ESRF	**Experiment title:** Kinetics of in-situ phase separation in glasses by 3D imaging part I: Interrupted in-situ experiments	**Experiment number:** HD501
Beamline: ID19	**Date of experiment:** from: 02 dec. 2010 to: 06 dec. 2010	**Date of report:** 29 feb. 2012
Shifts: 12	**Local contact(s):** Elodie Boller	*Received at ESRF:*

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Report:

Abstract The aim of the experiment HD501 was to follow the coarsening dynamics of a ternary glass (Barium-Borosilicate) in the phase separation domain i.e. at temperatures circa 1000°C. A first series of interrupted in-situ experiments (described in the following) has been performed from 02 to 06 december 2010 (12 shifts). A second series of in-situ experiments (described in the 2nd part of this document) has been performed from 10 to 14 february 2011. Good qualities 3D images and/or movies could be reconstructed and are currently analysed both at a statistical level (dynamic scaling of domain growth, evolution of domain size distribution) and a local level (growth and motion of individual clusters. Preliminary results have been presented in november 2011 at the 3D Microstructure Meeting in Saarbrücken.

Introduction

Lots of simple (binary or ternary) glasses exhibit phase separation in their liquid or supercooled state. Depending on temperature and composition, either spinodal decomposition (leading to interconnected domains) or nucleation (leading to droplets) can be observed. Everyday life example include PYREX or VYCOR glasses. Although this subject has been intensively studied up to the eighties in glass science [1], the interest for these remarkable materials has faded away since then. Yet phase separated glasses are ideal candidates model systems for studying phase transitions in 3D as well as for designing materials with a controlled microstructure.

Although known for a long time, phase separation in glasses remains difficult to study experimentally and few quantitative analysis in direct space are available so far [2]. A first difficulty stems from the high temperature range within which phase separation usually occurs.
Rather than trying a direct observation at high temperature one usually performs a quench after a heat treatment at a chosen high temperature. Observation can then be performed by optical or near field (AFM, SEM) microscopy depending on the characteristic size of the phase domains. The present experiment consisted of following by X-ray tomography the coarsening dynamics of a ternary glass (Barium-Borosilicate) in the phase separation domain i.e. at temperatures circa 1000°C.

Material and Methods
Barium Borosilicate samples (molar composition $(Si02)_{70}$-$(B2O3)_{20}$-$(BaO)_{10}$) of cylindric shape (diameter 2 mm height 5-6 mm) have been prepared in a phase separated state. The typical size of amorphous domains was about 5-10 micrometers. The preferential migration of Barium oxide in one of the two phases was checked to allow a significative X-ray absorption contrast in preliminary experiments by E. Boller. High temperature experiments have been performed in the range 900°C-1600°C using the furnace "Ecole des Mines". X-ray tomography projections have been acquired at 30 keV with an acquisition time around 1mn with the Frelon camera with a pixel size of 1.4 μm.

Preliminary results
Ten different samples were heat-treated and imaged. In the first experiments (1-6) imaging was performed in-situ. Heat treatments consisted either of applying a constant temperature (about 1000° C) or a ramp up to a very high temperature (above 1500°C) ensuring homogeneization of the glass melt before performing a quench at a lower temperature (about 1000°C) in the phase separation domain. In all cases HT dynamics finally appeared to be too rapid to allow high quality in-situ imaging. Moreover after heat treatment at very high temperature, phase separation appeared to be rather limited possibly because of a contamination of the glass by the alumina crucible. The second set of experiments consisted of heating the sample at a constant temperature about 1000°C and of performing regularly 3D images after an almost instantaneous quench obtained by lifting the furnace. This interrupted in-situ technique allowed us to acquire very good quality "snapshots" of the material structure upon heat treatment. An illustration is given in Fig. 1 where we have dispayed 2D vertical sections of the glassy structure after 2 min, 4 min, 6 min, 8 min, 11 min, 16 min, 23 mn, 32 min and 45 min of heat treatment at 1030°C. A beautiful coarsening phenomenon can be seen at work.

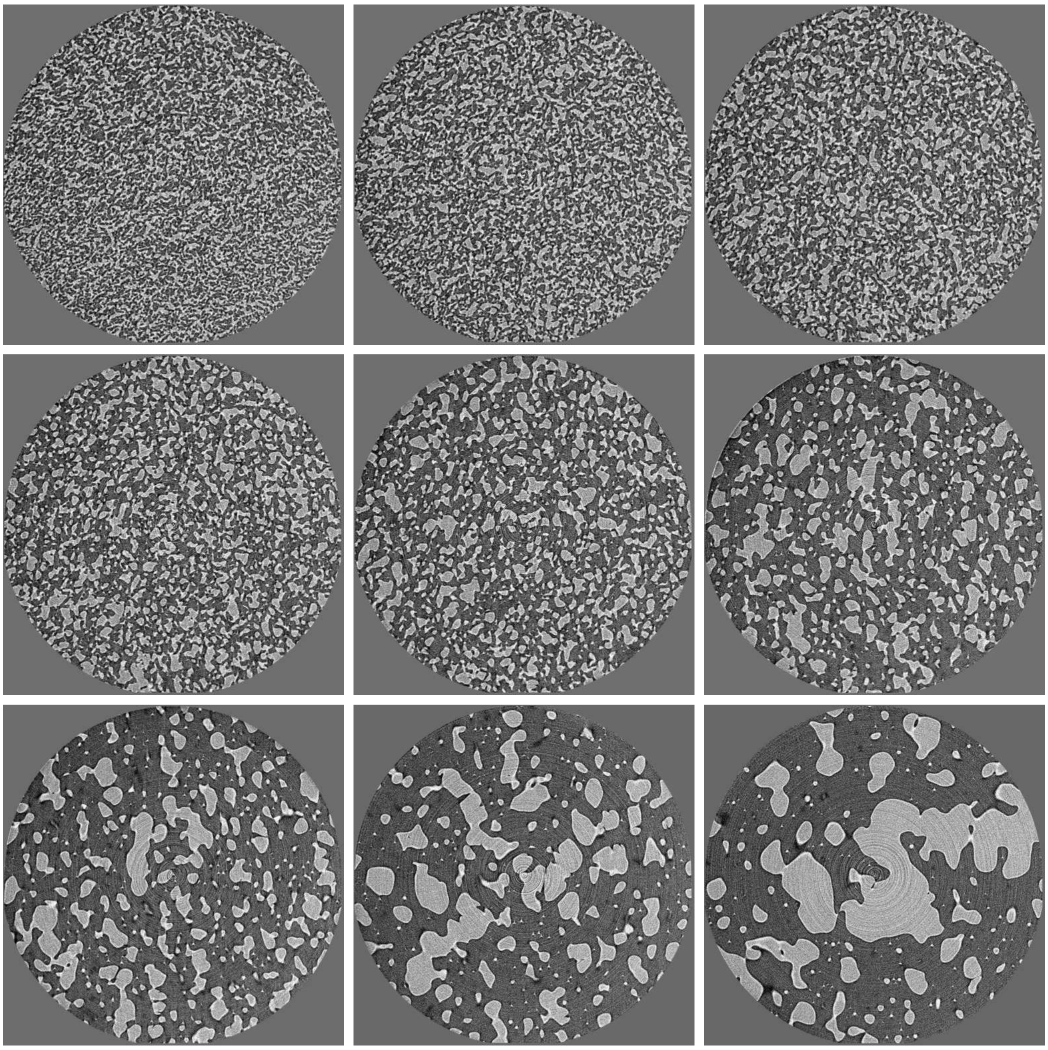

Figure 1: 2D sections snapshots of a phase-separated Barium-Borosilicate glass under heat treatment at 1030°C. Interrupted in-situ X-ray tomographic measurements have been performed after 2 min, 4 min, 6 min, 8 min, 11 min, 16 miin, 23 min, 32 min and 45 min. Domain growth is observed.

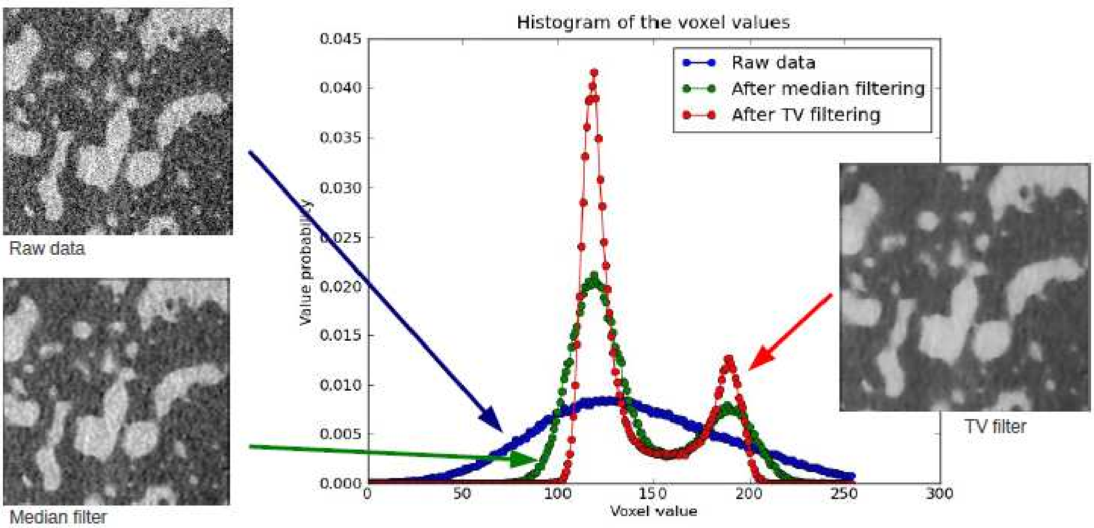

Figure 2: Filtering operations performed on the reconstructed 3D images. A median filter eliminates high-contrast outliers, a Total Variation denoising filter then improves the contrast between the two phases.

Three-dimensional image reconstructions (including ring correction) have been performed using the software tools developed at ESRF. Images obviously require additional treatments since we aim to perform statistical analysis of the time evolution of the domains of the two amorphous phases during coarsening. The current protocol we use consists of the following sequence: a median filtering is first applied in order to eliminate very high-contrast noise, a total variation denoising step[3] then allows us to clearly identify two peaks in the distribution of grey levels. The effect of these two filtering steps is summarized in Fig. 2.

These peaks are then used to initiate a segmentation step based on biased random walkers diffusion[4]. A systematic study is currently ongoing to estimate the effect of the parameters of these successive steps on the statistics of the final binary images to be used for statistical physics analysis.

First quantitative analysis seem to indicate that the typical domain size scales linearly with time. Such a scaling law would be consistent with a coarsening stage controlled by hydrodynamics rather than diffusion.

References

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[4] Leo Grady. Random walks for image segmentation. *IEEE Transactions on Pattern Analysis and Machine intelligence*, 28:1768–1783, 2006.

ESRF	**Experiment title:** Kinetics of in-situ phase separation in glasses by 3D imaging part II: in-situ experiments	**Experiment number:** HD501
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Report:

Abstract The aim of the experiment HD501 was to follow the coarsening dynamics of a ternary glass (Barium-Borosilicate) in the phase separation domain i.e. at temperatures circa 1000°C. A first series of interrupted in-situ experiments (described in the first part of this report – see previous pages) has been performed from 02 to 06 december 2010 (12 shifts). A second series of in-situ experiments (described in the following) has been performed from 10 to 14 february 2011. Good qualities 3D images and/or movies could be reconstructed and are currently analysed both at a statistical level (dynamic scaling of domain growth, evolution of domain size distribution) and a local level (growth and motion of individual clusters. Preliminary results have been presented in november 2011 at the 3D Microstructure Meeting in Saarbrücken.

Introduction

In the second part of this document we discuss the experimental campaign performed on beamline ID19 from 10th to 14th february 2011. We mainly insist on the differences with the 1st campaign.

Material and Methods

The experimental conditions were mainly identical to those of the previous campaign with a significative difference: the higher beam intensity (200 mA) and slight modifications of the exerimental set-up (removal of silica windows of the furnace) allowed us to obtain enough transmitted intensity to reduce acquisition time to about 15-30s and to perform real in-situ imaging of the glass upon heat treatment.

To avoid contamination at high temperature, a few experiments have been tested with a glass droplet attached to a platinum thread. However the increase of wettability at high temperature did not allow good imaging consitions.

Preliminary results

Fifteen different samples were heat-treated and imaged in situ. Most experiments consisted of a plateau at T=980°C, T=1030°C, T=1080°C or T=1130°C. This plateau was in a few cases peformed after a homogenization step at T=1480°C followed by a rapid quench.

As shown in Fig. 1 good quality images could be acquired in-situ even if not as good as with the interrupted in-situ protocol.

As discussed above in the first part of this document, two successive filtering steps and a segmentation step have ben applied on 3D reconstructed images. After segmentation, one obtains a large percolating cluster and a distribution of smaller domains. Figure 3 shows the temporal evolution of such a small domain during the heat treatment step. During this coarsening stage a significative growth is observed as well as a progressive regularization of the surface.

This coarsening process is basically driven by the advection/diffusion from regions of high curvature. In Fig. 4 we show the Surface to Volume dependence of individual clusters after 25 min of heat treatments at 1130°C. The smaller clusters are spheroidal while the larger ones are more fractal-like. The characteristic length between these two regimes progressively increases along the heat treatment.

In addition of such statistical investigations currently under way, the in-situ data also give us the possibility of finely following the dynamics of the coarsening process. In particular we have started to follow the motion of individual clusters.

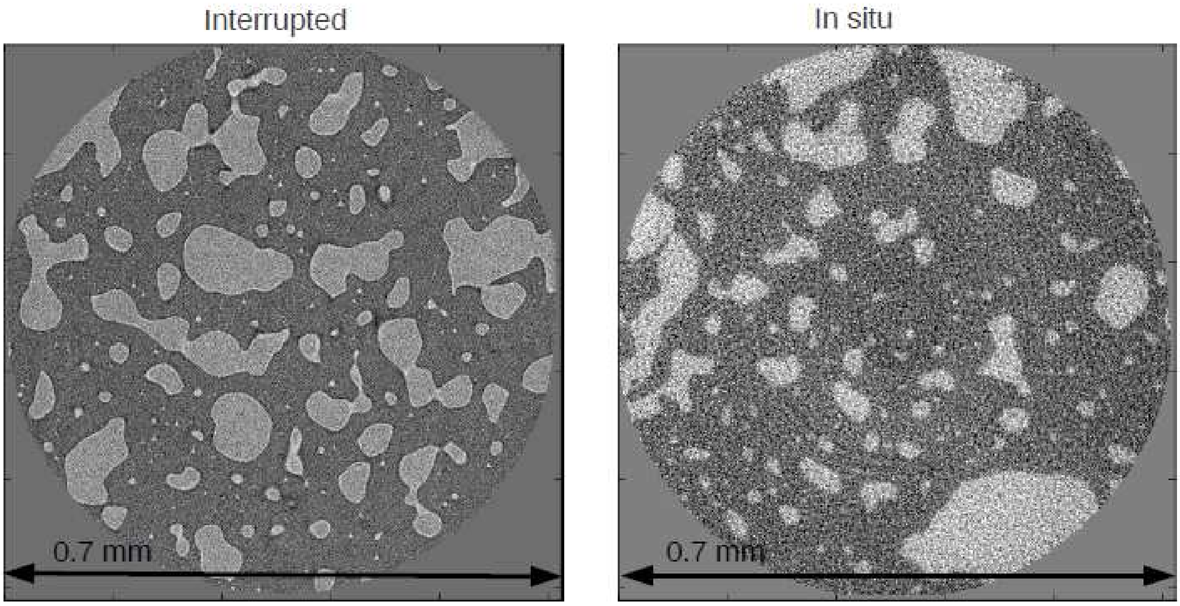

Figure 1: Comparisons of two sections obtained after circa 40 min at 1130°C with interrupted in-situ (left) and in-situ (right) protocols.

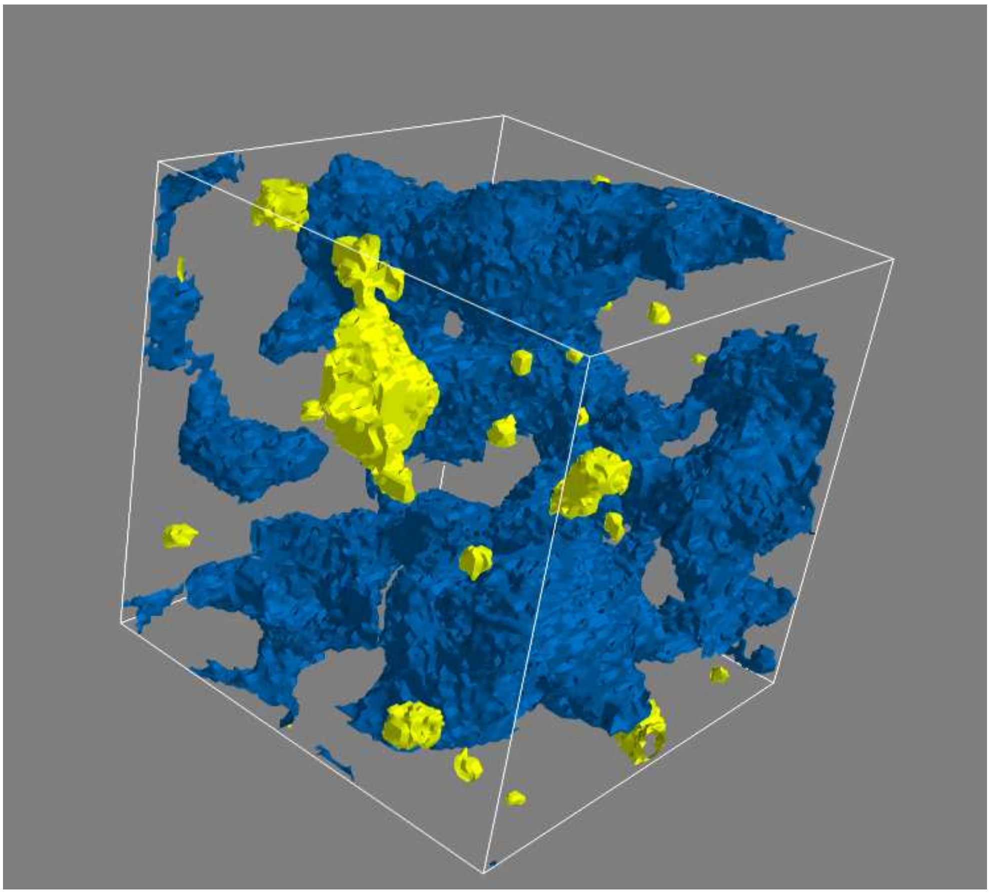

Figure 2: After segmentation, one large percolating domain and a distribution of smaller domains can be identified

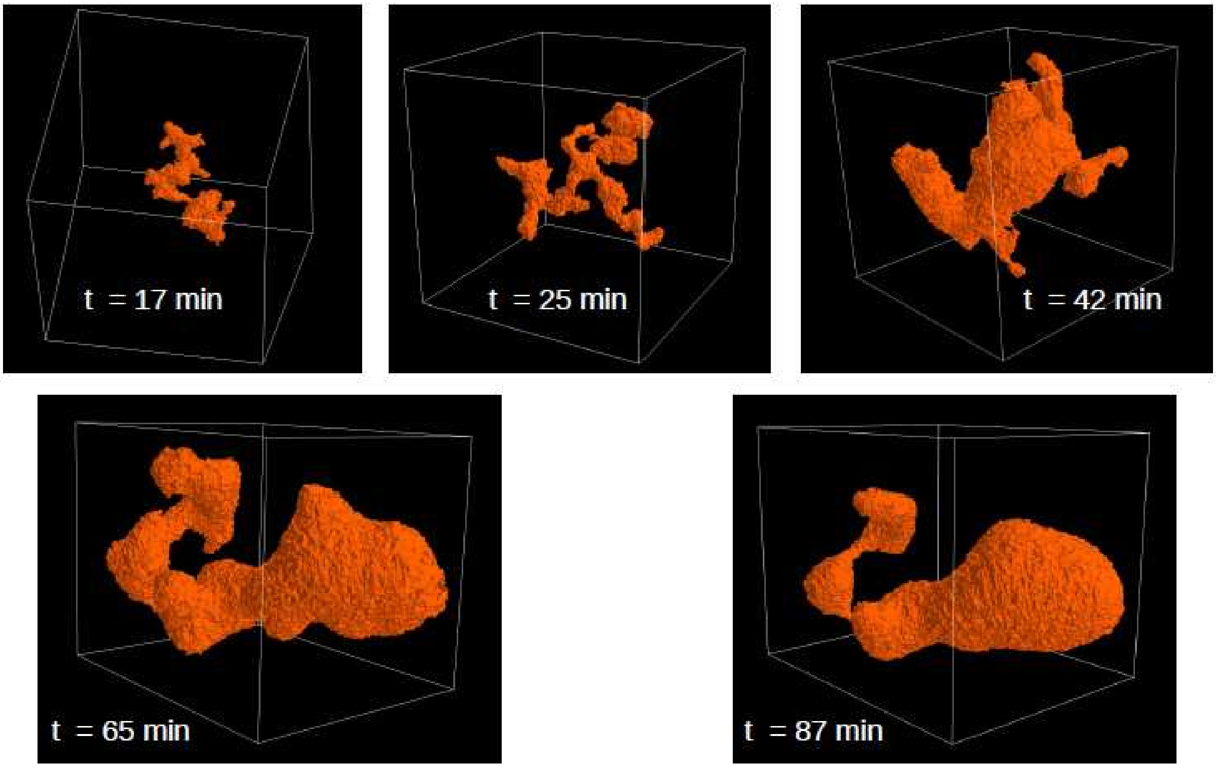

Figure 3: Individual tracking of a domain during a heat treatment at 1130°C.

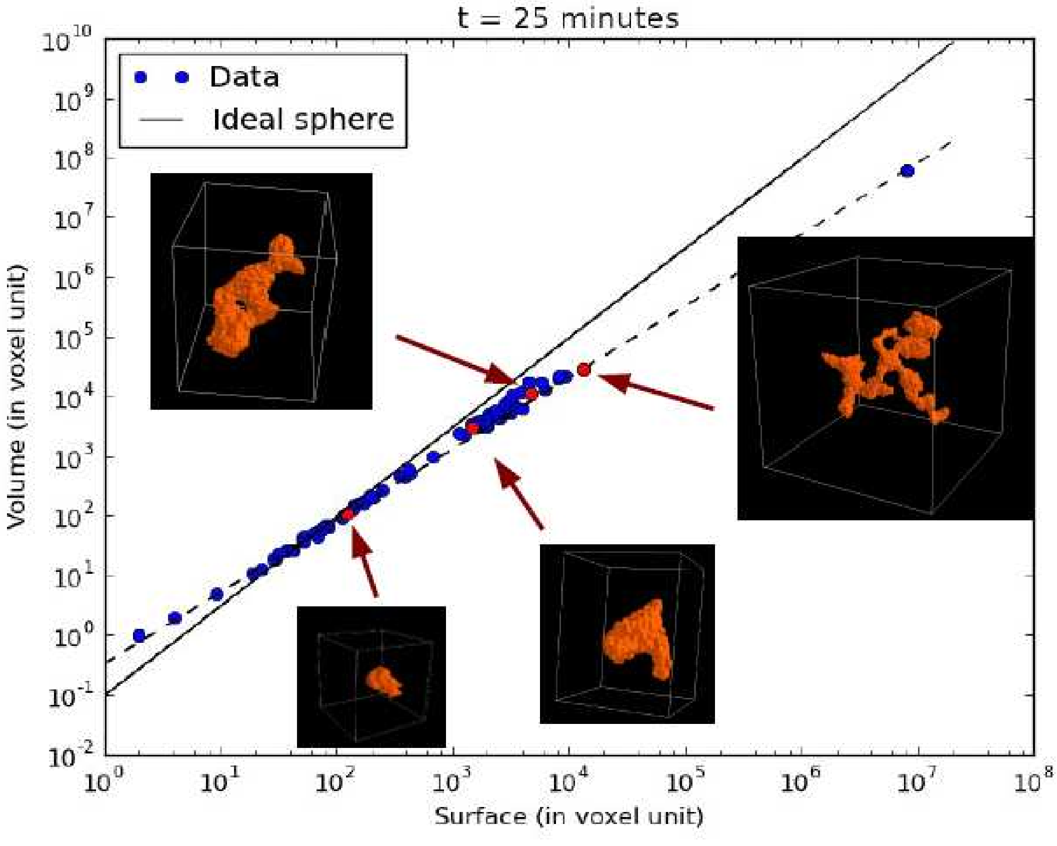

Figure 4: Surface to Volume dependence of individual clusters after 25 min of heat treatments at 1130°C. The smaller clusters are spheroidal while the larger ones are more fractal-like. The characteristic length between these two regimes progressively increases along the heat treatment.