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Comparative atomic force and scanning electron microscopic studies disclosing nanocrystallinity in cordierite glass-ceramics : examples of surface modification

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Abstract : The atomic force microscopy (AFM), because of its unique features, can be used for a variety of applications and provides excellent research and development opportunities in the area of nanoscience and nanotechnology of glass and glass-ceramics. In this study, microscopic experiments have been carried out using both AFM and SEM on polished and etched as well as fracture cordierite glass-ceramic surfaces to unfold their comparative capabilities. Most importantly, it has been exhibited that the AFM is capable to ascertain single tiny crystallites originated at the beginning of crystallization of glasses before scanning electron microscope (SEM) or X-ray diffraction (XRD) detects them. AFM provides extraordinary two-dimensional (2D), three-dimensional (3D), and quick surface plot (QSP) formats of images with unobscured (since no coating is necessary) views of nanostructures rather than obscured (since conducting coating is essential for insulators such as glass and glass-ceramics) and only 2D microstructural profiles of SEM. Development of interatomic forces (extended up to tens to hundreds of angstorms from the sample surface) between the atoms of the very sharp tip (probe) and those of surface (sample) during measurement results in unprecedented resolution (~0.1 nm) of images in AFM. While SEM produces images (resolution ~10 nm) based on secondary electron emission from the sample surface. By comparing the results with those of SEM experiments, the AFM is established as a simple and powerful technique for the characterization of nanostructures of glass-ceramics particularly of early stages of crystallization.

Keywords . Atomic force microscopy (AFM), scanning electron microscopy (SEM), cordierite glass-ceramics

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1. Introduction

Application of atomic force microscopy (AFM), a descendant of the Nobel Prize-winning scanning tunneling microscope (STM) developed in 1981, have grown and evolved at an incredible rate in the last decade. Inception in 1986 by Bennig, Quate and Gerber [1], the AFM is providing the excellent opportunity to examine a new world of nanoscience and nanotechnology of materials. The major advantages of applications of AFM in materials science are as follows :

(i) The AFM has a potential for providing three-dimensional (3D) information on the surface topography of samples at resolutions ranging from micrometer down to sub-nanometer scales.

(ii) The AFM enables the direct observation of non-conducting samples (*e.g.*, glass, ceramics, *etc.*), in contrast with scanning electron microscopy (SEM) of metal coated samples which often masks or even obliterates delicate microscopic structures so that the images may not provide an accurate picture of the studied surface.

(iii) The AFM can be operated not only in a vacuum but also in a non-vacuum (*i.e.*, air or liquid) environment, in contrast with SEM in vacuum only.

(iv) The AFM images contain quantitative information on the sample height, in contrast with qualitative SEM images.

(v) The AFM can provide new information which could not be obtained earlier with other microscopes.

Evidence for the successful application of AFM for investigation of glass and glass-ceramic surfaces comes from the studies of nucleation and crystallization because AFM is able to notice the formation of single tiny crystallites before XRD or SEM detects them [2]. The AFM reveals a continuous growing of ripples of the glass pattern with progress of heat-treatment time

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It is clear from the foregoing results that in order to obtain SEM images of glass ceramics, one has to etch the polished surfaces and coat with a metal such as gold. This coating

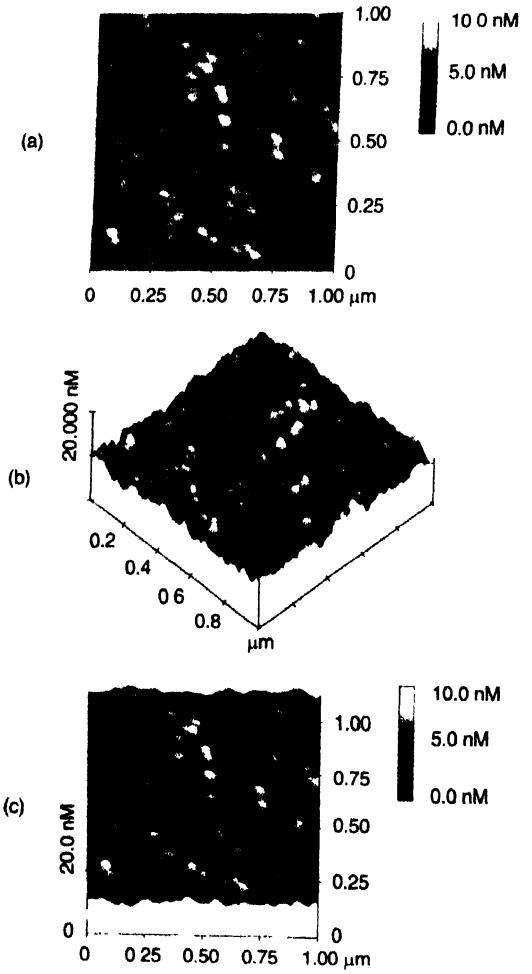

Figure 6. (a) 2D, (b) 3D, and (c) QSP formats of AFM images (height mode, z-scale : 10 nm) of a fracture surface of the crystallized glass (nucleation at 800°C for 2 h followed by crystallization at 1065°C for 1 h) without gold coating.

disguises or even erases delicate microscopic features. Furthermore, it is well known that the surface structures are

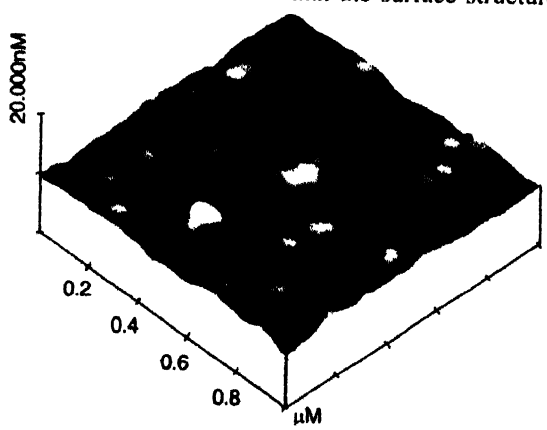

Figure 7. 3D format of AFM image (height mode, z-scale : 10 nm) of a fracture surface of the as-prepared glass without gold coating.

largely altered by the etchant concentration and etching tim [7]. Thus, the image obtained *via* SEM could not provide a accurate picture of the studied surface.

On the other hand, investigation with AFM does not requir any surface modifications such as polishing, etching or coating Fracture surface is most suitable for observation with AFM. S AFM can provide a more accurate (unobscure) surface structur than SEM. Moreover, the AFM images can be obtained in tw dimensions (2D), three dimensions (3D) and quick surface plo (QSP) formats with resolution from nanometer down t subnanometer range. This is possible due to development o interatomic forces between the atoms of the tip and those of th sample surface as shown in Figure 8. As the sample move

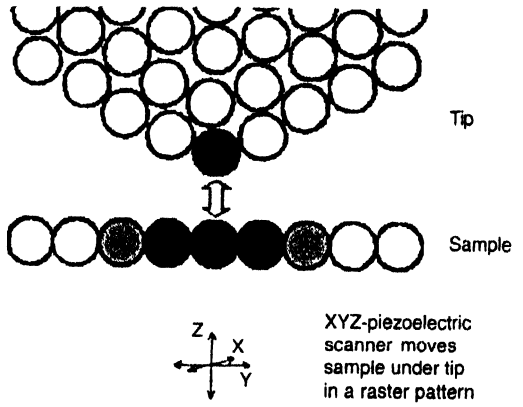

Figure 8. Interatomic interaction between probing tip and sample surfac (top), and sample movement (bottom) during imaging in AFM.

under the tip, the changing interatomic force causes th cantilever to bounce up and down with the contours of th surface. The topographic features of the surface is mapped ou by measuring the deflection of the cantilever which can b expressed as follows. The force, $F(r)$, between probing tip an sample is given by

$$F(r) = \frac{dU(r)}{dr} < 0 \qquad (1)$$

(where U = sample potential, r = distance between tip and sampl surface)

and the spring deflection, b, by

$$b = \frac{F(r)}{k} \qquad (2)$$

(where k = spring constant).

The 3D images are constructed by recording the cantilever motion in Z direction as a function of X and Y positions (shown in the bottom, Figure 8) of the sample (*i.e.*, in a raster pattern). In contrast, SEM images are constructed based on the secondary electron emission from the sample surface. It is not possible to obtain 3D images from the secondary electron emission.

4. Conclusions

This work provides a comparative information concerning the study of early stages of crystallization and nanostructuring of cordierite glass-ceramics using AFM and SEM techniques. AFM gives evidence of nanostructural features while SEM fails to reveal it. Because AFM imaging originated from the development of interatomic forces between the atoms of tips and those of sample surfaces, and AFM does not require any further surface modifications such as polishing, etching and coating. Fracture surface is most suitable to visualize unaltered micro-down to nano-structural features of glass-ceramics. By comparing the images obtained from AFM technique and the traditional SEM, he AFM has been established as a simple and powerful echnique for the characterization of evolutionary processes of crystallinity of glass-ceramics.

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