

Cementation of Silver Ions on Metallic Copper

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Abstract

The silver ion cementation on metallic copper was investigated in the presence or absence of oxygen. The influence of sulphuric acid and copper sulphate concentration on the silver cement morphology was studied in details, and results were linked with the previously determined kinetics data of the process. The morphology of silver deposit was found to be independent of the presence of oxygen in the system as well as the sulphuric acid concentration. Contrary, the concentration of copper sulphate strongly influenced the morphology of silver deposit. Two-stage mechanism of cementation was proposed.

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Keywords: Silver ion cementation, cementation on copper, kinetics of cementation, surface morphology.

1. Introduction

One of the oldest and most effective hydrometallurgical processes which allow recovering metals from solutions is cementation. This process is known since the ancient times of human culture, but in Europe the early knowledge of cementation spread only at the beginning of the Middle Ages. The famous medieval work of Agricola *De Re Metallica* should be mentioned here (Fig.1). At that time, the cementation process was used by alchemist in order to perform the transmutation of metals. For several decades, cementation has been commonly used in the industry for the recovery of metals, removal of metal ions from dilute wastes and purification of solutions.

Many new technologies used in the environmental protection and purification are based on cementation. The main advantage of this process is the possibility of removal of ions of very low concentrations (traces) from the great volumes of various electrolytes (i.g. in situation where other methods are much more expensive or unapplicable).

Typical industrial applications of cementation are:

- of copper with iron (for example the production of copper metal in the refinery Rio Tinto in Spain),
- of gold from cyanide solutions with zinc powder,
- of cadmium ions (purification of zinc sulphate solution) during zinc processing.

Intensive investigations on cementation process have been undertaken recently which allowed to attain significant improvement in technology and in apparatus construction like the introduction of industrial practice of the so called cementation towers, instead of leaching tanks used until now.

Although cementation has been used in practice for a long time, the theoretical backgrounds of this process still

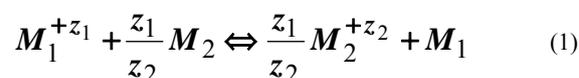
remains questionable. There are lots of papers devoted to cementation of various ions, but usually they are concerned about the kinetics of process and not about the mechanism itself. The problem becomes even more complex when the metal used for cementation of the ions may occur at different states of oxidation.

One of the important fields for the use of cementation is the recovery of noble metals, and we have concentrated our interest on the cementation of silver ion on metallic copper from industrial baths, used for electrowinning and electroplating of copper and containing sulphuric acid and copper sulphate. This problem has a great importance not only for the recovery of silver but also to obtain high purity copper for electronic purposes.

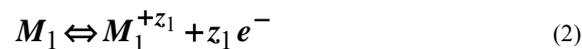
This problem is especially important in Poland, because concentration of silver in Polish copper ores is relatively high.

2. Theory

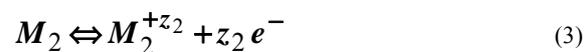
The overall cementation reaction can be expressed by the following equation:



Cementation process present a system of many short-circuited microcells and the overall reaction can be expressed as the sum of half-cell reactions:



and



Cementation is an electrochemical process, but it differs from the electrolytic deposition where the electrons are supplied from the external source as well as from

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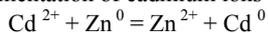
A—FURNACE. B—POT. C—LID. D—AIR-HOLE.

Fig.1 The reprint of the book De Re metallica from Agricola

electroless plating where the oxidation of an organic additive occurs.

For many cementation reactions, free enthalpy ΔG has very high negative value therefore, from thermodynamic point of view, these reactions go to completion.

The change of ΔG can be evaluated from the standard potentials of given half cells. For example for the cementation of cadmium ions on zinc one has



The change of free enthalpy ΔG is given by

$$\Delta G = -nFE^0$$

where E^0 is the standard emf of the appropriate cell and F and n are Faraday constant and the number of electrons respectively.

Thus

$$\Delta G = -2 \text{ equl/mol} * 23.06 \text{ kcal/volt.equl} * 0.36 \text{ V} = -16,6 \text{ kcal/mol}$$

And one can further calculate that the reaction attains equilibrium if

$$\frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} > 10^{12.2} \quad (4)$$

3. The simple model of cementation reaction

The simple accepted model of cementation is based on two assumptions:

1. Appearance of many anodic and cathodic places on the surface of more negative metal (dissolving metal)
2. Reduction of ions of more noble metal in the Helmholtz layer at cathodic places.

For the heterogeneous cementation reaction at the smooth metal surface under well defined hydrodynamic conditions and in the absence of other “impurities”, generally two processes are proposed to take place: 1) surface reactions and 2) mass transport.

Usually the chemical processes (surface reactions) are faster than the transport processes, and therefore the total rate is controlled by the transport process. In such cases of transport limitation, one can expect the kinetics of first order.

The increase in temperature results in increasing the total process rate, independently of limiting stage, but the observed effect is bigger in the case of chemical reaction control. The investigation of the temperature influence is important because it allows one to understand the nature of limiting stage.

Among the various factors that influence the process and its kinetics the following should be also mentioned

- the form and shape of deposit (cementate),
- the presence of “impurities” e.g. compounds which influence the stoichiometry and kinetics of reaction.

Mass transport takes place by convection, migration of ions under electric field, or by diffusion caused by concentration differences. Under given circumstances, it is possible to calculate the mass transport rate and compare it with experimental values. Finding which transfer mode is process-limiting is important to find out whether the surface reaction, which is going slowly, or that the mass transfer through cementate deposit layer, is in control of the process.

The description of kinetics of cementation process is similar to the metal deposition and the process rates may be expressed by the current densities. A more detailed analysis, made by Wadsworth [1], gives the following equation describing the rate of cementation reaction

$$\frac{dc_1}{dt} = c_1 k_0 \left(1 - \frac{c_2^{z_1/z_2}}{c_1} \exp \left[\frac{-z_1(E_2^0 - E_1^0)F}{RT} \right] \right) \quad (5)$$

where

- c_1 - concentration of noble metal ion M^{+z}
- c_2 - concentration of active metal ion M_2
- z - charge of ion
- E^0 - standard half-cell potential
- k_0 - rate constant (the complex function of overpotentials, potential drop in double layer, diffusion coefficients etc).

Based on equation (5), the back reaction is important when

$$\frac{c_2^{z_1/z_2}}{c_1} \exp \left[\frac{-z_1(E_2^0 - E_1^0)F}{RT} \right] > 10^{-2} \quad (6)$$

Usually the above condition (equation 6) is not fulfilled, and the rate of backward reaction is very small. The backward reaction should be taken into account only if the difference of standard potentials is about 0.5 V.

The cementation reaction is of the 1st order with respect to the concentration of metals ions:

$$\frac{dc_1}{dt} = k \frac{A}{V} c_1 \quad (7)$$

and its rate depends strongly on surface area (A) and electrolyte volume (V). Other parameters like initial concentration of ions, temperature, stirring, current density, presence of additives or other complex forming substances influence the magnitude and character of active area of electrode. The influence of these parameters is as follow:

- in thick crystalline, incompact and spongy deposits are created at higher temperatures, higher current densities and higher concentrations of metal ions,
- while the organic additives (like glue, gelatine), lower concentrations of metal ions and lower temperatures prefer deposition of shiny and fine crystalline deposits.

The present review is based on papers published by the author [2-8] concerning the kinetics and mechanism of silver ion cementation on metallic copper, Different results that are devoted to the morphology of the silver deposit were obtained under various experimental conditions. The detailed mechanism of the proposed process is also presented.

4. Experimental Work

Cementation experiments were carried out, using the rotating cylinder system, allowing the controlled hydrodynamical conditions (Fig. 2).

The rotating cylinder, made from stainless steel, had the working surface area of 27.50 cm². The cementation cell has the volume of 200 cm³. All solutions before the use were purged by bubbling with high purity argon or high purity oxygen for 20 minutes. The oxygen free atmosphere or oxygen atmosphere was also maintained over the solution throughout the whole duration of the process. Before each cementation experiment, the surface of the cylinder was covered electrolytically with fresh layer of copper. The copper layer was then polished electrolytically, rinsed and dried.

The changed parameters of cementation experiments were: concentrations of copper sulphate and sulphuric acid, initial concentration of silver ion and temperature.

During the experiment, the samples of solution were taken for the determination of the silver concentration by atomic absorption spectrometry (AAS) using the Philips PU 9100X. Additionally, the concentration of silver ion was monitored during the cementation by measuring the potential of silver ion selective electrode (EMF) immersed into the solution.

After each run, copper with cemented silver was rinsed, dried and carefully separated from the cylinder. The samples were dissolved in nitric acid and analysed for silver content. Also the SEM pictures of the surface

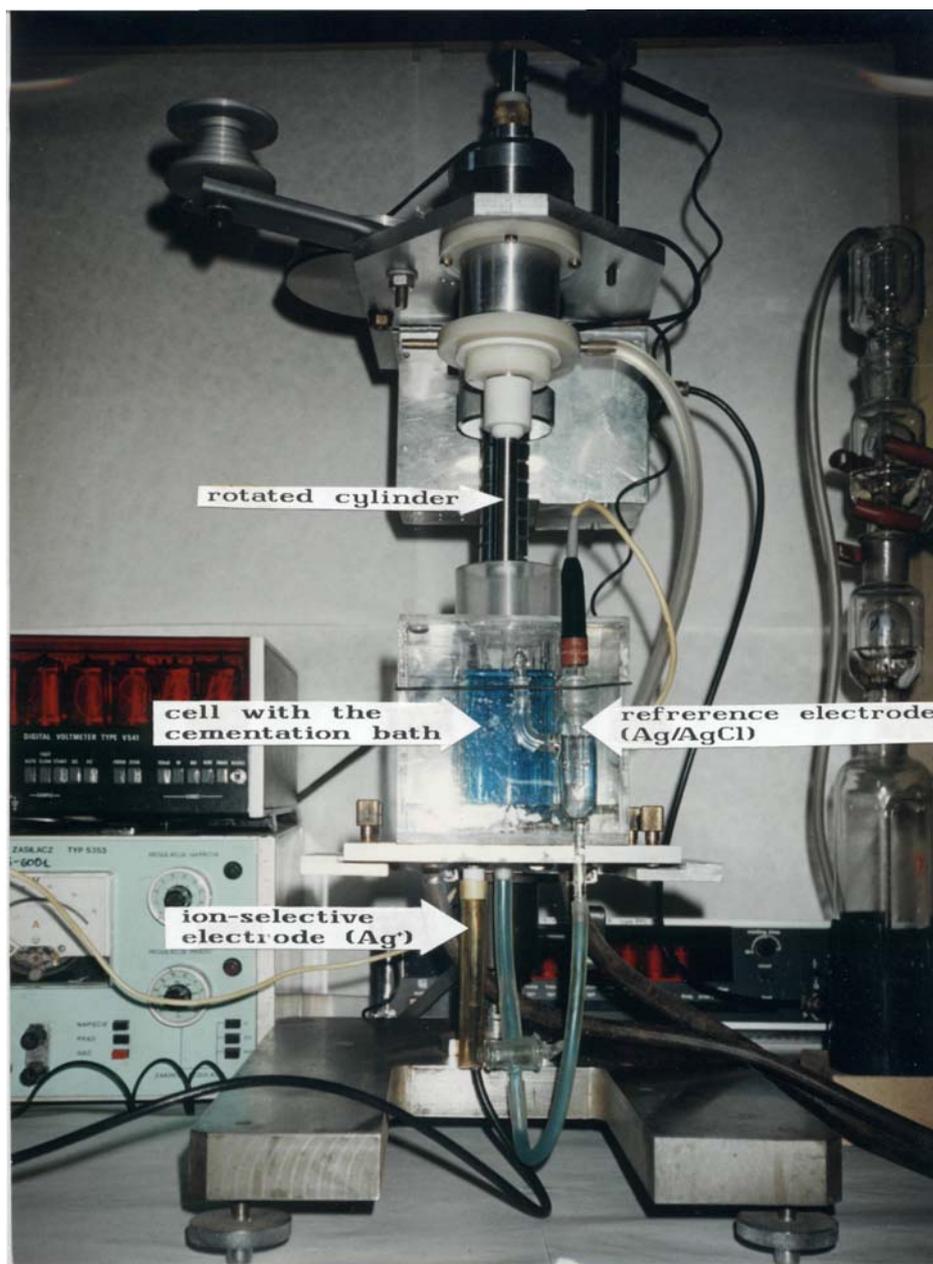


Fig 2 The rotating cylinder system used for investigation of cementation.

deposit were recorded. All details of experiments and used apparatuses were described in details previously [3, 6].

5. Results and Discussion

Fig.3 shows some examples of kinetics plots. It is seen that both used independently analytical methods i.e. atomic absorption spectroscopy (where total silver content was found in solution) and ion-selective electrode where only ionic part gave the same (or similar) results only in the case when the oxygen was presented in the system over the whole duration of the experiment. In the deoxygenated solutions and after first few minutes of experiment, the growing discrepancies were observed.

For the initial period of cementation the linearity of the concentration versus time plot (Fig. 4) was retained. This is in agreement with the assumption about 1st order reaction. Therefore the appropriate rate constants were determined.

Table 1 shows the values of activation energy calculated from the experimental data and compared with theoretical values obtained based on the Pang-Ritchie equation describing the transport to the rotating cylinder [10]. The tabulated values confirm that the cementation process kinetics, at its initial step, is of first-order.

Fig.5 shows SEM images of cemented silver which were formed during the cementation conducted in 0.5 M sulphuric acid without copper sulphate taken from different parts of the surface. The value of Θ denotes the percentage of cemented silver on copper in comparison

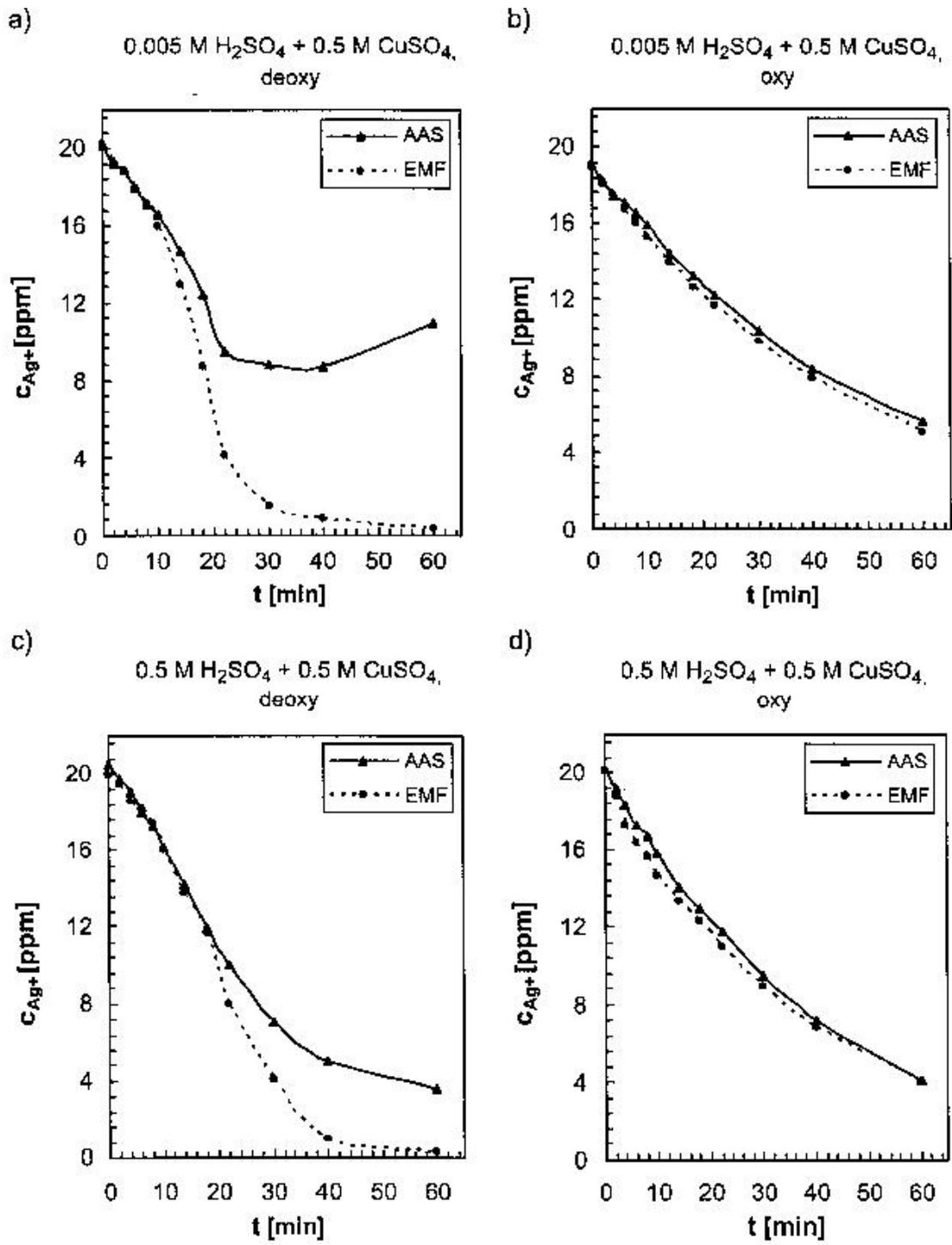


Fig.3 Variations in [Ag⁺] concentrations with time in deoxygenated and oxygenated solutions 298K, [Ag⁺]_{initial} = 20 mg/L, f = 500 rev/min, [CuSO₄] = 0.5 M, [H₂SO₄] = 0.5 M or 0.005M

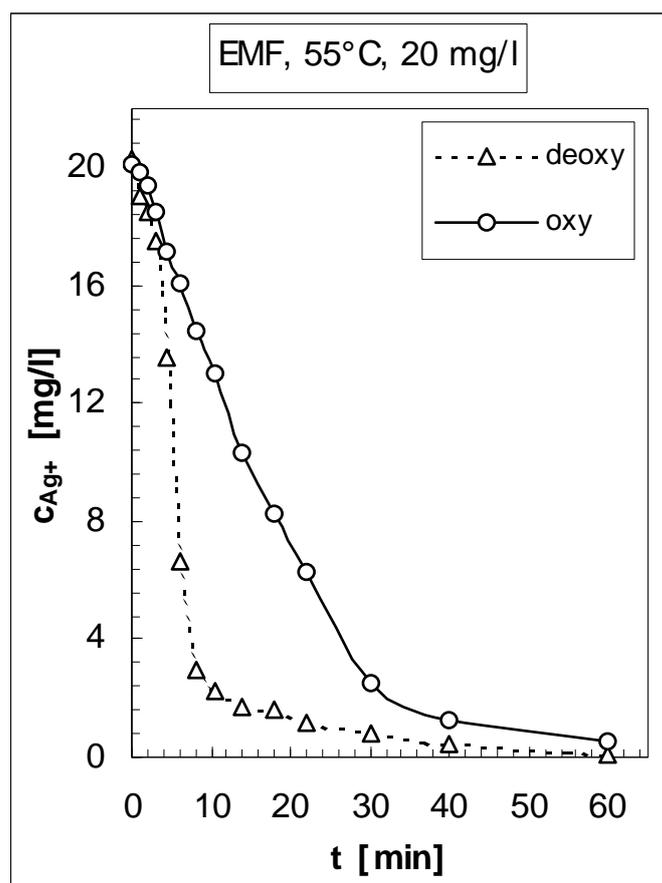


Fig 4. Concentration of silver ion versus time of cementation

Table 1. Activation energy values for the initial period of cementation

Conditions	Temperature range [°C]	E_a [kJ · mol ⁻¹]		
		P-R	AAS	EMF
20 mg/L Ag ⁺				
deoxy	7-55	16.14	21,35 ± 0.38	20.45 ± 0.29
oxy			15.61 ± 0.40	15.78 ± 0.84
100 mg/L Ag ⁺				
deoxy	15-55	16.14	19.36 ± 0.49	19.03 ± 1.04
oxy			18.63 ± 0.45	18.13 ± 0.10

with the initial silver content in solution, determined by the AAS method. It was found that the morphology of cemented deposit is highly non-uniform. Some parts of copper surface are covered with tiny Ag crystals (Figs 5A and 5B), but other parts are occupied by “fern leaf-shaped” dendrites. There is no visible effect of the oxygen presence on the morphology of formed silver deposit.

The presence of oxygen in the system does not modify the tight Ag deposit as well as Ag dendrites. On the relatively smooth parts of silver deposit (Figs. 5A and 5B), germs of pre-dendrites are already visible as white spots. These germs can further develop in huge silver dendrites as we can see in Fig 5C and 5D.

Fig. 6 shows the typical curve $\log c_t/c_0$ versus time and illustrates the moment when in the smooth surface of

cementate, the dendrites start to grow. Moreover, figure 7 shows the dendrites observed in the solution where a little amount of copper sulphate was introduced (concentration of CuSO₄ 0.005 M). When the concentration of copper sulphate in the solution was increased (up to 0.5 M), no dendrites were found on the surface and the surface was smooth (Fig. 8).

In Table 2, the Θ values (percentage of cemented silver found on the surface) are shown. The amount of cemented silver remains constant in oxygenated solution but in the absence of oxygen it depends strongly on the content of copper sulphate and sulphuric acid.

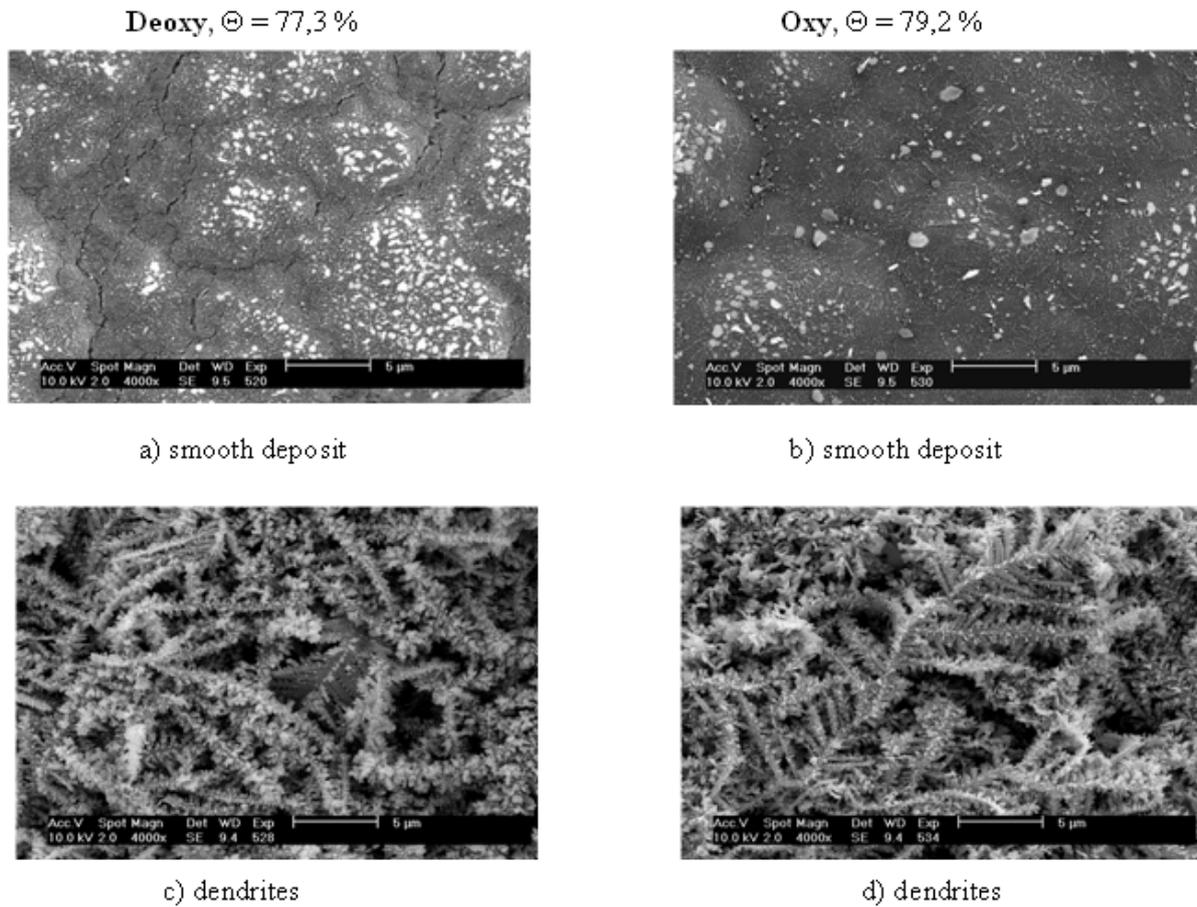


Fig. 5 SEM micrographs of Ag cements obtained from 0.5 M H₂SO₄.

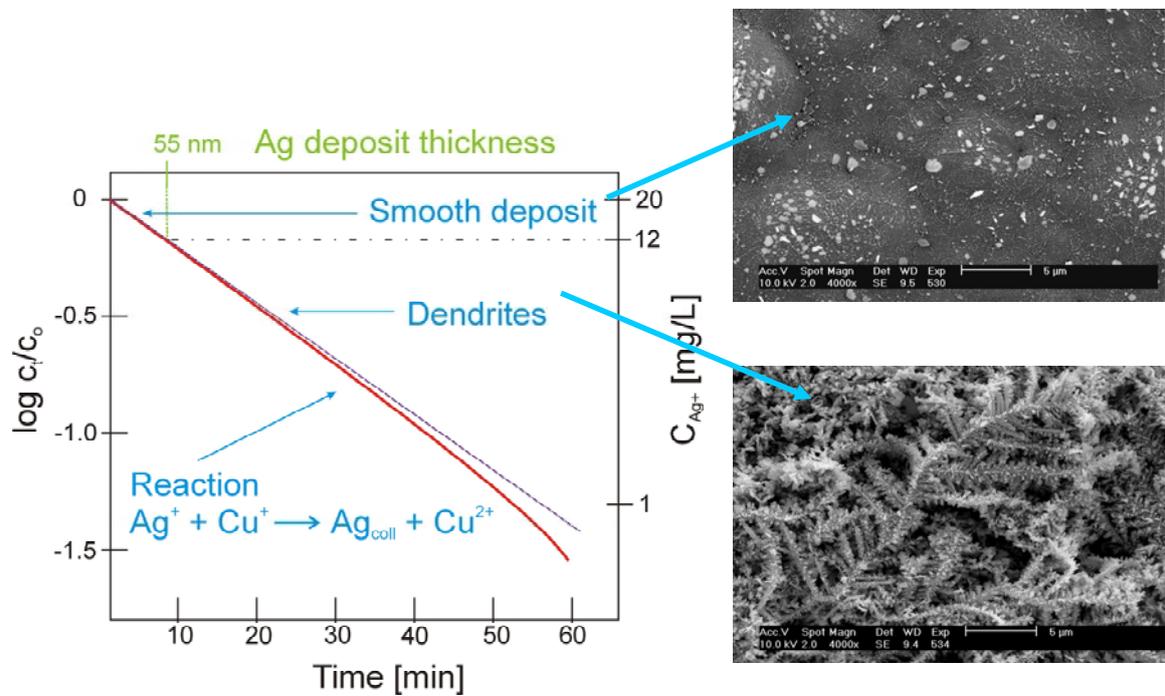


Fig. 6 The growing of dendrites

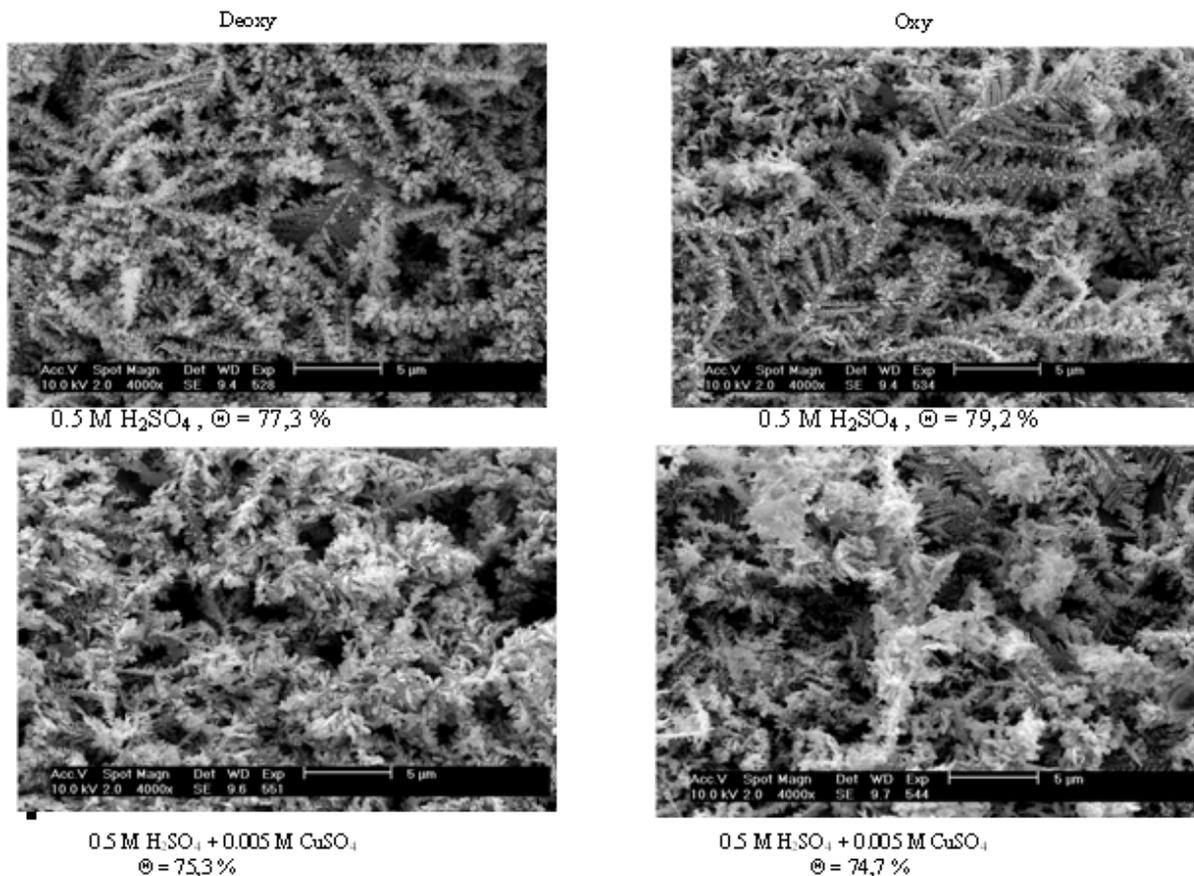
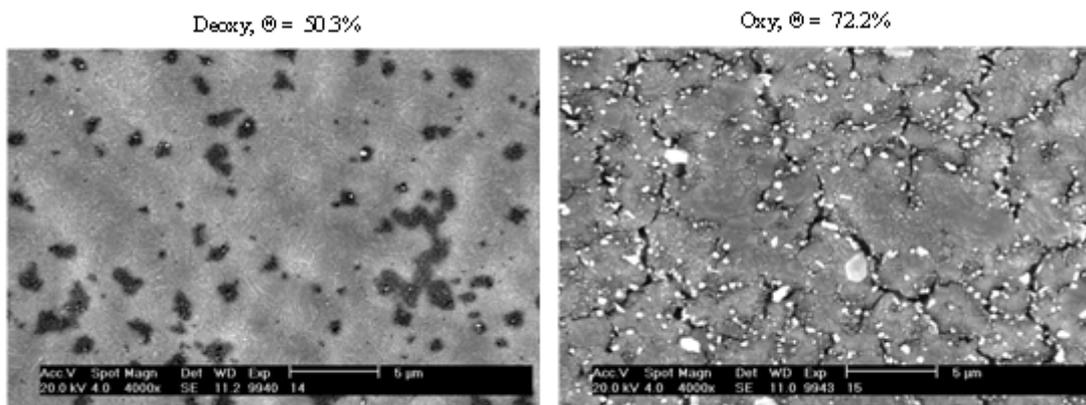


Fig. 7 SEM top-view images of the surface with cemented silver formed in the deoxygenated or oxygenated solution containing 0.5 M H₂SO₄ and 1.85 × 10⁻⁴ M Ag⁺. Cementation was conducted for 60 min at 25°C. (a and b) Smooth deposit and (c and d) Ag dendrites.



Only smooth surface without dendrites

Fig. 8 SEM top-view images of the surface with silver deposited in a 0.5 M H₂SO₄ + 0.5 M CuSO₄

Tab 2. The percentage of cemented silver on copper

Composition of solution		deoxy		oxy	
CH ₂ SO ₄	CCuSO ₄	n	Θ [%]	n	Θ [%]
0,5	0	3	77.7	3	78.4
0.5	0.005	4	78.0	4	77.5
0.5	0.05	3	64.7	3	71.8
0.5	0.5	9	52.7	6	73.8
0.005	0.5	3	37.6	3	74.8

The above results allow proposing the two-stage cementation process mechanism as shown in Fig. 9 and described by the following steps:

Step 1:

The first step of the cementation reaction generates Cu^+_{ad} ions in both deoxygenated and oxygenated solutions.

Step 2:

The second step is different and depends on presence or absence of oxygen:

- In oxygenated solution, the part of copper (I) ions created during the first step at the copper surface reacts immediately near to this surface with diffusing silver ions. The other part starts to diffuse away into the bulk of solution but on the way the copper (I) ions meet the oxygen and transform to the non reactive copper (II) ions.

- In the deoxygenated solution the copper (I) ions diffuse without obstacles into the bulk and then they react with silver ions creating the silver colloid. In many cases, the subtle haze of silver colloid was observed.

Sulka and Jaskula [3] showed that in the deoxygenated solution containing 0.5M H_2SO_4 and 0.5 M $CuSO_4$ the consumption of about 8 mg/L of silver ions (their concentration at the beginning was 20 mg/L) in cementation process corresponds to the production of about 4.7 mg/L of copper (I) ions. This concentration is high enough to initiate the progress of the reaction between Cu^+ and Ag^+ ions in the bulk of solution. Thermodynamics calculations⁽¹⁾ show that practically all silver ions could be cemented before reaching the equilibrium between copper (I) and copper (II) ions.

Mechanism of cementation

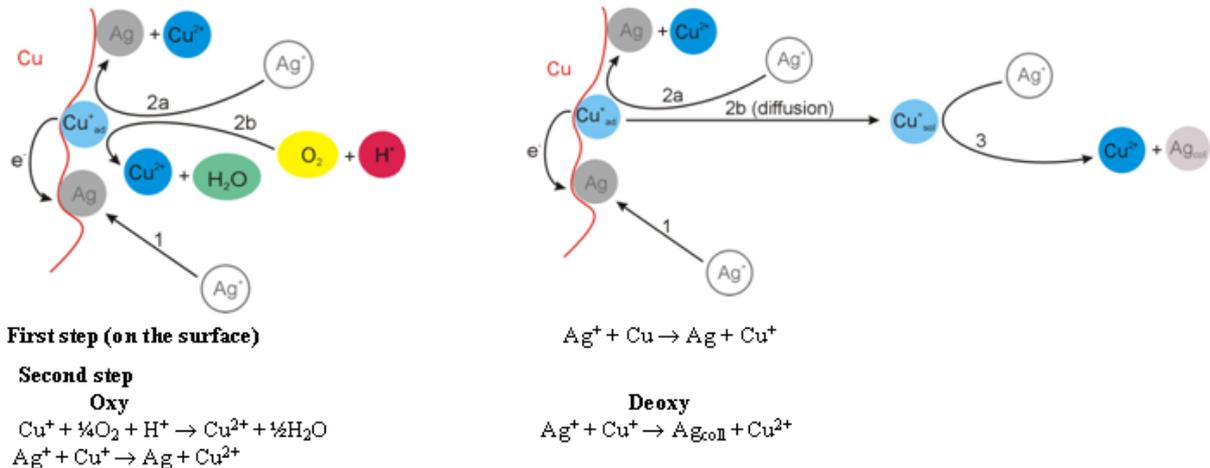


Fig. 9 Mechanism of silver ion cementation.

The SEM images presented in Fig. 10 show formation of cathodic sites on the reacting surface in the cementation process. The images were taken from various sites of the same sample. The study was performed for a cementation test conducted in deoxygenated solutions containing 0.5 M H_2SO_4 . At the beginning of the process, silver covers uniformly the copper surface as shown in Fig. 10A. Ag crystallites are very small and cover surface uniformly and compactly. Regular, hexagonal, sticking out Ag crystals are also visible on the surface. There are germs of dendrite growth.

¹Calculations:

There are two ionic equilibria in the studied system

(a) $2Cu^+ = Cu + Cu^{2+}$

$K_a = [Cu^{2+}]/[Cu^+]^2 = 1.13 \cdot 10^6$ (at 298K). It means that the equilibrium concentration of Cu^+ ions is equal to $6.6 \cdot 10^{-4}$ M. and

(b) $Cu^+ + Ag^+ = Cu^{2+} + Ag_{colloid}$ $\Delta G^0 = -61.6$ KJ

$\Delta G^0 = -RT \ln K$ since $K_b = [Cu^{2+}]/[Cu^+][Ag^+] = 6.3 \cdot 10^{10}$

From the above values, equilibrium constants may be calculated that

if $[Ag^+] = 1.85 \cdot 10^{-5}$ M i.e. 90% was cemented

then $[Cu^+] = 4.3 \cdot 10^{-7}$ M

Afterwards, a growth of dendrites is initiated on preferential parts of the surface, usually on small protrusions (Fig 10B). At the early stage of dendrites growth, “twig-shapes” appear on the protrusion (Fig 10C), which are transformed into “lycophodium twigs-shapes” or “fern leaves-shapes” (Fig. 10D). Their further growth leads to huge crystallite (Fig. 10E). The higher magnification of this crystallite shows tiny silver crystals deposited on the previously formed silver fern leaf (Fig. 10F).

The growing dendrite (Fig.10C) behaves as a cathodic site and promotes a creation of an anodic site in a close neighbourhood.

Finally, the anodic site surrounds a dendrite island and develops in the copper material. Such an anodic site is visible on Fig. 10D as a crack encircling the protrusion.

The close examination of the anodic site is presented in Fig.11. Deposited tiny silver crystals are visible on the edges of the valley. Inside the deep valley much bigger Cu

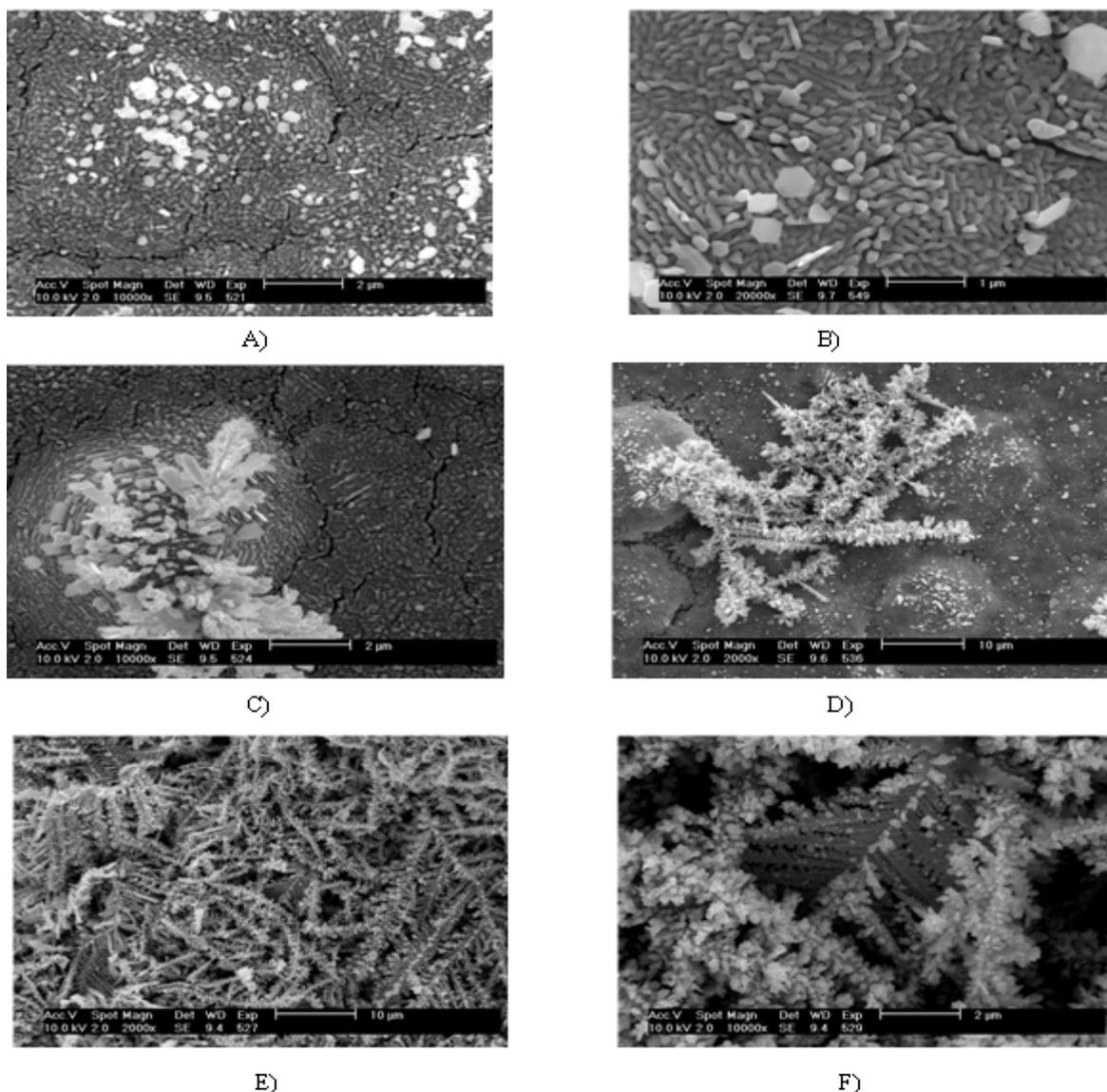


Fig. 10 Growth of the cathodic site in the cementation process conducted in the deoxygenated 0.5 M H₂SO₄ containing 20 mg/L Ag⁺ at 25 °C.

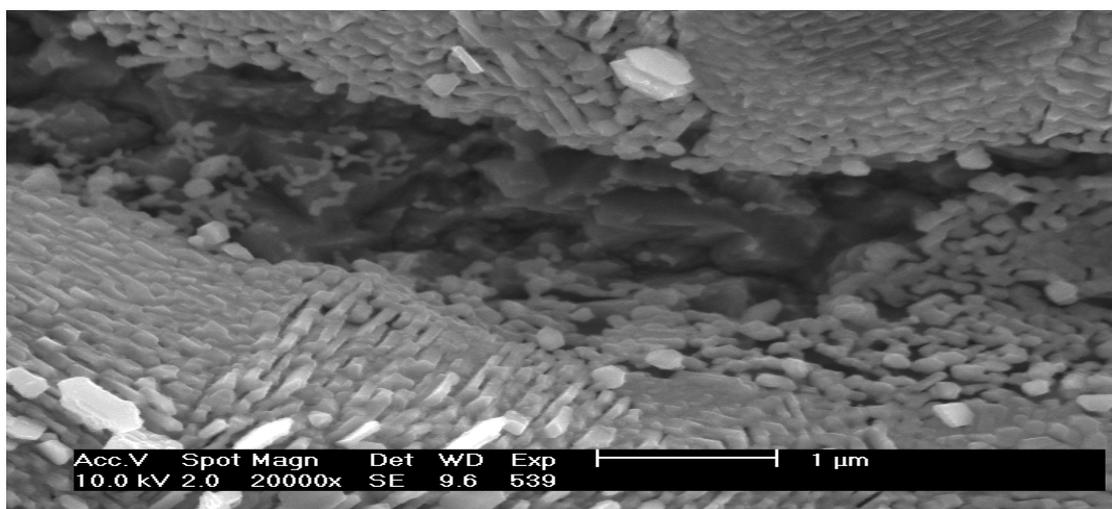


Fig. 11 The anodic site formed in the cementation process (deoxygenated 0.5 M H₂SO₄, 20 mg/L Ag⁺, 25 °C)

crystals appear. Results showed that anodic sites develop their working surface area in the copper material just under the deposited silver, with a formation of big cavities. The depth of these cavities was estimated to be about 3 μm .

6. Conclusions

1. The morphology of silver cements practically does not depend on oxygen content in solution.
2. The concentration of copper sulfate in the electrolyte has a great impact on the morphology:
 - a) In the solutions containing pure sulfuric acid or acid with small amount of copper (II) ions some parts of the surface are covered with smooth deposit, but other exhibit also huge dendrites.
 - b) The increase in concentration of copper sulfate up to 0.5 M results in a total disappearance of dendrites from the surface. Only tight deposit layer with tiny Ag crystals is observed.
3. The percentage of cemented silver found on the surface after the reaction in oxygen saturated solution remains practically constant whereas in oxygen free solution depends mainly on copper (II) ion concentration. It is caused by parallel side reaction, which produces colloidal silver in the bulk of solution.
4. The observed morphology of the deposits is consistent very well with the results obtained from kinetic.

measurements and confirms the proposed two-stage mechanism of cementation reaction.

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