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Investigation by neutron diffraction of texture induced by the cooling process of zirconia refractories

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Abstract

New fused cast refractories with a high content of zirconia have been developed to face corrosion in glass furnaces. The controlled cooling process is responsible for thermal gradients. So, thermal mismatches appear between core and edge zones of blocks. Besides, the multiphasic nature of ZrO_2 based refractories is associated to thermal mismatches during cooling. Finally, the expansive transformation of ZrO_2 can lead to stress generation.

This paper is an application of neutron diffraction to study texture generated during the cooling process of zirconia based materials. In fact, it is shown that ZrO_2 crystallographic variants have particular crystallographic texture regarding the main direction of the thermal gradient in the block. It was hypothesized that a selection of crystallographic variants could be done depending on the field stress. Tensile-compressive tests at high temperature have been done, to reproduce stress environment during the transformation of zirconia.

Keywords: Refractories; Texture; Variants; Cooling process; Neutron diffraction

1. Introduction

New compositions of refractory materials with high zirconia content have been developed. They are casted using a melting process in arc furnaces followed by a controlled cooling step in moulds. Microstructure features at room temperature are complex, with a 3D skeleton of ZrO_2 crystals surrounded by a glassy phase. The different phase transitions have been detailed elsewhere and are resumed in Fig. 1.[1] Dendrites of zirconia initially grow under the form of cubic domains (C) with primary and secondary ramifications (tree structure) and probably transform into tetragonal domains (T) at around 2300 °C. Down to 1700 °C, the mixing is not supposed to be fully solid, and nucleation-growth of zirconia dendrites is rather active. Below 1700 °C, the material can be considered as fully solid with zirconia dendrites embedded in a glassy phase. Between 1000 °C and 900 °C, the martensitic transformation of zirconia occurs, where ZrO_2 goes from tetragonal structure to monoclinic (M) one. Depending on the nature of the glassy phase (soda-siliceous or boron-siliceous for example), the refractory exhibits different thermo-mechanical behaviour,[1,2] probably due to different viscous behaviour around the T-M transition.

The glassy phase as well as the different zirconia domains are characterized by different thermal expansion coefficients. Moreover the tetragonal to monoclinic transition at about 1000 °C is associated with a large volume expansion (4%), which can generate important local strains. Thereby kinetic of the cooling stage must be minimized to limit the formation of local thermo-mechanical stresses which can lead to the damage of the material (microcracking). Different authors have studied previously the thermo mechanical behaviour of fused-cast

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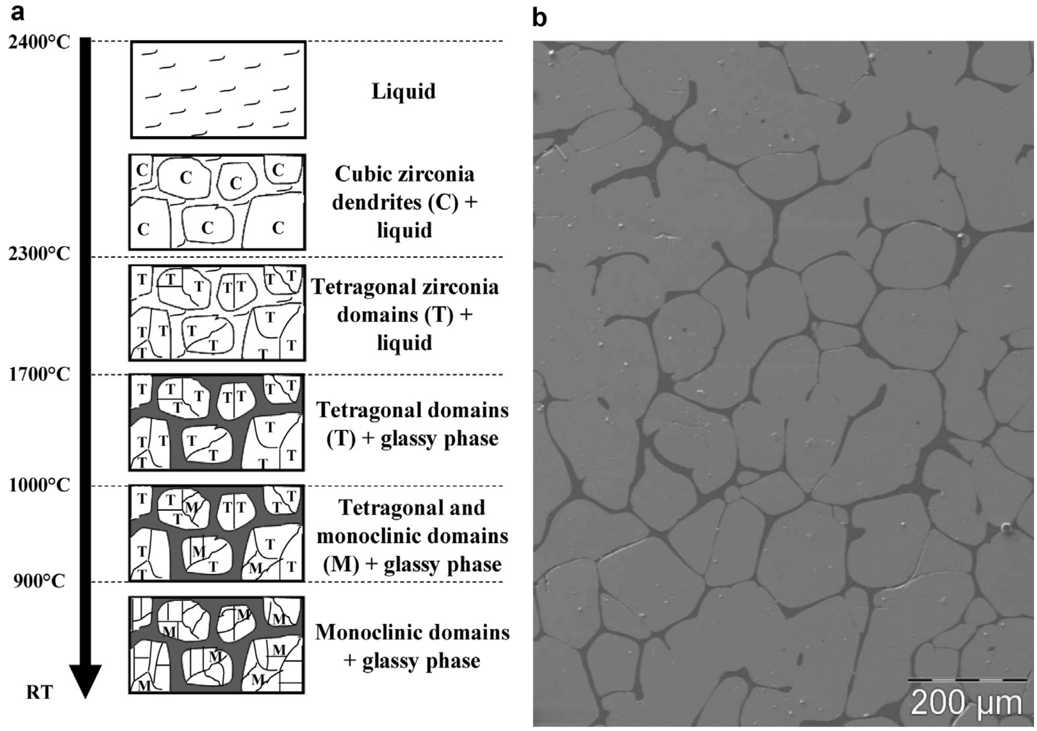

Fig. 1. Evolution of the microstructure during the cooling process (a) and final microstructure observed at room temperature by SEM (b).

refractory to avoid the appearance of important thermo mechanical stresses.[3] Cockcroft[4,5] performed a statistical analysis of macroscopic cracks in ZrO_2 refractory block and highlighted longitudinal and transverse cracks. The study showed that transversal cracks are rather due to mechanisms involved at high temperature while longitudinal ones appear below the glass transition temperature of the amorphous phase. Using conclusions of Thomas,[6] the author showed through a 3D thermo-elastic-type model, the appearance of high tensile stress after passing the T → M transformation of zirconia. In the same way, Evans[7] used a Drucker–Prager type model to study a block of Alumina–Zirconia–Silica refractory material. It was shown that passing the T → M transition in the skin area of the block is responsible for significant tensile stresses in the core, causing plastic deformation leading to its final rupture. These deformations depend on the blocksize, the transformation strains and the cooling profile. In 2000, Madi[8] computed simulation of a mesoscopic volume (some μm^3) of HZ material between 800 °C and room temperature. This model used an elastic behaviour for zirconia and a viscoplastic one for the glassy phase. A maximum level of tensile stress at the surface of the block and at interfaces between zirconia and glassy phase was measured, with interfacial debonding and cracking phenomena in the glassy phase.

Characterization of texture associated to the cooling process is of prime importance to understand stress field and damage occurrence. In-situ characterization is difficult due to high temperature conditions. Moreover crystallographic texture after cooling process in moulds has been investigated mainly for metal based materials (using X-Ray Diffraction (XRD) or Electron Backscattering Diffraction (EBSD),[9,10] but few studies are available for ceramics and especially for ZrO_2 based refractories.

Thereby crystallographic texture is studied by neutron diffraction on materials sampled in different areas of the refractory blocks. Relationships between preferential orientation of zirconia variants and main direction of thermal gradient in the block are highlighted for two different types of ZrO_2 refractories. Complementary tensile/compressive tests on samples are done during cooling to reproduce conditions of block casting. Corresponding strains are analysed to get information on the local stress field.

2. Materials

2.1. Casting process

Raw materials (zircon sand, alkali salts) are fused in electric furnaces. After refining, the molten liquid is poured into moulds before undergoing a slow controlled cooling stage. The block was cooled by adapting the external thermal conductivity with a “thermal calibrating” agent (Fig. 2).

The type of mould, geometry of blocks as well as the nature of the calibrating agent greatly influence the thermal behaviour of

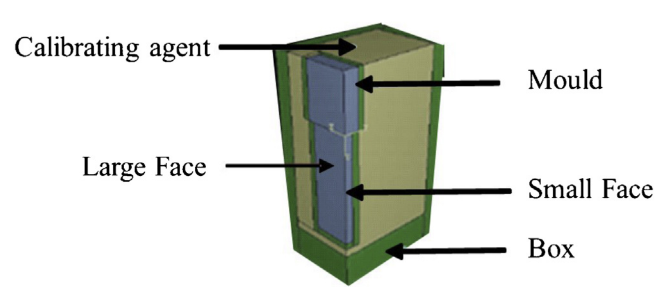

Fig. 2. Refractory block inside the mould with the presence of calibrating agent.