Electrochemical Synthesis of Nanocrystalline Materials

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Due to their ultra-fine grain structure, nanocrystalline materials exhibit significant improvements in selected mechanical, physical and chemical properties compared to their polycrystalline counterparts. For this reason the preparation of nanostructured materials by electrochemical methods [1-3] has found worldwide much attention, because these techniques allow a controlled variation of the crystallite size, and therefore the chemical and physical properties can be controlled.

The electrochemical production of nanomaterials is very advantageous because the most important steps in nanocrystal formation, the nuclei formation and nuclei growth, can be controlled by the physical- (e.g. current density, current characteristics, temperature, hydrodynamic conditions) and chemical parameters (grain refiners, complex formers, additives, pH-value).

In this contribution we discuss how these parameters influence the nuclei's growth and how it can be used to control the crystallite size of metallic deposits prepared from aqueous solutions (e.g. Pd, Cu, Au, Fe, Fe_xNi_{1-x}) or from ionic liquids (Al, In, Al_xMn_{1-x}).

The **p**ulsed **e**lectro**d**eposition technique (PED) is a versatile method for the preparation of nanostructured metals and alloys by a pulsed current deposition. It allows the preparation of large bulk samples with high purity, low porosity and enhanced thermal stability.

The pulse reverse technique was used to prepare nanostructured nickel samples which show a thermal stability up to 873 K. During the cathodic pulse the formation of nickel crystallites takes place and during the anodic pulse we observe a doping of the grain boundaries with nickel oxide resulting from oxygen formation. The nickel oxide content in the grain boundaries can be controlled by the intensity of the anodic pulse. In this way it is possible to vary the oxide content between 900 and 6000 wt.-ppm. The oxide-doping in the grain boundaries impedes the diffusion of the nickel atoms, and thus crystallites were stabilized. Samples with a oxygen content of 6000 wt.-ppm could be stabilized with 40 nm at 873 K.

The results received from the experiments in aqueous solutions can be transfered to depositions from ionic liquids (IL) [4,5]. The ionic liquids employed for theses studies consist of mixtures of an inorganic (e.g., $AlCl_3$) and an organic component (e.g. 1-Butyl-3-methyl-imidazoliumchloride, [BMIm]Cl or 1-Ethyl-3-methyl-1H-imidazoliumchloride, [EMIm]Cl). These mixtures are liquid in the temperature range between –50 and 200°C and exhibit low viscosity (ca. 10^{-2} Pa s), sufficient conductivity (10^{-2} $\Omega^{-1}cm^{-1}$, 25°C) and a broad electrochemical window of up to 6 Volt. Most of these ionic liquids are inflammable, and they have no measurable vapour pressure. The high thermal stability allows process temperatures up to 200°C. Due to a good solubility for many inorganic metal salts ionic liquids can be used for electrosynthesis of polycrystalline and nanostructured materials. The use of such salt mixtures enables the deposition of metallic materials like Al, In, W, $Al_xMn_{1-x,}$ or Al_xFe_{1-x}. The variation of physical and chemical process parameter allows the deposition of samples with crystallite sizes from 10 up to several hundred nm. Figure 1 and 2 show how the crystallite size can be influenced by the chemical (amount of additives) and physical (current density) parameters. A disadvantage of $AlCl_3$ based systems is that they are extremely hygroscopic. New systems with organic anions like e.g. bis-(trifluoromethyl-sulfonyl)amide, trifluoromethane-sulfonate or tosylate show a sufficient stability against water and can be heated, even under air, without decomposition up to 300°C. Experiments with these compounds are very promising and in the opinion of the authors IL will gain importance for the electrodeposition of nanocrystalline metals/alloys in the future.
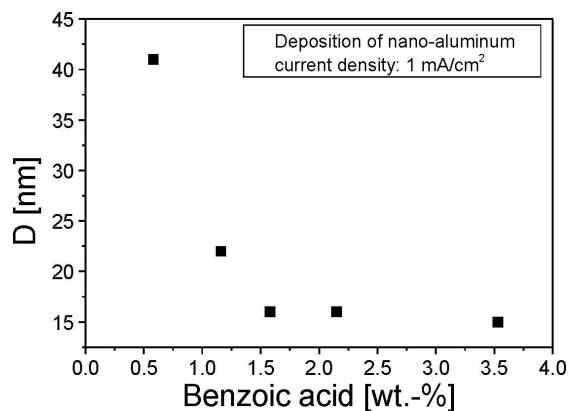

Fig. 1: Electrochemical deposition of nanostructured aluminum from an ionic liquid (65 mol.-% $AlCl_3$ / 35 mol.-% of [BMIm]Cl). Benzoic acid was used as grain refining additive.
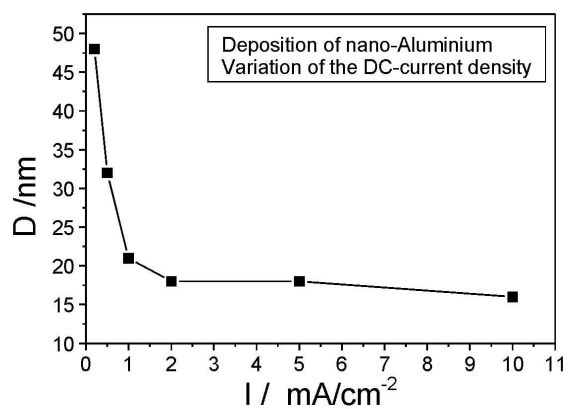

Fig. 2: The influence of the physical process parameter (current density) on the crystallite size of n-aluminum.

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