Electrodeposition of Nanocrystalline Silver: Study of Grain Growth by Measurement of Reversible Electromotive Force

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Electrodeposition of pure nanocrystalline silver from a highly concentrated potassium iodide solution containing silver nitrate was described and discussed. The reversible electrode potential of the nanocrystalline material was measured versus polycrystalline silver. Grain growth of the deposit could be quantitatively determined from the decrease of the electrode potential with time. A parabolic law of growth is fulfilled, which gives the initial grain size of silver by extrapolation.

Introduction

Nanostructured and nanocrystalline materials, i.e., materials with a typical grain size of some tens of nanometers or less, have interesting properties; especially mechanical performances, ductility, hardness, and corrosion resistance can be much improved.[1] Electrodeposition is a powerful technique for the preparation of some of these materials, especially metals and alloys.[2]

The density of crystal defects in these substances is very high, thus causing an excess Gibbs free energy. For metals, this quantity can, in principle, be determined electrochemically from the emf between nanocrystalline and polycrystalline electrode samples.

It is known from practice that even in the polycrystalline state only a very limited number of metals, among them silver, exhibit their reversible potentials at ordinary temperature, where the grain growth of extremely small crystals is not too fast.

The objective of this work is thus twofold: to present a special electrolyte for the electrodeposition of nanocrystalline silver and to study its grain growth by measuring the electrode potential versus polycrystalline silver.

Experimental Section

The electrolytic solution[3] was prepared from a highly concentrated potassium iodide solution (40 g in 60 mL of water) and a second solution containing 3 g of silver nitrate in 20 mL of water, which was slowly added under fast stirring to avoid the precipitation of silver iodide. After mixing, the solution was diluted to 100 mL without precipitation. It was stable against oxidation by air, as tested with starch solution.

The anode was a high-purity silver cylinder of 2.4 cm diameter and 0.4 cm thickness. Cathode materials should be inert against silver and permit a good adherence of the electrodeposits: silver, copper, vitreous carbon, and nickel as wires or rods were used. They were previously polished carefully with diamond paste and a chamois leather; this was decisive for deposition of the nanocrystalline silver.

A thermostated double-wall cell was used for electrodeposition. The cover had openings for the three electrodes. The cathode substrate was made of different materials (see above),

and the anode and a reference electrode were made of polycrystalline silver; there was an in- and outlet for inert gas. The electrolytic solution was kept at 25.0 °C under a nitrogen flow and was stirred at constant velocity. A constant current was imposed during a short time (typically about 10 s). This corresponded to a thickness of deposit in the range of 10 μm. Its electrode potential was then measured for some hours versus the polycrystalline silver reference electrode. After that, all deposits were observed ex situ by scanning electron microscopy, and an EDX analysis was performed.

Results

Faraday's law was checked by weighing the cathodes before and after electrodeposition: more than 98% of theory was achieved in the case of copper and silver as substrates. Taking the uncertainty of the weighing procedure into account, the agreement with Faraday's law is good. With nickel and vitreous carbon as cathode, the adherence of the silver deposits was unsatisfactory.

Due to grain growth, grain sizes from SEM micrographs are not representative of the original deposits in the solution. However, one can see in a typical micrograph (Figure 1) that the grain size of the deposit and probably the velocity of grain growth are determined by the surface morphology of the substrate. Distinctly larger silver grains are formed at polishing scratches.

EDX analysis showed no particular impurities, except for the presence of iodine near the detection limit. This may be due to an incomplete rinsing of the electrode. A specific adsorption of iodide ions on the silver surface, which was studied recently,[4] could reduce the surface free energy of the nanocrystalline aggregates and stabilize the nanostructure. This is also indicated by the fact that accelerated grain growth starts immediately when the deposit is taken out of the electrolytic solution; the black nanocrystalline silver transforms into the polycrystalline material, which is gray in appearance.

The emf is a quantitative indicator: it remains stable on a plateau value immediately after electrodeposition. The duration of this plateau depends on the starting value of emf; after this period a steady decrease of emf is observed (Figure 2), which can be correlated with the visible aspect of the deposit in the solution. Another interesting and typical feature for electrodeposition is the existence of a minimal current density to obtain nanocrystalline silver. Indicatively, this limit is here 0.04

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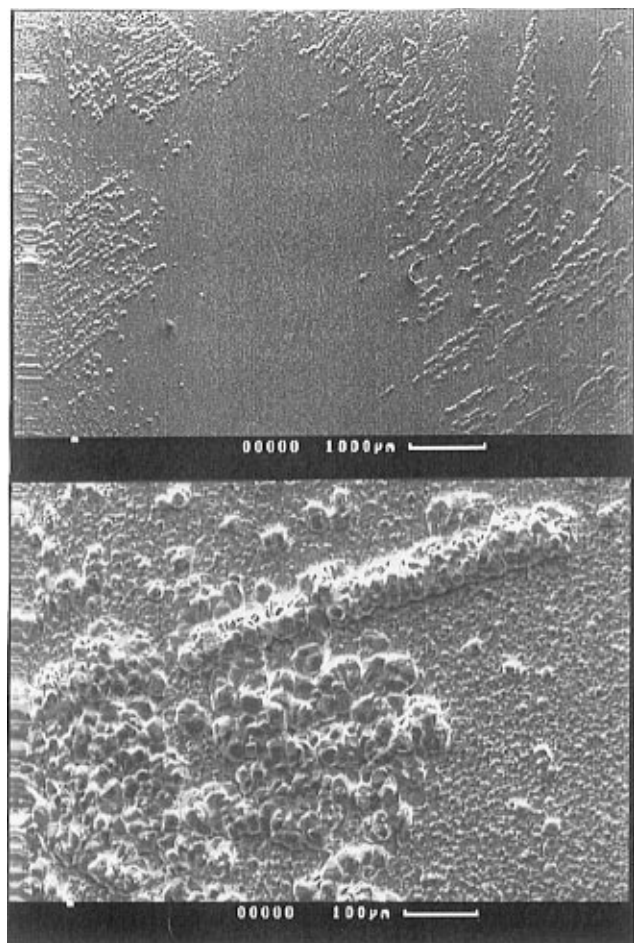
Figure 1. SEM micrographs of a grown silver deposit on a copper cathode. Enhanced grain growth occurs near polishing scratches ($i =$ 0.04 A/cm^2).
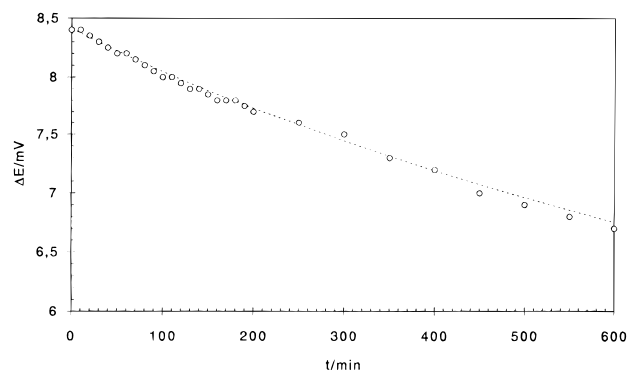
Figure 2. Emf decrease after deposition of nanocrystalline silver on a polycrystalline silver cathode ($i =$ 0.21 A/cm^2, $t =$ 10 s). Dotted line: calculated curve using eqs 4 and 5 with $r_0 =$ 3.3 nm and $k =$ 0.3 nm^2/h.

A/cm^2. On the other hand, high current densities are not favorable for good adhesion.

Discussion

Electrodeposition as a physical phenomenon and as a preparation procedure depends on thermodynamic, kinetic, and structural factors. The main thermodynamic parameters are the potential of deposition and the concentration of electroactive species in the electrolyte. From a kinetic point of view, mass transport in the electrolyte, surface diffusion of adatoms on the substrate, and formation and growth of nuclei are most important aspects. Concerning structural factors, the morphology of the

substrate and the structural relationship with the deposit are central. The weak adhesion of nanocrystalline silver on nickel and on vitreous carbon is obviously caused by the lack of epitaxial nucleation sites on the substrate: the nickel surface is probably covered by hydrated nickel oxides,[5] which are amorphous like vitreous carbon.

The mechanistic steps of electrodeposition of nanocrystalline silver include transport of silver ions and complexes ($AgI_n^{(n-1)-}$, $n \geq 0$) to the cathode by diffusion and convection, charge transfer at the cathode, and finally crystallization of the deposit. It is well-known that, depending on the experimental conditions, either growth of existing crystals or nucleation of new crystallites occurs.[6] Factors increasing the kinetics of nucleation with respect to kinetics of growth are favorable to a small grain size and thus the formation of nanostructured deposits. A decrease of silver ion concentration in the electrolyte leads to a large concentration polarization and thus a high overpotential, which increases the number of nuclei and is favorable for the deposition of small-grain materials. This condition was very well fulfilled in our electrolyte, because the high concentration of iodide ions, which form iodoargentate complexes, reduces the concentration of free silver ions. Furthermore, iodide ions seem to stabilize the deposits probably by adsorption on the silver surface, thus reducing the surface free energy of the nanostructured material and, as a consequence, the driving force for recrystallization. Ag−I adsorption layers are well-known in the field of electrochemical sensors.[7] High cathodic current densities also increase the overpotential by an additional lowering of the silver ion concentration.

The second interesting point of this work is the measurement of the emf of the cell consisting of the nanocrystalline cathodes and the polycrystalline silver anode in the same solution as used for the electrolysis. Under the assumption that the nanocrystalline silver electrode is reversible with respect to the electrochemical exchange reaction, although its crystal state is metastable, the emf ΔE gives the excess Gibbs free energy ΔG^{xs} of the nanocrystalline material ($F =$ Faraday's constant).

$$\Delta G^{xs} = -F\Delta E \qquad (1)$$

$\Delta G^{xs} < 0$ is an energetical measure of all crystal defects, but mainly of interfaces. If we suppose that the contribution of other structural defects (e.g., dislocations) is negligible, it can be related to the mean interfacial energy γ and the interfacial area A of the material:

$$\Delta G^{xs} \approx \gamma A \qquad (2)$$

The interfacial area A can be calculated using the mean grain radius r, the molar volume of the material ($V(Ag) = $ 10.3 cm^3/mol), and a geometrical factor, which takes the distribution of grain shapes and sizes into account.

$$A/V = g/r \qquad (3)$$

In this apparently simple equation, the complexity of the nanostructured material is hidden in the geometrical factor g. Chen and Spaepen[8] calculated a mean value from different grain size distribution functions ($g = 1.3 \pm 0.2$). Combining eqs 1−3 leads to relation 4 between the emf of the electrochemical cell ΔE and the mean grain radius r of the electrodeposited material:

$$\Delta E = -\gamma g V/(Fr) \qquad (4)$$

The decrease of cell voltage ΔE after an initial constant plateau was interpreted by normal grain growth of the silver
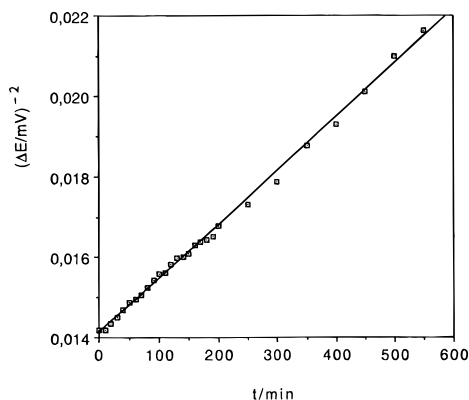
Figure 3. Growth law for nanocrystalline silver according to eq 6.

particles. To check the validity of this assumption, we now introduce Turnbull's parabolic law describing normal grain growth[9] with an initial grain radius r_0 and an interfacial mobility k.

$$r^2 = r_0{}^2 + 2kt \qquad (5)$$

Inserting this relation into the fundamental eq 4 yields the dependence of cell voltage during normal grain growth,[10] which can be written in the form of eq 6:

$$1/\Delta E^2 = A r_0{}^2 + 2Akt \qquad \text{with } A = (F/(\gamma g V))^2 \qquad (6)$$

When $1/\Delta E^2$ is plotted versus time t, a straight line should be obtained, which permits to calculate an initial mean grain radius r_0 of the nanocrystalline deposit from the intercept as well as the rate of grain growth k from the slope. Figure 3 shows that a straight line is actually obtained for a period as long as 10 h after deposition. With $g = 1.3$ and a mean interfacial energy of silver determined on nanostructured samples[11,12] (0.2 J/m^2), the calculated initial grain size of the silver particles is 7 ± 1 nm and the rate of growth about 0.3

nm^2/h at 25 °C. The latter value is 1 order of magnitude higher than for pure aluminum.[8] The initial grain size is comparable to electrodeposited nanocrystalline copper (10 nm).[13,14]

An experimental check of the initial mean grain radius by an independent technique is very desirable, but it should be done "in situ" or with rapidly cooled samples. On the other hand, all aspects of the fast silver deposition from our solution are very interesting fundamental questions to be investigated by tunneling microscopy.

Conclusion

Pure nanocrystalline silver deposits were obtained from an electrolytic solution containing silver nitrate in a highly concentrated potassium iodide solution. The electrode potential of the nanocrystalline silver was measured and its increase with time quantitatively interpreted as due to a grain growth process.

References and Notes

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