Preparation, Structure, and Sintering of Nickel Nanoparticles

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Summary: Nickel nanoparticles in the size range 3 – 20 nm are prepared in an inert gas condensation process and subsequently sintered in the gas phase. Morphology and microstructure of the sintered particles are investigated by means of (high resolution) transmission electron microscopy. We observe the occurance of both, polycrystalline agglomerates and multiply twinned particles (MTP's: icosahedra, decahedra). Whereas in the polycrystalline particles sintering starts at temperatures $T_S \cong 400°C$, the MTP's are found to remain stable and almost unaffected by the gas-phase annealing.

1. Experimental

Nickel nanoparticles are prepared by means of DC magnetron sputtering from nickel targets in Ar under pressures 0.3 mbar ≤ p ≤ 0.9 mbar at room temperature (RT). In order to allow for investigations on the (non-agglomerated) "primary" particles, an amorphous carbon substrate supported by a copper grid is placed at a distance x = 10 cm opposite to the sputter gun. Alternatively, the directed flow of the sputter gas is used to transport the nickel particles through a sintering tube to a liquid nitrogen (LN_2) cooled substrate holder, where the particles are also deposited onto amorphous carbon. In the following, all particles, which have passed the sintering tube, are referred to as "sintered particles". Sintering temperatures are $RT \leq T_S \leq 1000°C$, and the typical sintering time (i.e. the time during which the particles are exposed to the sintering temperature, T_S) is 5 s. Structural investigations on the deposited particles are carried out by means of transmission electron microscopy (TEM) utilizing a Philips CM12 (Twin lens) for morphological studies and dark field experiments and a Philips CM200 (Super-Twin lens) for high resolution investigations (HRTEM).

2. Results and Discussion

Depending on both, sputtering power and Ar gas pressure, the non-agglomerated primary particles exhibit log-normal size distributions with mean particle sizes of 2.5 nm ≤ d_{prim} ≤ 6 nm and a typical relative standard deviaton of $\sigma = 0.17$. From electron diffraction experiments the lattice constant is found to increase by about 5% with respect to the value of bulk nickel when reducing the mean particle size to 2.5 nm. Simple model calculations on the effective surface stress imply that this dilation is due to a lattice mismatch between the metallic Nickel particles and NiO surface layers, which form when the samples are exposed to ambient air. Though in HRTEM images no indication for the formation of contineous surface oxide layers is found, we often observe that very small crystallites ($d_{cryst} \leq 2$ nm) with lattice plane spacings comparable to what is expected for NiO are attached to the surface of the nickel nanoparticles. Thus the assumption lies close that the lattice mismatch between elemental nickel and NiO prevents the surface from homogeneous oxidization and rather results in the breaking off of small oxidic crystallites.

TEM studies on samples with particles sintered at T_S = RT show the occurance of both, single particles and particle agglomerates. The variety of particle morpholgies and sizes is due to the fact that the geometrical design of our preparation chamber allows the particles to take significantly different pathways before entering the sintering tube.

Dark field imaging experiments on single particles with 3-fold morphological symmetry indicate that they are of icosahedral structure. Clear evidence for this finding stems from HRTEM investigations, which show the existance of both, decahedral and icosahedral MTP's with sizes of up to 20 nm and larger. Theoretical predictions on the critical sizes of nickel particles, up to which decahedral or icosahedral structures are expected to be energetically stable, range from 4 nm to 15 nm [1-3]. However, in experiments the occurance of significantly larger MTP's is often observed [4]. Figure 1 shows as an example a HRTEM image of a nickel decahedron lying with its 5-fold axis perpendicular to the image plane. The power spectrum obtained by Fourier transformation of the HRTEM image is in good agreement with the results of HRTEM image simulations on decahedral nanoparticles [5]. Taking into account the expected lattice deformations within individual tetrahedra the measured lattice parameters are in good aggreement to what is expected for nickel.

Besides such MTP's, polycrystalline particles with sizes in the range 20 nm $\leq d_{cryst} \leq$ 50 nm are also observed. These particles consist of small crystallites (4 nm $\leq d_{cryst} \leq$ 8 nm) and are found to be mostly coagulated to larger agglomerates.

Investigations on particles that are exposed to higher sintering temperatures show that for $T_S > 400°C$, the polycrystalline nickel nanoparticles start to undergo a sintering process. The surfaces of the particles, which are rough due to the surface extension of individual crystallites in the case of RT-sintering, are smoothened, and intra-particle growth of the crystallites is observed. Quantitative analysis of the morphology of agglomerated particles reveals that the measured shrinkage (i.e. the relative length change of an agglomerate with respect to the original particle diameter) is comparable to the results of Andrievski [6] obtained for the sintering of ultrafine Nickel powders (d_P = 50 nm).

Although the number of MTP's is reduced at sintering temperatures $T_S > 400°C$ with respect to those obtained in the case of RT-sintering, we still observe the occurance of decahedral and icosahedral particles. They are comparable to those we find in RT-sintered samples and thus do not exhibit any sintering effects. As an example we show in figure 2 a HRTEM image of a nickel icosahedron (seen along its 3-fold symmetry axis), which is deposited after sintering at T_S = 600°C. Obviously, the multiply twinned structure of these particles is energetically sufficiently favoured to withstand sintering temperatures of up to T_S = 600°C and higher.

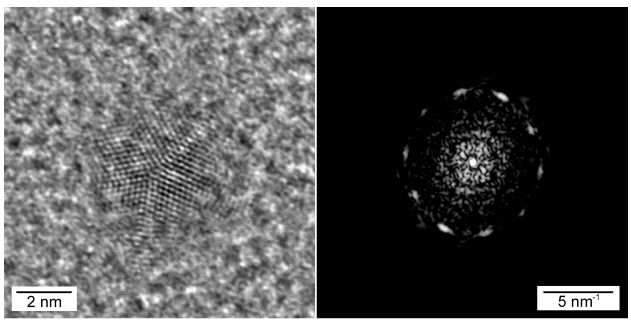

Figure 1: *Left: HRTEM image of a RT-sintered nickel decahedron along its 5-fold axis supported by an amorphous carbon film. The image is contrast enhanced by Fourier filtering. Right: Power spectrum of the original image.*

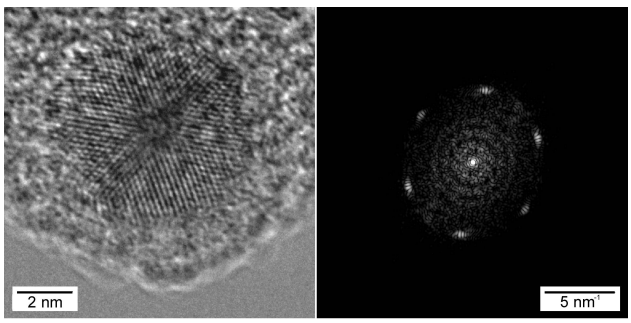

Figure 2: *Left: HRTEM image of a nickel ikosahedron sinterd at T_S = 600°C seen along its 3-fold symmetry axis supported by an amorphous carbon film. Right: Power spectrum of the image.*

References

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