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# Measuring Agglomerates in Ceramic Fibres using AFM

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## Abstract

*The presence of agglomerates in ceramic powder compacts has a detrimental effect on the strength of fired ceramics. In this paper, it is shown how an atomic force microscope has been used to image the surfaces of ceramic powder compacts containing polymer and solvent. Particular agglomerates were observed on the surface of these mouldings in the pre-fired state and the evolution of agglomerates was studied over a period of time. The size of these was related to the final microstructure of the fired ceramic. These observations were found for both the water and solvent based mouldings investigated. © 1998 Elsevier Science Limited. All rights reserved*

## 1 Introduction

It is now well accepted that the strength of ceramics is governed by the grain size[1] which, in turn, is predominantly influenced by the size of particles in the ceramic powder compact prior to firing. A way to control the particle size of the mouldings is to colloidally process the raw material to give a fine suspension.[2] After the addition of polymers to this suspension, the excess solvent is removed, leaving a paste of a high particle concentration from which ceramic parts can be moulded, fired and used. However, despite the fine particle size (i.e. $< 1\,\mu$m) in the original suspension, the fired ceramics have low strength. This is attributed to the presence of large grains. So, why are there large grains in the ceramic which have been made from a fine suspension? The presence of large grains in fired ceramics arises from either agglomerates (that are clusters of particles from which the bulk ceramic is comprised) or the sintering temperature.[3] Also, the soaking time at the sintering temperature is critical and can determine the final grain size.[3] Therefore, it is important to know the size of particles and agglomerates especially in the pre-fired state so the properties of ceramics can be more closely controlled.

Traditionally, techniques such as electron microscopy and laser light scattering, have been used to determine the particle size and distribution within suspensions. However, the measurements are done on dilute systems, either in the wet or dry states, which may not represent the bulk properties of a concentrated dispersion. There are techniques[4–6] available which can determine the particle size of concentrated dispersions (i.e. $> 1\%$ g/g solids). However, there are still problems. For example, in electroascoustic[4,5] determinations of particle size, the interpretation of results is complicated, particles need to have an electrical charge, they must differ in density from the surrounding medium and the technique is only suitable for particles $< 10\,\mu$m in size. The Coulter counter[6] is also limited to $<10\%$ (v/v) solids. Many of the problems discussed above have recently been overcome using atomic force microscopy (AFM).[7] This apparatus was used to determine the size of particles and foreign matter in ceramic powder mouldings containing an initial composition of 73% (g/g) zirconia, 17% (g/g) polymer and 10% (g/g) water. In this study, the growth of crystals on the surface of ceramic powder mouldings was closely followed with the AFM over a period of 24 h. It was observed that these crystals were not present on the surface immediately after extrusion but gradually appeared with drying at room temperature. The size of these crystals observed on the unfired compacts was found to cause flaws of a similar size as the crystals in the sintered ceramic. The presence of these flaws consequently reduced the strength of ceramic rods by 80 MPa.

AFM is an attractive tool to use in the processing of ceramics as it allows examination of samples whilst still wet. Furthermore, a ceramic powder compact that has a high solids concentration can be probed without changes to its immediate environment. For example, specimens viewed in the scanning electron microscope (SEM) have to be completely dry and often require a coating with a conducting material in order to be imaged. This can dramatically change the surface features and thus not be representative of the true surface. The advantage of using the AFM to image pre-fired compacts is that the material can be rejected from a production line and potentially recycled. This has enormous implications in the processing of ceramics.

The work presented in this paper shows how the AFM has been used to follow the growth of surface agglomerates in ceramic powder compacts, using extruded fibres as a case study. The appearance of agglomerates on the surface of the mouldings was imaged with the AFM over a period of time. The size of agglomerates on the fibres was related to the final ceramic surface microstructure. Both water and solvent based fibres were investigated in order to study the effect of solvent removal on the rate of formation of agglomerates.

## 2 Experimental Procedure

### 2.1 Preparation of ceramic powder compacts

The water based ceramic powder compacts were made with material obtained from Viking Chemicals (Follenslev, Denmark). The plastic sheets of raw material contained 66·1% (g/g) zirconia (8 mole % yttria stabilised), 25·3% (g/g) total polymer [which includes poly(acrylate) as the dispersing agent, cellulose as the binder and glycerol as the plasticiser], and 8·6% (g/g) water. More information about the material is described elsewhere.[6] Ram extrusion was used to make fibres of 150 $\mu$m diameter and these were fired to 1420°C, 2 $h^{-1}$.

The solvent based ceramic powder mouldings were prepared in our laboratories. A zirconia powder containing 8 mole % yttria [Grade HSY8, Daiichi, Zirconia Sales (UK) Ltd.] was vibro-milled for 130 min in the presence of 3% (g/g) hypermer KD1 (ICI Surfactants, UK) and acetone. Zirconia beads of 10 mm diameter and a polyethylene container was used. After milling, the particle size of the dispersion was $< 1\,\mu$m as measured by laser light scattering (Mastersizer E, Malvern Instruments, Inc.). To 26·2 g of this slurry, 1·3 g octanol and 1·3 g of paraloid, B7-MEK [Rohm and Haas (UK) Ltd] was added. Excess solvent was allowed to evaporate under ambient conditions whereby a thick paste was formed [87·4% (g/g) zirconia, 4·8% (g/g) total polymer and 7·8% (g/g) total solvent]. This paste was then immediately used to make 150 $\mu$m diameter fibres and sintered to 1400°C for 1 h.

### 2.2 Atomic force microscopy

A contact mode AFM, Nanoscope E, from Digital Instruments was used to image the surfaces of the wet and fired ceramic powder compacts. Details of the experimental set-up are described in more detail in Ref. 7. A 250 $\mu$m scanner was used but only 20 $\mu$m areas were imaged to avoid the AFM cantilever crashing into the sides of the fibre due to the curvature. Fresh cantilevers were always used for a new experiment to ensure that the apex of the tip was not worn from repeatedly imaging hard ceramic surfaces and was not covered with matter picked up during imaging.

## 3 Results

### 3.1 Water based fibres

AFM was used to image the surface of a wet fibre as a function of drying time. Immediately after extrusion, it normally took about 5 min to commence imaging with the AFM whilst the epoxy resin used to fix the fibre to the AFM stub set. Prior to gluing the extruded fibre onto the stub, it was stretched by pulling the ends of the fibres. This was done to force agglomerates to the surface of the small diameter fibre. If the agglomerates are present in the fibre, then they should protrude through the surface. It must also be mentioned that the slurries used to make the plastic sheets from which the fibres were extruded, were passed through a 1 $\mu$m filter to ensure that no large agglomerates were present. Therefore, any agglomerates $> 1\,\mu$m in size found in the AFM study are either already present in the plastic material or have formed after extrusion.

An AFM image (400 $\mu m^2$) of the water based fibre is shown in Fig. 1, 10 min after extrusion. The size of the zirconia particles, the major constituent of the fibres, measures to be approx. 0·7 $\mu$m and can be clearly seen on the surface. The topology of the fibre surface is uneven, with a 1 $\mu$m height difference measured between the peaks and troughs. There are mounds of varying diameter protruding from the surface. These protuberances were not caused by the extrusion die which normally produces striation lines. It is important to mention that no mounds were observed on the surface of the plastic material used to make the fibres (Fig. 2).

The section of the fibre surface shown in Fig. 1 was imaged at regular intervals over a 20 h period to follow surface topology changes. Figures 3 and 4 are images of the fibre surface after 1 h and 20 h drying under ambient conditions. The scanned areas in these figures are not identical to that shown in Fig. 1. Thermal drift, piezo hysteresis and

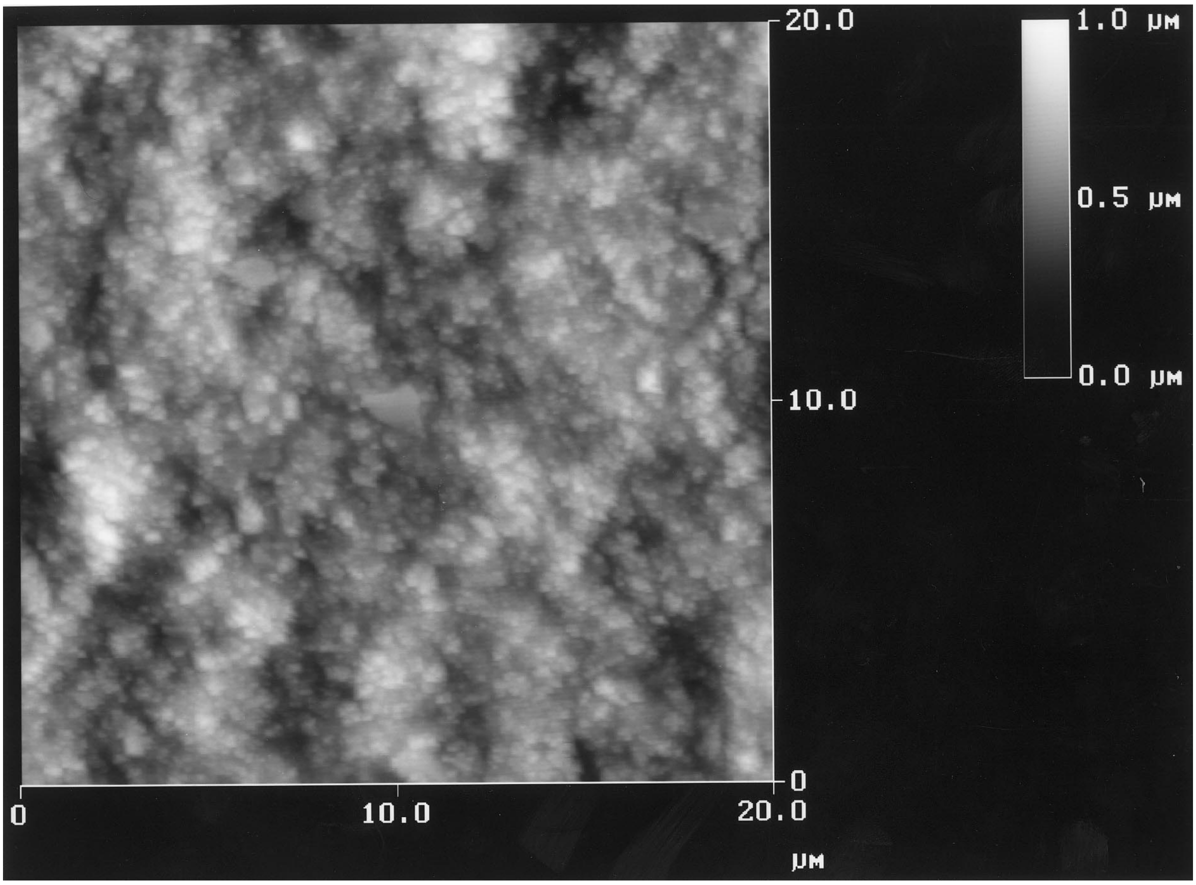

**Fig. 1.** An AFM profile of the surface of a water based fibre of 150 $\mu$m diameter, 10 min after extrusion. The right hand scale bar indicates the local surface height (normal to the plane of the figure).

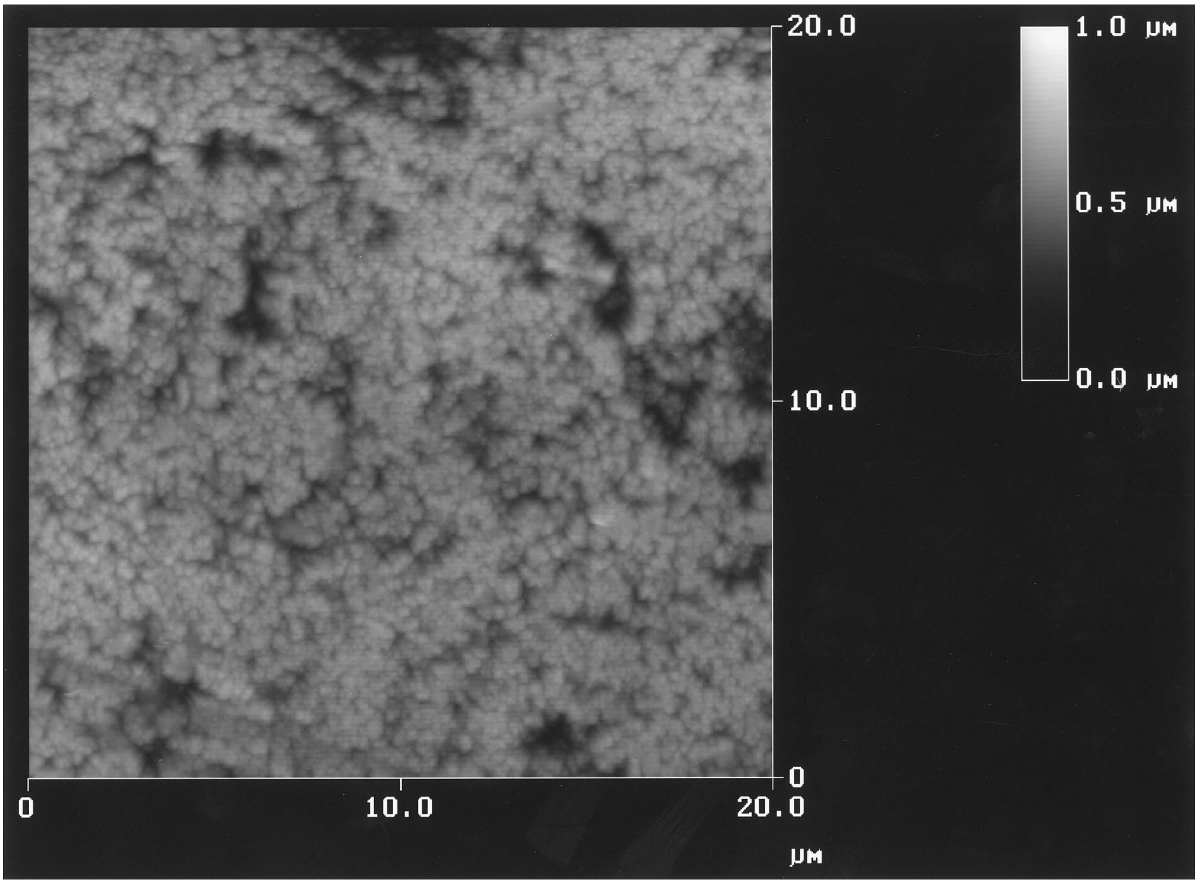

**Fig. 2.** The topology of the surface of the plastic material prior to rehydrating, mixing and extrusion of fibres as observed with AFM.

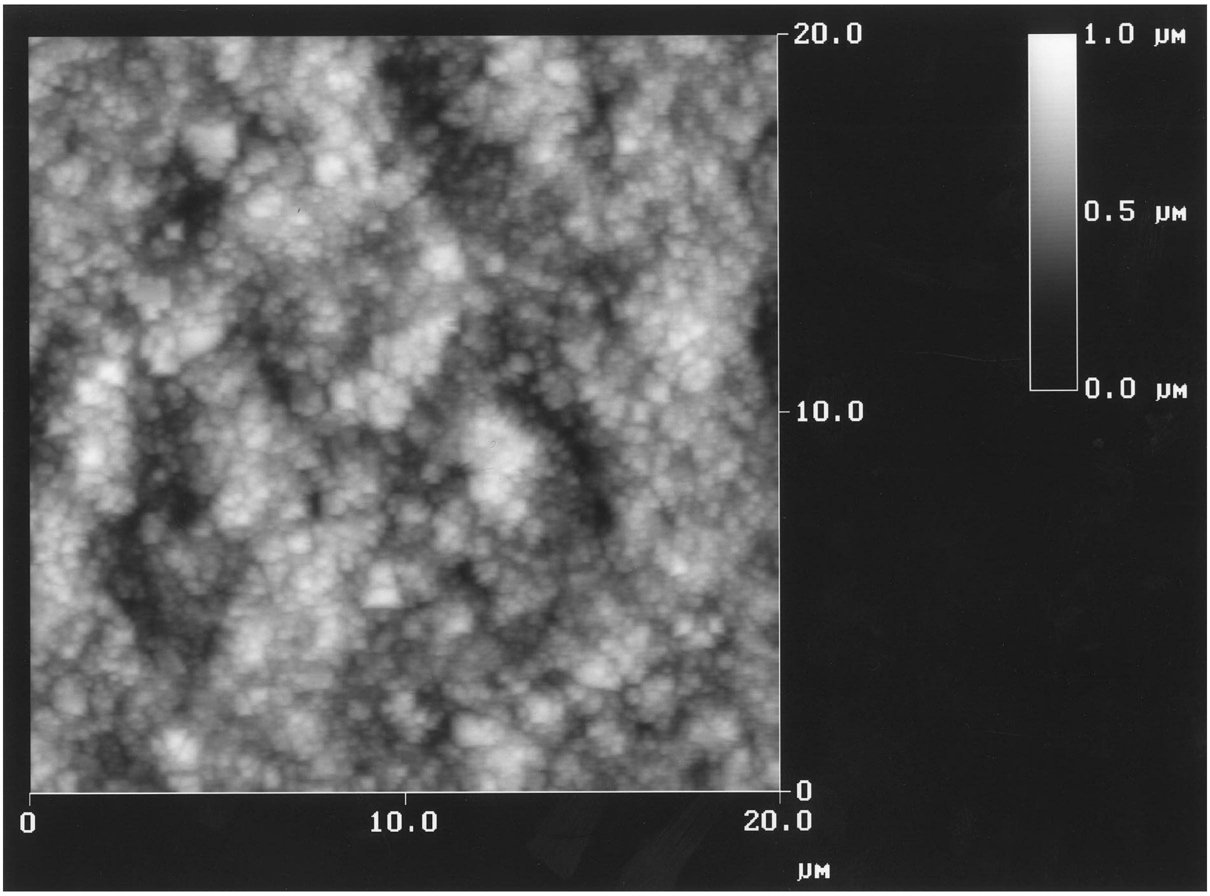

**Fig. 3.** The same area of the fibre surface 1 h after extrusion as observed with the AFM.

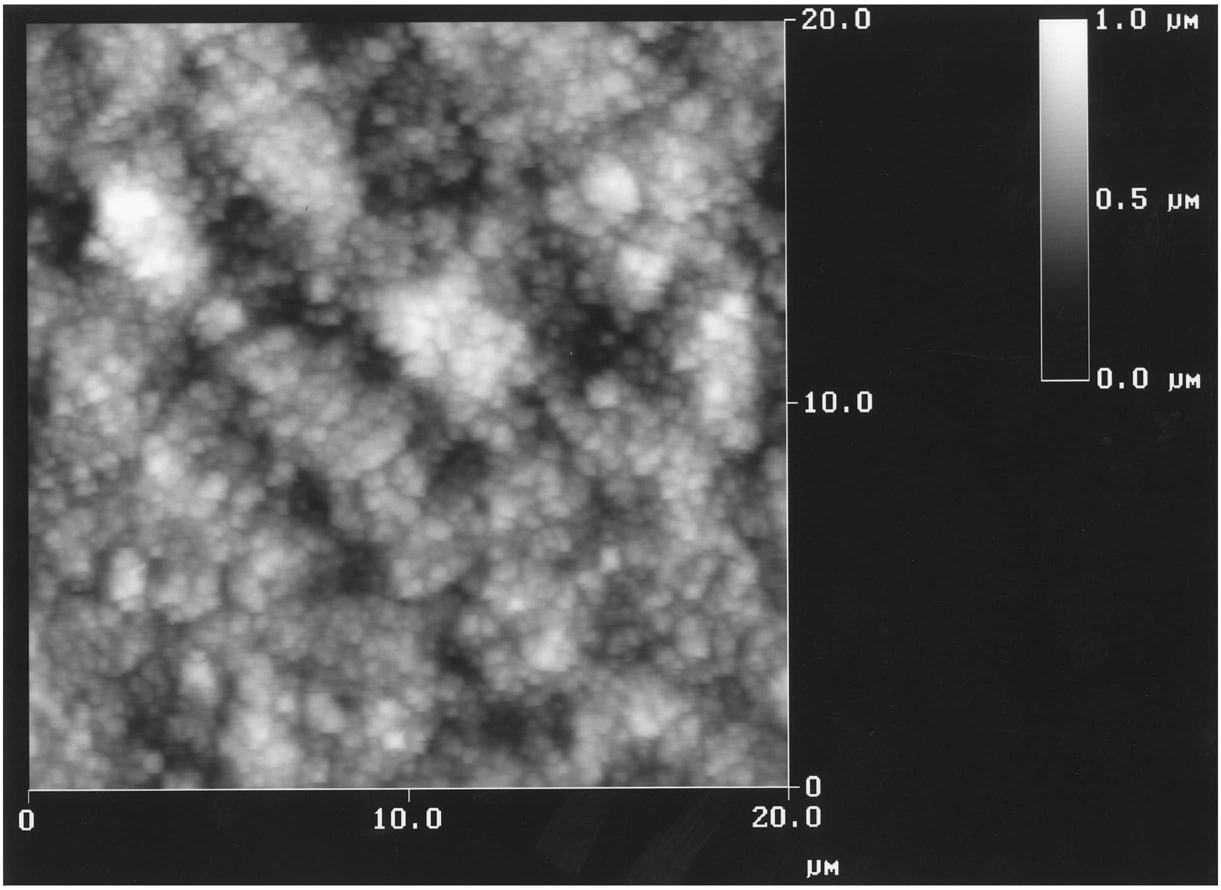

**Fig. 4.** An AFM micrograph showing topographical features of the fibre surface, 20 h drying time at room temperature.

fibre shrinkage make it difficult to image exactly the same area. Therefore, only sections of Fig. 1 are visible in the proceeding figures. The most striking feature is that the surface of the fibre has not changed dramatically with time. For example, the particle size of the zirconia is still the same at $< 1\,\mu$m, the mounds are still present and protrude from the surface as observed in Fig. 1. Therefore, it may be concluded that the mounds are either already present in the paste prior to extrusion or formed immediately upon extrusion and it is not possible to see the growth of these mounds with an AFM.

These water based fibres were fired to 1420°C for 2 h and the microstructure was assessed using AFM. It was not possible to image the same fibre surface after firing because the fibre was destroyed when the resin was removed and prying the fibre loose from the glue damaged the fibre. Therefore, another section of the fibre strand was fired and imaged. Figure 5 shows the typical topographical features of the fired fibre surface. The microstructure of the fibre varies with grains ranging from 0·56 to 5·80 $\mu$m in size. It is much smoother and the mounds which stuck out from the surface in the pre-fired state are not as pronounced.

In order to ascertain if the size distribution of mounds observed in the pre-fired fibre corresponded to that measured for the fired fibre, random areas of the wet and fired fibres were imaged and analysed. Table 1 shows the results of measuring the mounds and the grains on the wet and fired fibre surfaces. In both cases, the size distribution of the mounds and the grains are broad. After taking into consideration the ~20% shrinkage upon firing, it is interesting to point out that the range of mound sizes for the wet surface concurs with that for the sintered surface as does the frequency of their occurrence.

### 3.2 Solvent based fibres

A similar set of imaging experiments was also carried out on the solvent based fibre. This was done to closely follow surface changes with time and to compare with the observations noted for the water based fibre. It is important to note that the zirconia powder used to form the mouldings from which the fibres were made, was different in the two systems studied and, therefore, a direct comparison was not possible. These experiments additionally investigated the effect solvent had upon the rate of formation of the mounds as the surface was exposed to the atmosphere.

Figure 6 presents a 400 $\mu m^2$ micrograph of the fibre surface taken 10 min after extrusion. This fibre was also stretched to force agglomerates to stick out from the surface. The zirconia particles are fine being $< 1\,\mu$m in size, similar to that

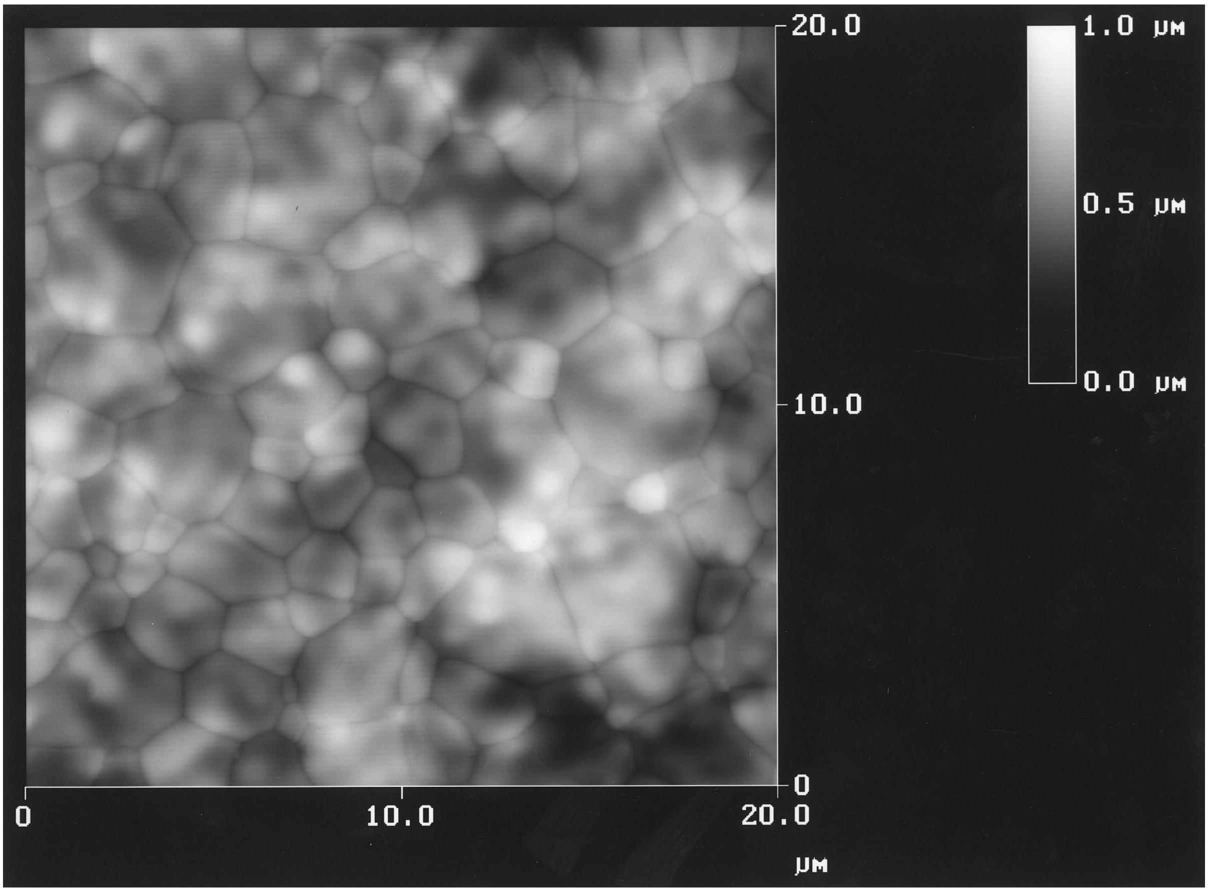

**Fig. 5.** AFM image of the fired fibre surface that shows the microstructure of 400 $\mu m^2$ area.

**Table 1.** A summary of the size range of mounds observed with AFM on the surfaces of both water and solvent based fibres

| *Type of fibre* | *State* | *Size range (μm)* |
|---|---|---|
| Water based | Pre-fired | 0·7—4·7 |
| | Fired | 0·4—4·2 |
| Solvent based | Pre-fired | 0·7—5·3 |
| | Fired | 0·6—4·9 |

observed in Fig. 1. Surface protuberances are also evident on the surface, matching the observations found for the water based fibre. There are a few streaked areas in this image, either caused by loose material present on the surface of the fibre or capillary forces. This same section of the fibre surface was also imaged as a function of time. Figures 7 and 8 show the surface of the fibre after 1 h and 20 h of contact with air, respectively. These images have fewer streaks than Fig. 6 because the loose matter on the surface has been removed with the AFM tip and the capillary forces have been reduced with solvent evaporation over time. It is apparent from studying Figs 6–8, that the scanned areas are not identical for the reasons explained earlier in the case of the water based fibre. The mounds did not change after 20 h exposure to the atmosphere, suggesting that again the mounds have formed immediately upon extrusion or were already present in the extrudate. Upon firing the fibre to 1400°C for 1 h, the surface protuberances have decreased in height as shown in Fig. 9. The size distribution of grains on the fired fibre was randomly measured (Table 1). After considering shrinkage, the range of 0·7 to 5·3 $\mu$m for the pre-fired fibre agrees well with the limits found for the fired fibre, similar to that recorded for the water based fibre.

## 4 Discussion

It has been demonstrated that the AFM can be used to image fibres containing polymer and solvent during the forming stage of the compacts. Topographical images show that the surfaces of both water and solvent based fibres do not change markedly during 20 h of drying in air. In particular, mounds protruding from the fibre surfaces were evident in both types of fibres. It was found that the size range and frequency of these mounds in the pre-fired state correlated with the values measured for the fired fibres. From these observations, it can be concluded that these mounds are agglomerates. However, it is difficult to say if they have either formed immediately upon extrusion or they were present in the original paste used to

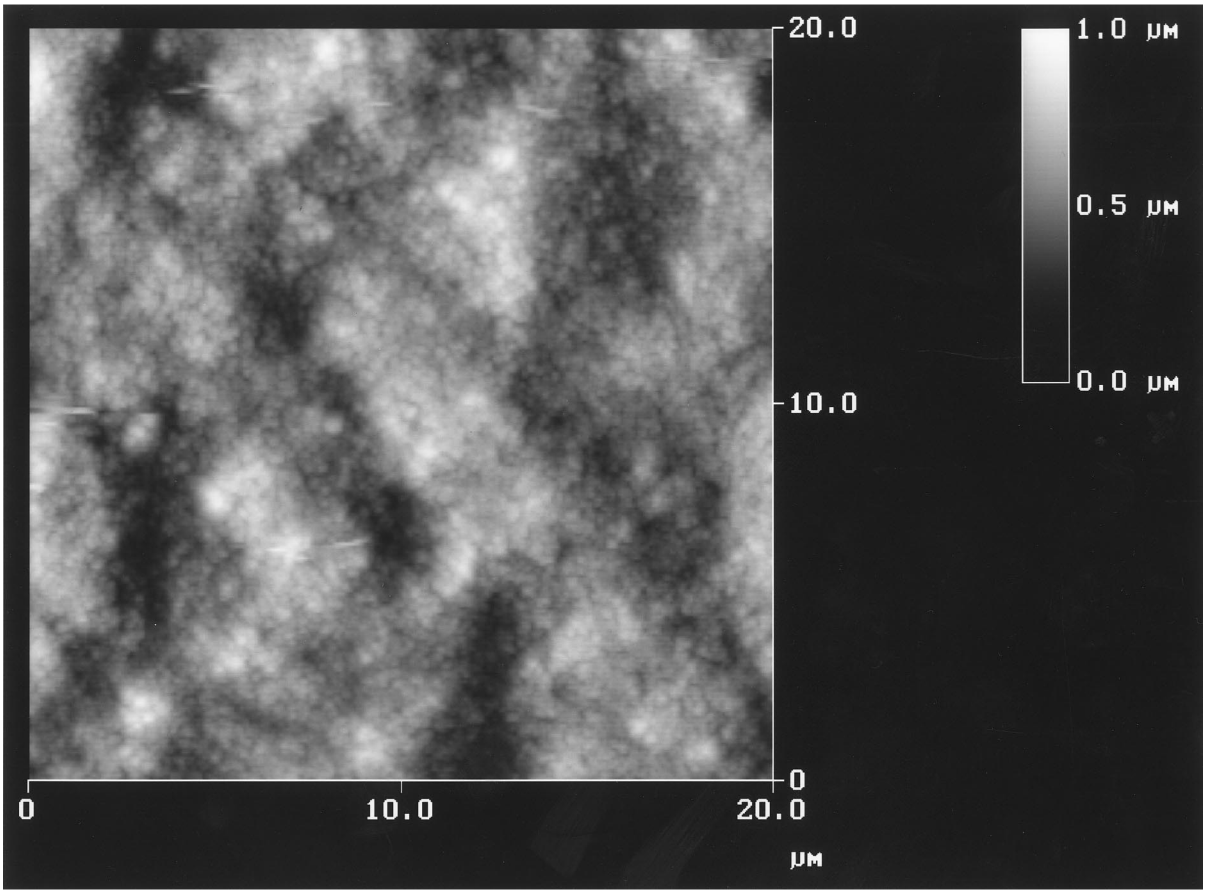

**Fig. 6.** The surface of a solvent based fibre immediately after extrusion as viewed by the AFM. An area of 400 $\mu$m$^2$ of the 150 $\mu$m

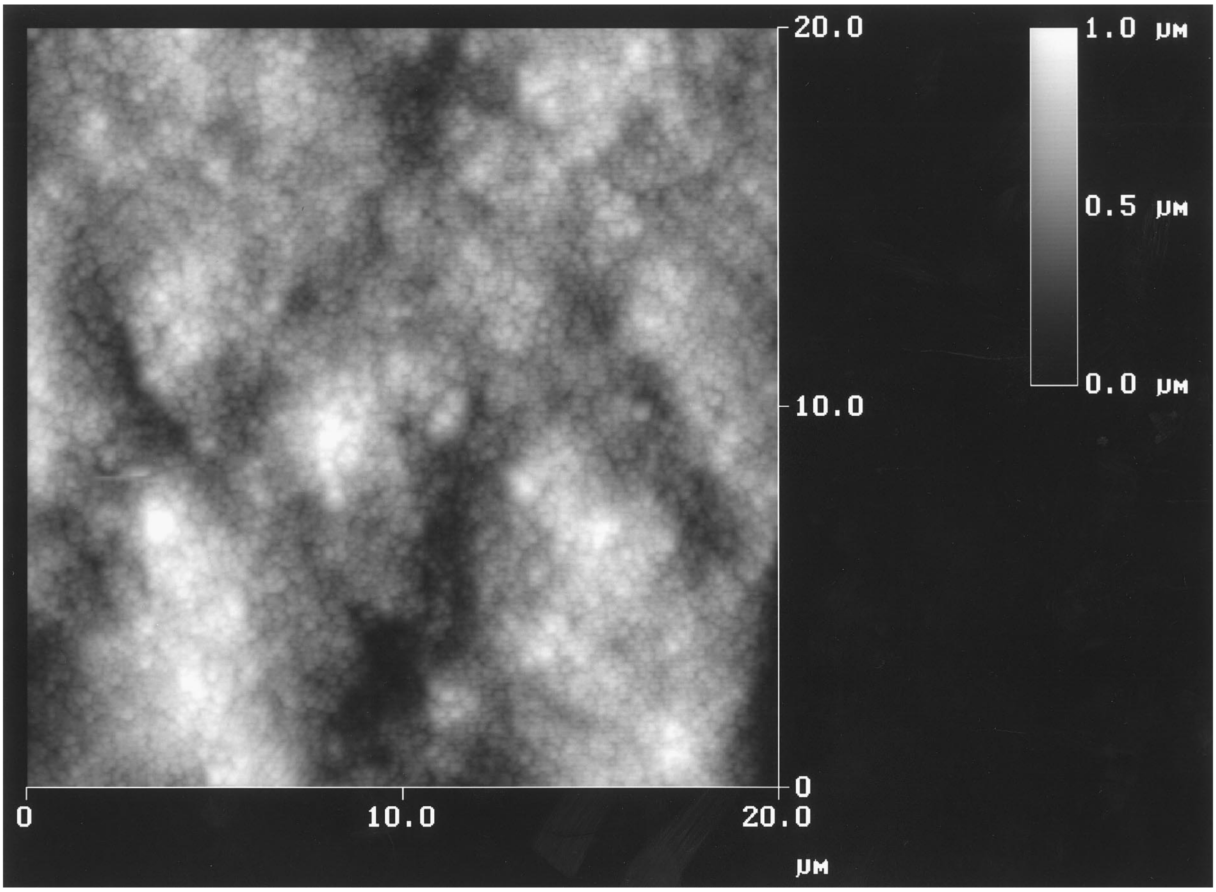

**Fig. 7.** The same section of the fibre surface, after 1 h exposure to the atmosphere.

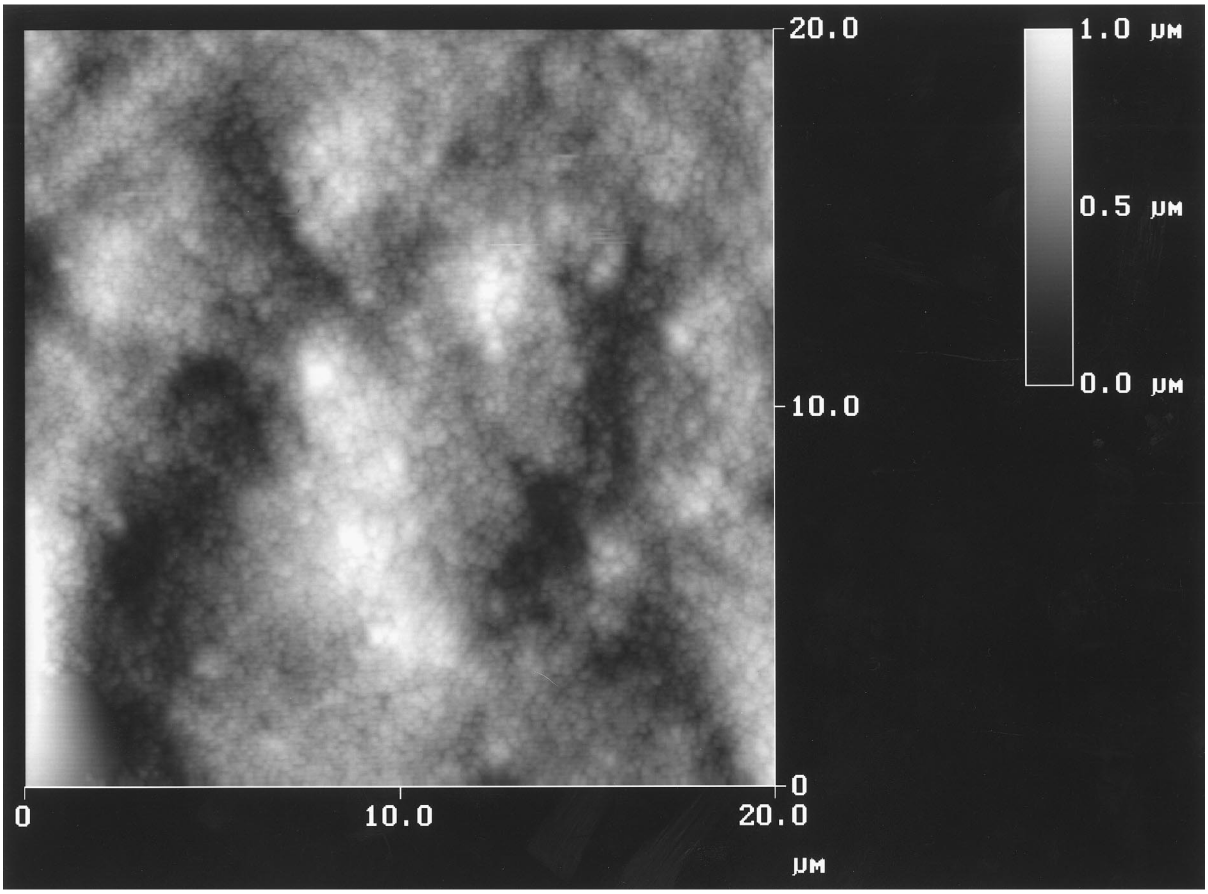

**Fig. 8.** An AFM image of the fibre surface. 20 h drying under ambient conditions.

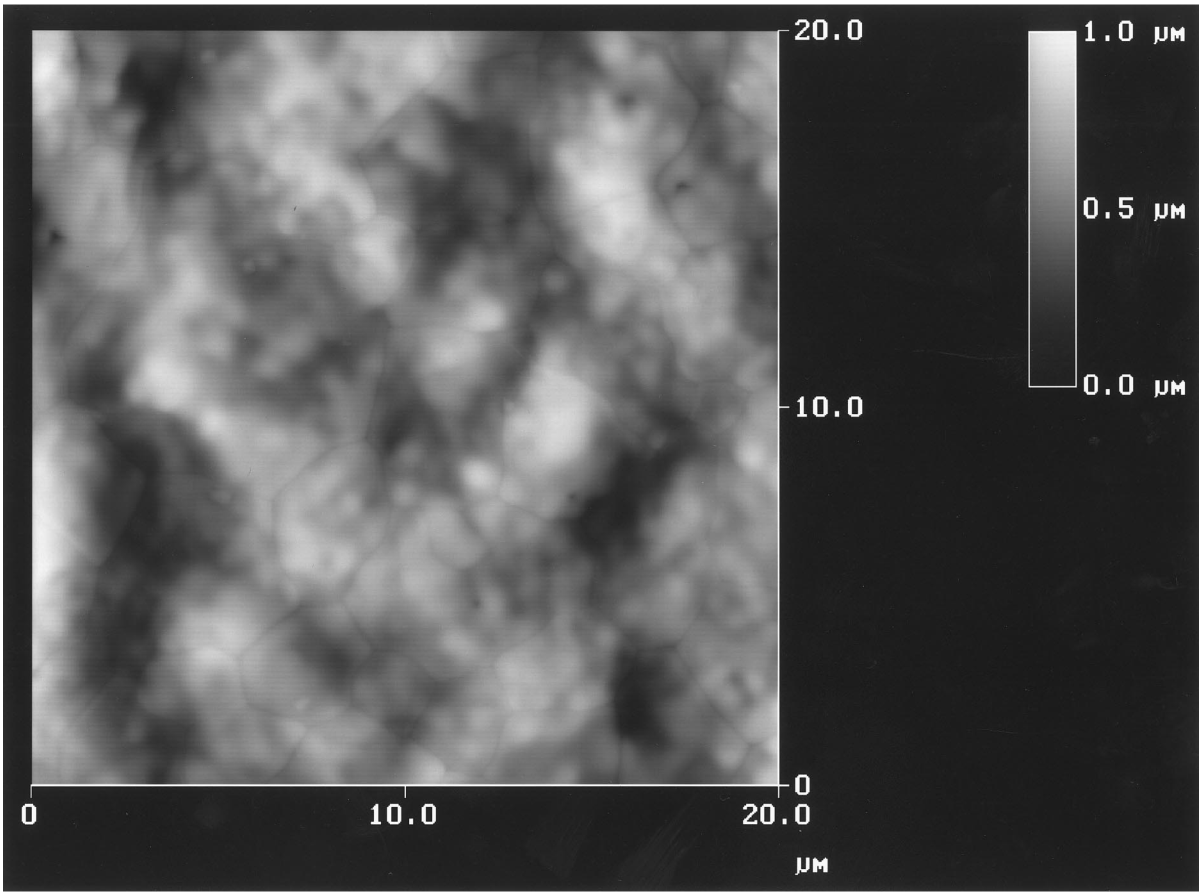

**Fig. 9.** A micrograph of the grains of a fired fibre surface as imaged with AFM.

make the fibres. Although the original material of the water based fibre was also imaged and no agglomerates were visible on the surface, they may still reside below the surface. Stretching the fibres after extrusion must force the agglomerates to the surface. This may be the reason why the surface of the fibres did not change with drying time because the agglomerates were fully formed in the paste and only exposed after extrusion and stretching. This is further supported by the experiments carried out on the solvent based fibre where the growth of agglomerates was also not seen. Surface changes should have been more pronounced in this example due to the rapid removal of solvent compared to loss of water. This was found not to be the case.

## 5 Conclusions

An AFM was successfully used to obtain topographical profiles of the surfaces of water and solvent based fibres as a function of drying time. Agglomerates were observed on the surfaces of the fibres. The size distribution of agglomerates in the pre-fired state correlated to the range measured for the fired fibres. These agglomerates did not form after extrusion as evidenced from the AFM images. This technique could be used to detect the size of agglomerates in ceramic powder mouldings. Size plays an important role in the final strength of fired ceramics.

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