X-RAY INVESTIGATION OF TiN AND CoCr, CoCr-N COATINGS

RENTGENOGRAFICKÁ ANALÝZA TiN A CoCr, CoCr-N POVLAKŮ

Z. Budinská, R. Králová, R. Novák

The coatings of the mechanical parts have a great importance in the mechanical engineering. Recently, the coating technology has developed considerably, including the sputtering techniques. We study two kinds of sample prepared by the PVD method, in which the thin films are deposited using the DC (dirct current) sputtering with an unbalanced pulsed magnetron. Namely (i) The TiN layer deposited on the steel 12050 is studied in connection with the residual stress distribution and the machining of the substrate. The target Ti was used. (ii) CoCr and CoCr-N   films were deposited on the glass substrate (the target of CoCr 66/34 wt. % was used in a mixture of Ar and N_2). The composition and the grain size of the films is studied in dependence on the condition under which the sample were prepared.

Keywords: X-ray analysis, magnetron sputtering, thin film, TiN, CoCr, CoCr-N, residual stress

Experimental details

(i)   TiN coatings:

The surface of the substrate was machined by milling and then covered by a TiN layer using the magnetron sputtering method (see Table 1). The size of all samples were $15 \times 15 \times 5$ mm. The details of samples are presented in Table 2.

Table 1: Parameters of magnetron sputtering procces

Temperature of deposition	$100°$ C
Gas atmosphere	$Ar + N_2$
Pressure	0,4 Pa
Deposition time	40 min (thickness 1,3 μm) 60 min (thickness 2,5 μm)
Bias voltage	-60 V (1,3 μm) -80 V (2,5 μm)

Mgr. Zuzana Budinská, ČVUT Praha, Technická 4, Praha 6, 166 07 Czech Republic, budinska@fsid.cvut.cz

Doc. RNDr. Rudolfa Králová, CSc., ČVUT Praha, Technická 4, Praha 6, 166 07 Czech Republic, kralova@fsid.cvut.cz

Doc. RNDr. Ing. Rudolf Novák, DrSc. ČVUT Praha, Technická 4, Praha 6, 166 07 Czech Republic, novakr@fsid.cvut.cz

Table 2: Samples parameters

Sample	Treatment of substrate	TiN coating thickness
A	none	none
B	milling	1,3 μm
C	none	2,5 μm
D	milling	2,5 μm

Residual stress measurements are made using the standard Bragg-Brentano X-ray diffraction geometry with CrK_α radiation. The measurements were made with respect to milling direction (see Fig. 1,2). The texture was determined using CoK_α radiation.

If a biaxial stress exists in the surface, the strain is related to the principal stresses σ_1 and σ_2 as follows (Fig.3):

$$\varepsilon_{\phi,\psi} = \frac{S_2}{2}\sigma_\phi \sin^2\psi + S_1(\sigma_1 + \sigma_2),$$

where S_1 and S_2 are the X-ray elastic constants and $\sigma_\phi = \sigma_1 \cos^2\phi + \sigma_2 \sin^2\phi$. For an elastically isotropic solid then,

$$S_1 = -\frac{\nu}{E},$$

$$\frac{1}{2}S_2 = \frac{1+\nu}{E},$$

where E is Young's modulus and ν is Poisson's ratio. Instead of the X-ray data, the bulk elastic constants were used for the steel 12050 [2] ,[3]:

$$S_1 = -1,368.10^6\,\text{MPa}^{-1},$$

$$\frac{1}{2}S_2 = 6,085.10^6\,\text{MPa}^{-1}\left(E = 212\,\text{GPa},\ \nu = 0,29\right)$$

for TiN coating:

$$S_1 = -0,34.10^6\,\text{MPa}^{-1},$$

$$\frac{1}{2}S_2 = 1,52.10^6\,\text{MPa}^{-1}\left(E = 640\,\text{GPa}, \nu = 0,30\right).$$
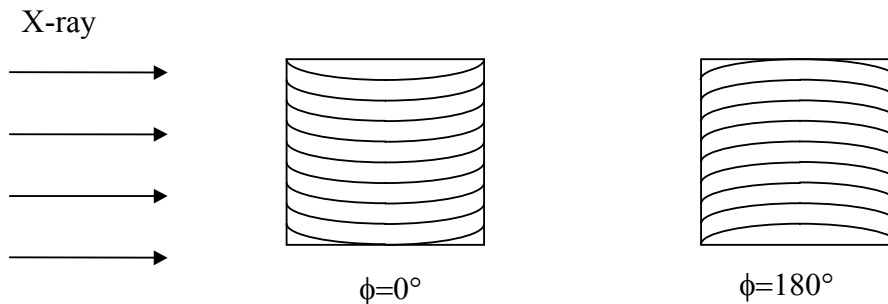

Fig.1

Fig.1 Substrate surface after milling with respect to measurement direction.
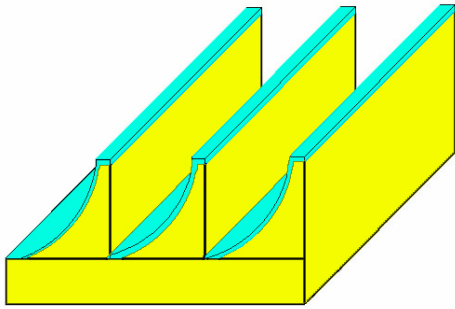
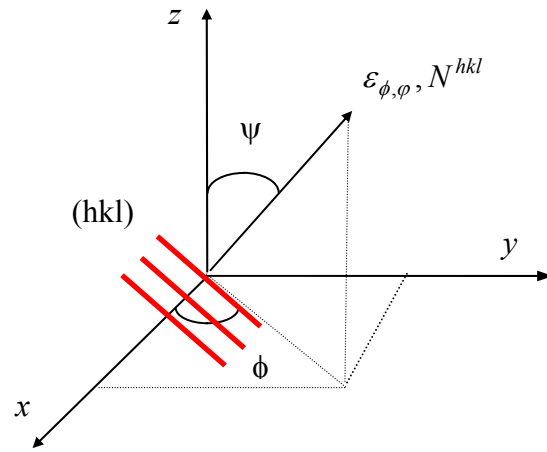| Fig. 2 | Fig. 3 |

Fig. 2   Surface roughness of the sample after milling

Fig. 3   Direction N^{hkl} of the measurement of the deformation $\varepsilon_{\phi,\psi}$ and orientation of angle ψ and ϕ. Direction z is direction of surface normal N^{hkl}.

(ii)   CoCr and CoCr-N coatings

CoCr and CoCr-N films were prepared. The thin films were deposited by DC sputtering using an unbalanced pulsed magnetron (the target of CoCr 66/34 wt % was used in a mixture of Ar and N_2 on the gas substrate.

The conditions of the deposition follow:
- the partial pressure of nitrogen was varied from p_{N_2} =0,06 Pa to 0,3 Pa ;
- the substrate temperature was in the range from T=50°C to 300°C ;
- the substrate biases were varied from -3V to -150 V.
- the thickness of the films, measured by interference microscope, is about 2 μm.

The x-ray diffraction (XRD) is made using the x-ray powder diffractometer Siemens with Bragg-Brentano geometry and CrK_α radiation.

Results

TiN coatings:

- The compressive residual stress can be determined on sample A (nonmilled surface of substrate).

- The results obtained on samples B, D (milled substrate with TiN coating) and C (nonmilled surface of substrate with TiN coatings) show the presence of texture (nonlinear independence of lattice parameter a vs. $\sin^2 \psi$ and I/I $_{MAX.}$ vs. $\sin^2 \psi$), see Fig. 4. The preferred orientation of (111) planes is determined on sample C, the preferred orientation of (100) is determined on sample D. So the texture has been changed after milling of surface of substrate.

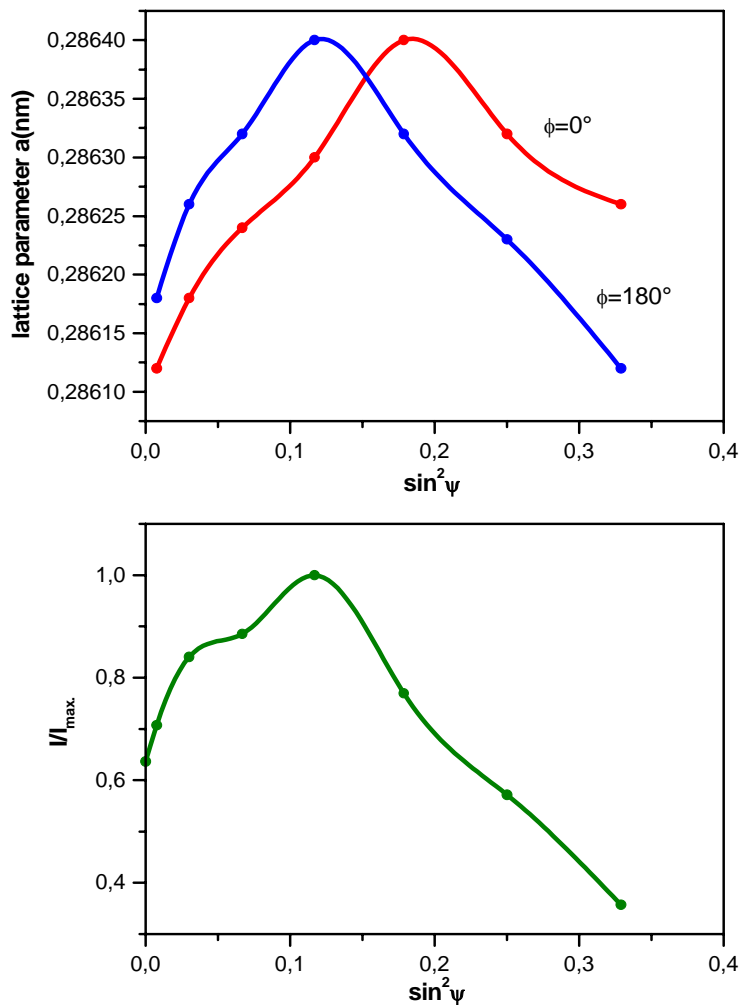- The residual stress in the TiN coating could not be determined because of weak intensity of (200) line at large ψ.

Fig. 4

Fig. 4   Lattice parameter a and relative intensity $I/I_{max.}$ vs. $\sin^2\psi$- sample B (TiN)

CoCr coatings

- The identification of diffraction lines in the XRD patterns gives the following possibilities of the association with structural components of a pure (without nitrogen) CoCr film: CoCr σ-phase [6], Co, Cr and CoCr .

- Pure CoCr films sputtered on an unheated substrate, are polycrystalline films with a strong preferred orientation at $2\Theta \approx 68°$. At this angle two reflections (110) Cr   and (002) Co overlap. The extent, to which   this preferred orientation occurs, depends on the substrate bias.

- The angle 2Θ of the most intensive peak does not change with temperature, however, the overall intensity this peak is temperature dependent. At 300 °C when the maximum at $2\Theta \approx 68°$ is already weak, a new peak appears at $2\Theta \approx 129°$. This new line is tentatively ascribed to σ-phase of CoCr.

- The full-width at half maximum of the reflection $2\Theta \approx 68°$ is about 0,5°. An estimation of the grain size from the Scherrer formula shows, under the assumption that strains are not contributing to the peak broadening, that the size of grains in the sputtered films is approximately 30 nm.

CoCr-N coatings

Addition of nitrogen into the argon gas strongly changes the properties of the sputtered films. The main changes are the following:

- T=50°C, U=-3V

  Under the pressure of p_{N_2} = 0,06 Pa the XRD patterns of CoCr-N does not differ from XRD patterns of CoCr, as far as the position of the reflection are concerned, only the intensities of the lines are different. At the pressure p_{N_2} = 0,1 Pa we observe a substantial change, namely a reflection at $2\Theta \approx 77°$ appears. This reflection is not observed in XRD patterns of CoCr, Therefore, this line could be associated with σ-phase of CoCr. The intensity of this reflection increases with the pressure.

- T=50°C, p_{N_2} = 0,1 Pa

  The position of the reflection in XRD patterns does not depend on the bias, while the intensities are weakly temperature dependent.

- U= -3V, p_{N_2} =0,1 Pa

  The position of the diffraction lines change significantly with temperature (see Fig.5). The reflection shift to higher angles. This shift corresponds to the change of lattice spacing, which causes macroscopic deformation. As a results a destruction of the layer may occur.

- The full width at half-maximum of the reflection $2\Theta \approx 77°$ is about 2,25°. Under the assumption that the strain are not contributing to the peak broadening, the size of grains in the sputtered CoCr-N films is approximately 7 nm.
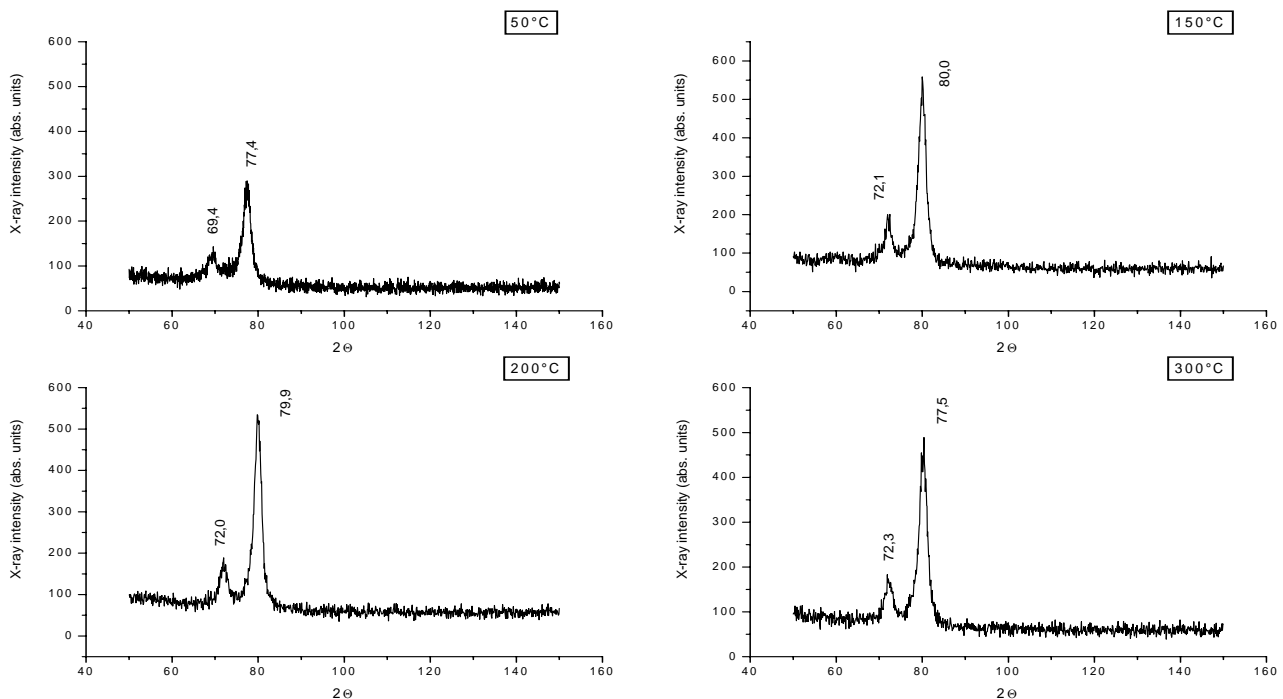

Fig. 5

Fig. 5   XRD patterns of CoCr-N films at various values of the temperature T of the substrate (substrate bias U=-3V, partial pressure of N_2 p_{N2}=0,1 Pa).

Conclusion

TiN coatings

The process of milling a substrate leads to the strong plastic deformation in the surface and consequently to changes of preferred orientation of crystallites of TiN coating. These changes are responsible for inhomogenous distribution of residual stress in TiN coatings.

CoCr and CoCr-N coatings

X-ray analysis of CoCr and CoCr-N films magnetron sputtered from the alloy CoCr (66/34 wt %) target onto the glass surface can be summarized as follows:

- The pure CoCr films sputtered at the substrate bias ranging from –3V to –150V and substrate at the temperature ranging from 50°C to 300°C are polycrystalline. The grain size is approximately 30 nm.

- The addition of nitrogen into CoCr film, converts the polycrystalline films into the nanocrystalline films. The size of the grains is then about 7 nm.

- The increase the temperature results in the shift of the diffraction lines in the direction of larger angles 2θ and to appearance of the macroscopic deformation inside the films.

- The films CoCr-N deposited at the nitrogen pressure $p_{N_2} \leq 0,3$ Pa and at the substrate temperature T$\leq$ 300°C showed an XRD patterns corresponding to σ-phase of CoCr.

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