# GROWTH OF INERT PARTICLES LYING ON A HORIZONTAL CATHODE

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The intergrowth of inert particles lying on a horizontal cathode into a metallic deposit was studied. The growth of individual particles was examined under the microscope, and the lifting of the particles by the growing deposit was also analyzed by means of a specially-developed instrument. All the inert particles examined grew into the cathodic deposit. The thickness of the deposit for which the intergrowth process began was determined by the nature of the particle, its size, the type of electrolyte employed, and the polarizability of the cathode.

Composite coatings have become widely employed for the protection of metal surfaces in the last few years, but the mechanism underlying their formation has been little studied.

We have now developed a method of studying the intergrowth of inert particles on a horizontal cathode, enabling us to simulate the growth of a single particle; the part of test particle is played by the thin (10-16 $\mu$ diameter) end of a glass or polyfluorethylene (Teflon) beam (Fig. 1, 1) touching the cathode surface

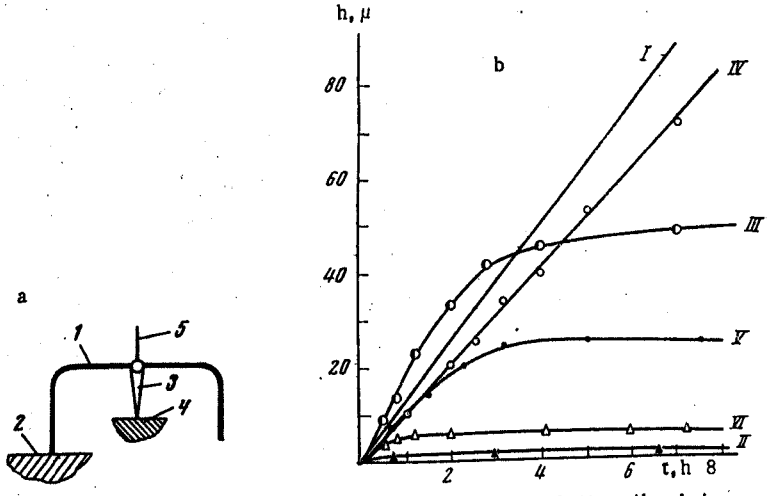


Fig. 1. a) Arrangement of apparatus for simulating the intergrowth of particles into an electrolytic deposit: 1) beam; 2) cathode surface; 3) tungsten filaments; 4) steel prism; 5) mirror; b) curves characterizing the lifting of the beam end with increasing thickness of a copper deposit obtained from a solution of 1 M $CuSO_4$+1 M $H_2SO_4$: 1) increase in the thickness of a deposit without any inclusions for acid of $D_K$=10 mA/cm$^2$; II) lifting of the end of the Teflon beam; III)-VI) lifting of the end of the glass beam; V) solution of 1M $CuSO_4$; VI) allyl thiourea added to the solution.

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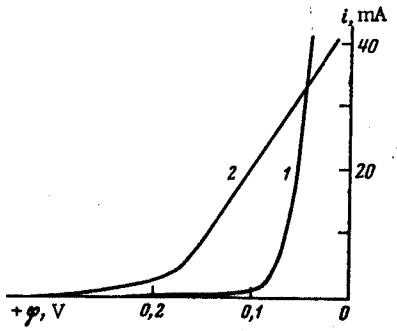

Fig. 2. Polarization curves characterizing the deposition of copper from a solution of 1 M $CuSO_4$+1 M $H_2SO_4$: 1) after adding smoothing agent A to saturation point; 2) after adding 0.1 g/liter of allyl thiourea.

(pressure 2-100 g/cm$^2$). The end of the beam is melted into the form of a hemisphere or ground to a plane. The beam is attached to an axle with tungsten filaments 3, which rest on a steel prism 4. The light beam of an LG-56 gas laser is reflected from the mirror 5, and from the motion of the spot the height to which the end of the beam is lifted may be read to an accuracy of $\pm 0.5\ \mu$.

This method enabled us to follow the changes taking place in the incubation period characterizing the growth of the end of the beam into the cathodic deposit in relation to the shape and material of the latter, the composition of the electrolyte, and the current density of the deposition process.

At the same time we studied the growth of individual particles (glass, corundum, and silicon carbide 10-30 $\mu$ in size) under the microscope, these particles being carried on the end of a wire 0.3 mm in diameter and examined in a cell analogous to the cell used for observing the growth of individual crystals [1]; we also carried out a metallographic analysis of microsections of cathodic deposits containing inert particles.

We studied the growth of particles into a cathodic copper deposit derived from sulfate and pyrophosphate electrolytes. The electrolyte compositions are indicated in the captions of the figures.

The end of the beam nearly always grew into the cathodic deposit, but the thickness of the metal deposit for which this process commenced varied from 0 to 100 $\mu$.

The polyfluorethylene beam started growing into the deposit immediately after the current had been connected (Fig. 1, II), whereas the glass was sometimes lifted up by the growing deposit to a height of 30-100 $\mu$ (Fig. 1, III, IV). The glass end of the beam with the plane surface started growing into the cathode for smaller thicknesses of the deposit than the rounded end. A deposit formed in a more acid solution lifted the beam to a greater height.

The presence of 0.005-0.01 g/liter of smoothing agent A or allyl thiourea in the solution increased the thickness of the deposit at which intergrowth of the beam end began by a factor of several times. In the presence of 0.1 g/liter of allyl thiourea at current densities of 3-5 mA/cm$^2$ intergrowth began for very thin deposits (Fig. 1, VI); at current densities of 10-20 mA/cm$^2$, however, the end of the beam failed to grow into the deposit until a thickness of 50-60 $\mu$ had been reached. On introducing smoothing agent A into the solution up to saturation, no intergrowth occurred for low current densities (up to 3 mA/cm$^2$) but this process did take place at 10-20 mA/cm$^2$.

The occasionally-observed anomalously high rates of lifting of the beam end (Fig. 1, III) were due to the formation of rapidly-growing single whiskers under the beam.

Microscope examination revealed that, after the initial ingrowth of the particle into the deposit, the rate of growth of the metal crystals close to the particle was greater than the mean rate of growth of the deposit, particularly for high current densities. The copper deposit enveloped the particle until the thickness of the metal layer became equal to the transverse dimension of the particle. This was observed with particular clarity on using pyrophosphate electrolytes.

The possible growth of an electrolytic deposit under a particle or beam end is determined by the following factors: 1) the disjoining pressure of the solution [2-6], 2) the micro-throwing power of the electrolyte [7,8], which for constant electrical conductivity and viscosity of the solution is determined by the polarizability of the cathode.

The disjoining pressure is determined by the extent to which the electrolyte wets the surface of the inert particle. In the absence of wetting (Teflon beam) the disjoining pressure is almost zero, so that there is no interlayer of electrolyte between the beam end and the electrode; no electrolysis occurs, and the beam grows into the deposit. In the case of a lyophilic surface such as glass or quartz, a liquid film appears between the particle or beam end and the cathode surface. For a specific gravity of the particle equal to ~4 g/cm$^3$ and a diameter of ~16 $\mu$ the specific pressure of the particle on the surface of the deposit is ~10 g/cm$^2$ and the layer of liquid under the particle may amount to several microns [2,3,6].

For a pressure of the end of the beam on the cathode equal to 2-4 g/cm$^2$ the thickness of the underlying layer of liquid is ~1 $\mu$ [2, 6]. Under these conditions the possibility of the particle or beam end growing into the cathodic deposit is determined by the micro-throwing power of the solution, and for similar values of the electrical conductivity and viscosity it will depend on the polarizability of the electrode in the particular solution. The higher the polarizability of the cathode, the less will be the difference between the rates of growth of the deposit on the closed and open parts of the cathode. Hence under conditions of high cathode polarization (low current densities) the ingrowth of the particles should begin after reaching a greater thickness of the deposit. This is supported by the fact that for high current densities the growth of the beam end into the copper deposit started at a smaller thickness of the latter than for low current densities. A reduction in the acidity of the solution also led to a reduction in the polarizability of the cathode, and hence the thickness of the deposit at which ingrowth of the inert particles into the metal began was also reduced.

The polarizability varies particularly sharply with current density on adding smoothing agent A to the solution (Fig. 2). In this case, for low current densities, no ingrowth of the beam end was observed until the deposit became very thick. For high current densities, the polarizability of the cathode fell sharply and the end of the beam grew into the deposit.

However, in the presence of allyl thiourea, for low current densities (high cathode polarizability) the end of the beam started growing into the metal for smaller thicknesses of the deposit than those corresponding to high current densities. This disagreement may best be explained by considering the difference between the adsorption of allyl thiourea on the free surface of the cathode and under the beam end. For low current densities, corresponding to potentials close to the desorption limit of the additive, the cathode acquired a state in which the additive was adsorbed under the beam end, and there retarded the deposition of the copper, while on the free surface characterized by higher current densities and corresponding cathode potentials, it was desorbed. For higher current densities the state of the free surface was similar to that under the beam end, and ingrowth of the latter failed to begin until greater thicknesses had been achieved.

The accelerated growth of individual crystals observed under the end of the beam is evidently associated with the creation of crystal-lattice defects at the point of contact between the beam and the cathode surface, favoring the rapid growth of crystals [9].

The foregoing arguments are supported by a study of some microsections of copper deposits containing silicon carbide particles. Silicon carbide powder was placed on a horizontal cathode and the current was then connected. On deposition from a sulfate solution the particles started growing into the deposit after reaching a thickness of 40-120 $\mu$ for a current density of 3 mA/cm$^2$ (greater cathode polarizability) and after reaching a thickness of 10-50 $\mu$ for one of 8 mA/cm$^2$ (smaller cathode polarizability). The cross sections of deposits obtained from sulfate solutions containing allyl thiourea showed that for a current density of 3 mA/cm$^2$ practically all the particles lay at the base/deposit interface, while for one of 8 mA/cm$^2$ some of the particles were lifted up by the growing deposit.

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