Modelling of ceramic coatings grow during Arc-PVD deposition

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Abstract. This paper presents the results of modeling the growth of ceramic coatings obtained by the kinetic Monte Carlo method. In the considered model, the possibility of forming misoriented grains in the direction of coating growth and in the plane of coating is realized. To verify the model, three coatings of different compositions were prepared, and their structure and composition was studied by TEM and EDS.

1. Introduction

Nowadays, various approaches are used to improve the operational properties of coatings: cerametallic TN-Me, (where T is a transition metal and Me is a plastic matrix of a metal that does not form nitrides), high-hardness coatings (TiN, TiCrN), hardened by ion bombardment, diamond-like coatings (nc-TiN / a-Si3N4), super stoichiometric coating systems TiC1+x or TiC / aC [1–4]. In general, there is a tendency to obtain composite coating materials, where each element has a specific role to play. For example, in CrMoN coatings, chromium provides high oxidation resistance, and molybdenum leads to a decrease in the friction coefficient [5, 6]. The introduction of the copper or nickel into this system leads to an increase in hardness due to the grinding of nitride grains by the metal phase, as well as to an increase in the resistance to viscous fracture due to the same metal matrix [3,7]. This coating technologies are developed is primarily since single-phase systems can no longer satisfy modern requirements. For instance, titanium nitride is characterized by low heat resistance, which levels its high hardness, and as a result limits its use [8]. As a result, scientists have to work with systems consisting of three or more chemical elements. This leads to the difficulty of studying such coatings, since a decrease in the concentration of one component occurs due to an increase in the concentration of other elements. As a result, both the growth regimes thermodynamic parameters of the system can change. In other words, the behavior of such coating systems, depending on the ratio of element concentrations, as well as other application conditions, becomes unpredictable.

In this paper, we propose a model based on the kinetic Monte Carlo method, which, based on data on the concentration flux and phase equilibrium of the system, models the process of coating growth at the atomic level. The use of a stochastic approach reduces the requirements for computing power. In addition, unlike the methods of molecular dynamics, in this model it is much easier to link the evolution of the system to real time [9, 10].
2. Model description
Most computer models of growth of both coatings and other systems are based on the representation of space in the form of cells (Figure 1), which allows us to solve complex geometric problems of crystal formation, however, such approaches are characterized by a significant drawback - the lack of disorientation of crystals relative to each other, binding of all sizes crystal to cell size, as well as the ability to simulate the phases of only one syngony [11,12]. Figure 1 at the bottom shows an advanced approach that does not fix the center of the atom strictly in the center of the cell, but it can be displaced [13]. It turns out that the cells no longer reflect the space itself but serve only as a tool to accelerate computer calculations. However, even with this approach, the system is characterized by rigid positioning of crystallographic directions in one of the planes. Therefore, if this approach is applied in three dimensions, these models remain pseudo-three-dimensional.

Figure 1. Schematic representation of cell space.

Figure 2 presents a new approach to representing space. As can be seen from the figure, there are no more cells (although they are used in the computer model similarly to the previous approach), the possible positions of neighboring atoms with this approach are determined depending on the group of atoms. If the atom is single, then the possible position of its neighbors is determined by a sphere whose radius depends on the atomic number of the neighbor. The diffusing atom occupies a position characterized by the shortest distance to the atom. As a result, a dimmer is formed - two connected atoms, the axis between which describes the crystallographic direction. Subsequently, upon diffusion of the third atom to the dimmer, it also occupies a position to the nearest accessible position. However, unlike a single atom, in a dimmer, the possible positions are described not by a sphere, but by circles whose radius is determined based on the position of atoms in the lattice sites. And after the addition of the third atom, a full-fledged crystal is formed, for which the possible position of the sites is obtained already by translating the atoms of the crystal lattice.

Figure 2. An example of a geometric representation of the formation of dimmers and crystallites.

In this work, we studied the multicomponent Ti-Cr-N system, which is characterized by the formation of solid solutions of TiN and CrN nitrides with unlimited solubility in each other. To verify
the model, three series of coatings were prepared at pAr 0.8 Pa, pN₂ 0.4 Pa, a substrate temperature of 450 °C, and the composition shown in Table 1.

Table 1. Elemental composition of coatings obtained by X-ray microanalysis

| Bias, V | Ti   | Cr | Ni | N  |
|--------|------|----|----|----|
| 80     | 22   | 9  | 14 | 55 |
| 120    | 13   | 36 | 11 | 40 |
| 140    | 10   | 51 | 9  | 30 |

According to the TEM data, the image of which is shown in Figure 3, all coatings are characterized by a multilayer structure formed as a result of planetary rotation of the substrates. As shown, this multi-layer structure composed by layers formed as result of substrate rotation around table axis, and sublayers formed as result of substrate rotation around own axis.

In order to simulate the growth process of the entire coating with a thickness of more than 3 μm, an array of data from 10¹² atoms is required. In this paper it is proposed to simulate the process of formation of one layer shown in Figure 3. Given the fact that coatings consist of such layers, we can predict the properties of the entire coating by the properties of one layer. Thus, the dimension of the studied system was given 100x100x1000 atoms. As input data, the plasma concentration profiles for Ti and Cr, calculated earlier, are used. Because charged particles begin to move perpendicular to the surface of the sample under the influence of the bias potential, the model uses a simple ballistic model of atom condensation at an angle perpendicular to the surface of the growing coating. As a nitrogen source, the same stream of nitrogen atoms was formed with zero energy and charge, so that one nitrogen atom per one atom of the deposited metal.

Since during the modeling process an array of data is formed in which grains are already defined, as well as their characteristics (atoms included in grains, orientation in global coordinates), it becomes possible to accurately study the microstructure of the simulated material without the use of additional data processing methods. First, the texture of the coatings was analyzed as a projection of the crystallographic direction [100] of all grains on a plane parallel and perpendicular to the coating. Figure 4 shows the characteristic distributions for all calculations. It can also be seen from these data that grains formed mainly upon the addition of two adatoms, while the fraction of grains formed upon condensation of an atom from plasma source at the site of condensed atom is minimal. This can be concluded by concentration points near the axis because these points correspond to the directions, formed in step 2 as shown in Figure 2. The difference with the electron diffraction observed by TEM is
since for each grain only one crystallographic direction [100] is projected on plots, while on the electron diffraction for each grain four crystallographic directions [100] are projected.

**Figure 4.** (a) Projection of the crystallographic direction [100] on the growth plane, where points on the radius of circle corresponds to the fraction of grains with a specified angle of rotation relative to the growth direction; (b) Electron diffraction from cross-section of coating prepared at 80 V.

Figure 5 shows the distribution of grains by volume. As expected, an increase in particle energy leads to an increase in the sputtering coefficient of the growing coating, and as a result, a decrease in grain size. It should be noted that the ratio of the average grain size in the direction of growth to the average grain size in the growth plane slightly decrease with increasing particle energy. Most likely this is due to an increase in grain boundary diffusion of adatoms, because the distance to the available sites in the neighboring grains in most cases will be greater than the distance to the available sites on the current grain. As result, the diffusion energy barrier will be greater.

**Figure 5.** (a) Distribution of grain volume at different bias; (b) The effect of the bias potential on the ratio of grain size in the direction of coating growth to grain size in the coating plane.

The same effect of the bias potential on the coating thickness was observed. From Table 2 it can be seen that the difference between the calculated data and the experimental is more than 30%. This difference is possibly caused by an error in the determination of the binding energies in Ti-Cr-N compounds, as well as by the nonlinear nature of the influence of ion energy on the sputtering coefficient, which was not taken into account in this model. According to the calculations, the energy distribution of ions is characterized by Maxwell equations with a shift towards higher-energy ions. And since the average value of those distributions was used in the model calculations, this can lead to a decrease in the sputtering coefficient of coating atoms by a high-energy particles.
Table 2. Thickens of the layer formed during one full rotation of substrate around table axis

| Bias, V | Layer thickness, nm |
|---------|---------------------|
|         | Model prediction | TEM analysis |
| 80      | 92                 | 61           |
| 120     | 78                 | 52           |
| 140     | 70                 | 47           |

3. Conclusion
Based on this, we can conclude that the presented model allows us to predict the texture and microstructure of multicomponent coatings. However, the presented model is still far from real physical experiments, which is especially manifested in the sputtering coefficient of the growing coating with a stream of high-energy particles. In the future, it is planned to expand the methods of analysis of simulated data, including for constructing a concentration profile of coatings, determining porosity and morphology of coatings.

4. Acknowledgments
The reported study was funded by RFBR, project number 19-38-90113.

5. References
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