

Electrochemical investigation of cementation process

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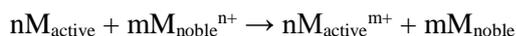
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Cementation of metals is a spontaneous electrochemical reaction at the interface of an active metal and the electrolyte containing ions of more noble metal. In this work the electrochemical behaviour of the redox couples was studied experimentally with a special emphasis the mixed cementation potential compared to the potentials of the individual couples at open circuit state. This approach allows determining the values of both the anodic and cathodic polarisations but not the reaction kinetics. The potentiodynamic method separately applied to the iron and the copper electrodes was used to elucidate the nature of the kinetics of the half-reactions of the electrodes. The intersection of the anodic branch of the polarisation curve of the iron electrode with the cathodic one of the copper electrode corresponds to the rate of copper deposition at the iron surface, represented indirectly by the deposition current density. The determined corrosion potentials, however, are more positive with respect to the open circuit potentials when direct copper cementation by iron takes place. More accurate results about the reaction rate were obtained by plotting of the values of the open circuit potentials of a real cementation process onto the polarisation curves of a copper electrode. The intersection is located in the area corresponding to an active iron dissolution and copper deposition under a transport control. These results correspond adequately to those obtained by inductively coupled plasma spectroscopy applicable to kinetic measurements.

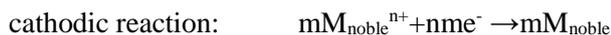
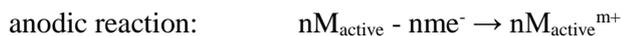
Key words: copper cementation, mixed potential, potentiodynamic,

INTRODUCTION

Cementation of metals is spontaneous electrochemical oxidation-reduction reaction taking place at the interface active *metal/solution containing ions of more noble metal* ($M_{\text{active}}/M_{\text{noble}}^{n+}$), [1-4] namely:



The ratio of the electrode potentials (E) of the oxidation-reduction couples is $E(M_{\text{active}}^{m+}/M_{\text{active}}) < E(M_{\text{noble}}^{n+}/M_{\text{noble}})$. The cementation process can be considered as a work of short circuit galvanic element where two half-reactions of oxidations and reduction take place simultaneously on one and the same surface [5]:



The common approach in the cementation kinetics is the use of physical methods analyzing the solution [6-9]. The electrochemical dynamic methods cannot be applied directly for the analysis

of the cementation processes. The high reaction rate results in rapid changes in the interface (i.e. contact areas, structures of the anodic and cathodic sites, etc) and the chemical content of the electrolyte.

A real analysis of the electrochemistry of the sub-processes involved in the cementation reaction can be done on the basis of the mixed potential of the system $M_{\text{active}}/M_{\text{noble}}^{n+}$ [10] and of the potentials of the separate couples $M_{\text{active}}^{m+}/M_{\text{active}}$ and $M_{\text{noble}}^{n+}/M_{\text{noble}}$ at the open circuit conditions. The determination of the potentials of the separate couples allows to assess the values of the anodic and cathodic polarisations. When the volume of the solution is quite enough and the contact area ($M_{\text{active}}/M_{\text{noble}}^{n+}$), enough small, then the measured values of OCP are independent of the area of contact. This is an advantage, because the cementation is commonly performed by using particles (iron spheres, scrap, iron wool, etc) which surface area taking place in the solid/fluid contacts is hard to be defined.

This paper demonstrates the possibility to apply two electrochemical methods in investigation of copper cementation by iron in solutions containing different anions: the open circuit potential measurements (OCP) and potentiodynamic method. The results contributed to the development of a

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kinetic model of the cementation of the couple Cu^{2+}/Fe and to determine the rate of the process.

EXPERIMENTAL

The electrochemical experiments used copper and iron electrodes with a surface of about 2 cm^2 . At the beginning of each experiment the metal surface was grinded mechanically by SiC paper № 600 and degreased in ethanol-ether mixture. The electrolytes are based on bivalence salts of copper and iron with SO_4^{2-} , SeO_4^{2-} , TeO_4^{2-} , PO_4^{3-} , NO_3^- , Cl^- и IO_3^- and concentration of $0,08\text{M}$ (or 5 g/L M^{2+}). Due to the instability and the low solubility of some compounds of Fe^{2+} , the equilibrium potential of the iron electrode were determined in solutions of FeSO_4 , FeCl_2 и $\text{Fe}(\text{NO}_3)_2$ only.

The electrochemical tests were carried out in a classical three-electrode cell with a platinum counter electrode and a reference saturated calomel electrode. The time variation of OCP was registered up to its almost stationary level, but for a time not less 30 min. The potentiodynamic relationships were obtained at a potential scan rate 10 mVs^{-1} by a potentiostatic-galvanostatic device PAR 273 and treated by a software package PowerSuit. The potentials reported in this paper are presented with respect to normal hydrogen electrode (NHE). All the experiments were carried out at ambient temperature of about $25 \text{ }^\circ\text{C}$ without initial de-aeration of the electrolyte solutions.

The elemental analysis of the solutions before and after the cementation process was performed by inductively coupled plasma (ICP) device (model High dispersion ICP-OES "Prodigy" of Teledune Leeman Labs).

RESULTS AND DISCUSSION

Open circuit potential - time measurements

The difference in the equilibrium potentials at $0.08 \text{ mol/L M}^{2+}$ of the more-noble metal, i.e. the copper (0.308 V) and the iron electrode (-0.472 V) is the theoretical value of the electromotive force ($\Delta E^0 = 0.78 \text{ V}$) of the cementation reaction $\text{Cu}^{2+} + \text{Fe} \rightarrow \text{Cu} + \text{Fe}^{2+}$. This value can be used only as a theoretical benchmark referring to the

Table 1. The OCP and polarization values (vs. NHE) of the copper and the iron electrodes in 0.08 mol/L solutions containing different anions.

| | SO_4^{2-} | SeO_4^{2-} | TeO_4^{2-} | Cl^- | IO_3^- | NO_3^- | PO_4^{3-} |
|---|--------------------|---------------------|---------------------|---------------|-----------------|-----------------|--------------------|
| $E(\text{Cu}^{2+}/\text{Cu}), \text{V}$ | 0.317 | 0.300 | 0.190 | 0.203 | 0.344 | 0.296 | 0.300 |
| $E(\text{Fe}^{2+}/\text{Fe}), \text{V}$ | -0.430 | --- | --- | -0.360 | --- | -0.120 | --- |
| $E(\text{Cu}^{2+}/\text{Fe}), \text{V}$ | -0.340 | 0.270 | 0.070 | -0.300 | 0.830 | -0.110 | -0.240 |
| $E(\text{Cu}^{2+}/\text{Fe}) - E(\text{Cu}^{2+}/\text{Cu}), \text{V}$ | -0.657 | -0.030 | -0.183 | -0.503 | 0.486 | -0.406 | -0.540 |

cementation reaction under standard conditions. The measured values of OCP in electrolytes with $0.08 \text{ mol/L M}^{2+}$ containing different anions are summarized in Table 1.

The data summarized in Table 1 indicate that the nature of the anions affects strongly the values of the potentials. Generally, the measured potentials in the sulphate environments are too close to the theoretical values. The values corresponding to the iron electrode are more positive than the theoretical ones which can be attributed to the aerated neutral solutions.

The time evolution of the open circuit potentials in the case of the iron electrode when the solutions containing of various salts of Cu^{2+} with a concentration of 0.08 mol/L (or 5 g/L Cu) is shown in Fig. 1. In almost all cases the OCP values was established for 5-10 minutes and the stationary levels are strongly affected by the anion contents of the solutions.

Depending on the direction of the OCP change in time it is possible to detect two typical cases:

- a sharp shift of the potential in the negative direction and a gradual change to the equilibrium level (in solutions of SO_4^{2-} , for instance) and
- slow and almost smooth shifts of the potential in the positive direction.

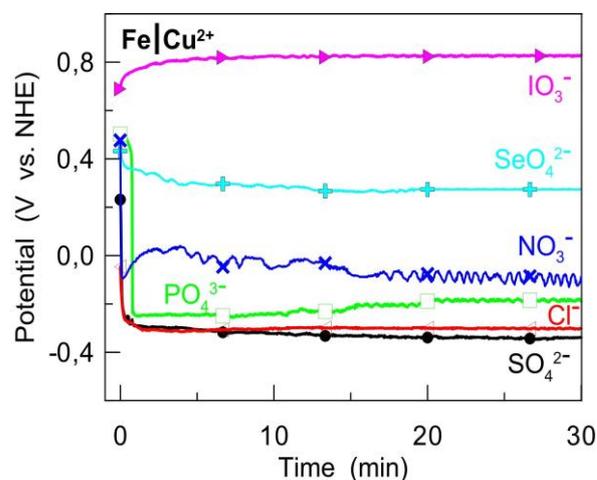


Fig. 1. Time evolution of the Open Circuit Potential (OCP) in case Cu^{2+} cementation by Fe in various solutions with concentration of 0.08 mol/L .

The first case can be considered a typical one for the cementation processes taking place under the diffusion control of the cathodic process when the mixed potential is established to levels close to that of the anodic half-reaction (dissolution of Fe) due to the high cathodic polarization. In accordance with this standpoint, the initial shift in the potential in the negative direction is caused by the depletion of copper ions at the vicinity of the iron surface and consequently the demand copper ions to be transported from the bulk of the solutions. Moreover, if it is supposed that the movement of the OCP in a negative direction is totally due to the depletion Cu^{2+} , the initially shift of the potential may be used as an indicator of the cementation rate. In addition, in sulphate electrolytes, for instance, the copper cementation occurs with highest rate because the slope of the initial linear section is the highest (27 mV/s) while in the selenate solution it is only (4.5 mV/s).

The second case characterizes the behaviour in the iodate solution. The high value of OCP in this case does not indicate the dominating role of the cathodic half-reaction in the process of metal deposition but the hindered anodic reaction of Fe dissolution. The observations of the iron surfaces in copper iodate solutions for the period of the experiments do not indicate any changes which may be attributed to surface passivation and missing cementation processes.

The cathodic polarization can be adequately represented by the difference in potentials of cementation in $\text{Fe} | \text{Cu}^{2+}$ and the equilibrium values at the electrodes $\text{Cu} | \text{Cu}^{2+}$. The calculated values of the cathodic polarization are summarized in last row of Table 1. In all the case all values are negative with only exception related to the case of the iodate solution. In contrast to the OCP, the values of the polarization can be used to establish the electromotive force of the cementation reactions. This suggestion can be easily explained by the results obtained from the cementation of Cu from solutions of SO_4^{2-} , Cl^- , NO_3^- , PO_4^{3-} . However, when positive cathodic polarizations take place the cementation processes cannot be performed.

The experimental results allow elucidating the strong effect of the anion nature in the electrolyte on the cementation process. The change in the OCP during a real cementation process and the comparison of the stationary level with the equilibrium potentials of the two half-reactions provide only qualitative information of the ability of a cementation process of a particular system but are not informative about its kinetics.

Potentiodynamic tests

The kinetics of the cathodic reaction of the cementation process was investigated by recording potentiodynamic relationships of copper electrodes $\text{Cu} | \text{Cu}^{2+}$ (0,08 mol/L) with various anionic contents of the electrolyte. The electrodes were cathodic polarized with an initial potential of 0.25 V, more positive than OCP up to -1.0 V. The anodic reaction of iron dissolution was investigated through anodic polarization of iron electrodes with concentration 0.08 mol/L Fe^{2+} of the solution, starting from OCP and a shift in the positive direction up to 0.4 V. The concentration of the iron ions was taken equal to that of the deposited metal (0.08 mol/L) with the assumption that the entire quantity of the noble metal from the solution (Cu^{2+}) is replaced by iron ions.

The polarization curves of copper sulphate and chloride electrodes are shown in Fig. 2.

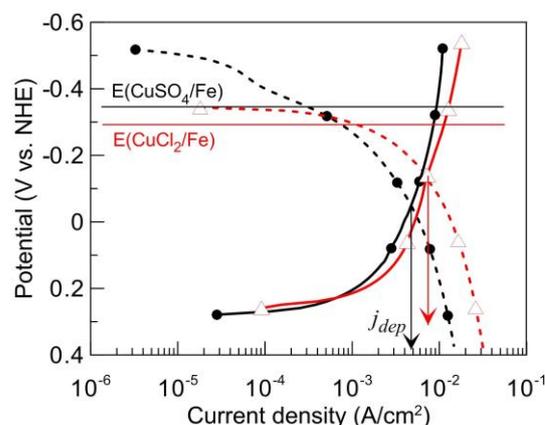


Fig.2. Potentiodynamic relationships of copper (solid lines) and iron (dashed lines) electrodes in sulphate (●) and chloride (Δ) solutions with a concentration of 0.08 mol/L copper salts.

Table 2. Current density and rate (electrochemical and through ICP) of contact deposition of copper on iron electrode from solutions of various copper salts with concentrations 0.08 mol/L.

| | SO_4^{2-} | SeO_4^{2-} | TeO_4^{2-} | Cl^- | NO_3^- | PO_4^{3-} | IO_3^- |
|--|---------------------|---------------------|----------------------|---------------------|---------------------|---------------------|-----------------|
| j_{dep} , A/cm ² | $4,8 \cdot 10^{-3}$ | $6,8 \cdot 10^{-4}$ | $1,8 \cdot 10^{-5}$ | $7,3 \cdot 10^{-3}$ | $1,6 \cdot 10^{-2}$ | $1,9 \cdot 10^{-2}$ | - |
| ν_{Cu} , (el.chem.) mg/h cm ² | 5,69 | 0,81 | $2,13 \cdot 10^{-2}$ | 8,64 | 18,9 | 22,5 | - |
| ν_{Cu} , (ICP) mg/h cm ² | 93.2 | 27.4 | 1.3 | n.a. | 49.4 | 87.2 | - |

The intersection of the anodic curve of the iron electrode with the cathodic section of copper electrode theoretically should coincide with the rate of copper deposition on the iron surface represented as a current density, j_{dep} [5]. The current densities by these points of intersection in the case of sulphate and chloride solutions are $4.8 \cdot 10^{-3}$ и $7.3 \cdot 10^{-3}$ A/cm², respectively with corresponding potentials of -0.05 V and -0.13V. These potentials, however, are more positive than the experimentally determined OCP in the case of copper cementation by iron in sulphate (-0.34 V) and chloride (-0.30 V) electrolytes. The difference in the mixed potential of the real cementation process (OCP) and the value determined potentiodynamically separately with iron and copper electrodes indicates that the real anodic polarization is too low and this can be attributed to some reasons, among them:

- The Fe²⁺ concentration in the electrolyte during the real cementation process varies, while in the model iron electrode it is constant. At the onset of the real cementation process, iron ions in the electrolyte are missing but after that their concentration rises in time and at the vicinity of the electrode surface it probably exceeds the value of 0.08 mol/L. Such a difference in the concentration most likely affects the potential and shifts the potentiodynamic plot along the ordinate.

- The ratio of the areas of the anodic and cathodic sites of the real cementation process varies in time, while in the model the polarization relationships corresponds to constant ratio of 1:1. The differences in the area of the anodic and cathodic sites could result in shifts of both relationships with different extents along the abscissa that finally results in different current densities determined by the potentiodynamic method used.

As a consequence of these experiments and the analysis performed it may be decided that the use of a separate iron electrode for the study of copper cementation is not the adequate approach.

However, when the OCP values for the systems Fe|CuSO₄ and Fe|CuCl₂ are plotted over the polarization plots of the copper electrodes Cu|CuSO₄ и Cu|CuCl₂ they corresponds to the sections of active iron dissolution and copper deposition under diffusion control (see Fig. 2). This result corresponds adequately to the initial suggestion about the process control based on the OCP measurements.

The polarization relationships of copper electrodes with various anionic contents are shown in Fig. 3. In accordance with these plots, the lowest rate of metal deposition was observed in the

solution of copper tellurate. In iodate solution the OCP line crosses the anodic curve of the copper electrode which indicates that the deposition of the copper does not take place, but the value of the mixed potential is due to occurrence of auxiliary reactions at the iron surface such as the release of iodine.

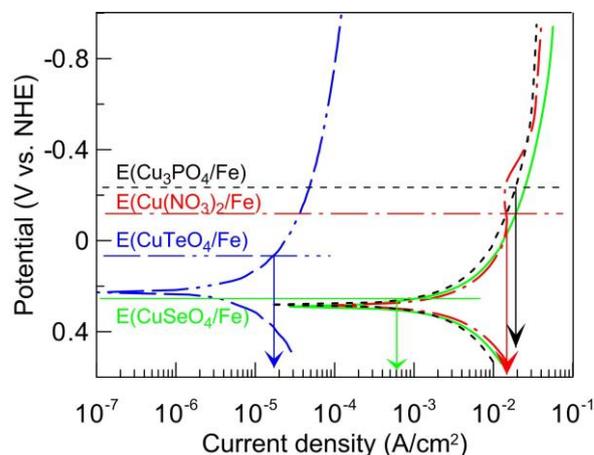


Fig.3. Potentiodynamic relationships of copper electrodes in solutions with a concentration of 0.08 mol/L copper salts.

The intersection of OCP corresponding to Fe|Cu²⁺ and the cathodic section of the polarization relationship of the copper electrode Cu|Cu²⁺ can be used for an experimental determination of the rate of the cementation process, represented as the density of the current of copper deposition onto iron (j_{dep}).

The rate of a heterogenic cementation reaction (v) is generally expressed by the relationship:

$v = dm/S \cdot dt$ where dm is the mass of copper deposited on unit surface S per time dt . The mass of copper deposition can be calculated by the current density (j_{dep}) through the Faraday law. As a result the cementation rate assumes the form:

$$v = m_{\text{Cu}}/t \cdot S = I \cdot A M_{\text{Cu}} / 2 \cdot S \cdot F = j_{\text{dep}} \cdot A M_{\text{Cu}} / 2 \cdot F$$

where $A M_{\text{Cu}}$ is the atomic mass of copper in g/mol; $F = 96495$ C/mol is the Faraday constant and j_{dep} is the cathodic density of current of copper deposition. The rates of copper depositions calculated by this methodology are summarized in Table 2.

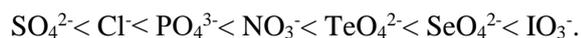
Results from ICP spectroscopy

The ICP results about the copper content in 50 mL of the solutions before and 1 h after the cementation (on 1.14 cm² iron surface) under intensive mixing are presented in the last row of Table 2 as a cementation rate. They are calculated on the basis of the reduction of the concentration of Cu²⁺ in the solution. The cementation rates determined by both methods are different that is an

expected result due to the differences in the experimental conditions. In addition, the cementation times are different: the electrochemical method requires several minutes and a clean surface of the cementer, while the ICP results correspond to the situation after 1h after the end of the cementing process carried out under intensive mixing; the intensive mixing allows permanently creating fresh contacting sites on the cementer surface. As a confirmation of the prescreening comments, it is obvious that the lowest rate of cementations are observed in solutions of selenate and telluride, while in the iodate solution the copper cementation does not take place.

CONCLUSIONS

The paper reports the effect of the nature of anions in the electrolyte on the copper cementation by iron. It was established that the stationary values of OCP strongly depend on the anionic content of the solution and can be arranged in the following order:



In the first five solutions, the OCP shifts sharply in negative direction which indicate diffusional control of the cathodic process (diffusion control of Cu^{2+} transport from the bulk of the solution towards the cementer surface). The only exception was

observed in the iodate solutions where a positive polarization was determined.

It is assumed as possible that the rate of the cementation process can be determined by the superposition of the OCP values and the potentiodynamic relationships in case of copper electrodes $\text{Cu} | \text{Cu}^{2+}$. The fast recovery of copper by cementation was observed in the sulphate electrolyte, while in the iodate solutions the process does not take place.

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ЕЛЕКТРОХИМИЧНО ИЗСЛЕДВАНЕ НА ЦЕМЕНТАЦИОННИ ПРОЦЕСИ

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(Резюме)

Цементацията на метали е спонтанна електрохимична реакция, протичаща на границата на активен метал и електролит, съдържащ йони на по-благороден метал. В тази работа е изследвано електрохимичното поведение на окислително-редукционни двойки като са сравнявани смесените потенциали при цементация със съответните, експериментално получени потенциали на отделните двойки. Този подход позволява да се определят стойностите на анодната и на катодната поляризация, но не и кинетиката на цементационната реакция. За изследване на кинетиката на електродните полуреакции са снети потенциодинамични зависимости на железни и медни електроди. Скоростта на отлагане на мед върху желязна повърхност е представена чрез плътност на тока, получена при наслагване на анодната поляризационна зависимост на железен електрод с катодната на меден електрод. Корозионните потенциали, определени в пресечната точка на двете зависимости, са значително по-положителни от съответните потенциали на отворена верига при директна цементация на мед върху желязо. По-точни резултати за скоростта на цементационната реакция се получават чрез нанасяна на стойността на смесения потенциал на реален цементационен процес върху поляризационната зависимост на меден електрод. Така получената пресечна точка попада в областта от потенциали, съответстващи на активно разтваряне на желязо и на отлагане на мед при дифузионен контрол. Тези резултати съответстват в достатъчна степен на получените чрез ICP спектроскопия.