Multilayer Coating Formation at the Deposition from Plasma

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Abstract. The numerical experiment was carried out for the process of the coating composition formation during deposition from plasma. The chemical reactions between elements are taken into account. The nonuniform composition of the coating is determined by various transfer processes, including diffusion under stress action. To find the stress field the equilibrium problem was solved numerically because all physical and mechanical properties depend on composition. Stress field has been also obtained nonuniform.

1. Introduction

The increase in physical-mechanical properties of protective coatings allows refining the operating characteristics of cutting materials. Structure and properties of the coatings depend on numerous factors [1,2]. Therefore, it is necessary to study the regularities of properties evolution varying the deposition conditions. The coatings from nitride of transition metals, especially TiN [3,4], are widespread, because their properties are unique. For example, TiN - coating elastic module reaches up 466 ± 15 GPa [1]. Material per se (chemical composition) does not ensure the wear resistance growth. Deposition mode, configuration of engineering accessory; preliminary etching or alloying etc determine the coating and interface structure [2].

The experimental results demonstrate that nanohardness is seriously affected by the residual stress [5]. Residual stresses depend on properties of substrates, surface finishing methods and processing parameters [6,7] It was shown that the residual stresses in the coatings deposited with ion assistance depend on the thickness of the coating and the flux and energy of the bombarding ions [8]. It was marked in [9] that residual stresses can arise from three sources: thermal, intrinsic and lattice mismatch. However, there are many other causes for stresses in multicomponent and multi layered coatings. The simplest analytical evaluations of stresses in the coated materials were made in [10].

Since experimental investigations are very expensive and labor-consuming, the mathematical modelling can help in the study of physical phenomena which effect coating structure and properties. Simple model of thickness change of the coating is contained in [11]. Physical and chemical phenomena do not taken into consideration in this model. Monte Carlo method have been used, for example, in [12,13] to understand the fundamental phenomena. There are many papers where finite elements commercial programs are applied for coated material modeling. Limitations of finite elements analysis were discussed for example in [14]. Multi physical model of coating formation is presented in [15]. And multi layered coating growth with chemical conversion and residual stresses evaluation is described in [16]. Numerical experiment had allowed revealing the numerous causes for inhomogeneous stresses field in the coating for the system Ti-Cr-C.

Here we numerically investigate the regularities of the formation of multi layered coating on the iron substrate.

2. Problem formulation

We assume that coating grows at the deposition from plasma with the composition changing due to successive arrival of ions Ti,N and Al,N into the chamber. The interval between arrivals of different ion is given. The stage of ion redistribution in chamber is not considered. Cylindrical specimen made from iron rotates around their axis that provides the same plasma composition along the lateral surface. General mathematical formulation of the problem is presented in [15] and includes three sub-problems: thermal-diffusion, kinetical and mechanical ones. Total mathematical model takes into account the various cross-effects additionally to fundamental transfer mechanisms for the heat and species. This leads to the appearance of additional term in the equations for the heat and mass fluxes. Really, when four elements

$$Ti, N, Al, Fe$$

can present in growing coating (with the mass concentrations C_i, $i = 1,2,3,4$ correspondingly), following summary chemical reactions

$$4Fe + N_2 = 2Fe_2N \; ;$$
$$8Fe + N_2 = 2Fe_4N \; ;$$
$$2Al + N_2 = 2AlN \; ;$$
$$2Ti + N_2 = 2TiN$$
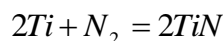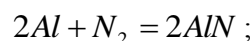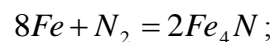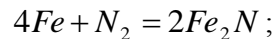
should be taken into account. Therefore, the chemical compounds $Fe_2N; Fe_4N; AlN; TiN$ will be contained in the coating and in the transient layer. C_i are their concentrations, $i = 5,6,7,8$. In this case, the defining relationships for the elastic body (temperature is more less then melting temperature) turn to

$$\sigma_{ij} = 2\mu\varepsilon_{ij} + \delta_{ij}\left[\lambda\varepsilon_{kk} - Kw\right]$$

where

$$w = 3\left[\alpha_T\left(C_k\right)\left(T - T_0\right) + \sum_{k=1}^{4}\alpha_k\left(C_k - C_{k0}\right) + \sum_{k=5}^{8}\alpha_k'\left(C_k - C_{k0}\right)\right],$$

where λ, μ are Lame coefficients; $K = \lambda + 2\mu/3$ is the bulk module; α_T is the thermal expansion coefficient, α_k and α_k' are the concentration expansion coefficients for diffusing elements and for compounds. Index '0' relates to unstrained state.

In accordance with the irreversible thermodynamics, the diffusion fluxes include the terms corresponding to the usual diffusion and to the diffusion of species due to presence of concentration gradients of other species; to the thermal diffusion and diffusion (mass transfer) due to stress (or/and strain) gradient action:

$$\mathbf{J}_k = -\rho\sum_{i=1}^{3}D_{ki}\nabla C_k + B_k C_k \nabla\sigma_{kk}^e - C_k D_{kk} S_{Tk}\rho\nabla T \; ; \; \sum_{i=1}^{4}\mathbf{J}_i = 0, \; k = 1,2,3$$

where $B_k = \dfrac{D_{kk}^0 m_k}{RT}\left(\alpha_k - \alpha_4\right)$ are transfer coefficients under stress gradient action; D_{kk}^0 - are self-diffusion coefficients; m_k are molar masses. Partial diffusion coefficients depend on the structure and composition of the substance

$$D_{kj} = D_{kk}^0\left(g_{kj} - g_{kn} + \frac{C_k m_k}{C_n m_n}\left(g_{nn} - g_{nj}\right)\right),$$

where g_{kj} are thermodynamical coefficients; $n = 4$.

Cross terms appear in the equation for the heat flux:

$$\mathbf{J}_q = -\lambda \nabla T - \sum_{i=1}^{3} A_i \nabla C_i + A_q \nabla \sigma_{kk}^{e},$$

where

$$A_i = \sum_{j=1}^{3} D_{ji} Q_j^{*}, \ i = 1,2,3 \ ; \ A_q = T \sum_{k=1}^{3} D_{kk}^{0} C_k S_{Tk}(\alpha_k - \alpha_4) \ ;$$

Q_j^{*} are the transfer heats.

Other equations stay the same.

3. Results
Thermal-physical properties were taken in [17] and are contained in the Table 1.

Table 1. The properties of the individual substances

Paremeter	N	Fe	Ti	Al	AlN	TiN	Fe2N	Fe4N	Dimension
λ	0.026	80.1	21.9	203.5	30.14	36.2	67.3	60.1	Vt/(m·K)
ρ	0.8	7.87	4.54	2.7	3.12	4.93	6.68	7.6	·103, kg/m^3
C_p	29.1	25.14	25.1	24.35	30.1	34.23	98.449	29.5	J/(mol·K)
m	14	55.84	47.8	26.98	40.98	61.8	125.6	237.2	·10^{-3}, kg/mol
E	0.14	190	112	70	310	261	217	200	GPa
ν	0.24	0.28	0.26	0.28	0.3	0.29	0.3	0.29	
α_T	2	4	2.8	3.1	3.4	3.2	3.8	4.7	·10^{-6}, K^{-1}

Formal-kinetical parameters used for the calculations are presented in the Table 2. They were found based on chemical thermodynamics similarly to [18].

**Table 2.** The kinetical parameters for the reactions

Compound	Activation energies, J/(mol K)	Pre-exponential factors	Reaction heat KJ/mol
Fe$_2$N	80508	2.9·108	-7.54
Fe$_4$N	79225	3.67·108	-21.78
TiN	200204	2.46·1014	11.64
AlN	319000	3.69·1018	9.63

Since thermal-physical properties of the coating depend on the composition changing in the time, the effective properties

$$\lambda(C) = \sum_{\kappa=1}^{8} \lambda_\kappa \cdot C_\kappa, \ \rho(C) = \sum_{\kappa=1}^{8} \rho_\kappa \cdot C_\kappa, \ E(C) = \sum_{\kappa=1}^{8} E_\kappa \cdot C_\kappa$$

of the growing coating depend on the space coordinate and on the time. Therefore, as opposed to [15, 19], here the sub-problem on mechanical equilibrium was solved numerically.

Below we present the illustrations to some interested result: due to changing composition of plasma, the coating forms with inhomogeneous structure. Due to the diffusion and chemical reactions the transient zones between the layers contain the chemical compounds (Figure 1). This leads to the diffusion retardation, and Fe2N presents only in the layer between the coating and substrate. All elements are distributed not uniformly.
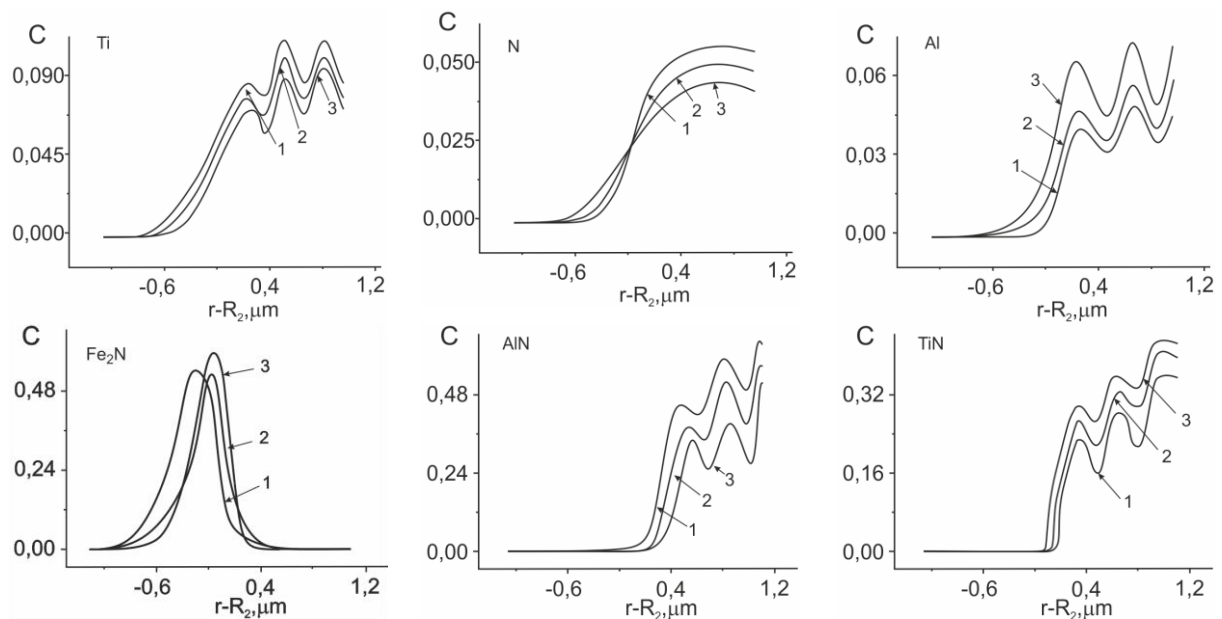
Figure 1. Concentrations of some substances in the coating for the different plasma compositions:
1. – y1=0.5, y2=0.4; 2. – y1=0.55, y2=0.45; 3. – y1=0.6, y2=0.5;

Not uniform stress field in the coating connects immediately with the concentration distribution is shown in the Fig. 2. Obviously, radial stresses equal to zero in the free surface. Axis and tangential stresses are discontinuous in interface.
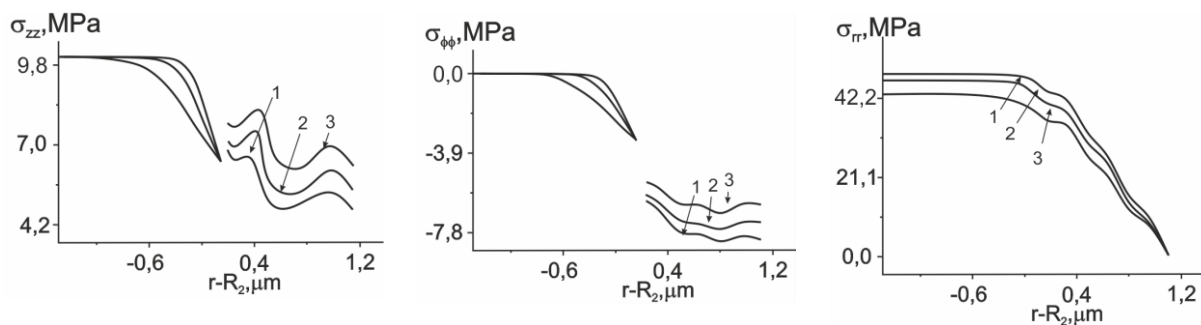
Figure 2. Stress tensor components in the coating depending on the plasma composition. The curves numbers correspond to the curves numbers in the Figure 1

4. Conclusion

The features of the model for multi layered coating formation were described. The coating composition was investigated depending on plasma conditions. It was detected that nonuniform stress field is determined by coating composition.

Acknowledgement

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