14. Nanomaterials and nanotechnology

14.0 Introduction

Nanomaterials: heterogeneous materials with a grain size (crystallite size) below 100 nm, at least in one direction (colloidal size range), usually measured by X-ray diffraction (Scherrer line broadening). The width of the interfacial region (phase boundary) between two nanosized (nanocrystalline) grains is usually estimated to be approx. 1 nm. Many of the exceptional properties of nanomaterials are due to the fact that with decreasing grain size the interfaces become an increasingly important (and below a grain size of approx. 10 nm the decisive) factor of the microstructure. In terms of volume fraction all grain boundary phases together make up approx. 50 % when the grain size is approx. 5 nm. A recent point of concern are the uninvestigated health hazards of nanopowders. Of course, these health hazards are especially relevant when nanopowders are to be used in upcoming commerical technologies.

14.1 Synthesis of ceramic nanopowders

Synthesis methods can be classified according to the strategy applied (bottom-up or top-down approach), the nature of the process (physical, chemical, biological, e.g. biomineralization), the energy source (laser, plasma, ion sputtering, electron beam, microwave, hydrothermal, freeze drying, high-energy ball milling, combustion, flame, supercritical) or by the media (synthesis in gas, in liquid or in solid).

- *Bottom-up approach*: Nanoparticles are built up atom by atom or molecule by molecule, e.g. flame synthesis of TiO₂ from gaseous TiCl₄ or flame synthesis of SiO₂ from gaseous SiCl₄, chemical vapor reactions using resistant heating, laser or plasma, aerosol pyrolysis (spray pyrolysis, vapor pyrolysis) applied to produce nanosized BaTiO₃ from hydrolyzed TiCl₄ and BaCl₂; further examples are chemical (reactive) precipitation or coprecipitation, e.g. the wet-chemical precipitation of needle-shaped hydroxyapatite nanocrystals, hydrothermal synthesis (thermal hydrolysis), forced hydrolysis, solvothermal synthesis, supercritical hydrothermal processing or supercritical fluid processing, sol-gel synthesis, microwave heating synthesis, synthesis in microemulsions or reverse micelles and sonochemical synthesis.
- Top-down approach: Nanoparticles are synthesized by breaking down bulk materials gradually into smaller sizes, e.g. synthesis of nanocrystalline α -Al₂O₃ (surface area up to 100 m²/g) by high-energy ball milling (mechanical milling) of γ -Al₂O₃ (by this route nanocrystalline high-temperature phases can be obtained without going through extreme heat treatment for long times, which would promote grain growth and surface area loss), mechanochemical processing (mechanical activation) for the preparation of nanosized (50-100 nm) BaTiO₃ by milling BaCO₃ and TiO₂ with a large amount of NaCl for several hours, cryochemical processing, combustion synthesis (self-propagating high-temperature synthesis) for BaTiO₃ note that it is extremely difficult to produce nanosized BaTiO₃ directly via solid-state synthesis (BaCO₃ + TiO₂ \rightarrow BaTiO₃ + CO₂); synthesis of nanosize yttrium-stabilized zirconia (Y-ZrO₂) by selective leaching of bulky yttrium-doped BaZrO₃ or Na₂ZrO₃ (produced via conventional solid state reactions).

14.2 Examples of nanoceramic materials

Nanocrystalline Al_2O_3 , ZrO_2 , SiC, Si_3N_4 , TiO₂, titanates, ferrites and others (CeO₂, Y_2O_3 , ZnO, AlN), ceramic nanocompsites (preparation methods, properties, application).

14.3 Structure and properties of nanomaterials

14.3.1 Nanoparticle size by XRD (Scherrer equation)

XRD can be used to measure *microstrains* (microdeformations) from the *peak broadening* (line width at half maximum height $2w_{\varepsilon}$) via the relation $2w_{\varepsilon} = 4\varepsilon \tan \theta$, where $\varepsilon = \Delta d/d$ is the microstrain (with Δd being the half width of the distribution function of the lattice spacings inside a grain or crystallite), and to measure an *average crystallite size* D for grains $< 0.2 \mu m$ (nanoparticle size) from the peak broadening (line width at half maximum height $2w_D$) via the Scherrer equation $2w_D = k\lambda/(D\cos\theta)$, where k is a constant close to unity (theoretical value $k = 2\sqrt{\ln 2/\pi} = 0.94$). Since the *effective XRD peak broadening 2w* can be caused by microstrain $(2w_{\varepsilon})$ and / or by small crystallite size $(2w_{D})$, these two effects have to This be distinguished. can be done calculating by the quantity $B = 2w\cos\theta/\lambda = (k/D) + (4\varepsilon\sin\theta/\lambda)$, and plotting B in dependence of $\sin\theta$ (Williamson-Hall graph). This dependence should be linear, with the slope determining the microstrain ε and the intercept determining the crystallite size D.

14.3.2 Interface structure

The main characteristic of nanocrystalline materials is the enhanced volume fraction of their interface component, i.e. grain boundaries and triple junctions, compared to their microcrystalline counterparts. 3D studies using the tetrakaidecahedron shape and assuming a grain boundary thickness of 1 nm have shown that the grain boundary volume fraction increases from a few percent at a grain size of 100 nm to about 45 % at a grain size of 3 nm. For grain sizes below 20 nm the triple junctions become more important than the grain boundaries. These findings are not significantly changed when other model grain shapes are used or when the grain boundary thickness is varied from 0.5 to 1.5 nm.

14.3.3 Nanoindentation with depth sensing

Depth-sensing indentation, where a material's resistance to a sharp penetrating tip is continuously measured as a function of depth, is a widely used method for estimating the mechanical properties of nanostructured materials and thin films \rightarrow load-displacement curve with loading and unloading segments that describe material response. Indentation testing uses the maximum point of the load-displacement curve to determine the hardness of the material, defined as the ratio of the applied load to the projected indenter / material contact area. Young's modulus *E* is another property that can be determined by nanoindentation testing (Doerner-Nix method or Oliver-Pharr method).

14.3.4 Typical grain size effects in the properties of nanomaterials

Many properties observed for nanocrystalline materials are directly associated with grain boundaries and / or triple junctions, e.g. the increase of thermal resistivity in ZrO_2 thermal barrier coatings (see Pabst – monograph chapter in Nalwa and Tseng, in press).