ABSTRACT

Dealloying is a selective leaching of one component in a multicomponent alloy so as to produce a nanoporous structure. In this study, it was aimed to produce nanoporous Ni coating by selective leaching of Zn in a Zn-Ni alloy. To achieve this, first the Zn-Ni alloy was obtained by electrodeposition in a bath containing Zn and Ni salts. Then, dealloying was performed at different concentrations of NaOH solution. Dealloying led to crack formation in the coatings which thus prevented the formation of porous structure. This was attributed to insufficient surface diffusion of nickel which for the leaching rate employed was too slow to form an interconnected skeleton of Ni as porous structure.

Keywords: Nanoporous Ni; Ni-Zn; Electrodeposition; Dealloying

INTRODUCTION

Nanoporous materials have pores with sizes in the range of 1 to 100 nm [1,2]. With their high surface-to-volume ratio, nanoporous materials are able to adsorb and interact with atoms, ions and molecules and as such have a variety of applications [1]; adsorbent materials, catalysis and battery and fuel cell electrodes; filters etc.

Nanoporous materials can be produced by a variety of methods. These include casting [3], powder sintering [3], metal deposition, full-replication process using templates [4] and dealloying/electrochemical dealloying [5-8]. Among these, dealloying is particularly attractive. Dealloying is simply a corrosion process in alloys where the less noble component is selectively dissolved out. This leaves behind the other component which forms ligament structure by surface diffusion. As a result, a porous structure is evolved in the material. The process may occur in a suitable selected corrosive media or the process may be accelerated electrochemically. [9]

Various alloys were used to produce nanoporous Ni. Qi [10] used Ni-Al alloys and dealloyed them in a 20 wt.% NaOH aqueous solution. Sun [11], Chang [12] and Hakamada [13] have used single phase Ni-Cu alloys to produce nanoporous Ni in solution containing 1.6 M Ni(H$_2$NSO$_3$)$_2$.H$_2$O and 0.1 M CuSO$_4$.5H$_2$O buffered to pH 2.5 with H$_3$BO$_3$, in a solution containing 1 M NiSO$_4$, 0.01 M CuSO$_4$, and 0.5 M H$_3$BO$_3$ (pH=4) and in 1 mol/l (NH$_4$)$_2$SO$_4$ respectively. Also, Hosseini [14] and Cai [15] tested to produce nanoporous Ni by dealloying Ni-Zn alloys. These studies have shown that for a successful nanoporous structure dissolved constituent should have a greater fraction of the alloy preferably in the neighborhood of 15-40 at% Ni. [10, 14, 19]

In this study, an attempt has been made to produce nanoporous Ni coatings to be used as substrate for hydrogen separation membrane. For this purpose, first Ni-Zn coatings were obtained in metallic substrate via electrodeposition. The coatings were then dealloyed in Zn – Ni salt solutions at different concentrations.

EXPERIMENTAL PROCEDURE

Substrate used in electrodeposition was Ni. This was chosen with the intention that nanoporous Ni membrane to be developed in this study would be fragile and need a mechanical support. Sintered Ni or sintered stainless steel filter would be suitable as support material.

Parameters used in electrodeposition are reported in Table 1. As shown in this table the solution used was adapted from Matsuda et al. [16] which contain ZnCl$_2$ and NiCl$_2$. Current density employed was 0.15 A/dm$^2$. The substrate Ni to be coated was connected as cathode which had been prepared by grinding with a series of abrasive papers down to 1200, and then polished with 1 μ Al$_2$O$_3$. The cathode was then cleaned by ultrasonically in acetone. They were immediately dried.
Table 1. Electrodeposition experimental parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>Nickel (2.5x20 cm², ~0.7 μ)</td>
</tr>
<tr>
<td>Anode</td>
<td>Zinc (5x20 cm²)</td>
</tr>
<tr>
<td>Solution</td>
<td>1 M KCl, 1.25 M NH₄Cl, 0.75 M ZnCl₂ + 1 M KCl, 1.25 M NH₄Cl, 0.1 M NiCl₂·6H₂O</td>
</tr>
<tr>
<td>Current</td>
<td>0.15 A</td>
</tr>
<tr>
<td>Time</td>
<td>6 hours</td>
</tr>
</tbody>
</table>

For dealloying coated substrates were dipped into NaOH solutions. The solutions for this purpose were prepared in four concentrations; 0.75 M, 1 M, 1.5 M and 2 M.

Coatings and dealloyed samples were examined with FEG-SEM. Chemical compositions of coatings were determined with EDS analysis.

RESULTS AND DISCUSSION

Using the experimental conditions given above Ni sheet was electroplated for duration of 6 hours. Figure 1 shows a cross-section of the sample where the coating layers are clearly visible. Measurements showed that the coating was 20 micron thick. Results of EDS analysis are given in Fig.2 This shows that the coating is made up of Ni and Zn and that the amount of Ni is around 15 at%.

One of the key parameters in dealloying is alloy composition. According to Ni-Zn phase diagram, Zn-15 at% Ni falls within a single phase region and thus dealloying was not complicated by the presence of second phases. Moreover, according to the studies of Qi [10], Hosseini [14] and Qiu [19] for successful dealloying the noble phase has to be between than 15-40 at. %. The coating produced here satisfies this requirement also.

Figure 1. SEM image of electrodeposited Zn-Ni coating.

Following the successful deposition of Zn-Ni coatings, deposited samples were leached NaOH concentrations. Fig. 3 (a) shows the surface of the coating after leaching the sample for 4 minutes in 2M NaOH solution. Cracks are clearly visible in the surface. So as to reduce the dissolution rate additional samples were leached in less concentrated solutions. 1.5 M, 1 M and 0.75 M solutions were used. Fig. 3 (b) shows the surface of the coating after 3 hours of leaching. This again led to crack formation in the coatings.

Figure 2. EDS analysis of coating. Note that the coating is rich in Zn.
Results reported above indicate that during dealloying the coatings are leached but rather than producing a porous structure this has led to cracking of coatings. According to Erlebacher [20] so as to develop a porous structure, noble element has to reorganize itself as ligament forming a continuous porous structure. For this to occur there ought to be a balance between dissolution rate of zinc and the surface diffusion of Ni. Failure to produce the porous structure is then most probably due to the fact that leaching rate employed was too fast to allow the formation of ligament structure.

Surface diffusion coefficient of Ni extrapolated from data given by Seebauer and Allen [21] has a value of $2.14 \times 10^{-17}$ cm$^2$/s. This value is quite low as compared to for instance Cu where the coefficient is $1.02 \times 10^{-14}$ cm$^2$/s. To compensate this slow surface diffusion of Ni, the dissolution rate may be reduced by employing less severe leaching solutions. This would then require an extensive leaching time or the process may be carried out electrochemically in a more controlled conditions.

**CONCLUSION**

In this study, two-step processes were investigated to produce nanoporous nickel. In the first step, Zn-Ni coating was obtained in the composition of 15 at. % Ni and average thickness of 20 μ was obtained. This composition is suitable for dealloying because of being in single phase region. In the second step, Zn-Ni coated samples were dealloyed in 0.75 M, 1 M, 1.5 M and 2 M NaOH solutions. This has led to cracking of coatings which run throughout the surface. This was most probably due to slow surface diffusion of nickel atoms. It was suggested that so as to compensate this, leaching rate can be decreased further decreasing the concentration of NaOH solution.

**REFERENCES**


AUTHOR INFORMATION

Seda Oturak is a senior from METU, TURKEY majoring in metallurgical and materials engineering. Her advisor for this project is Tayfur Öztürk, Professor at METU Metallurgical and Materials Engineering Department. Her academic interests include nanoporous metals and energy storage materials/devices, biomimetics and materials characterization. Beside academic interests, her personal activities are false-colouring electron microscope images, popular science journalism, astronomy and astrophotography.