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Determination of residual stresses in cathodic arc coatings by means of the parallel beam glancing X-ray diffraction technique

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ABSTRACT

A method based on the parallel beam glancing X-ray diffraction geometry has been applied to the measurement of the residual stresses present in cathodic arc plasma $(Al_{0.66}Ti_{0.34})N$ coatings deposited on hardmetal substrates. This procedure avoids the problems associated to the strong overlapping between the diffraction peaks of the coating and the substrate. The method has been validated by comparison with the results obtained with $\sin^2\psi$ technique on other combinations of coatings and substrates in which no important overlapping occurs (i.e. $(Al_{0.66}Ti_{0.34})N$ on steel and TiN either on steel or on hardmetal substrates). The elastic moduli of the different coatings, required for the calculation of the residual stresses, have been obtained from nanoindentation experiments.

1. Introduction

Hard $Al_xTi_{1-x}N$ coatings obtained by cathodic arc plasma deposition technique are used in a wide variety of tribological applications [1–3]. The implementation of this technique at industrial scale is based on its high deposition rates and the strong adhesion of these coatings both to steel and hardmetal substrates [4]. In addition, this technology is compatible with typical tolerance requirements of high precision tools. It is commonly agreed that hardness and residual stresses are two critical properties for the optimization of these coatings either for high speed steel (HSS) or hardmetal substrates. Hardness measurements on thin cathodic arc plasma coatings are difficult to perform due to their high roughness compared to those of sputtered films [5]. Deep indentations are affected by the substrate and shallow ones by the presence of protuberances and depressions at the film surface. On the other hand, residual stresses are typically measured by using the $\sin^2\psi$ technique [6,7]. However, for hardmetal substrates, a strong overlapping is found between peaks of WC and Co phases and those of the B1 NaCl $Al_xTi_{1-x}N$ phase. Deconvolution techniques are applied in these cases but error estimations are not provided by these authors [8]. In this work, residual stresses are calculated by using a parallel beam glancing X-ray diffraction technique (XRD) which does not require the deconvolution of overlapped peaks [9]. Additionally, the calculation of the residual stresses from XRD methods requires an independent determination of the coating elastic modulus. Some authors assume that the elastic moduli of TiC_xN_{1-x} type coatings are similar to that of TiN (450 GPa according to Ref. [10]), although it is well known that the hardness and bonding strength of TiCN materials differ significantly from those of TiN. Others apply the Oliver and Pharr method to nanoindentation results [11], but the values obtained are abnormally large, especially on hardmetal substrates [6,8]. In this work, nanoindentation results will be analyzed as a function of the penetration depth in order to provide a more reliable value of the Young's modulus.

2. Experimental procedure

Four different coating–substrate combinations were obtained by depositing either TiN or $Al_xTi_{1-x}N$ on M2 HSS steel and K25 hardmetal substrates by the cathodic arc plasma technique. Substrates were produced as cylinders 5 mm high and 25 mm in diameter. Before coating, the bases of the cylinders were polished down to 1 μm diamond paste and carefully degreased and cleaned. PLATIT PL50 equipment was used under the following conditions: temperature: 430 °C, pressure: from 1 to 5 Pa, cathode current: 200 A, axis voltage: 80 V. Thicknesses ranging from 1.6 to 3.9 μm were produced by means of a threefold rotating substrate holder with variable speed. The actual thickness of each coating was measured by the Calotest method (Table 1) and its adhesion strength to the substrate was qualitatively estimated by means of the VDI 3198 standard procedure [12]. Roughness was characterized by means of the roughness average parameter (R_a) which was obtained with an atomic force microscope (AFM). Chemical analyses, carried out by energy dispersion spectroscopy, show that Al/Ti at. ratios are

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Table 1
Residual stresses of the different coating–substrate combinations calculated from the $\sin^2\psi$ method (Bragg-Brentano configuration).

Coating	Substrate	Calotest thickness (μm)	Residual stresses (MPa)	Stress free lattice parameter (nm)
TiN	M2 steel	2.1	−4400 ± 200	0.4245
TiN	M2 steel	3.4	−4400 ± 180	0.4244
TiN	M2 steel	3.7	−4600 ± 200	0.4245
TiN	WC-Co	1.6	−1800 ± 170	0.4246
TiN	WC-Co	2.6	−2200 ± 200	0.4243
TiN	WC-Co	3.6	−2500 ± 180	0.4246
$(Al_{0.66}Ti_{0.34})N$	M2 steel	2.1	−6800 ± 500	0.4170
$(Al_{0.66}Ti_{0.34})N$	M2 steel	2.8	−6700 ± 250	0.4173
$(Al_{0.66}Ti_{0.34})N$	M2 steel	3.9	−6900 ± 200	0.4174

between 1.63 and 1.65 (clearly below 2, which is the composition of the target). More precise chemical analyses were carried out by glow discharge optical emission spectroscopy (RF-GD-OES) with a JY-GD-PROFILER 2 obtaining an average composition of 17.5 at.% Ti, 34.2 at.% Al, 47.3 at.% N and 1.0 at.% O, which corresponds to the $(Al_{0.66}Ti_{0.34})(N_{0.98}O_{0.02})_{0.93}$ stoichiometry. Oxygen levels are typical of industrial processing conditions. For simplicity, the coating composition notation will be, hereafter, based on the GD-OES data, but assigning a stoichiometric ratio to the nitride phase: (i.e. $Al_{0.66}Ti_{0.34}$)N. The coating microstructure was studied by transmission electron microscopy (TEM) on cross sections obtained by focused ion beam machining. A JEOL JEM 2100 microscope, operating at 200 kV with a point to point resolution of 2.3 was used for this work. Phase identification by XRD was carried out using the glancing angle method with Cu Kα radiation and a constant incident angle of $\omega = 3°$. Parallel optics was used for the incident beam and a crossed-slit collimator and a flat graphite monochromator for the diffracted beam. The size of radiated zone was 6 by 3 mm and was always centered with the specimen axis.

2.1. Nanoindentation

Nanoindentation tests were carried out with a Nano Indenter II machine using a Berkovich diamond tip. Raw hardness and modulus data were obtained from load vs. displacement curves using the method proposed by Oliver and Pharr [11]. For each sample (i.e. each combination of coating and substrate) a set of 30 tests was carried out with a minimum distance of 30 μm between indentations. Indentation locations were manually selected in order to avoid the presence of droplets. After testing, all load vs. displacement curves were revised for removing non valid data.

Loading was performed under displacement control (at 5 nm per second) up to different penetration depths: 100 nm, 200 nm, 300 nm, 400 nm and 1100 nm. Below 100 nm, a high dispersion of results is obtained since roughness values are of the same order of magnitude. The dwelling time at each penetration distance was 85 s in order to reach the stable regime. For correcting thermal drift effects, load variations vs. time are recorded at 10% of the maximum applied load for 50 s. Substrate effects on hardness were analyzed by means of the model proposed by Korsunsky et al. [13]. This model, based on the correlation between hardness and the total energy of the indentation, provides an estimation of the film hardness, "H_f" from:

$$H_c = H_s + \frac{(H_f - H_s)}{1 + k\beta^2} \tag{1}$$

where "H_c" is the composite hardness (i.e. film + substrate) and "β" the relative indentation depth, defined as the penetration depth divided by the film thickness. "H_f" is the film hardness and k is the fitting parameters. The pairs (H_c, β) were obtained experimentally by changing not only the maximum penetration depth but also by using coatings with different thicknesses (Table 1). The substrate hardness "H_s" was measured independently for both M2 steel and K25 hardmetal (at a max. penetration depth of 500 nm) obtaining values of 10 and 18 GPa respectively.

The determination of the coating elastic modulus from nanoindentation data also requires the correction of substrate effects. In this case, the method developed by Saha and Nix [14] (based on a previous model of King [15]) has been used to analyze the indentation experiments. This model assumes that the coating–substrate system behaves as a series composite with a constant Poisson's ratio equal to 0.21. The reduced modulus "E_r" obtained from indentation unloading graphs is related to the film modulus by the expression:

$$\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_f^2}{E_f}\left(1 - e^{-\frac{\alpha(t-h)}{a}}\right) + \frac{1 - \nu_s^2}{E_s}\left(e^{-\frac{\alpha(t-h)}{a}}\right) \tag{2}$$

where E_s and E_f are the modulus of the substrate and the film respectively. E_i and ν_i are the Poisson's coefficient and the Young's modulus of the diamond indenter (0.07 and 1140 GPa respectively). "a" is the square root of the projected contact area, "t" is the film thickness and "h" is the total indenter displacement. Finally, "α" is a numerically determined scaling parameter, which is a function of a/t and the indenter geometry (i.e. Berkovich pyramid in our case).

2.2. Residual stresses

X-ray diffraction analyses using the Bragg–Brentano configuration [9] were carried out on TiN and $(Al_{0.66}Ti_{0.34})N$ coatings on M2 steel substrates and TiN coating on the hardmetal substrate. For these three systems the conventional $\sin^2\psi$ method was used to calculate the coating residual stresses. Different peaks have been chosen depending on the coating/substrate pair. For TiN films deposited on WC-Co substrates, the (220) peak was selected with $2\theta = 99°$ for Cr Kα radiation whereas for M2 steel substrates, the (311) peak was used for both TiN and $(Al_{0.66}Ti_{0.34})N$ coatings (with $2\theta \sim 130°$). The interplanar spacings were measured in 39 different orientations (thirteen ψ and three ϕ). From these measurements, the entire stress tensor could be determined and a state of biaxial stress was confirmed, as expected in a thin coating on a substrate. In the rest of the measurements only 13 different orientations φ orientations were measured and the $\sin^2\psi$ analysis was used. Assuming a biaxial state of stress of magnitude "σ" and isotropic elasticity (E and ν), the interplanar spacing varies with ψ in the following way:

$$d_\psi = \frac{\sigma}{E}(1 + \nu)d_n \sin^2\psi + d_n \tag{3}$$

where d_n is the interplanar spacing normal to the film surface ($\psi = 0°$). Therefore, by plotting the measured lattice spacings d_ψ vs. $\sin^2\psi$, the residual stresses are determined from the slope, provided that the elastic properties are known and a good linear fitting is obtained in the regression analysis. In our case, elastic moduli are calculated from nanoindentation tests as described above. Fig. 1 shows representative $\sin^2\psi$ curves for the systems without peak overlapping. A linear plot was obtained in all cases, validating the hypothesis made. Results are summarised in Table 1.

As described by other authors, strong overlapping has been found between diffraction peaks corresponding to the $(Al_{0.66}Ti_{0.34})N$ coating and the hardmetal substrate (Fig. 2).

In this case, residual stresses were calculated by using the parallel beam glancing incidence geometry (Fig. 3). In this configuration, diffraction occurs at a small constant penetration depth, since a constant incident angle is used (in our case, $\omega = 3°$). All peaks within the instrumentally permitted range are used for the determination of residual stresses.