smaller compared to the initial material, and its surface melting and high-rate quenching during the process provides cellular crystallization with a cell size of 500-600 nm and with a surface relief typical of martensite transformation (figure 1).

![Figure 1. Surface structure of steel 420 irradiated with three pulses at 40 J/cm$^2$, 200 µs](image)

On such high-rate quenching, a lath martensite structure with a transverse lath size of 70–90 nm arises in the steel (figure 2). It should be noted that the transverse size of martensite laths formed by furnace heating with water or oil quenching is 150-200 nm or 1-1.5 µm in individual cases [11, 12]. Likely, it is the much higher quenching rate provided by electron beam treatment which is responsible for the difference in martensite structures in two cases.

Our study also suggests that under intense electron beam irradiation at an energy density of 40 J/cm$^2$, the globular M$_{23}$C$_6$ particles present in the initial steel are fully dissolved, and $\sigma$-FeCr, Cr$_7$C$_3$, and Cr$_{23}$C$_6$ precipitates are found in its crystallized structure and Fe carbide particles in its martensite structure. An example of $\sigma$-FeCr precipitates ranging in size to 35-40 nm is presented in figure 3.
Figure 2. Martensite structure in steel 420 irradiated with three pulses at 40 J/cm², 200 µs

Figure 3. Second phase precipitates in steel 420 irradiated with three pulses at 40 J/cm², 200 µs: a – bright field; b – dark field in reflection [110]α-Fe + [410]σ-FeCr; c – microdiffraction pattern for dark field. Arrows indicate σ-FeCr particles (a, b) and dark field reflection (c).

Thus, our study demonstrates that intense pulsed electron beam irradiation dissolves the (Cr, Fe)$_3$C$_6$ particles initially present in steel 420, enriches its surface in Cr atoms, provides cellular crystallization, and forms a quenched lath martensite sublayer with anomalously small transverse lath sizes. The solid solution is dynamically disintegrated with the precipitation of σ-FeCr particles and particles of Fe and Cr carbides, decreasing the grain size in the steel three times compared to its initial state. As a result of all these factors, the surface hardness of the steel increases 1.5 times and its wear resistance increases 3.2 times.

When nitrided in the plasma of a low-pressure gas discharge, the polished steel surface is etched (Ra=0.44 µm). Figure 4 shows a typical surface structure formed after nitriding. According to electron diffraction microscopy, ellipsoidal Cr$_3$(C, N)$_2$ particles of size 10×50 nm appear in the nitrided steel layer (figure 5).
Figure 4. Surface structure of steel 420 nitrided at 550°C for 4 hours.

The surface microhardness of the nitried steel increases 2 times, its wear resistance increases more than 800 times, and its friction coefficient decreases 1.15 times. After complex treatment (irradiation and further nitriding), the steel surface assumes a wave structure with round inclusions (figure 6). Our X-ray spectral analysis shows that these inclusions are enriched in nitrogen and are likely Fe and Cr nitrides (figure 7). According to electron diffraction microscopy, such complex treatment of the steel forms a martensite structure with lath and lamellar morphology in its surface layer. The volume of martensite crystals reveals second phase particles (figure 8) composed mainly of Cr$_3$(C, N)$_2$ (figure 8c) and rarely of Fe carbides and (Fe, Cr)$_{23}$(C, N)$_6$.

The results of mechanical and tribological tests suggest that after complex treatment through pulsed electron beam irradiation and further plasma nitriding in a single vacuum cycle, the surface hardness of the steel increases 2.3 times, and its wear resistance increases more than 100 times.

Figure 5. Structure of steel 420 nitrided in low-pressure gas discharge plasma at 550°C for 4 hours: a, b – bright fields; c – electron diffraction pattern for bright field with chromium carbonitrides indicated by arrows (b).
Figure 6. Surface structure of steel 420 after electron beam irradiation (40 J/cm², 200 µs, 3 pulses) and plasma nitriding (550°C, 4 hours).

Figure 7. Electron micrograph of surface structure (a), energy spectrum for its region marked by plus sign on micrograph (b), and percentage of elements for same region (inset) in steel 420 after irradiation (40 J/cm², 200 µs, 3 pulses) and nitriding (550°C, 4 hours).

| Element | Wt % | At % |
|---------|------|------|
| N(αK)   | 35.03| 67.94|
| Cr(αK)  | 12.68| 06.62|
| Fe(αK)  | 52.29| 25.43|

Figure 8. Structure of steel 420 after electron beam irradiation and plasma nitriding: a – bright field; b – dark field in reflection [220]Cr₃(C, N)₂ with Cr carbonitrides particles indicated by arrows; c – microdiffraction pattern for bright field.
4. Conclusion
Thus, we have analyzed the surface structure and properties of high-chromium steel 420 exposed to three types of surface modification: intense pulsed electron irradiation (40 J/cm², 200 µs, 3 pulses), nitriding in low-pressure arc plasma (550°C, 4 h), and their combination in a single vacuum cycle. The analysis shows that all types of treatment enhance the surface microhardness and the wear resistance of the steel: their values are increased respectively 1.5 and 3.2 times after irradiation, 2 and more than 800 times after nitriding and 2.3 and more than 100 times after irradiation and further nitriding in a single vacuum cycle.

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