13th International Research/Expert Conference
”Trends in the Development of Machinery and Associated Technology”
TMT 2009, Hammamet, Tunisia, 16-21 October 2009

MECHANISM OF ELECTROCHEMICAL FORMATION OF PURE METAL AND ALLOY POWDER

Branka A. Jordović, Olivera Pešić,
Aleksa Maričić
Technical Faculty Čačak
Svetog save 65, Čačak
Serbia

Jasna T. Stajić Trošić
ICTM, Institute of Chemistry Beograd
12 Njegoševa, 11000 Beograd
Serbia

Jasmina Stevanović
ICTM, Institute of Electrochemistry Beograd
12 Njegoševa, 11000 Beograd
Serbia

ABSTRACT

Pure metal and alloy powders are obtained from utilization of alkaline, ammonia electrolyte containing one, two or three different elements Co, Ni, Mo, through electrochemical deposition at constant density current. The reaction of powder formation is simultanuous with reaction of hydrogen separation. Obtained powders Ni and Co mutually deposit anomalously, and both metals induce precipitation of Mo that cannot be depostited by itself from water electrolytes. The effect of deposition current density on morphology and chemical composition of the extracted powders has been investigated.

Key words: powder Co-Ni-Mo alloys, electrochemical deposition

1. INTRODUCTION

Iron alloys obtained from electrochemical deposition in the form of powders or coating, belong both to essential magnetic materials [1,2], as well as to good catalysts for the reaction of hydrogen separation [3,4].

2. RESEARCH

Powder samples are deposited from electrolytes composition: $CoSO_4$, $NiSO_4$, $(NH_4)_6Mo_7O_{24}$, NH_4Cl and NH_4OH. The ratio of salt concentration of Co and Ni has varied and has amounted to 0,1M Ni and 0,1 M Co (1:1) and 0,16 M Ni and 0,04 M Co (4:1), as well as the salt concentration of Mo from 0,005 mol/dm^3 to 0,06 mol/ dm^3. Concentration of NH_4Cl has amounted to 74.13 g/ dm^3 with the addition of NH_4OH with which pH of the solution was maintained on level 10,6.

The effect of the alteration of salt concentration of Co, Ni and Mo in the electrolyte for deposition into electrochemical parametres of deposition has been investigated, as well as the effect of change of deposition current density from 200 mA/cm^2 to 1200 mA/cm^2 on the structure and mass composition of the obtained alloy powders.

The volume of the electrochemical cell into which alloy powders were deposited is 5.5 dm^3 with the addition of a separate part with Luggin cappilary in which saturated calomel electrode was used as a reference electrode. The anode was made of lead, Pb/PbO_2 within the area of 100 cm^2 and the catode was made of titanium, a plate of 32 sqare meters and 0,5 cm in diameter. The cell was thermostatic and working temperature of 25 ºC was maintained. The solution was made of p.a. chemicals and twice distilled water. During the research standard electric circuit was used.

The morphology and the particle size of electrodeposited powders was observed using scanning electron microscope (SEM) JEOL JSM-6460 LV.

Testing of thermal behaviour of the obtained alloys has been carried out by DSC-TGA analysis on SDT Q 600 device, TA Instruments.

2. RESULTS AND DISCUSSION

Electrochemical deposition of pure metals consists of Ions transport(ation) from electrolytes, adsorption of Ions, multiple electrical charge transfer, nucleation and other phenomena of sediment increase [5-14]. These processes may be limited by the concentration of the absorbed types on the surface of the electrode (hydrogen, anion, additive molecules). Concurrently with nickel and cobalt deposition, electrical discharge of metal ions and protones takes place, therefore the coefficient of electricity use of deposition depends on composition of electrolytes and deposition current density. According to the supposed mechanisms of iron metals deposition, reduction represents a two-stage electrochemical reaction and it can be explain with the following equations:

$$M^{2+} + e^- \rightarrow M^+_{ads} \tag{1.1}$$

$$M^+_{ads} + e^- \rightarrow M \tag{1.2}$$

Adsorbed intermediar ion, Ni^+_{ads}, is more or less hydrated comlex and can be presented as neutral MOH_{ads}.

Increase of the amount of the surface covered by the adsorbed metal complex, at low polarization has an effect on the increase of spreading rate of the adsorbed intermediar M^+_{ads}. At low polarizations, metal deposition takes place according to the equations (1.1) i (1.2), and the obtained coatings are relatively compact. At higher polarizations, after the first stage the disproportion reaction shown in the equation below can follow:

$$M^+_{ads} + M^+_{ads} \rightarrow M + M^{2+}_{ads} \tag{1.3}$$

Obtained coatings are substantially porous (dispersive) and they have finer grain than the coatings obtained at lower polarizations. Concurrently with reactions of metal reduction, hydrogen separation takes place, as shown in the following equation:

$$2\,H^+ + 2e^- \rightarrow H_2 \tag{1.4}$$

On the surface of the coating a firmly bound adsorbed kind of M^*_{ads}, that appears due to the M^+_{ads} concentration, is formed according to the equation:

$$M^+_{ads} + H^+ + e^- \rightarrow M^+_{ads} + H^*_{ads} \tag{1.5}$$

and/or due to the reaction between M^+_{ads} and moleculs of water

$$M^+_{ads} + H_2O \rightarrow MOH^+ + H^*_{ads} \tag{1.6}$$

The adsorbed hydrogen atoms take part in reaction of recombination (inclusion) according to the equations:

$$2\,H^*_{ads} \rightarrow H_2 \tag{1.7}$$

$$M^+_{ads} + H^*_{ads} + e^- \rightarrow M + H_{inkl} \tag{1.8}$$

Processes occuring concurrently with the process of metal deposition have an effect on the structure of the obtained nickel and cobalt deposit (according to the equations (1.1), (1.2) (1.3)), such as hydrogen separation, adsorption and inclusion into metal lattice (according to the equations (1.4 – 1.8)). Hydrogen adsorbtion blocks nucleus growth, resulting formation of delicately granulated coatings. At low polarizations and long time depositions a compact metal structure with a small hydrogen concentration is obtained, however at higher polarizations and short time peoriods of deposition a porous compact with much higher hydrogen concentration is obtained.

Metal that has low hydrogen concentration dissolves at more positive potentials than that of high hydrogen concentration, which shows that the latter exhibits higher corrosion stability since more compact coating is obtained.

Hydrogen separation taking place during the process of electrochemical deposition of metals and alloys has an effect on both the substrate and the characteristics of metal coating. The effects of hydrogen separation taking place during the process of electrochemical deposition of metals are as follows:

a) hydrogen adsorption on the substrate and its concentration around vacancies which leads to hydrogen brittleness;
b) occlusion of adsorpted hydrogen atoms and bubbles on the surface along with the formation of coating around the adsorption place result in hydrogen atom inclusion that is to say embracement and occlusion of hydrogen bubbles within the coating;
c) the effect of electrolyte mixing caused by hydrogen bubbles

Increase in hydrogen separation rate results in adsorption increase and higher inclusion of hydrogen in metal substrate. Hydrogen adsorption depends on kind of metal being deposited, as well as on electrolysis conditions. Increase in deposition current density, decrease in operating temperature and decrease in pH of a solution leads to the increase in hydrogen adsorption. A number of characteristics of metal have a major effect on adsorption and inclusion of hydrogen in metal substrate:

a) mechanism of electrical discharge that includes the formation of M-H coupling
b) capability of hybrid formation
c) hydrogen bubbles embracement on the borders of pores and vacancies as the aftereffect of physical adsorption
d) metal tension too high for hydrogen adsorption

The occurrence of hydrogen in metal has an effect on electrical, magnetic and corrosive characteristics as well as on plasticity and hardness. Inclusion of hydrogen in metal leads to plasticity decrease and metal hardness and brittleness increase. The concentration of hydrogen in nickel coating is usually between 0,01 and 0,02 mass percent and it results in the increase in microhardness of the coating.

Nickel belongs to the group of metals which have partially filled d-orbitals on which hydrogen is well chemisorbed and hybrids can be formed as well. Non-stoichiometric nickel-hybrid (NiHn, $0,1< n < 0,9$), the result of cathode reduction, has surface centered cubic lattice whose lattice parameter is approximately 6% higher than pure nickel. It is unstable at room temperature. Hydrogen concentration is much lower after thermal treatment at 400°C. Inclusion of hydrogen in electrochemically deposited nickel and cobalt coating depends on the adsorption level. It influences microstructure and is responsible for the formation of dislocations which leads to coating tension increase. When recently deposited nickel coating is concerned, hydrogen bubbles are not formed easily and they occlude on the surface without any indication of bubble embracement or adsorption, although pores are formed in the coating.

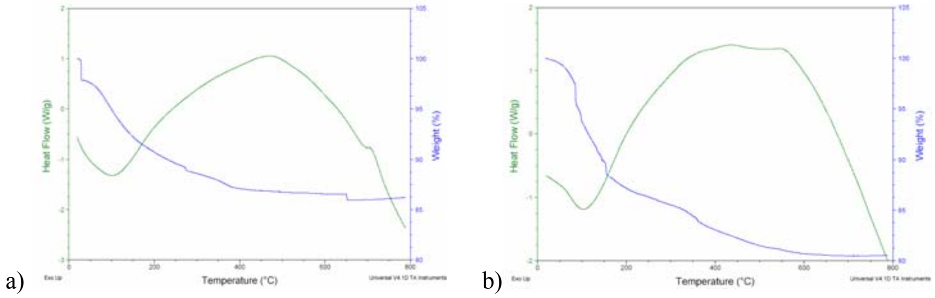

Figure 1. DSC-TGA anlysis of Co-Ni-Mo-O powder samples a) obtained at deposition current density of 800 mA/cm^2 and 0,03 mol/l Mo in deposition electrolyte, b) at deposition current density of 400 mA/cm^2 and 0,06 mol/l Mo in deposition electrolyte.

Results of TGA formed powders analysis show that total mass loss is up to 20%. At heating up to 100 °C mass loss may be ascribed to water evaporation, however the loss is less than 2%. After that, the mass loss (fig.1 a) and b)) occurs probably due to release of inclusive hydrogen from metal powder.

Figure 2. shows the results of SEM analyses of electrochemically formed pure Co and Ni powders, whereas figure 3 shows SEM images of electrochemically formed binary Co-Ni alloy as well as of ternary Co-Ni-Mo alloy.

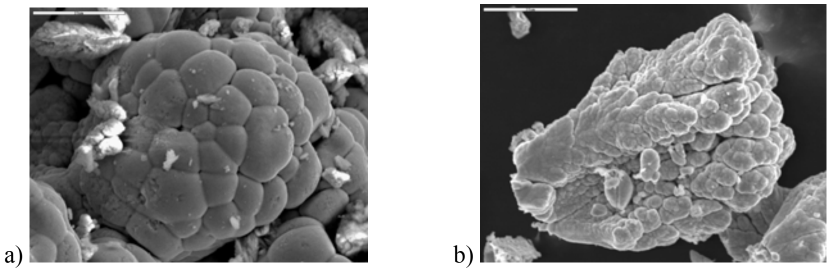

Figure 2. SEM images taken at deposition current density of 400 mA/cm^2 a) pure Co b) pure Ni

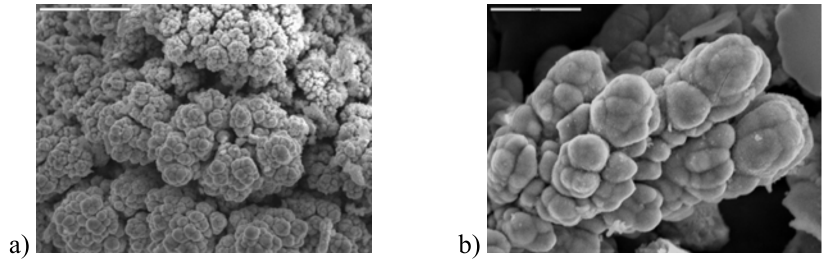

Figure 3. SEM images taken at deposition current density of 400 mA/cm^2 a) Co-Ni alloy b)Co-Ni-Mo alloy

3. CONCLUSION

Appropriate choice of deposition electrolytes, as well as electrolysis conditions enable the formation of powders of defined chemical composition and desired electrical, magnetic and other characteristics. This paper explains the mechanism of electrochemical deposition of binary and ternary Co, Ni, Mo based alloys, as well as the hydrogen inclusion during the process of deposition. Hydrogen inclusion in electrochemically formed powders is rather hard to prove using the existing conventional methods.

4. REFERENCES:

[1] P.J. Grundy, J.Phys. D 31 (1988) 2957-2990
[2] D.E. Laughlin, B.Lu, Y.N. Hsu, J. Zou, D.N. Lambeth, IEEE Trans. Magn.36 (2000) 48-53.
[3] M.M. Jaksic, Electrochim. Acta 29 (1984) 1539
[4] M.M. Jaksic, Int. J. Hydrogen Energy, 11(1986) 519-532
[5] A. R. Despić, Comprehensive Tretease on Electrochemistry, Vol. 7, ur. J. O´M. Bockris, B. E. Conway,E. Yeager, Plenum Press, New York (1983).
[6] A. Brenner, Electrodeposition of Alloys; Principles and Practise, Academic press, New York (1963).
[7] A. Slawska-Waniewska, P.Didukh, H.K.Lachowicz, T.Kulik, J.Magn.Magn.Mater. 215 (2000) 495-498
[8] J. O´M. Bockris, D. Dražić, A. Despić, Electrochim. Acta, 4 (1961) 325.
[9] E. Chassaing, K. Vu Quang, R. Wiart, J. App. Electrochem., 17 (1987) 1267.
[10] E. Chassaing, K. Vu Quang, R. Wiart, J. App. Electrochem., 19 (1989) 839.
[11] E. Gomez, C. Müller, W. G. Proud, E. Valles, J. Appl. Electrochem., 22 (1992) 872.
[12] S. Nakahara, E. C. Felder, J. Electrochem. Soc., 129 (1982) 45.
[13] N. A. Galaktinova, Vodorod v metallah, Metallurgiya, Moskva, 1967, 250.
[14] S. Nakahara, E. C. Felder, J. Electrochem. Soc., 129 (1982) 45.