Monitoring sintering of nanoparticle clusters by X-ray microtomography

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Abstract

There has been much effort in recent years to develop methods for producing materials with nanometer scale substructure. The desire is to control the macroscopic material properties such as toughness, elasticity and porosity by tailoring the microstructure. For ceramic materials, one approach is to synthesize nano-scale particles and develop methods for compressing and sintering these powders. The sintering of complex materials and mechanisms involved in morphological changes are still not very well known. An experimental X-ray microtomography system has been designed to observe evolution of nanoparticle assemblies during sintering. It is a non-destructive technique providing 3-D information on materials processing. Traditional imaging techniques do not give much needed 3-D information to understand these mechanisms. The initial green part is observed first, then full 3-D scan of the object is carried out while heating up to 285 °C. The agglomeration of nanoparticles in general decreases the density of green bodies when pressed from those nanopowders. Depending on the strength and morphology of the agglomerates, different density profiles can be achieved. The shrinkage during heating is observed and the amount of particle agglomeration of polymer-silica nanoparticles is examined.

Introduction

There are important issues, which are still not well understood in the sintering of powders with complex morphology and composition related to industrial processes such as drying, sintering, compaction etc. The causes of particle agglomeration, shrinkage, evolution of defects or cracks and the densification process during sintering are a few of them. While much work to date has focused on the study of microscopic powders, little has been reported on the corresponding behaviour of nano-scale particles.

The application of X-ray Computed Tomographic (CT) techniques to Non-Destructive Evaluation (NDE) of materials, outside of the medical field for which they were initially developed, is a rapidly expanding area of research [1,2,3]. The expensive body-sized medical CT machines have been replaced by relatively inexpensive bench-top sets. The typical spatial resolutions of 0.5 mm for medical systems have also been improved down to 5 mm. These improvements are mainly due to the advancement in pixelated X-ray detectors and the simultaneous development of micro-focus X-ray tubes. For example, third generation (cone-beam geometry, single source, two-dimensional detector) medical CT systems use 12-inch X-ray Image Intensifiers (detector pixel pitch of 0.5 mm) and 1 mm focal-spot size X-ray tubes in a proximity focused geometry. This compares to a modern NDE CT set which often uses flat-panel pixelated CsI coated CMOS arrays (detector pixel pitch of 50 mm) and X-rays tubes with a 5 mm focal-spot size in a geometry which magnifies the sample on the detector. The use of improved detectors has the additional benefit

of better contrast resolution and signal digitisation is higher (x-ray image intensifiers, XRIIs, are digitised to 8-bits, CMOS arrays are digitised to 12-bits). The use of NDE CT sets in the study of nano-powder assemblies is only just coming to fruition as the spatial and contrast resolutions are approaching the limits for which useful information can be obtained. X-ray microtomography is a very useful tool for imaging nano-powder assemblies but does not have the resolution to image individual nano-particles. Nevertheless, it can provide valuable information about nanoparticles systems in micro scale. The formation of the assembly can be studied as the suspension medium is evaporated and information regarding the packing density and large area defects can be obtained. The samples can then be mechanically tested and desirable properties can be linked to the formation and structure of the final assembly. The drying process can then be adapted allowing the evolution of better harvesting techniques. The formation of vacuum sintered nano-particle assemblies can also be studied and refined using the vacuum-furnace rotation stage. The sintered regime can be carefully controlled and the effects of heating cycles, axial loading impulses and vacuum conditions can all be assessed against desirable mechanical properties.
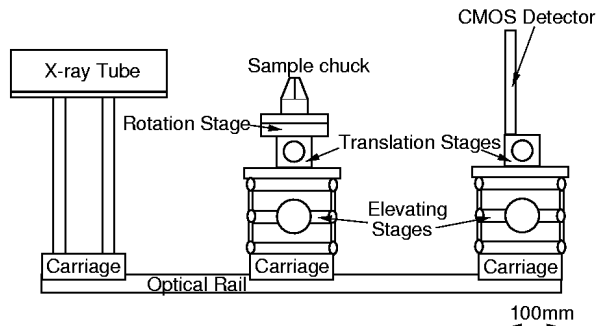

Figure 1. Schematic diagram of the high-resolution X-ray CT set.

Figure 1 shows the experimental apparatus used for high-resolution X-ray CT. The detector is a Hamamatsu C7942 flat-panel CMOS array (2400 x 2400 pixels at a 50 mm pixel pitch with a CsIcoating) and a Hamamatsu L6731-01 micro-focus X-ray tube (Mo target 80 kVp, 100 mA, 5 mm focal-spot size) [1,2]. The sample stage is a computer controlled rotational stepper motor with a resolution of 0.01°. The ring-artefact commonly associated with third generation scanners (caused by the repeated use of the same detector elements in each projection) is minimised by mechanically translating the detector sideward by a random integer number of pixels for each projection. The sample is rotated through 360° in a number of steps determined by the Nyquist sampling theorem (typically, number of steps = p/2 * number detector elements). The projection data are then stored and at a later stage reconstructed using a Feldkamp et al. [4] based three-dimensional backprojection routine on the Beowulf parallel-processing cluster into a three-dimensional data set of the linear attenuation coefficients. This can then be processed using a variety of signal-processing methods to extract useful information from the data.

A beryllium or carbon fibre windowed environmental chamber can replace the normal rotational stage. The samples can then be heated (up to 1000 K) and compressed (up to 6 kPa) under partial pressure (1 atm to below 10-6 mbar).

Powder System

Here, we describe the application of the microtomography technique to the study of thermallyinduced morphological changes in silica-polymer hybrid nanoparticles. The hybrid particles are produced by a catalytic silica precipitation reaction, using bipyridinium polymers ('polyviologens; PVs) as catalyst [5]. A slightly modified version of the procedure reported by Marvel and Sekera [6] was used for the synthesis of 1,4-butane ditosylate. Pyridine (20 ml) and 1,4-butanediol (2.019 g, 1.98 ml, 22.4 mmol) were added to a 100 ml round bottom flask equipped with a magnetic stirrer.

The flask is cooled to 0ºC and p-toluenesulfonyl chloride (8.701 g, 45.6 mmol) added in portions over 5 minutes, taking care to ensure that the temperature does not rise above 15ºC. The mixture is stirred for 3 hours below 20ºC before addition of hydrochloric acid (15 ml) in ice-cold water (50 ml). The ester that crystallises is collected on a chilled Buchner funnel and sucked as dry as possible. Recrystallisation from methanol yielded a crystalline white powder, which was then dried under vacuum for 24 hours. The purity of the monomer was checked by 1H NMR spectroscopy and elemental analysis.

Equimolar amounts of 4,4-bipyridyl and 1,4-butane ditosylate were stirred in dry acetonitrile at 80ºC for 120 h under an atmosphere of nitrogen according to the previously reported procedure [7] for the synthesis of poly(butylviologen ditosylate) (PBV-OTs). The resulting polymer was dried under vacuum at 80oC for 24 h. The structure of PBV-OTs is depicted in Figure 3.
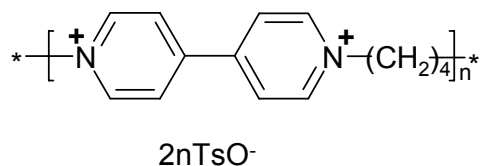

$$2nTsO^-$$

Figure 3. Structure of PBV-OTs.

The method used for silica precipitation was that employed by Coradin and Livage [8] Sodium silicate solution (0.5 ml) was added to the buffer solution (150 ml) in a 250 ml conical flask. The mixture was stirred for 10 minutes before a solution of polymer (15x10-5 M) in buffer (15 ml) was added. After 2 hours, the reaction mixture was centrifuged and the recovered solids dried under a flow of air at room temperature.

Polyviologens (bipyridinium polymers) are effective catalysts for the polymerisation of silicic acid at room temperature and neutral pH [5]. Variations in the alkylene spacer length and the associated counter ion appear to have little, if any, effect upon the rate of polymerisation. The resultant silica-PV hybrids are amorphous aggregates of roughly spherical particles of approximately 100 nm diameter. Particle sizing by scanning electron microscopy (SEM) shows that there are also occasional monolith structures which are much larger and do not appear to consist of an aggregate of spherical particles. We have shown previously that calcination of related silica-

PV hybrids can lead to formation of mesoporous silica [7]. The effect of thermal treatment on the hybrid structures formed in the current work was studied by microtomography.
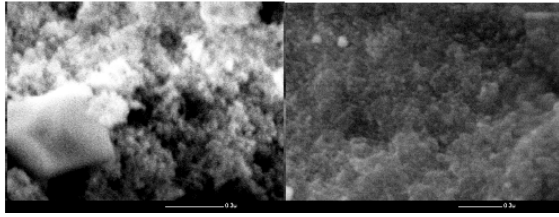
Figure4. SEM micrographs of silicas polymerised by typical PVs.

Experimental Procedure

The powder was put into a crucible with 7.5 mm inside diameter and 20 mm height. It was placed onto a temperature controlled heating system already fitted onto the rotating sample holder. The source to sample distance was 53 mm and sample to detector distance is 447 mm. The X-ray microtomography tube was operated at 65 kV and 101 mA and 900 projections were taken as the sample was rotated via a stepper motor. The geometrical magnification of the sample projection onto the detector resulted in a linear pixel resolution of 7.9 mm. The sample was heated up to 280°C starting from 40°C at a rate of 1°C/min.

Figure 5 shows X-ray projections for two different temperature values. As can be seen, even at this temperature range there is a considerable amount of shrinkage. The sol-gel techniques can often lead to low-density compacts with nanoparticles, while the high shrinkage rate can limit the ability of sol-gel techniques to produce bulk nano assemblies.
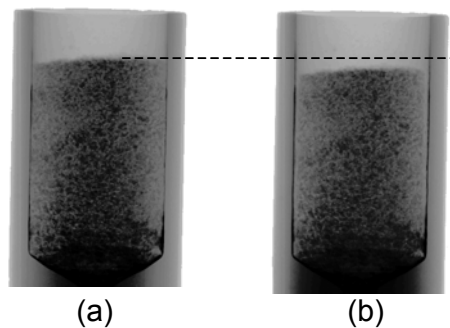

(a)   (b)

Figure 5. X-ray projections at a) 40 °C and b) at 285 °C

Figure 6 shows the corresponding two images captured by using a video camera where blackened polymer residues are still apparent in Figure 6b. At about 280°C the polymer is going to soften, before it starts to blacken (carbonise). What is being seen is the aggregation and densification of the silica network coupled with pooling and carbonisation of the melted polymer.
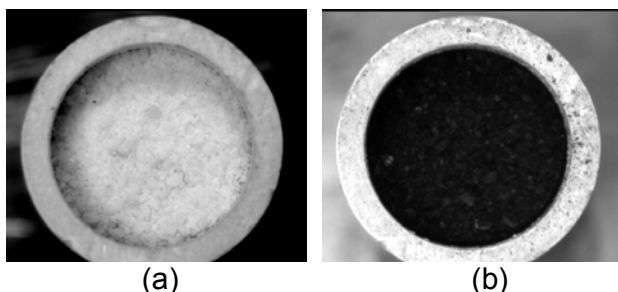

(a)   (b)

Figure 6. Video images taken from the top of the sample at a) 40 °C and b) 285 °C
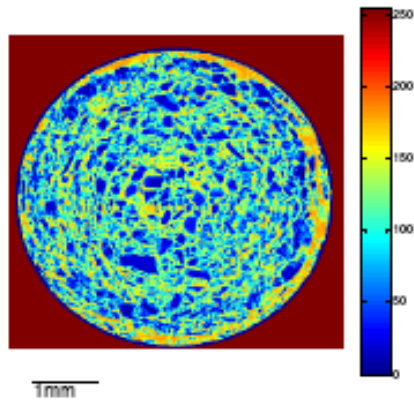
1mm

Figure 7. Reconstructed central slice of a thermally-treated silica-PV hybrid

Figure 7 shows a centrally reconstructed slice for the sample after the heated sample was left to cool down to ambient temperature. One can see the presence of rather large nano clusters. The lateral shrinkage from the sides of the crucible is also obvious in this figure, as polymer is being melted. Figure 8 shows 3-D reconstructions where silica agglomerates are clearly visible.
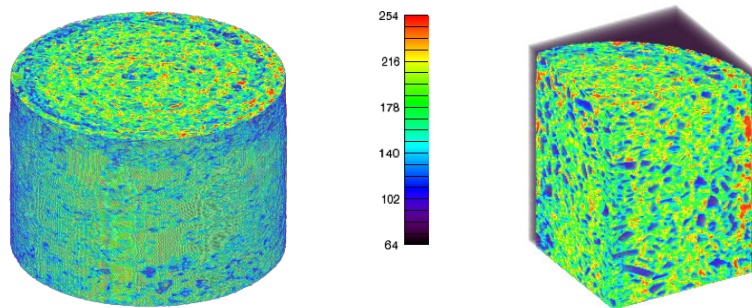

Figure 8. 3-D reconstructions of a thermally-treated silica-PV hybrid.

Conclusions

As can be seen, X-ray microtomography can provide important insight into the dynamical morphological changes in nanostructured materials. From these reconstructions, it is now possible to extract information about dynamic changes in particle shapes, particle agglomeration, the amount of shrinkage and its dependency on the heating, compaction etc.

Several well-known chemical and physical processes occur upon heating the polymer-silica hybrids and result in the shrinkage that is observed [9]. When the sample is heated from room temperature to 120ºC, desorption of water occurs resulting in weight loss but little shrinkage of the silica network. As the temperature is increased to approximately 550ºC a variety of processes account for shrinkage and weight loss, which are both significant, and these are attributed to the removal of the polymer (which essentially results in weight loss), condensation of the silica network

(with shrinkage proportional to weight loss) and structural relaxation (which results in shrinkage but no weight loss). Although the polyviologen (PBV-OTs) induces polymerisation and subsequent precipitation of monosilicic acid from solution, a significant number of hydroxyl moieties remain in the material synthesised at room temperature. Condensation of these groups occurs upon heating (Eq. 1) leading to shrinkage and a proportional weight loss as the water formed is removed.

$$Si\text{-}OH + HO\text{-}Si \quad Si\text{-}O\text{-}Si + H_2O \tag{1}$$

As the temperature is increased, carbonisation (ca. 200ºC) followed by oxidation of the polymer (up to ca. 450ºC) results in its removal from the hybrid. Some shrinkage occurs as a result of this but it essentially results in weight loss from the hybrid. Diffusive motions of the silica network upon heating can result in structural relaxation as the excess free volume of the silica is removed and the resulting skeletal density starts to resemble that of melted glass [10]. This process gives rise to an irreversible shrinkage.

Acknowledgement

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