	Experiment title: In-situ XRD quantitative analysis of phase and stresses amounts at high-temperature into pure-zirconia	**Experiment number**: 02-02-829
Beamline: BM02	**Date of experiment**: 2015, Sept. 3 - 2015, Sept. 8	**Date of report**: 15, Sept. 2015
Shifts: 15	**Local contact(s)**: Nils Blanc	*Received at ESRF:*

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Report:

Aim

The studied samples were part of large zirconia blocks elaborated through a specific fused cast process developed by the St Gobain company in order to manufacture large bricks (sub-meter scale) used as refractory components in industrial furnaces devoted to the production of glass. During the cooling process, after solidification at high temperature (2700 °C) zirconia is cubic (Fm$\bar{3}$m space group). Under normal pressure, a cubic–tetragonal transition occurs at lower temperature (2300 °C). The tetragonal phase (P4$_2$/nmc) transforms into the monoclinic one (P2$_1$/c) at 1150 °C. This last structural phase transition (SPT) is accompanied by a spontaneous large volume increase inducing large stresses. A large part of the microstructural characteristics and thermomechanical properties of the material is due to these successive SPTs and the related stress states. The aim of this experiment was to determine through in-situ high-temperature XRD measurements the coupling between the monoclinic-tetragonal (SPT) and the strain state into pure zirconia crystals. From the experimental point of view, the main idea was to follow the evolution of both the cell parameters into the monoclinic and tetragonal phases and the relative amount of these phases crossing the M$\rightarrow$T and then T$\rightarrow$M SPTs. The experiments were conducted using the new prototype furnace developed in the frame of the QMAX research program (ANR-09-NANO-031-01) and available at the BM02 beamline. The XRD patterns were collected at 17.9 keV (just before the zirconium absorption edge) using the XPad 3.1 detector allowing a direct 2D collection of the Debye-Scherer rings.

Experiment

A typical illustration of the diffraction signal that we were able to collect is reported fig.1. At room temperature, Debye-Scherrer rings are clearly spotty and some high intensity spots are observed at specific part of the rings. One interesting point that we have to interpret is the fact that at high temperature the rings due to the tetragonal phase are roughly continuous.

Before the measurement, at room temperature the samples are made of a huge number of monoclinic crystals (or domains) which are produced by the two successive SPTs. We have shown previously [1] that the initial cubic crystals appearing after the solidification during the elaboration process are very large (typically in the range of several hundred micrometers). Moreover it seems clear that at such very high temperature the thermal gradient is inducing textural effect of these

Fig.1. XRD images collected at 17.9 keV on bulk sample.
(a) as elaborated sample at 20°C ; (b) at 1500°C ; (c) after cooling at 20°C.

cubic crystals [2]. In XRD experiments on polycrystalline material, the use of 2D detector is associated to parallel geometry. In such geometry the width of the diffraction lines is directly related to the imprint of the X-ray beam onto the sample. The size of the beam must thus be as low as possible. In our case, we estimate that the primary beam irradiated an area of the sample corresponding to very few, maybe one, initial cubic crystal. This might explain why spotty rings are observed.
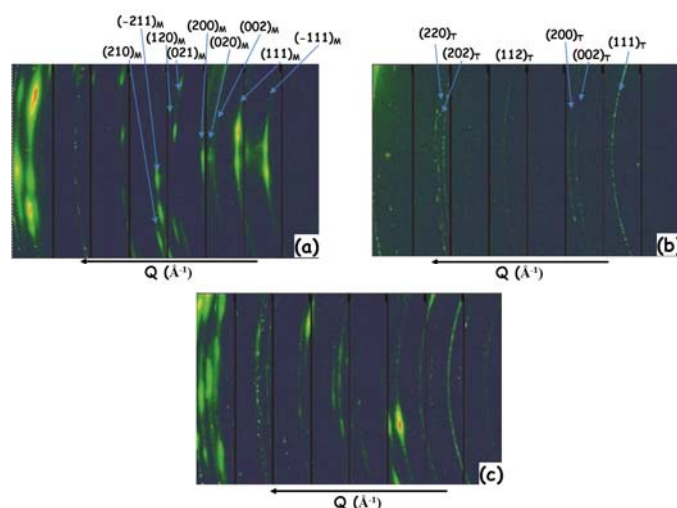
As a consequence of this observation, accurate determination of the relative amount of monoclinic and tetragonal phases require full texture measurements which are in principle feasible on the beamline, even at high temperature, but were out of the scope of this experiment. Qualitative determination of the M/T ratio with respect to the temperature will nevertheless be accessible.

(1) Determination of the used temperatures

One of the tricky points on high temperature measurements is the determination of the true values of the temperatures. The actual interesting temperature is of course not that one of the resistor or the expected one with respect to the applied electrical power but the one of the sample. The thermal behavior of the resistor and sample couple is strongly depending on the thermal properties of the sample. We thus decided to first determine the temperature of a powder put onto the sample holder. For that purpose, we followed the evolution of the cell parameters of the α-alumina NIST standard sample and evaluate the true temperature by using the thermal expansion of alumina which is given in the literature [3]. Results are illustrated in fig.2. One can see that we were able to realize experiments on powder at temperature as high as 1600°C. During the following experiments, we introduced alumina powder into our powdered samples and in the case of bulk samples we have put a thin layer of alumina powder on the top of the surface of these samples.
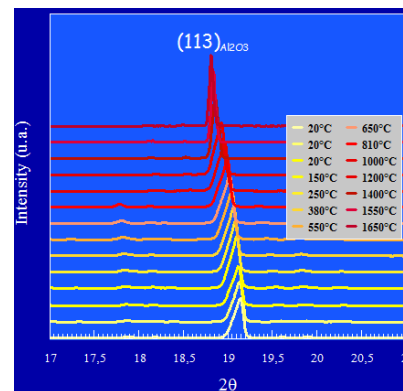
(2) Cell parameters and strains

Because experiments have been realized only one week ago (3-7 Sept. 2015), we are not yet able to propose quantitative analysis of the results concerning the zirconia samples. Nevertheless, preliminary fittings of the diffraction patterns obtained by radial integration of recorded images reveal important behaviors. As already quoted in the literature, the thermal expansion of monoclinic pure zirconia crystals is clearly anisotropic. With increasing temperature, enlargement of the a and c cell parameters is observed whereas the b cell parameter is quasi-constant. After cooling back to the room temperature, the cell parameters of bulk samples are significantly higher than those determined prior to the thermal treatment. This behavior is clearly the signature of a discrepancy of the stress states of the samples after and before the thermal treatment. One particularly interesting point is that this behavior is not observed for powdered samples.
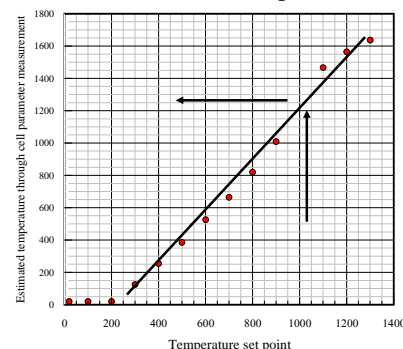
Because of the texture, for some (hkl) planes, the diffracted intensity is located only on a same part of the corresponding Debye-Scherrer ring. We have reported fig.3a a part of the reciprocal space corresponding to a part of the (-111) and (111) rings. On each of these rings, two main spots are observed, they are corresponding to the contribution of two monoclinic variants due to twinning process. The four observed spots are forming a cross in the center of which a less intense spot corresponding to the position of the (111) tetragonal node is observed. A clear diffuse scattering

(a) Evolution of the position of the (113) diffraction line of NIST 674a alumina powder as a function of the temperature.

(b) relationship between temperature set point and the actual temperature of powdered samples
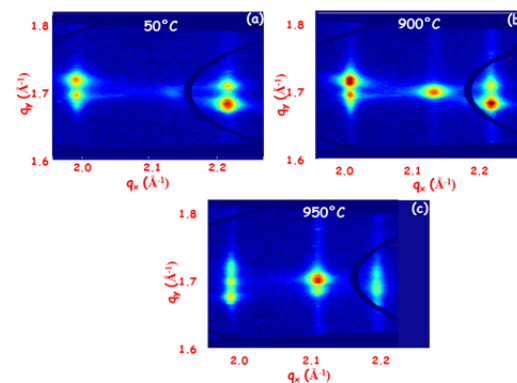
Fig. 2. Temperature calibration through XRD on a standard powder

Fig.3. Observation of diffuse scattering around the 111 nodes.

contribution is observed joining all those diffraction spots. Diffuse scattering around zirconia reciprocal space nodes has been largely discussed in the literature (see for example [4]), nevertheless the zirconia under consideration was doped-zirconia and the diffuse scattering signal was due to ion or vacancy ordering. In our case, pure zirconia is of concern. Thus this diffuse scattering can only be due to strain distribution into the monoclinic zirconia crystals. Increasing the temperature (see fig.3b and 3c), we observed simultaneously the increase of the intensity of tetragonal (111) node and a decrease of the diffuse scattering signal. This behavior is the signature of the coupling between stress relaxation and M➔T SPT.

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