Effect of reference accelerating voltage on formation of TiN structural coatings during vacuum ion-plasma treatment

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Abstract. In this article the matters of the structure of TiN coatings in the function of the parameters of ion-plasma vacuum treatment are addressed and their temporal evolution is considered.

Protection of the parts and products from the destructive influence of the working and external environments is related to application of various surface treatment methods allowing efficient performance of the outer layers of the constructional metallic materials during their exploitation period.

One of the processing methods is ion-plasma vacuum treatment [1]. This type of technologic treatment is addressed in many works and manuscripts [2–4]. However, the temporal evolution, which is responsible for sinergic self-reduction of the coating of the system Me–N, where Me is transitional metall, had not been considered enough.

One of the most popular types of protective coatings is Ti-N systems, which are resistant to aggressive environments and protect the surface of the main material from corrosion. These coatings, however, tend to crack and divide into layers.

In the present work, the formation of the protective coatings was realised on the polished “40X” steel substrate of the 15x15x5 (mm) size using the NNV6I5. Formation of the coating was performed at $J = 110$ A, residual pressure of $p = 3.5 \times 10^{-3}$ mm of Hg and sputtering time of $\tau = 60$ minutes. The value of accelerating reference voltage on the substrate varied from $-15$ V to $-100$ V. Samples were aligned with cathode axis of $\text{BT 1-00}$. In uncompensated coatings, during exposure to the air, the alteration of the properties occur due to the self-fitting caused by the presence of vacancies and free electron bonds, decrease of the inner tension of the coating. All of these factors ultimately lead to the alteration of the properties of the crystalline lattice and structural composition of the coating (the elimination of planes (hkl)).

Lattice parameter (a) is a size of the elemental crystal plane. In our case TiN possesses a face-centred cubic lattice alike to NaCl lattice.
As it can be observed from the obtained X-ray patterns (figure 1 a), during the formation of TiN without applying of the reference voltage (–15V), the formation of the untextured coating occurs, in other words there are many crystallographic directions (indexes) of the lattice.

This coating is not dense, but is porous, does not possess high value of microhardness of ~50 GPa and demonstrates wide diffusion zone from 3 to 8 mkm. After storing, increase in lattice parameter is observed (figure 1 b). Due to non-stoichiological nature of TiN, this coating is dominated by one type of the defects – vacancies. Increase in non-metallic content of MeN compound leads to formation of cation vacancies or interstitial anions, while the increase in metallic content leads to formation of anion vacancies and interstitial cations.

![Figure 1. X-ray patterns of the TiN surface, formed at p = 3,5·10⁻³ mm Hg, J = 110 A, Uref = –15V, τ = 60 minutes in initial state (a) and after 8 months of storing at normal conditions (b).](image)

Hence, the increase in lattice parameter (figure 2) and volume of the crystal occurs due to the filling of the “void” vacancies and their potential rise to the surface as a result of the thermodynamic processes of coating formation.

![Figure 2. The alteration of the lattice parameter (a) of the TiN coating (Uref= –15 V).](image)
The described changes in the structure of the coating are indicative of the process of self-assembly, thus the system is thermodynamically unstable and is not fixed energy wise, just as in case of coating formation at applied accelerating potential of -100V at the surface. Temporal parameter brings the system to equilibrium.

The coating obtained at –100V is different. It possesses a well-defined texture, represented by the plane indexes such as (111), (200) and (222), figure 3.

![Figure 3](image)

**Figure 3.** X-ray patterns of TiN coating at $p = 3.5 \cdot 10^{-3} \text{ mm Hg}$, $J = 110 \text{ A}$, $U_{\text{ref}} = -100 \text{ V}$, $	au = 60$ minutes in initial state (**a**) and after the 8 months of storing at normal conditions (**b**).

In this case the decrease in lattice parameter with time is observed, since the denser structures are formed and, most likely, the inner tensions are increased in the coating. Since the system is compensated by the applied energy, the alteration of the lattice parameter in it should be less significant and influence only texture components of the (110) and (200) (figure 4).

![Figure 4](image)

**Figure 4.** X-ray patterns of the TiN surface, formed at $p = 3.5 \cdot 10^{-3} \text{ mm Hg}$, $J = 110 \text{ A}$, $U_{\text{ref}} = -15 \text{ V}$, $	au = 60$ minutes in initial state (**a**) and after 8 months of storing at normal conditions (**b**).

Microhardness of such a coating is varied from 8 to 10 GPa and diffusion zone is not higher than 2–4 mkm. However, these coatings are more dense and possess anticorrosive properties, while TiN coatings, formed at $U_{\text{ref}} = -15 \text{ V}$ are less dense and possess high value of microhardness and can perform if lubricated.
Conducted research has shown that texture of TiN coating depends on the intensity and density of plasma fluency during interaction with the surface of the sample and reference accelerating voltage \( U_{\text{ref}} \) (while other parameters are constant).

Nonetheless, complete stabilization of coating's non-operation mode occurs during the 8-month period, independent of regimes of coating formation. The most uncompensated coating mostly influences the lattice parameters over time, which in term influences the performance parameters. This data can be used for further approval of the functional cathode-obtained coatings, along with the uniformity evaluation of new types of coatings during their manufacturing application.

References
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