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Dynamic aspects of cerium dioxide sintering: HT-ESEM study of grain growth and pore elimination

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Abstract

Sintering of CeO_2 is studied *in situ* by high temperature scanning environmental microscopy (HT-ESEM) at $T = 1400\,^{\circ}C$. The morphological modifications of a single grains population are recorded for 6 h. Kinetic parameters are extracted from image series. The local grain growth determined from the single population studied *in situ* is compared to the general grain growth obtained by classical *ex situ* technique. Using HT-ESEM for sintering study is validated. The grain boundary velocities range between 0 and 5 $\mu m\,h^{-1}$, with a mean value of about 1 $\mu m\,h^{-1}$. The migration of the intragranular surface pores is described. Their velocities range between 0.4 and 1.2 $\mu m\,h^{-1}$ and depend on pore diameters: the smaller the pore, the faster the pore velocity. The time required to fill a pore that arises at the sample surface is determined as a function of pore diameter. The time for pore elimination dependence with the pore diameters is also established.

Keywords: A. Sintering; A. Grain growth; Grain boundaries; Electron Microscopy; CeO2

1. Introduction

The final stage of sintering involves two major phenomena occurring simultaneously: pore shrinkage and grain growth. The microstructure evolution of a solid during sintering is then related to the kinetics of change in the grain size and pore distributions. These modifications are directly linked to atom and pore mobilities (and more generally to mass transfers) that generate displacements of grain boundary and pores.[1,2] Numerous models were developed to predict these processes but associated direct observations remained very rare. Indeed, even if the knowledge of experimental data is of great importance, only very few direct determinations of kinetic parameters are available, due to some difficulties to develop *in situ* observation methods that allow the visualisation of high temperature processes at the grain scale. Three main methods based upon recent technological developments have been used to observe *in situ* sintering process during heating:

- Transmission (and scanning transmission) electron microscopy,[3–6] and associated imaging techniques (high resolution imaging,[7,8] aberration-corrected high-angle annular dark-field – HAADF – detection[9]) which provide direct information at the atomic and nanometer grain scale.
- Synchrotron radiation X-ray computed tomography associated with *in situ* heating of the sample provides bulk material 3D imaging of samples.[10,11]
- Scanning electron microscopy (SEM) that provides information at the grain scale with nanometer resolution. It was extensively used to observe sintered materials, but generally after sample cooling at room temperature,[12–14] and surface preparation. The main problems linked to this technique are associated to the difficulty to perform successive analyses on materials at the same location.

One of the latest developments in electron microscopy is the environmental scanning electron microscope (ESEM),[15,16] which allows observing materials under a gaseous atmosphere. Its association with specific attached devices offers the possibility to perform direct observations of native surfaces evolution with temperature or atmospheric pressure modifications.[17]

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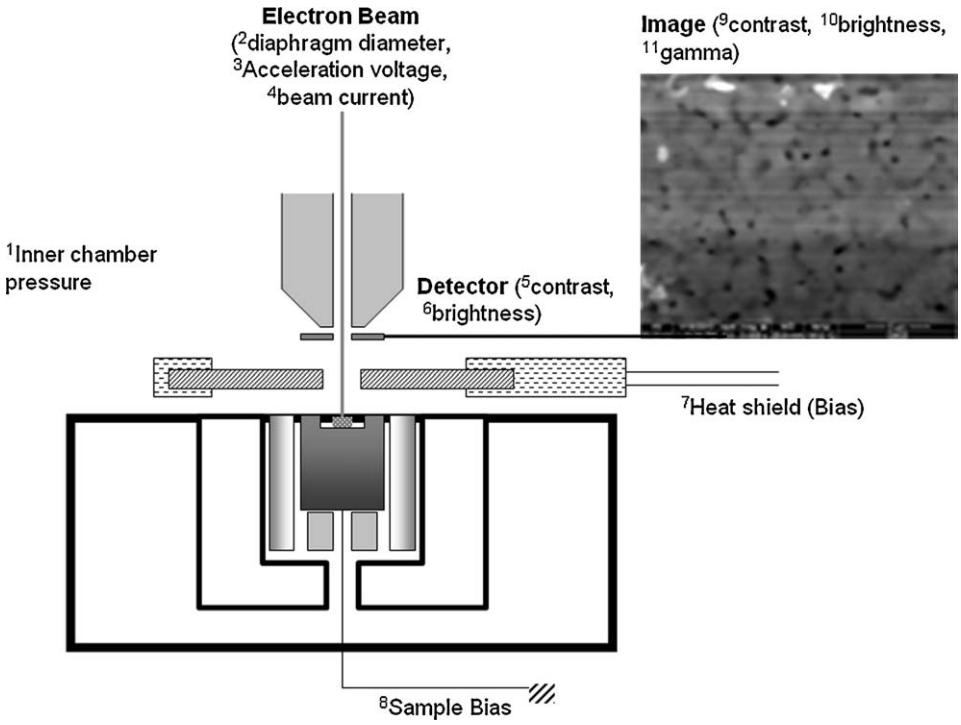

Fig. 1. Scheme for the use of the HT-ESEM with all possible image condition adjustments.

In situ scanning electron microscope imaging of materials at high temperature is a challenging problem to which ESEM can bring interesting answers. Indeed, even if electron microscopes have been successfully adapted to observe the behaviour of materials at high temperature for long,[18,19] the technological solutions developed limited the investigations to relatively low temperature experiments since heating materials above 1000 °C generally results in the emission of infrared and visible light along with increased thermo-ionic emission of electrons.[20] This is the main limitation in obtaining ESEM images at high temperature ($T > 1150$ °C). For example, Subramaniam[21] reports that the increase of electron emission with the temperature results in poor signal to noise ratio on recorded images since a "white-out" effect is observed. The accompanying loss of contrast also results in poor image quality and loss of details. The degradation of imaging conditions becomes drastic as one approaches temperatures encountered in conventional ceramic sintering processes ($T \sim 1300$ °C). Nevertheless, specific devices were recently designed to allow observations at very high temperatures: among them, a furnace was developed by Gregori et al.[20] to perform conventional SEM (under vacuum) *in situ* imaging at temperatures as high as 1450 °C while Knowles and Hardt[22] designed a system coupled with a heat shield assembly reaching up to 1500 °C (Fig. 1). This system was used during this study.

The challenges of the present study are mainly to record HT-ESEM image series of oxide grains with a submicrometer resolution during 8 h at $T = 1400$ °C in order to obtain new information on the sintering process of ceramic nanograins through the mathematical treatment of the obtained images. The selection of CeO_2 as model ceramic was motivated by its numerous applications such as its use as a surrogate for PuO_2 in the nuclear fuel industry[23,24] as well as its potentialities within the framework of cathode materials in Solid Oxide Fuel Cells[25,26] which both requires the preparation of sintered components.

2. Experimental

2.1. Powder synthesis and characterization

Powdered CeO_2 samples were obtained by firing cerium oxalate decahydrate, $Ce_2(C_2O_4)_3 \cdot 10H_2O$ at $T = 500$ °C for 6 h.[27] This resulted in the formation of oxide nanopowders, constituted with 40–50 nm diameter aggregates (average crystallite size of 15 nm). The specific area of this powder, determined using a Micrometric ASAP 2020 apparatus under nitrogen atmosphere (BET method) was found about $47 \pm 3\ m^2\ g^{-1}$. XRD patterns of the final oxides exhibited all the characteristic XRD lines of the FCC fluorite-type structure (space group $Fm\bar{3}m$) according to JCPDS file # 81-0792.[28]

2.2. Sample preparation

Cylindrical pellets of 5 mm diameter were shaped by uniaxial pressure under 200 MPa at room temperature. About 1 mm diameter part of the disc was considered to perform the HT-ESEM *in situ* experiments. The small size of the samples ensured a fast temperature homogenization of the studied piece of ceramic. Furthermore, the displacements of the sample coming from its sintering remained limited, avoiding the possibility of loosing the region of interest during analysis.

Complementary *ex situ* experiments were also performed at $T = 1300$ and 1400 °C. The density of the pellets sintered