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Excess Gibbs free energy and kinetics of grain growth of nanostructured silver

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Abstract Samples of nanostructured silver were prepared by a mechanochemical technique and by electrodeposition. In the former, the microstructure was stabilized by intergranular cosegregation of Mg and O atoms. The excess Gibbs free energy of these samples was investigated by e.m.f. measurements at 453 K in a solid state electrochemical cell with AgI as a solid electrolyte. Electrodeposited pure silver samples had a labile microstructure even at 298 K. Their structural relaxation process was monitored in situ by chronopotentiometric measurements in an aqueous iodoargentate electrolyte. The time dependence of the e.m.f. could be quantitatively described by a parabolic law of grain growth without any adjustable parameter.

Key words Silver · Nanostructure · Gibbs free energy · Kinetics · Grain growth

Introduction

During the past two decades, a number of advanced synthetic techniques for ultra-fine grained materials have been developed, including inert gas condensation, electrodeposition and ball milling. Following a suggestion by Gleiter [1, 2], nanocrystalline materials, i.e. compacts of very small crystallites with grain diameters less than 100 nm, may present unique properties. The thermodynamic data of these materials are thus an interesting subject for investigation. Modified thermodynamic properties, like anomalous melting points [3], can indeed be observed for certain materials with a crystallite size below 100 nm, because of the excess interfacial free energy. One can ask at which size a cluster of atoms can be regarded as a phase in the sense of classical thermodynamics.

Extremely sensitive methods are necessary to measure the specific thermodynamic properties of grain boundaries in a coarse-grained material. Experimental studies have focused on the measurement of dihedral angles, which are an indirect measure of the interfacial energy [4]. However, as the grain size decreases, grain boundaries begin to contribute significantly to macroscopic properties of a material and can then be studied by a variety of experimental techniques. The preparation of nanocrystalline materials with a high-grain boundary area opens thus a new field for experimental investigation of the thermodynamics of interfaces. In contrast to dihedral angle measurements, the calorimetric determination of interfacial enthalpies can be direct, and absolute: measurements on nanocrystalline materials were made with commercial calorimeters [5, 6]. Electrochemical e.m.f. measurements have been applied for a long time to study Gibbs free energies of solids; they have also been used to study the excess Gibbs free energy of nanocrystalline or amorphous materials [7, 8].

The thermally activated relaxation of non-equilibrium structures in nanocrystalline materials, especially grain growth, is important both from a fundamental point of view as well as for applications, because it limits the time and temperature of operation of nanocrystalline devices. The decrease of interfacial free energy is the driving force for the formation of larger particles. The microstructure relaxes at temperatures high enough to overcome the activation barrier for grain boundary motion. Strategies for inhibiting grain growth are chiefly based on solute segregation, which can influence interfacial thermodynamics (reduction of interfacial energy) and kinetics (reduction of grain boundary mobility). Grain growth is usually studied by observation in the optical or electron microscope, but these techniques can give only kinetic but no thermodynamic information. However, in

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nanocrystalline materials, scanning calorimetry [5, 6] and chronopotentiometric experiments can monitor structural relaxation phenomena, like grain growth, and can be used to obtain thermodynamic and kinetic data.

Silver is a model material for an electrochemical investigation, because reversible electrochemical cells can be designed with silver iodide as a solid electrolyte above 420 K as well as in aqueous solution at room temperature (only a very limited number of metals exhibit their reversible potential at ordinary temperatures). Furthermore, silver is a noble metal and this reduces the risk of parasitic corrosion processes. The stability of small silver particles in redox buffers was studied by Konstantinov et al. [9]. Fletcher et al. [10] investigated the nucleation and growth of microcrystalline silver deposits on glassy carbon electrodes by voltammetry. In our work, nanocrystalline silver samples were prepared by two different routes: electrodeposition and mechanical deformation/internal oxidation. In the latter process, solute segregation was used to reduce the grain boundary mobility; consequently, the microstructure of the nanostructured silver was sufficiently stabilized to allow e.m.f. measurements at moderate temperatures. Contrariwise, the microstructure of the electrodeposited pure silver was very labile. Here, the e.m.f. technique permitted us to monitor the recrystallization process in situ; the time dependence of the e.m.f. was accurately described without any adjustable parameter.

Experimental

Sample preparation

Electrodeposition, especially by pulse techniques, is a powerful and rather inexpensive way to prepare nanocrystalline metals [11]. The mechanosynthesis techniques include ball milling [12] and severe plastic deformation [13]. In our work, two different preparation techniques were worked out. One used a mechanical treatment to obtain small crystallites and an interfacial cosegregation of solutes to stabilize the microstructure and inhibit grain growth [14, 15]; the other was electrodeposition from a special aqueous electrolyte [16]. Details of the experiments can be found elsewhere [14–16].

Mechanical deformation and internal oxidation

The idea was to prepare a nanocrystalline material by cold-rolling and to stabilize the microstructure by internal oxidation [15]. First, a solid solution of 1 at% magnesium or aluminum in silver was prepared by fusion; both solutes have a high affinity for oxygen. Second, a high density of dislocations was created by heavily cold-rolling the silver sample (98% deformation); dislocations act as nucleation sites for numerous grains during the following annealing. Finally, the sample was internally oxidized in air at relatively low temperature (723 K, 21 days); clusters of aluminum or magnesium atoms with oxygen were formed. The solubility of Al or Mg in silver is negligible in the presence of oxygen and the Raoultian activity of silver is thus practically one. The clusters are located at the grain boundaries; the process is equivalent to an interfacial cosegregation of Al-O or Mg-O in silver, which inhibits subsequent grain growth.

Electrodeposition

Silver could be deposited in nanocrystalline form using a special electrolyte [16], prepared by addition of a diluted silver nitrate solution to a concentrated solution of potassium iodide. Under these conditions, iodoargentate complexes $[\mathrm{AgI}_x]^{(x-1)-}$ were formed and silver iodide did not precipitate.

Different cathode materials were studied for deposition. The best results were obtained on polycrystalline silver and copper. The cathodes must be carefully polished to obtain nanocrystalline deposits. Distinctly larger silver crystallites were observed at polishing scratches; the average grain size of the deposit and probably the rate of grain growth were determined by the morphology of the cathode.

The anode was a high-purity cylinder of polycrystalline silver. A constant current was imposed during a short time, typically 10 s. The deposition current must be higher than a certain lower limit, in our experiments 0.04 A/cm^2, to obtain nanocrystalline deposits.

Sample characterization

High-impedance electrometers were used for the e.m.f. measurements (Keithley 617) and the reversibility tests were performed with a high-precision current source (Keithley 220). The e.m.f. of the electrochemically deposited nanocrystalline silver was recorded immediately after deposition in the electrolytic solution. The mechanically prepared silver was studied in a silver iodide solid electrolyte cell at 453 ± 1 K under argon. Silver iodide is a well-known fast ionic conductor for Ag^+ ions above 420 K [17]. Coarse-grained polycrystalline silver was the reference electrode in both cases.

All investigated nanocrystalline samples were checked by X-ray diffraction (XRD) and scanning electron microscopy (SEM) before and after the experiments. High-resolution electron microscopy studies, however, were unsuccessful, because of preparation problems. The average grain size of mechanochemically prepared silver (≈40 nm) was estimated from Scherrer's equation using XRD [15]. However, SEM observations showed that we have actually a relatively broad distribution of grain sizes, probably due to an inhomogeneous distribution of dislocations in the sample after the mechanical treatment. Scherrer's equation neglects possible line broadening caused by other structural defects, like dislocations, and by internal strain in the samples. Taking into account the possibility of residual internal strains due to the mechanical processing even after annealing, we consider that the calculated average grain size is actually a lower bound value.

Results and discussion

Excess Gibbs free energy of nanostructured silver samples

The excess Gibbs free energy of nanocrystalline silver samples, prepared by cold-rolling with an internal oxidation treatment, was determined from e.m.f. measurements at 453 K with silver iodide as a solid electrolyte. The cell can be written:

$$(-)\mathrm{Ag}\ (\mathrm{nc})\ |\mathrm{AgI}|\ \mathrm{Ag}\ (\mathrm{pc})\ (+) \tag{1}$$

At 453 K, the microstructure of the nanocrystalline material remained unchanged during several weeks and a reproducible and stable e.m.f. was obtained: $\Delta E = 1.5 \pm 0.2$ mV. The reversibility of the cell was tested by the usual polarization technique with small currents. No significant difference was observed between samples containing magnesium or aluminum as solutes.

The accessible temperature domain for measurements was rather restricted, because of the phase transition of α-AgI into the much less conducting β-phase at 420 K [17] and a possible microstructural transformation of the nanocrystalline material at higher temperatures. Between 423 and 523 K, the e.m.f. variation was less than the experimental uncertainty.

The cell reaction is the transfer of silver from the nanocrystalline to the coarse-grained silver electrode and the electrochemical equilibrium condition is:

$$\Delta G^{\mathrm{ex}} = G\Big(\mathrm{Ag}_{(\mathrm{nc})}\Big) - G\Big(\mathrm{Ag}_{(\mathrm{pc})}\Big) = -F\Delta E \tag{2}$$

The excess Gibbs free energy ΔG^{ex} of the nanostructured silver amounts to 0.13 ± 0.02 kJ mol^{-1}. This is a complex value, which includes all atoms of the electrodes in their local environment: atoms in the bulk, at interfaces or near other structural defects, like dislocations. Few electrochemical studies of metastable metallic phases have been reported in the literature. Kirchheim and colleagues [7] found large excess Gibbs free energies for nanocrystalline copper, nickel and palladium, but the reversible e.m.f. was measured in acidic aqueous solutions. The temperature dependence of the e.m.f. was also much higher than in our work and the e.m.f. even changed sign at higher temperature. It is difficult to compare the experiments, because the investigated elements and electrolytes are different. However, a main problem of acidic solutions is the risk of protonic corrosion. From the negligible temperature dependence of the e.m.f. between 423 and 523 K in our experiments, we estimate that the temperature coefficient of the grain boundary free energy must be smaller than 3×10^{-4} J m^{-2} K^{-1} (see below).

The molar interfacial area A is related to the mean grain radius r of the material by a geometrical factor g:

$$A = gV/r \tag{3}$$

where V is the molar volume of the material under study [$V(\mathrm{Ag}) = 10.3$ cm^3 mol^{-1}]. The geometrical factor g takes the distribution of grain shapes and grain sizes in a real material with complicated microstructure into account. Chen and Spaepen [5] estimated a mean value of the geometrical factor, $g = 1.3 \pm 0.2$, for different grain shapes (spherical, cubic, tetrakaidecahedral) and different grain size distribution functions (identical grains, lognormal distribution, Wagner-Hillert and Louat distribution) and used it to study a nanocrystalline Al-Mn alloy. The value of g and its confidence limits were later experimentally confirmed by Terwilliger and Chiang [18] for nanocrystalline titanium dioxide. We thus accord some confidence to this approach, which may appear simplistic in the first view, but works reasonably for very different materials with fine grains.

Under the assumption that the excess Gibbs free energy of the nanocrystalline material is exclusively due to the high density of interfaces, we can calculate an average interfacial free energy. The contribution of other structural defects, such as dislocations, is neglected; this assumption is not unrealistic, because there is now convincing evidence that the density of extended crystal defects inside nanometer-sized crystallites is generally very low [19]. The excess Gibbs free energy due to interfaces is defined by

$$\Delta G^{\mathrm{ex}} \equiv \sigma A \tag{4}$$

with the specific interfacial free energy σ and the interfacial area A. Combining with Eq. 3, one obtains the relation:

$$\Delta G^{\mathrm{ex}} = g\sigma V/r \tag{5}$$

which is similar to the generalized capillary equation obtained for polycrystalline solids by Weissmüller and Cahn [20].

Combining Eq. 5 with Eq. 2, the dependence of e.m.f. on the grain radius can be written:

$$\Delta E = -\sigma g V/Fr \tag{6}$$

A similar equation was validated in the case of small silver particles by Konstantinov et al. [9]. Using the mean grain radius found from X-ray diffraction ($r = 20$ nm), we obtain a mean specific interfacial free energy of nanocrystalline silver: $\sigma(\mathrm{Ag}) = 0.2$ J m^{-2}. This value is somewhat lower than the literature value for the specific free energy of high-angle grain boundaries in polycrystalline silver (0.4 J m^{-2} [4]). Our specific interfacial free energy can be regarded as a lower bound value, because the grain radius r is probably underevaluated by the use of Scherrer's equation. Furthermore, the cosegregation of solute and oxygen atoms tends to reduce the interfacial free energy. The precision is therefore not sufficient to conclude if a particle size effect on the grain boundary free energy exists in nanocrystalline silver.

Kinetics of grain growth of electrodeposited nanocrystalline silver

Nanocrystalline silver without segregated solutes at the interfaces has an unstable microstructure and grain growth starts immediately after the electrodeposition. The grain growth in the solution can be monitored by measuring the time dependence of the e.m.f. (Fig. 1). The electrolytic solution seemed to stabilize the material; the interfacial energy, which is the driving force for grain growth, was probably reduced in the electrolytic solution by adsorption of iodide ions. If the deposit was taken out of the electrolytic solution, grain growth was very fast, and the colour of the deposit changed instantaneously from black to metallic grey.

To confirm our interpretation, we tried to describe the time dependence of the e.m.f. in solution quantitatively by Turnbull's parabolic law, which describes normal grain growth processes in polycrystalline materials [21]:

$$r^2 = r_0^2 + 2kt \tag{7}$$

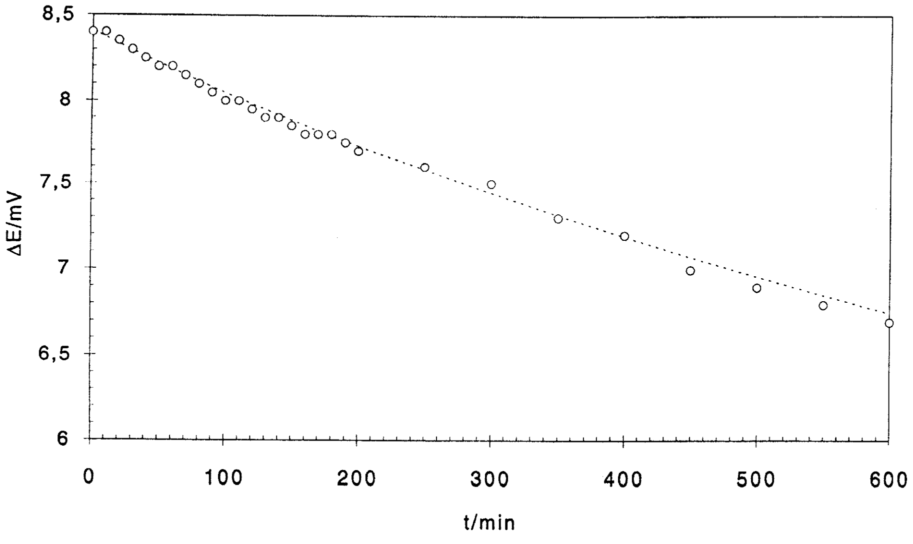

Fig. 1 Time dependence of the e.m.f. of a cell with nanocrystalline pure silver: $Ag_{(nc)}$ $|[AgI_x]^{(x-1)-}(aq)|$ $Ag_{(pc)}$. *Dotted line*: calculated curve according to Eqs. 6 and 7

where r_0 is the initial grain size and k the rate of growth, which is related to the interfacial mobility. Inserting Eq. 7 into Eq. 6, we obtain after a slight rearrangement:

$$1/\Delta E^2 = A\left(r_0^2 + 2kt\right) \quad (8)$$

with $A = \{F/(\sigma g V)\}^2$.

A linear relation between $1/\Delta E^2$ and time should thus be observed and this is actually the case (Fig. 2). We can calculate the initial grain size of our material from the intercept and the rate of growth from the slope. We used the previously derived mean interfacial free energy for silver ($\sigma = 0.2$ J m^{-2}). This may introduce a little error into the calculation, because the material is not the same, but this factor can be corrected easily if better data for the interfacial free energy become available. With the present data, we obtain an initial grain size of silver: $d_0 = 2 \times r_0 = 7 \pm 1$ nm and a rate of growth $k \approx 10^{-18}$ cm^2 s^{-1} at 298 K. The initial grain size is comparable to that of electrodeposited copper (10 nm [22]). The rate of growth is in the same order of magnitude as the grain boundary self-diffusion coefficient D_{gb} in conventional silver, extrapolated to 298 K from the data of Hoffman and Turnbull ($D_{gb} \approx 10^{-17}$ cm^2 s^{-1} [23]). The time dependence of the e.m.f. is perfectly described without any adjustable parameter (dotted line in Fig. 1).

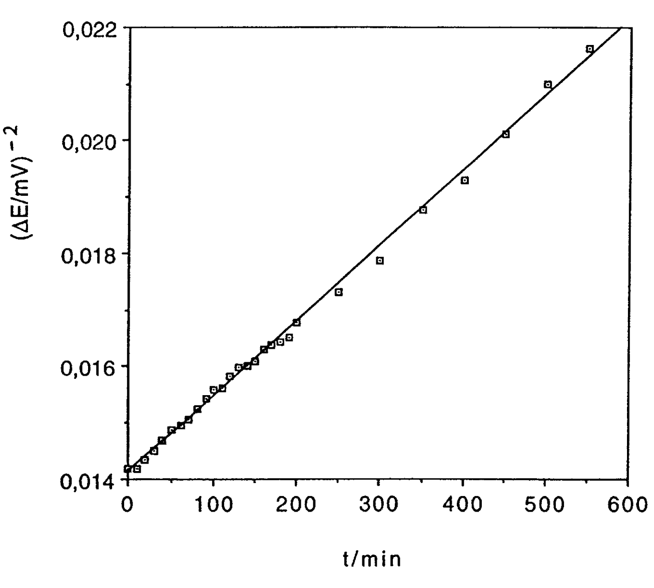

Fig. 2 Growth law for nanocrystalline pure silver according to Eq. 8

It may be surprising that an ideal parabolic law is applicable to a nanocrystalline material. However, the grain growth exponent was experimentally investigated for several nanocrystalline metallic phases. Chen and Spaepen [5] found $n = 1.9 \pm 0.2$ for $Al_{83}Mn_{17}$ alloys, and Huang et al. [24] found 1.85 and 1.92 for copper; they are close to the value $n = 2$ used in most theoretical models and in our derivation.

Concerning the mechanism of grain growth in solution, measurements of dissolution rates of polycrystalline metals indicate that the dissolution at grain boundary sites is two to three orders of magnitude faster than in single crystalline samples at the same driving force (overpotential) [7]. This is equivalent to a higher exchange current density at grain boundaries. On a larger time scale, this may cause the grains to grow at the expense of grain boundary regions. A grain growth mechanism via the electrolytic solution (a sort of local corrosion) is therefore quite possible. Since diffusion in aqueous solution is orders of magnitude faster than in the solid state, the overall rate of grain growth would be determined by diffusion processes in the nanocrystalline material and grain boundary diffusion is obviously dominant at room temperature.

Conclusion

The importance of the preparation technique for the properties of nanocrystalline materials is evident: electrodeposited silver grew in minutes even at room temperature, whereas mechanically deformed silver with segregated solutes had a metastable microstructure during several weeks at moderate temperature.

The excess Gibbs free energy of nanocrystalline silver was determined from electrochemical measurements. The calculated mean interfacial free energy is only an estimation because it averages over interfaces with different structure and energy.

The grain growth kinetics of nanocrystalline silver could be perfectly described by a parabolic law with a rate of growth consistent with grain boundary diffusion data. This in situ observation is made possible by the high interface density of the nanocrystalline material.

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