Mn nanoparticles produced by inert gas condensation

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Abstract. The results from experiments using the inert gas condensation method to produce nanoparticles of manganese are presented. Structural and compositional data have been collected through electron diffraction, EDX (energy dispersive X-ray) and EELS (electron energy loss spectroscopy). Both Mn₃O₄ and pure Mn particles have been produced. Moisture in untreated helium gas causes the particles to oxidize, whereas running the helium through a liquid nitrogen trap removes the moisture and produces β−Mn particles in a metastable state. The particle sizes and the size distribution have been determined. Particle sizes range from 2 nm to above 100 nm, however the majority of particles lie in the range below 20 nm with a modal particle size of 6 nm. As well as the modal particle size of 6 nm, there is another peak in the frequency curve at 16 nm that represents another group particles that lie in the range 12 to 20 nm. The smaller particles are single crystals, but the larger particles appear to have a dense region around their edge with a less dense centre. Determination of their exact nature is ongoing.

1. Introduction

Inert gas condensation is a well established nanoparticle production technique, and is popular due to the flexibility and control over the materials it can produce. Material is evaporated in a clean helium atmosphere, and the surrounding helium atoms cool the vapour produced. This results in the atoms condensing and forming nanometer sized particles, which are then carried by convection to be collected and examined. A number of different variables such as inert gas pressure, source temperature [1], inert gas type [2] and forced gas flow [3, 4] have been experimented with. This is in an attempt to gain greater understanding and control over the nanoparticle powder (nanopowder) samples produced. One of the reasons that nanoparticles have received a lot of attention is due to their capability to be composed of structures that normally only occur at higher temperatures in the same material when in bulk form. The reduced dimensions of nanoparticles mean that size related effects such as surface energy can hold materials in metastable states or stabilise high temperature phases [5]. Nanoparticles can also be useful when dispersed in a matrix of a different material, for example, when studying the giant magnetoresistance (GMR) effect [6]. If enough material is produced a nanopowder sample can be compacted to produce a nanocrystalline material. In this case the initial size of the grains in the material is dictated by the size of the crystals in the nanoparticles, and the grain boundary component of the material takes up a substantial volume fraction of the whole material. For example, in a nanocrystalline material where the crystallites are around 6 nm across, the total volume fraction of the material occupied by grain boundaries is around 50% [7]. These consolidated nanocrystalline
materials and the majority of applications for nanopowders require an accurate measure of median particle size and a narrow size distribution.

This paper describes preliminary experiments producing manganese nanoparticles using inert gas condensation. The size distribution of the particles has been analysed, and the composition of the particles determined using analytical TEM techniques. Manganese has been chosen for a material to investigate as it is one of the most interesting pure metals. Its low temperature phases form very complex structures, with a total of 58 and 20 atoms per unit cell in the cubic alpha and beta phases, respectively [8]. Mn can also exist in different metastable states which have relatively similar energies, and this has been observed in manganese nanoparticles produced in other experiments [5].

2. Experimental
The apparatus consists of a large vacuum chamber containing a resistively heated tungsten boat. A support tree holds copper TEM grids coated with continuous carbon support films at various heights above the source to catch the particles for subsequent examination. A schematic diagram of the apparatus can be seen in figure 1.

![Figure 1. A diagram illustrating the inert gas condensation equipment used to produce nanoparticles.](image)

The tungsten boat containing a small manganese granule (99.99% pure) was placed inside the chamber with the support tree holding the grids directly above the sample. The chamber was then sealed and evacuated to around $1.1 \times 10^{-9}$ mbar. Once UHV was reached, the chamber was backfilled with helium that had passed through a liquid nitrogen cold trap. Every effort was made to keep the system as clean as possible to prevent any contamination of the sample. Once the helium pressure was set the power supply to the tungsten boat was switched on and increased until a temperature of 1533 K was reached. Evaporation took place, the particles condensed in the helium and natural convection carried the particles up to be caught by the grids. The system was allowed to cool and the grids were then removed and stored ready for examination.

The samples were observed using a Philips FEI CM200 FEGTEM equipped with a UWT Oxford Instruments EDX detector and Gatan GIF200. Images of the samples were taken. 450 particles from each sample were measured, and from these measurements particle sizes and size distributions were calculated. Electron diffraction patterns were also taken from a selection of areas to identify the phases which had been produced. EELS and EDX spectra were taken to analyse the particle composition. EELS spectra were recorded in diffraction mode over a 200 nm diameter area.
3. Results and discussion

Samples prepared by the procedure described above were first analysed using electron diffraction, EELS and EDX. EDX spectra were taken from a sample produced using untreated helium that had not passed through a cold trap. The helium was set to 20 mbar pressure during the evaporation. The sample was found to be composed of oxygen and manganese. EELS analysis and quantification using hydrogenic cross sections with a white line correction indicated a Mn/O atom ratio of approximately 0.7. Indexing of an electron diffraction pattern taken from the same sample indicated the sample was composed of Mn$_3$O$_4$. It was apparent that moisture in the helium had completely oxidized the particles. Mn$_3$O$_4$ is not the most stable manganese oxide phase at room temperature. Its production must be due to the partial pressure of oxygen and temperature conditions near the source during particle formation. The small dimensions of the nanoparticles may also help to stabilise this phase at normal pressure and temperature.

A cold trap was used to remove the moisture from the helium before it was used in the experiment, and EELS analysis showed that almost pure manganese particles were produced. In a sample produced in 40 mbar of helium a Mn/O atom ratio of 3.3 was recorded, indicating a much larger proportion of Mn than oxygen in the sample. The presence of oxygen in the sample can be explained by the pure Mn particles having oxidized surfaces, which would most likely occur during transit of the samples following production. This information agrees well with selected area electron diffraction data taken from the same sample. Diffraction rings from $\beta$-Mn were indexed, as well as diffuse rings corresponding to the oxide MnO. The $\beta$-Mn phase is a high temperature phase that must be held in a metastable state. It was most likely created when the particles were forming close to the heated source. MnO is the most stable manganese oxide, and the diffuse rings indicate a thin, possibly nanocrystalline surface coating on the metal nanoparticles that may have formed when they were exposed to air.

The distribution of particle sizes for a sample produced at 40 mbar is illustrated in figure 2. The sample contained a few particles larger than 100 nm, but the vast majority of particles were less than 20 nm in size. The majority of particles were in the range of 2 to 10 nm diameter, as can be seen from the large peak in figure 2. A second, smaller peak can be seen over the range 12 to 20 nm diameter. This peak in the distribution curve represents a second set of particles different in nature to the smaller particles. The particles occur connected in stringers, however the particles themselves display quite an interesting structure. The difference in contrast between the dark outer edge and the lighter centre indicates a difference in density between the two regions. This could be due to the particles having a

![Figure 2. Distribution of particle sizes in a sample produced using 40 mbar helium pressure. The large peak corresponds to the modal particle size of 6 nm, whereas the smaller peak to the right of it represents another group of similarly-sized particles around 16 nm but which are different in nature to the smaller particles (see figure 2).](image)
core shell structure with a less dense region in the core, or could possibly be due to the particles having a disc or ‘doughnut’ shape with a thick outer edge and thinner or non-existent centre. If the particles were doughnut shaped, they could have been formed by several of the smaller particles joining in a circular stringer. The width of the dark edge is roughly equal to the diameter of the smaller particles (roughly 6 nm). A bright field TEM image showing both of the types of particle is shown in figure 3. High resolution SEM and TEM will be used to identify the exact morphology and structure of these larger particles.

4. Conclusions
Inert gas condensation has been used to produce nanoparticles of β-manganese. The size of the particles ranged from 2 to over 100 nm, although the majority of particles produced were less than 20 nm in diameter. Two main types of particles were observed. The first type consisted of small particles that fell into the size range 2 to 10 nm, with a modal particle size of 6 nm. The second type of particle was in the size range 12 to 20 nm. These larger particles appeared to have a more dense outer edge than centre, observed in TEM by the difference in contrast between the two regions. They could be explained as being hollow particles, or doughnut shaped with a thick outer edge with little or no centre. More high resolution imaging and analytical data are now needed in order to fully characterise the exact nature of the particles.

Acknowledgements
MBW acknowledges EPSRC for a studentship, and Dr Andrew Brown for help with using the different TEM techniques.

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Figure 3. A bright field TEM image from an area of sample produced at 40 mbar helium pressure. The smaller particles that fall into the size range 2 to 10 nm can be seen isolated across the image (a). The larger particles fall into the size range 12 to 20 nm and are formed in stringers (b). A clear difference in contrast can be seen between their centre and outer edge of the larger particles.