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Cryogenic-Scanning Electron Microscopy as a Technique to Image Sol-to-Gel Transformation in Chelated Alkoxide Systems

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Abstract: Direct imaging of wet sol-to-gel microstructures in chelated alkoxide systems is reported for the first time by using fast-freeze and freeze-fracture techniques for sample fixing. The system chosen for microstructural imaging is that of a chelated alkoxide, in an effort to observe sol-to-gel transformation. The batch composition corresponds to a 1 : 1 molar ratio of aluminum sec-butoxide and ethyl acetoacetate made using isopropyl alcohol as a mutual solvent. About 100 μl of samples in varying stages of sonogelation, at a water addition rate of 0·4 ml per hour per gram of alkoxide, were injected between two 300-mesh TEM grids mounted on 0·1 mm copper plates and plunged into melting Freon to bring about a rapid solidification. The sample was cryo-transferred into an SEM, equipped with a cold stage maintained at −170°C, using liquid N_2. The specimen was fractured and imaged for microstructural detail under the electron beam. The direct imaging techniques developed here have been applied to chelated alkoxides for the first time, showing the morphology and microstructure in unhydrolysed as well as fully hydrolysed sols, which were found to indicate complex shapes that were not previously known to exist in such systems. Thus, more microstructural information could be directly gained as a result of this cryo-SEM technique.

1 INTRODUCTION

Cryogenic-Scanning Electron Microscopy as a means for direct imaging of fluid, labile microstructures has so far been applied successfully on kaolin clays, latex samples and cellulose.[1–2] More recently, this technique has been applied to gain microstructural and morphological information about surfactant aggregates, liposomes and vesicles.[3] However, microstructure development in the vast majority of high-purity, liquid-phase systems, particularly the high-purity, sol–gel processed metal alkoxides, remains uninvestigated and until now the cryo-TEM technique for observing sol-to-gel transition in alkoxide sols,[4] was considered suitable.

In the processing of ultrafine aluminum hydroxide from alkoxide precursors, the most crucial step is that of controlling the high rate of alkoxide hydrolysis. Alkoxides react rapidly and irreversibly to form a range of hydroxides varying widely in properties and microstructures.[5,6] As a result of having fast-reacting liquid phases in the reaction mixture, following microstructural evolution in the sol-to-gel metamorphosis using conventional SEM techniques was not possible (Haridas, M. M. *et al.*, unpublished). As compared to all other, indirect, techniques employed to gain microstructure information, the SEM offers the advantage of direct visualization. Hence, to observe microstructural evolution directly, without using the TEM sample preparation procedure, the cryo-SEM technique, employing fast-freeze and freeze-fracture methods

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of sample preparation was developed and applied to alkoxide systems. In order to retard the hydrolysis of the aluminum sec-butoxide precursor, and enable the imaging of microstructures devoid of incipient hydrolysis, the alkoxide was chelated with a 1 : 1 molar ratio of a tautomeric, Lewis base, i.e. ethyl acetoacetate, as has been recently reported in literature.[7–12]

The object of our research was to evaluate the suitability of the cryo-SEM technique in generating microstructural data in a chelated alkoxide system, and subsequently to document the microstructures observed as a result of direct imaging.

2 EXPERIMENTAL

2.1 Materials

The aluminum sec-butoxide (ASB) used in the experiments was of 97% assay and was used as received. The isopropyl alcohol (IPA) (Fluka) with a 96% assay was dried by a 4-h storage in a desiccator containing calcium oxide previously heated to 800°C. The ethyl acetoacetate (EAA) (Spectrochem) with a 96% assay was used as received. Milli-Q water (18 MΩ-cm) was used to hydrolyse the chelated alumina sols. The copper sheets used in the preparation of sample holders were 0·1 mm thick and were of commercially available grade. These were ultrasonically agitated in 0·1 M H_2SO_4 for 200 s to clean the surface of residual oils and subsequently sonicated in a large excess of Milli-Q water in order to make them usable for electron microscopy. The nickel TEM grids (Agar, UK) used for sample mounting, were of 3·0 mm diameter, and 300 mesh size.

Electron microscopy was done on a JEOL : JSM 6400 electron microscope, at an accelerating voltage of 5 kV, at a scanning probe current of about 10^{-9}A with the working distance focused between 30 and 34 mm. The resolution hence obtained for a secondary electron image was estimated as about 10 nm or better. The samples were mounted for imaging, using fast-freeze and freeze-fracture techniques, as will be described later.

2.2 Methods

2.2.1 Preparation of samples by the sol–gel process
About 3·0 g of ASB was weighed out in a Teflon-coated, screw-capped sample bottle in a glove box, under inert gas flow, so as to minimize atmospheric hydrolysis. About 15 ml of previously dried IPA was added to it and the mix ultrasonically agitated at 18·750 kHz at 90 W output for approximately 600 s on a Branson-450 probe type sonicator, using a 12-mm diameter probe disruptor horn tip. The immersion of the probe tip was adjusted to about 2 mm below the liquid level in order to achieve maximum turbulence.[13] The alkoxide was enclosed in a cooling jacket and a temperature of 28°C was maintained throughout the sonication process. About 3·0 ml of EAA corresponding to a 1 : 1 molar ratio with ASB was added to the alcoholic alkoxide and sonication was performed for 900 s, to complete the room temperature chelation process, as reported in literature. IPA served as a mutual solvent for the ASB–EAA system and improved the optical transmittance of the chelated or structurally modified precursor. Water required to hydrolyse the chelated alkoxide was added at the rate of 0·4 ml g^{-1} h^{-1} of precursor, using a calibrated micropipette, operating on an electric suction and release. From previously conducted pilot experiments, it was determined that a 1 : 1 chelated system sonogels at 1·0 ml of water added, when water is added at the specified rate. The samples taken up for direct observation on the cryo-SEM, were those of the unhydrolysed chelated alkoxide, and fully hydrolysed sonogelled species.

2.2.2 Preparation of samples for SEM mounting
Copper plates used for the mounting of the chelated alkoxide, were cut into approximately rectangular sections of 12 mm by 8 mm, with a 4 mm by 2·5 mm projection along the width (Fig. 1). A single TEM grid was placed on the projecting arm of the copper plate with its overhanging edges

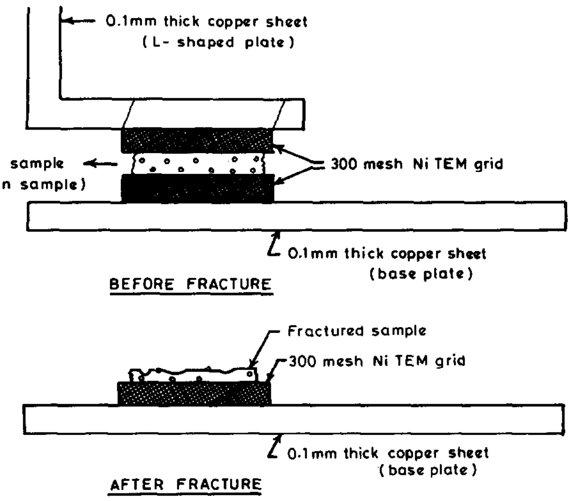

Fig. 1. Fabrication of the copper base plates to be used in the mounting and fixing of fluid labile samples for cryo-SEM imaging. Commercially available copper sheets about 100 nm thick are cleaned according to the procedure specified in the text and 300-mesh TEM nickel grids provide a 'holey' support for the sample. The smaller copper sheet is bent into an 'L', to facilitate specimen fracture inside the SEM by means of lateral shear. In the mounting of the specimen, the sample undergoes a fast-freeze and a freeze-fracture step which makes 'direct' imaging possible.

glued to the underside of the copper plate with a quick-setting adhesive. Another copper section was cut in an 8 mm by 2·5 mm size, to complement the projection of the base plate designed earlier. An identical TEM grid was fixed and glued to this section. This plate was then bent to an L-shape (Fig. 1) to facilitate fracture of the specimen inside the microscope's airlock chamber and make direct imaging possible. Both the copper plates, with the TEM grids on their facing edges were then used to sandwich the fluid sample, before mounting under the electron beam. The 12 mm by 8 mm section of the larger copper plate was used as the clamping area under the cryo-specimen holder mounted on the cold stage, for microscopic viewing.

The sol samples of the 1 : 1 chelated alkoxide, one before the addition of any water, and the other on complete gelling as a result of controlled hydrolysis, were collected from their screw-capped bottles. The batch volume was approximately 20 ml. Under the controlled environment of the glove box, about 100 μl of each sample was extracted from the sample bottle using a microsyringe, and sandwiched between the TEM grids using forceps. The sandwich containing the fluid, labile sample, was transferred to a standard electronic desoldering tool which was used as a plunger. The sandwich containing the sample was plunged into liquid Freon at −160°C at very high speeds, to initiate a rapid solidification into a glassy state. Crystallization was prevented, and the liquid state of matter preserved within the rapidly solidified sample. Hence, the samples were thermally fixed, as opposed to the conventional, chemical means of sample fixation. The samples were clamped under the base plate of the specimen holder, mounted on the cryo-stage, and the entire assembly kept immersed under liquid nitrogen at −196°C, until they could be taken up for imaging.

The electron microscope was maintained at a temperature of about −170°C, using the JEOL cold stage, consisting of two specially designed Dewar flasks. One of these cooled the fracture stage in the airlock chamber, while the other cooled the viewing stage in the specimen chamber. To bring about a rapid cooling of the stages, cooling was achieved by conduction through a copper braid at liquid nitrogen temperatures, which functioned as a heat sink.

When the microscope was ready for use, the cryo-stage on which the samples were mounted was introduced into the airlock chamber onto the fracture stage of the electron microscope. The samples were allowed to stabilize inside the airlock chamber for about 900 s. Some etching may take place during this time. Using the specially designed fracture knife, present on the JEOL stage, the sandwiched samples were subjected to a lateral shear of a sufficient magnitude to separate the adjoining copper plates, so as to rupture the rapidly solidified surface and expose the fluid, labile surface to the electron beam (Fig. 2). The fast-frozen and freeze-fractured samples were gold-coated to a film thickness of about 100 mm using the cryo-evaporator specially constructed for this purpose. The cryo-stage carrying the samples was transferred to the specimen chamber for microscopic imaging. The electron beam was turned on and the samples viewed for microstructural information.

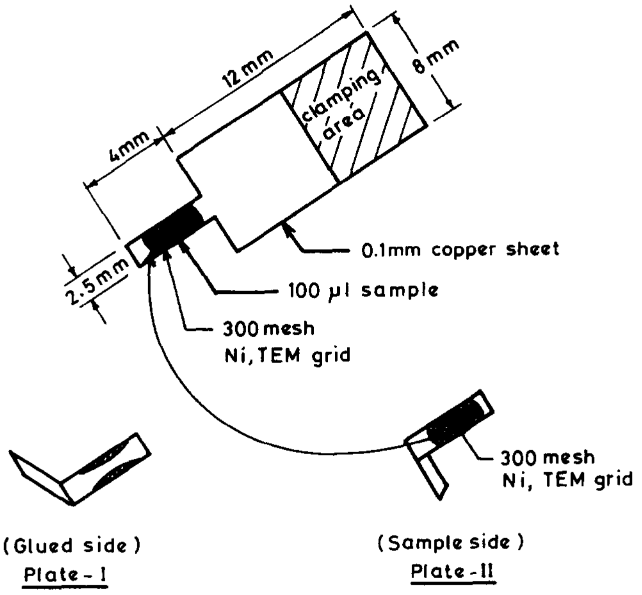

Fig. 2. Fractured specimen mounted on the TEM grid, as seen by the electron beam. The liquid state of matter is preserved inside the rapidly frozen sample.

2.2.3 Generation of microscopic contrast

Microstructural detail, i.e. contrast generation in the SEM, in SEI mode, is usually achieved either by a variation in the chemical composition along the depth of field (compositional contrast) or by an intensity difference of the secondary electrons generated due to topography and edges (topological contrast). Microstructural information from the homogeneously chelated alkoxide system was obtained as a result of a topological contrast. The electron flux pinning centres appear bright in the photomicrograph and generate a good topological contrast over the dark major phase of the matrix. However, in the absence of sharp boundaries, edges and faces in non-crystalline, fluid media, microstructural detail does not stand out in relief and hence the contrast generated in the microscopy of fluid samples is far less than that in the microscopy of solid samples, where the number

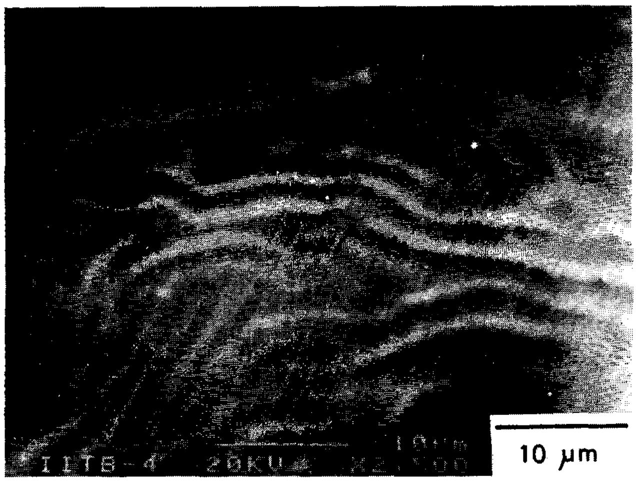

Fig. 3. Electron micrograph of an unhydrolysed, chelated, alcoholic alkoxide after probe-type sonication, showing a flat microstructure, characteristic of a homogeneous, isotropic, liquid phase. Bar = 10 µm.

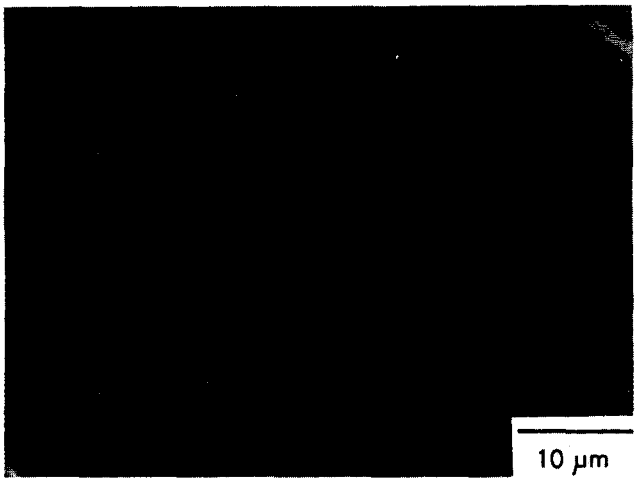

Fig. 4. A 1 : 1 chelated system at its gelling point is seen to possess a wavy microstructure which emerges in low relief and a faint topological contrast over the major phase. Such a wavy matrix is a characteristic of a polymeric alumina gel. Bar = 10 µm.

density of the electron flux pinning centres is higher due to the presence of grains and grain boundaries. Some contrast enhancement, to get a well-defined particulate morphology, was done by subtracting the adjoining gray shades from the images, so as to achieve an improvement in image quality.

3 RESULTS AND DISCUSSION

The first sample viewed for microstructural detail, was an unhydrolysed, alcoholic, 1 : 1 chelated alkoxide, synthesized in the controlled environment of the glove box, under carefully controlled conditions. Visually, the sample appeared fully transparent and its electron micrograph as seen in Fig. 3, shows a flat microstructure, characteristic of a homogeneous, isotropic, liquid phase with no microstructural or morphological detail. Incipient and uncontrolled hydrolysis has been reduced or perhaps avoided, by conducting the process in a glove box under inert gas flow, by using a chelating agent, and the incorporation of alcohol into the sol under continuous sonication conditions. Agglomerated alumina is absent in the micrograph, and this suggests that such a control over the hydrolysis process is adequate.

When the unhydrolysed sol obtained as described, is hydrolysed at the specified water addition rate, under constant temperature, under continuous sonication conditions, it sonogels at the addition of 1·0 ml of water. The sonogel, forming the second sample to be imaged for microstructural detail, yields the micrograph shown in Fig. 4. The microstructure in this case, is characterized by the emergence of a wavy matrix—a characteristic of a polymeric alumina gel.

In order to ascertain the reproducibility of the cryo-SEM data, and to eliminate the possibility of artifactual information being recorded, about 10 samples, having an identical batch composition and processing to those chosen as sample points, were imaged for microstructural detail. The micrographs obtained at every sample point were similar and microstructural information collected from each of them identical, suggesting a good technique reproducibility.

4 CONCLUSIONS

The microscopic interactions in chelated alkoxides at the unhydrolysed sol and the sonogelled stage, have been imaged by cryo-SEM for the first time, by using a direct imaging technique for *in-situ* visualization. Samples are prepared by a fast-freeze and a freeze-fracture process conducted in liquid cryogen, to preserve the fluid, labile state of matter within a rapidly solidified sample. Samples are thermally fixed, and fracture exposes the fluid phase to the electron beam and makes direct viewing, without the appearance of microscopic artifacts, possible. Results obtained from the characterization technique, developed and applied to chelated alkoxides, are highly reproducible and we have demonstrated that the cryo-SEM provides a new access to morphologies, microstructures, and microstructure evolution in chelated aluminum alkoxide systems.

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