ESRF	**Experiment title:** Competition between diffusion and precipitation of C and N in nitrided steels.	**Experiment number**: 02-01 809
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Report:

Nitriding of steels involves a complex microstructural gradient both in time and depth including diffusion of nitrogen and precipitation of nano-nitrides but also coarsening, dissolution and re-precipitation of carbides accompanied by transverse diffusion of carbon.

Despite of the large characterization of nitrided surface, the chemical composition of nano-scale precipitates remains controversial. On one hand, the determination of nitrogen-absorption isotherms coupled with specimen weight measurements concluded on the nature of alloying elements in nitrides MN (M : Cr, V…). On the other hand, transmission electron microscopy and tomographic atom probe analyses showed an iron substitution of alloying elements in nitrides (up to 30 at.%). These controversial results arise from the respective limitations of the techniques used.

The purpose of this experiment is to bring some new insight on the composition of the nano-scale phases at different time and temperature of nitriding, as well as different depths in order to explore the precipitation state under various conditions of carbon and nitrogen local compositions.

Small-angle X-ray scattering is a powerful technique for investigation of nanometric particles and provide statistical data. Moreover the use of the anomalous mode at the Cr-edge was expected to bring essential data on the composition of the nano-phases.

<u>Experimental method</u>

The first challenge of this experiment was the low energy of the Cr K-edge (5.96 keV) that requires the preparation of relatively thin samples around 30 µm in thickness to ensure a satisfactory transmission. The second challenge arose from the investigation of the whole thickness of the nitrided surfaces, which can reach 1mm, using a 25 µm step in depth. Such a step was used within the depth in order to collect accurate data especially where the chemical composition changes abruptly. Therefore in order to limit the number of samples, they were cut along a bevel so that all depths can be studied by a profile measurement along samples. A preparation procedure was so optimised and consisted in gently polishing 20 x 10 mm surfaces using a bevel of 3 to 7 degrees depending on the nitrided layer thickness. 500 µm steps were then used for profile measurement along samples that correspond to a 25 µm step within the depth of the nitrided layer.

A small-angle set-up was chosen to well characterise nano-precipitates in the 5-50 nm radius range, i.e. in a q-range going down to 0.003 $Å^{-1}$. Different energies around the Cr K-edge (5.96 keV) were used to carry out the anomalous investigation.

Two different samples were studied with the same composition (0.35 wt.% C, 1.0wt% Cr, Fe balance) and different nitriding conditions (10 or 100 h at 550 °C).

Results

Example of spectra measured at different energies around the Cr-edge (E < 5.959keV) at one position is displayed in Figure 1 in the Iq^2 versus q mode. It clearly shows the increase in the integrated intensity due to the anomalous effect (modification of the atomic scattering factor of Cr).

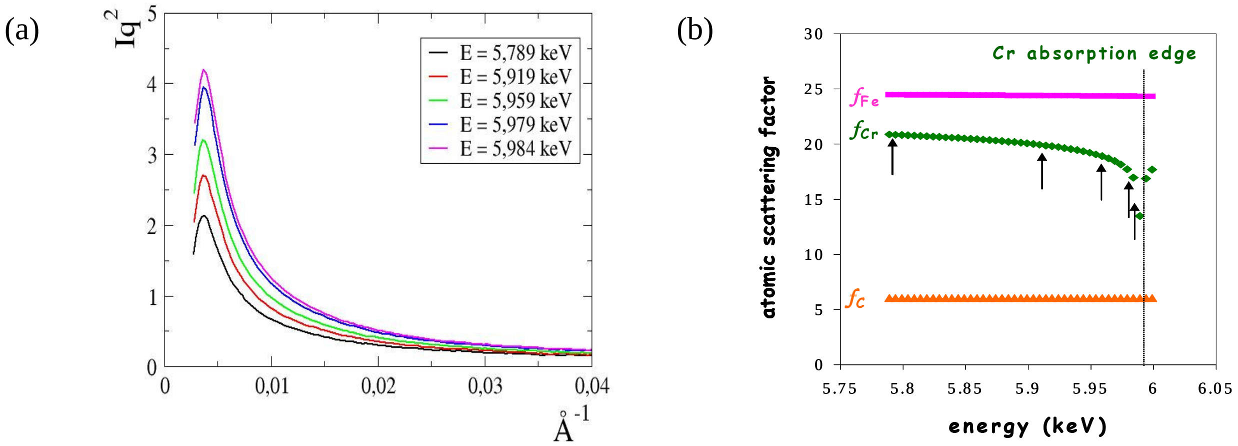

Figure 1: Evolution of the scattering effect at the Cr-edge vicinity. Iq^2 vs q. plot (a) showing the increase of the integrated intensity and evolution of the atomic scattering factors of Fe, Cr and C at the Cr-edge.

The evolution of the integrated intensity as a function of depth was evaluated and is displayed in figure 2 for the 10h@550°C nitrided sample. The figure clearly renders the three expected zones, i.e. the compound layer close to the surface, the diffusion layer caracterised by the precipitation of nitrides and the bulk material away from the surface. For each point, the Cr-content can then be determined by the exploitation of the anomalous effect. It can be shown that the square root of the integrated intensity is expected to evolve linearly with the atomic scattering factor of Cr, as $\sqrt{Q_0}) = p\ f_{Cr} + \theta$, where p and Θ can be related to the Cr-content in the precipitates :

$$\frac{\Theta}{p} = \frac{f_{Fe}\left[\frac{(1-X_{C/N}^{P}-X_{Cr}^{P})}{V_{at}^{P}} - \frac{1}{V_{at}^{Fe}}\right] + f_{C/N}\frac{X_{C/N}}{V_{at}^{P}}}{\frac{X_{Cr}^{P}}{V_{at}^{P}}}$$

Such mathematical treatment was carried out and the resulting Cr-content in the nitrides was determined and is displayed in Figure 2(b).

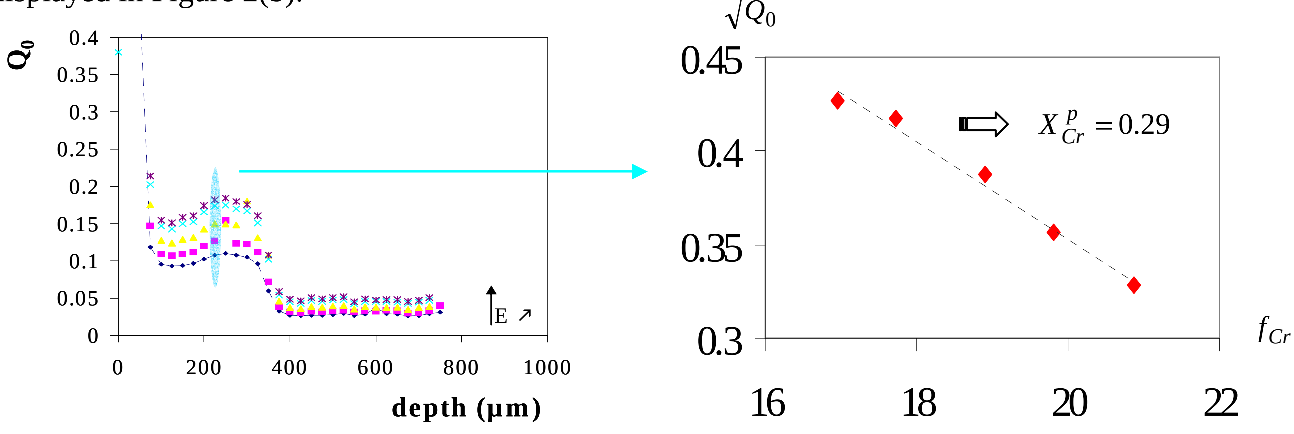

Figure 2: Evolution of the integrated intensity as a function of depth in the 10h@550°C sample (a) and linear treatment of the anomalous effect in order to extract the Cr composition (b).

Conclusions and acknowledgments:

In spite of technical challenges this experiment was a success, in particular regarding the anomalous measurements which are expected to give essential data on the chemical nature of nano-precipitates in the nitrided zone. We are grateful to the ESRF staff, especially on the BM02/D2AM beam line for giving us the opportunity to perform this challenging experiment and for their help during the experiment. Special acknowledgement is addressed to Dr. Frédéric De Geuser for his support before, during and after the experiment.