XRD, Thin Film, Stress Analysis
FOX2D CU 12_INF

Application Note n° AN-2D13

Abstract

Line-focus sealed tubes coupled to one-dimensional multilayer optics are standard solutions for powder diffraction measurements or reflectivity measurements as it provide high flux on a large surface area. The microstructure analysis of thin films requires the variation of the diffraction vector with respect to the sample and consequently a two-dimensional beam is preferred.

The FOX 2D 12_INF optics have been previously validated as a high performance solution for such applications providing high flux and low divergence (Wohlschlögel et al., J.Appl.Cryst. (2008). ***41****, 124-133). Such mirror was installed on a Bruker D8 diffractometer set-up at OC Oerlikon Balzers AG (see Fig. 1).*

This application note reports stress analysis on modern high performance CrN thin films produced and characterized at OC Oerlikon Balzers AG.

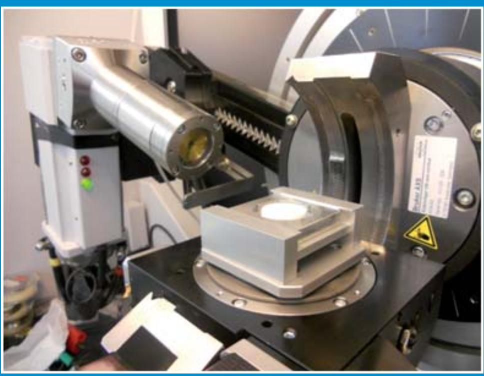

Fig. 1 : FOX 2D Cu 12_INF mechanics mounted on a sealed tube

State-of-the-art X-ray diffraction stress analysis of modern nano-sized coatings - An approach to track coating performance

Data courtesy of Dr. Matthias Sobiech, OC Oerlikon Balzers AG, Balzers, Liechtenstein.

Introduction

Generally, coatings deposited on substrates (e.g. tools or components) are present in a (mechanically) "stressed" state. The analysis of such (residual) stresses is of great technological importance regarding coating performance during field application. X-ray diffraction offers a very powerful possibility to investigate accurately and non-destructively the state of mechanical stress in coatings and surface regions of bulk materials. Thus, in order to demonstrate practically the capabilities of the approach mentioned above, dedicated X-ray diffraction stress analyses of standard PVD (physical vapor deposition) arc-evaporated CrN coatings (chosen as an suitable example) are presented in this report. In addition, for the sake of completeness, a brief overview of the microstructural and tribological characteristics is given.

Preparation and characterization of specimens

CrN coatings were prepared by cathodic arc evaporation using an Oerlikon Balzers INNOVA deposition machine (see Fig. 2). As substrate material polished steel substrates (alloyed cold working steel) were used.

In the as-deposited state the investigated CrN coatings exhibited a surface roughness of 0.3 µm (Ra) due to the presence of surface droplets which represent separated massive particles from the Cr target during arc evaporation. By Calo grinding as well as by cross-sectional SEM investigations a coating thickness of about 5 µm was determined (see Fig. 3).

As obtained from X-ray diffraction measurements the fine-grained coating morphology is composed of nano-crystalline CrN exhibiting crystallite sizes of about 15 nm and a lattice

Fig. 2 : Left: Oerlikon Balzers INNOVA deposition machine (www.oerlikon.com/balzers), Right: Illustration of a driller coated with Balzers BALINIT® coating enabling high-performance machining.

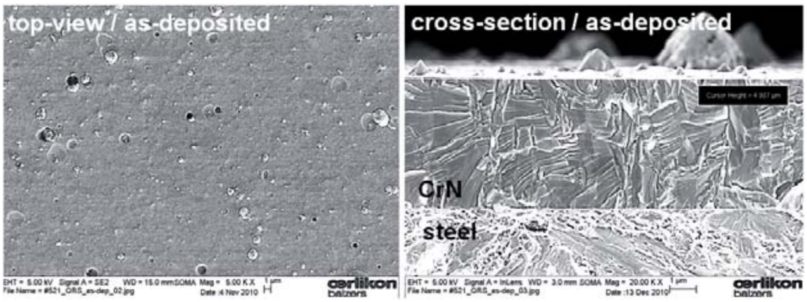

Fig. 3 : Top-view and cross-sectional SEM micrographs of the investigated CrN coating in the as-deposited state.

constant of 0.4157 nm (see Tab. I). On the basis of instrumented micro-indentation and ball on disc tests the mechanical and tribological properties of the coating were determined as follows: E = 280 +/- 15 GPa, H = 20 +/- 1.5 GPa and COF = 0.3 (see Tab. I). Therefore it can be concluded that the investigated arc-evaporated CrN coating represents a hard, nano-sized coating which is suitable for different tribological applications, such as e.g. machining of copper, plastic injection molding or motor sport and aviation applications. In the following state-of-the-art X-ray diffraction stress analyses of the same CrN coatings are presented.

Table I : Compilation of some CrN coating properties.

Lattice constant [nm]	Crystallite size [nm]	Young's modulus [GPa]	Hardness [GPa]	Coefficient of friction
0.4157	15	280 +/- 15	20 +/- 1.5	0.3

X-ray diffraction setup at Balzers

The X-ray diffraction setup installed at OC Oerlikon Balzers AG (see Fig. 4) is dedicated to perform state-of-the art X-ray diffraction stress and texture analysis. The Bruker D8 Advanced Diffractometer operates with Cu Kα radiation and is additionally equipped with Xenocs FOX 2D 12_INF optics, an Eulerian cradle, a parallel-plate collimator and an energy-dispersive detector. Apart from the Eulerian cradle (which allows tilting and rotating the specimen), a two dimensional highly parallel X-ray beam is absolutely mandatory for the above mentioned measurements in order to avoid instrumental aberrations which usually obstruct proper diffraction analysis. A FOX 2D 12_INF optic was installed on the point focus sealed tube in order to produce a two-dimensional low divergence beam. In the following a brief characterization of the performance of the Xenocs FOX 2D optic is given:

i) The residual beam divergence was measured on a {100} cut single-crystal Si wafer by recording rocking curves, as shown in Fig. 5 (see for further details M. Wohlschlögel *et al.*, J. Appl. Crystallogr. **41**, 124, 2008). The difference between the full width at half-maximum of the measured rocking curve on Si 400 diffraction line (without any optical components in the diffracted beam) and the intrinsic line width of Cu Kα radiation (about 0.01°) allow to estimate the residual divergence which is in the present case about 0.05° (< 1 mrad), i.e. the X-ray beam is highly parallel.

ii) The comparison of X-ray diffraction survey scans on pure α-Al_2O_3 reference material (NIST standard reference material SRM 1976a) measured with two different X-ray mirrors is shown in Fig. 6a. The difference in diffracted intensity is due to significantly different beam sizes of the optics used (1D-Göbel with about 15x1.5 mm^2; Xenocs FOX 2D 12_INF optics with about 1x1 mm^2). However, it is clearly obvious that by use of the Xenocs FOX 2D optics only diffraction lines belonging to α-Al_2O_3 appear, i.e. "artificial" diffraction lines which do not belong to α-Al_2O_3, as observed when using the 1D-Göbel, can be avoided.

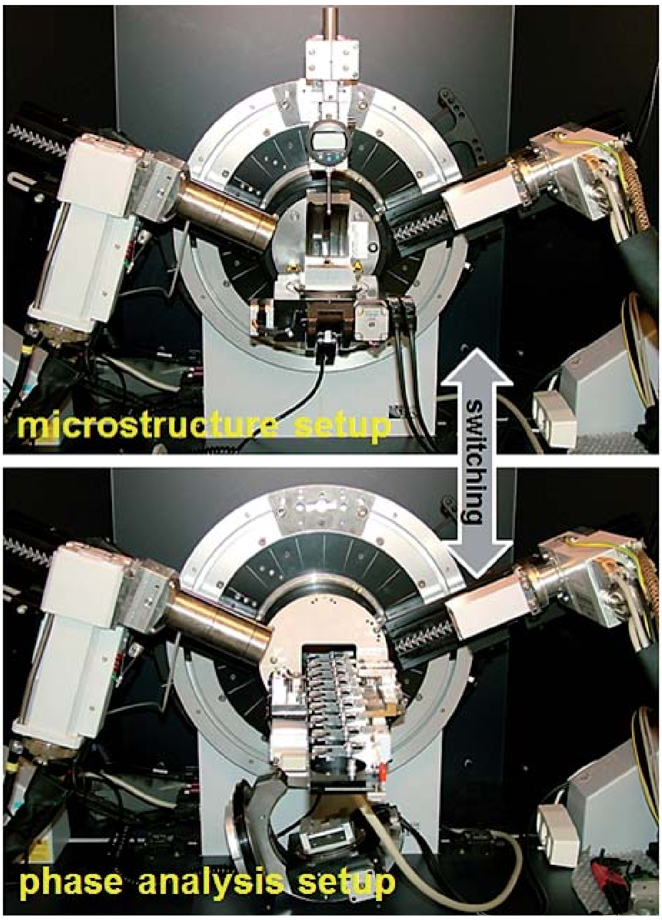

Fig. 4 : X-ray diffraction setup at OC Oerlikon Balzers AG (Balzers, Liechtenstein) dedicated to perform state-of-the art X-ray diffraction stress and texture analysis. By using different specimen holders (i.e. an Eulerain cradle as well as a 7-fold specimen holder), two different diffraction setups can be realized allowing high-throughput phase analysis and detailed microstructural investigations.

X-ray diffraction stress analyses of PVD arc-evaporated CrN coatings

The specimen was mounted on the Eurelian cradle in order to allow tilting and rotating the specimen (see "microstructure setup" in Fig. 4) as required for diffraction stress analysis. The residual stress of the CrN coating was measured without and with control of penetration depth (according to the diffraction strategy proposed by A. Kumar *et al.*, J. Appl. Crystallogr. **39**, 633, 2006) and thus stress-depth profiling of the near-surface region of the coating was possible. The CrN coating was investigated in the as-deposited state as well as after micro-blasting in order to demonstrate the capabilities of the employed diffraction strategy by tracking accurately and non-destructively changes in the residual state of stress.

The mechanical macrostress state of the CrN coating was found to be planar and rotationally symmetric and thus only one stress component oriented parallel to the coating surface was determined. The mechanical stress was calculated from lattice strains measured employing the 200 reflection of cubic CrN on the basis of the $\sin^2\psi$-method (U. Welzel *et al.*, J. Appl. Crystallogr. **38**, 1, 2005). The specimen was assumed to be macroscopically elastically quasi-isotropic and therefore the *hkl*-dependent diffraction elastic constants S^{hkl}_1 and $\frac{1}{2}S^{hkl}_2$ were derived from single-crystal data (K. J. Martinschitz *et al.*, J. Appl. Crystallogr. **42**, 416, 2009) using the elastic grain interaction model of Neerfeld-Hill (U. Welzel *et al.*, J. Appl. Crystallogr. **38**, 1, 2005).

In order to ensure that instrumental aberrations do not occur during diffraction stress analysis, i.e. upon tilting and rotating the specimen, a ceramic plate composed of sintered α-Al_2O_3 (NIST standard reference material SRM 1976a) was investigated with respect to its state of strain. The obtained $\sin^2\psi$-plot for the 104 diffraction line (i.e. a straight-line behavior with no slope) proofed the material to be strain/stress-free (see Fig. 6b), i.e. for this XRD setup instrumental aberrations do not have to be taken into account upon diffraction stress analyses.

The residual mechanical stress (without control of penetration depth) of the CrN coating was determined for the as-deposited state as well as after micro-blasting. The corresponding residual stress-depth distributions were measured as well and the results are shown in Fig. 7. It demonstrates in a straightforward manner that diffraction stress analysis using the XRD setup described before is very suitable in order to track precisely the changes in mechanical (surface) stress, as e.g. induced by micro-blasting. In the as-deposited state the CrN coating exhibited a compressive stress (averaged within the probed

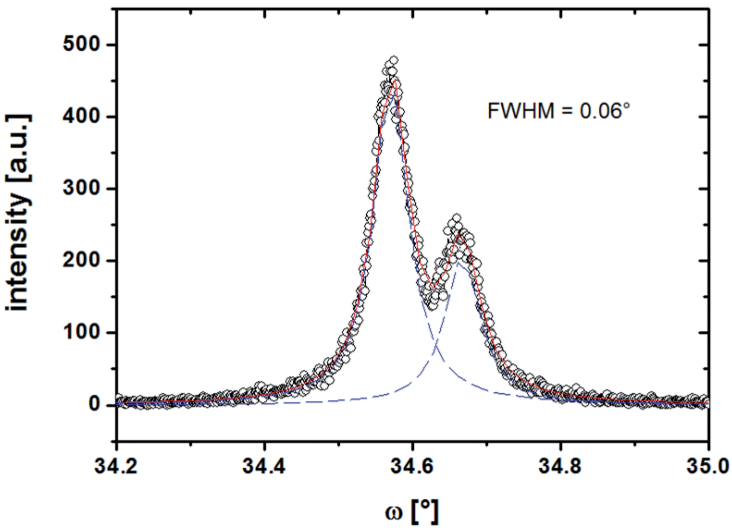

Fig. 5 : Rocking curve of the Si 400 reflection without any optical components in the diffracted beam path.

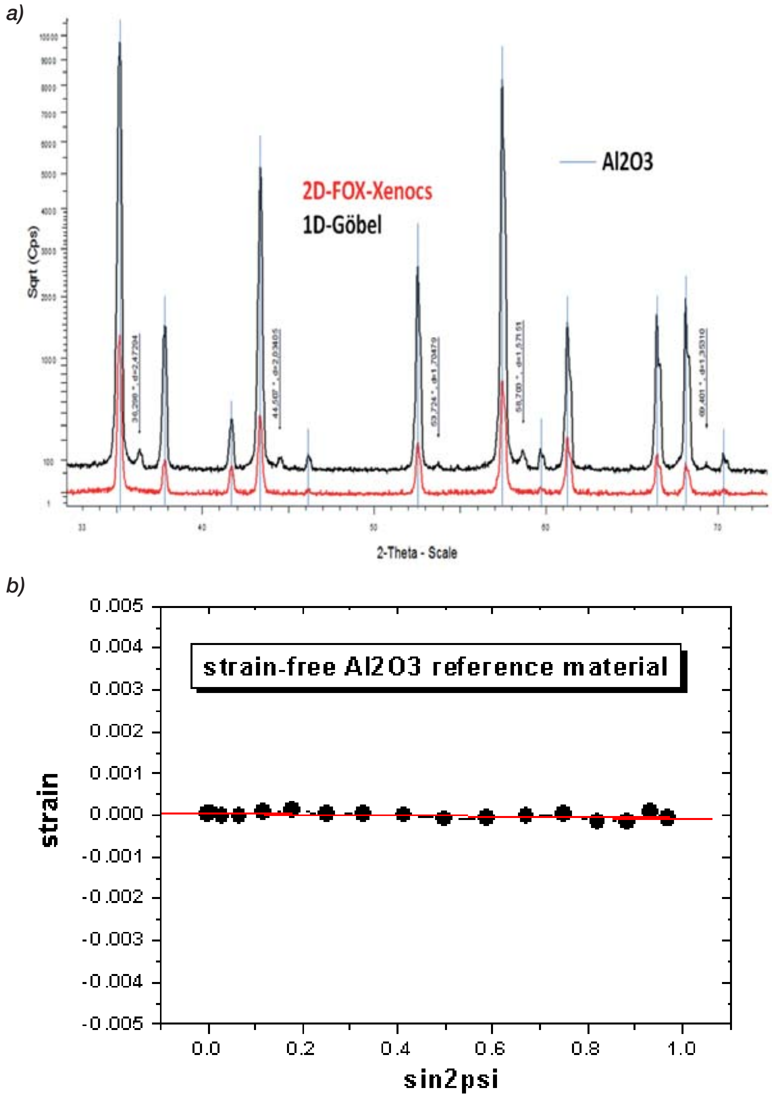

Fig. 6 a : X-ray diffraction patterns of α-Al_2O_3 measured with two different X-ray mirrors;
Fig. 6 b: $\sin^2\psi$-plot for the 104 diffraction line of α-Al_2O_3.

diffraction volume) of about -2.3 GPa which increased significantly by a factor of about 1.5 upon micro-blasting. Furthermore, as visible in the both sin²ψ-plots, the straight-line behavior deviates significantly for sin²ψ-values of 0.8-1. This sin²ψ- range is representative for the "very near-surface regions" (as upon specimen tilting the penetration depth of the X-ray decreases), i.e. deviations from the straight-line behavior within this sin²ψ- range are typically indicative for the presence of stress-depth gradients. However, in order to measure the stress as function of specimen depth (i.e. in order to perform diffraction stress-depth profiling), a state-of-the-art XRD setup is required which allows measuring accurately the diffraction signals at very small incidence angles (of the order of some degrees) neglecting the influence of instrumental aberrations which usually occur at such diffraction conditions (see section above). As already mentioned before, the stress-depth distributions were measured according to the diffraction strategy proposed by A. Kumar *et al.*, J. Appl. Crystallogr. 39, 633, 2006. The stress-depth profiles demonstrate very nicely that this experimental approach is very suitable for accurately tracking the change of mechanical stress at the near-surface regions of the coating (see Fig. 7 right).

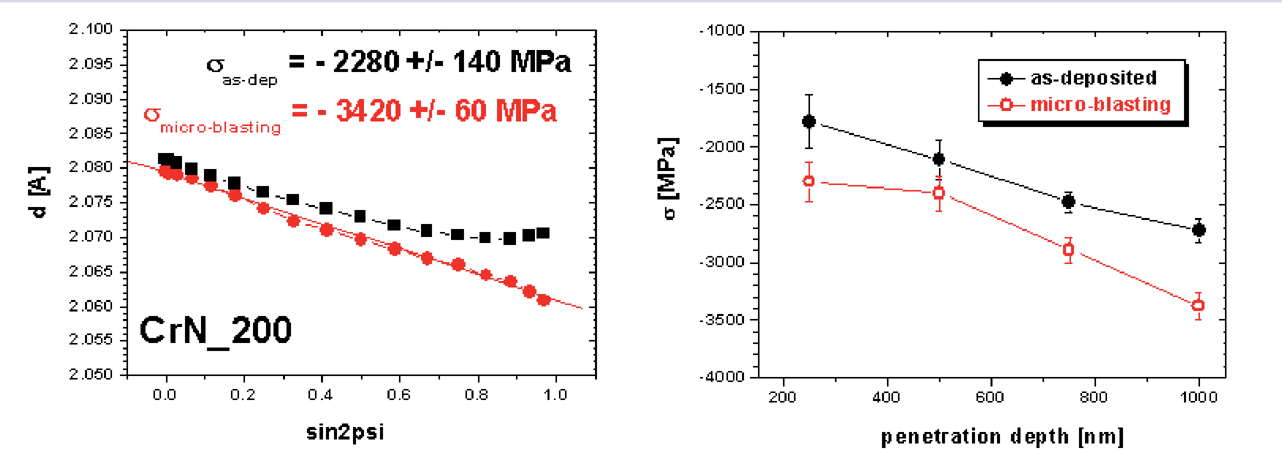

Fig. 7 : Residual stress measurements (without and with control of penetration depth) of the CrN coating in the as-depoisted state as well as after micro-blasting.
Left: Sin²ψ-plots of the 200 diffraction line of CrN;
Right: Stress-depth profiles obtained using the 200 diffraction line of CrN.

Conclusion

It has been shown in the present work that X-ray diffraction is a very powerful tool in order to measure the mechanical stress of modern, high-performance coatings. The combination of dedicated diffraction methods and a state-of-the-art XRD setup, as used in this work, enables to perform stress-depth profiling of the near-surface region of the coating. On this basis sound interrelations between coating stress and its performance can be drawn, i.e. residual stress engineering becomes possible.

About OC Oerlikon Balzers AG

OC Oerlikon Balzers AG is a highly innovative, leading global-player in the field of hard and wear-protective PVD coatings and other state-of-the-art surface technologies (see Fig. 2) (www.oerlikon.com/balzers). With almost 90 coating centers in more than 30 countries Oerlikon Balzers offers its customers the largest sales, service and after sales network in the industry.

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