

# BULK- AND SURFACE-MODIFIED HYDROGEN STORAGE MATERIALS ON THE BASIS OF TiFe

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## Introduction

TiFe intermetallic compound is a well-studied hydrogen storage material known for more than 30 years [1,2]. It is still one of the most promising hydrogen storage alloys, due to its reasonable storage capacity (~1.8 wt% H), abundance and low cost. Main drawback of TiFe and its derivatives is that they have poor activation performances and poisoning tolerance resulting in the suppression of hydrogen sorption even by trace amounts of gas species including oxygen and water vapours [3,4]. Attempts to address these problems included ball milling of the parent alloy together with an additive of Pd (H<sub>2</sub> dissociation catalyst [5]) or carbon (to prevent surface oxidation [6]). It was also shown [7] that Pd deposition onto TiFe promotes hydrogenation of the non-activated substrate, and the hydrogen uptake rate can be further increased by annealing of the Pd-capped TiFe in air. Most probably, the latter takes place due to formation of oxygen-containing phases (e.g., Ti<sub>4</sub>Fe<sub>2</sub>O<sub>1-x</sub>) which were shown to easily absorb hydrogen at mild conditions [8]. Interesting, that the formation of such phases was observed in the course of sintering of Ti and Fe powders in non-purified hydrogen (0.2% O<sub>2</sub>), to yield TiFe as a major product [9].

This work presents experimental results on comparison of structure, morphology and hydrogen absorption characteristics of core and surface-modified by Pd electroless deposition samples of TiFe prepared by arc-melting and sintering.

## Experimental

TiFe alloy was prepared by arc melting of the starting metals (99.99%) taken in equiatomic amounts (total charge weight ~5 g) in argon. Prior to further procedures (hydrogen sorption and surface modification experiments), the ingot was pulverised by ball-milling in argon for 10 minutes.

The sintered TiFe was prepared from metal powders (99.99%; particle size of 10 μ) mixed in atomic ratio Ti:Fe = 1.1:0.9. The mixture (~10 g) was placed into a quartz sample holder positioned in a quartz tube inside a tubular furnace. The tube was flushed with Ar for 1 hour at room temperature followed by heating to 1000 °C, maintaining the high temperature during 1 hour,

and cooling down to room temperature under Ar flow (estimated concentration of O<sub>2</sub> impurity below 0.01%).

Surface modification of the TiFe samples was done by electroless deposition of palladium in a hypophosphite-based plating bath [10].

The samples were characterised by XRD (Cu-K<sub>α</sub>; 2θ=30...85°), SEM / EDS, and volumetric measurements of hydrogen absorption (sample weight ~0.5 g; T=20 °C, P<sub>0</sub>~30 bar; no vacuum heating before first hydrogenation; further hydrogenations were preceded by heating the sample in dynamic vacuum to T=400 °C during 1 hour). Further details were presented in [10].

## Results and discussion

Fig.1 presents XRD patterns of the arc-melted (a) and sintered (b) samples of TiFe. Both samples contain bcc-TiFe, space group *Pm-3m*, as a major phase; the lattice periods (*a*= 2.9803(1) Å and *a*= 2.9780(2) Å for arc-melted and sintered material, respectively) were close to the reference data [11], *a*= 2.976 Å. At the same time, the sintered material additionally contained two impurity phases identified as η-Ti<sub>4</sub>Fe<sub>2</sub>O (*Fd-3m*; *a*= 11.316(1) Å) and Ti<sub>3</sub>O (*P312*; *a*= 5.115(2) Å, *a*= 14.458(8) Å). The presence of oxygen (2.86 wt.%) in the sintered sample was also confirmed by EDS and, most probably, originated from capturing trace amounts of O<sub>2</sub> from gas phase during sintering.

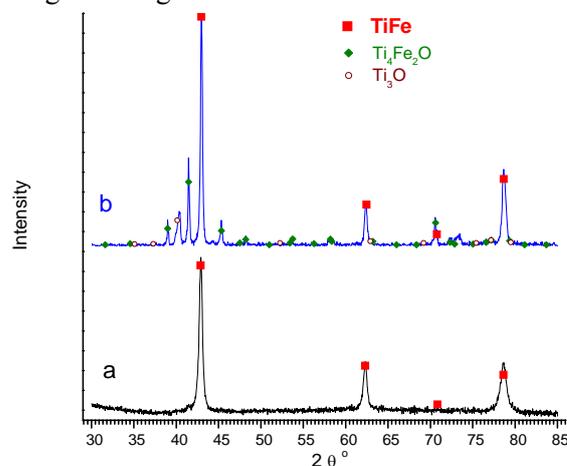


Fig. 1. XRD patterns of the arc-melted (a) and sintered (b) TiFe.

SEM images of the arc-melted and sintered samples of TiFe are shown in Fig.2. The arc-

melted material (A) is a dense alloy exhibiting characteristic flake-like structure of its fracture. The material prepared by sintering (B) consists of agglomerates of micron-size flakes exhibiting a smooth, “fused” surface. Discontinuous deposits of fine Pd particles on the surface were observed after electroless Pd deposition (C, D); the concentration of Pd on the surface (EDS) varied within 12–18 wt.%.

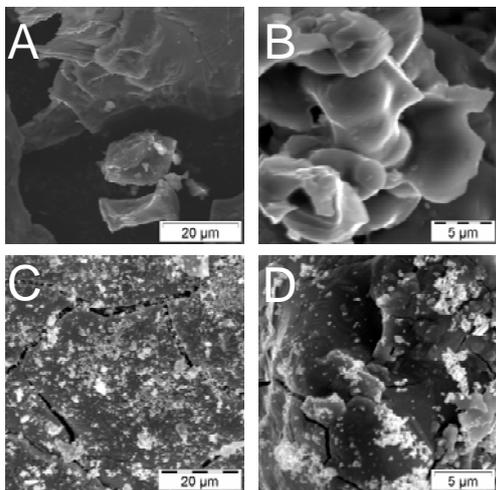


Fig. 2. SEM images of the arc-melted (A,C) and sintered (B,D) samples of TiFe: A,B – unmodified; C,D – surface-modified by electroless deposition of Pd.

Both arc-melted and sintered samples do not absorb hydrogen during the first hydrogenation. After heating in vacuum, slow hydrogen absorption was observed for the arc-melted sample (Fig.3, curve 1). For the sintered material the second hydrogenation proceeds much faster (curve 2).

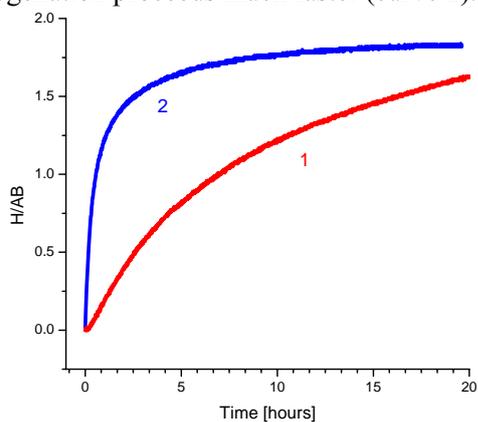


Fig. 3. Dynamics of hydrogen absorption (hydrogenation #2) by the unmodified arc-melted (1) and sintered (2) samples of TiFe.

So, the activation and hydrogenation performances of the sintered TiFe are significantly better than for the arc-melted one. This effect was associated with the presence of the oxygen-containing phases in the sintered sample acting as hydrogen transfer catalysts.

Surface modification results in further improvement of activation performances and

hydrogen absorption kinetics (Fig. 4). Hydrogen absorption was observed even on the first hydrogenation cycle carried out without activation by vacuum heating. The sintered surface-modified sample exhibited better hydrogenation performances than the arc-melted one showing shorter incubation period of first hydrogen absorption and very fast hydrogenation kinetics after vacuum heating.

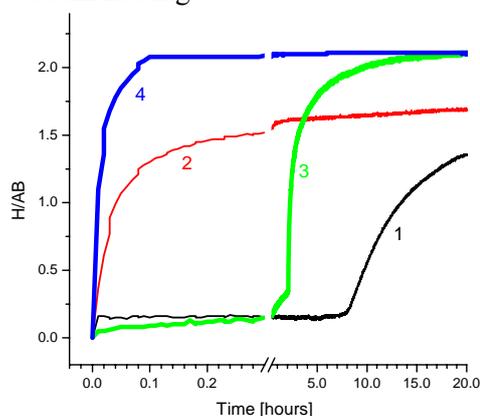


Fig. 4. Dynamics of hydrogen absorption by surface-modified arc-melted (1,2) and sintered (3,4) samples of TiFe: 1,3 – hydrogenation #1 (no vacuum heating); 2,4 – hydrogenation #2 after vacuum heating to 400 °C.

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