

PREPARATION OF THE COPPER COATINGS ON FE POWDER BY ELECTROLESS PLATING TECHNIQUE

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Abstract

The electroless coating technique is one of the elegant methods available for the production of protective coatings on surface. Our study has been aimed at the conditions of the electroless deposition of copper coating onto the iron powder particles from sulphate electrolyte. The course of the electroless process depends on the composition and pH of the electrolyte as well as on the size and concentration of the iron powder particles in the electrolyte. After analysis, the most convenient electrolyte was chosen ($\text{pH } 3.3$, $c \text{ Na}_3\text{cit} = 0.25 \text{ mol dm}^{-3}$), suppressing mostly the rate of the electroless process and shifting at the same time its equilibrium to the reactants. Another parameter is quantity of Fe powder particles. With increasing particle size fraction the effective surface for electroless process is reduced. The highest amount of copper is deposited on the smallest grain class of powder particles. At higher suspension density of iron the effective surface for deposition of copper is enlarged. The coated and uncoated powders have been subjected to microstructural studies by microscopic methods.

Keywords: electroless, copper coating, Fe particles, complex forming agent

INTRODUCTION

The electrochemical plating of iron powder particles by metallic coatings has been studied in our laboratory for a period of time, in order to prepare convenient powder material with the required properties. At first, we investigated the electrolytic deposition of one-component nickel coatings [1-3]. Reactivity of the basic iron powder was a very important property in the electrolytic coating of nickel [4]. Next, we were interested in deposition of a two-component nickel-copper coating onto the particulate iron. This process is fairly complicated. The problem of the simultaneous deposition of two metals with both standard redox and deposition potentials rather far apart was successfully solved [5,6]. The process of the electrolytic deposition of copper as a considerably electropositive metal is accompanied by an electroless deposition process that is very difficult to control. Two types of electroless processes are known. First, the donor of electrons is a reducing agent present in the electrolyte. Second, the donor is a substrate, which produces free electrons for chemical redox reaction [7]. In our case, the iron powder substrate supplied the electrons and, consequently, was transferred into the solution as Fe (II) ions.

The process proceeds at a system, where the dispersed particulate Fe creates a suspension with the electrolyte through intensive stirring. The rate of the spontaneous process decreases with time until a stationary state is reached and the dissolution of Fe is stopped. The electroless deposition of copper is influenced by several parameters. One of

the most important is the concentration of sodium citrate in the electrolyte, which, as a complex-forming agent, is aimed at preventing copper ions from being reduced to metallic Cu. With a change of pH, the sort and number of complex compounds with sodium citrate characterized by different values of stability constants, also changes [8-11]. Further more, it is the ratio of Fe powder to Cu²⁺ ions in the solution and, finally, the particle size fraction of the powder particles.

EXPERIMENTAL

The Fe powder material used was sieved into the five granulometric classes: 0–45 µm, 45–63 µm, 63–100 µm, 100–125 µm, 125–160 µm. The powder was chemically activated in 10% solution of hydrazine dihydrochloride before measurement. The electrolyte for the electroless process consists of 0.25 mol·dm⁻³ CuSO₄·5H₂O and 0.15, 0.25 or 0.4 mol·dm⁻³ sodium citrate, Na₃(cit). The pH of the solution was adjusted to 2.0, 3.3 or 4 by diluted sulphuric acid. The suspension was prepared by adding 1.5, 2.5, 3.5 g of iron powder into 150 ml of electrolyte corresponding to the suspension density 10.0, 16.7, and 23.3 g·l⁻¹, respectively. A mechanical stirrer with the rotation speed 800 r.p.m intensively stirred the reaction system. The temperature applied was kept at the laboratory value, 24±1°C.

The amount of the deposited copper on the surface of Fe powder as well as the concentration of Fe (II) ions transferred into the electrolyte were analysed during the time period 150 minutes, in which the stationary state was reached and the spontaneous redox process was brought to an end in all studied cases. At the same time, the quantity of the copper ions remaining in the solution and not participating in the process was determined in order to control the material balance of Cu. For analysis, AAS method was used. After dissolving the powder in diluted nitric acid, Fe in solution was determined at 249 nm, Cu at 326 nm wave lengths. The calibration line method was used for evaluation of experiments. The average thickness of the Cu layer was calculated from the total amount of deposited Cu determined by analysis and the total surface area of the powder participating in the reaction. Specific surface area of the powder was either determined experimentally by BET analysis - S_{exp}, or calculated according to a model presented elsewhere - S_{calc} [1].

The thickness and character of the Cu layer deposited on iron powder particles were also observed by metallurgical microscope.

RESULTS AND DISCUSSION

The spontaneous process of electroless deposition of copper by heterogeneous redox process of Fe powder dissolution is largely influenced by the composition of solution, by the amount of Fe powder in a unit volume of solution and by the particle size fraction of Fe powder.

Trisodium citrate, Na₃(cit) was examined as a complexing agent forming rather strong complexes with Cu ions in solution and preventing thus their reduction to nulvalent copper by Fe powder. Figure 1 shows the course of reaction (1) with time at two different concentrations of Na₃(cit), during which the electroless deposition of Cu proceeds:



It may clearly be seen that higher complexing agent concentration slows down the rate of the exchange redox reaction and reaching the stationary state takes more time.

The influence of pH is presented in Fig.2. At lower pH 2, the reaction runs faster and to higher extent than at pH 4. If the electroless process runs at pH 4.0, the quantity of Fe dissolved into the solution and Cu deposited on the powder is nearly equimolar. At low pH 2.0 the equivalency between the deposited copper and dissolved Fe is disturbed,

quantity of Fe in solution is higher than would correspond to the deposited copper. The iron is dissolved not only by redox reaction with Cu, but also by other side reactions, such as the chemical dissolution of iron in acidic solution. With a change of pH, the sort and number of complex compounds with sodium citrate characterized by different values of stability constants, also changes.

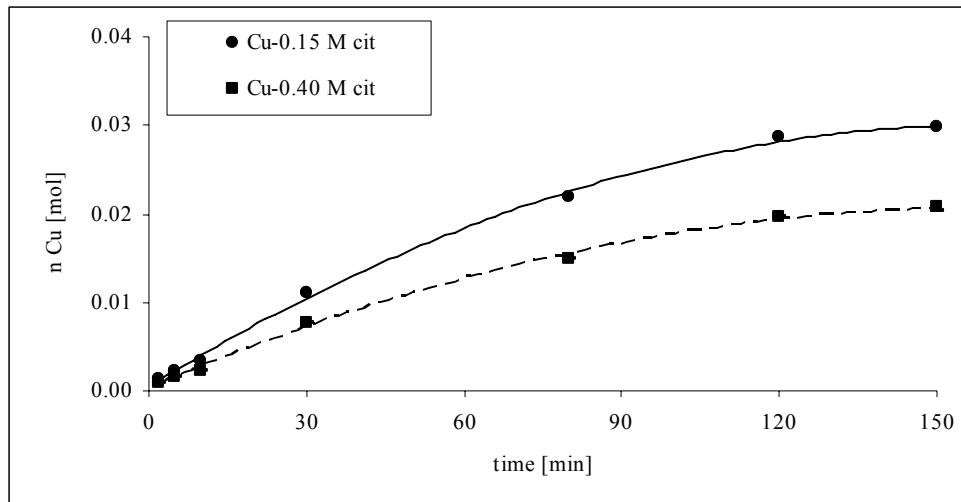


Fig.1. The amount of Cu deposited on Fe powder for various concentrations of the sodium citrate, $c\text{ CuSO}_4 = 0.25\text{ M}$, particle size $63\text{--}100\text{ }\mu\text{m}$, suspension density $16.7\text{ g.l}^{-1}\text{ Fe}$; $t = 24 \pm 1^\circ\text{C}$; $\text{pH} = 3.3$.

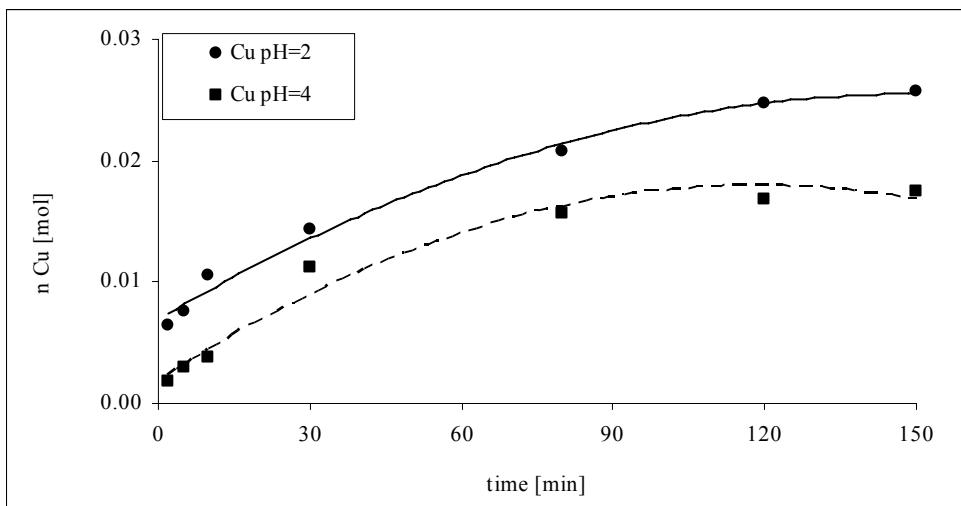


Fig.2. Content of the copper deposited on Fe powder in dependence on pH, $c\text{ CuSO}_4 = 0.25\text{ M}$ $c\text{ Na}_3(\text{cit}) = 0.25\text{ M}$, particle size $63\text{--}100\text{ }\mu\text{m}$, suspension density $16.7\text{ g.l}^{-1}\text{ Fe}$, $t = 24 \pm 1^\circ\text{C}$.

The heterogeneous kinetics of the exchange process was evaluated as first-order reaction kinetics. The rate constants of reaction in the first 30 minutes, signed as k_{0-30} , actually reflect the situation, when most of the surface of Fe powder is free for the redox exchange, Table 1. After this time period the reaction slows down significantly and proceeds toward the stationary state. On the basis of rate constant values, such electrolyte composition was chosen for further experiments giving the lowest reaction rate, i.e. 0.25 mol. dm^{-3} Na₃(cit) and pH 3.3.

Tab.1. Rate constant of the electroless copper deposition for different concentrations of the sodium citrate and for different pH values in the electrolyte, c CuSO₄ = 0.25 M, particle size 63-100 μm , suspension density 16.7 g.l⁻¹ Fe, t = 24±1°C.

c Na ₃ (cit) [mol. dm^{-3}]	0.15	0.25	0.40
k_{0-30} [min ⁻¹ .10 ²]	1.12	0.74	0.92
k [min ⁻¹ .10 ²]	0.88	0.37	0.60
pH	2	3.3	4
k_{0-30} [min ⁻¹ .10 ²]	0.87	0.74	1.14
k [min ⁻¹ .10 ²]	0.61	0.37	0.60

A further parameter to influence the process of electroless deposition of copper is the particle size fraction of the powder particles, in regard to the change of the total efficient surface for deposition. Five particle size fractions were used, see Experimental. Figure 3 presents the effect of various particle size fractions with time upon the content of the copper deposit on the Fe powder particles. The largest specific surface belongs to the smallest grain fraction (0–45 μm). It was experimentally confirmed that the highest amount of copper was coated on the smallest grain fraction of iron powder. If the particle size fraction increases, the quantity of deposited copper on their surface decreases.

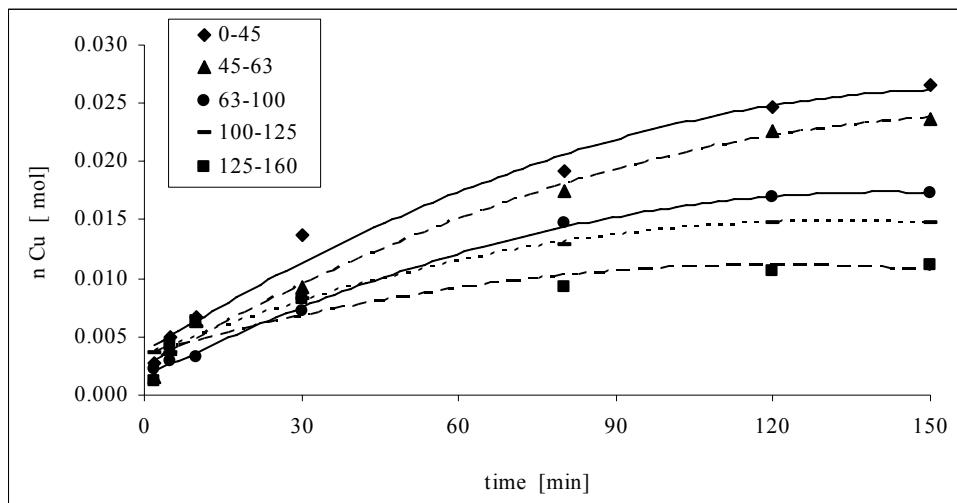


Fig.3. Content of the copper deposited on Fe powder in dependence on time for various particle size fractions, c Na₃(cit) = 0.25 M, c CuSO₄ = 0.25 M; suspension density 16.7 g.l⁻¹ Fe, t = 24±1°C, pH = 3.3.

As to the time when the deposition of Cu reaches the stationary state, it is also affected by the particle size. Steady state was reached in shortest time in the case of the largest grain fraction. As can be seen in Figure 3, steady state in the case of the fraction 125–160 μm occurs roughly in 70 minutes, in the case of smaller grain classes this time increases, and for particle size fraction 0–45 μm it reaches approximately 130 minutes. The rate of the reaction decreases with the decreasing specific surface area of Fe powder.

The stationary state was characterized, first by the degree of heterogeneous conversion of solid Fe particles to dissolved Fe, and second by the thickness of the deposited layer of Cu on the Fe particle surfaces. The amount of dissolved iron in solution after 150 minutes was determined and expressed as a degree of conversion of iron α and is presented in Table 2. With increasing particle size the degree of conversion of iron in solution has a decreasing nature. Table 2 also presents the values of thickness of Cu layers σ coated on Fe powder for individual grain fractions, for calculated and experimentally determined specific surface area. All calculated values of specific surface area are higher than the experimentally measured ones due to the differences between spherical shape simplifications used in the model and the actual surface of particles, determined by BET analysis. The thickness of the layer is the smallest for grain fraction 0–45 μm , with increasing particle size fraction the thickness of deposited Cu layer increases, at the largest particles it is approx. three times higher than for the smallest ones.

Tab.2. Degree of conversion of iron α and the thickness of the deposited layer of Cu σ on Fe particles for various particle sizes reached after 150 minutes, $c \text{ Na}_3(\text{cit}) = 0.25 \text{ M}$, $c \text{ CuSO}_4 = 0.25 \text{ M}$, suspension density $16.7 \text{ g.l}^{-1} \text{ Fe}$, $t = 24 \pm 1^\circ\text{C}$, pH 3.3

Particle size [μm]	α	$\sigma [\mu\text{m}]$	
		S calc.	S exp.
0–45	0.597	2.24	0.75
45–63	0.536	4.90	1.65
63–100	0.414	5.28	2.25
100–125	0.362	6.22	2.28
125–160	0.319	5.96	2.39

Figures 4 a, b present the optical micrograph of the electroless deposited copper coating on the Fe powder particles of various sizes after 80 minutes. Some places on the particle surface show the displacement of Fe by Cu. Formation of the hollow copper particles is also observed. The surface of the particle is created only by Cu deposit, separated by vacant space from the surface of the basic Fe particle. The layers are homogenous and uniform and the thickness of coating ranges from 0.5 μm to 12 μm .

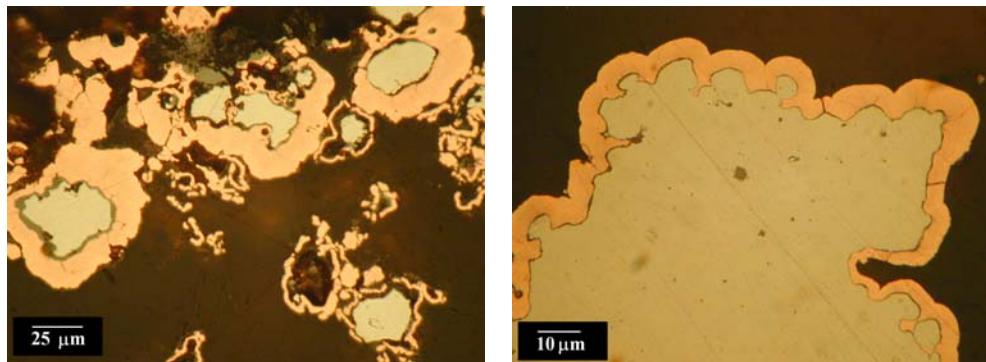


Fig.4. The optical micrograph of the electroless deposited Cu coating on Fe powder taken after 80 minute of the process, the particle size a) 0–45 μm , b) 125–160 μm .

The last studied parameter influencing the process was the amount of iron powder particles added into the electrolyte expressed as suspension density. For study of this effect the powder grain size fraction 63–100 μm was used. As already mentioned, the quantity of the deposited copper on iron powder depends mainly on the effective surface area available for the electroless process, which in turn, is directly proportional to the amount of powder added into the electrolyte. As is evident from Figure 5, the smallest amount of copper is deposited at the lowest suspension density value. If the value of suspension density increases, the quantity of deposited copper as well as the rate of reaction increases.

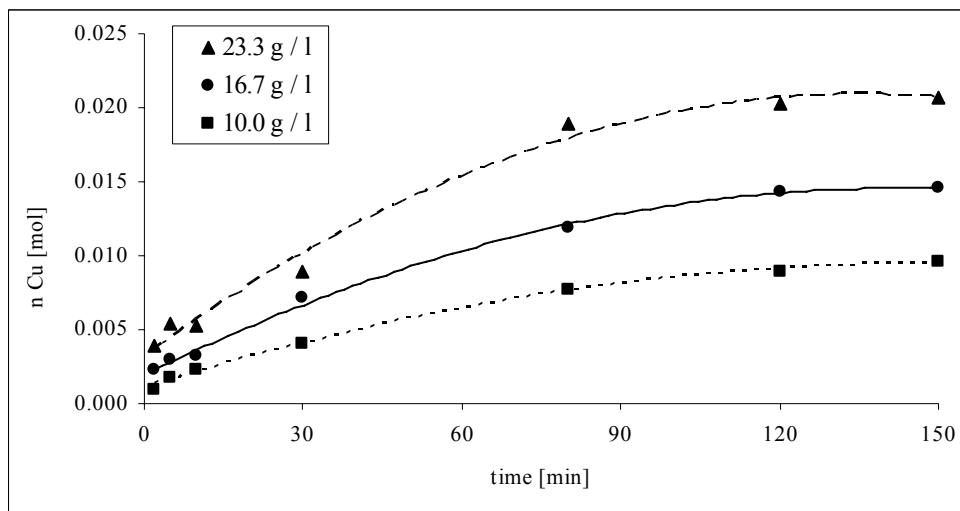


Fig.5. Content of the copper deposited on Fe powder in dependence on time for various suspension densities, $c \text{ Na}_3(\text{cit}) = 0.25 \text{ M}$, $c \text{ CuSO}_4 = 0.25 \text{ M}$, particle size fraction 63–100 μm , $t = 24 \pm 1^\circ\text{C}$, $\text{pH} = 3.3$.

In Table 3, the values are presented for the degree of conversion of iron for individual suspension densities after the process reaches the stationary state. The value of degree of conversion has a decreasing character. The values of the thickness of the Cu layer

σ for individual suspension densities are also presented. The thickness of the deposited copper layer is roughly independent on the suspension density value as it can be seen from the values in the last two columns of the Table. This independence may be attributed to the fact that for a respective grain class the effective surface area for 1 g of powder is always equal and independent to the total quantity of powder particles added into the electrolyte.

Tab.3. Degree of conversion of iron α and the thickness of the deposited layer of Cu σ on the Fe particles for various suspension densities after 150 minutes, particle size $63 - 100 \mu\text{m}$, $c \text{Na}_3(\text{cit}) = 0.25 \text{ M}$, $c \text{CuSO}_4 = 0.25 \text{ M}$, $t = 24 \pm 1^\circ\text{C}$, pH 3.3.

Suspension density [g.l ⁻¹]	α	$\sigma [\mu\text{m}]$	
		S calc.	S exp.
10.0	0.563	5.04	2.19
16.7	0.414	4.50	1.89
23.3	0.362	4.51	1.93

Figures 6 a, b present the optical micrographs of the electroless deposited Cu coating on Fe powder surfaces where the suspension density is 10.0 g.l^{-1} and 23.3 g.l^{-1} . If the suspension density is high, the adhesion of the deposited Cu layer is worse. The high amount of Fe particles causes more frequent contacts between them and may lead to damage of the deposited layer.

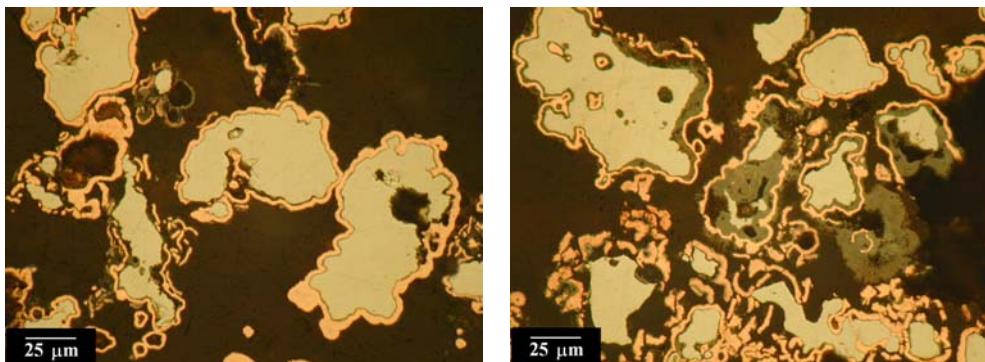


Fig.6. The optical micrograph of the electroless deposited Cu coating on Fe powder taken after 80 minute of the process, the suspension densities a) 10.0 g.l^{-1} b) 23.3 g.l^{-1} .

CONCLUSIONS

The electroless deposition of copper may be realized in a system where the dispersed particulate Fe creates suspension with the electrolyte. The product possesses superior properties as to the quality in general and as to the homogeneity in particular, and is used in powder metallurgy and microelectronics. For practical reasons it is useful to suppress the spontaneous electroless process of Cu deposition since it is difficult to control. After the analysis of the two main effects, influence of the complexing agent - trisodium citrate and value of pH, the most convenient electrolyte was chosen ($\text{pH } 3.3$, $c \text{Na}_3(\text{cit}) = 0.25 \text{ mol dm}^{-3}$), suppressing mostly the rate of the electroless process and shifting at the same time its equilibrium to the reactants.

Another research parameter is quantity of Fe powder particles, which form the suspension with the electrolyte and their particle size. The process is to a remarkable extent influenced by the effective surface area available for electroless deposition. With increasing particle size fraction, the effective surface for electroless process is reduced. The highest amount of copper is deposited on the smallest grain class of powder particles. At higher suspension density of iron, the effective surface for deposition of copper is enlarged. The thickness of deposited copper is, however, not influenced by this parameter, because the effective surface area for the weight unit of the powder is unchanged.

Acknowledgements

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REFERENCES

- [1] Gálová, M., Oriňáková, R., Lux, L.: J. Solid State Electrochem., vol. 2, 1998, p. 2
- [2] Lux, L., Gálová, M., Oriňáková, R., Turoňová, A.: Particulate Science and Technology, vol. 16, 1998, p. 135
- [3] Turoňová, A., Gálová, M., Lux, L., Gál, M.: Journal of Solid State Electrochemistry, vol. 5, 2001, p. 502
- [4] Oriňáková, R.: Surface and Coatings Technology, vol. 162, 2003, p. 54
- [5] Turoňová, A., Gálová, M., Šupicová, M.: Journal of Solid State Electrochemistry, vol. 7, 2003, no. 10, p. 684
- [6] Turoňová, A., Gálová, M., Šupicová, M., Lux, L.: Journal of Solid State Electrochemistry, vol. 7, 2003, no. 10, p. 689
- [7] Schlesinger, M., Paunovic, M.: Modern Electroplating. New York : John Wiley & Sons, Inc., 2000
- [8] Green, TA., Russell, AE., Roy, S.: J. Electrochem. Soc., vol. 145, 1998, no. 3, p. 875
- [9] Daniele, PG., Ostacoli, G., Rigano, C., Sammartano, S.: Transition Met. Chem., vol. 9, 1984, p. 385
- [10] Daniele, PG., Ostacoli, G., Zerbinati, O., Sammartano, S., De Robertis, A.: Transition Met. Chem., vol. 13, 1988, p. 87
- [11] Martell, AE., Smith, RM.: Critical Stability Constants, vol. 3. (Other Organic Ligands). New York : Plenum Press, 1976