Two-step Processing for Hydrogen Storage FeTi alloys: Influence on Reaction Temperature

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Abstract

In the present work, nanostructured FeTi powders were produced by mechanical alloying, avoiding the unfavorable agglomeration problem by using a low energy milling (e.g. 300 rpm) of pure metallic constituents, Fe and Ti, followed by subsequent heat treatment at 800ºC. A major achievement of this research was to show that by modulating the milling intensity and total milling time, the high temperature synthesis reaction of FeTi (1100ºC) can be partially or totally suppressed, reverting instead to a metastable reaction path at low temperature (650ºC). The mechanical "activation" modifies the reactivity of the system, producing a very thin Ti /Fe layers. That in conjunction with a high level of defects induced mechanically may be responsible for the metastability.

Keywords: *Hydrogen storage, mechanical alloying, nanostructured intermetallics, FeTi, sodium borohydride, heat treatment.*

1 Introduction

FeTi intermetallic powders are very promising media for reversible hydrogen storage [1-4]. However, difficult activation treatments including annealing at elevated temperatures in high pressure H_2 gas atmosphere are mandatory. Mechanical alloying/milling (MA), is a high energy powder metallurgy (PM) processing technique involving dynamic cold welding and fracturing of particles to synthesize equilibrium or non-equilibrium microstructures including nanocrystalline materials. MA introduces a high density of crystal lattice defects such as dislocations, vacancies and grain boundaries, into the synthesized products. This mechanical activation facilitates hydrogen diffusion and absorption in nanocrystalline storage materials. The small grain size of obtained powders contributes as well for a larger available surface per volume for hydrogen absorption [5-11]. However, the undesired occurrence of complete cold-welding to container and milling balls during ball milling processing of Fe and Ti is frequent, inhibiting (or retarding) the full conversion of the starting materials to the target intermetallic compound FeTi and consequently making difficult the control of the microstructure and hydrogen properties of this alloy [12-15].

2 Experimental procedures

Synthesis of FeTi by ball milling of an equimolar elemental powder mixture composed of pure Ti (99.9wt%; 105μm) and pure Fe (99wt%; 44μm). A Retsch planetary ball mill Model PM100 was used in this work. A 250 ml stainless steel container was charged with a 20 g mixture of starting powders and 400 g of 10 mm diameter stainless steel balls. In order to prevent powder oxidation, the container was evacuated and filled with argon. The mill was operated at rotation speeds of

200-400 rpm. Phase identification of the as-milled and annealed powders was performed by x-ray diffraction (XRD) using Cu-Kα radiation. Differential thermal analysis (DTA) was carried out in the initial mixture and in the as-milled powders. The DTA runs went up to a maximum of 1100 ◦C, with heating and cooling rates of 20 ◦C/min, under argon at a flow rate of 15 cm3/min. Thermal stability of the as-milled powders was evaluated through analysis of material submitted to interrupted DTA runs.

A new approach to the production of the intermetallic phase was used. A set of experiments designed to prepare nanocrystalline FeTi phase consisted of:

a) Low energy milling (e.g. 300 rpm) to redistribute both elemental powders, Fe and Ti, in thin alternated lamellae without reaction, therefore avoiding the agglomeration/welding associated with the release of the heat of formation of the FeTi phase.

b) High temperature reaction of the milled powders leading to the synthesis of FeTi at much lower temperature (650ºC vs 1100ºC) than that of the conventional melting process.

3 Results and discussion

The milling energy for Fe+Ti mixture was set to a low value initially (200 rpm), with the objective of trying to reduce the extent of the FeTi synthesis reaction and thus agglomeration in the elemental powder mixture. However, with such low energy, 200 rpm, XRD peaks are essentially identical to those of the starting materials; **Fig. 1** depicts the effect of milling energy on the synthesis reaction of the Fe+Ti pre-milled mixture. Using higher energy, 400 rpm, the XRD peaks from Fe and Ti are no longer visible, but the FeTi peaks were more intense after the annealing. It was thus concluded that 200 rpm, while solving the agglomeration problem, was probably insufficient milling intensity to induce significant modification in the pristine powders.

Higher milling intensity (400 rpm), on the other hand, while having agglomeration difficulties, clearly shown the potential to induce metastable transformation. The DTA, in **Fig. 2**, shows two smooth exothermic peaks (675ºC and 807ºC), probably associated with synthesis reactions. As it is possible to observe in the XRD patterns, in **Fig. 1**, the peaks of intermetallic FeTi were more intense after annealing.

In the next set of experiments, the milling energy was adjusted to a low values (200 and 300 rpm), and a milling time of just one hour was used, with the objective of trying to reduce the degree of the FeTi synthesis reaction of the elemental powder mixture, and thus the extent of powder agglomeration. The microstructure in the particles is more homogeneous in samples milled at 300 rpm, than at 200 rpm, showing higher degree of mixture between components and, thinner lamellae, **Fig. 3**. So, the best compromise between powders homogeneity, size and energy seems to correspond to 1 hours of milling at 300 rpm. Thence, these conditions were used in the subsequent experiments.

Acceptably low values of both oxygen and nitrogen were obtained, Table 4. With respect to nitrogen this represents an order of magnitude improvement relative to prior millings in air (**Table 1**).

Table 1 Nitrogen and oxygen levels analysed by Leco.

	wt%O	**wt %N**
FeTi – 1H 300rpm	0.4195	0.0449

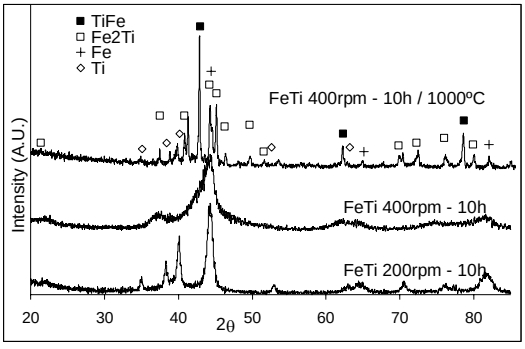

Fig. 1. XRD of the Fe+Ti after milling and annealing.

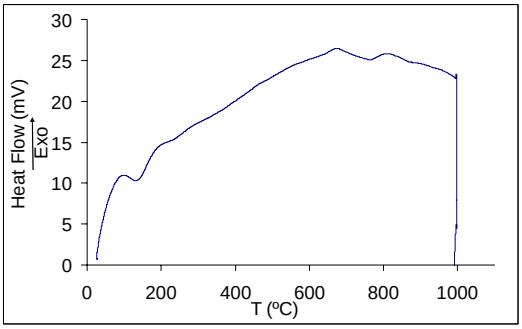

Fig. 2. DTA curve of the mixture FeTi 400rpm – 10h.

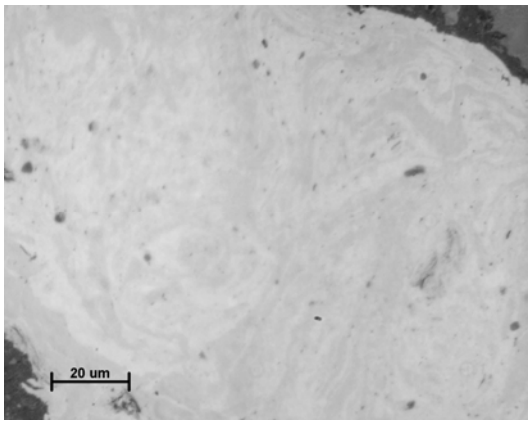

Fig. 3. Optical micrograph of Fe+Ti milled for 1h at 300 rpm.

After cleaning the container and balls in an argon filled glove box, to take a sample to DTA and DRX, the milling was continued for two additional periods of 30 minutes. The obtained powders are very fine and homogeneous, without agglomeration problems.

The DTA of Fe+Ti mixture, **Fig. 4**, shows two exothermic peaks (650ºC less intense and 1100ºC very intense), probably associated with two reaction paths. Increasing the milling time, the high temperature synthesis reaction (1100ºC) becomes less intense. A major achievement of this research was to show that by modulating the milling intensity and total milling time, the high temperature synthesis reaction (1100ºC) can be partially or totally suppressed, reverting instead to a metastable reaction path at low temperature (650ºC). It is possible to observe in the XRD patterns (**Fig. 5**), full conversion to intermetallic FeTi was achieved with a short milling time (1 hour) plus heat treatment. Similar phase constitution is obtained by high temperature synthesis reaction (from elemental powders), but with a short milling "activation" plus annealing, FeTi peaks are more intense and there are less secondary phases.

Based on the DTA and DRX results, the FeTi powders milled for 2 hours total at 300 rpm, were selected to continue the experiments. Consequently, these powders were annealed at 800ºC in a vacuum furnace (LPA furnace). From XRD data the average crystallite size, using the Scherrer's equation with the most intense FeTi reflection (110) of FeTi is 77 nm, indicating a nanostructured material.

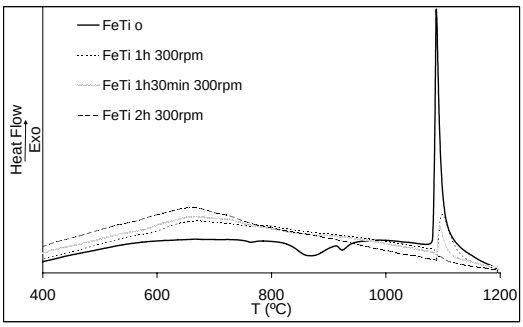

Fig. 4. DTA curves of the Fe+Ti mixture before milling and after milling for different times at 300 rpm

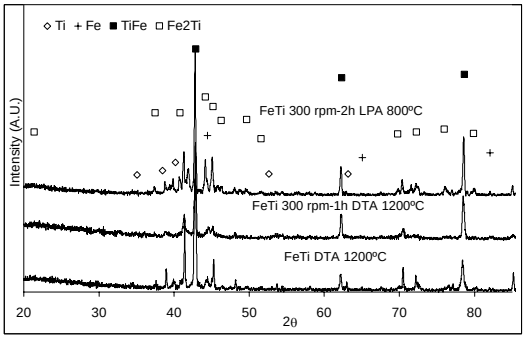

Fig. 5. XRD results of Fe+Ti mixture and miled samples after annealing

One possible explanation for the way that mechanical "activation" modifies the reactivity of the system is the formation of very thin Ti /Fe layers that in conjunction

with a high level of defects induced mechanically.

4 Conclusions

A novel two-step nano-FeTi powder synthesis routine was developed in which reduced extent of nano-FeTi synthesis in the powder is followed by supplemental heat treatment to complete the formation of FeTi phase for hydrogen absorption. The synthesis of FeTi takes place at much lower temperature (650ºC vs 1100ºC) than that of the conventional melting process, yielding essentially only the desired FeTi phase.

Acknowledgements

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