

High-temperature 3D-RSM, phase transition and stress relaxation in pure zirconia

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It is well-known that the temperatures of structural phase transitions (SPTs) observed in actual polycrystalline materials are usually very different from that defined in stress-free, perfect infinite crystals. Bulk materials subjected to martensitic transformations are typical illustrations of such a fact. Zirconia is certainly the most famous case of an oxide material subjected to a martensitic transformation. Without any external pressure or stress, pure zirconia crystallizes at about 2700 °C in cubic crystal structure (c-ZrO₂, Fm $\bar{3}$ m space group), it transforms to tetragonal (t-ZrO₂, P4₂/nmc) at 2300 °C and finally it becomes monoclinic (m-ZrO₂, P2₁/c space group) at 1170 °C (see for example [1]). This last SPT is a first order one and exhibits a martensitic behavior. Moreover, it induces a large volume expansion which, in absence of any stress, is typically close to 4.5%. This specific behavior is at the origin of the well-known toughening effect observed in zirconia based materials [2].

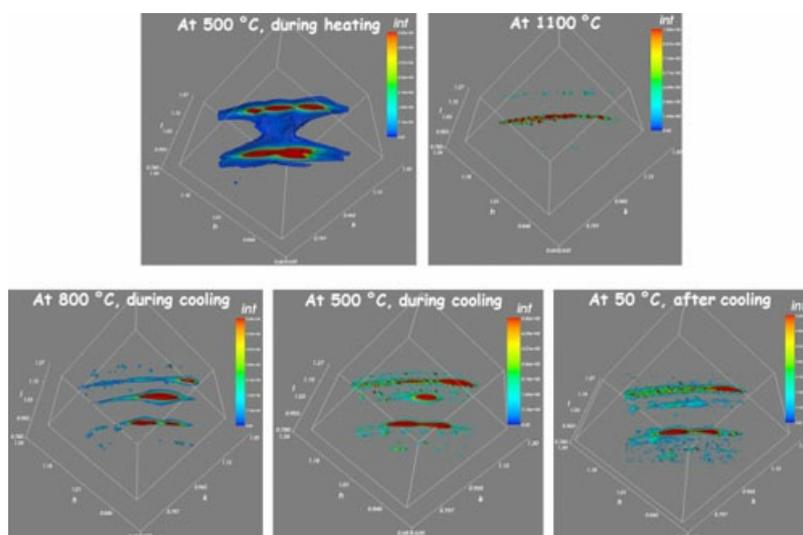
The manufacturing of large refractory zirconia based blocks through fuse-casting results in the formation of large pure zirconia cubic crystals embedded in a glassy phase. After cooling down, these submillimeter crystals are transformed into large number of pure zirconia monoclinic sub-micrometer crystals exhibiting crystallographic relationships inherited from the SPTs [3]. The initial cubic crystals are mechanically quasi-independent from each other since they are fully embedded in the glassy phase. Because of the phase transition process and the associated volume variation, large internal stresses are created within the monoclinic crystals.

Stresses induce large elastic strains which result in large distributions of d-spacing. Very recently we have evidenced the existence of this d-spacing distribution through 3D reciprocal space mapping (3D-RSM) around the 111 diffraction nodes. At room temperature, large amount of diffuse scattering is present and this signal is spread continuously from the -111m to the 111m node crossing the 111t node. Because the crystals are made of pure zirconia, the diffuse scattering signal can only be attributed to atomic displacement field. We thus follow the phase transition process through in-situ high temperature 3D-RSM up to more than 1200 °C i.e. in a temperature range where the stable phase is the tetragonal one. The experiments have been realized using a new prototype furnace developed in the framework of a joint research program associating the BM02 beamline at the ESRF. At each considered temperature, two hundred 2D reciprocal space maps were recorded in roughly one hour using a 2D pixel detector. The 3D maps are then reconstructed using a specific python routine developed at the beamline. We very clearly observe the disappearance of the diffuse scattering signal during heating (mt SPT), this behavior being associated to stress relaxation. Moreover, this signal does not reappear after cooling! Indeed, the tm SPT, which induces large volume increase, is mainly associated with microcracking as also evidenced by acoustic emission during complementary experiments. To our knowledge, this experiment is the first direct in situ observation of the coupling between stress relaxation and phase transition in pure zirconia crystals.

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