

# ***HIGH TEMPERATURE SYNCHROTRON NANO HOLOTOMOGRAPHY TO FOLLOW THE SINTERING OF TiO<sub>2</sub> NANO PARTICLES AGGLOMERATED AS MICROSPHERES***

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**Summary:** A challenging experience using X-ray synchrotron nano holotomography was developed in order to follow, in 3D, the sintering of a single TiO<sub>2</sub> microsphere between 1100 °C and 1300 °C. Microstructural evolutions were precisely characterised at nano-scale on each critical thermal steps.

## **1. INTRODUCTION**

Titanium oxide is widely used in a broad range of applications (electronics, spintronics, sensing, photocatalysis, photovoltaic...) due to both its unique electronic and optical properties and a remarkable versatility of processing and shaping [1-4]. Recently, we used microspheres of TiO<sub>2</sub> to build innovative 3D composites such as low-loss all-dielectric metamaterials and ferroelectric ceramics with tunable properties [5-6]. The dielectric properties in terms of permittivity and loss values can be accurately controlled over a broad frequency range provided that the microstructure is mastered.

TiO<sub>2</sub> microspheres prepared by spray drying from nano-crystalline rutile powder and sintered in two steps (1200 °C and 1400 °C) have been observed by Scanning Electron Microscopy (SEM) putting into evidence drastic changes of their microstructure. As the final properties of the composites using these spheres as inclusions strongly depend on this microstructure, we looked for a better understanding of the observed evolution using X-ray nano holotomography at high temperatures (1100 °C - 1300 °C).

## **2. EXPERIMENTAL METHOD**

The experiment was conducted at the ID16B beamline of the European Synchrotron Radiation Facility (ESRF), in Grenoble, France. The experimental protocol was designed in order to follow the internal sintering of a single TiO<sub>2</sub> microsphere (approx. 40 µm diameter), between 1100 °C and 1300 °C (Fig.1a and b). The beamline offers the opportunity to perform nano-holotomography using a divergent X-ray beam focused by a KB optics system. The achievable focal spot size is below 50 nm. During the experiment, the energy was set to 17 KeV, in pink beam mode, and the voxel size to 50 nm. Samples were prepared having in mind that the sample holder must be: i) low X-ray absorbing materials; ii) chemically inert; and iii) able to withstand high temperatures. Alumina tubes (0.2 mm inner diameter, 2 mm height) were selected due to their good thermal and X-ray attenuation properties. A few TiO<sub>2</sub> microspheres were mixed with 100 µm SiC particles in order to avoid contacts between TiO<sub>2</sub> microspheres, and the mixture placed into alumina tubes. Tubes were sealed by high temperature ceramic glue, and placed on top of a mullite tube containing an S type thermocouple reaching the sample bottom in order to monitor the temperature.

After positioning the sample on the tomographic stage, a bell-type furnace (FibHeat 200 from MHI) was used for heating the sample. At the time of the experience *in situ* acquisitions were not feasible due to the complicated

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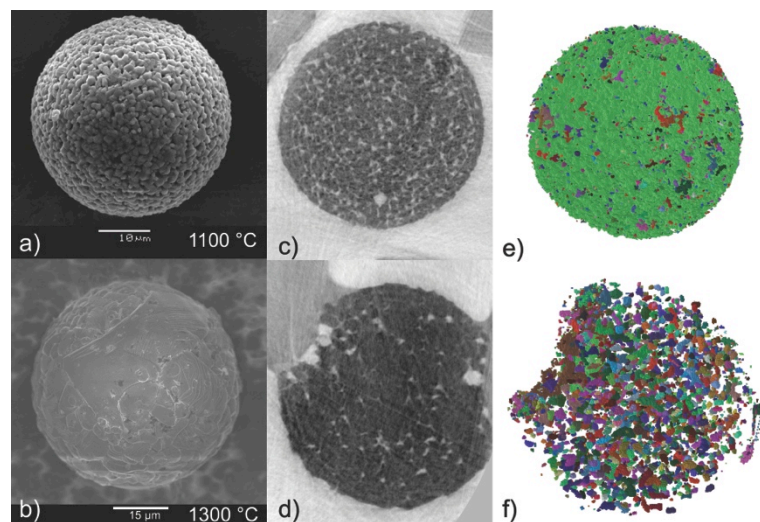
experimental conditions (local tomography, high resolution, high temperature, strong phase contrast). An interrupted sintering experiment was then performed, the furnace being alternatively lowered and raised around the sample. Because of the sample smallness, the effect of these interruptions on the microstructure evolution can be considered as negligible. With the sample out of the furnace it was possible to acquire tomographies at different distances in order to obtain complete phase contrast information for the sample [7]. A series of 7 tomographic acquisitions were performed at different temperatures between 1100 °C and 1300 °C. Final reconstructed volume dimensions were 128  $\mu\text{m}$  x 128  $\mu\text{m}$  x 108  $\mu\text{m}$ .

### 3. RESULTS

The results presented in this section were obtained between 1100 °C and 1300 °C (Fig.1c and d). Several difficulties were encountered. First, the maximal temperature sintering (1400 °C) was hard to achieve due to a limited power of the furnace. This leads to investigate only the preliminary modification of the microstructure. Secondly, SiC particles, initially used to avoid contact between microspheres started to sinter. Nevertheless, the evolution of the porosity and grain boundaries was precisely observed. The initial volume fraction of pores was 12.9 % at 1100 °C, and drastically decrease during the first thermal steps (4.5 % at 1200 °C) (Fig.1e and f). Between 1200 °C and 1300 °C, the porosity slightly decrease towards 3.2 %. In the first sintering steps, diffusion mechanisms are more efficient due to a large number of grain boundaries. During the last thermal steps, a reduction of the number of grain boundaries leads to very slow porosity evolutions.

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**Figure 1:** (a) and (b) SEM image of TiO<sub>2</sub> microspheres sintered at 1100 °C and 1300 °C. (c) and (d) Tomographic section obtained on a single microsphere at 1100 °C and 1300 °C (voxel size = 50 nm). (e) and (f) 3D rendering of the connected porosity (each colour corresponds to a unique connected component).