EFFECT OF THE ELECTRODE POSITION CONDITIONS
ON THE MORPHOLOGY AND CORROSION BEHAVIOR OF Ni-Co ALLOYS
PART 2: PHASE COMPOSITION AND CORROSION BEHAVIOR
OF Ni-Co ALLOYS, ELECTRODEPOSITED FROM CITRATE ELECTROLYTE

Katya Ignatova¹, Georgi Avdeev²

¹ University of Chemical Technology and Metallurgy
Department of Inorganic and Electrochemical Technologies
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: katya59ignatova@gmail.com

² Bulgarian Academy of Sciences
Institute of Physical Chemistry “Rostislav Kashev”
“Acad. G. Bonchev”, bl. 11
1113 Sofia, Bulgaria

ABSTRACT

The changes in the phase composition (through X-Ray analysis) and the corrosion behaviors (through potentiodynamic polarization studies in 4 % NaCl) of Ni-Co alloys, electrodeposited from a citrate electrolyte by changing the Ni/Co ratio, content of organic additive (saccharine) and the content of sodium citrate in the solution, are studied. It is found that the increase of Ni/Co ratio from 1 to 5 increases the content of Ni in the Ni-Co alloy to 48 mass %. The proportion between the phases of Co and Ni with cubic face-centered crystal lattice is in approximate compliance with the proportion of the two metals in the alloy. The peaks in the difractograms are weak and stretched, which corresponds to the nano-sized structure of the alloy. Ni-Co alloys with highest content of Ni have a higher corrosion resistance compared to those containing a higher percentage of Co. It is also shown that the Ni-Co coatings obtained in the presence of addition of saccharine show a much higher corrosion resistance than the coatings obtained in absence of additive. Ni-Co alloys, deposited from electrolyte with more sodium citrate show only a slight growth of Ni content and the effect of sodium citrate on corrosion behaviors of the alloy is insignificant.

Keywords: phase composition, corrosion behavior, Ni-Co alloys, nanostructured alloys.

INTRODUCTION

For decades the Ni-containing alloys have been successfully applied because of their high both corrosion resistance and mechanical strength in a number of industrial areas, such as nuclear power systems, chemical and oil industry, automotive industry [1]. Recently, the interest in Ni-Co alloys has grown due to their specific magnetic and catalytic properties that are dramatically enhanced upon reaching the nanometric structure [1 - 4]. Apart from their application in magnetic data storage devices, the nano-structured coatings of Co, Ni and Ni-Co alloys display excellent catalytic and hydrophobic properties [5], which expand their scope of application.

The micro-structure and the properties of the electrodeposited Ni-Co alloys strongly depend on the ratio Ni/Co in the alloy that may be controlled through the parameters of electrodeposition, such as composition and pH of the electrolyte, temperature and current density [6, 7]. There are a lot of data available in the reference sources about the effect of a number of organic addition agents on the micro-structure and the corrosion resist-
Hence of Ni-Co alloys [8 - 10]. There is also a relationship between the phase content of the alloys and their corrosion resistance [13, 14]. According to the phase diagram of Ni-Co alloy [11], there is an independent α-phase for pure Ni, a solid solution for the alloy with the increase of Co content up to 65 mass %, two phases (α+ε) in the area from 65 mass % Co to 75 mass % Co, and independent ε-phase at Co content up to 100 mass %. In a number of cases of electrodeposited Ni-Co alloys the occurring phases correspond to the phase diagram of the system. There is a correspondence in the conclusions of the most publications on the point that at Co content up to about 50 - 60 mass % in the electrodeposited Ni-Co alloys the structure transforms from α-phase with cubic face-centered lattice (fcc) to ε-phase with hexagonal lattice (hcp), while the compactness and the hardness of the coatings reach their maximum, the coefficient of friction decreases [12], and the corrosion resistance is improved [13 - 15]. It is also found that in alloy with the above content the coercive force reaches its maximum [14], which is explained with the following factors [14]: (1) defined proportion of the two crystalline modifications; (2) size of crystallites below the critical value; (3) corresponding texture of the two phases; (4) influence of internal stresses on the magnetization vector in fcc crystallites.

The aim of this study is to evaluate the effects of the ratio Ni/Co in the citrate electrolyte, the addition of saccharine and the increase of sodium citrate in the electrolyte on the phase composition and anodic behavior of the electrodeposited Ni-Co alloys.

**EXPERIMENTAL**

The subject of investigation are 9 groups of Ni-Co alloy coatings, depending on the content of the electrolyte [16]. The ratio Ni/Co in the solution was changed (from 1 to 5), the content of Na₃citrate varied from 0.2 to 0.6 g dm⁻³ and the addition of saccharine (SHR) varied from 0 to 2 g dm⁻³. All electrochemical experiments were carried out in a thermostatic three-electrode cell without stirring includes a platinum counter electrode arranged concentrically around the working electrode, and saturated calomel reference electrode in a special pan with Lugin’s capillary (Eₛₑₑ = 0.241 V) and working electrode. Corrosion behavior of Ni-Co alloy coatings, deposited at different conditions on Cu plates (99,97 %, MERC) was studied. The thickness of coating was maintained at 8±2 µm.

The anodic potentiodynamic polarization dependencies were obtained using Wenking Electrochemical Analysis System (Germany). The scanning rate of 10 mV s⁻¹ was applied. The test sample was loaded in a Teflon holder and the surface area exposed to a model corrosive medium (4,0 % NaCl) was 1,023 cm⁻². The measurements were performed at room temperature, non-stirred and free air conditions.

The phase composition of the Ni-Co alloy coatings

<table>
<thead>
<tr>
<th>Electrolytes No</th>
<th>Ni/Co</th>
<th>Co, mass %</th>
<th>Ni, mass %</th>
<th>CCE, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pure Co, 0,3 M Co</td>
<td>100</td>
<td>0</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>pure Ni, 0,3 M Ni</td>
<td>0</td>
<td>100</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>3,0 (0,3 M Co)</td>
<td>83</td>
<td>17</td>
<td>69</td>
</tr>
<tr>
<td>4</td>
<td>1,5 (0,3 M Co)</td>
<td>92</td>
<td>8</td>
<td>81</td>
</tr>
<tr>
<td>5</td>
<td>1,0 (0,3 M Co); 0,6 M Na₃citrat</td>
<td>90</td>
<td>10</td>
<td>77</td>
</tr>
<tr>
<td>6</td>
<td>1,0 (0,3 M Co)</td>
<td>94</td>
<td>6</td>
<td>81</td>
</tr>
<tr>
<td>7</td>
<td>1,0 (0,3 M Co) + 1 g dm⁻³ SHR</td>
<td>95</td>
<td>5</td>
<td>48</td>
</tr>
<tr>
<td>8</td>
<td>4,0 (0,1 M Co)</td>
<td>68</td>
<td>32</td>
<td>57</td>
</tr>
<tr>
<td>9</td>
<td>5,0 (0,1 M Co)</td>
<td>51</td>
<td>49</td>
<td>64</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition of Ni-Co alloys and cathodic current efficiency (CCE) depending on Ni/Co ratio in the solution (pH = 5,5) and the contents of the SHR and Na₃citrat (at E = -1.150 ÷ -1.180 V vs. SCE).
were identified using X-ray analysis with powder diffractometer Philips PW 1050 and CuKα radiation. The operating voltage was 20.0 kV.

RESULTS AND DISCUSSION

Phase composition of Ni-Co alloys

The Ni-Co alloys were deposited from solutions with Ni/Co ratio from 1 to 5 (Table 1), all of them containing 0.485 M H₃BO₃ and 0.4 M Na₃citrate (with exception of solution No 5, which contains 0.6 M Na₃citrat).

The summarized data about the chemical composition (mass % Co) and the cathodic current efficiency (CCE, %) of Ni-Co alloys, deposited from different solution are presented in Table 1.

The XRD patterns of Ni-Co alloys with different chemical composition are shown in Fig. 1. The binary Ni-Co phase diagram [17] indicates that the structure consists of α-phase, which is a substitutial solid solution of Ni and Co and has a face centered cubic (fcc) structure.

Very weak and stretched reflection peaks from Ni- and Co-phases are visible within the entire range of the studied chemical compositions of Ni-Co alloys due to the fact that the coatings have almost nanometric size of crystallites. For pure Co (Fig. 1а) and Ni (Fig. 1g) such clear and high peaks of reflection are not visible too. However, the reflection peaks from the substrate (copper electrode) are very clear since the deposited alloys have insufficient thickness of about 8±2 µm. The phases found are only such of Ni and Co with cubic face-centered (fcc) lattice.

There is a good correlation between the X-rays diffractograms and the data about the chemical composition and SEM-images already discussed [16]. The more fine-crystalline structure of the alloys deposited in presence of SHR (Fig. 2а) corresponds to more stretched maximums for Co (compared to those in Fig. 1а).

The increase of sodium citrate (Fig. 2b) leads to more pronounced occurrence of reflections of cubic Ni, which corresponds to the previous results [16]. The correspondence observed in the morphology and the phase composition of Ni-Co alloys with the cobalt content should affect their corrosion behavior, as is shown below.

Corrosion behaviors of Ni-Co alloys

The anodic potentiodynamic polarization dependencys of Ni-Co coatings were obtained in corrosion medium of 4 % NaCl. In Fig. 3 are shown the anodic curves of Cu plate (curve 1), coatings of pure Ni (curve 2) and pure Co (curve 3) on copper electrode, compared with the anodic curves of Ni-Co alloy coatings deposited from solution No 6. Obviously, the anodic curve of dissolution of the copper plate (Fig. 3, curve 1) runs through
a maximum of the current having the lowest value in comparison with the maximum for Co coating (Fig. 3, curve 3), and that for Ni coating (Fig. 3, curve 4). The latter two have almost equal values, which suggest approximately equal corrosion resistance of Ni and Co. The deviation of the potential to more positive values results in a more rapid decrease of the current to very low values followed by a long retention due to reaching the area of passivation. While the anodic maximums for Cu and Co correspond to the same potential, the anodic maximum for Ni is shifted to much more positive potentials. The highest anodic maximum is registered for the Ni-Co coating (Fig. 3, curve 9). The anodic dependencies, and more precisely the section of active dissolution of Ni and Co, run through a weak retention of current before the sharp drop due to reaching the potential of passivation. This can be explained with occurrence of two types of products on the surface during the dissolution of Ni and Co, the first of which is incompact and hence does not block the surface, and the second is more compact and insoluble and leads to a permanent passivation of the surface.

The anodic maximum of current for Ni-Co alloy is observed at potential close to the Flade-potential of Co, but yet between the Flade-potentials of Ni and Co. This fact proves that the passivation results from formation of insoluble products of both Ni and Co with the chloride ions from the model corrosion solution. After passivation the current does not reach the same values in all cases of Cu, Co, Ni, and Ni-Co discussed, which evidences formation of chemical products of different nature on the surface. The morphology of the obtained electrochemical coatings discussed [16] also influences the corrosion behavior of the pure metals and the alloy.

More clear conclusions can be drawn from the comparison between the anodic curves of alloys with different contents of Co in the range from 82 mass % to 94 mass %, in which the morphology is approximately equal [16].

The anodic behavior of Ni-Co coatings deposited at different values of Ni/Co ratio in the solution is illustrated in Fig. 4. As already shown [16], the increase of Ni/Co ratio in the solution from 1 to 3 results in increase of the content of Ni in the alloy. It follows from Fig. 4 that upon dissolution of Ni-Co alloys with higher content of Ni (curve 1) the anodic maximum is lower compared to alloys with lower content of Co (curve 3). The anodic maximums grow normally with the increase of the content of Co in the alloy and are observed at the same anodic potential. In all alloys the maximum of current is followed by a sharp drop to the same value of current, which means that the current of passivation of about 10 mA cm\(^{-2}\) is reached. The conclusion that can be drawn from the results obtained is that the alloys with the highest content of nickel have a higher corrosion resistance in the studied model environment compared to those containing a higher content of Co.

The anodic dependencies of Ni-Co coatings in 4 % NaCl deposited from electrolytes with compositions No 7 and No 9 are compared in Fig. 5, i.e. at higher content of sodium citrate (0.6 M) in the first case, and at lower content of sodium citrate (0.4 M) in the second case but
at equal Ni/Co = 1 in the solution.

As already shown [16] sodium citrate in the solution leads to only a slight growth of Ni content in the Ni-Co alloy. However, the presence of higher concentration of the complexing agent in the solution leads to formation of Ni-Co coatings with more coarse-crystalline structure. The slight increase of corrosion resistance of the alloys in presence of more sodium citrate (Fig. 5) is possibly attributable to the increase of Ni content in the alloys. As a whole, the effect of sodium citrate on the anodic behavior of Ni-Co alloy is insignificant.

Fig. 6 indicates that Ni-Co coatings obtained in the presence of SHR addition show higher corrosion resistance than the coatings obtained in the absence of additive. It should be noted that the coatings deposited in the presence of additive have more fine-crystalline structure, as proved by SEM observation [16].

CONCLUSIONS

The results are reported about the effects of the ratio Ni/Co in the citrate electrolyte, the addition of saccharine and the increase of the content of sodium citrate in electrolyte on the phase composition and the corrosion behavior of the electrodeposited Ni-Co alloys.

It is shown that the increase of Ni/Co ratio from 1 to 5 increases the content of Ni in the Ni-Co alloy to 48 mass % and the proportion between the phases of Co and Ni with cubic face-centered crystal lattice is in approximate compliance with the proportion of the two metals in the alloy. The increased content of Ni in the alloys, the presence of SHR and the higher content of sodium citrate in the solution for electrodeposition, lead to increased corrosion resistance of the coatings.

REFERENCES

4. J.L. McCrea, Industrial implementation of nanostructured cobalt as an alternative to hard chrome, Surface Engineering, 26, 3, 2010, 149-152.