Electrodeposition of La–Ni alloy films in a nonaqueous system

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Abstract

The codeposition of La–Ni alloy films in a nonaqueous system was investigated. The effects of several factors including the concentrations of main salts, pH, temperature, current density and substrates on the lanthanum content in the deposit were studied. The results show that the lanthanum content in the deposit can reach 18 wt % by controlling the system composition and deposition conditions. X-ray photoelectron spectrometry, X-ray diffraction and scanning electron microscope were used to characterize the morphology and structure of the deposit. The results show that the majority of lanthanum exists in the form of LaH2, while the rest exists as metal and its oxide in the deposit, and the structure of the alloy deposited is amorphous.

1. Introduction

Of all the elements in the periodic table only about one-quarter may be electrodeposited from aqueous electrolytes in their elemental form or as alloys suitable for coatings, the rest are of engineering and scientific interest because of their specific properties, and methods of depositing them are desirable. The deposition of certain metals and alloys has been successfully achieved from nonaqueous electrolytes, and they have been used on a commercial scale. However, these electrolytes are often used in the laboratory to obtain deposits and electroforms with characteristics unattainable by other coating methods.

Although the standard electrode potentials of rare earth elements are unknown in nonaqueous systems, the electrodeposition of rare earth elements or their alloys from nonaqueous electrolytes has been recently reported. Bhattacharya has successfully deposited YBaCu superconductor precursor films in DMSO [1] and Yuichi Sato has made a great achievement in electrochemical preparation of Sm–Co magnetic thin films [2]. Co–Gd magneto-optical thin films were also obtained by an electrochemical process [3]. Other rare earth elements or their alloys such as yttrium [4], dysprosium [5] and La–Fe alloy [6] in organic solvents have been successfully deposited. In addition, electrodepositions of Dy–Ba–Cu alloy films [7] and Sm–Te alloy films [8] in an aqueous system and electrodeposition of rare earth elements and their alloys in molten chlorides has been reported [9, 10].

The codepositions of La–Ni alloy films in molten [11] and aqueous system [12] have been reported. The former requires a very high temperature. In the latter, the lanthanum content in the coating is very low, and all lanthanum exists in the oxidized state. Up to now, there has been no report on the codeposition of La–Ni alloy in organic solvents.

The present paper describes the research on the electrodeposition of La–Ni hydrogen storing alloy functional thin films in an organic solvent system. Our primary objective is to increase the La content in the coating because the alloy only has a hydrogen-storing function if the La content is not less than 30%.

2. Experimental details

Analytical grade reagents including lanthanum nitrate [La(NO3)3], nickel nitrate [Ni(NO3)2], lanthanum chloride [LaCl3] and nickel chloride [NiCl2] were used. The electrodeposition of La–Ni alloy was studied in the following four solvents: N,N-dimethylformamide [DMF], dimethylsulphoxide [DMSO], ethanol, and acetonitrile [AN]. Ethylene diamine tetraacetic acid [EDTA], nitrilotriaacetic acid, ammonium bifluoride and triammonium citrate were used as complexing agents. Boric acid was used to adjust the pH of the solution.

Stainless steel, copper, brass and titanium alloy plates with a surface area of 2.5 cm² were used as substrates. The surfaces of the substrates were smooth and mirror polished. Two high purity graphite plates were used as the anode. The distance between the anode and the cathode was 1 cm. A closed system was adopted for the plating bath. The electrolysis cell was flushed with dry nitrogen before and during plating. Constant current
electrolysis was carried out by using a potentio-galvano
test. The electrolysis was performed isothermally.

A spectrophotometric method was applied to analyse
the lanthanum content in the deposit. X-ray diffraction
(XRD) and scanning electron microscope (SEM) were
used to detect the structure and the morphology of the
deposited coating. X-ray photoelectron spectrometry
(XPS) was used to test the chemical states of lanthanum
and nickel in the deposit.

Because the traditional three-electrode system is
inconvenient and aqueous reference electrodes must be
avoided in nonaqueous systems, we used a microelec-
trode technique to determine the voltammograms of the
plating solution. The working electrode was a Pt
microdisc electrode 30 µm in diameter and the counter
electrode was a Pt plate of 1 cm² surface area, which
also functioned as reference. The scan rate was
100 mV s⁻¹.

3. Results and discussion

3.1. Electrolysis systems

The solvents used were DMF, DMSO, AN and ethanol,
formamide etc. The following conclusions can be
obtained by comparison: (i) High content La coating
cannot be obtained with DMSO as solvent because of
the low solubility of La salt; (ii) codeposition of La and
Ni can be obtained only at pH < 1 with formamide as
solvent; (iii) coating is relatively coarse and porous with
AN as solvent; (iv) the plating bath is unstable with
ethanol as solvent due to the high volatility of ethanol.
With DMF as solvent, good bath stability, high metal
salt solubility and relatively high lanthanum content in
the coating are obtained. Therefore, DMF was selected
as solvent.

It is well known that the solubility of inorganic salts is
generally very low in organic solvents. Improvement of
the solubility of the main salts is problematic. Based on
complex theory, similarity and compatibility principle,
the following salts with different anions were studied:
LaCl₃, La(NO₃)₃, (p-CH₃C₆H₄SO₃)₂La and NiCl₂,
Ni(NO₃)₂, (p-CH₃C₆H₄SO₃)₂Ni. The results show that
(p-CH₃C₆H₄SO₃)₂La and (p-CH₃C₆H₄SO₃)₂Ni readily
dissolve in DMF because of their large anions, whereas
the lanthanum content in the deposit was low. The
solubilities of LaCl₃ and NiCl₂ in DMF were low.
Adding solubilizer can increase the saturation concen-
tration of NiCl₂ in DMF greatly so as to meet the
requirement for electrodeposition. The solubility of
La(NO₃)₃ was fairly high due to the formation of a
stable complex with DMF. The experimental results
show that a fine and closely woven and porous-free
deposit with a high lanthanum content can easily be
obtained from the system containing La(NO₃)₃ and
NiCl₂. Therefore, these were used as the main salts. The
preparation process of anhydrous La(NO₃)₃ was as
follows. First, La₂O₃ was reacted with nitric acid in
solution to form La(NO₃)₃. Then, the solution was
dewatered and dried by heating for at least 12 h at
140 °C in order to obtain raw particles. Next, the raw
particles were ground into fine particles. Finally, the fine
particles were further heated in an oil bath so as to lose
crystalline water under reduced pressure at 170 °C. The
dehydration process of La(NO₃)₃ · 6 H₂O is

\[
\text{La(NO₃)₃} \cdot 6 \text{H₂O} \overset{140 ^{0} C}{\longrightarrow} \text{La(NO₃)₃} \cdot 4 \text{H₂O} \overset{170 ^{0} C}{\longrightarrow} \text{La(NO₃)₃}
\]

The reaction of a complexing agent in a nonaqueous
system may be greatly influenced by other ions. The
chloride ion functions as a catalyst in the electrodepo-
sition of cobalt in DMF. However, the chloride ion is
also an inhibitor if SCN⁻ is added [13]. Therefore four
kinds of complexing agents – ethylene diamine tetra-
acetic acid (EDTA), nitrilotriacetic acid, ammonium
bifluoride and triammonium citrate – were investigated.
The following results were obtained. EDTA and nitrilo-
triacetic acid not only improved coating quality, but
also increased La content. However, their solubility in
the plating solution was low. Ammonium bifluoride
increased the coating lanthanum content by four to six
times, compared with no complexing agent. Even
though the solubility of ammonium bifluoride in DMF
is poor, fluorine can easily be adsorbed on the cathode
and hinder the adsorption of O₂ or O²⁻. Therefore, the
conductivity of the system can be improved. The
fluorine function is similar to a surfactant. In addition,
fluorine can greatly increase the solubility of NiCl₂ in
DMF by functioning as an assistant solubilizer. The
coating quality can also be improved by using triam-
onium citrate. However, it can result in a decrease in
La in the coating. By comparison, ammonium bifluoride
as complexing agent is the best for increasing La content
and for improving the coating quality.

The effects of the five substrates on the electrodepo-
sition of La–Ni alloy are shown in Table 1. It can be
seen that the compositions of the coatings and the

<table>
<thead>
<tr>
<th>Substrates</th>
<th>La content/wt %</th>
<th>Current efficiency/%</th>
<th>Surface morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>18.0</td>
<td>65.2</td>
<td>brightness</td>
</tr>
<tr>
<td>Brass</td>
<td>17.5</td>
<td>60.1</td>
<td>a little dark</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>10.4</td>
<td>59.0</td>
<td>very bright</td>
</tr>
<tr>
<td>Titanium</td>
<td>12.7</td>
<td>53.4</td>
<td>some black pot on surface</td>
</tr>
<tr>
<td>Titanium alloy</td>
<td>20.8</td>
<td>55.3</td>
<td>a little dark</td>
</tr>
</tbody>
</table>

Table 1. The effects of substrate on the electrodeposition of La–Ni alloy
(C₅⁺ = 0.05 mol dm⁻³, C₆ IPV = 0.2 mol dm⁻³, pH 4.0, Jₑ = 0.6 A dm⁻², T = 50 °C)