Particle size and morphology of hydrothermally processed MnZn ferrites observed by atomic force microscopy

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Atomic force microscopy (AFM) was employed to analyse ultrafine MnZn ferrite powders, obtained by precipitation from metal sulphates and sodium hydroxide at 110 and 190 °C, under hydrothermal conditions. Particle sizes measured on AFM images taken at the surfaces of pressed samples ranged from 10 to 40 nm, as a function of synthesis temperature, and were in good agreement with measurements made using X-ray diffraction and the Brunnauer–Emmett–Teller (BET) technique. Direct observation also showed that the particles were monodispersed and approximately spherical in shape, meeting the requirements for the production of high density sintered components. Using a straightforward sample-preparation technique, AFM proved to be a powerful tool for direct analysis of ceramic powder particles on the nanometre scale.

1. Introduction

Manganese–zinc ferrites form an important group of ceramic materials used in the fabrication of electric and magnetic devices. Specific sets of properties are achieved by appropriate control of powder characteristics and purity, which have a strong influence on the microstructure and properties of the sintered components. The hydrothermal synthesis of ferrite powders is increasingly gaining importance as a low energy process for obtaining ultrafine (submicrometre), highly reactive, crystalline and impurity free particles, having controlled stoichiometry and particle size [1]. Physical characterization of hydrothermal powders is generally performed using X-ray diffraction, the Brunnauer–Emmett–Teller (BET) technique, scanning and transmission electron microscopy (SEM and TEM, respectively). Morphology is often the most difficult characteristic to be analysed, because direct observation of ultrafine particles is only possible using high resolution techniques such as TEM, which require sophisticated sample preparation procedures.

Techniques of the new family of scanning probe microscopy (SPM) [2], some of them with atomic resolution capacity, are very promising tools for imaging particles in the submicrometre range. These techniques have been used to image surfaces of various materials [3], biological cells [4], and magnetic domains [5]. However, imaging non-conductive powder particles is not an easy task. As the particles are not attached to a surface, contact with the probe, when using atomic force microscopy (AFM), could remove them. The deposition of a film for coating and binding the particles to the surface can distort the actual particle image, especially when their size is in the nanometre range. In spite of these difficulties the choice of a proper technique with adequate sample preparation can make SPM a powerful tool for morphological analysis of powders.

This paper reports observations using atomic force microscopy, performed on samples of pressed MnZn ferrite powders, obtained by hydrothermal synthesis. Results concerning particle sizes determined with this method are compared with those measured using XRD and the BET technique.

2. Experimental procedure

2.1. Preparation of ferrite powders

Manganese–zinc ferrite powders were prepared with stoichiometric amounts of the appropriate metal sulphates and sodium hydroxide, treated hydrothermally at 110 and 190 °C (saturated vapour pressure). The stoichiometry obtained under these conditions was $Mn_{0.48}Zn_{0.52}Fe_2O_4$ as determined by chemical analysis. Powders were uniaxially pressed at 196 MPa into the form of discs, 11 mm in diameter and 2 mm in height, which were then glued on AFM sample holders.

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2.2. Characterization

Images of the surface of the pressed discs were obtained by AFM with a Nanoscope III (Digital Instruments) operating in tapping mode (TM), using a commercial silicon probe. AFM was used because these ferrites showed very high resistivity, so that scanning tunnelling microscopy (STM) could not be performed. TM was chosen because contact mode (CM) led to very noisy images, indicating that particles were being removed by the probe. In spite of operating in TM, contamination of the probe with powder particles could not always be prevented; when it occurred, the probes were changed, and the same results as before contamination were obtained. For each sample, the particle size was measured directly on AFM images taken in a total of 100 particle diameters at five different regions of the specimen. The average diameter of the particles, which were only approximately spherical in shape, was taken as the mean of the largest and the smallest dimensions, at perpendicular directions.

To determine the average particle size by XRD, a Philips diffractometer operating with CuK_α radiation and having a graphite crystal monocromator was used. The particle size was calculated from X-ray line broadening, using Hall's equation [6]

$$\varepsilon = \lambda/(\beta\cos\theta - \eta\sin\theta) \quad (1)$$

where ε is the particle size; λ is 0.1542 nm for CuK_α; β_{hkl} is the half-width of the (2 2 0), (3 3 3), (4 4 0) and (5 5 3) lines; θ is the Bragg angle; and η is the lattice stress.

Quantasorb equipment (Quantachrome Corp.) was used to determine the specific surface area by the BET technique. Helium picnometry (Micromeritics) was used to obtain the actual density of the powders. From the results of the specific surface area and density, the particle size, t_{BET}, was calculated by means of Equation 2

$$t_{BET} = F/(S_{BET} \times D) \quad (2)$$

where F is the particle's form factor ($F = 3$ for spherical, $F = 4$ for cylindrical and $F = 6$ for cubic geometry), S_{BET} is the specific surface area and D is the density obtained by picnometry.

3. Results and discussion

Fig. 1 shows AFM images of the surfaces of the two pressed powders. The powder in Fig. 1a was treated hydrothermally at 110 °C and the powder in Fig. 1b at 190 °C. Monodispersed particles approximately spherical in shape can be observed in these images. Measured particle sizes for the powder treated at 110 °C were 18 ± 2 nm, and 30 ± 3 nm for powders treated at 190 °C.

XRD data showed the presence of crystalline particles without impurities. Particle sizes obtained with this method were 13 ± 3 nm for powders treated at 110 °C, and 27 ± 3 nm for powders hydrothermally treated at 190 °C. Results obtained with the BET technique led to particle sizes of 14 ± 2 nm, for powders treated at 110 °C, and 25 ± 3 nm, for powders obtained at 190 °C.

From the above it can be seen that the results obtained using AFM are in good agreement with the other measurements, although there is a tendency for AFM to measure higher particle size values. This tendency can be understood considering the sample preparation procedure and the interaction between the specimen and the tip of the probe, i.e. tip convolution. If the particles are dispersed on the specimen surface, as illustrated in Fig. 2a, lateral interaction between the tip and the particles distorts the shape of the particles, increasing their size [7]. If the particles are closely packed, i.e. if they touch one another, as illustrated in Fig. 2b, interaction with the

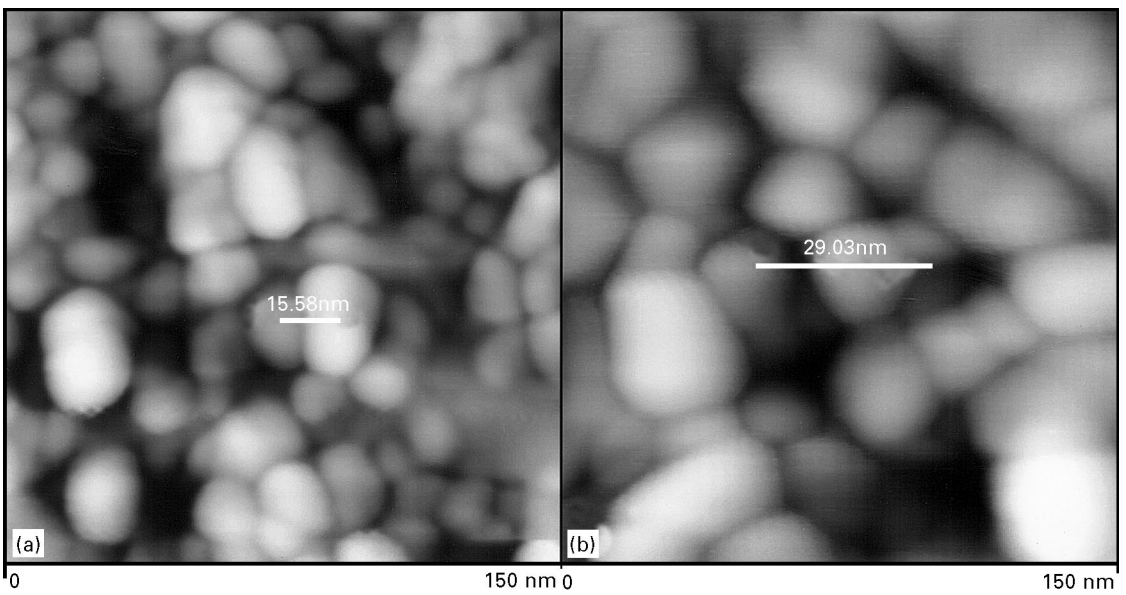

Figure 1 MnZn ferrite hydrothermally synthesized at (a) 110 °C, and (b) 190 °C (Data type: height). Z range: 30 nm for (a) and 50 nm for (b).

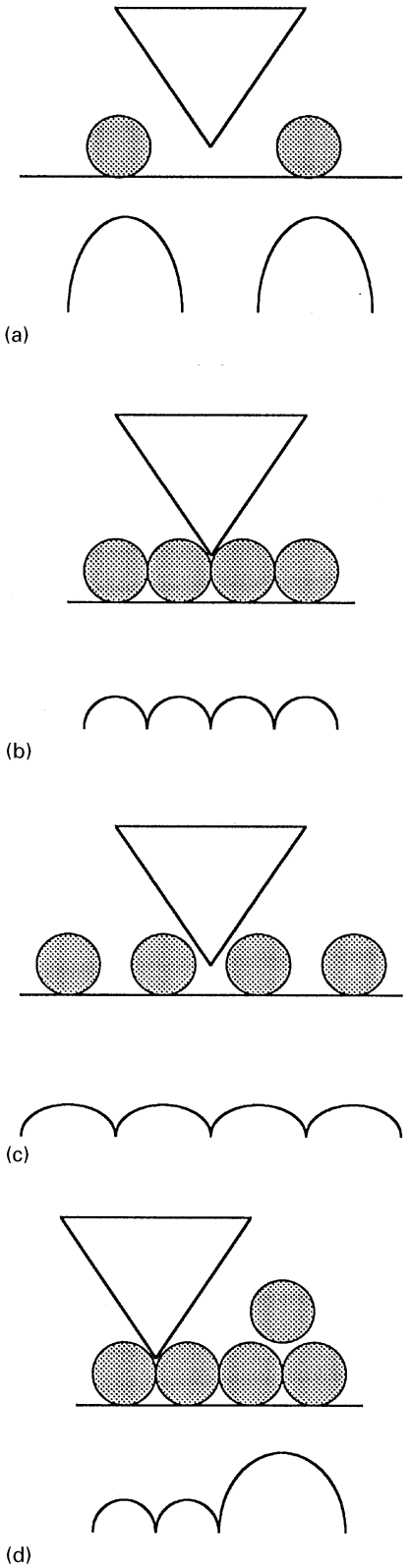

Figure 2 Interaction between the tip of the probe and the particles at the surface of the specimen: (a) dispersed particles, (b) particles touching one another, (c) particles not touching one another, and (d) a cluster of particles.

probe occurs mainly at the top of the particles, so that actual particle sizes should be adequately measured.

The sample preparation technique described in this paper was employed aiming to attain the configuration depicted in Fig. 2b. For this, the powders were compacted in order to minimize tip convolution.

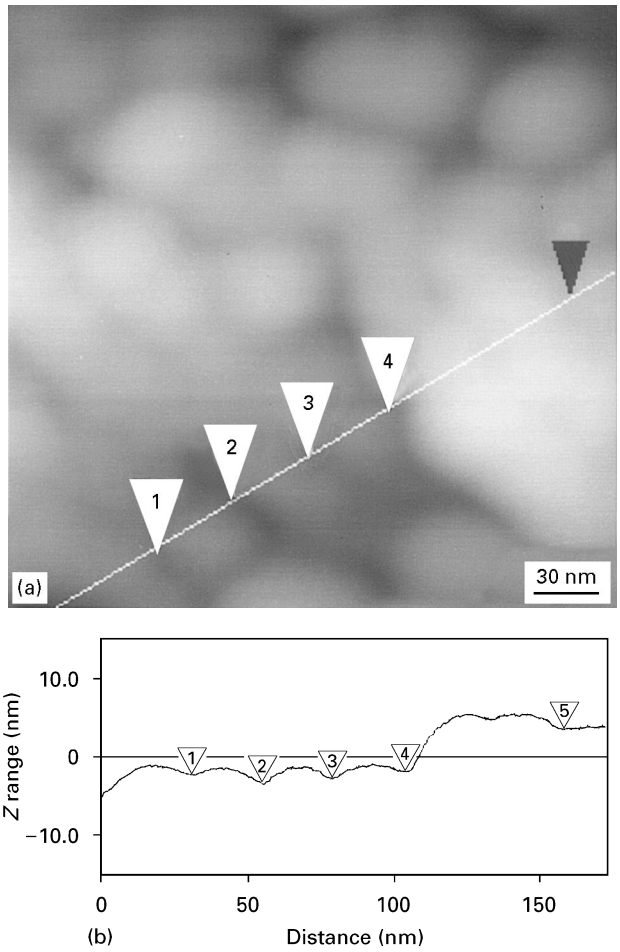

Figure 3 Topographical analysis of a MnZn ferrite prepared at 190 °C: (a) image of particles touching one another, and (b) topographical profile.

However, it is possible that in certain regions of the specimens, the particles were very close together but did not actually touch one another, as shown schematically in Fig. 2c. In this case, also due to tip convolution, the image exhibited larger particles, and was not taken into account for measurement purposes. A fourth case should also be considered, which arises when clusters of particles are formed at the surface of the specimen, leading to images of very large particles (Fig. 2d). The topographic profile of the surface shows that these larger particles are also higher than other particles, clearly indicating the presence of a cluster. The effect of the tip of the probe was investigated in order to measure the cluster regions. Many probes have been used that always give the same results. These "particles" were thus not considered in the measurements performed to obtain the "real" particle size.

Fig. 3 shows a topographical analysis of a cluster region of a sample synthesized at 190 °C. Particles touching one another and a distorted "particle" can be seen at the right hand side of Fig. 3a. The line drawn in this image indicates the position where the topographical analysis was performed. Fig. 3b shows the topographical profile, where it can be observed that the distorted "particle" between points 4 and 5 is located at a higher position than the other particles. A size larger than 57 nm can be measured for this

particle, in contrast to sizes of particles touching one another laterally located at points 1–2, 2–3 and 3–4 with 24, 24 and 22 nm sizes, respectively. This kind of analysis clearly shows the presence of particle cluster on the surface of the sample.

4. Conclusions

Atomic force microscopy is a powerful tool for analysis of submicrometre powders. Particle size and morphology can be directly observed and measured using this technique, if the powders are pressed in order to minimize tip convolution. Very simple specimen preparation is required and quick measurement procedures are available, in comparison with conventional electron microscopy and to indirect techniques such as XRD and BET.

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