ESRF	**Experiment title:** Characterisation of nano-clusters in oxide dispersion strengthened alloys using anomalous SAXS	**Experiment number**: MA-700
Beamline: BM02	**Date of experiment**: from: 14th Feb. 2009 to: 17th Feb. 2009	**Date of report**: 23/10/09
Shifts: 9	**Local contact(s)**: Isabelle Morfin, Françoise Bley	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Myriam Dumont * (IM2NP, Université Paul Cézanne Aix-Marseille III, France)

Dr. Fabrice Legendre * (SRMP, CEA-Saclay)

Dr. Loreleï Commin * (AMPT, Chalons)

Dr. Marie-Vanessa Coulet (IM2NP, Université Paul Cézanne Aix-Marseille III, France)

Report:

Synchrotron radiation was used to study nano-oxides in ODS (oxide dispersion strengthened) steels using small angle X-ray scattering. The anomalous mode was used to investigate the chemistry of nano-clusters in early stages of processing of these materials. The processing route consists in high-energy milling of powders followed by thermal ageing. The resulting material is a powder with nano-meter sized grains (~50-100nm) inside which 1-2 nm Y-based oxides are uniformly distributed. However the nature of oxides remains unclear in particular in the presence of titanium. Only few experimental investigations are available concerning the nano-clusters and they are controversial about the chemical composition which may vary with size. On one side, recent tomographic atom probe analyses have shown that oxide dispersoids should be in form of nanoclusters containing yttrium, titanium and oxygen with a non-stoechiometric ratio [1]. On the other side, crystallised pyrochlore $Y_2Ti_2O_7$ phase has been identified by high-resolution TEM in a similar ODS alloy [2].

In this framework, the aim of this experiment is to bring some new insight on the composition of the dispersoids at different steps of the processing route, in particular in the as-milled condition and after annealing. 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 Y-edge was expected to bring essential data on the composition of the nano-clusters.

Experimental method

One challenge of this experiment was the powder nature of the material. In fact 30µm-thick samples have to be prepared to optimise the transmission of the sample and this, using a powder with aggregates around 10-50µm in size. A preparation procedure was optimised and consisted in putting down powder on a kapton adhesive film. The thickness was assessed using a gauge of Ni-Cr 20µm in thickness.
A small-angle set-up was chosen to well characterise nano-cavities in the 10-100 Å size range (in terms of Guinier radius), i.e. in a q-range varying from 0.02 to 0.6 $Å^{-1}$. Different energies around the Y K-edge (17.040 keV) were used to carry out the anomalous investigation.
Different kinds of samples were studied with different compositions (0.25wt% and 1wt% equivalent Y_2O_3, with or without Ti), and taken at different steps of the processing route (just after milling and after different annealing).

Results

- *General considerations*

Examples of SAXS signal measured for different samples are displayed on figure 1. It appears that all samples, including the matrix alone (without nano-oxides), scattered a lot in the range of small q-values ($q < 0.05$ Å^{-1}). This effect, due to the nanometric scale of the powder, was detrimental for the measurement of the scattering effect arising from the nano-oxides in the q-range $q > 0.05$ Å^{-1} since the acquisistion time was limited by the scattering from the powder and then the signal/noise ratio remains large for the interesting q-range, in particular for the as-milled samples containing a low volume fraction of nano-oxides.

In spite of this, the scattering signal from nano-oxides can be interpreted in terms of Guinier radius and volume fraction in the case of annealed samples after removal of the signal arising from the powder. Comparison of the samples allows us to study the effect of the composition and processing route on the evolution of the nano-oxide population.

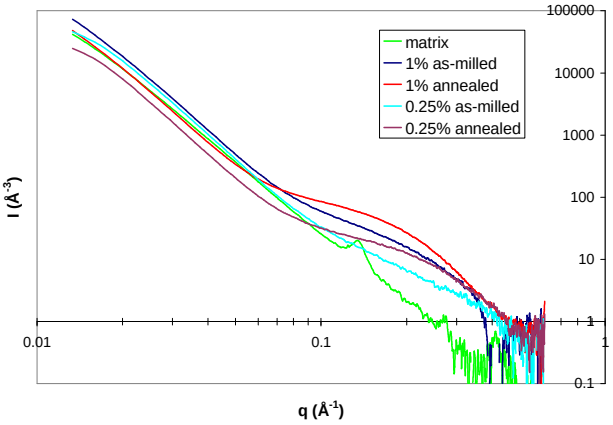

Figure 1: Scattering signal measured on different samples (matrix, 1% and 0.25% equivalent Y_2O_3) in the as-milled condition and after 5 minutes at 800°C annealing.

- *Anomalous measurements*

The results of anomalous measurements performed on a sample 1% equivalent Y_2O_3 around the K-edge of yttrium are displayed in figure 2 in the Iq^2 *versus* q plot.

One can observe that the signal arising from the nano-oxides (q-range > 0.05 Å^{-1}) is increasing with increasing the energy ($E < 17040$ eV). This effect has now to be interpreted in terms of Y-composition of the nano-oxides using the variation of the Y scattering factor around the K-edge.

Regarding the poor signal to noise ratio, this study is not expected to succeed in the case of the 0.25% equivalent Y_2O_3. Unfortunately most of the samples were prepared with this composition, in particular the interesting Ti-free samples.

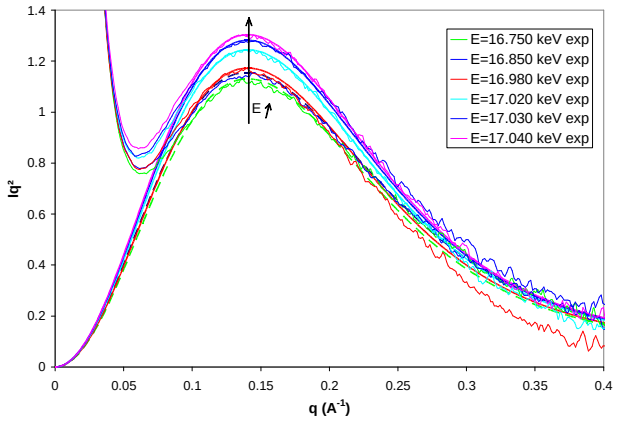

Figure 2: Anomalous SAXS response in the $Iq^2=f(q)$ plot for the different energies around the Y K-edge for the sample 1% equivalent Y_2O_3 annealed .

Conclusion and acknowledgements

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-oxides in early stages of the processing route. 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. Françoise Bley and Dr. I. Morfin for her support before, during and after the experiment.

References

[1] M.K. Miller, K.F. Russell, D.T. Hoelzer, Journal of Nuclear Materials, Vol. 351, 2006, pp. 261-268.

[2] M. Klimiankou, R. Lindau, A. Möslang, Journal of Nuclear Materials, Vol. 329-333, 2004, pp. 347-351.