ESRF	**Experiment title:** Microcracking and strain relaxation in bulk pure zirconia polycrystals probed by *in situ* high temperature Laue microdiffraction	**Experiment number**: MA-4959
Beamline: BM32	**Date of experiment**: from: 26 Jan. 2022 to: 2 Feb. 2022	**Date of report**:
Shifts: 18	**Local contact(s)**: J.S. Micha	*Received at ESRF:*

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Objective & expected results:

Pure-zirconia under atmospheric pressure solidifies into a cubic structure (c, $Fm\bar{3}m$) at about 2700 °C, transforms to tetragonal (t, $P4_2/nmc$) upon cooling to 2300 °C and becomes monoclinic (m, $P2_1/c$) at 1170 °C [1]. The solid-state phase transition (SPT) between the *t* and *m* phases induces a large volume expansion that creates huge internal stresses, which promote the development of a huge stresses state and the formation of microcracks. The understanding of the coupling of this phase transition and strain relaxation process is a key point for the development of zirconia based polycrystalline materials exhibiting enhanced thermomechanical properties [2]. We have shown previously that Laue microdiffraction is a very efficient approach for the measurement of the local strain state that can be mapped on polycrystalline samples with a sub-micrometric step [3, 4]. Moreover, associating to this experimental approach a very fast Laue patterns indexing process based on neuronal network [5] allows in principle to follow the evolution of the strain state *in situ* during any external constraints (temperature, tensile or compressive strain etc.). The aim of the present proposal was to follow in situ the evolution of the strain state in a pure zirconia polycrystal at high temperature during the t→m SPT. The phase transition starts around one thousand degrees C, we thus have to record Laue microdiffraction patterns at such high temperature. As far as we know such experiment has never been done previously at the qualitative nor quantitative level. Beside the scientific interest concerning the zirconia polycrystalline materials behavior, a key point was thus to be able both to measure and to calibrate Laue microdiffraction patterns on a polycrystalline sample *in situ* at temperature higher than 1000°C.

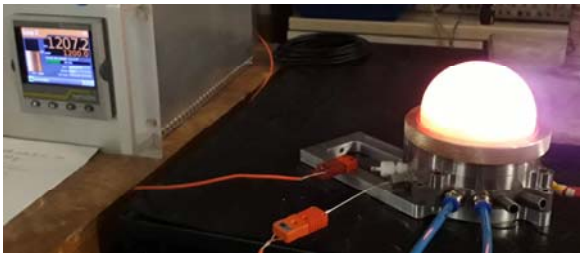

Fig. 1. The QMAX-V2 furnace at 1200 °C well suited for Laue microdiffraction experiments.

Results and conclusions of the study:

The *in situ* thermal loading has been performed using the QMAX furnace [6] specially designed for scattering and diffraction at synchrotron beamlines up to 1700 °C. The first version of this furnace was developed for the BM02 beamline and its use for Laue microdiffraction measurements needed technical modifications allowing to reduce its global size (see Fig. 1). This was done thanks to a strong implication of the engineering BM02 staff (S. Arnaud) and technicians from the SERAS service in Grenoble.

During Laue microdiffraction experiments, the *Q*-space calibration require a very accurate estimation of the sample to detector distance. The classical method is to record the diffraction pattern of a well-known single crystal and to calibrate this distance with respect to the position of the diffraction nodes of this crystal onto the detector. However, the use of this method requires that the position of the probed volume along the normal to the diffracting sample surface be exactly the same for the studied sample and the single crystal used for the calibration. This is usually done by putting the


Fig. 2. Laue microdiffraction pattern of a sapphire single crystal recorded at 1200 °C. Many of the small diffraction spots spread on the diffraction image are due to the beryllium done

sample and the calibration crystal in the focal plane of a high quality optical microscope. Temperature confinement above the sample however requires the use of a beryllium or PEKK dome and thus this procedure cannot be used. We have solved this experimental bottleneck using the sapphire thermal expansion along both the $\vec{c}$ and $\vec{a}$ sapphire cell vectors and a specific process that iteratively minimizes the errors associated with strains thereby identifying the actual temperature on the saphire, as well as calibrating properly the detector geometry. Accordingly, a flat piece of sapphire cut parallel to the (006) planes and roughly free of strain was located very near to the studied Region Of Interest and Laue microdiffraction pattern of this calibration sample was recorded at each temperature (see Fig. 2).

After selection of interesting polycrystalline zirconia sample parts, we were able to record the diffraction patterns on square areas of few tens of microns wide with a sub-micrometric step size. We report on Figure 3 two typical Laue patterns recorded at room temperature and at 1250 °C on the same area. It is important to note that all the monoclinic or tetragonal diffracting crystals are coming from only one parent cubic crystal (see [2] and [7] for more information on this specific feature). The pattern recorded at room temperature and reported Fig. 3a exhibits a very large number of diffraction spots but they are corresponding to the diffraction of a number of monoclinic nanosized zirconia crystals exhibiting similar orientation and we were able to indexed such pattern. Comparison between Fig. 3a and 3b clearly evidences the phase transition. At 1250 °C zirconia is under its tetragonal form. As far as we know such image is the first Laue microdiffraction pattern obtained on a polycrystalline sample at such a high temperature. Indexing such pattern allows to plot the local fluctuation of the tetragonal zirconia cell parameters with a sub-micrometric lateral resolution. Such a map is reported Fig. 4 for the *c* cell parameter. Very few data on the values of the cell parameters of tetragonal zirconia crystals free of any stresses are available in the literature. The most cited paper [7] give a *c* value of 5.27 Å at 1250 °C. It roughly corresponds to the mean value of the measurement reported Fig. 4. The maximal relative variation around this mean value is close to 1% and this corresponds to huge strain values.

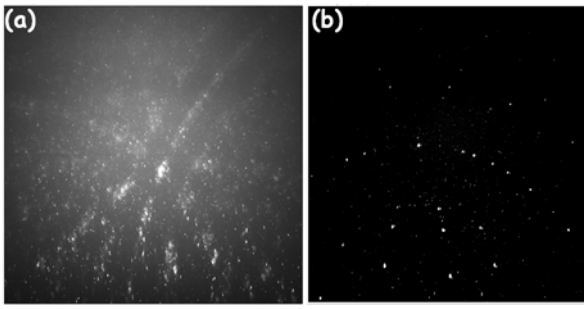

Fig. 3. Phase transition observed in situ in a zirconia polycrystal. (a) a diffraction pattern recorded at room temperature, zirconia crystals are monoclinic. (b) a diffraction pattern recorded at 1250 °C, zirconia diffracting crystals are tetragonal.

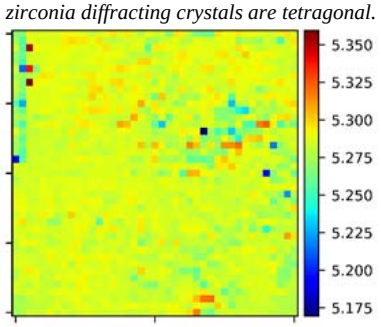

Fig. 4. Map of the local variations of the tetragonal zirconia c cell parameter recorded at 1200 °C. The size of the probed area was equal to 20 X 20 µm with a step size of 0.5 µm.

We have collected a large number of such maps as a function of the temperature with a temperature step as small as 10° in the interesting temperature range. After full data reduction, we will be able to follow the local strain relaxation process through the t→m SPT.

Justification and comment about use of beamtime

The Laue microdiffraction set-up implemented at the BM32 beamline is very well suited for such measurements. This experiment was the first one realized at such a high temperature. A significant part of the beamtime was used to elaborate an efficient reciprocal space calibration process associated to an accurate evaluation of the actual sample temperature. Moreover, we were able to record the evolution of the strain maps across the zirconia t→m phase transition. Overall, it is a great success and we already start, two weeks after the end of the experiment, to write a paper.

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