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Charge storage in 40/60 TiFe alloy electrodes

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Abstract Charge storage in 40/60 TiFe alloy has been investigated using electrode fabrication powder material, either of true alloy or of alloy precursor grades. The true alloy activated very reluctantly in that its maximum charge (i.e., hydrogen) capacity remained below 100 mA h g⁻¹. In contrast, the alloy precursor could be activated to an intrinsic capacity of ~300 mA h g⁻¹. Charge storage of the 40/60 TiFe alloy precursor was certainly affected by the redox reactions of surface Fe, but a large amount was stored as hydrogen absorbed by the material, as indicated by a dialometric test and the poison effect. X-ray and EDAX analyses of the two materials can account for their differing abilities to store charge.

Keywords Hydrogen · Hydrides · Intermetallic compounds · Titanium-iron alloy · Electrolysis

Introduction

The surface of the air-exposed, crushed 50/50 TiFe intermetallic compound (IMC), which is the usual form of the commercial product, is covered by a 10–30 nm thick oxide layer impervious to hydrogen, and hence hydriding of the virgin IMC requires previous activation by pressurized hydrogen at temperatures between 300 and 400 °C [1]. The surface of the activated TiFe thus shows the presence of metallic Fe [1], which predictably serves as the gating force for dissociative hydrogen absorption.

We recently found [2] that polycrystalline 50/50 TiFe can (in part) be hydrided also at room temperature when driven as a pressed powder electrode within the proper electrolytic environment. The activation consists of repeated charging-discharging cycles in aqueous K₂CO₃ where Fe surface oxides, attacked by carbonate anions, become suitable for cathodic reduction to metallic Fe. The activation rate is increased by using classical poisons of the hydrogen evolution reaction, such as thiourea or SeO₂.

When TiFe samples activated in carbonate were transferred to KOH (4–6 M), irreversible passivation occurred after cycling, which seemed to preclude this IMC from any electrochemical use. However, we subsequently found (Mengoli G, et al., unpublished results) that the cycle life of 50/50 TiFe is significantly improved when KOH is replaced by a 4 M KOH + 2 M LiOH mixture, as recommended for Ni-Fe and O₂-Fe alkaline batteries [3, 4].

All the data above point to one conclusion: that the presence of metallic Fe at the IMC surface and the actual reversibility of surface Fe redox reactions are the clue to both TiFe hydride formation and its cycle life in an electrochemical environment.

Therefore, the question remains: could electrode performance be improved with an alloy richer in Fe than the 50/50 compound? To address such a question we considered that Fe and Ti form two well-defined IMCs, stoichiometric TiFe and TiFe₂ [5] (AB and AB₁, families [6]). The latter does not absorb hydrogen but every composition richer in Ti than TiFe₂ does [7]. Thus, the present investigation concerns the commercially available 40/60 TiFe alloy.

Experimental

Materials

Two grades of 40/60 TiFe powder were used, both supplied by Goodfellow. One was already available by catalogue as the “alloy precursor”, having particle size ≤ 150 µm and melting point.
1380 °C (Goodfellow), which according to the producer is not a true alloy but is made by sintering a blend of powders of the component metals to achieve alloying by diffusion; the resultant cake is ground and sieved to the required particle size. The other “true alloy” was specially prepared at our request, again with particle size ≤ 150 μm and m.p. 1380 °C.

The 50/50 TiFe IMC was also supplied by Goodfellow. The Fe powder was of the following grades: “ferrum reductum” with particle size ≤ 50 μm supplied by Fluka and SNDC-NIFE material specially designed for Ni-Fe batteries.

The electrodes were prepared by inserting a weighed amount of powder(s) onto a weighed strip of Ni foam (“Sorapex”) followed by pressing at 100–300 atm, fixing by immersion in a dilute solution of epoxy resin, and drying in hot air.

The chemicals for the electrolytic solutions, K2CO3, KOH, LiOH, thiourea and SeO2, were all reagent grade. H2O was of Millipore grade. N2 was 99.9% purity gas from SIO.

Apparatus and procedure

TiFe powders were analyzed by X-ray diffraction with a Philips PV3710 instrument (Cu Kα radiation, 40 kV and 30 mA). The equipment included a silicon spinning holder and a graphite monochromator. The detected range was between 5° and 90° (2θ).

Scanning electron microscopy (SEM) observations were made with a Philips XL-40 LaB6 apparatus. Quantitative standardless microanalyses were obtained using an energy dispersive analysis (EDAX) X-ray spectrometer with a Be window.

The samples used as working electrodes in typical electrochemical tests were squares cut from the larger pressed powder strips prepared as above. Each square was pressure bonded to a Ni wire, which constituted support for the sample as well as the electrical connection. Table 1 gives the characteristics (composition, weight and dimensions) of the samples used for voltammetric and charging-discharging runs. The content of the active material for each sample was between 70% and 80% of the total weight.

The counter electrode was a Ni foil (diameter = 0.1 cm, l = 50 cm) rolled around the working electrode. The reference electrode was Hg/HgO-0.1 M KOH.

The three-electrode system was supported by the Teflon lid of a cylindrical uncompartmented Pyrex cell of 50 mL capacity. The cell was equipped with an inlet-outlet pipe system, which allowed a continuous N2 draft to remove the gas produced by electrolysis. All experiments were carried out at 25 °C.

The electrochemical instrumentation consisted of AMEL and PAR apparatus interfaced with either an x-y recorder or a PC. Voltammetric and charging/discharging data were directly versus HgO. In the plots, the discharges are represented as working minus reference potential differences, ∆E, decreasing with time, thus mimicking the behaviour of a real battery.

The volumetric increments involved in the charging/discharging processes were monitored from the mechanical stress induced in specially designed asymmetrical electrodes. These consisted of pressed powder strips with contact to the electrolyte on only one face. The other face was masked with an insulating coating. One end of the strip was fixed to a support whereas the other was free to move in consequence to any volumetric changes. Although the described specimens likely have a porous structure, they do account for the volumetric changes occurring in the component particles; in fact, not only the powder particles are in tight contact since they were compacted under high pressure, but they are also bound to a non-rigid, light support (Ni foam) whereby the stress originated in the particles is transferred to the specimen, causing visible bending.

Using a custom-made apparatus whose core is the arm of a balance directly applied onto the free end of the strip, any stress due to volumetric changes was directly measured by the weight (i.e., the force) necessary to offset it [8, 9].

Results and discussion

X-ray analysis

In order to set a standard for our X-ray analysis, the diffraction pattern of 50/50 TiFe IMC was first achieved by detecting three main lines at 43.104°, 62.49° and 78.77° (2θ), in full agreement with the provisions of the literature (JCPDS 19-636).

The “true” 40/60 TiFe alloy gave the diffraction pattern shown in Fig. 1. The lines marked by a cross can be ascribed to stoichiometric TiFe; those marked by a circle are likely due to TiFe2 species, whereas those marked by a square might be explained by a hypothetical Ti3Fe5 phase; this last is suggested by comparison with the peaks present on the diffraction pattern of Ti3Fe5 (JCPDS 12-594). SEM observation coupled with EDAX analysis, however, showed a very homogenous particle composition at 40/60 TiFe atom ratio, pointing to a true alloy.

The X-ray pattern of the alloy precursor is shown in Fig. 2. The lines marked by a cross are very similar to those of pure Fe (JCPDS 6-966); the lines marked by a circle are similar to those of Ti (JCPDS 44-1294) except for a non-negligible shift with respect to the pure metal. Minor peaks marked by a square can again be ascribed to either 50/50 TiFe or to TiFe2. Some of these lines are split due to the possible presence of hydrogen, the up-take of which might have occurred during the synthesis.

SEM observations coupled with EDAX analysis carried out in different spots and on different particles of this material have shown the presence of both Ti and Fe, but with a variable atom ratio which depended strongly upon either the sampled area or the sampled particle. In conclusion, X-ray and surface analysis point to a highly disordered system which more resembles a solid solution than an alloyed compound.

Electrochemical behaviour of 40/60 TiFe true alloy

The dotted curve of Fig. 3 shows the cyclic voltammogram (CV) (v = 1 mV s⁻¹) pattern achieved from sample 1 during one of the initial scans in 4 M KOH + 2 M LiOH. The currents were low and peak resolution was poor because of the high resistance of the surface layers. After 20 charging-discharging galvanostatic runs, carried out in aqueous K2CO3 with thiourea additive and then in KOH + LiOH (see below), the voltammetric