

Journal of Alloys and Compounds 441 (2007) 197-201

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Electrochemical hydriding of amorphous and nanocrystalline TiNi-based alloys

Boris Drenchev, Tony Spassov*

Department of Chemistry, University of Sofia "St.Kl.Ohridski", 1 J. Bourchier Str., 1164 Sofia, Bulgaria Received 13 July 2006; received in revised form 19 September 2006; accepted 19 September 2006 Available online 17 October 2006

Abstract

Amorphous and nanocrystalline TiNi_{1-x}M_x (M = Co, Fe, Sn; x = 0 and 0.2) alloys were synthesized by mechanical alloying. Powder particles with an average diameter of about 5 μ m were produced. X-ray diffraction analysis showed that after 10.5 h of milling the initial mixture of metal powders transformed into amorphous or fine nanocrystalline material. DSC analysis displayed high thermal stability of the as-milled amorphous alloys. Electrochemical hydrogen charge/discharge measurements of the as-milled as well as annealed alloys were carried out at galvanostatic conditions. It was found that among the alloys studied TiNi_{0.8}Fe_{0.2} revealed the highest discharge capacity of about 65 mAh/g in the as-milled state and 80 mAh/g after annealing at 500 °C.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Ti alloys; Mechanical alloying; Amorphous materials; Ni-MH

1. Introduction

Titanium-based alloys are promising materials for hydrogen storage [1-4]. AB-type TiFe and TiNi alloys react reversibly with hydrogen and form ternary hydrides. Some of these materials have shown excellent properties as reversible negative electrode for Ni-MH batteries. TiNi-based alloys reveal notable electrochemical hydrogen capacity (245 mAh/g [5,6]), low specific weight and good oxidation resistance, but the charge/discharge kinetics are slow. TiFe alloys, despite of their high hydrogen capacity at room temperature (up to 2 H/f.u.), have also limited application in batteries due to poor absorption/desorption kinetics and complicated activation [4]. Replacement of Fe/Ni or Ti by other transition metals is one of the approaches used to improve the activation of this type of alloys [4,7]. Cuevas et al. [7] have shown that martensitic (Ti_{0.64}Zr_{0.36})Ni exhibits much higher reversible capacity (330 mAh/g) than the austenitic phase (85 mAh/g), but the cycle life of the last is longer.

Ball milling is a suitable method to produce amorphous and nanocrystalline Ti-based alloys and is another effective way for

* Corresponding author. *E-mail address:* tspassov@chem.uni-sofia.bg (T. Spassov).

0925-8388/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2006.09.071

improving the hydrogen absorption rate, due to the reduction of the particle and grain size [4,8,9]. The influence of Ni content on the electrochemical properties of ball-milled nanocrystalline TiFe_{1-x}Ni_x (x = 0, 0.25, 0.5, 0.75, 1) alloys has been investigated and a maximum discharge capacity has been found at x = 0.75(155 mAh/g) [4,10].

In the present work, the influence of the alloying elements (Co, Fe, Sn) and microstructure on the electrochemical hydrogen capacity and cycle life of TiNi-type alloys has been studied.

2. Experimental part

Powders of Ni (99.5%), Ti (99.7%), Co (>99%), Fe (>99%) and Sn (99.8%) in appropriate amounts were mixed together in the reactors of high-energy planetary mill to produce TiNi, TiNi_{0.8}Co_{0.2}, TiNi_{0.8}Fe_{0.2} and TiNi_{0.8}Sn_{0.2}. Alloying started after 5 h of milling at ball to powder mass ratio of 9:1 under argon atmosphere (*n*-heptane) and ended after 10.5 h. After each 1 h of continuous milling 30 min relaxation time was applied. The alloys powders were studied by X-ray diffraction (XRD) using Cu K α radiation, scanning electron microscope (SEM, JEOL-5510), differential scanning calorimeter (DSC, Perkin-Elmer) and galvanostate "KRIONA-KR515".

The as-milled and annealed materials were used to prepare metal-hydride electrodes by mixing 100 mg alloy with 30 mg teflonysed carbon black (VULKAN 72 with 10 wt.% PTFE). The mixture was pressed at 1240 kg/cm². An electrode with a shape of pellet with a diameter of about 10 mm and thickness of 1 mm was prepared. The electrode was charged and discharged in a





 $TiNi_{0.8}Co_{0.2}$





 $TiNi_{0.8}Fe_{0.2}$



 $TiNi_{0.8}Sn_{0.2} \label{eq:rescaled}$ Fig. 1. SEM micrographs of the as-milled TiNi alloys.

three-electrode cell in 30 wt.% water solution of KOH at room temperature. The reference electrode was Hg/HgO and the counter electrode was a nickel net. The charge and discharge current was 100 and 50 mA/g, respectively.

3. Results and discussions

In the present study four TiNi-based alloys (TiNi, TiNi_{0.8}Co_{0.2}, TiNi_{0.8}Fe_{0.2} and TiNi_{0.8}Sn_{0.2}) were prepared by mechanical alloying (MA). SEM analysis displayed particles size in the range of 1–15 μ m with an average particle size of about 5 μ m, Fig. 1. Agglomerates of smaller particles (<2–3 μ m) were also detected. At higher magnifications a lamellar particle structure and a presence of cleavages was observed (Fig. 1). Noticeable difference in the particles size distribution and morphology of the different alloys was not detected.

X-ray diffraction patterns of the as-milled alloys are presented in Fig. 2. The alloy with Sn shows one broad diffraction peak around 41.5° (2θ) with a shoulder at about 36° , whereas the other three alloys, except the peaks at 36° and 42.5° , have an additional less intensive broad peak at 61° . On the base of the XRD results it can be concluded that the alloying has been realized successfully for all compositions studied. Although, due to the very large width of the diffraction peaks, it is difficult to assign them to those of exact phases they are all positioned in the range of Bragg angles (2θ) of the cubic and monoclinic TiNi phases. The microstructure of the as-milled materials is amorphous or extremely fine nanocrystalline. It was found that the addition of Sn favors the grain size refinement of the TiNi alloys during ball milling.

The electrodes prepared from the as-milled alloys were charged for 1 h at current density of 100 mA/g and discharged at 50 mA/g to cut-off potential of 650 mV ($E_{Hg/HgO} - E_{MH}$) for TiNi, TiNi_{0.8}Co_{0.2} and TiNi_{0.8}Fe_{0.2} and 500 mV for TiNi_{0.8}Sn_{0.2}. Typical charge and discharge curves can be seen in Fig. 3. The charging process occurred in the potential range of about 860–920 mV—the linear part of the charging curve. It was found that the hydrogen charging process practically ends when the potential establishes a constant value. Once the constant potential value fixes hydrogen bobbles evolution takes place. The discharging plateau was not observed for any of the compositions. The capacity as a function of charge/discharge cycle



Fig. 2. X-ray diffractograms of the as-milled alloys.



Fig. 3. Charge and discharge curves of TiNi_{0.8}Fe_{0.2} alloy (second cycle).



Fig. 4. Capacity as a function of cycle number for the different as-milled compositions.

number is presented in Fig. 4. A discharge capacity increase with the cycle number is observed for the TiNi, $TiNi_{0.8}Co_{0.2}$ and $TiNi_{0.8}Fe_{0.2}$ alloys and a slow capacity decrease for the $TiNi_{0.8}Sn_{0.2}$ alloy. Table 1 presents the initial and the capacity at the 11th discharge cycle for the four alloys studied. The iron-containing alloy possesses the highest discharge capacity and this with tin—the lowest. It is necessary to be mentioned that the type of the curves "discharge capacity versus cycle number" depends on the alloy composition as well as on the electrode

Table	1
-------	---

Initial capacity and the capacity at the 11th discharge cycle for the alloys studied

Composition	Initial capacity (mAh/g)	Capacity (mAh/g) at 11th cycle
TiNi	39	52
TiNi _{0.8} Co _{0.2}	23	56
TiNi _{0.8} Fe _{0.2}	48	60
TiNi _{0.8} Sn _{0.2}	36	30



Fig. 5. DSC analysis of the as-milled alloys.

preparation technique (mass ratio between alloy and carbon, amount of PTFE, degree of homogenization, electrode thickness and pressure). Electrodes prepared at different pressures $(900-1250 \text{ kg/cm}^2)$ revealed the highest capacity for the sample compacted with the highest pressure.

In order to obtain information about the thermal behavior of the as-milled hydrogen free alloys they were annealed in DSC up to 500 °C and then analyzed by XRD. Fig. 5 shows DSC curves of the powders and the corresponding XRD patterns of the annealed materials can be seen in Fig. 6. There are two endothermic effects for all as-milled alloys. There could also be some exothermic effects combined with the endothermic reactions, but it is difficult to separate the overlapping processes from the calorimetric curves measured. The enthalpy changes associated with the solid state reactions observed by DSC are substantial (>150 J/g). It is interesting to note that the processes associated with the DSC effects do not change the microstructure significantly, i.e. the annealed materials are still in a nanostructured state, Fig. 6. The average nanocrystals size of the annealed sam-



Fig. 6. XRD diffarctograms of the annealed alloys.



Fig. 7. Capacity as a function of cycle number for the different annealed alloys.

Table 2	
Initial capacity and the capacity at the 50th disch	arge cycle for the alloys studied

Composition (annealed)	Initial capacity (mAh/g)	Capacity (mAh/g) at 50th cycle
TiNi	4	67
TiNi _{0.8} Co _{0.2}	0.57	83
TiNi _{0.8} Fe _{0.2}	1.68	79
TiNi _{0.8} Sn _{0.2}	2.1	44

ples varies between 6 and 8 nm for the alloys studied. A detailed study on the nature of the solid state transformations occurring in the as-milled samples during heating is underway.

The hydrogen absorption properties of the annealed materials (500 °C for short time) are different compared to those in the as-milled state. Activation processes and capacity increase were observed, Fig. 7. It can be seen that for TiNi and TiNi_{0.8}Co_{0.2} alloys the activation lasts about five charge/discharge cycles and the maximum capacities attained are 67 and 83 mAh/g, respectively. The compositions TiNi_{0.8}Fe_{0.2} and TiNi_{0.8}Sn_{0.2} have longer activation period and their capacity increase start after the 15th cycle. The maximum value of the capacity for the TiNi_{0.8}Fe_{0.2} and TiNi_{0.8}Sn_{0.2} is ~80 and ~44 mAh/g, respectively. The discharge capacities of the annealed TiNi_{0.8}Co_{0.2} and TiNi_{0.8}Fe_{0.2} are almost the same, as the first one is slightly higher. Table 2 presents the initial capacity and the capacity at the fiftieth discharge cycle for the alloys studied.

4. Conclusion

Ni-substituted amorphous and nanocrystalline TiNi alloys (TiNi_{1-x}M_x, M = Co, Fe, Sn; x = 0 and 0.2) were synthesized by high-energy ball milling. A favoring effect of Sn on the grain size refinement of the alloy during milling was found. The as-milled alloys revealed high thermal stability. Significant microstructural coarsening of the nanostructured alloys starts at annealing temperatures above 500 °C only.

The electrochemical hydrogen capacity of the as-milled amorphous/nanocrystalline alloys is lower than that of the annealed nanocrystalline alloys with slightly coarser microstructure. The annealed samples need activation. Ni substitution by Co and Fe in the TiNi alloys results in improved hydrogen absorption properties and Sn addition makes them worse. TiNi_{0.8}Fe_{0.2} alloy exhibits the highest capacity in as-milled state, but after annealing both Fe and Co-containing materials show almost the same capacity of 80–85 mAh/g.

Acknowledgments

The work has been supported by the Bulgarian Scientific Research Fund under grant BYX-14/05 and by the National Science Fund, Project "University research center on nanotechnologies and new materials".

References

- L. Zaluski, A. Zaluska, J.O. Ström-Olsen, J. Alloys Compd. 253–254 (1997) 70.
- [2] K.H.J. Buschow, P.C.P. Bouten, A.R. Miedema, Rep. Prog. Phys. 45 (1982) 937.
- [3] D.H. Bradhurst, Metals Forum 6 (1983) 139.
- [4] M. Jurczyk, E. Jankowska, M. Nowak, J. Jakubowicz, J. Alloys Compd. 336 (2002) 265–269.
- [5] S. Miyazaki, Y. Igo, K. Otsuka, Acta Metall. 34 (1986) 2045.
- [6] Y. Lin, G.S. Tan, Intermetallics 8 (2000) 67.
- [7] F. Cuevas, M. Latroche, P. Ochin, A. Dezellus, J.F. Fernández, C. Sánchez, A. Percheron-Guégan, J. Alloys Compd. 330–332 (2002) 250–255.
- [8] H. Aoyagi, K. Aoki, T. Masumoto, J. Alloys Compd. 231 (1995) 804.
- [9] S.B. Jung, J.H. Kim, K.S. Lee, Nanostruct. Mater. 8 (1997) 1098.
- [10] E. Jankowska, M. Jurczyk, J. Alloys Compd. 372 (2004) L9–L12.