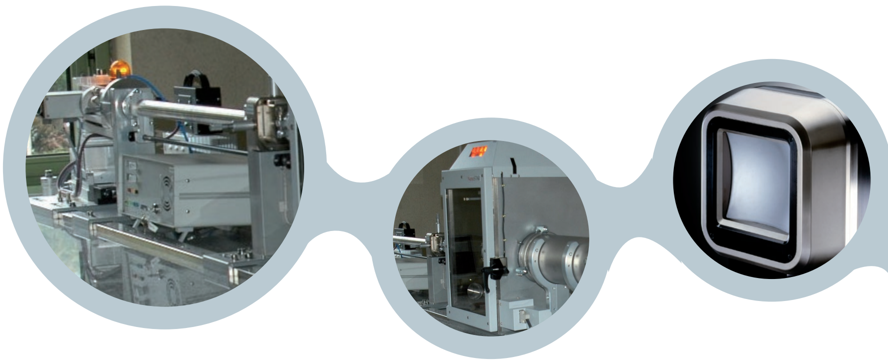

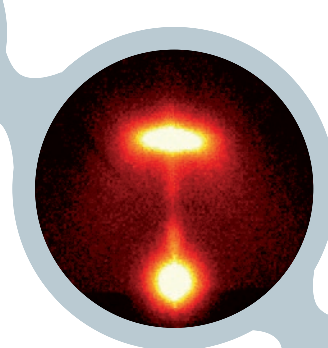

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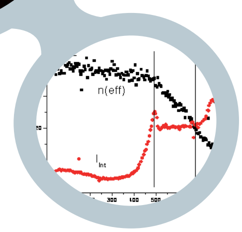
High Temperature in-situ GI-SAXS on W/C multilayer coatings in NANOSTAR



Principle of GI-SAXS and Goal

Grazing incidence small angle scattering (GI-SAXS) was introduced in 1987 [1] to probe the structural details of surface and near-surface regimes. Below the critical angle, the incident beam undergoes total external reflection and the scattering signal arises from structural arrangements of the first few Angstroem below the air-sample interface. Increasing the incident angle causes a gradual increase of the penetration depth of the incident beam. This in turn causes an increase of the scattering volume and thus the surface-sensitive scattering signal. If this incident angle becomes larger than the critical angle, then the penetration depth increases drastically. Finally, the bulk-sensitive scattering signal becomes dominant and the surface-sensitive signal disappears. The variation of incidence angle can therefore be used for non-destructive depth profiling. This physical phenomenon is also used for X-ray reflectivity (XRR) measurements, a technique widely used for the determination of roughness, periodicity and thickness of thin amorphous and crystalline layers perpendicular to the surface normal. In contrast to XRR, GI-SAXS measurements provide much more directly information about in-plane correlations and roughnesses, both important parameters for characterization of multilayer coatings [2].

The goal of the experiment was to investigate the thermal stability and decomposition process of nearly perfect X-Ray mirrors.

Experiment and Sample Material

The GI-SAXS investigations were executed using a NANOSTAR-U equipped with a micro-focus X-ray source (IμS, Incoatec GmbH, Geesthacht, Germany) and a 2-dimensional VÅNTEC-2000 detector (fig. 1). A high temperature heating chamber (DHS 900, Anton Paar, Graz, Austria) was implemented into the beam path. The measuring time was 10 s per frame and the heating rate was set to 30 °C/minute. The incidence angle was fixed to 0.6° just below the critical angle of total external reflection. A series of 172 frames was recorded while the sample temperature was increased from 40 °C up to 870 °C.

The samples under investigation were W/C multilayers. The coating was deposited on single crystalline Silicon wafers by Ar-plasma sputtering technology (Incoatec, Geesthacht, Germany). The period of multilayer stacking (thickness of W and C layer) was 1.375 nm and 80 individual layers were deposited.

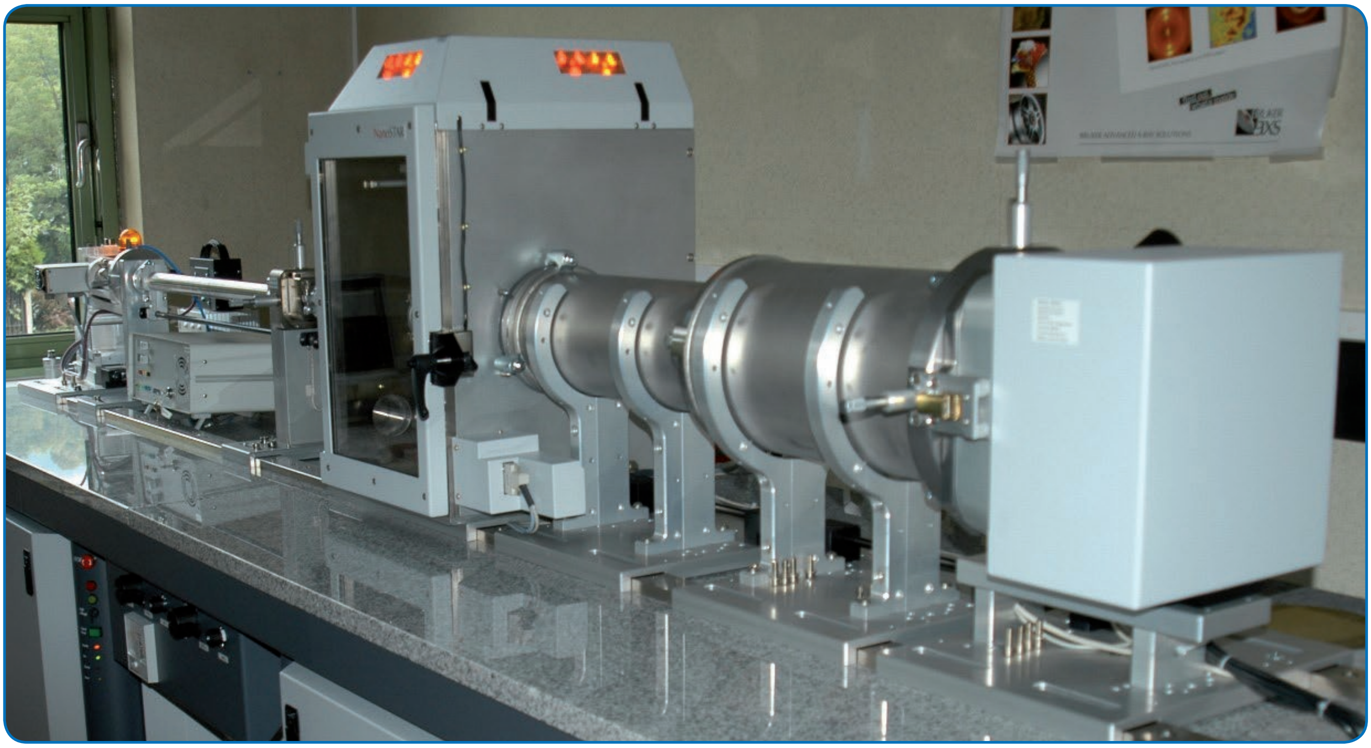


Figure 1: NANOSTAR-U with IμS (left), extended sample chamber with WAXS Image Plate detector (center), and a 20 x 20 cm^2 active area VÅNTEC-2000 (right).

Evaluation

The data reduction of the 2-D frames $I(q_y q_z)$ was performed in three different ways using SAXS NT software. The $I(q_{z1})$ scattering curves were calculated by arc-like integration of the $I(q_y q_z)$ patterns. An opening angle of 10° was used and $q_z=0$ was set at center of the detector where the direct beam was located. The $I(q_{z1})$ scattering curves were used to determine the multilayer period and the vertical correlation length. The $I(q_{z2})$ scattering curves, used for the determination of the integral intensities of uncorrelated scattering, were determined by integrating the $I(q_y q_z)$ patterns in arcs with an opening angle of 180° starting from the center position of primary reflected beam. $I(q_y)$ scattering curves were calculated by pixel-wise integration between $q_z = 0.63\ A^{-1}$ and $q_z = 0.42\ A^{-1}$. The $I(q_y)$ scattering curves were used to determine the lateral correlation length and the fractal dimension [3]. The fractal dimension is equal to the Hurst parameter [4].

The multilayer period and the vertical correlation length were determined by fitting the correlation peak with a pseudo-Voigt function, where the position represents the period and the width correlates to the size of the coherent scattering domains. The dimension of coherent domains was determined by applying the Scherrer formula on FWHM of the obtained peak. The FWHM was corrected for geometrical effects (large sample size), the beam divergence was not considered. From the multilayer period (d) and Scherrer size (S) the effective number of multilayer periods in coherent domains (n_{eff}) was derived by $n_{eff}=S/d$. The lateral correlation length was determined by using Guinier's approximation, the fractal dimension (D_{mass}) was determined by fitting q_y data at large q with an exponential function. The integral intensities, referred as I_{int}, were calculated by integrating the Lorenz corrected scattering curves between $q_{min} = 0.2\ nm^{-1}$ and $q_{max} = 1.8\ nm^{-1}$.

Results

The scattering pattern of an untreated mirror is dominated by the signal from primary reflected beam and the first main reflection of the multilayer (fig. 2). After the heat treatment, the main reflection peak basically disappears, while the intensity of the primary reflected beam and the diffuse scattering strongly increases.

The strong uncorrelated scattering signal indicates some roughening and the formation of clusters with uncorrelated distances.

Figure 3 shows results of a series of in-situ measurements while increasing the sample temperature. The effective number of layers in coherent domains - basically remain constant up to 490 °C. Above

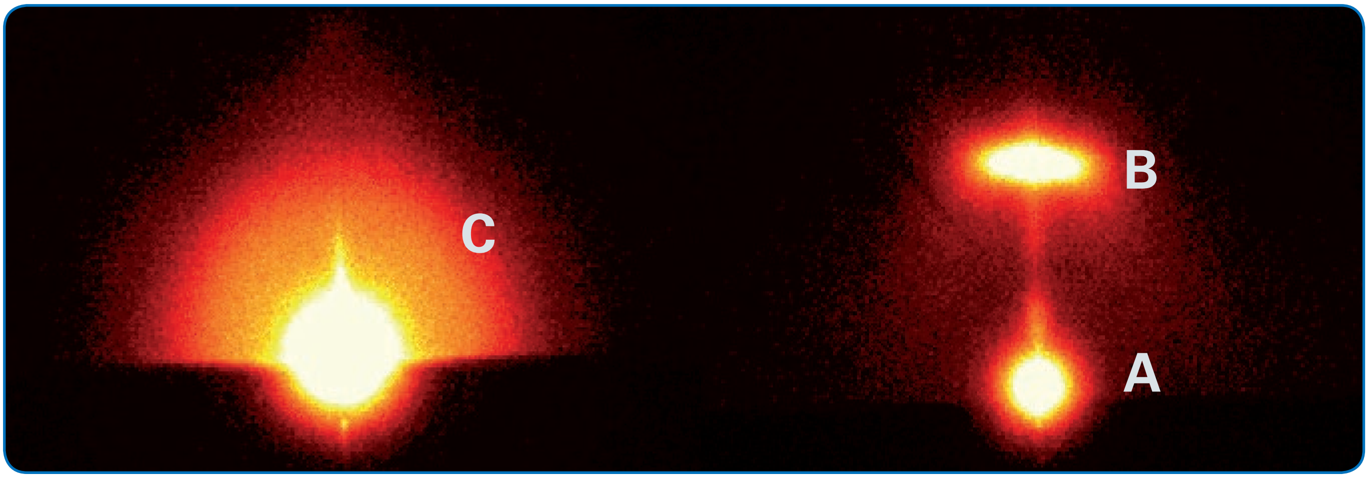


Figure 2: Scattering pattern of untreated mirror (right) and after heat treatment up to 900°C (left). A: reflected beam, B: main reflection of the multilayer, C: uncorrelated scatter (GI-SAXS signal).

this temperature, a linear decrease in n(eff) is observed. In parallel also the period of originally 1.375 nm slowly decreases with increasing temperature. Above 700°C the period rapidly drops down to 1.15 nm. Above 840°C the signal causes by the period of the multilayer disappears from GI-SAXS signal.

The uncorrelated scattering intensity around primary reflected beam (I_{int}) shows three main features: below 400 °C the scattering signal slightly decreases with increasing temperature. This can be referred to a slight loss of the signal from the pure reflection. Above 400 °C the GI-SAXS signal drastically increases with a maximum at 490 °C. This increase can be referred to a roughening of the top layers of the mirror. Above 490 °C the GI-SAXS intensity remains constant, while n_{eff} decreases which might by caused by a stimulated interdiffusion process. Above 680 °C, a steep increase of the GI-SAXS signal indicates the decomposition of multilayer structure. Finally the correlated signal from the period disappears.

The above described characteristic is clearly confirmed by the temperature dependence of the fractal dimensions and lateral correlation lengths (fig. 4). Up to 700 °C the vertical correlation length remains approximately constant at 8 nm. Above 700 °C it rapidly decreases with increasing temperatures down to 2 nm.

At the same temperature also the mass fractal dimension diminish from 1.8 down to 0.8. This change indicates a change in the shape of fractal structures from a plate-like to a filament-like.

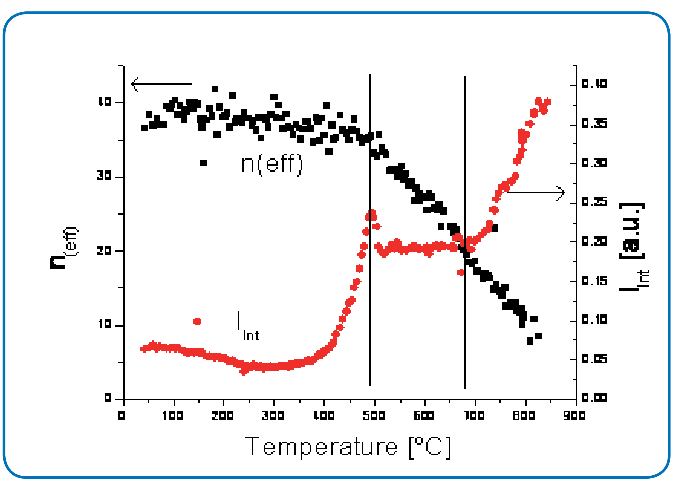


Figure 3: Effective number of layers in coherent domains (black dots, left y-scale) and integrated scattering SAXS signal (I_{int}) (red dots, right y-scale) plotted against temperature. The vertical lines indicate temperatures where main structural changes occur.

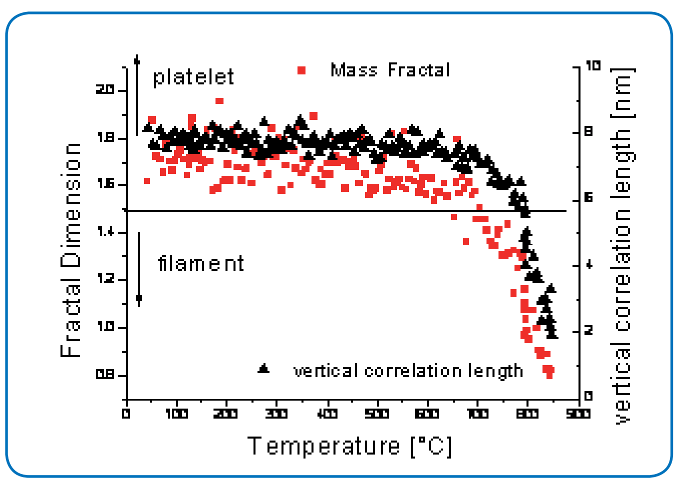


Figure 4: Fractal dimension and vertical correlation length plotted against temperature.

Conclusion

The thermal decomposition of a W/C multilayer coating with a period of 1.375 nm was studied using the NANOSTAR U. The initial step of the corrosion of the multilayer was the formation of surface roughness of the top layers. Above 490°C the lateral correlation lengths became shorter and so did the effective number of layers in the coherent domains. Above 690°C also vertical correlation lengths and fractal dimension changed dramatically which finally led to a complete loss of order in the multilayer.

The publication clearly shows that in-situ GI-SAXS investigations with good time resolutions and up to high temperatures are possible with the lab-based NANOSTAR-U Small Angle X-ray scattering system using a micro-focus X-ray source.

Acknowledgments: The work was performed in the framework of Comet-K2 program of FFG (Austrian Funding Agency) in cooperation with Bruker AXS (Karlsruhe, Germany). The authors thank Incoatec GmbH (Geesthacht, Germany) for supplying the samples. The authors thank Dr. Peter Siffalovic from Institute of Physics, Slovak Academy of Science (Bratislava, SK) and Prof. Jozef Keckes from University of Leoben for fruitful discussions and help during experiment.

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