Many of the physical and processing characteristics of copper powders used in powder metallurgy, such as particle size distribution, apparent density, and specific surface, must be precisely controlled. In this respect electrolysis is a particularly convenient process, enabling, thanks to its versatility, copper powders to be produced having properties that can be varied within wide limits [1]. This technique, however, is based on the use of an expensive raw material, namely copper cathodes. At present increasing attention is being focused on cementation as a comparatively simple method of manufacture of copper in finely divided form from relatively cheap raw materials [2, 3]. It has already been demonstrated [4] that, by varying such cementation parameters as the concentration of the solution being cemented and temperature, it is possible to vary substantially the properties of the resultant copper powder.

The properties of a copper powder produced by electrolysis are strongly affected by the presence of surface active agents (SAA) in the electrolyte [1]. As cementation, i.e., contact exchange, is an "internal electrolytic" reaction and has an electrochemical nature [5], it is of interest to determine also the effects of SAA on the physical properties of contact-deposited copper powder. Apart from this, data yielded by an investigation into the influence of SAA can be expected to prove useful in attempts to intensify cementation as a method of manufacture of copper powder.

In the present work a study was made, on the basis of an electrochemical representation of the cementation reaction and with the aid of electrochemical methods of investigation [4], of the influence of SAA — thiourea, gelatin, and chlorine ions — on the rate of cementation and the properties of the resultant copper powder.

The cementation reaction

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\text{CuSO}_4 + \text{Fe} = \text{Cu} + \text{FeSO}_4
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takes place as a result of the operation of iron—copper cementation (contact) electrolytic cells forming on an iron surface. The rate of cementation is directly proportional to the cementation emf and current of an individual electrolytic cell. Cementation polarization curves show (Fig. 1) that the addition of thiourea and gelatin to a copper sulfate solution reduces the cementation emf and current.

The decrease in cementation emf in the presence of thiourea and gelatin increases the time to the appearance of copper crystal nuclei on an iron surface (Fig. 2) and also leads to fewer copper crystallization centers being produced, as is confirmed by a shift of the compromise potential of iron toward negative values in the presence of thiourea and gelatin (Fig. 2). Thus, the addition of thiourea and gelatin to a solution undergoing cementation reduces the rate of deposition of copper powder (Table 1). At the same time thiourea decreases the cementation emf and current to a greater extent than does gelatin (Fig. 1), and consequently the rate of powder deposition in this case falls more sharply than in the presence of gelatin (Table 1).

Adsorption of thiourea and gelatin on growing crystals inhibits their growth. The action of the cementation emf, however, results in the formation of new crystalline copper nuclei, whose growth, too, is...
then inhibited by the adsorbed SAA. This pattern of crystal formation and passivation is maintained throughout the whole cementation process, and consequently a finer powder is deposited in the presence of thiourea and gelatin (Table 1 and Fig. 3). The action of thiourea and gelatin on the sedimentation deposit is primarily a dispersing one, as evidenced by an increase in the apparent density of the powder (Table 1). This must be a result of a comminution of the copper powder, since its specific surface undergoes little change.

Chlorine ions, too, decrease the cementation emf and current (Fig. 1). As a result of the lower cementation emf the number of copper crystallization centers also falls, as is borne out by a shift of the compromise potential of iron into the negative range (Fig. 2). As the presence of chlorine ions reduces both the number of contact electrolytic cells and the cementation current of each individual cell, the rate of the cementation process, i.e., the rate of powder deposition, in such a case might be expected to fall. In our experiments, however, the rate of powder deposition was found to increase rather than decrease with rise in chlorine ion concentration (Table 1). In the presence of chlorine ions a more dispersed powder is deposited as a result of transient passivity (Table 1 and Fig. 3). Chlorine ions promote the formation of a more dendritic deposit, and consequently the more dispersed powder has a smaller apparent density but a larger specific surface.

A deposited cementation layer hinders diffusion of the anodic reaction products into the main volume of the solution. At the same time the diffusion of the products of the anodic process depends on the structure (density) of the cemented copper layer being formed. With rise in chlorine ion concentration in the solution the structure of the copper particles becomes more dendritic, as a result of which the porosity of the deposit grows, thereby facilitating the iron ion diffusion process. Because of this, under conditions promoting the formation of a looser deposit the rate of cementation grows.

Thus, with rise in chlorine ion concentration the rate of cementation changes as a result of two opposing tendencies. On the one hand the rate of cementation would be expected to fall because the cementation emf and current decrease, but on the other hand the rate of powder deposition must grow because at higher chlorine ion concentrations the deposit produced is more dendritic, i.e., more porous. In the case of a solution containing chlorine ions we can conclude that the latter tendency predominates in the variation of cementation rate.