Materials Science Forum Vols. 660-661 (2010) pp 329-334
Online available since 2010/Oct/25 at www.scientific.net
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doi:10.4028/www.scientific.net/MSF.660-661.329

An Investigation on the Mechanical Alloying of TiFe Compound by High-Energy Ball Milling

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Keywords: mechanical alloying, intermetallic compound, high-energy ball milling

Abstract: This work reports the efforts to obtain TiFe intermetallic compound by high-energy ball milling of Ti and Fe powder mixtures. This process route has been used to provide a better hydrogen intake in this compound. Milling was carried out in a SPEX mill at different times. Strong adherence of material at the vial walls was seen to be the main problem at milling times higher than 1 hour. Attempts to solve this problem were accomplished by adding different process control agents, 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. Better results were attained with benzene and cyclohexane, but with partial formation of TiFe compound even after a heat treatment (annealing) of the milled samples.

Introduction

TiFe is a well-known intermetallic compound suitable for hydrogen storage [1,2]. TiFe powder has been produced by high-energy ball milling, since particles with high surface area, high concentration of crystal defects or nanostructure have improved properties for the hydrogen intake and desorption [3-12]. Two different process routes have been adopted to obtain TiFe powder by high-energy ball milling: mechanical alloying of a mixture from titanium and iron powders [5,9-19] and mechanical grinding of pre-melted and homogenized TiFe compound or TiFe alloy [3,5,8,15,18,20]. Mechanical alloying has also been used for producing TiFe-based alloys by adding a third element in powder form to previous TiFe powder [7] or to titanium and iron powders in the mill [9,10,17,21,22].

This work deals with mechanical alloying of TiFe from its elemental powders. Mechanical alloying is a solid-state process based on successive welding and fracture of the elemental powder particles that takes place under high energetic impact of the balls in a vial and between each other. A lot of variables can influence the final result and must be considered in order to get reproducible results. Some of them can be cited here like type of mill, ball to powder weight ratio, ball and vial size, ball and vial material, time of milling, atmosphere in the vial. Ductile metal powder particles plastically deform and exhibit strong tendency to weld each other and to stick on the surface of the vial and balls. Then for mechanical alloying succeeds is imperious to control the welding and stick tendency of the particles. The control of it is normally done by adding substances, known as process control agents (PCAs), to the mill charge. Good reviews about the use of PCAs (type and quantity) could be found in the technical literature [23,24].

Concerning the mechanical alloying of TiFe, information about milling equipment and control parameters are as a general rule not fully reported, which makes the reproducibility of the results an impossible task. None of the reviewed papers cited before have mentioned the use of any PCA. Only the paper of Lópes Báez *et al.*[10] describes a procedure to cover preliminary the balls and the vial with Ti and Fe powders by milling a small quantity of them before the main operation, which indicates their sticking behavior. However, preliminary work of the present authors has pointed out the necessity of using a PCA for avoiding strong sticking (cold welding) of both titanium and iron powders (mainly to the vial). This paper reports the author's efforts to overcome these difficulty not reported before.

Experimental

Elemental powders of Ti and Fe (99.5 % pure, -200 mesh) were mixed with the atomic ratio of the stoichiometric compound TiFe (1:1). Each milling charge consisted of 72 balls (∅ = 7 mm) made of Cr-V steel, 10 g of Ti-Fe powder mixture and a variable content of process control agents, performing a constant ball-to-powder weight ratio of 10:1 in all batches. Stearic acid (Vetec), Ethanol (Merck), low-density powdered polyethylene (Braskem), benzene (Carlo-Erba) and cyclohexane (Merck) were used as PCA in proportion varying from 0 to 20 weight % of nominal powder mixture mass grouped in two sets. In the *Set 1* the PCA amount has not exceeded 4 wt% and milling period varied from 0 to 3h). *Set 2* comprises experiments with PCA amount range from 10 to 20 wt% and milling period varying from 5 to 40 h. The mechanical alloying was performed in a high-energy ball mill (SPEX 8000 Mixer/Mill) with forced air cooling from a fan installed at the side of the mill. Milling was carried out for different times ranging from 1 to 40 hours. A rounded bottom vial (two parts) from hardened steel was built in-house and sealed with a viton O'ring. Powders were handled in glove box with 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. After milling, samples were heat treated (annealing) under vacuum ($\sim 10^{-5}$ mbar), performing two isothermal paths at 480ºC and 780ºC, both for 1h, at a fixed heating rate (10ºC/min.). As-milled and annealed samples (loose and adhered powders) were characterized by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM).

Results and Discussion

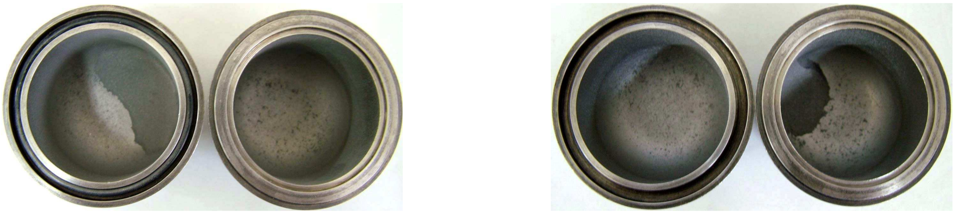
Powder adherence on the vial. Table I shows the loose powder mass (in wt% of the initial powder mass) for the various milling experiments. As a general rule by increasing milling time for the same kind and amount of PCA the loose powder mass is decreased. This can be particularly seen by comparing the results related to ethanol, polyethylene and "pure" samples (no PCA) from *Set 1*. Around 40 wt% of initial powder mass has become adhered after 1h milling without any PCA which increases to 96 wt % after 2h milling. This pointed out the necessity to use a PCA. For a constant milling time the loose powder mass increases with the amount of PCA which is another tendency. In the experiments from *Set 1* (two first columns in Table 1) polyethylene was the most efficient. This could be seen by comparing the results with 4 wt% of PCA and 3h milling time: with stearic acid and ethanol the amount of loose powder was 10 and 11 wt%, respectively, while for the samples with polyethylene this amount reached 65 wt%. With 2 wt% of PCA and 2h milling polyethylene is also better than benzene. In spite of that, the experiments from *Set 2* (PCA amount ≥ 10 wt%) have been done with benzene and cyclohexane mainly because they can be easily volatilized after milling.

Previous experiments were carried out in split bottom rounded vials. When the amount of the loose powder after milling was around 90 wt% or over, the adhered portion was homogeneously distributed at the balls and the vial walls and it is not possible to see a clear deposit of cold weld material. As the loose powder amount is lowering a localized sticking is clearly formed always occurring at the rounded portion of the vial. Fig.1 shows pictures of some typical sticking observed. No pattern was seen concerning the radial position of the cold welded material or systematic location on the upper or lower half of the vial. As the rounded part of the vial was seen to be the preferred place for the sticking, an experiment (PE2%2h) was made with a flat bottom vial (Spex original vial), but after 2h milling, about 49 wt% of the initial powder mass was cold welded at the corner between the vial wall and the cover. Opening the vial caused fracture of the welded material, so the broken peace was placed on the cover. Compared to the sample milled in the round-bottom vial, the amount of loose powder from the sample milled in the flat-bottom vial was, surprisingly, twice higher. Although there are no dead corners (regions not reached by the balls) in a round-bottom vial, these results indicate that flat-bottom vial could be better for lowering cold welding. In spite of that, previous work from other authors [5,9-19] has not reported any cold welding problem at rounded or flat bottom vials.

Table 1 – Loose powder mass (M) from each milling experiment (see code caption below*).

Experiments (*Set 1*)	M (wt%)	Experiment (*Set 1*)	M (wt%)	Experiments (*Set 2*)	M (wt%)
N0%1h	59	SA2%2h	6	B10%5h	95
N0%2h	4	SA4%3h	10	B10%10h	96
E1%1h	59	PE1%1h	92	B10%15h	40
E1%2h	5	PE1%2h	7	B15%20h	98
E2%1h	96	PE2%1h	91	B17.5%25h	101
E2%2h	20	PE2%2h	34	CH10%5h	94
E4%2h	90	PE4%2h	96	CH10%10h	91
E4%3h	11	PE4%3h	65	CH20%30h	96
SA1%2h	5	B2%2h	22	CH20%40h	103

*code: ACP kind (N = no ACP; E = Ethanol; SA = Stearic Acid; PE = Polyethylene; B = Benzene; CH = Cyclohexane), ACP quantity (0 to 20%) and milling time (1 to 40h).



E1%1h PE2%2h

Figure 1 – Photographs showing typical cold welded material inside the vials.

XRD analysis of as-milled samples. It can be seen from the diffraction patterns of as-milled samples in Fig. 2a that some peak broadening has occurred comparing to the peaks of the simple mixture sample (at the bottom of Fig. 2a). The peak broadening increased with the time of milling as expected. Diffraction patterns from cold weld portion of the milled samples (denoted with a "W" in the right column of Figure 2 showed some peaks more clearly defined than the parent samples. This is indicative that these portions of the samples have suffered less action of the milling balls, becoming apart from the milling after the cold welding event. Formation of TiFe compound after milling was not seen in both loose and cold weld powder as well. Diffraction patterns o samples from *Set 2* (higher content of benzene and cyclohexane) still shows Fe reflections, however with the appearance of TiC phase coming from the reaction with carbon supplied by the organic PCAs.

XRD analysis of annealed samples. Fig 2b shows patterns from samples milled with ethanol and polyethylene (up to 4 wt%) and benzene and cyclohexane (17.5 and 20 wt%, respectively). TiFe peaks can be only seen in the patterns from samples milled with lower content of PCA and for no more than 3h, along with Fe_2Ti, Fe and TiC peaks. Little beat strong reflections of TiFe were seen in PE4%3h-A. Patterns from samples with higher contents of benzene and cyclohexane show only Fe and TiC peaks, confirming that organic PCAs are sources of carbon, as observed on as-milled samples.

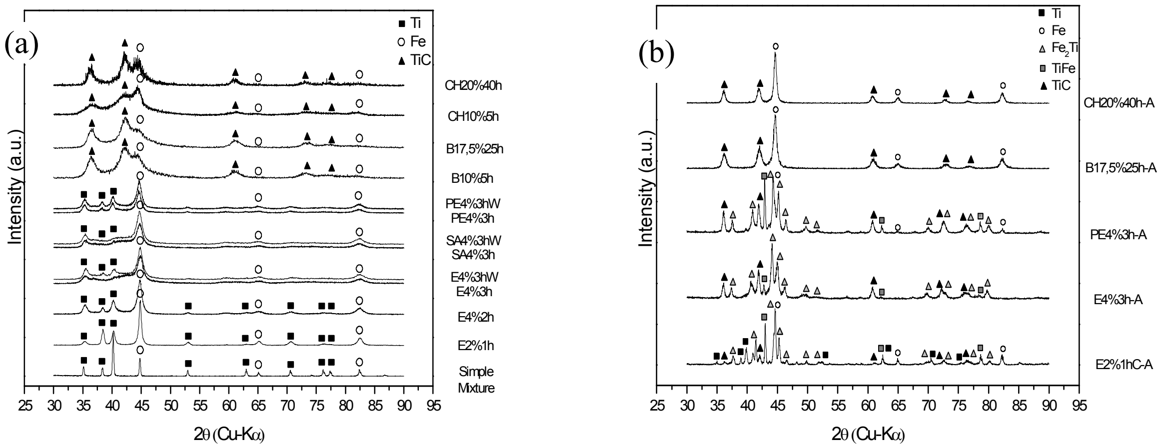
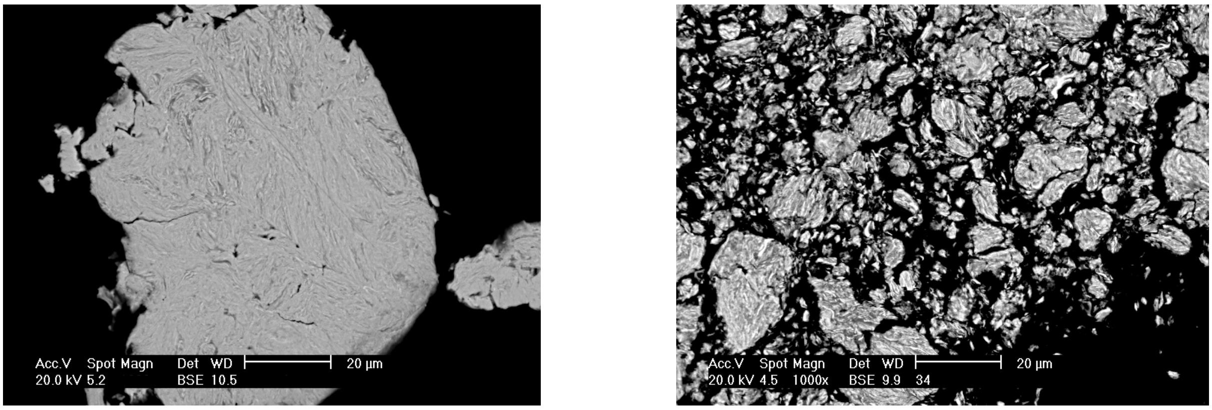


Figure 2 –XRD patterns of selected samples: (a) as-milled; (b) annealed. Simple mixture data was shown for comparison. Preparation conditions are indicated in the left column of each diffraction set. Patterns are not proportionally plotted.

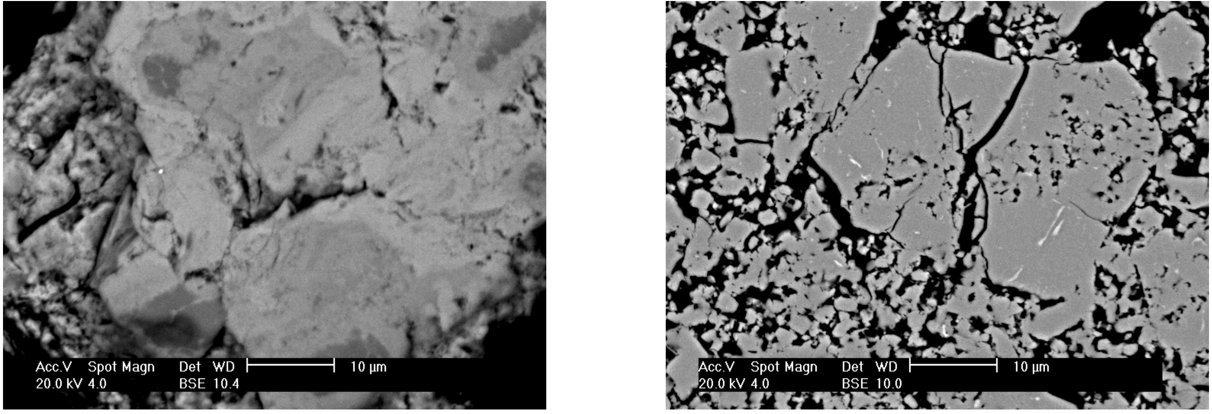
SEM analysis of as-milled and annealed samples. Figure 3 shows SEM micrographs of some milled and annealed samples (both from loose portion). Milling has promoted the formation of typical agglomerates having a lamellar structure, with alternate layers of titanium and iron, which can be distinguished by different tones of gray, since titanium layers are darker under back-scattered electronic images. These layers become thinner with the increase of the milling time (not shown in the micrographs), or thicker with the increase of the amount of PCA, as shown for samples with polyethylene (Figs. 3a and 3b). Low density polyethylene was the better tested PCA of *Set 1* concerning the prevention of adherence of the powder to the vial and balls, as seen before, however retarding mechanical alloying evolution, since agglomerates with lamellar structure were still present after three hours of milling. When compared to the other PCAs (same amount and milling time), the lamellar structure was not seen, which could be due to the formation of the compound TiFe. However, this is not the case, according to the XRD patterns. After annealing the lamellar structure from as-milled samples was not seen anymore. In some samples, heterogeneous structures are still seen, as observed in Fig. 3c (E2%1h-A) where different tones of gray can be seen (lighter and darker regions are richer in iron and titanium, respectively).

Conclusions

TiFe intermetallic compound has not been formed by high-energy ball milling of titanium –iron powder mixtures. A strong tendency to cold welding was seen to occur even when PCAs were utilized in amounts not exceeding 4 wt% (*Set 1*). This was the reason the formation of desired compound has been prevented. The higher the milling time the higher the formation of a cold welded deposit on the round part of the vial. Massive cold welding could only be prevented by adding higher amounts of PCAs (10 wt% or over), which makes possible more extended periods of milling (up to 40 h in *Set 2*). In spite of that, TiFe was only partially formed after a heat treatment (annealing) since TiC was formed as well, suggesting the decomposition of the PCAs during milling operation and their role as a carbon source.



(a) PE1%2h (b) PE4%2hC



E2%1h-A B17.5%25h-A

Figure 3 – SEM micrographs (back-scattered electrons) from as-milled and annealed samples (experiment is indicated below each image).

Acknowledgements

This work was supported by FAPESP (research grant 2007/50018-2) and CNEN (Comissão Nacional de Energia Nuclear). One of the authors (R. B. Falcão) is grateful to CAPES for a research fellowship. The authors would like to thank BRATS and Höganäs do Brasil for providing Ti and Fe powders, respectively.

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Advanced Powder Technology VII
doi:10.4028/www.scientific.net/MSF.660-661

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