Coefficient of friction of titanium oxynitride films deposited by hot target reactive sputtering

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Abstract. The influence of the oxygen flow rate on the friction coefficient of titanium oxynitride films deposited by reactive magnetron sputtering at a constant current of a hot target was investigated. The study used the plans of the active experiment and regression models of the first and second order. It is found that the increase of the oxygen flow rate in the gas environment leads to the increase of the film friction coefficient.

1. Introduction
TiO\textsubscript{x}N\textsubscript{y} films are materials drawing attention of many researchers [1]. They are widely applied to: produce solar [2] and lithium batteries [3], protect metals from the influence of aggressive media, increase the metal surface mechanical properties [4], etc. A wide variety of possible applications of oxynitride films stimulated the development of methods for their deposition. At present, both physical and chemical methods are used. Among the most popular methods are reactive magnetron sputtering with direct and alternating current, impulse and reactive high-power pulsed magnetron sputtering [5]. In these cases, magnetrons with both cold and hot targets are used [6].

The purpose of this paper is to study the effect of the independent parameters of the deposition process on the friction coefficient of titanium oxynitride films. The films were deposited by the method of reactive magnetron sputtering of a hot target with a direct current. The independent parameters include discharge current density, nitrogen consumption and oxygen consumption.

2. Experiment details
The films of titanium oxynitride were deposited by a magnetron with a hot titanium target operating on a direct current in argon, oxygen, and nitrogen. In order to deposit the films, a vacuum chamber with a volume of 7.8 ∙ 10^-2 m\textsuperscript{3} was equipped by a flat magnetron with a titanium target of 130 mm in diameter operating on a direct current. The hot target mode is provided by fixing a titanium disk of 1 mm thick with a gap of 1 mm on a copper plate of 4 mm thick cooled by running water. The residual pressure in the chamber did not exceed 10^-2 mTorr. In the research, the theory of active experiment was used. Two batches of samples were produced:
- films of titanium nitride (a special case of TiO\textsubscript{x}N\textsubscript{y} films at x = 0) were deposited at a pressure of \( P_{Ar} = 2 \) mTorr, nitrogen consumption (2–6) sccm, and discharge current density (14–33) mA/cm\textsuperscript{2}.

The batch contained four series of three samples, manufactured according to the plan of the first order, shown by round markers in figure 1(a). In this batch, an additional sample was made at the
current density of 22 mA/cm$^2$ with the addition of oxygen to the gas environment at the rate of 1 sccm (the square marker in figure 1(a));
- titanium oxynitride films were deposited at the pressure of $p_{Ar} = 2$ mTorr, discharge current density of 22 mA/cm$^2$, nitrogen flow rate of (4–6) sccm, and oxygen consumption of (1–3) sccm. The batch contained nine samples made according to the second-order plan on the cube, shown by round markers in figure 1(b).

Each sample was tribotested using a scanning hardness tester "NanoScan-4D" (manufacturer of FGBNU TISNUM). The measurement method is a multi-cycle friction by a spherical tip with the registration of the pressing force, lateral force and deepening of the tip into the sample. Tip: AISI 440C steel ball with a radius of 3 mm. Parameters of the measurement procedure:
- length of wear track 100 µm,
- number of cycles of reciprocating motion – 200,
- force of loading when tested — 1 mN,
- tip speed — 10 µm/s.

3. Results and discussion
The first batch of samples provided the following results. Figure 1 shows the average value of the friction coefficient below each point of the plan. The above value has a mean-square deviation of less than 0.01. The independent variables in this plan (the discharge current density $j$ and the nitrogen flow rate $Q_{N_2}$) were changed at two levels, as shown in figure 1(a).

The experimental plan used for this batch allowed determining the influence of the selected parameters on the TiN friction coefficient in the form of a polynomial of the first order:

$$\mu \approx 0.001j + 0.014Q_{N_2}. \tag{1}$$

The coefficients in the model (1) were determined by the method of least squares with the variables in measurement units indicated in figure 1(a). In accordance with the theory of experimental planning, expression (1) can be used for interpolation. Using this possibility, the authors estimated the value of $\mu$ for the sample of point $l$ shown in figure 1. Calculations resulted in $\mu = 0.1$. While the measurement yielded a value of $\mu = 0.135$. The observed difference obviously indicates an increase in the coefficient of friction when oxygen is introduced into the TiN film.
In the second batch, nine samples were produced (figure 1(b)). The experimental plan allowed to determine the influence of the selected parameters (\(Q_{N_2}\) nitrogen flow rate and \(Q_{O_2}\) oxygen) on the TiN friction coefficient in the form of a polynomial of the second order:

\[
\mu \approx b_0 + b_1 Q_{N_2} + b_2 Q_{O_2} + b_{11} Q_{N_2}^2 + b_{22} Q_{O_2}^2 + b_{12} Q_{N_2} Q_{O_2}.
\]  (2)

Just as in the model (1), the coefficients in the model (2) were determined by the method of least squares with the variables in units of measurement indicated in figure 1(b). The values of the model (2) parameters are given in the table 1.

**Table 1.** The values of the model (2) parameters.

| Model (2) parameters | \(b_0\) | \(b_1\) | \(b_2\) | \(b_{11}\) | \(b_{22}\) | \(b_{12}\) |
|----------------------|---------|---------|---------|-----------|-----------|-----------|
| Values               | –2.12   | 1.09    | –0.52   | 0.12      | 0.06      | 0.07      |

Figure 2 shows the surface modeled based on expression (2), where the dependence of \(\mu = f (Q_{N_2}, Q_{O_2})\) reflects a tendency for the coefficient of friction to increase when oxygen fraction increases in the gas environment. The films with the smallest value of \(\mu\) are deposited near the values of \(Q_{N_2}=4\) sccm and \(Q_{O_2}=2\) sccm.

**4. Conclusions**

The performed study revealed that:

- in the specified ranges of the discharge current density \(j\) and the nitrogen flow rate \(Q_{N_2}\), their influence on the friction coefficient of TiO\(_x\)N\(_y\) films at \(x = 0\) can be described by a polynomial of the first order;
- in the given ranges of the nitrogen flow rate \(Q_{N_2}\) and oxygen \(Q_{O_2}\), their influence on the friction coefficient of TiO\(_x\)N\(_y\) films can be described by a second-order polynomial. The smallest value of \(\mu\) can be obtained if the films are deposited at the current density of 22 mA/cm\(^2\) near the values of \(Q_{N_2}=4\) sccm and \(Q_{O_2}=2\) sccm;
- an increase in the consumption of oxygen during deposition leads to an increase in the friction coefficient of TiO\(_x\)N\(_y\) films.
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