STRESS AND COMPOSITION EVALUATION FOR GRADIENT NITRIDE COATINGS

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ABSTRACT

Thin gradient Ti-Cr-N layers have been formed by the cathodic arc vapour deposition in the nitrogen atmosphere using simultaneous bombardment of the surface by metal ions. The deposition was carried out by combining the titanium and chromium plasma flows of various densities. The deposited coatings were found to be two-phase (solid solution and titanium nitride) systems. The residual stress and density depth profile of the coatings have been studied. The stress profile was measured by using one- and two-dimensional detectors and calculated by modified sin^2ψ and XRD^2 methods. The density and concentration gradients were measured by several methods including specular X-ray reflectivity technique.

INTRODUCTION

The multicomponent ternary TiN-based nitrides, such as TiAlN [1], TiCrN [2], and TiZrN [3], are now widely used as protective coatings. Ti-Cr-N coatings have high hardness, good wear-resistance, and excellent high-temperature resistance [4–5]. Therefore, the Ti-Cr-N coatings have become popular in recent years as the hard-protective coatings for tools, in particular for high-speed cutting tools. However, the adhesion between the coatings and the substrate is usually not strong enough, especially at heating and cooling conditions. The reason is the difference in the composition, microstructure, and other properties of the Ti-Cr-N coatings and the substrate. The formation of the gradient ternary systems with a variable concentration of elements, both on interphase boundary and inside the coating, allows for an increase in adhesion and improvement in the mechanical properties [5] of the film. The ternary layers Ti-Cr-N demonstrate an increase in hardness [6] in comparison with the pure nitrides of titanium and chromium (CrN, TiN). At the same time, the Young’s modulus of the gradient layers is varied within the intermediate range of the modulus for CrN and TiN. This behavior of the hardness and the modulus of elasticity of gradient layers permits the creation of the hard and elastic coating by controlling the concentration depth profile of the solution (Ti\(_x\)Cr\(_{1-x}\))N at variable 0.60 < \(x\) < 0.84 [6].

This work presents the elemental and phase compositions of the gradient Ti-Cr-N coatings, formed by the vacuum arc deposition technique with changeable titanium or chromium flow during the deposition process. The elemental and phase compositions have been studied in relation to the residual stresses in the coatings.
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EXPERIMENTAL

The gradient Ti-Cr-N coatings were grown by cathodic arc vapor deposition (CAVD) technique. The growth process uses the plasma phases of the titanium and chromium of a variable density in a residual nitrogen atmosphere and with the concurrent ion bombardment of the sample surface [6]. Carbon steel St3 (< 0.18 wt% C) was used as substrate materials. Prior to the deposition, the surface of the substrate was cleaned and bombarded with chromium ions for 1 min with -1 kV substrate bias, 100 A arc current of chromium cathode, and vacuum in the chamber of 10^{-3} Pa. This stage prior to the deposition resulted in a heating of the substrate of 450 to 500 °C. All the film depositions were initiated by introducing N₂ gas at a pressure of 10^{-1} Pa into the vacuum chamber and the bias was fixed at -120 V.

The distribution of the titanium, chromium, and nitrogen elements in the coating was determined by Auger-Electron Spectroscopy (AES) with the step-by-step sputtering of the sample’s surface by Ar ions with energy of 3 keV. The scanning microprobe PHi-660 was used for the measurements. The density and concentration gradients at the depth range up to 100 nm were measured by specular X-ray reflectivity technique. The phase composition of Ti-Cr-N systems was investigated by grazing-incidence X-ray diffraction (GIXRD) using CuKα characteristic X-ray radiation. Additionally, the GIXRD data were analyzed using modified sin^2ψ method to evaluate the residual stress depth profile of the coating at the depth up to 450 nm. Two-dimensional XRD stress measurements with GADDs detector [7] allowed the evaluation of the residual stresses at the depth of ~1 µm.

RESULTS AND DISCUSSION

The gradient Ti-Cr-N coatings were deposited by varying the density of the plasma flows of titanium or chromium. The density of the plasma flows was changed during the deposition by changing independently the arc currents Iₜi and Iₖr of one of cathodes from 60 to 100 A. The deposition time was fixed at 2.25 min. The total thickness of the formed coatings was about 1.2 to 1.5 µm, depending on the deposition conditions.

Figure 1 shows AES concentration profiles of elements in the Ti-Cr-N coating deposited on steel substrate. The formation of the main layer Ti-Cr-N with variable concentration of Ti and Cr elements in depth is observed. The obtained AES data allowed the presenting of the composition of the gradient coatings in the form of TiₓCr₁₋ₓN, where x is changing in the range 0.60 to 0.84. Thus, a change in the current of the arcing of Ti and Cr cathodes makes it possible to control the composition of coatings and to obtain the gradient concentration profiles of the basic elements.
Surface and undersurface region of Ti-Cr-N coatings have been investigated by X-ray reflectivity (XRR) technique. For CuKα X-ray radiation, the informational depth of X-ray penetration is ~100 nm. Figure 2 shows the experimental and the fitted XRR curves as a function of the incidence angle in θ/2θ scanning geometry. The data interpretation was performed by LEPTOS software (Bruker AXS GmbH, Karlsruhe, Germany). Reflectivity curves display typical oscillations, associated with the sublayers of different thicknesses. The reconstructed profile of mass density in the undersurface region and corresponding simulated sample model are shown in Figures 3 and 4, respectively. The sliced sample model was used for data fitting. The standard deviations of the mass densities and the thicknesses of the sublayers are varied within the limits of ± 5 nm for the thickness and ± 0.3 g/cm³ for the mass density. On the surface of sample, there

Figure 1. Concentration profiles of TiₙCr₁₋ₓNₓ coating, obtained by AES (0.60 < x < 0.84).

Figure 2. Measured and fitted XRR curves.

Figure 3. Reconstructed density profile of the Ti-Cr-N coating resulting from the XRR curve fitting.

Figure 4. Sample model for fitting of the XRR curve.
is a 90 nm layer, enriched with chromium, followed by a 20 nm layer, enriched by titanium, and finally the main coating. The mass density profile for the undersurface region is related to the technology of the coating formation at the final stage of the deposition. For the CAVD technique, the formation of metal drops on the surface of the grown coating is typical, caused by the sputtering of the molten metal because of overheating of the cathode [8,9]. Investigating the samples by SEM in combination with EDF methods, we found that the drops mainly consist of pure chromium.

The phase composition of Ti-Cr-N system was investigated by GIXRD technique. Figure 5 shows \( \alpha/2\theta \) scans for five incidence angles \( \alpha = 0.45^\circ, 0.90^\circ, 1.35^\circ, 1.80^\circ \) and \( 2.30^\circ \) with respect to the sample surface (CuK\( \alpha \) radiation). The measured spectra demonstrate both peaks of the solid solution Ti-Cr-N and the titanium nitride. With the increase of the incidence angle \( \alpha \), the substrate Fe(110) peak shows up. Usually, no special measures are taken for X-ray penetration depth control in the measurements of the residual stress in polycrystalline materials. The sample rotation is used to set the selected \( \{hkl\} \) Bragg planes in the condition of diffraction. GIXRD method is used for the analysis of the residual stresses in the following cases: (1) determination of the residual stresses in undersurface regions and thin coatings, and (2) determination of the stress gradients in the sample.

The effective X-ray penetration depth for the incident angles \( \alpha \) far from the critical angle of the total external reflection is [10]:

\[
\tau = \frac{\sin \alpha \sin(2\theta - \alpha)}{\mu(\sin \alpha + \sin(2\theta - \alpha))}
\]  

where \( \mu \) is the linear attenuation coefficient depending on the wavelength of the radiation used and \( \theta \) is the Bragg angle. For use in the experimental incident angles \( \alpha \), the penetration depths are 0.090, 0.179, 0.266, 0.361, and 0.445 nm, respectively.

By \( 2\theta \) scanning at the constant incidence angle \( \alpha \), the positions of several Bragg reflections \( \{hkl\} \) are measured. Thus, with no sample rotation and no variation of depth \( \tau \), the direction of residual stresses can be identified. The angle of inclination \( \psi^{hkl} \) of the diffraction vector to the surface normal is:
When determining the residual stresses from the measurements at different crystallographic planes, the dependence of the elastic constants $S_{1}^{hkl}$ and $\frac{1}{2}S_{2}^{hkl}$ on $\{hkl\}$ should be taken into account. The traditional analysis of the residual stresses using fundamental equation [10] also requires further modification. Introducing the variable

$$g(\psi, hkl) = \frac{1}{2}S_{2}^{hkl}/S_{1}^{hkl} \sin^{2}\psi^{hkl}$$

and in approximation of biaxial stress (that is usually correct for thin films), the equation for the analysis of residual stress is transformed to

$$\varepsilon^{hkl}_{\psi} / S_{1}^{hkl} = g(\psi, hkl)\sigma_{\varphi} + (\sigma_{11} + \sigma_{22})$$

$$\sigma_{\varphi} = \sigma_{11}\cos^{2}\varphi + \sigma_{12}\sin(2\varphi) + \sigma_{22}\sin^{2}\varphi$$

where $\sigma_{\varphi}$ is the residual stress in the sample along the azimuthal angle $\varphi$. Further we use the additional condition of the axial diffraction symmetry, which takes place in the coating production process.

The expression for the strains $\varepsilon^{hkl}_{\psi}$ contains the interplanar distance for each $\{hkl\}$ plane in the absence of stress. To avoid the pseudo-distortion of the crystallographic structure, the parameters $d_{0}^{hkl}$ have to be related to each other according to this lattice symmetry:

$$\frac{d_{0}^{hkl_{2}}}{d_{0}^{hkl_{1}}} = \sqrt{\frac{h_{1}^{2} + k_{1}^{2} + l_{1}^{2}}{h_{2}^{2} + k_{2}^{2} + l_{2}^{2}}}$$

Figure 6 shows the dependence of the residual strains normalized to the X-ray elastic constants on the parameter $g(\psi, hkl)$ in the coating of thickness 1.2 $\mu$m, formed on the substrate and for the incidence angles $\alpha = 0.45^\circ$ and $2.30^\circ$. Figure 5 displays the presence of two phases: solid solution TiCrN and titanium nitride. In our case, we used the phase TiN for calculations, for which the maximal number of the reflections in the spectra is observed. For the analysis, the modified $\sin^{2}\psi$ method in biaxial approximation has been used. The linear character of the observed dependences confirms the validity of the approximations used in the analysis.

The calculated residual stresses for different X-ray beam incidence angles $\alpha = 0.45^\circ$, $0.90^\circ$, $1.35^\circ$, $1.80^\circ$ and $2.30^\circ$ are shown in Figure 7. Using Eq. (1), they can be associated to the thicknesses of probed layer $\tau = 0.09$, $0.179$, $0.266$, $0.361$ and $0.445$ $\mu$m, respectively. As the figure shows, in the angle region $\tau = 0.15$ to $0.45$ $\mu$m, the stress value is $\sigma_{\varphi} \approx -6.7$ GPa. At the informational depth of coating $\tau = 0.09$ $\mu$m, the evaluated magnitude of the residual stress is -6 GPa. This fact points to the presence of the layer, enriched by chromium (Figure 3). The residual
stress was also measured using two-dimensional X-ray diffraction (XRD²) technique [7]. The Bragg reflection (200) of the phase TiCrN was used for measurement. A Bruker D8 DISCOVER diffractometer was set up with a 2.2 kW Cu long, fine focus tube (mounted for a point focus), 0.8 mm collimators, ¼-circle cradle, two-dimensional HI-STAR detector with resolution 1024 × 1024 pixels (the distance from detector to sample was 150 mm), and brass foil in front of the detector to suppress fluorescence radiation. Two-dimensional frames (Figure 8) were collected in side-inclination mode at fixed angels \( \omega = 5^\circ \) (the rotation axis is perpendicular to the diffractometer plane) and \( \varphi = 0^\circ \) (azimuthal angle). Inclination angle \( \psi \) was varied from \( 0^\circ \) to \( 45^\circ \) with a step of \( 5^\circ \). The penetration depth at these conditions was not controlled and monotonically
decreased from 0.9 to 0.6 µm with an increase in the incidence angle. The data interpretation was done using LEPTOS software and resulted in the residual stress value $\sigma_\phi = -6.7 \pm 0.3$ GPa, which agrees well with the average values obtained previously by using the GIXRD method.

**CONCLUSION**

The combination of GIXRD, two-dimensional stress, and XRR methods is promising for the analysis of thin near-surface layers of variable concentration, and delivers information on the distribution of the phase composition and density as a function of the depth. At the surface of the deposited coating, the Cr-enriched layer is formed, which specifies a decrease of the residual stresses. Phases of TiN and solid solution Ti$_x$Cr$_{1-x}$N both are present in the coating and their fraction grows with the depth, which leads to raising the stress up to -6.8 GPa. Stress evaluation using two techniques, GIXRD method for different Bragg reflections of TiN phase and XRD$^2$ method for reflection TiCrN(200), correlate well with each other, which points to the consistency of the results obtained.

**REFERENCES**