Analysis of strain in manganese nanoparticles using the optical moiré technique

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Abstract. Manganese nanoparticles have been produced using the inert gas condensation technique. XRD has been used to analyse the particles, which contain a mixture of Mn–Mn oxide phases. Too few isolated reflections from any one phase have meant that broadening measurements are limited, and strain measurements are unreliable. Another way to measure strain in a sample is through analysis of lattice images taken using TEM. Observation of strains over long atomic distances can prove difficult, but a method of magnifying strain is by the optical moiré technique. A crystal lattice image with a grating superimposed over the top creates dark bands due to interference between the two. These dark bands are called moiré fringes and they can occur as an artefact in TEM images due to interference between two real crystal lattices. Here though they are implemented using a synthetic grating where the strain in crystalline solids can be studied. The manganese nanoparticle samples have been found to contain fully oxidised particles below 20nm diameter, and core shell particles above 20nm diameter. The technique has been used to study the core-shell particles, which consist of a β-Mn core and an oxide shell. The core is a single crystal and the moiré fringes show that there is no strain in that region. The oxide crystals in the shell are too fine for the technique to work, and so any strain in them must be measured using a different method.

1. Introduction
Manganese nanoparticles have been produced through inert gas condensation. Bulk manganese has been evaporated in a clean helium gas environment at low pressure. The resulting vapour cools quickly and condenses to form particles. These are carried by convection to collection points and can then be characterised [1]. They have been characterised using X-ray diffraction (XRD) and transmission electron microscopy (TEM). A feature of XRD is that any line broadening can be measured and analysed to show what the average crystallite size is in the sample and if there is any strain in the sample. This is done using the Scherrer’s equation to estimate size, with a similar approach to estimate strain and the two can be distinguished as they have different 2θ variance [2]. A number of individual peaks/reflections are needed to make an estimate of crystallite strain and this can then be used to provide a more accurate estimate of crystallite size. Manganese and its oxides have relatively complex structures and so a polycrystalline material that contains several Mn phases will give XRD plots that are very complicated with a large number of closely spaced peaks. This is the case with the manganese nanoparticles produced by inert gas condensation [1] (figure 1) resulting in diffractograms containing reflections from β-Mn, MnO and Mn₃O₄. In such cases it is difficult to make accurate broadening measurements as most of the high intensity peaks have contributions from many lower intensity peaks of other phases. As a result it is difficult to make a reliable estimate of the
strain from XRD data alone in any one phase of the sample; as there are not enough isolated peaks in the 2θ plot from just the one phase of interest.

Another method for detecting strain in a crystallite is directly from an atomic lattice image of the crystal, using the optical moiré technique [3]. Moiré fringes are formed when two superimposed grids interfere with each other, and appear as dark bands of larger spacing than the original grids running through the image. They occur in two different modes, rotational and parallel. Rotational moiré patterns come from two grids of the same spacing being rotated relative to each other through small angles. Parallel moiré patterns occur when two grids of dissimilar spacing are parallel to each other. Moiré patterns can also be formed as a result as a combination of the two types. TEM is capable of producing lattice images of crystals when a suitably thin specimen is viewed down a particular crystal axis. By superimposing an undistorted grid (reference grid) over such an image a moiré pattern can be formed. Further to this, any distortions in the lattice image (strains) are amplified in the moiré pattern.

The method of producing moiré patterns to observe distortions on lattices can vary but relies on the same principle of overlap and interference. Transparent reference grids have been placed over images of crystal lattices [3, 4]. Computer software has been used to generate a grid to overlay the image, producing moiré fringes in lattice images of multi-layer films [5]. Scanning lines from a computer monitor have been used to produce moiré fringes in lattice images of multi-walled carbon nanotubes [6]. Moiré patterns have also been formed using the scanning lines of a scanning tunneling microscope (STM) [7]. This investigation uses a transparent grid to generate moiré fringes in lattice images of core-shell manganese nanoparticles produced by inert gas condensation. This is in an attempt to identify whether there is any strain within the core of the particles, which can then be taken into account when analyzing the associated XRD data.

2. Experimental
Particles were produced using the inert gas condensation technique [1] and characterised using a Panalytical X’Pert Pro MPD with Cu kα source and X’cellerator detector. A continuous scan over 10-90° was performed.

The particles were then characterised using TEM techniques. The microscope used was an FEI CM200 field emission gun TEM running at 197KeV equipped with an ultra thin window (UTW) Oxford Instruments EDX spectrometer running ISIS software and a Gatan imaging filter (GIF200 running digital micrograph 3.3.1). Images were recorded and elemental and crystal phase data was acquired using energy-dispersive X-ray (EDX) analysis and electron diffraction. Energy filtered TEM (EFTEM) elemental maps of the oxygen and manganese distribution within the nanoparticles were taken. Maps were recorded using a 20eV slit width. Post, pre edge 1 and pre edge 2 windows were at 542, 517 and 502 eV for O K-edge and 650, 620 and 590 eV for Mn L-edge respectively.

For moiré pattern analysis, an atomic lattice image was recorded on a photographic plate, and developed as a negative. A standard enlarger was then used to project the image onto some photographic paper for a short time. Before the paper was developed, it was re-exposed with a transparent image of a grating which was used as a reference grid. Once the photograph had been developed it showed up moiré patterns due to the interference between the lattice fringes and the reference grid. The method was the same as that used by Hetherington and Dahmen [3].

3. Results
The presence of three phases (β-Mn, MnO and Mn₃O₄) was clearly evident in the XRD data recorded from the nanoparticles although due to the small amount of material produced during experiments (~0.1mg) the XRD data contained a lot of background noise (figure 1). It is not possible to identify the distribution of the phases using XRD and because of peak overlap assessment of crystallite strain and size is difficult.

Bright field (BF) TEM images showed that samples contained particles ranging in size from 5 to 200nm diameter depending on the inert gas condensation processing parameters (figure 2a). EDX showed individual particles contain both manganese and oxygen, and further to this electron
diffraction from clusters of particles confirmed the findings of XRD that the phases present in the samples were $\beta$-Mn, MnO and Mn$_3$O$_4$ (inset in figure 2a).

**Figure 1.** XRD plot from Mn nanoparticles produced by inert gas condensation. $\beta$-Mn (square), MnO (circle) and Mn$_3$O$_4$ (cross) are clearly present in the sample.

**Figure 2.** A bright field image of the Mn nanoparticles with inset electron diffraction pattern which can be indexed to a combination of $\beta$-Mn, MnO and Mn$_3$O$_4$ phases (a). Corresponding oxygen (K-edge) (b) and manganese (L-edge) (c) elemental EFTEM maps are also shown. These clearly demonstrate core-shell Mn-Mn oxide particles.

**Figure 3.** An image of the particle studied, showing the moiré fringes in the core running from bottom left to top right of the image (a). An enlarged area of the original image is shown (b), highlighting the $\beta$-Mn lattice fringes used to form the moiré pattern. A diffraction pattern from the particle viewed down the [526] axis is also shown (c), containing single crystal diffraction spots from the $\beta$-Mn phase, and polycrystalline rings from the MnO phase.
EFTEM maps were recorded (figures 2b and c) of an area containing particles of a range of sizes. Smaller particles (sub-20nm diameter) were found to have an even distribution of manganese and oxygen through their volume. Larger particles (20nm diameter and over) were found to have a concentration of oxygen in the shell.

Selected area electron diffraction from a single isolated core-shell nanoparticle (figure 3 and inset) indicates the core to be a \( \beta \)-Mn crystal (lying on its \([\bar{5}2\bar{6}]\) zone axis) with a polycrystalline MnO shell (confirmed by dark field imaging).

Observation of the moiré fringes produced by overlaying a lattice image with a reference grid indicates that there is not a large amount of strain in the sample. The fringes remain parallel and evenly spaced across the whole core section of the particle (figure 3a). A magnified section of the original lattice image and a diffraction pattern taken from the particle are also shown (Figures 3b and c). Magnified sections of the original image do reveal some small defects, but long-range strains are not shown by distortions in the moiré pattern. It can then be concluded that there is not a large amount of strain in the pure \( \beta \)-Mn core.

4. Discussion of results
EFTEM maps show a concentration of oxygen in the shell of particles over 20nm diameter and single particle electron diffraction shows that the core of such particles are single crystal \( \beta \)-Mn and the shells are mainly MnO. Smaller particles in the sample have an even distribution of oxygen and manganese throughout them so it can be assumed that these are completely oxidised. The inert gas condensation will form single crystal \( \beta \)-Mn particles at first which develop a polycrystalline oxide layer on exposure to the atmosphere. If the particles are below a critical size (20nm) then the oxide penetrates the entire particle. Where an oxide layer does form, lattice mismatch would create an incoherent interface, and this would explain a large number of small oxide crystallites at the particle surface and a relatively unstrained \( \beta \)-Mn core.

A representative crystallite size measurement can be taken from XRD of the \( \beta \)-Mn crystals in the sample as strain can now be neglected. A measured value of 150nm broadly agrees with TEM images from the same sample (TEM derived size distributions not shown here). Whilst smaller particles were used for the TEM analysis, it is assumed that these are representative of the sample.

5. Conclusion
Manganese nanoparticles have been produced using inert gas condensation and core-shell particles develop. These have been characterised using XRD and TEM. The particles have a pure \( \beta \)-Mn core and a MnO shell. Moiré patterns have been formed by placing a reference grid over an image of the crystal lattice of the core of the particle. These moiré patterns show that there is no strain in the lattice of the single crystal \( \beta \)-Mn core. The MnO crystallites are too small and irregular to measure using the moiré technique. This is a useful tool for estimating strain in the \( \beta \)-Mn crystallites, and can be used to inform XRD peak broadening analysis for representative crystallite size measurement.

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