	Experiment title: Strain relaxation through microcracking in zirconia polycrystals probed by *in situ* high temperature coupled Small Angle X-ray Scattering and X-ray diffraction experiments	**Experiment number**: MA-5547
Beamline: BM02	**Date of experiment**: nov. 29th to dec. 5th., 2022	**Date of report**: Nov. 2023
Shifts: 18	**Local contact(s)**: G. Chahine	*Received at ESRF:*

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Objective & expected results:

The aim of the experiment was to investigate the interplay between solid state phase transition (SPT), internal stress and crack network evolution during thermal loading of pure zirconia polycrystalline aggregates. SPT and strain relaxation by microcracking are two distinct phenomena that are strongly intricated in zirconia polycrystals [1, 2]. We have shown with our previous experiments at D2AM that while the tetragonal to monoclinic ($t \rightarrow m$) SPT occurs over a very large temperature range, ~1000°C, during cooling, it is very likely that a large amount of nanocracks appears in a narrow temperature range of about 50°C at the onset of the $t \rightarrow m$ transition [2]. With this experiment, we aimed to provide experimental proof of this strain relaxation by nanocracking. This experiment was carried out in the framework of the French-German (ANR-DFG) HoTMiX project (2 post-docs and 4 PhD students involved), which will end in 2024 and which focuses on the evolution of internal stresses in zirconia and aluminium titanate during thermal loading, both experimentally and through micromechanical modelling approaches. D. Fowan, PhD within HoTMiX, was involved in this experiment.

Results and conclusions of the study:

For this experiment, we used a setup allowing the simultaneous measurements of small angle x-ray scattering (SAXS) and x-ray diffraction (XRD) signals. The samples were irradiated in transmission mode by an incident monochromatic x-ray beam of 17.978 keV with a cross section of 60 × 70 microns. Two detectors were used simultaneously. The diffraction signal was recorded using the WOS detector installed at 0.17 m from the specimen, while the SAXS signal was recorded by the D5 detector positioned at 2.68 m from the specimen. It was necessary to put a thin Cu foil in front of the WOS detector to avoid pixel saturation.

Concerning sample heating, a new experimental configuration recently developed and commissioned at the BM02 beamline in collaboration with the ESRF Sample Environment Group, was used (figure 1). The setup is based on an induction heating coil for performing in situ scattering or diffraction experiments in a transmission geometry. It was made in a way to achieve high temperatures, to prevent heating the goniometer and the sample support and also allows a quick sample alignment as well as a complete 360° sample rotation around the vertical axis. Temperatures up to 1350 °C could be reached during this experiment. The sample temperature (difference between the set-point temperature of the furnace and the real specimen temperature) was calibrated prior this run by the ESRF group. Previous to the experiments, flat samples with a rectangular main face of 5 × 20 mm and a thickness of 0.1 mm were machined form large dense blocks of the material of interest. For the x-ray measurements, this samples were glued on top of a fine alumina rod. This new setup was perfectly adapted to our need.

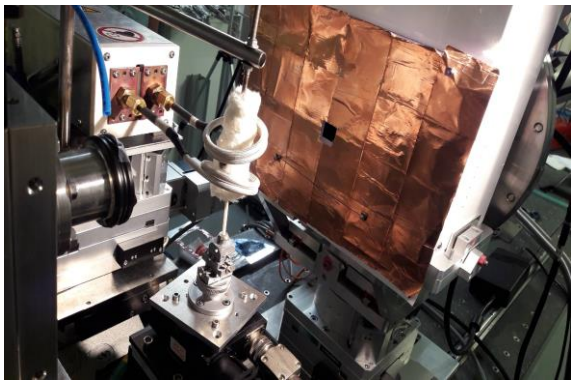

Fig. 1. View of the induction furnace and the WOS detector protected by a Cu foil.

The microcracking process that we mentioned above is related to at least two different phenomena. The first one is in zirconia related to the discrepancy between the ZrO_2 molecular volumes under the monoclinic and the tetragonal phases. In fact, this volume is typically 3.5 % higher under the monoclinic form [2, 3]. The second phenomenon to consider is the anisotropy of the thermal expansion. Due to the first point, it is well-known that microcracking occurs in zirconia polycrystals during cooling from the tetragonal to the monoclinic state. Consequently, in that case, we tried to evidence microcracking during the cooling process.

The relative amount of tetragonal and monoclinic zirconia was followed continuously during fast heating (20 deg./min) and slow cooling (1.5 deg./min). In some critical values of temperature, the recorded the whole 3D reciprocal space maps (RSM) around the 111 reciprocal space node (RLN) of the tetragonal phase. We have

already shown [4] that such measurement allows to follow carefully *in situ* the phase transition process. One of the 3D-RSM that we recorded, during the present experiment, by such a way is reported figure 2. In total, two zirconia samples could be measured. The second sample was subjected to four load cycles (from room temperature to 1350°C) to investigate the effects of cumulative nanocrack development during thermal cycling.

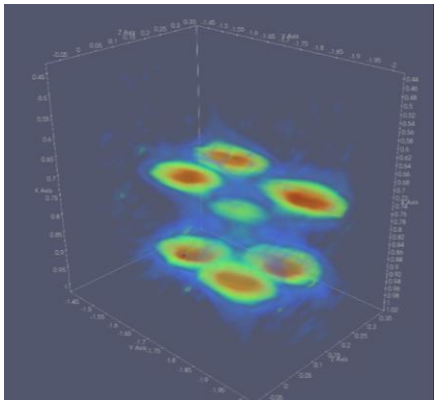

Fig. 2. A 3D-RSM around the 111_t RLN. The complete interpretation of such a map can be found in [4].

The tricky point of this experiment was to demonstrate on the one hand that microcracking can be observed by SAXS measurements and on the other hand that this microcracking process is triggered by the *t→m* SPT which can be followed quantitatively by XRD. The evidence for microcrack formation during the cooling process is illustrated in Figure 3. In Fig. 3a, the SAXS signal is plotted in the well-known Kratky plot where, after subtracting the background, the scattered intensity *I(q)* is multiplied by the square of the diffraction vector norm, q^2, and plotted as a function of *q*. A decrease in temperature induces a very clear increase in the scattered intensity. The simultaneous evolution of the amount of tetragonal zirconia is roughly evaluated by the evolution of the ratio of the $(111)_t$ and $(\bar{1}11)_m$ integrated diffracted intensities. We have plotted the evolution of both the appearance of the additional SAXS signal and the zirconia t→m SPT in Figure 3b. This plot seems to clearly demonstrate the coupling of these two processes. Quantitative analysis is underway.

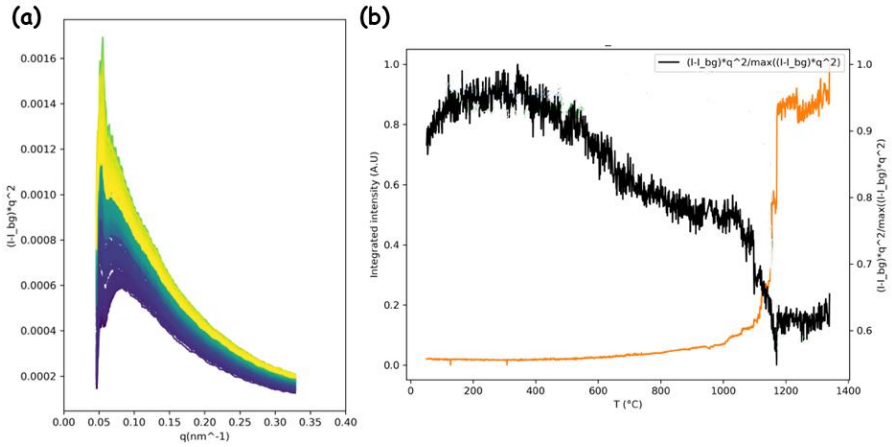

Fig. 3. Coupling of the increase of the SAXS signal and the zirconia t→m SPT during cooling. (a) Increase of the SAXS signal during the cooling process. The starting point at 1350 °C corresponds to the blue curve. (b) Combined evolutions of the amount of tetragonal zirconia (orange curve) and the normalized SAXS signal as a function of temperature during cooling.

Microcracking can also be promoted by thermal expansion anisotropy. Aluminium titanate (Al_2TiO_5), in its beta phase, exhibits a very strong thermal expansion anisotropy and the thermomechanical properties of polycrystalline materials made from this compound are strongly influenced by the presence of a complex microcrack network. In order to prepare possible future studies, a measurement was carried out on such a sample during a thermal cycle up to 1350 °C.

Justification and comment about use of beamtime:

Zirconia specimen #1 had already seen, prior this experiment, a heating up to 1300°C. It was therefore assumed that this specimen contained an already quite dense nanocrack network. On this specimen, we did only one thermal cycle, *i.e.* heating up to 1350 °C and cooling. Zirconia specimen #2 was a fresh one. On this specimen, we did 4 thermal cycles loading and we clearly observed variation of the SAXS signal during each cycle and between them. We spent the last day for preliminary investigation of an aluminium titanate specimen, which is another oxide for which the thermal dilation is extremely anisotropic at the crystal scale. Besides few minor problems with the furnace control, the experiment worked well. The D2AM beamline is very well-adapted to such SAXS - WAXS combined *in situ* high temperature measurements.

References

[1] T. Ors, F. Gouraud, V. Michel, M. Huger, N. Gey, J. S. Micha, O. Castelnau, R. Guinebretière “Huge local elastic strains in bulk nanostructured pure zirconia materials” Mater. Sci. Eng. A 806 (2021) 140817.

[2] R. Guinebretière, T. Ors, V. Michel, E. Thune, M. Huger, S. Arnaud, N. Blanc, N. Boudet, O. Castelnau “Coupling between elastic strains and phase transition in dense pure zirconia polycrystals” Phys. Rev. Mater. 6 (2022) 013602.

[3] M. Smirnov, A. Mirgorodsky, R. Guinebretière "Phenomenological theory of lattice dynamics and polymorphism of ZrO_2” Phys. Rev. B 68 (2003) 104106.

[4] R.R.P. Purushottam Raj Purohit, D.P. Fowan, E. Thune, S. Arnaud, G. Chahine, N. Blanc, O. Castelnau, R. Guinebretière “Phase transition and twinning in polycrystals probed by *in situ* high temperature 3D reciprocal space mapping” Appl. Phys. Lett. 121 (2022) 181901.