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Effect of centrifugal fields on the solid-state film formation as applied to gold electrodeposits

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Surfaces with lower fractal dimensions were generated during gold deposition under stronger centrifugal fields.

Centrifugal effects on physical phenomena have been reported.[1–3] However, there are few reports on chemical processes, *e.g.*, centrifugal effects on corrosion under centrifugal fields from 1 to 39 g were studied.[4]

The fractal structure of solid films is of interest for surface science. Fractal geometry[5] is widely used in physical sciences.[5–9]

In this paper, the effect of centrifugal fields on the fractal structure of solid-state films is described. For this purpose, gold electrodeposits were used because of their well-known properties and structures.

The deposition of gold onto a gold substrate was carried out electrochemically by the electroreduction of an oxide layer formed on a polycrystalline gold electrode.[10,11] The electrodeposition of the oxide layer was performed under potentiodynamic conditions in 0.5 M H_2SO_4 at 298 K and a potential sweep rate of 20 mV s^{-1}. The thickness of the gold electrodeposits was about 10^{-5}–10^{-4} cm (for the surface prepared under the Earth's gravity), and the growth rate of electrodeposits was in the range 10^{-6}–10^{-5} cm s^{-1}. The true surface area of an Au electrodeposit was estimated using cyclic voltammetry based on oxygen electroadsorption.[12] It was about 80 times larger than the true surface area of an Au substrate electrode, which is in agreement with published data.[13]

An electrochemical cell for controlling the centrifugal fields between 1 and 40 *g* was employed, which was described in the literature.[4,14] The centrifugal field was in perpendicular vector on the electrode surface to aggravate the applied force on the electrodeposition process. After the preparation, the Au electrodeposits were placed into a conventional cell for a fractal study.

The fractal dimension of solid film surfaces is determined based on the diffusion of electroactive species towards electrode surfaces.

The electrochemical reaction of ferricyanide, a well-characterised anion, on the gold surface was used as a redox probe to determine the fractal dimension of electrode surfaces. The electrolyte was an aqueous solution of 3 M NaCl, 15 mM $K_4Fe(CN)_6$ and 15 mM $K_3Fe(CN)_6$. The initial potential was 0.6 V, at which no electrochemical reduction of $Fe(CN)_6^{3-}$ occurs. By stepping the potential to zero, almost all ferricyanide was reduced to $Fe(CN)_6^{4-}$.

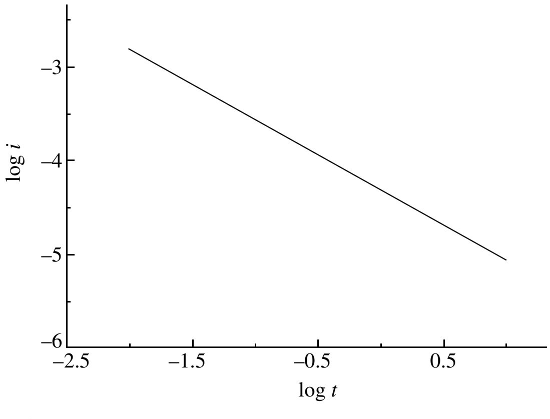

Figure 1 Typical current transient for the Au electrodeposit prepared under the Earth's gravity.

Table 1 Fractality of Au electrodeposits prepared under various centrifugal fields.

Electrode	Centrifugal acceleration force/*g*	Fractal parameter α	Fractal dimension D_f
1	1	0.756	2.51
2	10	0.733	2.47
3	25	0.709	2.42
4	40	0.695	2.39

The fractal parameter α can be easily transformed to the fractal dimension D_f according to the equation:[15]

$$\alpha = (D_f - 1)/2. \quad (1)$$

For determining the fractal dimensions of gold electrodeposits, a chronoamperometric technique was used. In the conventional planar case, the diffusion-controlled current shows the well-known inverse square root time dependence $I \propto t^{-1/2}$.[16] According to equation (1), the power of 1/2 (the fractal parameter) corresponds to a dimension of two from the standpoint of Euclidean geometry. For rough (fractal) electrodes, the Cottrell equation transforms to the extended form:[17]

$$I(t) = \sigma_F t^{-\alpha}, \quad (2)$$

where σ_F is a proportionality factor. This indicates that, in a certain time interval, the current is a power-law function of time, and the fractal dimension is included in the exponent, $\alpha = (D_f - 1)/2$. Therefore, the fractal dimension can be determined from the slope of the current plotted as a function of time on the logarithmic coordinates. The validity of this method was examined by numerical Monte Carlo simulations[15] and by experiments using artificial fractal electrodes and real ones.[17,18]

Figure 1 shows a typical diffusion-controlled current of a gold electrodeposit prepared under the Earth's gravity (1 *g*) in an aqueous solution containing the electroactive species. It was plotted in a log–log scale to determine the fractal dimension based on equation (2). Thus, the fractal dimension of the Au-electrodeposit surface can be estimated by equation (1). The results are summarised in Table 1. The fractal dimension of Au electrodeposits decreases with centrifugal field strength. This can be explained by the effect of centrifugal forces on squeezing the porous film of the Au electrodeposits. It is expected that the thickness of the electrodeposits decreases as higher centrifugal fields are applied. However, this decrease is not very noticeable.

Note that the proposed effect is stronger for other materials such as metal oxides, polymers, *etc*. The present case is the weakest example of this effect due to the constant structure of Au metal electrodeposits. In the context of this report, no attempt was made to formulate a theoretical model that can describe and predict this effect, although our ultimate goal is towards this direction.

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