

Synthesis of FeTi hydrogen storage material via ball milling: effect of milling energy and atmosphere

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Abstract

Attempts were made earlier to synthesize and activate the FeTi intermetallic during ball milling (BM), for H₂ storage using sodium boron tetra-hydride (NaBH₄) additive as a process controlling agent. Simple reactive milling starting from Fe and Ti powders resulted in heavy agglomeration of powders, due to the self sustaining nature of the reaction following an incubation period. When NaBH₄ was used as the process control agent to avoid agglomeration, this resulted in the production of titanium hydride besides FeTi, and as a consequence unfavorable irreversibility in the subsequent hydrogen charging/discharging cycles [1,2,12]. The present work reports on modifications introduced in the synthesis process by changing two processing parameters, namely the milling energy and atmosphere composition.

Keywords: Ball Milling, Atmosphere Environment, Intermetallic, FeTi, Nanostructure, Hydrogen Storage

1 Introduction

Lately there has been growing interest in FeTi intermetallic powders as a very promising media for reversible hydrogen storage, due to their high storage capacity, about 1.8 wt%, and low cost [3-6]. But two of the major obstacles of FeTi powders are the preparation and high H₂ gas pressure requirements for activation [3-11]. Currently it is known that this can be overcome if during ball milling (BM) processing of elemental Ti and Fe, sodium boron tetra-hydride is added (NaBH₄ is a powerful reducing agent with H content as high as 10.9 wt%) [2,11]. The decomposition of NaBH₄ being mixed with elementary powders, Ti and Fe, during BM processing, releases hydrogen, leading to *in situ* activation of the synthesized nanostructured FeTi and pre-charging with hydrogen. The activated powders are then ready to be subjected to H₂ absorption/desorption cycle near room temperature without the need of the difficult pre-activation processes required for FeTi alloys manufactured by the conventional process.

The aim of this research is to study the viability of using nanostructured FeTi based powders prepared by BM, activated with NaBH₄, for hydrogen storage. The effects on hydrogen storage capacity and on powder agglomeration of some milling

parameters, such as atmosphere composition, milling time and energy were studied.

2 Experimental

A molar ratio of Fe:Ti of 1:1 was used. Milling was executed in a P100 Retsch planetary ball mill in a 250 ml stainless steel container, at 200-400 rpm. The ball-to-powder weight ratio was 20:1, with stainless steel balls (10 mm diameter).

Pre-milling the elemental powders has the effect of slowing down the synthesis reaction and reducing powder agglomeration. XRD results and SEM observations showed that milling Ti for 4 hours and Fe for 2 hours results in adequate homogeneity and proper grain size distribution. These milling times were employed in the subsequent milling of single components. The handling and charging of the powders into the container were performed in a glove box with nitrogen (N₂) or argon (Ar) atmosphere with about 1% oxygen. In the second milling step the pre-milled Ti and Fe were milled altogether for 10 hours. The powders were handled and milled with an atmosphere of N₂ (the first 8hrs) or Ar (the last 2 hrs). After these 10 hours of milling the third step, the H₂ activation was performed. NaBH₄ powders were added, and milling was continued for additional 2 or 10 hours.

Powders were characterized by XRD using a Rigaku Geigerflex D/MAX III C diffractometer and by DTA. Microstructure and chemical composition were studied using a SEM/EDS Philips XL30 FEG with EDAX. Vickers microhardness were performed in a Shimadzu HMV2000. Chemical analysis (Leco) was made to assess the oxygen and nitrogen pick up during BM processing.

3 Results and Discussion

The milling energy for Fe+Ti mixture was set to a low value initially in order to reduce the reactivity of the elemental powder mixture. This procedure has shown in a similar system, NiTi, that the reactivity of the system is clearly modified by low energy mechanical “activation” [12]. Following this low energy milling the heat of reaction is released in a range of temperatures upon annealing at intermediate temperatures, instead of the highly exothermic reaction at high temperature. Although this procedure does not eliminate completely the agglomerating problem it is now manageable and the milling synthesis can be divided into three steps a) mechanical “activation”, b) synthesis reaction and c) hydrogen activation/charging with NaBH₄. Fig. 1 illustrates the effect of milling energy on the synthesis reaction of the Fe+Ti mixture. With low energy, 200 rpm, XRD peaks are essentially identical to those of the starting materials. Using higher energy, 400 rpm, the XRD peaks from Fe and Ti are no longer detectable, but FeTi peaks intensified after the annealing. One possible explanation for the way that mechanical “activation” modifies the reactivity of the system is the formation of very thin Ti oxide/nitride layers on the surface of the powders. Attempts were thus made for modifying the milling atmosphere, usually consisting of an inert gas such as Argon, by deliberately introducing small amount of the gases oxygen or nitrogen, in a controlled manner, in order to provide surface modification to the powders.

The usual characterization techniques do not provide sufficient discrimination to control the process. For instance, the formed phases are either nanocrystalline or amorphous thus providing very broad X-ray diffraction (XRD) peaks. Several characterization techniques were used to circumvent this problem, including SEM, Auger Electron Spectroscopy (AES) and chemical analyses. The latter proved to be especially important when working with modified milling atmosphere compositions.

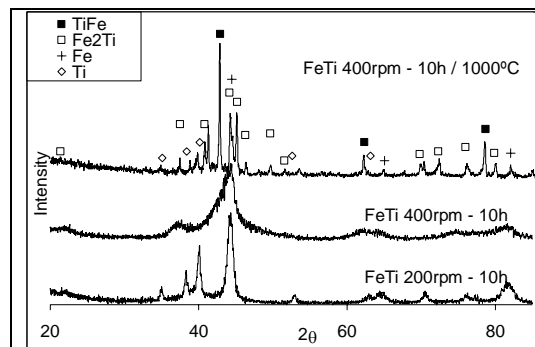


Fig. 1. DRX patterns of Fe +Ti milled for 10h.

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