Analysis of admixed CeO_2 Nanoparticles via TEM and X-ray Diffraction Techniques.

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The techniques used to identify nanoparticle size and shape characteristics are of vital importance in the development of functional nanoparticles. Each technique offers different advantages; this work compares the two techniques of transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis by characterising CeO_2 nanoparticle specimens. Whole Powder Pattern Modelling (WPPM) is used to quantify the specimen dislocations and size characteristics from XRD data. Using admixed samples we test and extend the techniques. We show that XRD accurately characterises small crystallite distributions and that larger crystallite distributions necessitate further investigation.

1 Introduction

Both transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis can be used to characterise a specimens crystallite size, shape and strain characteristics, but do so using two very different approaches. TEM is a direct measurement technique, while X-ray diffraction analysis involves solving a series of inverse problems. As TEM directly observes and measures crystallites size properties and lattice defects, it is a widely accepted technique and is often used to complement other methods. On the other hand, the practical basis of TEM poses some limitations namely: a very intensive effort is required to collect a sufficiently large number of samples. Conversely, X-ray diffraction analysis is performed in a fairly automated fashion and samples a relatively large volume of material. Experimentally, X-ray diffraction techniques have only investigated single mode size distributions. Using non-mixed and admixed specimens we experimentally test and extend the current techniques by resolving bimodal size distributions and dislocation content.

2 Methodology

Four cerium oxide (CeO_2) nanoparticle specimens were prepared and examined using TEM. XRD patterns of each sample were collected and analysed using Whole Powder Pattern Modelling (WPPM). Two CeO_2 nanoparticle samples were obtained from Advanced Powder Technology[1] Pty Ltd, Western Australia; nominally 30 nm diameter (or 100%A), and nominally 5 nm diameter (or 100%B). The particles were produced by mechanochemical processing (see [1]). These samples were mixed in weight ratios of 70:30 and 30:70 providing a total of four specimens for study: 100%A, 70%A30%B, 30%A70%B and 100%B.

2.1 TEM Analysis

The CeO_2 nanoparticles were examined using a Phillips[1] CM120 microscope operating at 120keV. For high resolution imaging a Jeol[1] 3000F was used operating at 300keV. The CeO_2 nanoparticles were dispersed in ethanol and sonicated for 60 minutes. A single drop of

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1: Certain commercial materials, equipment and software are identified in order to adequately specify the experimental procedure. Such identification does not imply a recommendation or endorsement by NIST, nor does it imply that the materials or equipment or software are necessarily the best available for the purpose.

suspension was placed onto a 200 Cu Mesh holey support film and dried. Previous studies showed that the choice sample preparation method influenced the observed particle size distribution [2]. Approximately 600 randomly selected particles from each sample were imaged. Each particle was approximated by an ellipse using ImageJ[1]. A histogram of the average major and minor axis was generated for each of the eight TEM data sets. A lognormal distribution was fitted to each TEM histogram. For the admixed samples a bimodal lognormal model was also used.

2.2 X-ray diffraction analysis

XRD patterns were collected on a Siemens[1] D500 diffractometer, for diffractometer specifications, see[3]. Patterns were collected over the angular range of 20° to 160° at 0.01° per step for a total scan time of 72 hours per sample. NIST SRM 660a (LaB_6) was used to model the instrument broadening of the diffractometer. A split-Pearson VII function was used to model the instrument function. The WPPM software only has a pseudo-Voigt function available for the purpose of modelling the instrument function. Using a WPPM approach, the collected raw data was fitted assuming a lognormal size distribution of crystallites and Wilkens [6,7,8] dislocation model. The WPPM approach was performed using PM2K[1] software developed and maintained by M. Leoni[‡] and P. Scardi [4,5].

3 Results

TEM size distributions were obtained for all four specimens, as shown in Figure 1. The mean crystallite size and variance are also presented in Table 1. The TEM size distributions were found to be dependent on sampling, sample size and preparation method as shown in previous work by Vella *et al.* [2].

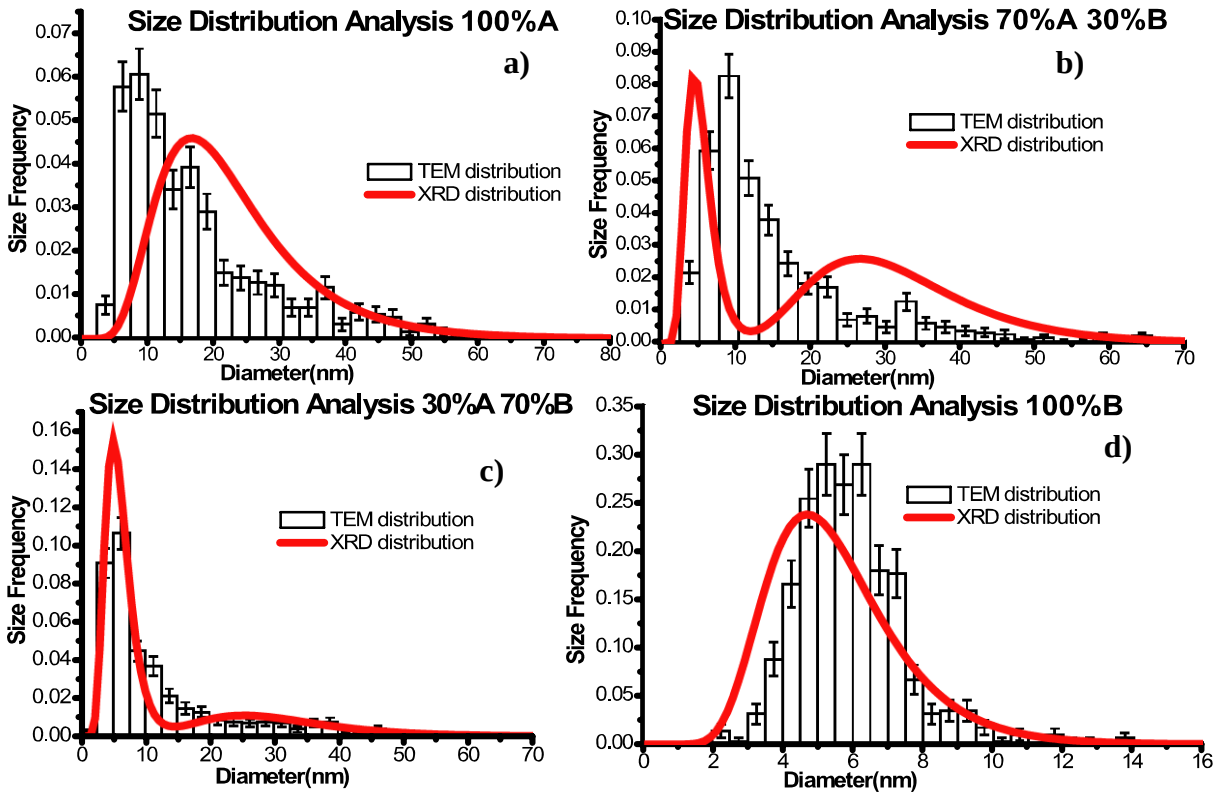

Figure 1: TEM and XRD crystallite size distributions, samples as labeled.

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Following a WPPM analysis [4,5] the specimen size and strain parameters were determined from the collected XRD patterns, for all four samples. This is also presented in Table 1. Parameters describing the size distributions obtained from XRD and TEM analyses are compared (see: Table 1, Figure 1). The TEM data collected for the admixed specimens was modelled using monomodal and bimodal lognormal distributions. It was found that the bimodal model provided a better approximation of the data for both mixed cases.

In the case of specimen 100%A, the disagreement between the XRD and TEM results may arise from an over accommodation of microstrain in the Wilkens model [6,7,8]. When examining the mixed cases using XRD it was necessary to use TEM information as starting parameters for fitting. Additionally, the outer cut-off radius *Re*, used in the Wilkens model [6,7,8] refines to a non-physical values (~0.1nm). In order for *Re* to retain a physical value, it was constrained to crystallite mode size taken from the TEM analysis (see Figure 1).

	XRD Analysis		TEM Analysis	
	100%A	100% B	100%A	100% B
$<D>$ (nm)	23.17(3)	5.57(6)	16.50	5.93
$\sigma^2_{<D>}$ (nm^2)	128.90(2)	3.64(5)	138.76	1.99
ρ (m^{-2})	4.47(1)x10^{13}	3.17(7)x10^{15}		
R_e (nm)	20.00	5.00		
	XRD Analysis		TEM Analysis	
	70%A:30%B	30%A:70%B	70%A:30%B	30%A:70%B
$<D_1>$ (nm)	32.07(2)	30.80(1)	17.96	18.39
$\sigma_1^2{}_{<D>}$ (nm^2)	135.89(2)	135.37(2)	206.23	345.52
$<D_2>$ (nm)	5.41(4)	5.99(5)	9.36	5.71
$\sigma_2^2{}_{<D>}$ (nm^2)	3.88(5)	4.97(7)	4.98	3.33
η	0.65(5)	0.27(5)	0.77	0.61
ρ (m^{-2})	1.50(1)x10^{14}	1.69(1)x10^{14}		
R_e (nm)	5.71	6.49		

Table 1: Lognormal size distribution parameters: <D> mean diameter, variance $\sigma_{<D>}{}^2$ and mixing ratio η. WPPM microstrain parameters: ρ dislocation density and R_e outer cut-off radius. 100%A: 30nm diameter CeO_2 sample. 100%B: 5nm diameter CeO_2 sample.

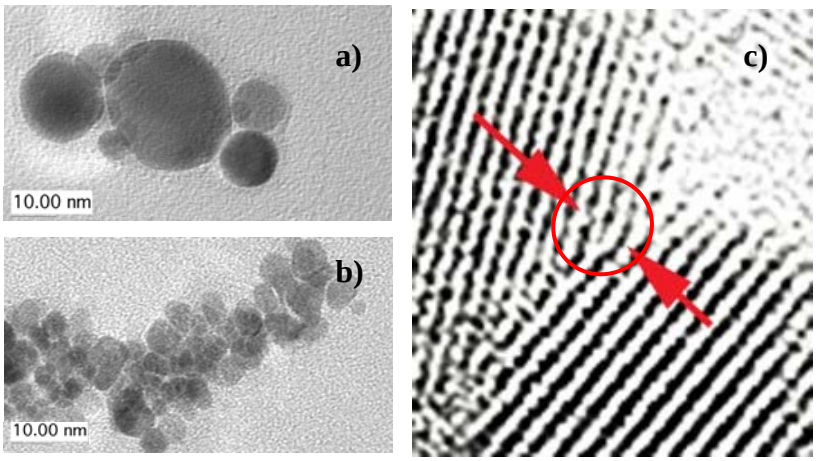

Figure 2: TEM Micrographs of specimen 100%A (top left), specimen 100%B (bottom left) and high resolution TEM showing an edge dislocation in sample 100%B (right).

Information on the specimen microstrain obtained from the WPPM analysis is presented in Table 1. In the case of 100%A the dislocation density was found to be relatively low. Moreover, for the 100%A and mixed cases, the dislocation density is at the lower limit of detectability for XRD, but at the higher limit for TEM methods [6]. Thus the two techniques operate at opposite ends of their detectability ranges. TEM evidence of edge dislocations (sample 100%B) is presented in Figure 2(c). The XRD analysis yields a large microstrain parameter for sample 100%B indicating that peak broadening arises from both size and strain effects. In general, the dislocation densities in Table 1 demonstrate that as the mixing ratio increases to 100%B, an increase in the dislocation density is also expected.

4 Conclusions

In summary, the size distributions determined from the TEM and XRD analysis showed a strong agreement for smaller crystallites. In the case of sample 100%A and 70%A30%B, the disparity observed arises from an over accommodation of microstrain in the XRD analysis and TEM sample preparation, sampling and sample size. XRD analysis of the mixed cases required *a priori* TEM information as the final solution was highly sensitive to starting parameter values. TEM results can resolve bimodality in size distributions. Bimodality was detected in all mixed samples using both XRD and TEM techniques. In addition, evidence of dislocations were found in both the TEM and XRD analysis. The large microstrain in specimen 100%B can be attributed to dislocations.

Acknowledgments

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