COMPARATIVE STUDY OF ELECTRODEPOSITED AND ION BEAM MIXED Fe-Ni-Cr ALLOYS

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Electrodeposited Fe-Ni-Cr alloys irradiated with 209 MeV energy $^{84}$Kr ions were investigated by conversion electron Mössbauer spectroscopy, X-ray diffraction and electron microprobe analysis. Significant dose dependent changes were found between Mössbauer spectra of the irradiated and non-irradiated deposits. These changes reflect the dose dependent transformation of the metastable ferromagnetic phase to the paramagnetic one.

1. Introduction

Non-equilibrium techniques for the treatment of alloys have received much attention in recent years, because they can produce materials with excellent properties of both industrial and scientific importance. Chromium-nickel-iron alloy electrodeposits have remarkable industrial importance because they possess considerable wear and corrosion resistance and can therefore be developed as protective coatings for softer and more corrosive substrate materials. Previous investigations [1,2] using Mössbauer spectroscopy and X-ray diffraction (XRD) have shown the structure of electrochemically deposited Fe-Ni-Cr to be microcrystalline and the dominant phase to be ferromagnetic. In contrast, the thermally prepared alloys of equivalent composition consisted only of a paramagnetic phase. For comparison, an analogous system, Fe-Ni-Cr multilayers of composition similar to electrodeposits were prepared by vacuum deposition and subsequent ion beam mixing, in which case a metastable ferromagnetic phase has also been found as a dominant phase [3].

The aim of the present work was to study the process of transformation of the metastable ferromagnetic phase into a stable paramagnetic one in an electrochemically deposited Fe-Ni-Cr coatings, in comparison with that occurring in ion beam mixed multilayers, transformation which might occur due to ageing and due to radiation effects. For these investigations $^{57}$Fe conversion electron Mössbauer (CEM) spectroscopy, XRD and electron microprobe measurements were performed on Fe-Ni-Cr alloys coatings electrochemically deposited and irradiated with energetic heavy ions.

2. Experimental

The Fe-Ni-Cr samples examined in this study were electrodeposited using a new plating process recently developed which allows thicker coatings to be deposited [4,5]. The deposition was carried out over a range of plating times to produce alloy deposits with different thicknesses.

Electrodeposition was carried out using copper cathode substrates of 25x25mm working area and 0.2 mm in thickness using a circulation cell. Table 1 shows the bath composition and Table 2 shows the other electrodeposition conditions.
Although the chromium concentration is almost forty times the iron concentration in the electrolyte, the average concentration of the deposits was 25% Cr, 35% Ni and 40% Fe (±10%) for deposition times of 9, 19 and 29 min.

<table>
<thead>
<tr>
<th>Table 1. Bath Composition</th>
<th>Table 2. Electrodeposition Conditions</th>
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<tbody>
<tr>
<td>CrCl₃·6H₂O 0.80 mol/l</td>
<td>Cathode potential -1.8 V (SCE)</td>
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<tr>
<td>NiCl₂·6H₂O 0.20 mol/l</td>
<td>Electrolyte temperature 20 °C</td>
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<tr>
<td>⁵⁷FeCl₂·4H₂O 0.02 mol/l</td>
<td>Flow rate (circulation cell) 100 ml/min</td>
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<tr>
<td>NaCl 0.50 mol/l</td>
<td>Anode (40x60 mm) graphite</td>
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<tr>
<td>NH₄Cl 0.50 mol/l</td>
<td>Cathode (25x25 mm) copper</td>
</tr>
<tr>
<td>H₃BO₃ 0.15 mol/l</td>
<td>Bulk pH 1.8</td>
</tr>
<tr>
<td>H₂O deionized 500 g</td>
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<tr>
<td>dimethylformamide 500 g</td>
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</table>

X-ray diffractograms were recorded by means of a computer controlled DKON-2 diffractometer using CuKα radiation and β-filter.

The irradiation was carried out at room temperature with 209 MeV ⁸⁴Kr ions with different fluences up to 3x10¹⁴ ions/cm² at the Laboratory of Nuclear Reactions, JINR, Dubna.

Conversion electron ⁵⁷Fe Mössbauer spectra of electrodeposited samples were recorded by a conventional Mössbauer spectrometer using a CEM detector (RANGER) at room temperature, a 10⁹Bq activity ⁵⁷Co(⁹₀) source used. Isomer shifts are given relative to the α-Fe. The evaluation of Mössbauer spectra was performed by a least-square fitting of the lines using SIRIUS [6] and MOSSWINN [7] programs. The hyperfine field distributions were obtained either by Window or modified Hesse-Rübbartsch methods.

3. Results and discussion

The XRD results are consistent with the amorphous or microcrystalline character of electrodeposits[2].

![Fig. 1. CEM spectra of electrodeposited FeNiCr samples prepared for plating time 9 min.: (a) non-irradiated and (b) irradiated with 209 MeV ⁸⁴Kr ions with a fluence of 5x10¹³ ions/cm² and (c) irradiated with a fluence of 3x10¹⁴ ions/cm².](image-url)
Fig. 1. shows CEM spectra of electrodeposited FeNiCr samples before and after the irradiation with two different fluences.

All CEM spectrum was decomposed into a sextet (with an average hyperfine field of 270 kOe), a singlet ($\Delta = 0.09 \text{ mm/s}$) and a doublet ($\Delta = 0.8 \text{ mm/s}$). The sextet is attributed to the typical spectrum of the ferromagnetic phase occurring in the electrodeposited samples [1,2]. The singlet is associated with the stable paramagnetic phase of the alloy because it is the fingerprint of the thermally prepared alloy with fully crystalline fcc structure in stable paramagnetic state [1]. The doublet is assigned to the paramagnetic phase occurring in the microcrystalline Fe-Ni-Cr alloys [1-3]. Nevertheless, it can not be ruled out that this doublet is due to amorphous iron oxide. Namely, the electrodeposits can contain some oxygen or oxide inclusions.

In the as-deposited alloy the ferromagnetic phase is the dominant and no contribution of the stable paramagnetic phase was observed (Fig. 1a).

In the Mössbauer spectra of the irradiated deposits the singlet component of stable paramagnetic phase was also identified. An increase of the relative area of the singlet can be observed with increasing fluence (Fig. 1b and 1c).

The changes found in the Mössbauer spectra (Fig. 1) reflect the dose dependent transformation of the ferromagnetic phase to the paramagnetic ones due to the effect of heavy ion irradiation. Irradiation induced phase transformation has already been shown in the case of other alloys, too [8].

In the case of alloys prepared by vapour deposition and subsequent ion beam mixing with 100keV Xe ions, the phase composition was found to be similar to that of electrochemically as-deposited alloy [3]. The dominant ferromagnetic phase of the ion beam mixed vapour deposited samples has been transformed to the stable paramagnetic phase upon the isothermal heat treatment at temperatures higher than 650°C. In this case, the same components were identified in the Mössbauer spectra as in the case of the irradiation induced phase transformation of electrodeposits [9].

Fig. 2. shows CEM spectra of electrodeposits prepared at different plating times and irradiated at the same conditions. We have observed that the relative amount of the paramagnetic subspectrum decreases with increasing plating time. In the earlier work [2] a correlation was found between the width of the hyperfine field distribution and the mechanical stresses occurring in these samples with the plating time.

Fig. 2. CEM spectra of electrodeposited FeNiCr samples, prepared for plating time of 29 min (a), 19 min (b) and 9 min (c) and irradiated with 209MeV $^{84}$Kr ions with a fluence of $3 \times 10^{14}$ ions/cm$^2$. 
Conclusion

We can conclude that an irradiation induced phase transformation of the dominant metastable ferromagnetic phase takes place in Fe Ni Cr electrodeposited coatings due to an effect of the energetic heavy ion irradiation.

It is hoped that the present research will help to develop new coatings that will be of interest to the industry because of their corrosion resistance.

Acknowledgements

This work was supported by the Hungarian OTKA Fund (project No 014970) and the Hungarian-Italian Science and Technology Program (project No I-17/95). The irradiation at JINR, Dubna, was financially supported by the Hungarian Academy of Sciences.

References