Crystallization of nanoscaled tungsten oxide powder particles

D. V. Szabó, D. Vollath

Forschungszentrum Karlsruhe, Institut für Materialforschung III, P.O. Box 3640, D- 76021 Karlsruhe, Germany

Nanostructured materials exhibit interesting new properties, which are correlated to the small size of the particles [1, 2]. These properties may be mechanical, magnetic, optical or electrical ones. Particles with sizes below about 10 nm are either monocrystalline or glassy. Within this study the attention is drawn to the phenomenon of partly crystallized or polycrystalline particles found in tungsten oxide. The material is synthesized in a microwave plasma [3] under different experimental conditions. Structural characterization is performed by high resolution electron microscopy.

Within this study the synthesis parameter varied was the mean temperature after the plasma zone, which depends on the microwave frequency. Two frequencies, 2.45 and 0.915 GHz were used. Performing the synthesis with 2.45 GHz means lower reaction temperature and shorter residence time in the plasma, as compared to a synthesis performed with 0.915 GHz. The reaction temperature was 250°C in the case of 2.45 GHz and 400-500°C in the case of 0.915 GHz. $W(CO)_6$ was used as precursor. The resulting products are characterized using a Philips CM 30 ST electron microscope operated at 300 kV. It is operated at 200 kV for the acquisition of digital electron diffraction pattern using a slow scan CCD camera. Based on the Scherrer formula, line profiles of these diffraction patterns are evaluated to estimate the particle size. To do this, the diffraction profiles are corrected for background and the peaks are deconvoluted. The samples were prepared by dipping carbon coated grids into the powder.

Depending on the process parameters, powders with different particle size, morphology and structure are obtained.

- The synthesis with 2.45 GHz at 250°C leads to a white powder. The particles are amorphous and droplet like in shape. These droplets with sizes around 10 nm contain some crystallites (Fig. 1a) with sizes below 3 nm. These crystallized areas show lattice fringes with a spacing of 0.38 nm. The electron diffraction pattern of these crystallites (Fig. 1b) may be interpreted as the pattern of monoclinic $W_{24}O_{68}$ (ASTM 36-103), a hypo-stoichiometric phase of WO_3. Considering this structure, the lattice fringes can be attributed to the (104) or (010) planes. In micrometer sized particles the color of this phase is blue; this is not consistent with our product. In this case, one has to take into account that, changing the particle size to the nanometer range, the color often changes. $W_{24}O_{68}$ is an intermediate phase, formed from WO_3 by crystallographic shear to maintain the octahedral coordination, although some oxygen atoms are missing. The evaluation of the Scherrer formula leads to mean particle sizes of 1.9 nm; dark field imaging reveals particle sizes of about 1.6 nm. Interestingly, these crystallized areas do not act as nuclei for crystallization of the glassy particles during observation in the electron microscope as it was found in Cr_2O_3 [2].
- The synthesis with 0.915 GHz at 400-500°C leads to a gray powder. The particles (Fig. 2a) with sizes in the range from 5 to 10 nm are crystallized. The lattice fringes exhibit a spacing of

0.375 nm. The diffraction pattern (Fig. 2b) can be correlated to several polymorphic or metastable non-equilibrium structures of WO_3. The most probable structure is the triclinic one. Considering the triclinic WO_3 (ASTM 20-1323) structure the lattice fringes can be attributed to the (001) or (020) planes. Assuming this structure the Scherrer formula leads to a particle size of 5.6 nm

Electron microscopy revealed different structures and various features of tungsten oxides. These features depend on the experimental conditions of the synthesis. A short residence time in the plasma combined with low temperature leads to the formation of amorphous material with crystallized inclusions. Longer residence time connected with higher temperature lead to a product crystallized in one of the metastable phases in this system. With increasing size of the crystallites the color changes from white to gray, but it always differs from the colors of micron sized tungsten oxides. Obviously, the amorphous material is white. Most interesting, a new phenomenon, partly crystallized or polycrystalline nanoparticles, was found.

References

[1] Gleiter, H., *Prog. Mater. Sci.* 33 (1989) 223

[2] Vollath, D. and Szabó, D. V., *Materials Letters* 29 (1996) 271

[3] Vollath, D., Szabó, D. V. and Haußelt, J., *J. Europ. Ceram. Soc.* 17 (1997) 1317

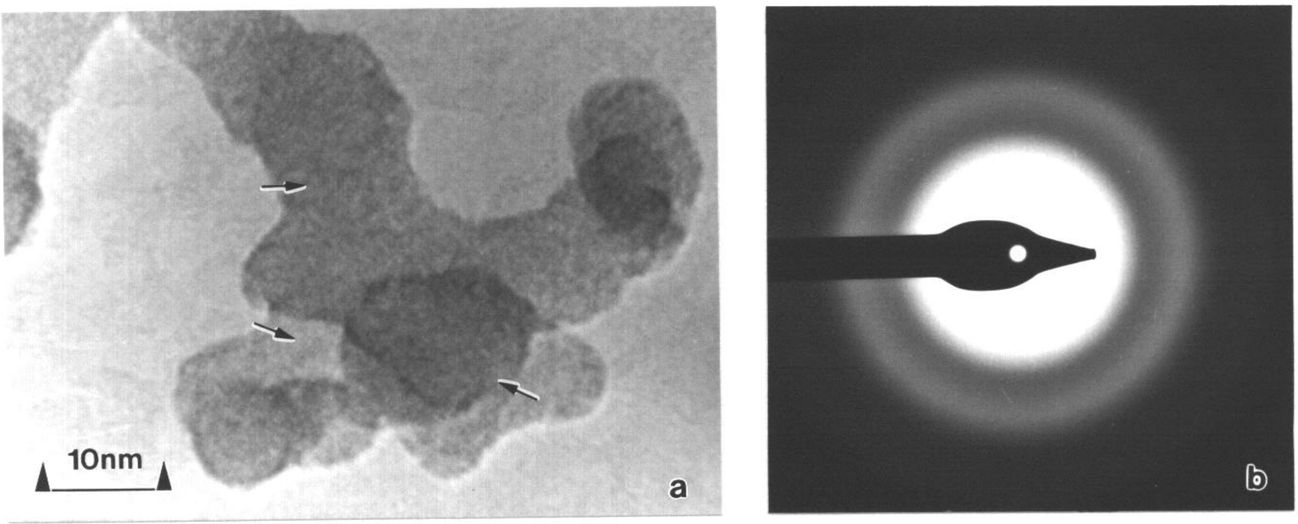

Fig. 1: Electron micrograph (a) and diffraction (b) of amorphous, droplet like tungsten oxide powder particles with crystallized $W_{24}O_{68}$ inclusions (arrows).

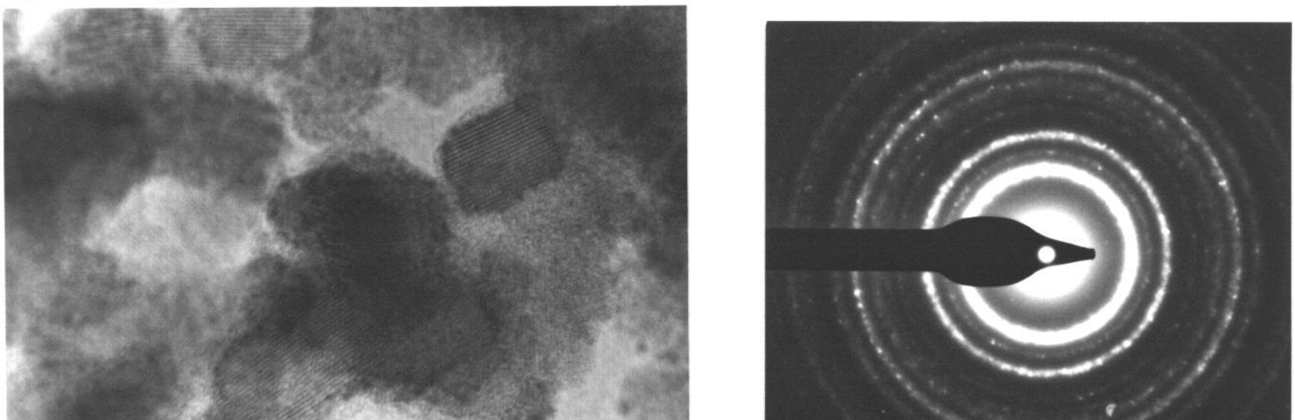

Fig. 2: Electron micrograph (a) and diffraction (b) of crystallized, triclinic WO_3 powder particles.