Formation of a silicon-niobium-based surface alloy using electron-ion-plasma surface engineering

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Abstract. The results of the development and study of the modes of formation of a surface alloy based on silicon and niobium on steel 40X using electron-ion-plasma engineering of the surface are presented. The surface alloy was created in several stages: first, layers of silicon and niobium were deposited successively, and then electron-beam remelting of the surface took place. After that, the samples were subjected to nitriding. The dependences of the change in the surface hardness of the samples on the processing modes are shown. In the optimal processing mode, the surface hardness increased by almost 70 times compared to the original material.

1. Introduction
Electron-ion-plasma surface engineering is a promising method used to create materials and products with predetermined surface properties that differ from the properties of a bulk material. Unlike the deposition of functional coatings, electron-ion-plasma surface engineering allows smooth change in the properties of materials on the film-substrate interface and, thereby, eliminates the problem of adhesive peeling of coatings under high mechanical loads or sudden temperature changes.

The authors designed equipment and identified regularities in the change of surface properties during the formation of a silicon-and-niobium-based surface alloys on the 40X steel using electron-ion-plasma surface engineering.

2. Experimental procedure and discussion of results
The Si-Nb coating was deposited on 40X steel samples by plasma-assisted magnetron (Si) and electric arc (Nb) deposition. After the deposition of the coating layers, subsequent high-speed melting of the film (Si-Nb) and substrate (40X steel) system was carried out by a pulsed electron beam. Then the film-substrate system was nitrided in the plasma of a non-self-sustained arc discharge in the PINK plasma generator. The experiments were carried out in the COMPLEX laboratory setup. The structural diagram of the setup is shown in figure 1. The setup was developed in the Laboratory of Plasma Emission Electronics, Institute of High Current Electronics SB RAS and included in the list of unique installations of the Russian Federation (UNIKUUM Complex, http://ckp-rf.ru/usu/434216/) [1]. The setup can be used to sequentially carry out plasma-assisted deposition of functional layers and coatings, nitriding and electron-beam processing including surface polishing and electron-beam mixing of the surface layers of samples and products in a single vacuum cycle. The setup consists of two sections (10 for electron-beam processing and 17 for coating deposition) that are separated by a shut-off gate 19.
Figure 1. The structural diagram of the COMPLEX setup: 1 – power supply for the arc discharge of the SOLO electron source, 2 – power supply for the auxiliary discharge of the SOLO electron source, 3 – redistributing electrode Ø 10 mm, 4 – emission grid Ø 40 mm, 5 – accelerating electrode of the electron source and the area of e-beam transportation, 6 – solenoid B1, 7 – diaphragm, 8 – solenoid B2, 9 – sample holder (manipulator) during electron-beam processing, 10 – electron-beam processing chamber, 11 – magnetron sputtering system (Si), 12 – power supply for the magnetron sputtering system, 13 – PINK gas plasma generator, 14 – power supply for the PINK gas plasma generator, 15 – arc evaporator (Nb), 16 – power supply for the arc evaporator, 17 – deposition chamber, 18 – manipulator during deposition of Si and Nb coatings, 19 – shut-off gate (separates the working chambers during deposition), 20 – bias voltage supply.

The sputtering part of the setup was modernized by installing a magnetron sputtering system with the target diameter of 100 mm, which made it possible to obtain silicon films at the rate of ~1 μm/h.

The coating was deposited in the working chamber 17 (figure 1) when the shut-off gate 19 was down. The gate only slightly reduced the pumping speed in the deposition chamber and prevented the materials sputtered in the chamber 17 from entering the electron-beam processing chamber 10.

After a cycle of vacuum pumping (at the ultimate pressure below 6.6×10⁻³ Pa), ion-plasma treatment was carried out. The working gas pressure was set using a gas flow meter. The samples were cleaned and heated with ion plasma in an argon atmosphere at the pressure of 0.1 – 0.5 Pa using the PINK plasma generator. 30 samples were placed on the holder of 100×150 mm that was mounted opposite the PINK plasma generator 13. The sample surfaces were cleaned with ion plasma during 20 minutes at the discharge current in the range of 10-80 A and the negative bias voltage supplied to the
sample holder gradually increasing up to its maximum value of -1000 V relative to the grounded chamber.

After cleaning, the sample surfaces were sequentially deposited with Si and Nb layers 0.2 μm thick. Silicon was deposited by plasma-assisted magnetron deposition (at simultaneous operation of the PINK plasma generator and the magnetron sputtering system) during 12 minutes to avoid cracking of the Si target. The samples were placed opposite the magnetron sputtering system 11. The target power was 300 W, the argon pressure was 0.5 Pa, the bias voltage on the samples was –35 V.

The Nb layer was subsequently deposited by plasma-assisted vacuum-arc deposition during three minutes. The samples were placed opposite the arc evaporator 15. The discharge current of the arc evaporator was 80 A, the PINK current was 30 A, the deposition bias voltage was –35 V and the deposition pressure was maintained within 0.1 Pa.

The mentioned parameters of surface cleaning and coating deposition were selected after preliminary optimization.

After coating deposition, the film-substrate system of the surface layer on each sample was subjected to electron-beam mixing.

A pulsed electron source of the SOLO series was used for high-speed melting of the film (Si-Nb) and substrate (40X steel) systems. The SOLO electron sources use a plasma grid cathode where an electron beam is emitted from the plasma of a low-pressure gas (arc) discharge. A relatively small accelerating voltage \( U = 10 \text{kV} \) was chosen to ensure a stable operation of the electron gun when processing the samples with possible intense melting of their surfaces and the evaporation of the processed material at desired high energy input. The configuration of the magnetic field was determined by the currents of the solenoids that created the field to transport the beam. It produced a well-focused beam and ensured sufficient beam energy density per pulse for the treated sample surface (up to 50 J/cm\(^2\) per pulse). The high energy density of the beam generated by the electron source of the COMPLEX setup could be obtained only in the almost maximum magnetic field of the solenoids (up to 0.12-0.14 T) because the beam was transported at a significant distance to reach the sample surfaces \((\approx 600 \text{ mm})\). The beam energy density was changed by changing the current of the electron beam.

After the Si-Nb coating was formed on the sample surfaces, the shut-off gate 19 (figure 1) was lifted and the manipulator was moved inside the chamber 10 for high-speed melting of the film (Si-Nb) and substrate (40X steel) system. A working gas (argon) was pumped through the pulsed electron source and the working pressure \((1-5) \times 10^{-2} \text{ Pa}\) was set using a gas flow meter before irradiation.

The manipulator was set in the position where the electron beam fell on the part of the holder (collector plate) that was free from the samples. The electron source was set in the operating mode. After the pulses of the beam current were generated with the required current amplitude, pulse duration and electron energy and when the accelerating gap of the gun was formed without breakdowns, the manipulator was sequentially placed in the position where the beam hit the samples and their surface was processed in accordance with the selected parameters, i.e. accelerating voltage 10 kV, pulse duration 200 μs, energy density on the sample surface 20 J/cm\(^2\), the number of pulses 3.

One, three and five cycles of coating deposition and surface melting were performed, 10 samples in each cycle. Then the samples were nitrided.

Similar to coating deposition, the nitriding of the samples was carried out in the working chamber 17 (figure 1). The samples were placed opposite the PINK plasma generator 13. Nitrogen was pumped into the chamber to the pressure of 0.6 Pa, a non-self-sustained arc discharge with the current of 65-85 A was ignited and a negative bias voltage was applied to the samples. The bias voltage was set at -990 V while heating the samples to the required temperature. Then the negative bias voltage was decreased to (500-700) V depending on the required temperature. In total, nine nitriding processes were carried out at 500, 550 and 600 degrees Celsius during one, three and five hours for each temperature. One sample after one, three and five cycles of coating deposition and surface melting were processed in each nitriding mode.

The microhardness of the processed sample surfaces was measured by a PMT-3 microhardness tester at the load of 100 g. Each sample was measured 20 times and the average surface hardness was
calculated. The hardness of non-nitrided samples is shown in figure 2 (a); the hardness of nitrided samples is shown in figures 2 (b), 2 (c) and 2 (d) for the temperatures of 500, 550 and 600 degrees Celsius, respectively.

![Graphs showing surface hardness](image)

**Figure 2.** Surface hardness: a) without nitriding; b) nitriding at 500 degrees Celsius; c) nitriding at 550 degrees Celsius; d) nitriding at 600 degrees Celsius. Designation of the signature on the graph: 1 c/1 h – 1 cycle of coating deposition and surface melting / 1 hour of nitriding, etc.

The surface microhardness graphs demonstrate that the surface hardness significantly increased even in non-nitrided samples from the initial 220 MPa for 40X steel to 5000-10000 MPa depending on the deposition/melting mode. Nitriding parameters also had a great impact on surface hardness. Nitriding at 500 degrees Celsius increased hardness of all samples, while five cycles of coating deposition and surface melting followed by nitriding during five hours resulted in the highest increase in hardness up to 15306 MPa. Nitriding at the temperatures of 550 and 600 degrees Celsius had a similar impact on the hardness of the samples: the minimum hardness was observed at 2000 MPa for the samples processed in one deposition/melting cycle. This is most likely due to the low thickness of the modified layer, which was etched off during nitriding by ion bombardment. The samples processed in three deposition/melting cycles had the hardness near 10000 MPa after nitriding at 550 degrees Celsius; the same samples nitrided at 600 degrees Celsius had the hardness of only 5000-7000 MPa, which is most likely associated with increased displacement stress and therefore increased rates of surface etching.
3. Conclusion
The COMPLEX setup for electron-ion-plasma surface engineering was modernized: a magnetron sputtering system was installed, which allows depositing silicon films on samples and products; the discharge system of the SOLO electron source was modernized, which made it possible to select the optimal mixing modes for the film/substrate system. The influence of nitriding parameters on the surface hardness was investigated for the samples with a Si/Nb surface alloy on 40X steel. Hardness of over 15000 MPa was obtained in the optimal processing mode of five coating deposition / surface melting cycles and 5 hours of nitriding. The maximum hardness was almost 70 times higher than the surface hardness of the original steel.

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References
[1] Koval N N and Ivanov Yu F 2019 Russ. Phys. J. 62 1161