Potentials of Metallic Powder Formation on the Mercury Dropping Electrode

THE formation of electrolytic metallic powders on solid electrodes at a certain potential in the region of the limiting current was first observed with copper, gold and cadmium[1,2]. However, the conditions of electrodeposition on the solid electrodes make it impossible to determine precisely the corresponding potentials[3] and to construct a series of potentials of metallic powder formation.

Using the phenomenon of metallic dendrite formation on the dropping mercury electrode[4], it is possible to determine the potential of the powder formation with a relatively high precision (± 25 mV) by microscopic observation. In the case of cadmium, for example, the powder begins to form at a potential more negative than $-0{\cdot}9$ V (Fig. 1). At the same time the concentration of the metal ion must be greater than a certain minimum value (0·0125 M for Cd^{2+}). In this way we determined the series of potentials of formation (ε_p) of various metallic powders on the mercury dropping electrode (Fig. 2). Fig. 2 shows that these potentials are independent of the concentration and that the minimum value is in general about 0·01 M. Experimentally it was found that the formation of powders is favoured by a certain value of the rate of growth of the surface of the drop. In the case of cadmium, in a range of concentration of 0·1–0·4 M, the metallic dendrites are formed when a fast capillary ($t_1 = 3$ sec) is used, while in the range of 0·025–0·05 M it is necessary to use a slow capillary ($t_1 = 75$ sec). The presence of gelatine favours the dendrite formation by diminishing the threshold of the concentration. The experimental observation shows also that the dendrites are not in close contact with the mercury; immediately after direct contact with mercury is established, the particles are rapidly dissolved in the mass of the drop and often (in the case of the cadmium, for example) an intense hydrogen discharge is observed on the non-dissolved dendrite portions.

These experimental results are in good agreement with the quantum mechanical mechanism suggested for the formation of electrolytic metallic powder[1,3] and make possible a more complete explanation of the phenomenon.

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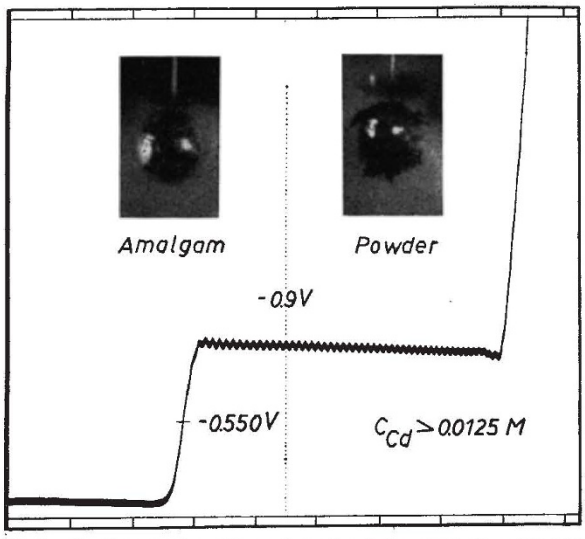

Fig. 1. Amalgam and powder regions of cadmium (cadmium chloride) discharge on dropping mercury electrode in 2 M potassium nitrate and 0·05 per cent gelatine solution. Beginning at 0 V, −200 mV/absc.

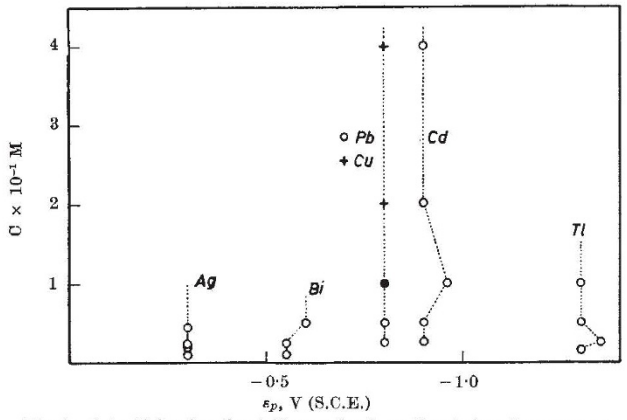

Fig. 2. Potential series of metallic powder formation (ε_p) on the mercury dropping electrode as a function of metal concentration. Silver nitrate in 3 M sulphuric acid, bismuth nitrate in 4 M hydrochloric acid and lead nitrate, cupric chloride, cadmium chloride and thallium nitrate in 2 M potassium nitrate base solution, 0·05 per cent gelatine.

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[2] Ibl, N., in *Adv. in Electrochemistry and Electrochemical Engineering*, edit. by Tobias, Ch. W., **2**, 49 (Interscience Publishers, New York and London, 1962).

[3] Călusaru, A., *Depunerea Electrolitica a Metalelor în Forma Dispersa*, **66**, 95 (Editura Academiei Române, Bucuresti, 1962).

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Nucleation of the Solid Phase by Cavitation in an Undercooled Liquid which expands on Freezing

HICKLING[1] has proposed that nucleation by cavitation in an undercooled liquid which expands on freezing is caused by adiabatic compression into a region where a high pressure phase is stable: the high pressure phase nucleates and later transforms to the stable low pressure phase. Originally, his arguments were intended to explain only the results on water, but were later extended to include other materials which expand on freezing[2], although no such observations were available.

In recent experiments we have found that gallium, which expands on freezing, behaves like water, benzene, nickel, etc., in that the solid phase can be nucleated

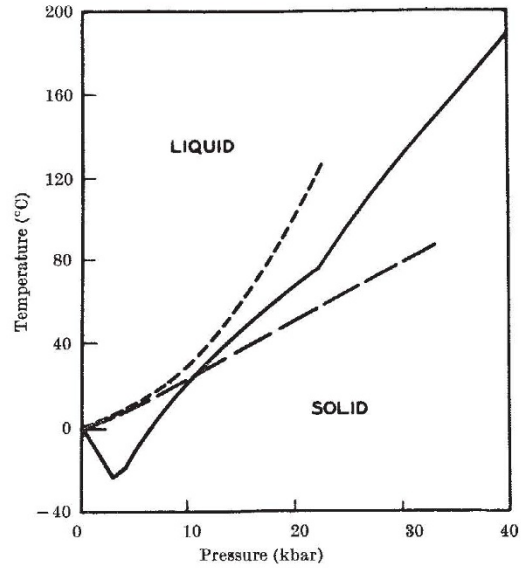

Fig. 1. Lines of adiabatic compression in water superimposed on a plot of the equilibrium melting line of ice. ——, Reversible adiabatic compression. - - -, Shock-wave adiabatic compression.