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Solidification structure in pure zirconia liquid molten phase

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Abstract

Up to now few studies concerning the crystallographic features of zirconia materials (HZ) used as refractory material have been performed. The elaboration process through raw material fusion followed by a controlled cooling step lead to a material containing 94 wt.% of dendritic monoclinic zirconia. During cooling, ZrO_2 passes through three different structural phase transitions (SPTs), inducing formation of a complex microstructure made of different crystallographic domains called variants. This study focus on formation of these different monoclinic variants in a non-doped zirconia based material and the possibility to reconstruct initial cubic parent crystals formed at high temperature using optical microscopy and Electron Back Scattering Diffraction (EBSD). EBSD experiments allow to identify 24 monoclinic variants issued from tetragonal parent crystal and to highlight the contours of the parent cubic crystal. Then, the microstructure appearing during the first steps of the solidification of the material can be evidenced.

Keywords: Monoclinic zirconia; Crystallographic variants; Solidification; EBSD; Optical microscopy

1. Introduction

Ceramic bulk materials are usually synthesized through sintering processes performed at temperature high enough to promote significant atomic diffusion associated with grains bridging and a subsequent reduction of the global porosity. Important contributions have been published on the relationships between this process and the resulting microstructure (see for example, Ref. 1). Beside this general situation, the fused cast ceramics are representative of a specific class of ceramic materials which is much less often encountered. High performance refractory materials based on zirconia in the building of continuous ovens are probably the most known example of those ceramics.[2,3]

The melting process differs from a classical sintering process inasmuch as it allows to obtain, at room temperature, a 3D microstructure constituted of monoclinic grains within larger dendritic zone surrounded by an amorphous phase. Indeed, because of the nature of the raw materials, silicate phases are the most important secondary phases (typically 6 wt.%). Thus the final microstructure results from a phase separation process which can be more or less described in the metastable pseudo-binary zirconia–silica phase diagram.[4,5] Thus, after fusion, during the cooling process, cubic zirconia dendrites start first to appear at around 2400 °C into the liquid phase. Then, at around 2300 °C, ZrO_2 transforms from cubic to tetragonal structure and due to the discrepancy of the $\vec{a}$ and $\vec{c}$ tetragonal cell parameters this phase transition is accompanied by the formation of orthogonal domains. The liquid phase surrounding zirconia grains is considered to be solidified at about 1700 °C. Finally, close to 1000 °C, the tetragonal zirconia transforms into a

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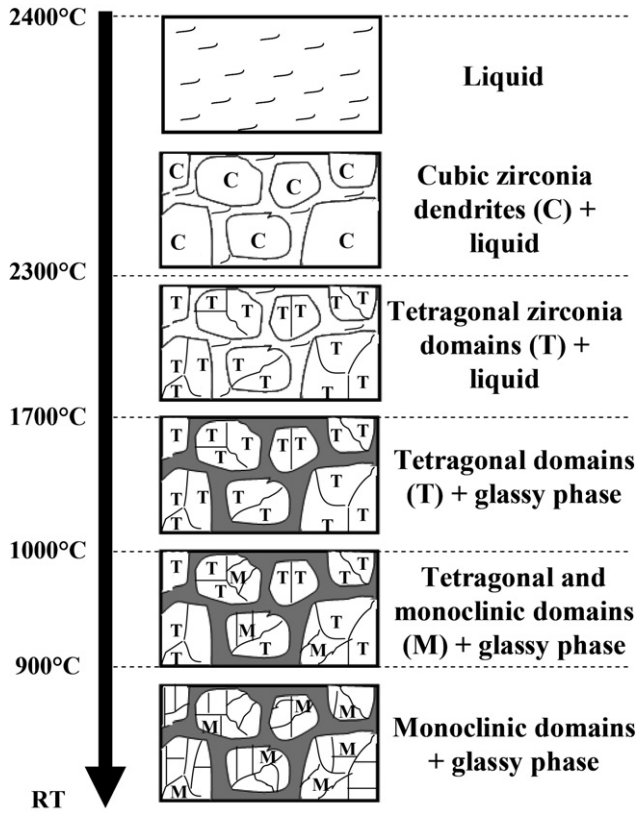

Fig. 1. Schematic representation of the microstructure of zirconia high containing refractory materials.

monoclinic structure and each tetragonal domain is transformed into different monoclinic sub-domains.[6–8] In fact, both cubic to tetragonal and tetragonal to monoclinic structural phase transitions (SPTs) lead to the formation of crystallographic variants. Moreover, it has been shown that, due to the homogenous character of the nucleation of these phase transitions, very small nanosized coherent domains are often observed and the resulting microstructure is typically a multi-scale herringbone tangle.[9] A schematic representation of the influence of the successive SPTs on the microstructure is reported in Fig. 1. Studying the same material, we have recently shown that, using Electron Back Scattering Diffraction (EBSD), it is possible to fully determine the relationships between the crystallographic orientations of monoclinic domains and the crystallographic axes of the initial cubic crystal they are inherited from.[10] A similar approach has been published, around the same time, by other authors[11] who have evidenced by micro-Raman measurements the complete relative orientation of domains in a monoclinic zirconia single-crystal. Moreover those resulting orientations are influenced by the external stress field. The next advance would be to take into account the SPTs to describe the observed hierarchical microstructure.

For decades, optical microscopy was used by mineralogists to determine the orientations of birefringent crystals. The orientation of a single crystal is deduced from the extinctions of polarized light beam though a polarized optical analyser for different angular settings of the sample[12] and a complete automated apparatus for mapping the orientations of grains in thin samples has been designed.[13] Besides, the EBSD technique is based on the automated acquisition and indexing of Electron Back Scattering Diffraction patterns in a Scanning Electron Microscope (SEM).[14] This technique was widely applied to characterize the microtexture of metallic material. However few works have been performed on ceramics and particularly on zirconia.

This paper aims to show how the optical microscopy observations and EBSD investigations are able to evidence the parts of the material formed of monoclinic domains, inherited all from the same initial cubic crystal. As far as we know, such an approach has never been successfully used to describe the microstructure of ceramic materials. Moreover, because of similarities in the elaboration processes, some comparisons with the microstructure of metallic alloys[15] are proposed.

2. Experimental

2.1. Material and crystallographic features

A new composition of zirconia rich refractory material, developed in the framework of a French National Research Program (NOREV) associating a refractory supplier, was investigated. To obtain this refractory, raw materials are melted at around 2500 °C, put into a mould and then cooled respecting a very controlled route to limit thermo-mechanical stresses. The cooling rate can be as low as 0.4 °C/min in critical temperature range. The control of this last step is always critical because the tetragonal to monoclinic transition occurring at about 1000 °C is associated with a large volume expansion (4%), which can threaten the integrity of the material. The observed sample was extracted from a large entity (500 mm × 200 mm × 600 mm) located at 30 mm from the surface and the normal direction to the observation plane always corresponds to the direction of the main thermal gradient in the considered slice of the initial wedge.

As said above, under normal pressure, three zirconia phases are observed as a function of the temperature. The C → T → M SPTs sequence corresponds to the successive $Fm\bar{3}m \rightarrow P4_2/nmc \rightarrow P2_1/c$ space group changes. Although those transitions have been, since the 'sixties', the subject of numerous studies,[16–19] the transition paths are not yet well established. One of the reasons is the lack of clear groups ⇔ subgroups relationships[e] and thus the space group changes cannot be described by a clear general crystallographic scheme as, for example, that established for perovskite structures.[20] Taking into account this observation, the microstructure developed through the successive SPTs is made of interwoven domains, the crystallographic orientation of which cannot be a priori formally described. Therefore, the microstructure is only explained from the experimental point of view.

Because of the volume expansion associated with the tetragonal to monoclinic SPT and the high temperatures under consideration, few studies concerning experimental observations of the microstructure of pure zirconia have been published.

[e] Note that the space group $P2_1/c$ is not a sub-group of $P4_2/nmc$.