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ORIGINAL PAPER

Electrochemical hydriding of nanocrystalline TiFe alloys

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Abstract Nanocrystalline TiFe alloys with different morphology and microstructure were synthesized by mechanical alloying from the elemental powders with varied milling time. The particle morphology distinctly changes from globular to slaty between the 10th and 15th h of milling and then becomes spherical again after 30 h. The average particle size decreases continuously with milling time from about 50 μm (10 h milling) to 1–2 μm for the 30 h milled sample. X-ray diffraction analysis showed that after 15 h of milling alloying has already started. The initial mixture of metal powders transformed into amorphous or fine nanocrystalline material after 20 h. Further milling did not change the microstructure noticeably, i.e. it remaied nanocrystalline with some amount of amorphous fraction. Nanocrystalline Fe was also present in the end product. DTA analysis displayed exothermic effects due to crystallization reactions, revealing that the end product also contains the amorphous phase. Electrochemical hydrogen charge/discharge measurements of the as-milled alloys were carried out under galvanostatic conditions. It was found that with increased milling time the discharge capacity increased and reached a value of 230 mAh g^{-1} for the 30 h milled sample, which is a substantially higher value than those published for this alloy composition. The cycle life of the alloy with the finest nanostructure is, however, shorter compared to the coarser nanostructures.

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1 Introduction

The development of Ni–MH batteries has broadened the application of hydrogen storage alloys as precursors for negative electrodes [1]. Hydrogen storage alloys used for negative electrode materials must satisfy the following criteria [2]: large electrochemical capacity, high catalytic activity, high durability against oxidation in concentrated alkaline solution and very slow degradation with cycling. Well-known hydrogen-storage materials include AB, A_2B, AB_2 and AB_5 type intermetallic compounds. AB_5-type hydrogen storage alloys, such as $LaNi_5$ and $MmNi_5$-based (Mm is mischmetal) multi-component systems and zirconium – titanium – vanadium systems (AB_2 Laves phase-type) have been studied and successfully used as negative materials for commercial Ni–MH batteries [3–5]. However, these materials have a low hydrogen storage capacity resulting in a low electrode energy density. Generally, these two systems are hard to activate electrochemically, and so many charge/discharge cycles are necessary to reach full battery capacity [6]. Moreover, the main alloying elements in AB_2 systems, such as Ti, Zr, V, are costly, and V is also toxic. In the last ten years magnesium-based hydrogen storage alloys have shown great potential for use as hydride electrode materials for Ni–MH batteries because of their higher theoretical electrochemical capacity (999 mAh g^{-1}) and lower cost [7–9]. However, the electrodes prepared from Mg-based materials show short cycle life, due to their low corrosion stability in strong alkaline solutions.

TiFe alloy, a typical hydrogen storage alloy of the AB-type, is a prime candidate for hydrogen storage systems [10]. Generally, the titanium-based alloys are among the most promising materials for hydrogen storage. For example, TiFe intermetallic compound, which crystallizes in the cubic CsCl-type structure, is lighter and cheaper than the $LaNi_5$-type alloys [11]. Nevertheless, the application of these types of polycrystalline materials in batteries has been limited due to slow hydrogen absorption/desorption kinetics in addition to a complicated activation procedure [12]. Activation involves heating TiFe to a high temperature (about 450 °C) in vacuum and annealing in H_2 at a certain pressure (about 7 bar) [10, 13]. To improve the activation of these materials several approaches have been adopted. The replacement of Fe by a transition metal to form a secondary phase has been used to improve the activation properties of TiFe [14, 15]. Moreover, excess Ti in TiFe, i.e $Ti_{1+x}Fe$ enables the alloy to be hydrided without activation [11]. On the other hand, ball milling of TiFe is an effective way of improving the initial hydrogen absorption rate, due to the reduction in particle size and the creation of new clean surfaces [16, 17].

Although reliable studies on the gas phase hydrogen sorption properties of TiFe alloys with different microstructure (amorphous, nanocrystalline and polycrystalline) already exist [18–20], investigation of the electrochemical hydriding/dehydriding of nanostructured TiFe with different microstructure is still needed with the aim of optimisation. Moreover, formation of an amorphous layer at the surface or at the boundaries of FeTi crystals was found to have an influence on their hydriding behavior [19, 20]. Thus, the objective of the present work was to study the influence of microstructure on the electrochemical hydrogen capacity and cycle life of nanocrystalline TiFe alloys.

2 Experimental part

Powders of Fe (99.5%) and Ti (99.7%) in appropriate stoichiometric amounts were mixed together in the vial of a high-energy planetary mill (Fritch 5) to produce TiFe alloys.

Ball to powder mass ratio of 10:1 was used. The milling was performed under a protective Ar atmosphere and liquid n-heptane as a process control agent. Four different milling times (10, 15, 20 and 30 h) were applied in order to produce powders with different morphology and microstructure.

The mechanically alloyed powders were studied by X-ray diffraction (XRD) using Cu-K_α radiation, scanning electron microscopy (SEM, JEOL-5510), differential thermal analysis (DTA – Perkin Elmer) and a three-channel software controlled galvanostatic setup (developed in IEES-BAS).

The as-milled powders were used to prepare metal-hydride electrodes by mixing 100 mg alloy with 30 mg Teflonized carbon black (VULKAN 72 with 10 wt% PTFE). The mixture was pressed at about 1000 kg cm^{-2}. The electrode was charged and discharged in a 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 high-surface nickel foam sheet. The charge and discharge current was 100 mA g^{-1} and 20 mA g^{-1}, respectively.

3 Results and discussion

Four TiFe alloys were prepared by mechanical alloying (MA) with differing milling duration (10, 15, 20 and 30 h). The X-ray diffraction patterns of the as-milled alloys are presented in Fig. 1. Milling for 10 h results in iron and titanium grain size reduction only, Table 1. The average grain size, calculated by the Scherrer equation, for Fe and Ti is 35 nm and 55 nm, respectively. With increased milling time the diffraction peaks of Fe and Ti additionally broaden and partially overlap, an indication of a solid-state reaction resulting in the formation of TiFe. The powder milled for 15 h contains about 25 wt% highly disordered TiFe phase. Milling for 20 h leads to a substantial increase in the amount of TiFe (~80 wt%), having a nanocrystalline microstructure (3–4 nm). During further milling (30 h) the quantity of TiFe did not change noticeably, only the TiFe nanocrystals become slightly larger (4–5 nm). Nanocrystalline Fe is also present in the end product of milling,

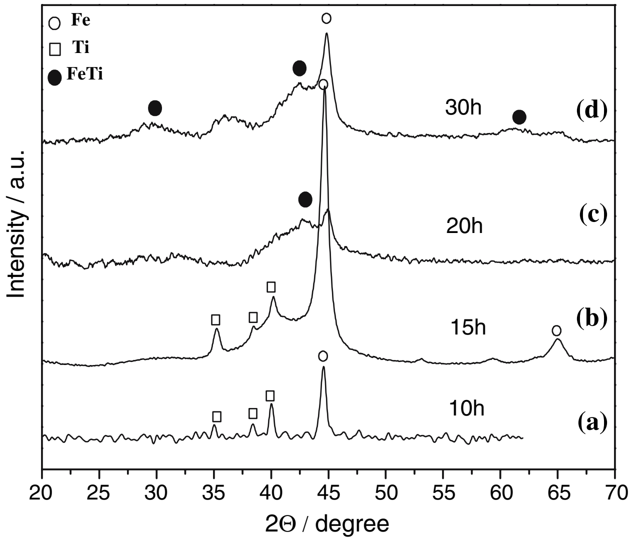

Fig. 1 X-ray patterns of the TiFe powders milled for different times

Table 1 Initial and maximum discharge capacity for the different as-milled TiFe alloys

Time of milling/h	Average grain size /nm			Initial discharge capacity/mAh g^{-1}	Maximum discharge capacity/mAh g^{-1}
	Fe	Ti	TiFe		
10	35	55	-	11	42
15	22	28	-	55	90
20	21	18	3–4	105	140
30	20	-	4–5	180	230

which probably means that Ti dissolves into TiFe. This is confirmed by the shift of the TiFe main diffraction peak ($2\theta = 43°$) to smaller angles (see Fig. 1).

To study the thermal behavior of the ball-milled alloys a DTA analysis of the as-milled (20 h and 30 h milled) alloys was carried out (Fig. 2). Several exothermic peaks in the range 350–550°C are clearly detected, most probably associated with the crystallization of amorphous (disordered) phase and/or with growth of existing nanocrystals, formed during milling. This result is in agreement with that obtained previously by Zaluski et al. [18–20]. A solid-state reaction resulting in TiFe formation is also possible during annealing of the ball milled material. In our study the enthalpy changes associated with the exothermic reactions observed by DTA are substantially larger for the alloy milled for 30 h compared to that milled for 20 h (see Fig. 2), showing that the amount of the amorphous (disordered) phase in both alloys is significantly different. The exothermic effects, obtained for the sample milled for 15 h, are substantially smaller than those of the 20 and 30 h milled samples and are hardly detectable by DTA, revealing that the amount of the amorphous phase in the samples milled for 10 h and 15 h is negligibly small. In order to analyse in detail the origin of the observed exothermic reactions XRD analysis of samples annealed after each of the thermal effects has to be carried out. A detailed study on the possibility of producing TiFe alloys with defined microstructures by combining ball milling with subsequent annealing is underway.

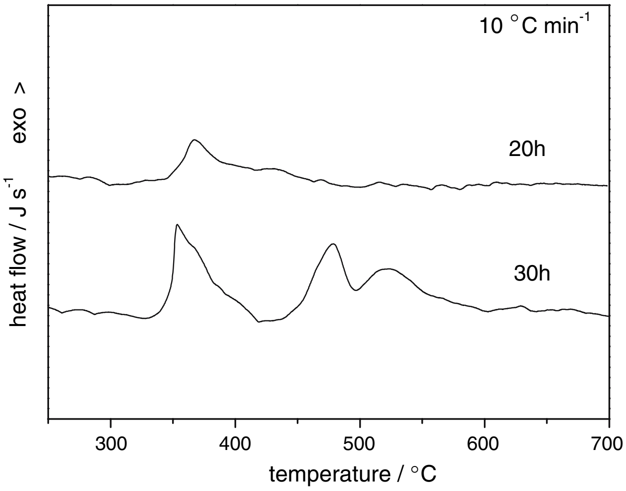

Fig. 2 DTA analysis of the as-milled alloys

Scanning electron microscopy (SEM) analysis showed particles size in the range of 10–100 μm with an average particle size of about 50 μm for the sample milled for 10 h as shown in Fig. 3a. The particles are agglomerates of smaller particles with almost spherical (oval) form. In contrast, the powders milled for 15 and 20 h contain particles with plate-like shape (Fig. 3b,c). The rather different morphology of the powders milled for different time is due

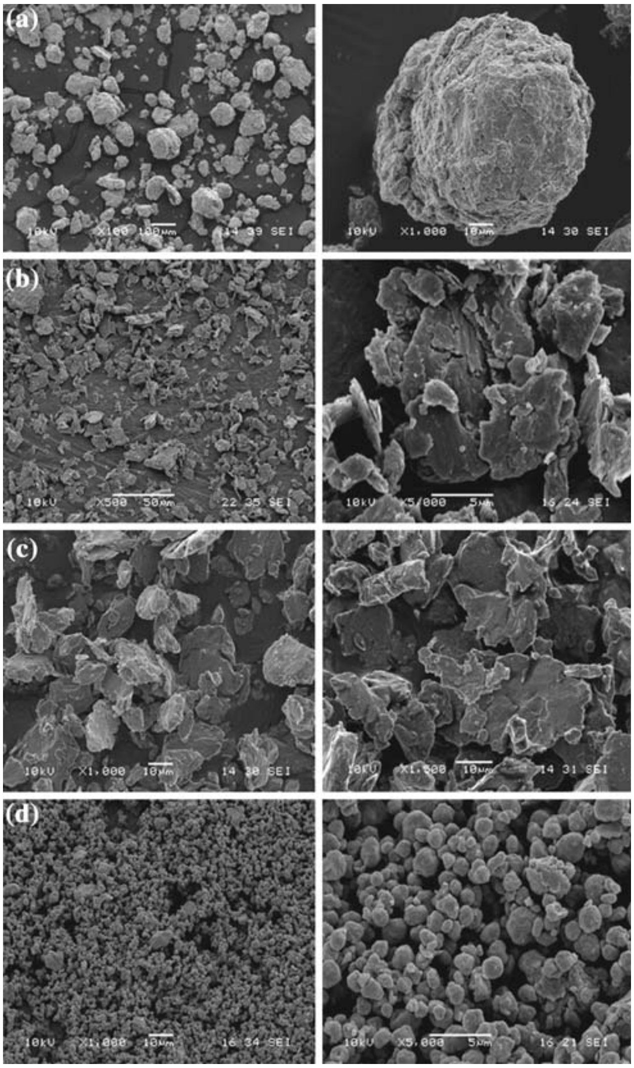

Fig. 3 SEM micrographs of the TiFe powders milled for (**a**) 10 h (**b**) 15 h (**c**) 20 h, and (**d**) 30 h

to a difference in the mechanical properties (hardness) of the materials, which is most clearly pronounced between the samples milled for 10 and 15 h. The particles of powder milled for 30 h again possess spherical shape, but the average size (1–2 µm) is drastically reduced compared to particles milled for 10 h only (Fig. 3d). During milling the particle size reduces progressively, as the first size-reduction (between 10 and 15 h) is larger (Fig. 4).

The electrodes prepared from TiFe alloys with different microstructure were charged for 10 h at current density of 100 mA g^{-1} and discharged at 20 mA g^{-1} to cut-off potential of –400 mV versus the reference electrode. Two discharge reactions were observed for all four alloys: the first at about 880 mV and the second at about 700 mV. While the first discharge reaction does not show a clear plateau, the second shows a near-horizontal line, Fig. 5. Obviously, the alloys contain two hydriding phases. Most probably these are the nanocrystalline and the amorphous phases, which may also differ slightly in their chemical composition. This result needs further investigation. The total discharge capacity as a function of charge/discharge cycle number is presented in Fig. 6. An initial discharge capacity increase with cycle number followed by a capacity decrease after a certain number of cycles is observed for all alloys. The discharge capacity maxima appear at different cycle number for the different alloys. For the sample milled for 10 h the activation lasts about 35 charge/discharge cycles and the maximum capacity attained is 40 mAh g^{-1}. The alloy milled for 30 h has shorter activation period (15 cycles) and its maximum capacity is 230 mAh g^{-1}. Table 1 presents the initial and the maximum capacity for the four alloys studied. With increasing milling duration the activation period falls and the maximum discharge capacity increases. The maximum capacity, measured for the alloy with the finest microstructure, 230 mAh g^{-1}, is substantially higher than all capacity values published for this alloy composition [11, 12]. The large difference between the electrochemical capacity measured in the present work and in previous studies can only be due to the microstructural difference. In the present study we use composite nanocrystalline/amorphous TiFe alloys, which are known to be appropriate for hydrogen storage. Additionally, the presence of nanocrystalline iron in the as-milled material might also be favorable for the hydriding process. The rate of capacity decrease, however, also increases with milling time (Fig. 6), most probably as a result of the decreased corrosion stability due to the finer microstructure of the long-time milled materials.

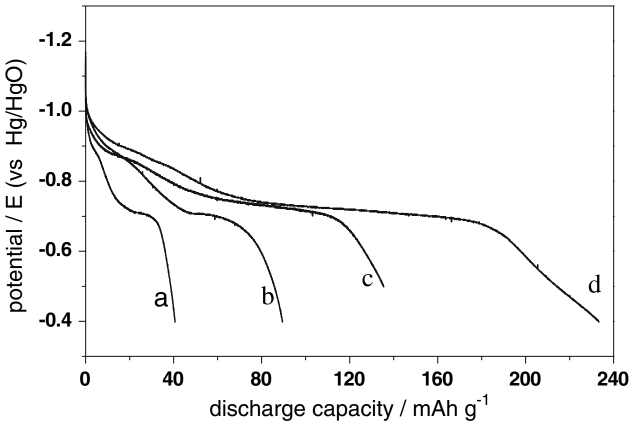

Fig. 5 Discharge curves of TiFe milled for different time (**a**) 10 h, (**b**) 20 h, (**c**) 25 h and (**d**) 30 h

4 Conclusion

Nanostructured TiFe alloys with different morphology and microstructure were synthesized by high-energy ball

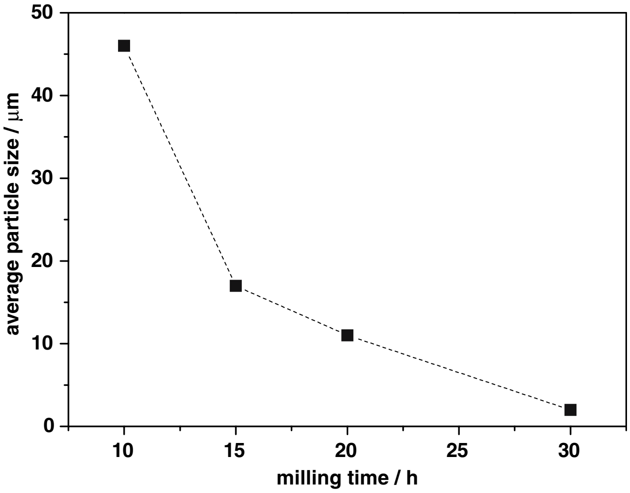

Fig. 4 Particle size vs. milling time

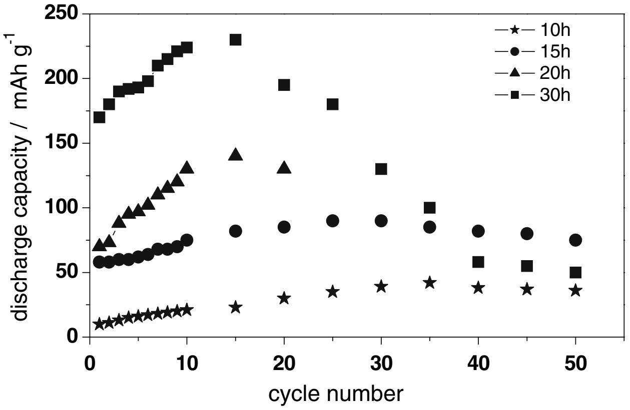

Fig. 6 Capacity as a function of cycle number for the different as-milled TiFe powders

milling. The evolution of the particle size was determined. The thermal stability and crystallization of the as-milled nanocrystalline alloys were investigated and formation of an amorphous phase during milling was found.

The electrochemical hydrogen capacity of the ball-milled nanostructured alloys depends on the microstructure. The alloy with the finest nanostructure, also containing an amorphous phase, shows the highest hydrogen capacity of 230 mAh g^{-1}, a value which is significantly higher than that obtained recently [11, 12]. All samples need activation, as refining the microstructure the activation time shortens. Whereas the alloys milled for 10 and 15 h have similar stability during continuous charge/discharge cycling those milled for 20 and 30 h show noticeably poorer cycle life, obviously due to the presence of a larger amount of amorphous phase in the last two alloys.

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