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Conference Abstract

Effect of Colloids on Electrocrystallization of Metals*

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It is an old experience in the field of electrochemical deposition of metals, that adsorption of electrochemically inactive molecules (primarily organics) has a profound effect on the morphology and texture of deposits¹. The phenomenon has found extensive application in the plating practice for producing leveling (decrease of surface roughness) and brightening effects.

It is interesting to note, however, that most of the substances reported in the literature as leveling and brightening agents²⁻⁴ are relatively simple organic compounds of low molecular weight. Effect of colloidal substances present in solution seems not to have been systematically investigated till recently. A group of Soviet scientists investigated codeposition of metals and alloys with polymers dispersed into aqueous solutions either with the help of surface active agent or by ionizing some of its ionogenic groups. The aim of their work was to obtain composite materials consisting of comparable amounts of metal particles intimately mixed with polymer. Although the obtained materials possessed useful properties (e. g. for corrosion protection), their work did not reveal clear effects of the polymer on the structure and morphology of the obtained metal particles.

In our laboratory, in the course of metal deposition studies, two cases of the effect of colloidal matter on the properties of the deposit have been investigated. In the process of deposition of cadmium onto copper electrodes, the conditions leading to the appearance of granular deposit have been sought. It has been established that, in simple cadmium salt solutions, the frequency or the appearance of the granular deposit (Figure 1) was strongly dependent on pH of the solution⁵. Granules have been obtained in the pH region 4.6 to 6.0 with the maximum at 5.2. This coincides with the pH above which the appearance of insoluble cadmium hydroxide is noted and it is very likely that it is the presence of colloidal hydroxide, which causes a decrease in nucleation rate and appearance of threedimensional outgrowth.

In another set of experiments^{7,8} the effect of dissolved organic polymer-polyvinyl pyridine-comethyl methacrylate on deposition of copper and zinc from solutions of their simple salts onto a graphite electrode has been investigated.

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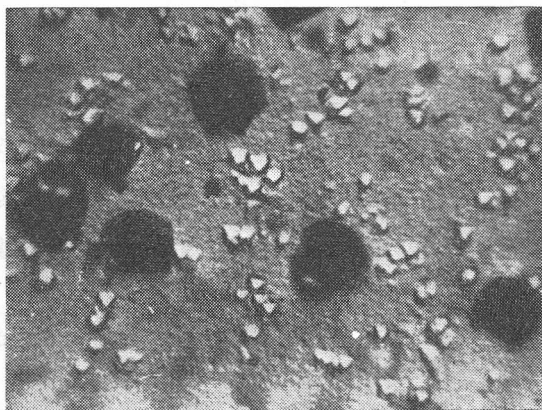


Figure 1. Granules of cadmium on a copper electrode

The polymer dissolves in slightly acid solutions ($\text{pH} < 3.5$) in cationic form and precipitates at the electrode if the solution pH is increased due to a cathodic process.

However, even before precipitation of the polymer occurs, potential sweep recordings revealed that its presence affects the crystallisation kinetics, delaying nucleation and reducing the rate of discharge at a given potential.

It was found by electron microscopy that under the same plating conditions which render dendritic deposits in pure salt solutions (Figure 2), the

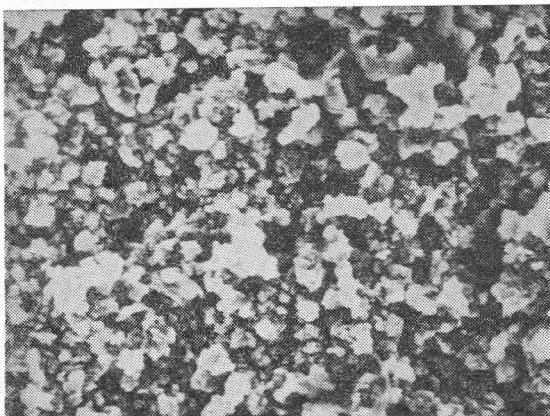


Figure 2. Deposit of zinc on graphite from pure zinc salt solution

presence of the polymer leads to spheroidization of metal particles. Although the crystal structure is maintained (X-ray examination) in external appearance the deposit consisted of well defined globules (Figure 3).

It is likely that the effect is that of strong adsorption of colloidal particles onto growing centers. It is known in the field of crystal growth that those crystal plains develop preferentially on which inhibition of growth is produced

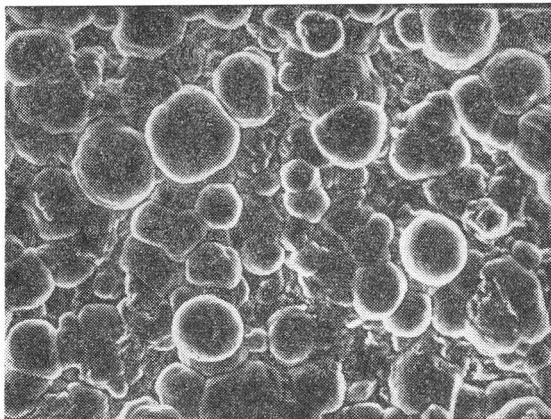


Figure 3. Deposit of zinc on graphite under the same conditions as in fig. 2, but in the presence of the polymer in osln.

by adsorption. Obviously, if adsorption is equally strong on all potential crystal plains, they are all likely to grow at the same rate and hence a sphere must result. Further experiments are on the way to investigate this model.

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SAŽETAK

Utjecaj koloida na elektrokristalizaciju metala

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Poznato je da se u tehnologiji elektroizlučivanja metala dodatkom u otopinu elektroinaktivnih, mahom organskih, molekula postižu znatni utjecaji na morfologiju i strukturu nastalog sloja. U istraživanjima izlučivanja kadmija na bakrenu podlogu, te bakra i cinka na grafitnu elektrodu, pokazalo se da dodatak kopolimera polivinilpiridin-metilmetakrilata prouzrokuje sferidizaciju izlučenih metalnih čestica, iako kristalna struktura ostaje ista kao i u odsustvu polimera.