

The Influence of Chemical Modification by Silver on Hydrogen Storage Properties of Nanocrystalline Ti₂Ni Alloy

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In this study mechanical alloying process with subsequent annealing at 750 °C for 0.5 h were used to produce Ti₂Ni-based nanocrystalline alloys and composite. To improve electrochemical properties, Ti-Ni-based alloy was chemically modified by 5 wt% of silver powder. X-ray diffraction analyses showed formation of nanocrystalline Ti₂Ni main phase. Electrochemical studies revealed a positive effect of chemical modification by silver on Ti₂Ni alloy. All synthesized materials were used as negative electrodes for Ni-MH_x batteries. The highest discharge capacity equaled 303 mAh/g, at 40 mA/g discharge current. All electrochemical measurements were done in 6 M KOH solution.

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1. Introduction

Ti₂Ni alloy have been recently examined for negative electrode in Ni-MH_x batteries. Theoretical electrochemical capacity of Ti₂Ni 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 Ti₂Ni 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 Ti₂Ni 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 handlings 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 Ti₂Ni alloy and the second one was chemically modified Ti₂Ni 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 Ti₂Ni-type structure MA powders were annealed in argon atmosphere at 750 °C for 0.5 h. Additionally Ti₂Ni-based composite was produced by 5 min milling of MA and annealed Ti₂Ni alloy with 5 wt% of Ag.

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

- Ti₂Ni alloy without changes is labeled as Ti₂Ni,
- Ti₂Ni with 5 wt% of Ag nanocrystalline alloy is labeled as Ti₂Ni+Ag,
- Composite of Ti₂Ni alloy with 5 wt% of Ag elemental powder is labeled as Ti₂Ni+(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.

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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-MH_x systems (electrochemical measurements). These 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

$$R_h = \frac{C_{18}}{C_{\max}} \times 100\%, \quad (1)$$

where C_{18} and C_{\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.

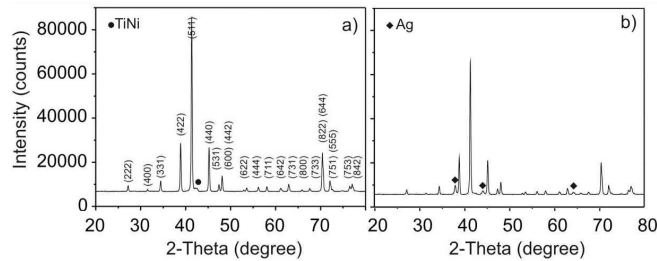


Fig. 1. XRD spectra of annealed powders of: (a) Ti₂Ni alloy, (b) Ti₂Ni+Ag.

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 data, 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

TABLE I

Crystallites size and average particle size of Ti₂Ni based materials.

Composition	Crystallites size	Average agglomerates
	of annealed powders [nm]	size of annealed powders [μm]
Ti ₂ Ni	32	45.3
Ti ₂ Ni+Ag	31	49.6

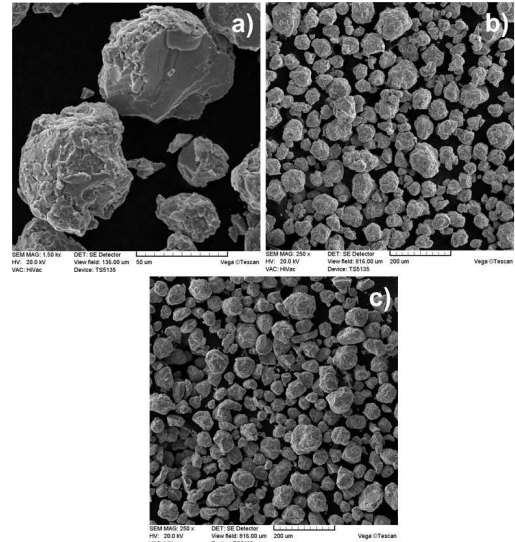


Fig. 2. SEM picture of Ti₂Ni (a, b) and Ti₂Ni+Ag (c).

size from a few to one 150 μm. 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

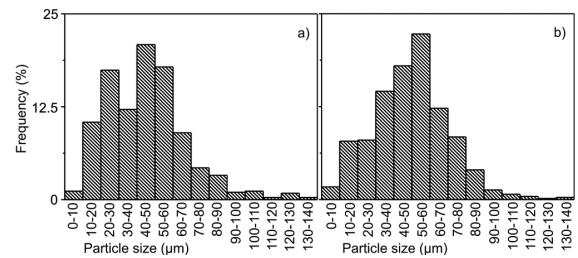


Fig. 3. Particle size dimension distribution histograms of: (a) Ti₂Ni, (b) Ti₂Ni+Ag.

agglomerates had size less than 100 μm. Average size of agglomerates is similar for Ti₂Ni and Ti₂Ni+Ag alloys. It equaled less than 50 μm (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

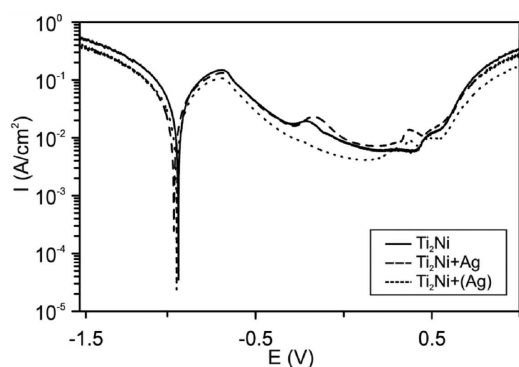


Fig. 4. Potentiodynamic curves of Ti_2Ni -based materials in 6 M KOH solution.

TABLE II

Maximum discharge capacity, capacity retaining rate after 18th cycle, corrosion current of Ti_2Ni -based materials.

Composition	Max. discharge capacity [mAh/g]	Capacity retaining rate after 18 th cycle [%]	Corrosion current [A/cm^2]
Ti_2Ni	256	31	1.15×10^{-2}
$\text{Ti}_2\text{Ni}+\text{Ag}$	294	14	1.25×10^{-2}
$\text{Ti}_2\text{Ni}+(\text{Ag})$	303	13	0.72×10^{-2}

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_2Ni alloy and composite improved the corrosion resistance of materials in 6 M KOH solution. The best corrosion resistance was obtained for $\text{Ti}_2\text{Ni}+(\text{Ag})$ 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

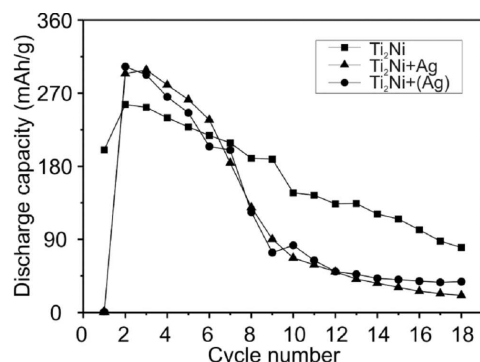


Fig. 5. Discharge capacities as a function of cycle number of electrode prepared with Ti_2Ni -based materials (solution 6 M KOH, room temperature).

properties had Ti_2Ni 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 $\text{Ti}_2\text{Ni}+(\text{Ag})$ 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 $\text{Ti}_2\text{Ni}+\text{Ag}$ alloy and for $\text{Ti}_2\text{Ni}+(\text{Ag})$ composite than for unmodified Ti_2Ni alloy. The best capacity retaining rate was obtained for Ti_2Ni material — 31% after 18th cycles.

4. Conclusions

Ti_2Ni -based alloys and composites with Ag were used as negative electrodes for Ni-MH_x rechargeable batteries. Based on this study the following conclusions can be obtained:

- Chemical modification of Ti_2Ni alloy by 5 wt% of Ag element did not affect crystallite size and average agglomerate size.
- Ag particles improves corrosion resistance of Ti_2Ni alloy in alkaline solution.
- Ti_2Ni with 5 wt% composite had the highest electrochemical discharge capacity which equaled 303 mAh/g.

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