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POWDERS OF BINARY AND TERNARY OF Co, Ni AND Mo ALLOYS OBTAINED BY ELECTROLYTIC DEPOSITION

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ABSTRACT

The Co-Ni and Co-Ni-Mo alloy powders were electrochemically deposited from alkaline ammonical electrolyte at a constant current density. Between them, Ni and Co are anomalously deposited, and both metals induce Mo deposition, which on its own cannot be deposited from aqueous solutions. Based on the obtained experimental results it can be concluded that by appropriate selection of chemical composition of the electrolyte for deposition, varying of Co, Ni and Mo ions ratios and current density it can be influenced on the particle sizes of deposited powders.

Keywords: powder Co-Ni, powder Co-Ni-Mo-O alloy, anomalous deposition, induced deposition.

1. INTRODUCTION

Powders of binary and multicomponent alloys and metal deposits are divided according to the type of deposition that they undergo, in a system defined by Brenner [1]. Deposition of alloy powders during which the deposition of more electronegative metal is favored is called anomalous deposition. Iron-group metals Fe, Co or Ni are deposited anomalously with Zn or between each other, regardless if it is from solutions of simple or complex salts. On the other side certain elements like Mo, W, Ti, can not be electrochemicaly reduced to metal from the aqueous solutions [2]. Reduction of these metals is induced by iron-group metals. There are a number of different hypothesis regarding the mechanism of the induced deposition. [3-12].

2. EXPERIMENTAL

The powders were electrodeposited from the electrolyte containing: $CoSO_4$, $NiSO_4$, $(NH_4)_6Mo_7O_{24}$, NH_4Cl and NH_4OH. Different Ni^{2+}/Co^{2+} concentration ratios were used Ni^{2+}/Co^{2+} (1:1) [0.1M Ni / 0.1 M Co] and (4:1) [0.16 M Ni / 0.04 M Co]. The molybdate concentration of was also varied from 0.005 to 0.06 mol/dm^3 and the NH_4Cl concentration was 74.13 g/dm^3. The NH_4OH was added to keep the pH of the applied solutions constant at 10.6.

As a referent electrode, the saturated Calomel electrode (SCE) was used, the anode was Pb/PbO_2 electrode with the surface area of 100 cm^2 and the cathode was 0.5 cm thick titanium plate with the surface area of 32 cm^2. The Co-Ni-Mo-O alloy powders were electrochemicaly deposited at a constant current density. After deposition, obtained powders were firstly rinsed few times with distilled water and then rinsed with 0.1% benzoic acid solution and left to dry at 110°C.

3. RESULTS AND DISCUSSION

During the co-deposition of Co and Ni from alkaline ammoniacal electrolyte anomalous Ni deposition occurs. It is well known that the equilibrium potential of Ni is for 20 mV more positive than that of Co. Polarization curves of electrochemical deposition of single metals show that pure Ni metal deposition takes place at more negative potential (for about 100 mV) than in case of Co deposition (Fig. 1, curve 1 and curve 2).

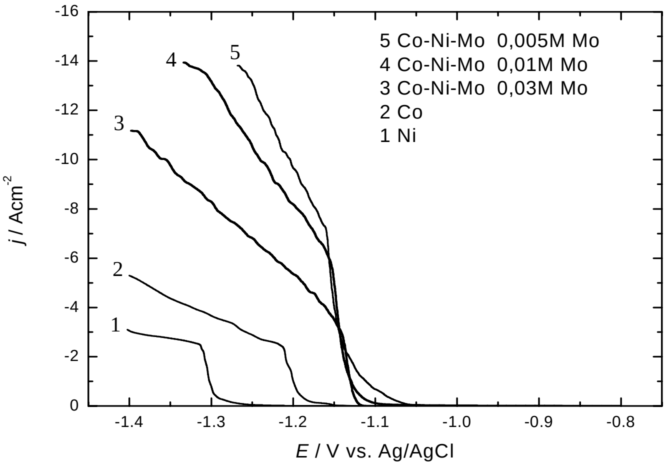

Figure 1. Polarization curves for the electrodeposition of:
1) pure Ni; 2) pure Co; 3) Co-Ni-Mo-O powder from 0.03 M Mo solution;
4) Co-Ni-Mo-O powder from 0.01 M Mo solution;
5) Co-Ni-Mo-O powder from 0.005 M Mo solution.

In the puffered ammonical electrolyte at the pH 10.6 the influence of all other ligands is negligible so that Co and Ni are only present as a complex ions of octahedral type: $[Co (NH_3)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ with the values of stability constant $10^{4.39}$ and $10^{8.01}$ respectively. The presented values of stability constants indicate that Co will be more easily deposited, since it is more weakly bonded in the complex than Ni. Anomalous deposition of Ni is the consequence of the significantly higher affinity of Ni ions to create complexes, so that its deposition potential becomes considerably more negative compared to essentially less noble metal Co. The polarization curve of Co-Ni alloy powder deposition lies between the polarization curves for the pure electrodeposition of Co and Ni powders, and its position depends upon the Ni^{2+}/Co^{2+} concentrations ratio in the basic electrolyte. Practically, for the Ni content to be higher than that of Co in the deposit, it is necessary that the Ni^{2+} concentration in the electrolyte for deposition is significantly higher than Co^{2+} concentration, even few times [13].

Although, Ni and Co powders as well as Ni-Co alloy powders by themselves are not the subject of this research, the conditions of their deposition were studied in order to clarify the mechanism of Co-Ni-Mo-O alloy powders deposition and to determine which of the iron-group metals (Co or Ni) preferentially influences the Mo deposition from ammonical electrolyte.

Mo was introduced into the electrolyte for deposition in a form of $[MoO_4]^{2-}$. Despite its affinity to form polymer ions, clusters of $[Mo_7O_{24}]^6$ that can be detected in a solution by diffuse reflection spectroscopy at pH levels higher than 9, Mo was preferentially present in the solution used for deposition (pH 10.6) in a form of molybdates.

It is only after the acid or essentially H^+ ions are added i.e. at pH level lower than 5 that Mo polymer ions are formed [14]. Deposition of powders from ammonical electrolyte strongly supports the hypothesis of adsorption and catalytic reduction of molybdate species [9-12]; having in mind that some corrections in the terminology should be made. Iron-group metals induce the Mo deposition and on the other side Mo acts as a catalyst for the deposition of iron-group metals. Mo moves the deposition potential of Ni for about 200 mV (Fig.1, curve 1) and of Co for more than 100 mV in the positive direction (Fig. 1, curve 2.). Electrodeposition of pure Ni from the ammoniacal electrolyte starts at the potentials more negative than -1.3 V, deposition of pure Co starts at potentials more negative than -1.2 V, while Co-Ni-Mo-O alloy starts to deposit at slightly more positive potential than those of pure metals i.e. about -1.1V.

Recorded polarization curves 3, 4 and 5 in Fig. 1 show that an increase of the Mo concentration in the electrolyte for deposition, with all other system parameters kept constant, shifts deposition potential of Co-Ni-Mo-O alloy to more negative values and lowers the plato of the limiting deposition current density. This means that the deposition of the powder from the electrolyte with the lowest Mo concentration begins at the most positive potentials. From the electrolyte containing 0.0005 M Mo concentration, alloy powder deposition starts at the potential of -1.07 V (Fig.1, curve 5) whereas deposition of the alloy from the electrolyte containing 0.03 M Mo starts at the potential for about 100 mV more negative than that (-1.123 V) (fig.1, curve 3). The increase of the Mo concentration in the plating bath was found to lower the plato of the limiting deposition current density, which is 7.183 A/cm^2 for 0.005 M Mo in the bath and 2.911 A/cm^2 for 0.03 M Mo concentration in the bath.

The mechanism of deposition suggested by the group of authors [9-12] is confirmed in this research work but only for the alkaline electrolytes, where Mo is present in a form of molybdates and not for acidic electrolytes, where Mo is present in a form of polymer ions. According to suggested mechanism Ni and Co should deposit in a two stage consecutive reaction of reduction and Mo should deposit in a form of pure metal, oxide or even compound with Ni and Co. Adsorbed reaction intermediates should be $\left[\mathrm{Co}^{2+}(\mathrm{aq})\mathrm{MoO}_2\right]_{ads}$ $\left[\mathrm{Ni}^{2+}(\mathrm{aq})\mathrm{MoO}_2\right]_{\mathrm{ads}}$. Due to greater stability of the ammoniacal complex it should be also expected that the Ni content in the deposit is lower, which obtained experimental results confirm.

4. CONCLUSION

In the ammonical alkaline electrolyte at pH 10.6 molybdenum is only present in a form of molybdate ions. Anomalous deposition of Ni is the consequence of the significantly higher affinity of Ni ions to create complexes, so that its deposition potential becomes for as much as 120 mV more negative, compared to essentially less noble metal Co.

In the Co-Ni-Mo-O alloy powder, Mo can be present as a pure Mo, in the form of oxides MoO, $\mathrm{Mo_2O_3}$, $\mathrm{MoO_2}$, $\mathrm{MoO_3}$ or $\mathrm{Mo_2O_5}$, as well as in a form of compounds with Co and Ni.

It can be assumed that adsorbed layer on cathode consists of $\left[\mathrm{Co}(\mathrm{NH}_3)_6\mathrm{Mo_xO_y}\right]^{2+}_{ads}$ and $\left[\mathrm{Ni}(\mathrm{NH}_3)_6\mathrm{Mo_xO_y}\right]^{2+}_{ads}$, where x ≥ 1 and y ≥ 0. However, it is obvious that $\left[\mathrm{Co}(\mathrm{NH}_3)_6\mathrm{Mo_xO_y}\right]^{2+}_{ads}$ is preferentially formed. This complex cation (behaves in such manner that it) prevents the Ni transport from solution to the surface of the electrode and at the same time enables unaffected Co and Mo deposition.

Due to the fact that the stability constant of Ni ammonia complex is about four orders of magnitude higher than the stability constant of Co ammonia complex, in the presence of Co, Ni is probably unable to form complex cation with Mo, which would make its deposition in the form of pure metal, oxide or some compound with Mo, much easier.

5. ACKNOWLEDGEMENT

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