

CORROSION BEHAVIOUR OF COATED HOLLOW SPHERES IN ACETATE BUFFER WITH KCl

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Abstract

The potentiodynamic polarization method was used to study the corrosion properties of coated hollow spheres. The copper hollow spheres created on porous iron powder particles by cementation were electrolytically coated with Ni layer in fluidised bed arrangement. Electroless deposition of Cu and electrolytical deposition of Ni allows suitable modification of the iron particles surface. The results, obtained from polarization curves performed in a deaerated 1 mol.dm⁻³ acetate buffer with KCl, indicated that increasing the amount of Ni in surface layer increased corrosion resistivity of coated hollow spheres. Surface morphology and composition of spherical particles were studied by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Deposition of Ni and Cu coatings on Fe hollow particles is a very simple and cost-effective technique for preparing novel materials for powder metallurgy and the chemical industry, with high corrosion resistance and favourable mechanical properties.

Keywords: corrosion, anodic polarization, nickel electrodeposition, copper electro-less deposition

INTRODUCTION

Copper can be deposited by wet chemical plating techniques such as electroplating and electroless deposition. These techniques have the advantage of a low cost of tools and materials, low processing temperature and high recovery of the process [1-3]. The main disadvantage of electroless deposition of Cu is the large amount of produced waste and lower quality of the deposited layer.

Electroplating is a process of metal deposition by electrolysis from an aqueous or non-aqueous metal salt solution. Coatings containing Cu and Ni have favourable protective and mechanical characteristics [4,5]. The electrochemical behaviour of these alloys was studied mainly in chloride solutions [6-10]. The corrosion potential can give a fundamental indication of the thermodynamic corrosion risk. Copper-based alloys are among the most important commercial metals in the marine environment due to their excellent electrical and thermal conductivities, good corrosion resistance and ease of manufacture. They are tested also in the automobile, aerospace and railway industry. At present, application oriented solutions for crash absorbents, heat insulators, sound absorbers and lightweight construction are being developed [11].

The copper hollow spheres were created by cementation on iron hollow spherical particles. The surface of copper particle is porous, rough and weak and thus the particles are

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difficult to handle. The Ni coating was deposited on copper hollow particles with the aim to improve mechanical properties.

Electroplating of metallic hollow particles can be realised in a fluidised state with good experimental results. In optimum conditions, the metal coating on the particles is equally distributed, even and adhering. Interesting results were obtained by a combination of electroless deposition of copper and electrolytic deposition of nickel [12,13].

In this work, the influence of Ni electrodeposition conditions on the surface morphology, composition and corrosion resistivity of copper hollow particles covered with nickel was investigated. Corrosion properties were examined in an acetate buffer with KCl. Corrosion behaviour of original iron particles, uncoated copper spheres and iron particles coated with nickel was considered as the reference state.

EXPERIMENTAL

Porous Fe particles produced from the iron oxide particles were obtained in pickling acid, recovering in a wire factory by the following fluidised bed line. The obtained oxide particles were reduced in a split ammonia atmosphere (75% H₂ + 25% N₂) for 6 hrs at 850 °C resulting in similar spherical hollow iron particles. After screening a fraction between 0.71 – 0.80 mm was used.

Fe particles were subjected to chemical pre-treatment before the coating: etching in a reductive solution of 10% hydrazine hydrochloride for 5 min. The chemical activation produced new active sites for coating deposition and removed the passivated layer from the particle surface.

The plating electrolyte used consisted of:

- Cu (electro-less): 1 mol dm⁻³ CuSO₄; 0.1 mol dm⁻³ H₂SO₄, pH = 1.2
- Ni (electrolytic): 1.42 mol dm⁻³ NiSO₄; 0.6 mol dm⁻³ H₃BO₃; 0.6 mol dm⁻³ NaCl, pH=3.2

A cell with separated anodic (glass, volume 300 ml) and cathodic (plastic, volume 170 ml) compartments was used for electrolysis, with an Ni plate as anode and stainless steel plate as cathode. Anodic and cathodic compartments were connected with a diaphragm (textile net with mesh size of about 0.04 mm).

A defined amount of Cu hollow particles in a cathodic compartment was kept in a fluidised state by a glass stirrer, the speed of which was controlled. All electrolyses of time dependence were realised with a constant current (1 A) and electrolyses of current dependence with a constant time (45 minutes). The cathode was cleaned in a nitric acid solution before each measurement.

The coated metallic hollow particles were rinsed in distilled water and dried by acetone after each electrolyse. Content of Ni and Cu deposited on hollow particles was determined after dissolution in nitric acid by atomic absorption spectrometry (AAS).

The morphology of coated metallic hollow spheres was studied using scanning electron microscopy (TESLA BS 340 with EDX LINK ISIS micro-analyser).

A conventional three-electrode arrangement was used for potentiodynamic polarization experiments in 1 mol.dm⁻³ acetate buffer with 1 mol.dm⁻³ KCl. Before measurement the electrolyte was deaerated with gaseous argon for 10 minutes. Polarization curves were obtained by varying the applied potential from -1000 mV up to 0 mV at a scan rate 25 mV/s. The working electrode (WE) was a carbon paste electrode (CPE), the reference electrode (RE) was Ag/AgCl with saturated KCl solution and the counter electrode (CE) was Pt plate. The surface of carbon paste electrode was renewed by the cutting and polishing of the electrode top-surface layer before each measurement. For determination of corrosion potential there was only one respective micro-particle immobilized on the surface of CPE by abrasion. Three cycles of potentiodynamic

polarization were registered for every hollow micro-particle immobilized on CPE. Size of the examined particle diminished due to its partial dissolution in each cycle of anodic polarization. As a consequence of diameter reduction the particle loosened and fell out from the cavity in the CPE surface, as a rule after the third cycle, thus it was not possible to register more cycles.

RESULTS AND DISCUSSION

Corrosion potentials of the iron hollow particle, Cu hollow particle prepared from iron particle by cementation and the iron hollow particle coated with Ni were measured as a reference state. The following differences have been found between the corrosion potentials of the above mentioned coated hollow spheres (Fig.1). The corrosion potential of the Cu hollow sphere was the most positive because copper is a noble metal. The corrosion potential of the Fe hollow sphere coated with Ni was shifted to more negative values and the E_{corr} of the Fe hollow particle was the most negative.

It was found, that E_{corr} values of metallic particles were slightly shifted to more negative values with increasing number of cycles. The iron particle had a nearly constant value of E_{corr} for all cycles.

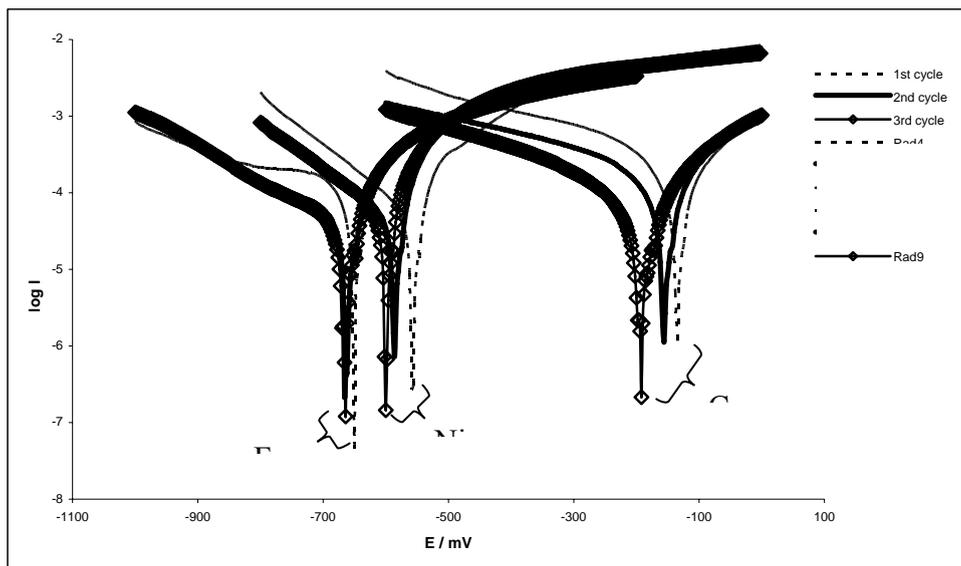


Fig.1. The potentiodynamic polarization curves obtained from de-aerated $1 \text{ mol} \cdot \text{dm}^{-3}$ acetate buffer with KCl for Fe particle, Cu particle and Fe particle with Ni layer.

The composition of metallic particles after electroless deposition of Cu and electrodeposition of Ni is summarized in Table 1. The value of partial current efficiency η_{part} characterizes the current efficiency of electrolytic deposition of Ni on Cu hollow particles:

$$\eta_{\text{part}} = \frac{M_{\text{pow}}}{M_{\text{total}}} \cdot 100\% \quad (1)$$

M_{pow} represents the mass of metal deposited on micro-particles and M_{total} stands for the theoretical total amount of deposited metal calculated according to Faraday's Law. The

maximum current efficiency of the hollow spheres coating was about 3% at given conditions. Nickel is deposited during electrolysis also on the stainless steel cathode, which is from our point of view the side reaction, lowering efficiency of the particular material plating. The copper content was about 80 % – 90% and iron content about 6% – 12% after cementation. The amount of nickel deposited on copper particles increased with time of electrolysis. Current dependence shows that the most suitable current intensity for Ni deposition was 1.4 A (Tab. 1).

Tab.1. Composition of Cu hollow particles electrolytically coated with Ni; size fraction 0.71 – 0.80 mm.

t [min] (I was 1 A)	Cu [wt.%]	Fe [wt.%]	Ni [wt.%]	η [%]
30	82.9	10.3	0.40	7.18
45	84.3	9.4	0.58	7.06
60	89.8	9.3	0.93	8.50
75	85.4	12.3	1.28	9.35
90	92.6	7.3	1.63	9.92
I [A] (t was 45 min)	Cu [wt.%]	Fe [wt.%]	Ni [wt.%]	η [%]
0.8	89.3	8.2	0.23	3.29
1.0	84.3	9.4	0.58	7.06
1.2	81.0	11.3	0.83	8.59
1.4	92.3	6.4	1.93	15.95
1.6	91.4	7.1	1.39	10.48

The effect of electrolysis time on the corrosion properties

Three cycles were registered during anodic dissolution of the coated hollow sphere in 1 mol.dm⁻³ acetate buffer with KCl. The E_{corr} values for all three cycles are summarized in Table 2. The protective nature of the metal film increases with the time of electrolysis, as with the amount of Ni deposited on particle surface. Also the surface morphology of the particle is apparently improved by the presence of a nickel layer on the surface of a spherical particle [14]. Values of E_{corr} for different electrolysis time decreases with an increasing number of cycles (Tab. 2). The passivated layer on the particle top-surface, which to some extent protected the particle, was dissolved during the first cycle of anodic polarization and thus in the next cycle particles showed a higher tendency to corrode. The E_{corr} values are shifted with time to more positive values for all three cycles (Fig.2). The highest scatter of E_{corr} values was obtained for the first cycle (about 450 mV) and the lowest difference was observed for the third cycle (about 60 mV) (Tab. 2).

Tab.2. The E_{corr} values for 1st, 2nd and 3rd cycle of anodic dissolution of Cu hollow particles electrolytically coated with Ni in an acetate buffer with KCl depending on time of electrolysis.

Time of Ni electrolysis [min]	E_{corr} [mV]		
	1 st cycle	2 nd cycle	3 rd cycle
30	-588	-735	-739
45	-467	-713	-727
60	-388	-702	-706
75	-356	-608	-687
90	-245	-587	-672

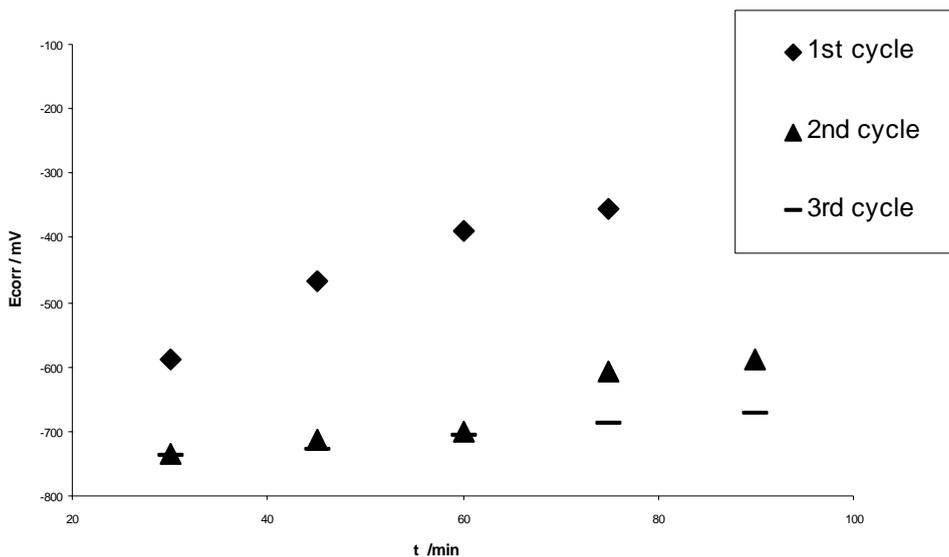


Fig.2. The E_{corr} for 1st, 2nd and 3rd cycle of anodic dissolution of Cu hollow particles electrolytically coated with Ni in acetate buffer with KCl depending on time of electrolysis.

The effect of electrolysis current on the corrosion properties

The E_{corr} values for 1st, 2nd and 3rd cycle of anodic dissolution of coated hollow spheres in acetate buffer with KCl are summarized in Tab.3 for different current intensities during Ni electrolysis. Values of E_{corr} for current intensity dependence varied in a smaller range in comparison with values of E_{corr} for time dependence (Fig.2). More positive values of E_{corr} were observed for higher current intensities and more negative values for lower intensities (Fig.3). Observed results correspond to the amount of Ni deposited on the particle surface (Tab.3). It was found that current intensity 1.4 A was the most suitable for Ni electrodeposition and subsequently for better corrosion resistivity of particles.

Tab.3. The E_{corr} values for 1st, 2nd and 3rd cycle of anodic dissolution of Cu hollow particles electrolytically coated with Ni in an acetate buffer with KCl depending on current intensity.

Current during Ni electr. [A]	E_{corr} [mV]		
	1 st cycle	2 nd cycle	3 rd cycle
0.8	-487	-692	-735
1.0	-467	-695	-728
1.2	-440	-691	-725
1.4	-400	-655	-692
1.6	-384	-636	-669

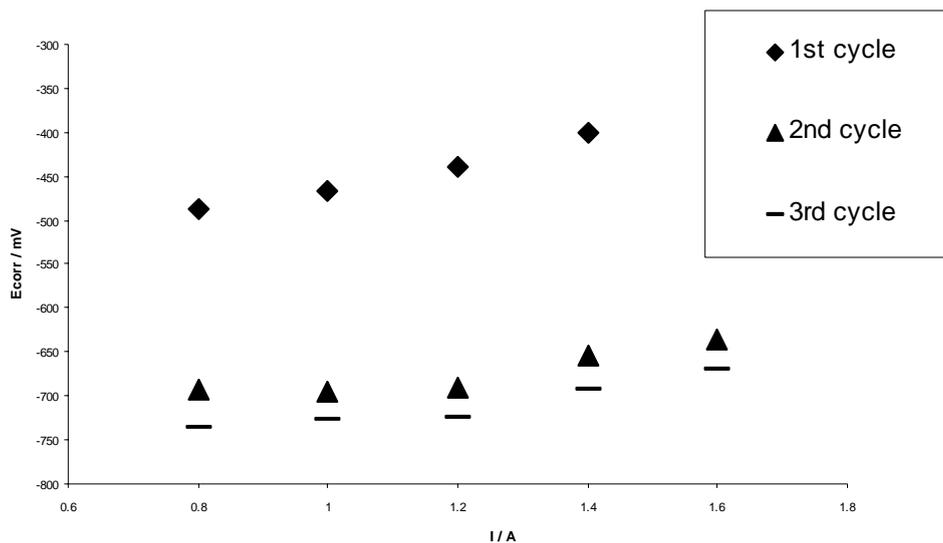


Fig.3. The E_{corr} for 1st, 2nd and 3rd cycle of anodic dissolution of Cu hollow particles electrolytically coated with Ni in acetate buffer with KCl depending on current of electrolysis.

Surface morphology of coated hollow spheres

In Figure 4 is shown as SEM micrograph of a Cu hollow particle covered with Ni during 45 min electrolysis at 1 A. The particle surface is rough and porous because of Fe diffusion from the inner surface during electroless deposition of Cu.

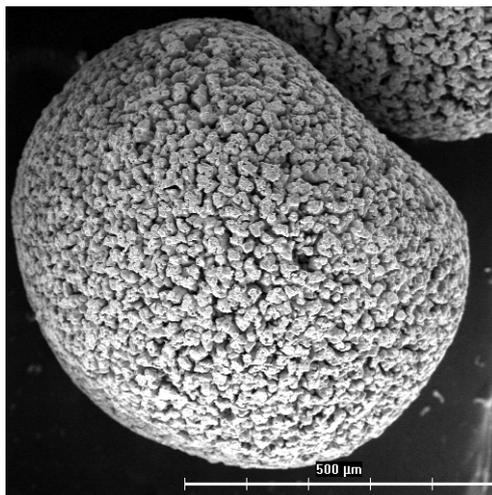


Fig.4. SEM micrograph of Cu hollow particle covered with Ni layer.

The cross-section of walls of two neighbouring particles is shown in Fig.5. The EDX line analysis was made from a starting point marked on Fig.5 as “START” to the ending point marked as “END”. In Figure 6 is shown the metal composition along line

START-END marked on Fig.5. From EDX line analysis it can be clearly seen that while iron is concentrated mainly on inner side of particle wall, copper and nickel are equally distributed across the outer side of the particle wall.

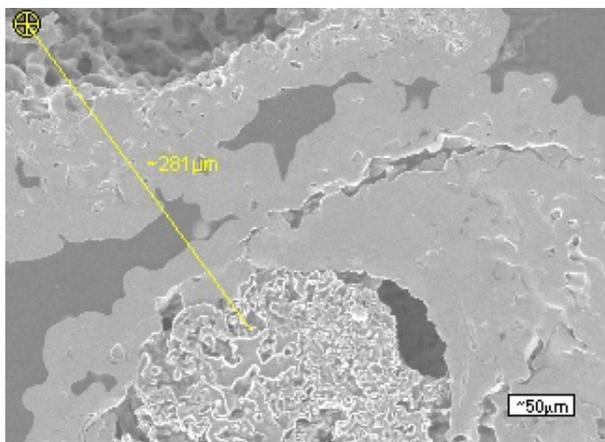


Fig.5. SEM micrograph of cross-section of Cu hollow particles covered with Ni layer.

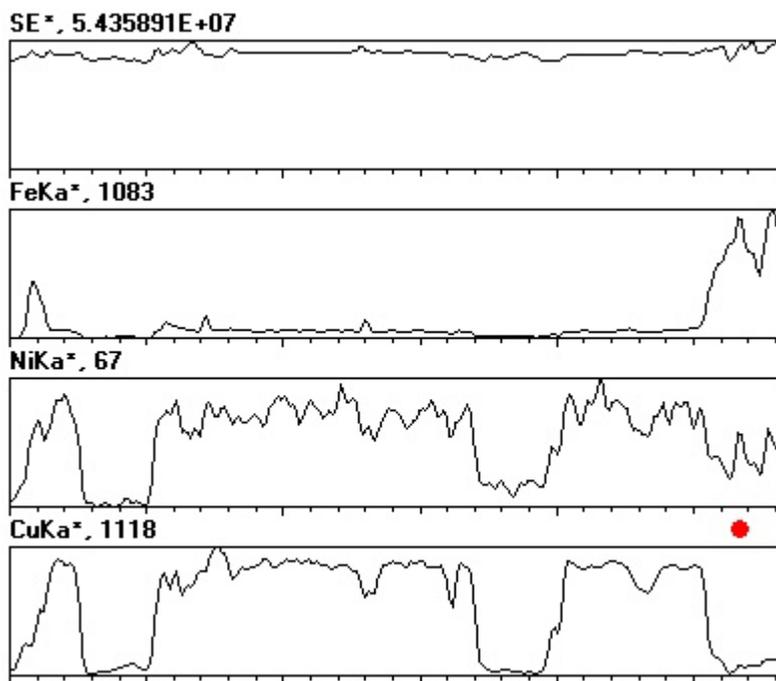


Fig.6. Content of Fe, Ni and Cu on the cross-section of Cu hollow particles covered with Ni layer obtained by EDX line analysis marked in Fig.5.

CONCLUSIONS

The copper hollow spheres were created on porous iron powder particles by electro-less deposition. The consequent Ni plating was applied to improve the mechanical properties of copper hollow particles. These structures have significant potential multifunctional applications where a combination of impact energy absorption, acoustic attenuation, thermal insulation, corrosion resistivity or heat dissipation is required.

Corrosion resistivity of coated hollow particles increases with the amount of nickel in the coating layer. Nickel content increases with time of electrolysis and current intensity. It was found that the most suitable current intensity for Ni electrodeposition is 1.4 A at given conditions. Corrosion resistance of Cu hollow particles coated with Ni also decreased with the increasing number of polarisation cycles.

The EDX line analysis proved that iron was concentrated mainly on inner side of the particle wall and copper and nickel were equally distributed across the outside.

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REFERENCES

- [1] Körner, C., Singer, RF.: *Advanc. Eng. Mater.*, vol. 2, 2000, p. 159
- [2] Banhart, J.: *JOM*, vol. 52, 2000, p. 22
- [3] Queheillalt, DT., Sypeck, DJ., Wadley, HNG.: *Mater. Sci. Eng. A*, vol. 323, 2002, p. 138
- [4] Beltowska-Lehman, E., Ozga, P.: *Electrochim. Acta*, vol. 43, 1998, p. 617
- [5] Green, TA., Russel, AE., Roy, S.: *J. Electrochem. Soc.*, vol. 145, 1998, p. 875
- [6] Milosev, I., Metikos-Hukovic, M.: *Electrochim. Acta*, vol. 42, 1997, p. 1537
- [7] Maciel, JM., Agostinho, SML.: *J. Appl. Electrochem.*, vol. 30, 2000, p. 981
- [8] Lalvani, SB., Kang, JC., Mandich, NV.: *Corros. Sci.*, vol. 40, 1998, p. 69
- [9] Ismail, KM., Fathi, AM., Badawy, WA.: *Corros. Sci.*, vol. 48, 2006, p. 1912
- [10] Nobe, K., Lee, HP.: *J. Electrochem. Soc.*, vol. 140, 1993, p. 2483
- [11] Kear, G., Barker, BD., Stokes, K., Walsh, FC.: *J. Appl. Electrochem.*, vol. 34, 2004, p. 659
- [12] Oriňáková, R., Kupková, M., Dudrová, E., Kabátová, M., Šupicová, M.: *Chem. Pap.*, vol. 58, 2004, p. 236
- [13] Šupicová, M., Oriňáková, R., Kupková, M., Kabátová, M.: *Surf. Coat. Technol.*, vol. 195, 2005, p. 130
- [14] Oriňáková, R., Oriňák, A., Arlinghaus, HF., Hellweg, S., Kupková, M., Kabátová, M.: *Appl. Surf. Sci.*, vol. 252, 2006, p. 7030