Nickel–metal hydride battery using nanocrystalline TiFe-type hydrogen storage alloys

E. Jankowska[a,*], M. Makowiecka[b], M. Jurczyk[b]

[a] *Central Laboratory of Batteries and Cells, Forteczna 12 St., 61-362 Poznan, Poland*
[b] *Institute of Materials Science and Engineering, Poznan University of Technology, M. Sklodowska Curie 5 Sq., 60-965 Poznan, Poland*

Abstract

Mechanical alloying (MA) process was used to synthesize nanocrystalline TiFe-type alloys. XRD analysis showed that, firstly, after 20 h of milling, the starting mixture of the elements had transformed into an amorphous phase and, secondly, the annealing in high purity argon at 700 °C for 0.5 h led to formation of the CsCl-type structures with crystallite sizes of about 30 nm. It was found that the respective replacement of Fe in TiFe by Ni and/or by Al and Cr improved both the discharge capacity and the cycle life of these electrodes. In the nanocrystalline $TiFe_{0.125}Cr_{0.125}Ni_{0.75}$ powder discharge capacity up to 154 mA h g^{-1} was measured (at 40 mA g^{-1} discharge current). Some of the produced nanomaterials were used as negative electrodes in sealed Ni/MH button cells. The results show that the sealed battery using the nanocrystalline $TiFe_{0.25}Ni_{0.75}$ or $TiFe_{0.3}Ni_{0.5}Co_{0.2}Zr_{0.05}$ alloys have about 1.5 times the capacity of the TiFe one.
© 2005 Published by Elsevier B.V.

1. Introduction

The nickel–metal hydride (Ni/MH) cell has a hydrogen storage material as its negative electrode, which is able to absorb and desorb reversibly a large amount of hydrogen at room temperature [1–4]. These batteries attracted increasing attention due to its various advantages. They widely are used from communication to hybrid electric vehicles.

The polycrystalline TiFe(Ni) system has been widely studied in the past [4–7]. TiFe alloy, which crystallizes in the cubic CsCl-type structure, can absorb up to 2 H/f.u. at room temperature. After activation the TiFe reacts directly and reversibly with hydrogen to form two ternary hydrides TiFeH (orthorhombic) and $TiFeH_2$ (monoclinic). The application of TiFe material in cells has been limited due to poor absorption/desorption kinetics in addition to a complicated activation procedure [6]. The discharge capacity of TiFe alloy in

polycrystalline form was 0.07 mAh g^{-1} at discharge current of 4 mA h [8]. The property of this alloy can be stimulated by partial replacement of iron by some amount of transition metals in the TiFe system or by modification of the microstructure which may improve the properties of the alloy for practical use, e.g. as active material in MH electrode [4,9,10]. Earlier, the effect of high-energy ball-milling (HEBM) on the electrochemical properties of TiFe electrode material has been investigated [10]. The discharge capacity of HEBM TiFe material increased to 64 mAh g^{-1}.

During last years, mechanical alloying (MA) has been proved to be a promising method for preparation of the wide range of materials for energy storage or other energy-related applications [4]. The use of mechanical alloying technique is very effective in lowering the cost of hydrogen storage materials.

In present work, we have shown that the properties of nanocrystalline TiFe-type alloys can be stimulated by partial replacement of iron by some amount of transition metals (Ni, Al, Cr, Co, Mo or Zr). These alloys produced by mechanical

* Corresponding author. Fax: +48 61 879 30 12.
E-mail address: jankowska_ewa@o2.pl (E. Jankowska).

alloying followed by annealing were used as negative electrode for testing the charge/discharge cycles in half-cells and in sealed Ni/MH cells.

2. Experimental details

The nanocrystalline TiFe-type powders were prepared by MA and annealing the stoichiometric amounts of the constituent elements (the purity more than 99.8 wt.%). These materials were processed under a high purity argon atmosphere using SPEX 8000 Mixer Mill (USA). The elemental powders were mixed in glove box (Labmaster 130) and poured into the vial. The mill was run up to 25 h for every powder preparation. The as-milled powders were heat-treated at 700 °C for 0.5 h under high purity argon to form CsCl-type phase. The MA process has been studied by X-ray powder diffraction analysis with Co Kα_1 radiation at the various stages during milling. Crystallite sizes were determined by atomic force microscopy (AFM).

The mechanically alloyed and annealed (nanocrystalline) materials with 10 wt.% addition of tetracarbonylnickel powder, were subjected to electrochemical measurements as working electrodes. A detailed description of the electrochemical measurements was given in Refs. [8–10].

The cyclic behavior of the nanocrystalline alloy anodes was examined in a sealed HB 116/054 cell (according to the international standard IEC no. 61808, related to the hydride button rechargeable single cell) [11]. The mass of the active material was 0.33 g. To prepare MH negative electrodes, alloy powders were mixed with addition of 5 wt.% tetracarbonylnickel. Then this mixture was pressed into the tablets which were placed in a small basket made of nickel nets (as the current collector). The sealed Ni/MH cell was constructed by pressing together the negative and positive electrode, polyamide separator and KOH ($\rho = 1.20 \, \text{g cm}^{-3}$) as electrolyte solution. The cell with electrode fabricated from nanocrystalline materials was charged at current density of $i = 3 \, \text{mA g}^{-1}$ for 15 h and after 1 h pause discharged at current density of $i = 7 \, \text{mA g}^{-1}$ down to 1.0 V. All electrochemical measurements were performed at $20 \pm 1 \, °\text{C}$.

3. Results and discussion

The effect of MA processing was studied by X-ray diffraction. For example, in the case of Ti–Fe powder mixture the originally sharp diffraction lines of Ti and Fe gradually become broader and their intensity decreases with milling time (not presented in Fig. 1). The powder mixture milled for more than 20 h has transformed completely to the amorphous phase ("X-ray-amorphous"), without formation of other phases (Fig. 1). Formation of the nanocrystalline alloys was achieved by annealing of the amorphous material in high purity argon atmosphere at 700 °C for 0.5 h. For all studied compositions, the diffraction peaks were assigned to CsCl-type structures
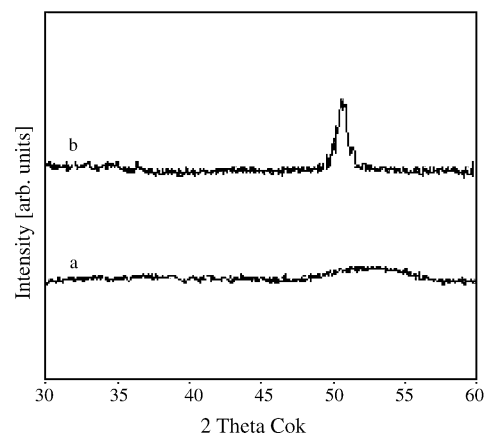

Fig. 1. XRD spectra of nanocrystalline Ti and Fe powders mechanically alloyed in argon atmosphere for 25 h (a) and heat-treated at 700 °C for 0.5 h (b).

(Table 1). When nickel is substituted for iron in TiFe$_{1-x}$Ni$_x$ the lattice constant a increases.

The average crystallite size of the nanocrystalline TiFe powders, according to AFM studies, was of the order of 30 nm.

The discharge capacity of electrodes prepared by application of mechanically alloyed TiFe alloy powder is very low (Fig. 2) though the MA TiFe alloys showed a higher discharge capacity ($0.7 \, \text{mA h g}^{-1}$) than the arc melted ones. The reduction of the powder size and the creation of new surfaces is effective for the improvement of the hydrogen absorption rate. Materials obtained by the substitution of Ni for Fe in TiFe$_{1-x}$Ni$_x$ lead to great improvement in activation behavior of the electrodes. It was found that the increasing nickel content in TiFe$_{1-x}$Ni$_x$ alloys leads initially to an increase in discharge capacity, giving a maximum at $x = 0.75$ (Fig. 2). In the annealed nanocrystalline TiFe$_{0.25}$Ni$_{0.75}$ powder, discharge capacity of up to $155 \, \text{mA h g}^{-1}$ was measured. The electrodes mechanically alloyed and annealed from the elemental powders displayed the maximum capacities at around the 3rd but, especially for $x = 0.75$ in TiFe$_{1-x}$Ni$_x$ alloy, degraded slightly with cycling. This may be due to the easy formation of the oxide layer (TiO$_2$) during the cycling. On the other hand, the discharge capacity of nanocrystalline

Table 1
Structural parameters and discharge capacities of nanocrystalline TiFe-type materials on 3rd cycle in half-cell (current density of charge/discharge was $40 \, \text{mA g}^{-1}$)

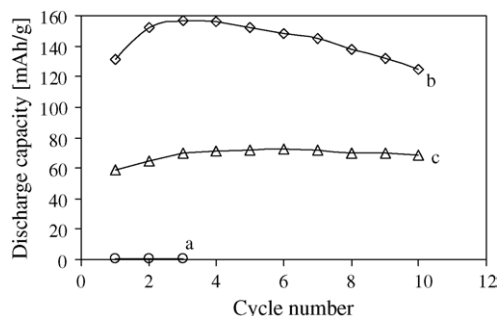| Composition	a	Discharge capacity	
		On 3rd cycle	On 10th cycle
TiFe	2.973	0.7	–
TiFe$_{0.25}$Ni$_{0.75}$	3.010	155	133
TiFe$_{0.125}$Al$_{0.125}$Ni$_{0.75}$	3.013	140	120
TiFe$_{0.125}$Cr$_{0.125}$Ni$_{0.75}$	3.011	154	134
TiFe$_{0.125}$Co$_{0.125}$Ni$_{0.75}$	3.010	113	105
TiFe$_{0.125}$Mo$_{0.125}$Ni$_{0.75}$	3.013	122	100
TiFe$_{0.3}$Ni$_{0.5}$Co$_{0.2}$Zr$_{0.05}$	3.012	128	126
TiNi	3.018	67	67

Fig. 2. Discharge capacities as a function of cycle number of electrodes prepared with nanocrystalline: (a) TiFe; (b) $TiFe_{0.25}Ni_{0.75}$; (c) TiNi powders (6 M KOH solution; the charge/discharge conditions were $40\,mA\,g^{-1}$ and the cut-off potential was $-0.700\,V$).
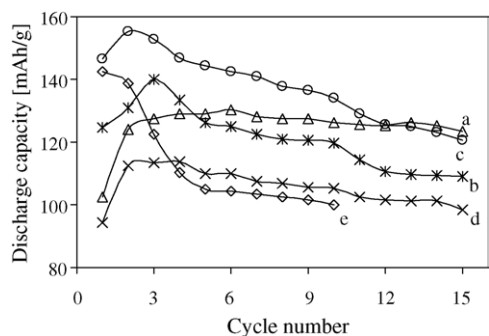

Fig. 3. Discharge capacities as a function of cycle number of electrodes prepared with nanocrystalline: (a) $TiFe_{0.3}Ni_{0.5}Co_{0.2}Zr_{0.05}$, (b) $TiFe_{0.125}Al_{0.125}Ni_{0.75}$, (c) $TiFe_{0.125}Cr_{0.125}Ni_{0.75}$, (d) $TiFe_{0.125}Co_{0.125}Ni_{0.75}$ and (e) $TiFe_{0.125}Mo_{0.125}Ni_{0.75}$ powders (6 M KOH solution; the charge/discharge conditions were $40\,mA\,g^{-1}$ and the cut-off potential was $-0.700\,V$).

Table 2
Discharge capacities of nanocrystalline TiFe-type materials on 1st and 3rd cycle in sealed HBL 116/055-type cell (current density of discharge was $7\,mA\,g^{-1}$)

Composition	Discharge capacity	
	On 1st cycle	On 3rd cycle
TiFe	–	–
$TiFe_{0.25}Ni_{0.75}$	29	42
$TiFe_{0.3}Ni_{0.5}Co_{0.2}Zr_{0.05}$	27	42
TiNi	26	30

$TiFe_{0.3}Ni_{0.5}Co_{0.2}Zr_{0.05}$ powder has not changed much during cycling. The alloying elements Ni, Co, Zr, substituted simultaneously for iron atoms in nanocrystalline TiFe master alloy prevented oxidation of this electrode material. On the other hand, it was found that the substitution of iron by Cr in $TiFe_{0.125}M_{0.125}Ni_{0.75}$ materials leads to an increase in

discharge capacity in comparison to basic alloy. In nanocrystalline $TiFe_{0.125}Cr_{0.125}Ni_{0.75}$ powders discharge capacities up to $160\,mAh\,g^{-1}$ was measured (Fig. 3) (Table 2).

4. Conclusion

In conclusion, nanocrystalline TiFe-based alloys synthesized by MA and annealing were used as negative electrode materials for Ni/MH cell. The discharge capacity of electrode prepared by application of MA and annealed TiFe powder displayed low capacity. It was found that the replacement of Fe in TiFe by Ni and/or by Al and Cr improved not only the discharge capacity but also the cycle life of these electrodes. Some of the studied alloys were used as negative electrodes for sealed Ni/MH cells. The results show that the sealed cells using the nanocrystalline $TiFe_{0.25}Ni_{0.75}$ and $TiFe_{0.3}Ni_{0.5}Co_{0.2}Zr_{0.05}$ alloys have about 1.5 times the capacity of the TiFe one.

References

[1] L. Zaluski, A. Zaluska, J.O. Ström-Olsen, J. Alloys Comp. 217 (1995) 245–249.
[2] G. Liang, S. Boily, J. Huot, A. van Neste, R. Schultz, J. Alloys Comp. 276 (1998) 302–306.
[3] G. Sandrock, J. Alloys Comp. 293–295 (1999) 877–888.
[4] M. Jurczyk, Curr. Top. Electrochem. 9 (2003) 105–116.
[5] J.J. Reilly, Z. Phys. Chem. 117 (1979) 155–160.
[6] M.H. Mintz, S. Vaknin, S. Biderman, Z. Hadari, J. Appl. Phys. 52 (1981) 463–467.
[7] C.S. Wang, Y.Q. Lei, Q.D. Wang, J. Power Sources 70 (1998) 222–227.
[8] M. Jurczyk, E. Jankowska, M. Nowak, J. Jakubowicz, J. Alloys Comp. 336 (2002) 265–269.
[9] M. Jurczyk, E. Jankowska, M. Makowiecka, I. Wieczorek, J. Alloys Comp. 354 (2003) L1–L4.
[10] E. Jankowska, M. Jurczyk, J. Alloys Comp. 346 (2003) L1–L3.
[11] J.M. Skowronski, A. Sierczynska, M. Kopczyk, J. Solid State Electrochem. 7 (2002) 11–16.