Surface alloying of high-chromium steel: structure and properties

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Abstract. Here we analyze the structure and mechanical properties of high-chromium steel AISI 420 after combined surface treatment in a single vacuum cycle on the COMPLEX setup through intense pulsed electron beam irradiation of a Zr-Ti-Cu film/steel AISI 420 substrate system and its further nitriding in low-pressure arc plasma at 550 °C for 4 h. The methods of research include scanning and transmission electron diffraction microscopies, X-ray diffraction analysis, and measurements of surface microhardness and wear resistance. The research shows that after pulsed electron beam irradiation, the microhardness of the Zr-Ti-Cu/steel AISI420 system increases by 11%, and its wear resistance by a factor of 3.5. After further nitriding, the hardness of the system increases 2.4 times, and its wear resistances more than 350 times.

1. Introduction
The method of synthesizing nonequilibrium surface alloys was pioneered in the 80s of the last century. Such surface alloys were formed using a nanosecond laser beam [1, 2] and a nanosecond (=50 ns) low-energy high-current electron beam [3-6]. Surface alloying of 20Cr13 steel and Zr-Ti-C film with a submillisecond intense pulsed electron beam revealed the formation of a submicro- and nanosized multiphase cellular structure in the system [7]. However, due to the high Zr concentration in the alloy, the method failed to provide hardening and high strength and tribological properties of the system [7].

Here we analyze the elemental composition, phase state, defect substructure, mechanical and tribological properties of high-chromium steel AISI 420 exposed to combined treatment through pulsed electron beam surface alloying and low-pressure arc plasma nitriding.

2. Material and research techniques
The test material was steel AISI420 (US grade, Russian analogue is 20Cr13) containing 0.16–0.25% C, 12–Cr, 0.6Ni, 0.8Si, 0.8Mn, 0.03P, 0.003S, and balance Fe wt.% [8]. The steel was exposed to pulsed electron beam irradiation with surface melting and rapid solidification and to low-pressure arc plasma nitriding as follows: (1) irradiation of steel AISI 420, (2) irradiation of its system with a Zr-Ti-C film, and (3) irradiation of the Zr-Ti-Cu/steel AISI420 system with further nitriding in a single vacuum cycle on the COMPLEX setup [9]. The irradiation and nitriding parameters were constant: irradiation with three pulses at a beam energy density of 30 J/cm², pulse duration of 200 µs, repetition frequency of 0.3 Hz, and residual Ar pressure of ≈3·10⁻² Pa; and nitriding for 4 h (550 °C) at a discharge current of 56 A, bias voltage of 400 V, duty factor of 85 %, frequency of 50 kHz, and nitrogen pressure of 0.6
Pa. The state of the modified 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 diffraction microscopy (EM-125 device), and measurements of its hardness (PMT-3 tester, normal indenter load 1 N) and specific wear rate at room temperature (TRIBOtechnic tester). The specific wear rate was determined 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 50-100 m, rotation rate 2.5 cm/s, number of revolutions 3000–8000, load 1-5 N). The surface wear resistance was assessed after wear track profilometry.

3. Results and discussion

According to optical and electron diffraction microscopies [10], steel AISI420 in its initial (unmodified) state is a polycrystalline aggregate with grains of average size 19 µm and globular M$_{23}$C$_6$ (Fe,Cr)$_{23}$C$_6$ carbide particles of size 0.15-0.35 µm inside the grains, at their boundaries, and in segregated dendrite structures.

When irradiated with an intense pulsed electron beam, the steel experiences surface melting and very rapid solidification (quenching) such that a cellular structure with a cell size of 400–450 nm is formed in its surface layer (figure 1). The defect substructure of the steel is represented by grains and subgrains (figure 2a) with a band structure in their volume (figure 2b).

![Figure 1. Surface structure of steel AISI420 after electron beam irradiation (30 J/cm$^2$, 200 µs, 3 pulses). Scanning electron microscopy.](image)

After intense electron beam irradiation with an energy density of 30 J/cm$^2$, the globular M$_{23}$C$_6$ particles present in the initial steel are completely dissolved in the surface layer, and nanosizedCr$_3$C$_2$ and Cr$_{23}$C$_6$ precipitates appear in its cellular structure. The surface hardness of the steel after such modification increases by 12%, and its wear resistance by a factor of 2.

The Zr-Ti-Cu/steel AISI 420 system after irradiation reveals a cellular structure similar to that shown in figure 1b. Its surface layer is composed of 2.2 Zr, 0.4 Ti, 12.2 Cr, 0.5 Cu, and balance Fe wt%. Along the boundaries of cells and at their junctions, there are ZrC particles of size 20–30 nm (figure 3).

Thus, our analysis of the Zr-Ti-Cu/steel AISI 420 system after intense pulsed electron beam irradiation reveals the formation of a surface alloy enriched in Zr, Ti, and Cu atoms, its cellular structure, and zirconium and chromium carbides resulting from solid solution decomposition. All these provide an increase in the surface hardness of the steel by 11% and a decrease in its specific wear rate (increase in its wear resistance) by a factor of 3.8.
Figure 2. Defect substructure of steel AISI 420 after electron beam irradiation (30 J/cm², 200 µs, 3 pulses). Transmission electron microscopy.

Figure 3. Electron micrographs of cellular structure with ZrC particles (arrows) in irradiated Zr-Ti-Cu/steel AISI420 system: a – bright field, b – microdiffraction pattern (arrow points to reflection for dark field), c – dark field in reflection [111] ZrC.

After intense pulsed electron beam irradiation and further plasma nitriding assisted by a gas-discharge source with combined hot and hollow cathode, the Zr-Ti-Cu/steel AISI420 system assumes a structure whose characteristic image is presented in figure 4.

Our X-ray spectral analysis shows that after nitriding of the irradiated Zr-Ti-Cu/steel AISI 420 system, the concentration of Zr in its surface layer increases more than 5 times (figure 5).

After irradiation and nitriding, the surface layer of the system reveals a grain-subgrainstructure with second phase inclusions represented mostly by zirconium nitrides in the volume of grains and at their boundaries (figure 6). There are also particles of Cr₃(C, N)₂ and (Fe, Cr)₂₃(C, N)₆ in the structure, but their occurrence is rare.

Our mechanical and tribological testing demonstrates that after combined treatment through pulsed electron beam irradiation and low-pressure arc plasma nitriding in a single vacuum cycle, the surface hardness of the Zr-Ti-Cu/steel AISI 420 system increases 2.4 times, and its wear resistance more than 350 times.
**Figure 4.** Surface structure of Zr-Ti-Cu/steel AISI 420 system after electron beam irradiation and low-pressure arc plasma nitriding (550°C, 4 h).

**Figure 5.** Electron micrograph of surface structure (a), its energy spectrum (b), and percentage of its elements in Zr-Ti-Cu/steel AISI420 system after electron beam irradiation and plasma nitriding (550°C, 4 h).

**Figure 6.** Electron micrographs of surface structure in Zr-Ti-Cu/steel AISI420 system after electron beam irradiation and low-pressure arc plasma nitriding (550 °C, 4 h): a – bright field, b – dark field in reflection [002] ZrN + [110] α-Fe, and c – microdiffraction pattern for bright field (arrow points to reflection in dark field).
4. Conclusion
Thus, we have analyzed the structure and properties of steel AISI420 exposed to three types of surface modification through intense pulsed electron beam irradiation and low-pressure arc plasma nitriding: (1) irradiation of steel AISI420, (2) irradiation of its system with a Zr-Ti-Cu film, and (3) irradiation of the Zr-Ti-Cu/steel AISI420 system with further nitriding. The analysis shows that after electron beam irradiation, the surface hardness of the steel increases by 12%, and its wear resistance by a factor of 2. The surface microhardness of the Zr-Ti-Cu/steel AISI420 system after electron beam irradiation increases by 11%, and its wear resistances by a factor of 3.5. After nitriding of the irradiated Zr-Ti-Cu/steel AISI420 system, its hardness increases 2.4 times, and the wear resistances more than 350 times.

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