Surface hardening of VT-22 alloy by inductively coupled plasma nitriding and magnetron deposition of TiN films

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Abstract. The surface of VT-22 Russian grade titanium alloy samples was modified by inductively coupled plasma (ICP) nitriding followed by magnetron deposition of TiN coatings. Different operating conditions of ICP nitriding and magnetron deposition were considered. The microhardness depth profiles were measured for samples after nitriding. The performance of TiN coatings was examined with a scratch tester.

1. Introduction
Titanium alloys are widely used in aviation industry. An attractive material for some construction applications is Russian grade titanium alloy VT-22. Certain applications require surface hardening of the alloy. The needed effect can be achieved by means of plasma nitriding or by TiN coating deposition. The techniques combining different approaches for surface modification (e.g. duplex methods) are considered to be prospective for improving the tribological performance of titanium alloys [1–5] and steels [6]. In particular, a number of studies have been focused on analyses of the duplex technology that combines plasma nitriding of titanium followed by TiN deposition [1–4]. As a rule, direct current or mid-frequency discharges are used for plasma nitriding. The coatings are mainly deposited by various physical vapour deposition (PVD) methods (e.g. arc plating [1] or electron beam evaporation [2]) as well as by plasma enhanced chemical vapour deposition (PECVD) methods [3, 4]. Papers [1–4] demonstrate that preliminary nitriding of titanium alloys aids in improvement of adhesive properties and wear resistance up to several times for TiN coatings as well as for multilayer TiN-Ti and TiN-DLC coatings.

Implementation of radiofrequency (rf) discharges for nitriding of materials including titanium and its alloys has not been studied well. It is therefore practically nothing known about performance of this technique in the combined (duplex) processing technologies. In this work, the surface hardening of VT-22 titanium alloy was carried out by nitriding in the inductively coupled plasma (ICP) followed by TiN deposition in a magnetron sputtering system. The surface hardness was studied at both steps of duplex treatment, and scratch tests of TiN coatings were performed for several regimes of nitriding and film deposition.

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2. Experimental
The samples were cylinders of VT-22 with the diameter of 30 mm and the height of 8 mm. The elemental composition of VT-22 alloy is presented in table 1.

| Element | Composition (%) |
|---------|-----------------|
| Fe      | 0.5–1.5         |
| C       | < 0.1           |
| Si      | 0.5–1.5         |
| Cr      | 4–5.5           |
| Mo      | 4–5.5           |
| V       | 79.4–86.3       |
| Ti      | 4.4–5.7         |
| Al      | < 0.7           |
| Other   |                 |

Plasma nitriding was performed in an experimental ICP facility in mixture of Ar and N₂. The vacuum chamber was pumped down to $1 \times 10^{-4}$ Pa with a turbomolecular pump backed by a dry scroll pump, and gas flow rate and composition were regulated by mass-flow controllers. The discharge was generated by a radiofrequency plasma generator RPG-250. The rf power was supplied by COMET cito 1330 series, through the automated matching network.

Prior to nitriding, the samples were sputter-cleaned in argon plasma at $p_{Ar} = 1$ Pa and $P_{rf} = 1.5$ kW. The bias voltage applied to the sample $U_b = -300$ V was used, and the cleaning time was 10 min.

The parameters of plasma nitriding procedures for five samples are given in table 2.

| Sample no. | Pressure (Pa) | Gas mixture | Forward rf power (kW) | Bias voltage (V) | Processing time (min) | Temperature (°C) |
|------------|---------------|-------------|-----------------------|-----------------|----------------------|-----------------|
| 1          | 0.33          | N₂:Ar = 1:2.3 | 1.5                   | –300            | 120                  | < 900           |
| 2          | 0.33          | N₂:Ar = 1:2.3 | 1.5                   | –100            | 30                   | < 700           |
| 3          | 0.33          | N₂:Ar = 1:2.3 | 1.5                   | –100            | 120                  | < 700           |
| 4          | 0.33          | N₂:Ar = 1:2.3 | 1.5                   | –100            | 240                  | < 700           |
| 5          | 0.33          | N₂          | 1.5                   | –1500           | 120                  | < 700           |

After the experiments, the samples were cooled in argon at $p_{Ar} = 130$ Pa down to 200°C. Each sample was then sectioned into four parts. One part was used for measurements of depth profiles of hardness and elemental composition, as well as the cross-section image analyses. Microstructure and elemental composition were analysed by Tescan Vega 3 scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectrometer (EDS) Oxford Instruments X-act. Two parts of each sample were used for coating deposition in a magnetron sputtering facility.

The vacuum chamber of the magnetron sputtering facility was evacuated to a base pressure of $1 \times 10^{-4}$ Pa with a turbomolecular pump backed by a multi-stage Roots pump. Argon and nitrogen mixture was regulated with mass-flow controllers. Prior to coating deposition, the samples were sputter-cleaned in glow discharge in argon at $p_{Ar} = 1.7$ Pa at $U_b = -1500$ V for 10 min. The magnetron deposition was then performed in either of two regimes (A or B). The deposition parameters corresponding to regimes A and B are shown in table 3.

| Regime | Pressure (Pa) | Gas mixture | Discharge power (W) | Bias voltage (V) | Deposition time (min) | Coating thickness (µm) |
|--------|---------------|-------------|---------------------|-----------------|----------------------|-----------------------|
| A      | 0.62          | N₂:Ar = 4.50:0.30 | 300                 | –300            | 60                   | 3                     |
| B      | 0.62          | N₂:Ar = 4.64:0.16 | 300                 | –300            | 120                  | 6                     |

3. Results and discussion
After the ICP nitriding of sample no. 1 at $T \sim 900$°C, redistribution of elements in the near-surface layer was observed. The regions of higher Al (α-phase stabiliser) concentration together with lower Mo (β-phase stabiliser) concentration were found. Cross-sectional SEM image of sample no. 1 accompanied by the Mo distribution map are shown in figure 1.
The observed behaviour of alloying elements is in accordance with the results of abnormal glow discharge plasma nitriding studies reported in [7]. This effect of nitriding at high temperature of 900–1000°C, as it was mentioned in [7], may lead to negative changes in mechanical properties. However, its influence on the performance of the above-deposited coatings has not been examined.

Samples nos. 2, 3, 4 were nitrided at the lower temperature ($T \approx 700\,^\circ\text{C}$) and under identical conditions except the time period (30, 120, and 240 min, respectively). Higher processing time caused improvement in surface hardness measured perpendicular to the surface (see table 4). The hardness depth profiles measured in the polished section for all samples are shown in figure 2. Increasing the processing time from 120 to 240 min did not cause substantial change in hardness profiles. However, the hardness measured on the surface noticeably increased presumably due to growth of the nitride layer. The microstructure of samples after plasma treatment (samples nos. 2, 3, 4, 5) did not exhibit noticeable changes with respect to the initial sample. Redistribution of elements was not observed in samples nitrided at $T \approx 700\,^\circ\text{C}$.

### Table 4. Surface hardness of samples after plasma nitriding.

| Sample no. | Hardness HV$_{0.1}$ |
|------------|---------------------|
| 1          | 1150                |
| 2          | 450                 |
| 3          | 640                 |
| 4          | 1030                |
| 5          | 620                 |

Hardness of TiN coatings deposited after the nitriding procedures was measured for all samples to be nearly constant at the level of 1600–1700 HV$_{0.1}$.

The coatings were analysed by a scratch-tester Anton Paar Revetest RST with Rockwell indenter (radius 200 μm) under linearly increasing load form 0.5 to 70 N. The track length was 7 mm. Three tracks were scratched on each sample. Typical indenter track after the test is shown in figure 3.

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Figure 1. Cross-section of sample no. 1 after ICP nitriding ($U_b = -300\,\text{V}$, $T \sim 900\,^\circ\text{C}$): (a) Mo distribution map; (b) secondary electron SEM image.

Figure 2. Microhardness depth profiles after ICP nitriding.
Figure 3. Typical scratch test results: $F_1$ — occasional cracking, $F_2$ — elastic deformations, $F_3$ — coating separation from the substrate.

The indenter track demonstrated three critical load points: $F_1$, $F_2$, and $F_3$. Critical load $F_1$ is characterised by low magnitude acoustic emission that correlates with the beginning of occasional cracking of coating. The second critical load $F_2$ corresponds to beginning of the plastic deformations. Eventually, critical load $F_3$ denotes the coating separation from the substrate.

Scratch tests (table 5) demonstrate that for samples nos. 1–4, deposited TiN coatings start to crack ($F_1$) at 10–15 N load in regime A, and at 25–35 N load in regime B. Coating separates from the substrate ($F_3$) at 35–45 N in regime A, and at 60–70 N in regime B. Hence, the coatings deposited in regime B mostly demonstrate better overall adhesive performance. One must also mention that cracking and exfoliation take place easier if nitriding is performed at high temperature (sample no 1).

Table 5. Mean critical loads for TiN coatings obtained by the scratch test.

| Sample no. | Regime A  | Regime B  | Regime A  | Regime B  | Regime A  | Regime B  |
|------------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1          | 12        | 26        | 25        | 40        | 33        | 61        |
| 3          | 15        | 28        | 28        | —         | 40        | 70        |
| 4          | 15        | 33        | 46        | 45        | 58        | 50        |
| 5          | 15        | 18        | 18        | —         | 65        | 50        |

However, sample no. 2 nitried in N$_2$ gas at high bias voltage of –1500 V demonstrates different result: regime A gives better adhesive properties than regime B.

4. Conclusion
Duplex ICP nitriding and magnetron TiN deposition technology ensures several times improvement of the surface layer hardness of VT-22 titanium alloy together with its high adhesive strength.

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