The Influence of Chemical Modification by Silver on Hydrogen Storage Properties of Nanocrystalline Ti$_2$Ni Alloy

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In this paper which is a continuation of our previous work, new obtained materials were measured. To the best of our knowledge, there are no reports on chemical modification of Ti$_2$Ni alloy by Ag element in order to improve electrochemical properties of electrode for Ni-MH$_x$ batteries.

1. Introduction

Ti$_2$Ni alloy have been recently examined for negative electrode in Ni-MH$_x$ batteries. Theoretical electrochemical capacity of Ti$_2$Ni hydride equals 500 mAh/g [1]. First experimental studies on this alloys were performed by Luan et al. [2-4]. In this works arc melting was used to obtain this alloy. The highest discharge capacity obtained by mentioned group was just 160 mAh/g which was caused by accumulation of irreversible metal hydride. Electrochemical properties can be improved by changing size of alloy crystals. Mechanical alloying (MA) is novel method for production of nanocrystalline hydrogen storage materials. This process which consists of repeated fracturing, mixing and cold welding provides formation of new nanostructured, non-equilibrium alloys [5]. In our previous work we studied Ti$_2$Ni alloy produced by MA process. Maximum discharge capacity for this system was 253 mAh/g. This improvement of electrochemical properties was due to creation of new clean surfaces, greater specific surface area and reduction in powder size [6].

Another way to improve mentioned properties is chemical modification of alloys for Ni-MH$_x$ batteries. Elemental substitution of Ni by other metallic or non-metallic elements can improve cycle stability and decrease metal hydride stability [7-10]. Silver is one of element which is used for chemical modification of hydrogen storage materials [11, 12].

In this paper which is a continuation of our previous work, structure, agglomerate size and morphology, corrosion and electrochemical properties in 6 M KOH were measured. To the best of our knowledge, there are no reports on chemical modification of Ti$_2$Ni alloy by Ag element in order to improve electrochemical properties of electrode for Ni-MH$_x$ batteries.

2. Experimental details

MA process was used to produce all of studied materials. In our work SPEX 8000 Mixer Mills were used. All synthesis and handleings were done in an argon atmosphere. Every powder milling lasted 8 h. Ti, Ni, and Ag powders which were used in our work had at least 99.9% purity.

Detailed description of synthesis procedure was described in our previous works [6, 13]. In this work two materials were synthesized. First one was pure Ti$_2$Ni alloy and the second one was chemically modified Ti$_2$Ni alloy with 5 wt% of Ag added to elemental powder mixture before MA. As a result of 8 h MA amorphous materials were obtained [6, 13]. In order to obtain Ti$_2$Ni-type structure MA powders were annealed in argon atmosphere at 750°C for 0.5 h. Additionally Ti$_2$Ni-based composite was produced by 5 min milling of MA and annealed Ti$_2$Ni alloy with 5 wt% of Ag.

To facilitate the reading of work, obtained materials were labeled as follows:

- Ti$_2$Ni alloy without changes is labeled as Ti$_2$Ni,
- Ti$_2$Ni with 5 wt% of Ag nanocrystalline alloy is labeled as Ti$_2$Ni+Ag,
- Composite of Ti$_2$Ni alloy with 5 wt% of Ag elemental powder is labeled as Ti$_2$Ni+(Ag).

X-ray diffraction (XRD) and scanning electron microscopy (SEM) was used to study structure, microstructure, and morphology of obtained materials. Based on XRD data average crystallite size were calculated using the Scherrer equation. SEM pictures were used to made particle size dimension distribution histograms.
Corrosion resistance behavior was examined during potentiodynamic tests. Measurements were made in 6 M KOH solution. Scanning range was from –1.5 to 1 V. Scanning speed equaled 1 mV/s.

Obtained materials in mixture with 10 wt% of Ni powder were used as negative electrodes in Ni-MHx systems (electrochemical measurements). This mixtures were cold pressed under 800 MPa to form pellets. Electrodes were charged and discharged at 40 MA/g. A cut-off potential vs. Hg/HgO/6 M KOH was –0.7 V. All electrochemical measurements were performed in 6 M KOH solution. Cycle stability of materials was evaluated by capacity retaining rate after 18th cycle

\[ R_h = \frac{C_{18}}{C_{\text{max}}} \times 100\% \]  

(1)

where \( C_{18} \) and \( C_{\text{max}} \) are discharge capacities at the 18th cycle and maximum discharge capacity, respectively.

Description of activation procedure and electrochemical measurements were described in our previous papers [6, 13].

3. Results and discussions

Ti2Ni-based materials were characterized by XRD, SEM, corrosion and electrochemical measurements. Addition of Ag to mixture of elemental powders did not affect MA process (not shown here). After MA process, amorphous powders were heat treated at 750°C for 0.5 h. Figure 1 shows XRD spectra of annealed materials.

Almost all of peaks are related to presence of Ti2Ni phase. Small amount of minor phase was also detected: hexagonal TINi. Small peaks related to presence of Ag crystals are visible on Ti2Ni+Ag alloy and Ti2Ni+(Ag) composite (not shown here) XRD patterns. Intensity of Ag peaks was much higher for composite material. Comparing both patterns of materials which had the same amount of silver, we think that most of silver in Ti2Ni+Ag alloy reacted with Ti and Ni creating Ti-Ni based phase. Small part of Ag did not react with other elements — residue is visible on XRD spectra (Fig. 1a). Based on XRD date, average crystalline size were calculated using the Scherrer equation. Silver addition does not affect the average crystallite size of alloy. For unmodified and modified alloy it equaled 32 and 31 nm, respectively (Table I).

SEM pictures of Ti2Ni and Ti2Ni+Ag alloys are shown in Fig. 2. Both of them had crystallite agglomerates in size from a few to one 150 \( \mu \)m. Materials after MA and additional annealing had cleavage fracture morphology (Fig. 2a). Based on SEM pictures particle size dimension distribution histograms were made (Fig. 3). Most of agglomerates had size less than 100 \( \mu \)m. Average size of agglomerates is similar for Ti2Ni and Ti2Ni+Ag alloys. It equaled less than 50 \( \mu \)m (Table I). Particle size dimension distribution histogram of Ti2Ni+Ag seems to be more uniform. Figure 4 shows potentiodynamic polarization curves of the uncharged studied alloys and composite. All curves have a very similar shape. Initially occurring area of resistance is followed by active dissolution of formed hydroxide layer. Subsequently passivation process was observed. During this process the hydroxide layer is rapidly formed. In case of Ti2Ni and Ti2Ni+Ag

<table>
<thead>
<tr>
<th>Composition</th>
<th>Crystallites size of annealed powders [nm]</th>
<th>Average agglomerates size of annealed powders [um]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti2Ni</td>
<td>32</td>
<td>45.3</td>
</tr>
<tr>
<td>Ti2Ni+Ag</td>
<td>31</td>
<td>49.6</td>
</tr>
</tbody>
</table>

Fig. 2. SEM picture of Ti2Ni (a,b) and Ti2Ni+Ag (c).

Fig. 3. Particle size dimension distribution histograms of: (a) Ti2Ni, (b) Ti2Ni+Ag.

Fig. 1. XRD spectra of annealed powders of: (a) Ti2Ni alloy, (b) Ti2Ni+Ag.
the hydroxidation process was disturbed for some reason which resulted in a creation of new clean surface. The surface was then quickly hydroxidized to reach the passive state. This situation was not observed for studied composite where passivation process proceeded continuously. Corrosion current of all measured materials is summarized in Table II. Ag element in Ti$_2$Ni alloy and composite improved the corrosion resistance of materials in 6 M KOH solution. The best corrosion resistance was obtained for Ti$_2$Ni+(Ag) composite. Observed slight improvement of corrosion properties may be caused by suppressed pulverization of electrode due to the anticorrosion effect of silver addition.

Electrochemical properties of materials are shown and summarized in Fig. 5 and in Table II. The best activation properties had Ti$_2$Ni alloy. Both materials with Ag in their composition showed almost zero discharge capacity in first charge/discharge cycle. The maximum discharge capacity of studied alloys and composite was obtained in 2nd or 3rd cycle. The highest discharge capacity showed Ti$_2$Ni+(Ag) alloy — 303 mAh/g. However both Ti-Ni-Ag materials had much higher maximum discharge capacity. Decrease of discharge capacity during cycles was observed for all of materials. This situation can be due to formation of oxides, hydroxides and irreversible hydride phases. The mentioned decrease of discharge capacity is much bigger for Ti$_2$Ni+Ag alloy and for Ti$_2$Ni+(Ag) composite than for unmodified Ti$_2$Ni alloy. The best capacity retaining rate was obtained for Ti$_2$Ni material — 31% after 18th cycles.

### 4. Conclusions

Ti$_2$Ni-based alloys and composites with Ag were used as negative electrodes for Ni-MH$_2$ rechargeable batteries. Based on this study the following conclusions can be obtained:

- Chemical modification of Ti$_2$Ni alloy by 5 wt% of Ag element did not affect crystallite size and average agglomerate size.
- Ag particles improves corrosion resistance of Ti$_2$Ni alloy in alkaline solution.
- Ti$_2$Ni with 5 wt% composite had the highest electrochemical discharge capacity which equaled 303 mAh/g.

### References