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Investigation of the Correlation Between Internal Stresses and Adhesion of Magnetron Deposited crn Coatings for Different Bias Voltage

KEYWORDS: CrN coatings; internal stresses, nanoindentation, scratch test; adhesion; cohesion

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ABSTRACT *CrN coatings have been deposited on X10CrNi18-10 steel substrates by magnetron sputtering with chromium target at substrate temperature Ts=500 oC and four bias voltages Us= 0, -50, -100 and –200 V. The phase composition, lattice parameter, hardness and Young's modulus of the coatings have been determined. The internal stresses, adhesion and cohesion of the coatings at each bias voltage have been investigated. The influence of bias voltage and internal stresses of the coatings on their adhesion and cohesion has been discussed.*

INTRODUCTION

To accomplish their protective and decorative functions it is necessary that all adhesive coatings should firstly have strong adhesion to the parts on which are deposited. One of the factors that influences the adhesion between the substrate and coatings is the internal stresses in these coatings.

The focus of this work is the comparative analysis of the influences of internal stresses in magnetron deposited CrN coatings on their adhesion for different bias voltage of the substrate.

2. THEORETICAL PREMISES

According to a lot of authors [3, 5-9] all metallic and ceramic films are in a state of stress. This behavior is independent of the method of deposition and applies [1, 9]. The total stress σ_{tot} is composed of a thermal stress σ_{th} and a intrinsic σ_{in} stress of the coating. Then the following equation is valid [9]:

$$\sigma_{tot} = \sigma_{th} + \sigma_{in} \qquad (1)$$

The thermal stress σ_{th} is due to difference in the thermal expansion coefficients of the coating and substrate materials. The intrinsic stress σi_n is due to the accumulating effect of the crystallographic flaws that are built into the coating during deposition.

The total stresses σ_{tot} in the coatings can be determined out of a change of the lattice spacing, which is a result of the influence of these stresses in the coating. This can be done by using the data of the XRD analysis and after that using the equation [3]:

$$\sigma_{tot} = -\frac{E_f}{\nu_f}.\left(\frac{d_E + d_O}{d_O}\right), \qquad (2)$$

where: E_f - Young's Modulus of the coating; the values of E_f for investigated coatings are determined by nanoindentation; ν_f – Poison's ratio of the coating; d_E – experimental lattice spacing of the coating under stress; d_o – nominal lattice spacing of the coating; because the lines of direction <200> appears in all XRD diagrams, so d_o of investigated CrN films are calculated for it.

The values of d_E are calculated by Bragg formula

$$d_E = \frac{\lambda}{2\sin\Theta}\sqrt{H^2 + K^2 + L^2} \qquad (3)$$

where: λ = 0,179021 nm – wavelength of the used X-rays; ÐΘ – angle of peaks in XRD diagrams of the coating for direction <200>.

When the sign of the calculated values of the stresses is "-", they are stresses of pressure, and when it is "+", they are stresses of strain.

The size of thermal stresses σ_{th} in the coatings is calculated from the equation [4, 9]:

$$\sigma_{th} = \frac{E_f}{(1-\nu_f)}.(\alpha_f - \alpha_S).(\grave{O}_S - \grave{O}_0) \qquad (4)$$

where: α_f and α_S - thermal expansion coefficients of the coating and the substrate.

After the values of the total and thermal stresses are calculated by means of equations (2) and (4), the intrinsic stresses can be calculated from equation (1) in form:

$$\sigma_{in} = \sigma t_{ot} - \sigma_{th} \qquad (5)$$

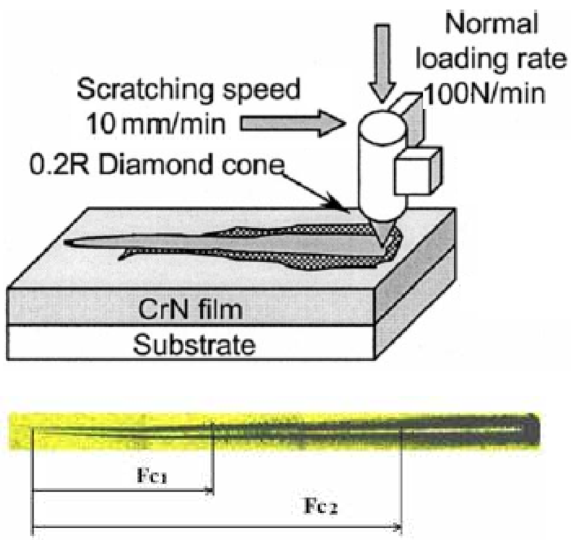
The adhesion and cohesion strength of the CrN coatings in the current article are determined according to the Scratch test method (Figure 1-a) [2], which is in the group of the indirect quantitative methods.

Quantitative indicators are critical values of the normal compressive force F (Figure 1-b): F_{C1} – a force of first appearance of wrenching on the surface of the coating and F_{C2} – a force of its destruction (at over 50% separated coating from the substrate) [2, 3].

In that case, F_{C1} and F_{C2} are indirect indicators of the adhesion and cohesion of the coating to the substrate. Direct indicators are cohesion stress σ_c and adhesion stress σ_a of the coating to substrate. These stresses can be calculated with the formula of Xie and Hawthorne [10]:

$$\sigma_i = \frac{0{,}15}{R}.\sqrt{\frac{F_C.HV_f}{HV_S}}.E_f^{0,3}.E_S^{0,2}, \qquad (6)$$

where: R – radius of the diamond cone of Scratch-tester; F_C - value of the critical force, defined by Scratch-test; HV_f and HV_s – micro hardness of the coating and the substrate; E_f and E_s – Young's modulus of the coating and the substrate.



b)

Figure 1. Scratch test method: a) scheme of testing; b) trace of Scratch-test and scheme of determining the values of the F_{C1} and F_{C2}.

If F_C, HV_f, HV_s, E_f and E_s are the measured values of the specific coating, then the calculated value of the stress s_i is its real value.

3. EXPERIMENTAL PROCEDURE

CrN coatings have been deposited in a single-chamber vacuum furnace with a built-in planar DC unbalanced magnetron. The coatings have been deposited on X10CrNi18-10 stainless steel substrates with size Ø20x4 mm by reactive magnetron sputtering, using Cr target in (Ar + N_2) atmosphere. The substrates temperature have been T_s=500°C and bias voltage U_s=0, -50, -100 and -200 V.

The phase composition and crystallographic structure of the films have been analysed by XRD using CoK_α radiation. The thickness of the films was investigated on a cross section, using a NIKON®-OPTIPHOT metallographic microscope and was confirmed with GDOES analysis. The microhardness and Young's modulus have been determined by a Vickers Nanoindentation tester FISCHERSCOPE® H100 using a load force of 50 mN. Adhesion and cohesion of the coatings are determined by the Scratch test method, using a Scratch tester CSEM-REVETEST®. A diamond cone is used with an angle α=120o and radius R = 200 μm, which moves in a straight line at a speed υ = 10 mm/min and increasing load F from 0 to 100N with intensity dF/dt = 100 N/min until destruction of the coating (Figure 1).

4. RESULTS AND DISCUSSION

4.1. Thickness and Phase composition

The thickness h of the coating decreases with the increasing of the bias voltage Us: h = 5,62, 4,45, 3,76 and 3,32μm respectively for Us = 0, -50, -100 and -200V.

According to the XRD analysis all coatings have only one phase – CrN at preferred orientation <200>. The crystal lattice of the CrN is strongly deformed in the interval of Us = 0 to –200 V and the lattice space is bigger than the theoretical one.

4.2. Internal stresses of the coatings

As it's shown in Table 1, all stresses in the coatings are compressive. With increasing of the substrate bias voltage from 0 to –200 V, all stresses in the coating are increasing too. This tendency is regularly and is also observed by other investigators [9]. The influence of bias voltage on the intrinsic stresses σ_{in} is stronger than in the thermal stresses σ_{th}. This is due to the accumulating effect of the crystallographic flaws that are built into the coating, during deposition process (vacancy, interstitial, and dislocation movement). In Table 1 is also shown, that with increasing the bias voltage at U_S= 0 V to -200 V there is permanent tendency of increasing of the intrinsic stresses in the coating from –6,754 GPa to –14,620 GPa. The reasons for this strong alteration of the intrinsic stresses in the coatings with increasing of the bias voltage this is the simultaneously influence of thermal stresses and main energetic vector $\vec{R}$.

The total stresses in the CrN coating are in result of the application of the principle of the superposition. What makes impression in Table 1 is, that the common regularities and peculiarities, ascertained before of thermal and intrinsic stresses, are also valid for the total stresses σtot. With the increasing of Us the total residual stresses in the coating are increasing, because the processes of recovery and recrystallization, that are cause for decreasing of the intrinsic stresses, is feebly.

4.3. Adhesion and cohesion stresses

The impact of bias voltage Us on adhesion and cohesion stresses of coatings is different. With the increasing of Us cohesion stress σc does not change significantly, while adhesion stress σa shows steady upward trend - Table 1.

The main reason for this is the higher collision velocity of the evaporated atoms of chromium target to the surface of the substrate, caused by an increase of bias voltage Us from 0 to -200V, which improves adhesion interconnections between coating and substrate. At the same time the large number of crystallographic defects in the coating lead to a relaxation of its cohesion stresses and that is why they do not increase.

5. CONCLUSIONS

Based on the obtained results the following important conclusions about the relationship between the internal stress and adhesion of the investigated CrN coatings can be made:

The bias voltage affects directly proportional both the internal stress and adhesion stress of the coatings;

The increase of internal stresses in the coatings does not reduce adhesion stresses of the border coating-substrate;

The influence of the internal stresses in the coatings on their adhesion is weak. By increase of internal stresses 1,95 times, the adhesion stresses increase only by 12%, which is due to the process of stress relaxation of the border coating-substrate due to the high coating homologous temperature of deposition. By Thornton's model (Fig.2), the processes of recovery in the coating are started at homological temperature T_s/T_m>0.3 and the processes of recrystallization are started at T_s/T_m > 0.5 (where T_s(K) is the substrate temperature and T_m(K) is melting or destructive temperature of the coating). For CrN coatings, for which T_m=1083°C [7] these temperatures correspondingly are 410 and 680°C. This means, that for all investigated CrN coatings, the processes of recovery are in action.

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TABLE 1. Measured and calculated data of CrN coatings, deposited at substrate temperature t_s = 500 °C and different bias voltage.

№	Bias voltage U_s, V	Lattice spac-ing $d_E^{<200>}$, nm	Hard-ness HV_f, GPa	Young's modulus, E_f, GPa	Thermal stress, σ_{th}, GPa	Intrinsic stress, σ_{in}, GPa	Total stress, σ_{tot}, GPa	Criti-cal force F_{C1}, N	Criti-cal force F_{C2}, N	Cohe-sion stress σ_c, GPa	Adhe-sion stress σ_a, GPa
1	0	0,418902	11,551	268	-2,776	-6,754	-9,530	19,1	52,4	3,204	5,307
2	-50	0,418902	13,109	288	-2,983	-7,259	-10,242	15,6	48,0	3,152	5,530
3	-100	0,418902	14,574	320	-3,314	-8,066	-11,380	11,5	42,8	2,945	5,682
4	-200	0,420455	17,098	379	-3,926	-14,620	-18,546	10,6	36,7	3,222	5,996

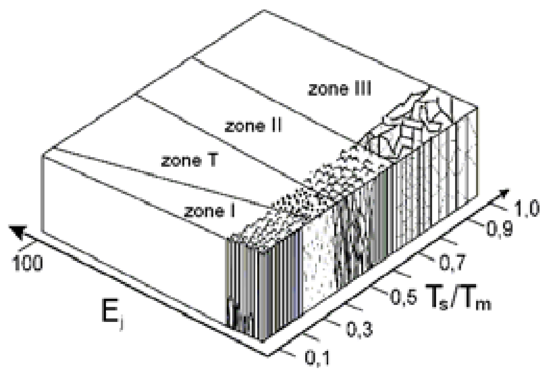

Figure 2. Schematic representation of the Thornton's model for influence of homological temperature T_s/T_m and ion energy E_j of magnetron deposition process on microstructure of the coatings [9].

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