The Role of Coating in the Cellular Material Preparation

[a]R. ORIŇÁKOVÁ*, [b]M. KUPKOVÁ, [b]E. DUDROVÁ, [b]M. KABÁTOVÁ, and [a]M. ŠUPICOVÁ

[a]*Institute of Chemistry, P. J. Šafárik University, Faculty of Natural Sciences, SK-041 54 Košice*
e-mail: orinako@kosice.upjs.sk

[b]*Institute of Material Research, Slovak Academy of Sciences, SK-043 53 Košice*

The hollow metal spheres represent the interesting substance, suitable for the cellular material production by the powder metallurgical method. Thick-walled and thus stronger hollow particles are of interest for less extremely light-weight but mechanically stronger components. The basic material properties improving by metal coating deposition is described. The electrolytical and electroless coating of iron hollow spheres with Cu and Ni, in fluidized bed arrangement, is demonstrated here. The influence of the deposition method and the coating conditions on the mechanical properties, surface morphology, and coating composition of the covered spheres were investigated. The effect of current intensity on current efficiency was also studied there.

It was found that the cell structure, surface morphology, composition, and mechanical properties of prepared samples are strongly affected by the coating method.

Porous materials such as metal foams, sponge-like metals or complex sintered products play an important role in many innovative industrial applications. The research interest in these materials still increases. The hollow metal spheres are used for the production of highly porous metallic structures by the powder metallurgical method. The metal coatings can be applied to improve the mechanical properties, the surface morphology, and the wear and corrosion resistance of the basic material.

Cellular solids (an assembly of cells with solid edges and/or faces, packed together so that they fill the space) represent the materials used in a human history for the centuries (animal bones, wood, cork, sponge, coral, *etc.*). More recently man has begun to produce his own cellular materials, which are increasingly used for new light-weight structural components [1]. One of the ways how to produce the cellular solids consists in the sintering of the components made of hollow metallic particles. The properties and mechanical behaviour of the final product strongly depend on the properties of original hollow metallic particles and also on the structure of the cell. Therefore, the preparation of reliable hollow metallic particles of defined parameters represents an important step within the cellular solid production by means of the powder metallurgical route. The modification of the mechanical characteristics of hollow spheres by coating offers an alternative method of changing their properties and structure, requiring relatively inexpensive equipment.

The aim of the present work was to study the copper-nickel coatings on porous hollow iron particles. Three ways of the coating deposition were studied: binary Ni-Cu alloy obtained by electrodeposition; at first Cu layer and then Ni layer originated during the electrodeposition; at first Cu deposition during the cementation and after that the Ni film was obtained by the electrodeposition.

Electroplating of powder materials is made advantageously in fluidized bed. Coating deposited in this way is of a good quality, uniform and adherent. Fluidized bed electrolysis is frequently used in many fields of the modern technology [2, 3]. Mainly two types are discussed in the literature: powder particles get into the fluidized state either by vertical flow of the electrolyte [4] or by horizontal circular stirring of the electrolyte [5]. Dispersed particles come into contact with the solid electrode obtaining the charge. The model describing fluidized bed with circular movement of suspension was developed in [6] and extended in [7]. The papers dealing with the possible ways of the charge transfer in such system were also published [8—10]. The electrolytic plating of the powder particles by the metallic coating is a new way of fluidized bed application and it is used for upgrading the basic material properties in powder metallurgy. Several procedures can be adopted in order to modify the base of metal material in powder metallurgy. Electrochemical deposition of the metal film on the powder is one of the processes giving the best homogeneity of the product.

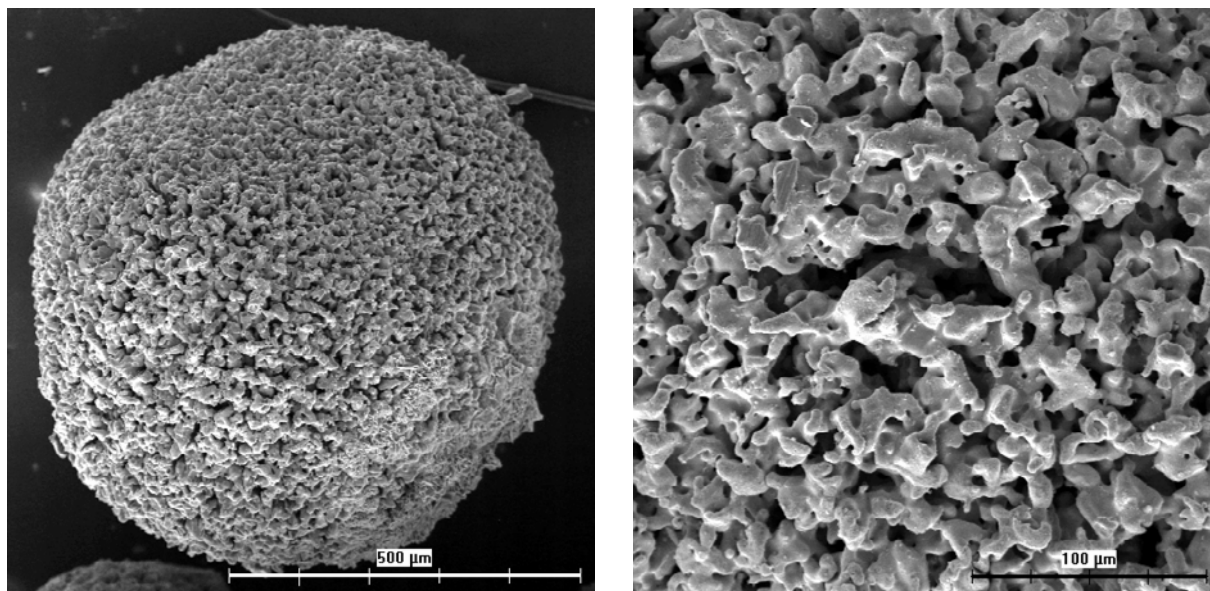*The author to whom the correspondence should be addressed.

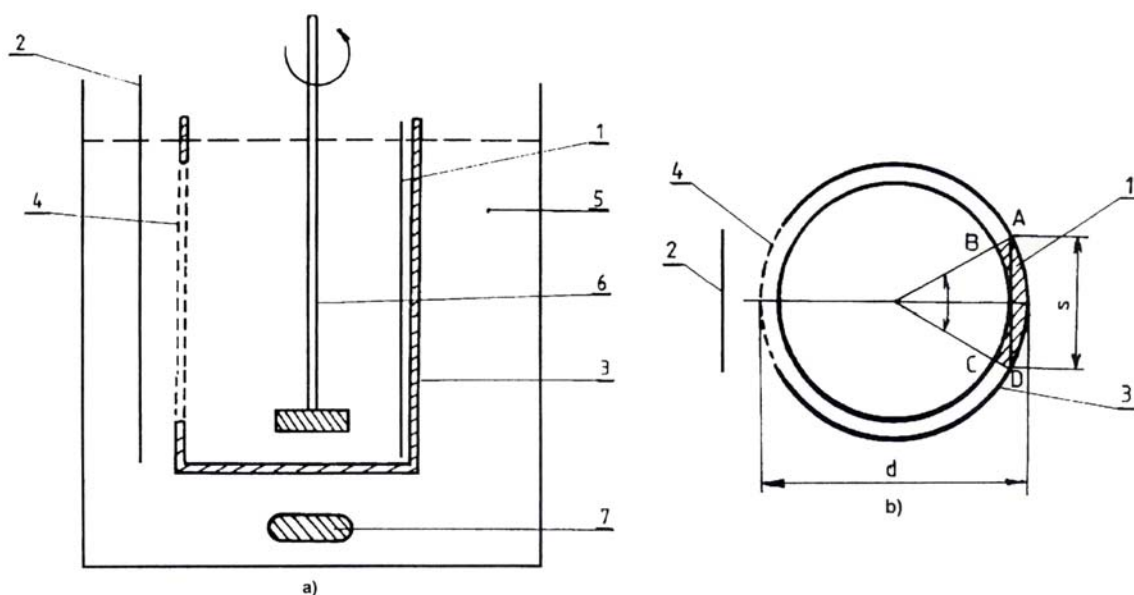**Fig. 1.** Morphology of Fe hollow particles (right); detail, SEM.

Fig. 2. *a*) Schematic representation of the electrolytic cell used. *b*) Base projection of the cathodic compartment. *1.* Cathode, *2.* anode, *3.* cathodic compartment, *4.* diaphragm, *5.* anodic compartment, *6.* glass propeller, *7.* magnetic stirrer, *d* – diameter of the cathodic compartment, *s* – width of the cathode.

Coatings containing Ni have favourable protective and mechanical characteristics. Ni-Cu alloys have a good corrosion resistance.

EXPERIMENTAL

The porous spherical Fe powder produced from iron oxide was obtained in pickling acid recovering in a wire factory by the following fluidized bed line. This oxide was reduced in flowing hydrogen for 6 h at 850 °C to yield similarly spherical iron powder (Fig. 1). After screening the fraction between 0.63—0.71 mm was used there.

The powder material was subjected to the chemical pretreatment before the coating: etching in a reductive solution of 10 % hydrazinium chloride for 5 min.

The electrolytic cell with separated cathodic compartment was used for the electrodeposition (Fig. 2). The cathodic compartment was formed by cylindrical vessel. A window with diaphragm, enabling diffusion of the electrolyte and preventing the particles from contacting the anode, was suitably placed into vessel. Stainless steel cathode and nickel or copper sheet anode were used. The suspension was held in the fluid state by intensive circular stirring during the
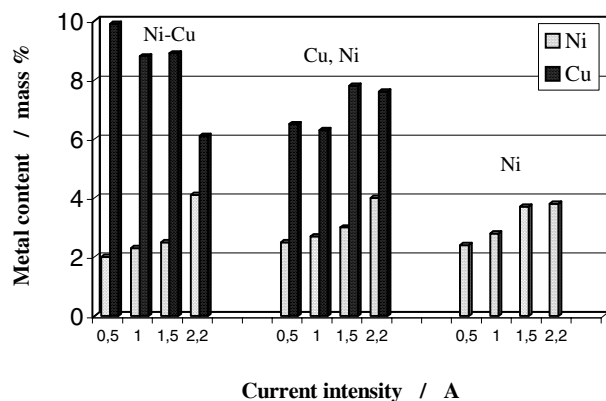
Fig. 3. The influence of current intensity on metal content for different coating deposition ways.

galvanostatic electrolysis. The rate of the stirring was $1800 \ \mathrm{min}^{-1}$.

The electrolyte, containing 1.42 M-NiSO$_4$, 0.33 M-NiCl$_2$, and 0.4 M-H$_3$BO$_3$, was used as a nickel-plating bath. The electrolyte used as nickel-copper-plating bath was 0.7 M-NiSO$_4$, 0.13 M-CuSO$_4$, 0.5 M-citric acid. The composition of the electrolyte used for copper deposition (electrolytic and electroless) was 1 M-CuSO$_4$ and 0.1 M-H$_2$SO$_4$. The electrolytic coating process was run galvanostatically for 30 min. 2.5 g of Fe powder and 200 cm^3 of electrolyte were taken for the electrolysis.

Electroless coating with copper was done by pouring the Fe powder into the solution. The suspension was stirred (1800 min^{-1}) and cooled (30 ± 5 °C).

After dissolution the content of Cu, Ni, and Fe was determined by atomic absorption spectrometry (AAS).

The particle surface was investigated by the scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Experimentally obtained amount of the metal coating on powder particles was used for evaluation of coating process. The metal deposition on the solid cathode is the main side reaction that lowers the amount of electrochemically deposited metal on particles. The electrodeposition of metals on solid cathode was of no interest and therefore the amount of metal coating on the solid cathode was not determined. The other side reactions, such as hydrogen evolution contributed also to the decreasing of current efficiency of the particles electroplating.

The difficulty in defining the exact value of the current density applied is one of the problems of fluidized bed arrangement. The surface area of working electrode is influenced with three factors: roughness of solid electrode surface and its change during the electrolysis due to the metallic coating deposition on it; the statistically followed changing of the electrode sur-

face area as a consequence of the frequent, replicate, short contacts of the hollow spheres with the solid cathode during the electrolysis; and the contribution of surface area of the hollow particles in the vicinity of the electrode to the solid electrode surface. The iron particles are very porous and exact determination of the surface area is very complicated. The current intensity is, therefore, more accurate than current density. The approximate specific surface area of the used hollow particles was determined by the BET method: 1.1263 m^2/g. This method is not very suitable for so large particles and so this value is deformed.

The influence of current intensity on the amount of Ni and Cu in the coat on the powder particles is shown in Fig. 3 for different original procedures. It is worth mentioning that the amount of each metal in Fig. 3 refers to the electrolysis time of 30 min, with the exception of bars denoted as "Ni-Cu". In this case, the sum of the Ni amount and Cu amount refers to the same electrolysis time. The first group of bars denoted as "Ni-Cu" represents the result obtained from the electrodeposition of binary Ni-Cu coating. The increasing of the current intensity favours the Ni deposition and suppresses the Cu deposition in two-component coating. The Cu content is always higher than Ni content. The codeposition of Ni-Cu binary coating was possible by using the complexing agent – citric acid. Complexation of copper ions brought the potentials, both copper and nickel, to that one they are codeposited at.

The surface of Fe particle covered with binary Ni-Cu coating is shown in Fig. 4. These micrographs suggest a uniform distribution and compact morphology of the film. The Fe particle is very rough and porous and so it is a very large surface. The thickness of binary coating is consequently small but coated particles are still sturdy. After deposition the surface is less rough and porous, but does not change significantly. The film thickness and so surface smoothing increases with higher current intensity. The approximate average thickness of the Fe particle wall is about 130 μm and thickness of the Ni-Cu film is about 10—20 μm.

The individual electrodepositions of Cu layer and then Ni layer are represented by the second group of bars in Fig. 3, denoted as "Cu, Ni". The combination of individual electrodepositions results in increasing of both metal contents with current intensity. The quantity of Cu is again higher in the whole current intensity range compared with the quantity of Ni. It is assumed that the electroless deposition occurs in addition to electrolytic deposition of Cu. The cementing process can be preceded at the beginning of the electrolysis, while the deposited layer is not coherent. The contribution of cementation is increasing with the decrease of the current intensity, as one can see from Table 1. The particle cavity dilates nonuniformly because of the replacement of Fe by Cu. The approximate average particle wall thickness is about 100 μm
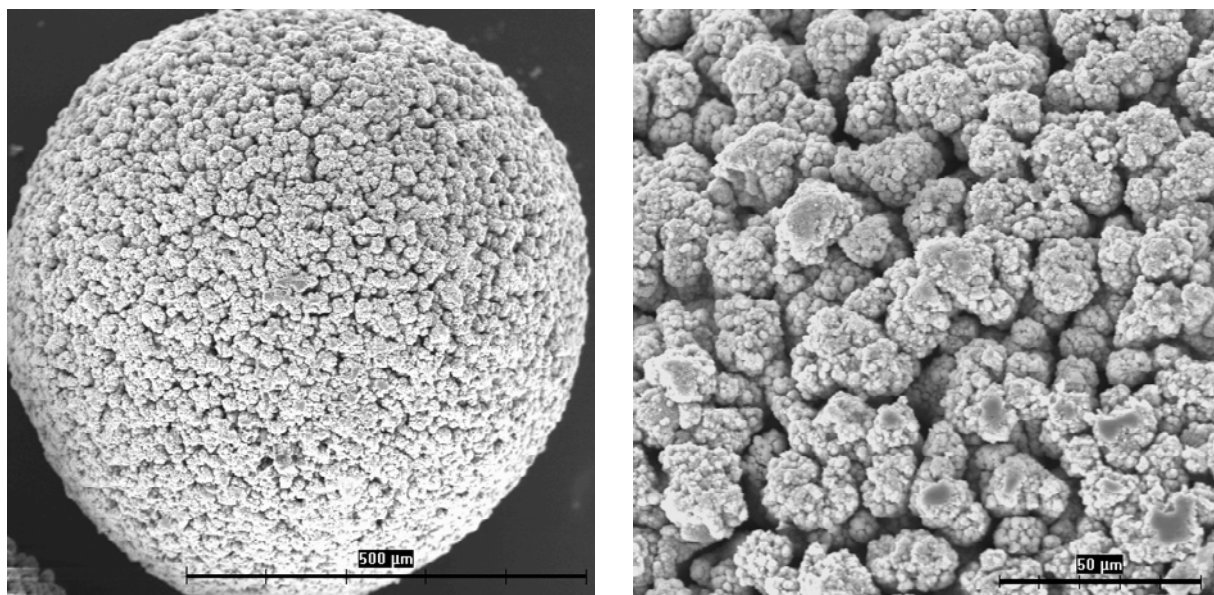
Fig. 4. Morphology of Fe hollow particles covered with binary Ni-Cu coating by electrodeposition; detail, SEM.

Table 1. The Values of Partial Current Efficiency (η) of Electrolysis on Powder Particles for Different Electrodeposition Ways

	$\eta/\%$				
	Ni-Cu binary		Cu, Ni – electrodep.		Cu – electroless, Ni – electrodep.
I / A	Ni	Cu	Ni	Cu	Ni
0.5	14.6	66.9	18.2	43.9	17.5
1.0	8.4	29.7	9.9	21.2	10.2
1.5	6.1	20.0	7.3	17.5	9.0
2.2	6.8	9.4	6.7	11.7	6.3

and varies from place to place and the thickness of the two-layered coat is about 10—20 μm, too. This way coated particles are mechanically strong.

Table 1 summarizes the partial current efficiency values for different current intensities and electrodeposition ways. Generally, the electrolysis efficiency lowers with increasing current intensity. It was found, in earlier studies [11], that the current efficiency of powder particles plating process ranged in optimal conditions between 33 % and 35 %. The low values of current efficiency on powder result mainly from the competitive deposition on solid cathode. The hydrogen evolution is the next process bringing the current efficiency down. High copper electrodeposition efficiency is due to simultaneous currentless copper deposition, which is the most significant for the lowest current intensity. The quantification of the currentless copper deposition contribution is investigated at the present time.

Fig. 5 is SEM photograph of the sample made of Cu electrodeposition and next Ni electrodeposition. The surface morphology is changing essentially, it is more compact and smooth. The consolidation is higher with the increasing current intensity. The surface area is much smaller. The deposited metal layer is thicker due to the double electrolysis time. A compact, uniform layer is distributed homogeneously on the surface of the particles. The surface structure becomes smoother and less rough in comparison with pure Fe and other investigated coatings.

The thin-walled hollow particles with large cavity are interesting from a cellular material production viewpoint. On account of that the currentless copper deposition on iron hollow particles was investigated. During the electrolysis deposition, it was found that the iron particle was dissolved from within and the copper layer was deposited from outside. Thus the cavity inside the particle was enlarged and the wall of particle has become thinner.

The results of Ni film electrodeposition on powder particles following currentless copper deposition are shown in the last group of bars in Fig. 3, denoted "Ni". Generally the deposition of Ni – less noble metal is favoured with increasing of current intensity. After cementation the composition of particles was usually
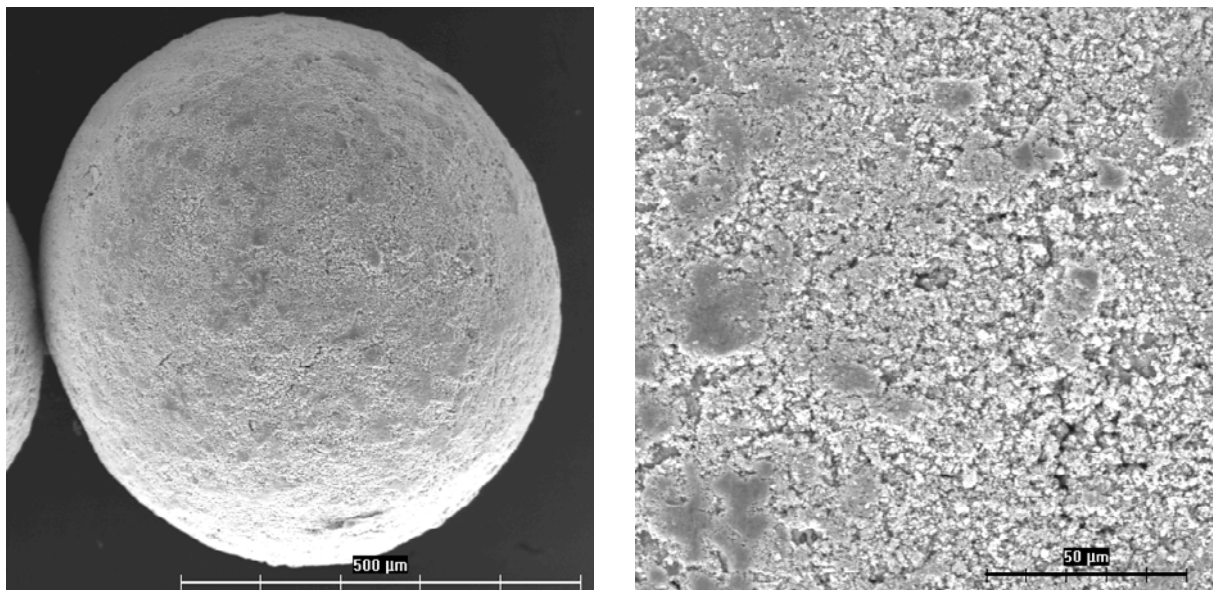
Fig. 5. Morphology of Fe hollow particles covered with Cu by electrodeposition and next with Ni by electrodeposition; detail, SEM.
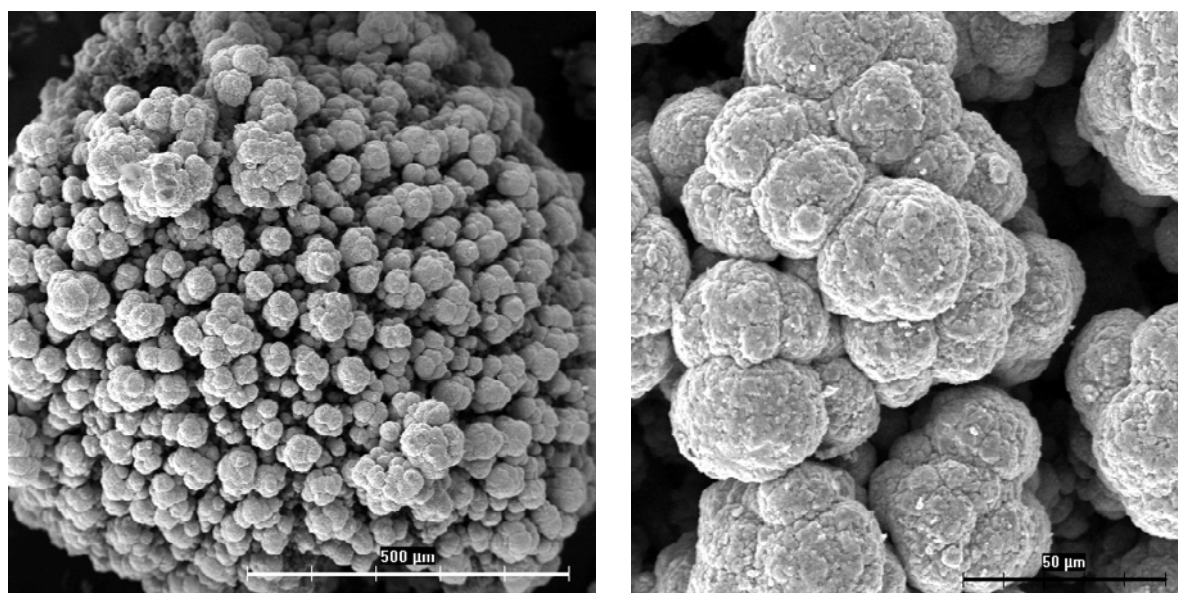

Fig. 6. Morphology of Fe hollow particles covered with Cu by cementation and next with Ni by electrodeposition; detail, SEM.

about 95 % of Cu and 5 % of Fe. It was found that considerable amount of copper could be deposited on the Fe particles during cementation. Even the complete replacement of Fe by Cu was possible. The powder amount to electrolyte volume ratio must be chosen according to the amount of Cu in the solution sufficiently with regard to the amount of Fe dissolved. The deposited copper layer is porous and enables the diffusion of the Fe ions from the Cu-Fe interface into the solution (Fig. 6). The iron particle is almost fully dissolved during the cementation and so the final product is composed mainly from copper. It was found that if the complete replacement of Fe by Cu took

place, the arising Cu particles were very crisp and were disintegrating. The same happened, if the cementing progressed very quickly. The optimal conditions were 180—200 min, 30 °C, 30 g of Fe, and 600 cm³ of electrolyte. In this case the usual content of Cu was 95 %, the spheres were hollow, with large cavities and thin walls, and the coat was compact. The particles were still fairly weak and difficult to handle. It was found that the consequent Ni plating results in the significant strengthening and consolidation of powder particles. Fig. 6 shows the surface of Fe particle covered with Cu by electroless deposition and next with electrodeposited Ni layer. The surface is very rough

and porous in contrast with the other coating deposition ways. The structure of roughness is rather different. Due to the fast deposition of copper this has thick deposit, even under stirring conditions, dendritic morphology. The coating layer forms the new particle wall with average thickness about 50 μm.

CONCLUSION

Cellular materials offer the attractive potential for the production of light-weight components by the powder metallurgy route. The hollow iron spheres are suitable substance for the preparation of the regularly structured cellular material. The properties of the original hollow particles can be modified by metallic nickel + copper coatings utilization.

From the comparison of electrolytic deposition it follows that the most amount of metal film was obtained for binary Ni-Cu coating. The cavity inside the Fe particle and the walls of Fe particle were the same size. The coating layer was thin and following the surface roughness. The increasing of the current intensity supports the Ni deposition and suppresses the Cu deposition in two-component coating.

In spite of double electrolysis time the amount of metallic film for two-layered electrolytic Cu + Ni coating was lower. However, the superficial morphology of prepared sample was less rough and smoother than for other coating methods used. Both the metal contents are increasing with current intensity increasing for individual electrodepositions of Cu layer and then Ni. The currentless copper deposition is preceded by that at low current intensity in the beginning of the electrolysis. Owing to the nonuniform dissolving of the particle wall the coherent copper layer is formed during the electrodeposition. The cavity inside the Fe particle is enlarged only while and where the ions can be diffused.

The Cu content in coating deposit is always higher than Ni content. This is assumed to be the consequence of the electroless deposition in addition to electrolytic deposition of Cu.

The main advantage and the difference of currentless copper deposition is the replacement of Fe by Cu and in consequence of it the regular enlargement of cavity inside the particle and constriction of the particle wall. This experience found is important for the light-weight porous cellular material production.

REFERENCES

1. Danninger, H., Strobl, S., and Gurtenhofer, R., in *Proc. Powder Metall. World Congress 1998, Granada,* Vol. *1,* p. 185.
2. Lux, L., Oriňáková, R., and Gálová, M., *Acta Metall. Slovaca 3*, 603 (1997).
3. Doherty, T., Sunderland, J. G., Roberts, E. P., and Pickett, D. J., *Electrochim. Acta 41*, 519 (1996).
4. Fleischmann, M. and Oldfield, J. W., *J. Electroanal. Chem. 29*, 211 (1971).
5. Held, J. and Gerisher, H., *Ber. Bunsen – Ges. Phys. Chem. 67*, 921 (1963).
6. Lux, L., Stašková, R., and Gálová, M., *Acta Chim. – Models in Chemistry 133,* 115 (1996).
7. Gálová, M., Lux, L., and Oriňáková, R., *J. Solid State Electrochem. 2*, 2 (1998).
8. Sabacky, B. J. and Evans, J. W., *Metall. Trans. 8B*, 5 (1977).
9. Yen, S. Ch. and Yao, Ch. Y., *J. Electrochem. Soc. 138,* 2344 (1991).
10. Gabrielli, C., Huet, F., Sarah, A., and Valentin, G. J., *J. Appl. Electrochem. 22*, 801 (1992).
11. Gálová, M., Lux, L., Dudrová, E., and Stašková, R., *Trans. Tech. Univ. Košice 3—4,* 185 (1994).