

Synthesis of TiFe Compound from Ball Milled TiH₂ and Fe Powders Mixtures

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Abstract. TiFe compound was produced by high-energy ball milling of TiH₂ and Fe powders, followed by heating under vacuum. TiH₂ was used instead of Ti in order to avoid the strong particles adhesion to grinding balls and vial walls. Mixtures of TiH₂ and Fe powders were dry-milled in a planetary mill for times ranging from 5 to 40 hours. The amount of sample, number and diameter of the balls were kept constant in all experiments. After milling, samples were heated under dynamic high-vacuum for the synthesis reaction. As-milled and heat-treated materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential thermal analysis (DTA). The mean crystallite sizes and microstrains were determined by XRD line profile analysis using the Warren-Averbach method. As-milled materials presented only Fe and TiH₂ phases. Nanostructured TiFe compound was formed after heat treatment. TiH₂ was effective for providing low adherence of the powders during milling.

Introduction

TiFe intermetallic compound has been normally produced by mechanical alloying through high-energy ball milling of titanium (Ti) and iron (Fe) powder mixtures in order to improve their properties concerning hydrogen storage (absorption and desorption) [1-9]. Several authors associated this improvement with formation of nanostructures during the milling process (nanocrystalline TiFe) [5-9]. However earlier attempts of present authors to synthesize TiFe by this route (in a shaker mill) have failed due to a strong sticking (cold welding) of both Ti and Fe powders (mainly to the vial), preventing mechanical alloying to succeed [10]. The first approach to solve this problem consisted of adding different process control agents (PCAs), like ethanol, stearic acid, low density polyethylene, benzene and cyclohexane at variable quantities and keeping constant other milling parameters like ball to powder ration and balls size. In spite of preventing strong adherence, it was seen that higher the amount of PCA, particularly benzene and cyclohexane, longer the time of milling to form TiFe phase, but only partially, since TiC was also formed as result from the decomposition of the PCAs during prolonged milling operation. The investigation was then proceeded but without adding any PCA and also using a planetary ball mill. Different procedures were compared in order to avoid or minimize cold welding: preliminary dirtying of the vial walls and the balls surfaces with powder mixture before milling the main charge; stepwise milling with stops for pausing, for opening the vial to follow the behaviour of the powder or for performing rotation and inversion of the vial between the steps; hydriding Ti powder and milling with Fe powder. The best yield (in terms of loose powder mass) was obtained with the last procedure carried out on a planetary mill (93% yield), but major TiFe formation was only attained after an annealing treatment [11]. That result has encouraged us to perform a more systematic investigation concerning the production of nanocrystalline TiFe compound after heating and reacting a milled mixture of TiH₂ and Fe powders.

Experimental

Ti and Fe powders (99,7 % pure, -325 mesh) were supplied by AEE (Atlantic Equipment Engineers). Initially titanium hydride (TiH_2) was produced by heating Ti powder under 10bar hydrogen atmosphere up to 500°C. TiH_2 and Fe powders were then weighted according to the TiFe compound stoichiometry. TiH_2 was selected as precursor powder, instead of Ti powder, due its fragility, beneficial to decrease adherence of powders on grinding tools. A planetary mill (Pulverisette 5 from FRITTSCH) were used to perform mechanical alloying. Each milling charge consisted of balls ($\varnothing=8$ mm) made of tool steel and 30g of TiH_2 and Fe powders mixture, being the ball-to-powder weight ratio equal to 20:1, which was kept constant in all batches. A cylindrical rounded-bottom vial, made from hardened steel and also built in-house (vol. ~ 250 cm³), was used for planetary milling, always operated at 300 rpm. Powders were handled in glove box with purified argon atmosphere during charge and discharge operations in order to guarantee an inert atmosphere inside the vial and to prevent burning of the milled product after opening the vial. Samples were dry milled for 5, 10, 25 and 40 hours. X-ray diffraction from Cu-K α radiation (XRD), scanning electron microscopy (SEM) and differential thermal analysis (DTA) were used for characterizing microstructure and phase transformations of the as-milled powders and after heat treatments. The mean crystallite sizes and microstrains were determined by XRD line profile analysis using the Warren-Averbach method. DTA was performed with a heating rate of 10°C/min up to 1000°C under an argon flow (1L/h).

Results and Discussion

It should be said that in spite of using TiH_2 instead of Ti, most powder mixture was adhered to the vial. Adherence however was weak enough that the adhered powder could be easily removed by using a stainless-steel orthodontic spatula (rounded ends). In any as-milled powder samples was observed the formation of compound TiFe, as shown powder diffraction patterns in Fig. 1, only reflections peaks corresponding to TiH_2 and Fe phases were detected. The intensity of the peaks decreased with the milling time due to the crystalline defects produced by the impact of the balls. TiFe compound non-formation also was observed in SEM micrographs from loose powders (Fig. 2). These micrographs (secondary electrons) show very fine particles and large agglomerates. The quantity of fine particles seems to decrease after prolonged milling time, e.g. 25h and 40h. From micrographs (back-scattered electrons) it can be seen that former particles are actually aggregates whose microstructure is made from alternated layers of TiH_2 (gray) and Fe (white) phases, which is particularly visible after 5h milling. After 10h milling, however, the aggregates microstructure is homogeneous, even when it is observed at higher magnification as in the case of the sample milled for 40h (indicated in Fig 3). White areas in the microstructure of samples milled for 25h and 40h are Fe reach and resulted from balls wear.

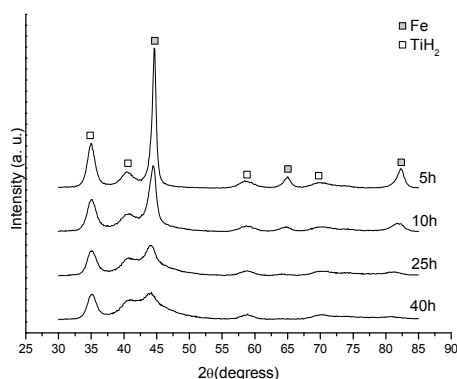


Fig. 1. Powder diffraction patterns from as-milled samples.

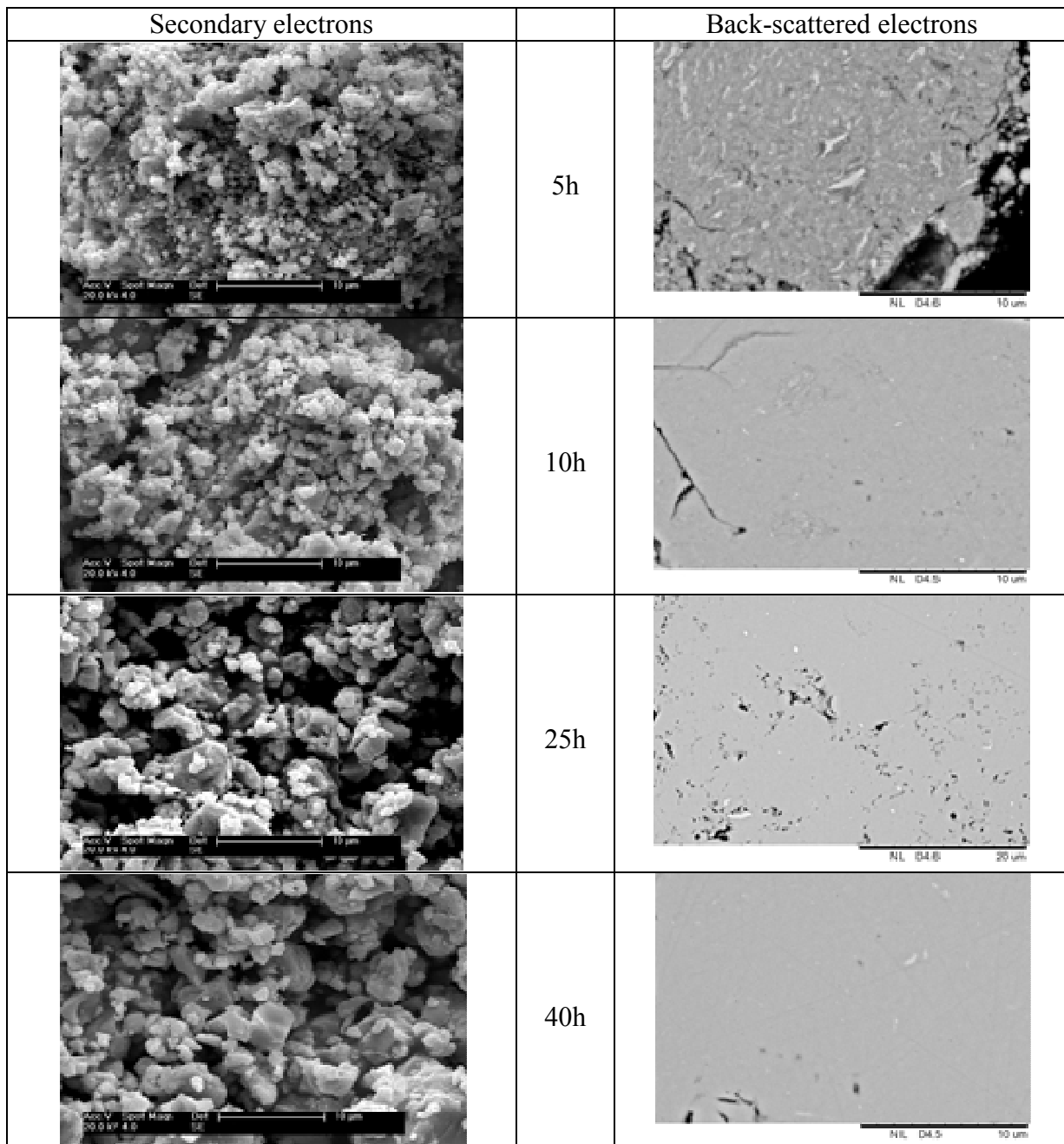


Fig. 2. SEM micrographs (secondary and back-scattered electrons) from as-milled samples.

Previous results indicated that a post heat treatment would be necessary to obtain TiFe compound. In order to verify the annealing temperature a differential thermal analysis was performed on as-milled samples. Results are shown in Fig.3. First endothermic peak occurred about 100°C and can be attributed to the water lost. Second and third endothermic peak going from 220°C to 240°C and from 420°C to 450°C, respectively can be related to the decomposition of TiH₂, according to the work of other authors [12,13]. Before the end of this third endothermic event it can be seen a exothermic peak ranging from 490°C to 510°C. Sample milled for 5h presented two small exothermic peaks in that range. It seems that the exothermic events in this case was weaker than the events from samples milled for longer times. The first exothermic event on each curve from Fig.4 can be related mainly to the TiFe compound formation. It should be said that in the temperature range of this first peak other authors verified a recrystallization of the amorphous TiFe [1,9]. A second and last exothermic event, weaker than the first one, is seen on each curve ranging from 730°C to 740°C. Novakova *et al.* also verified a second exothermic peak on a DTA and related this to the transformation of TiFe to TiFe₂ and α -Ti(verified by Mössbauer spectroscopy). Work is presently under way in order to confirm that result.

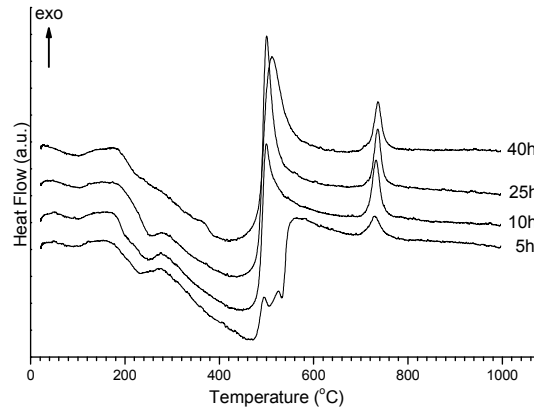


Fig. 3. Differential thermal analysis from as-milled samples.

TiFe compound formation was confirmed by DRX analysis from as-milled powders after a heat treatment under dynamic high-vacuum up to 600°C (and immediately cooled). Fig. 4 shows diffraction pattern from samples after this treatment. In any cases can be observed majority TiFe phase formation, however, samples milled for 5h and 10h showed second phases as Fe and TiO₃₂₅. In this cases TiO₃₂₅ was probably formed during the heat treatment due free Ti presence.). The mean crystallite sizes ($\langle L \rangle_A$) and microstrains ($\langle \epsilon^2 L \rangle^{1/2}$) from TiFe phase were determined by XRD line profile analysis using the Warren-Averbach method. Fig. 5 shows these results for each milled performed. In any milled was observed nanostructured TiFe compound formation ($\langle L \rangle_A < 20\text{nm}$) and relative low values for microstrain ($\langle \epsilon^2 L \rangle^{1/2} < 3.10^{-4}$). These microstrains results suggest that first exothermic peak observed in Fig. 3 are also related to a partial recrystallization of material.

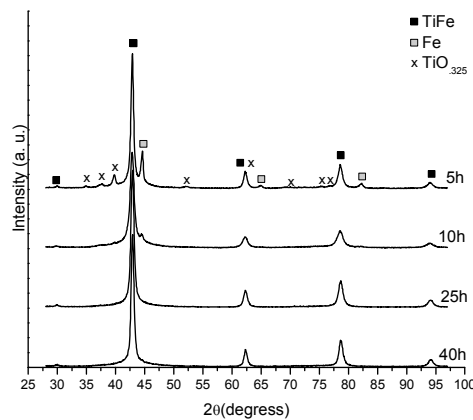


Fig. 4. Powder diffraction patterns from heat treated samples.

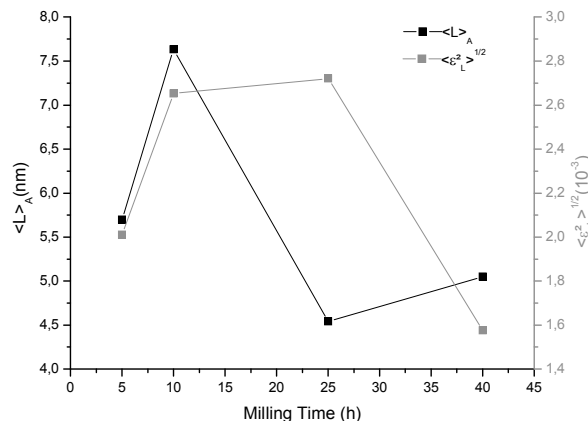


Fig. 5. Mean crystallite sizes ($\langle L \rangle_A$) and microstrains ($\langle \epsilon^2 L \rangle^{1/2}$) from TiFe phase.

Conclusions

In this study, we have successfully avoided strong adherence of the powders during milling, by starting with TiH₂ and Fe powder mixture. Nanostructured TiFe compound (<L>A<20nm) could be obtained after a heat treatment (600°C) from as-milled samples presented only Fe and TiH₂. These results suggest that milling route performed is viable to produce TiFe compound with suitable properties for hydrogen storage.

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