

An Investigation on the High-Energy Ball Milling of Iron-Titanium Powder Mixtures without Process Control Agents

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ABSTRACT

Results of high-energy ball milling of Ti and Fe powder mixtures to obtain TiFe intermetallic compound are reported. Previously, we used various process control agents (PCAs) to solve a cold welding problem in a SPEX mill. In this work, we continue that investigation but without adding PCAs and also using a planetary ball mill. Four different strategies were tried to avoid or minimize cold welding: (a) preliminary milling of a small quantity of the mixture, dirtying the vial walls and the balls surfaces before milling the main charge, (b) stepwise milling with the rotation and the inversion of the vial between the steps (only in SPEX), (c) milling Ti and Fe powders (apart from each other) before milling the mixture of them, and (d) finally milling Fe powder with Ti hydride powder. The loose powder mass and the crystalline phases formed (identified by XRD analysis) after milling were used to compare the procedures. High loose powder yields could be attained but with no major TiFe formation.

INTRODUCTION

This work reports the efforts to obtain TiFe intermetallic compound by mechanical alloying through high-energy ball milling of Ti and Fe powder mixtures. Previous works of the present authors [1,2] have pointed out the necessity of using a PCA (Process Control Agent) for avoiding strong sticking (cold welding) of both titanium and iron powders (mainly to the vial), preventing mechanical alloying to succeed. In order to make possible high periods of milling (e.g. 40 h), which are necessary to obtain the desired compound, large amounts of PCAs (10 wt% or over) were utilized. However, in doing so, PCAs act as carbon source, leading to the formation of TiC, as titanium is a strong carbide former. Most papers found in the literature about mechanical alloying of TiFe have not mentioned the use of any PCA or reported problems with sticking behaviour [3-14]. Information about milling equipment and control parameters are as a general rule not fully reported either, which makes the reproducibility of the results an impossible task. Only the paper of López-Báez *et al* [12] 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, in order to prevent sticking.

In this paper, we describe four procedures used to attempt overcoming sticking problems during high-energy ball milling with no PCA added to the powder mixture. Both shaker and planetary mills were used this time.

EXPERIMENTAL

Titanium and iron powders (99,5 % pure, -200 mesh), supplied by BRATS and HOGANAS, respectively, were weighted at 1:1 ratio (TiFe compound stoichiometry). A shaker mill (Mixer-

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Mill 8000 from SPEX), with forced air cooling from a fan installed at the side of the mill, and a planetary mill (Pulverisette 6 from FRITSCH) were used to perform mechanical alloying. Shaker milling was accomplished by using a split rounded-bottom vial (two parts), made from hardened steel, built in-house (vol. $\sim 95 \text{ cm}^3$) and sealed with a viton o'ring, as described elsewhere [1,2]. Each milling charge consisted of balls ($\varnothing = 7 \text{ mm}$) made of tool steel and 10 g of Ti-Fe powder mixture (mixed with the atomic ratio of the stoichiometric compound TiFe (1:1).), being the ball-to-powder weight ratio equal to 10:1, which was kept constant in all batches, as well as the shaker frequency (1060 cycles per minute). A cylindrical rounded-bottom vial, made from hardened steel and also built in-house (vol. $\sim 250 \text{ cm}^3$), was used for planetary milling, always operated at 500 rpm. Tool steel balls ($\varnothing = 5 \text{ mm}$) and a ball-to-powder ratio of 25:1 or 50:1 were used. 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 that, a cleaning operation was carried out to remove the adhered mass. This was done by adding pure ethanol to the vial, performing a short milling operation (5 min), and filtering the powder containing liquid. Generally, the vial and the balls were totally cleaned after repeating three or four times this operation. The powder mass removed by this way was weighted after drying and stored separately from the original loose powder. Milled loose powders (not adhered) were characterized by X-ray diffraction analysis using Cu K-alpha radiation.

The procedures adopted to overcome the sticking problem are described in the following:

Procedure 1 – The vial walls and the ball surfaces were dirtied before milling the main charge by previously milling a small quantity of titanium and iron powder mixture (0.5 g) for 2 hours, similarly to what was done by López-Báez et al. [12]. After that, the milling charge was completed and the sample was milled continuously for 5 hours (experiment 1) on the shaker mill (SPEX).

Procedure 2 – It is similar to Procedure 1, but milling was carried out in stepwise manner, with intermediate openings of the vial to follow the behaviour of the powder. The vial was opened inside the glove box under pure argon atmosphere and was left there overnight. Further, the vial was taken out to the air atmosphere to check better the adherence and to register it photographically. Two experiments were carried out with different intervals of milling and total milling time. In experiment 2A, the stops occurred every 1 hour for a total milling time of 5 hours (5x1). In experiment 2B, the stops occurred every 5 hours totalizing 25 hours of milling (5x5).

Procedure 3 – It was a stepwise milling but with inversion and rotation of the vial between steps; the vial was not opened after interruptions. The purpose here was to avoid possible preferential locations for sticking. Inversion was done by alternating the head and the bottom of the vial on the shaker mill. Rotation was accomplished by turning the vial 90 degrees after each interruption. The milling operation was interrupted every 1 hour and the total milling time was 5 hours in experiments 3A and 3B. Experiment 3B included the dirtying operation described for experiment 1.

Procedure 4 – First, the weighted mass of each powder (4.62 g of Ti and 5.38 g of Fe) was milled on the shaker mill separately for 30 min to introduce a previous cold work in order to verify if it could reduce powder particles tendency to welding (by decreasing its ductility). Titanium was milled before iron, using the same vial and balls that were used in subsequent mechanical alloying. After the milling of the Ti powder, it was discharged from the vial and the milling of the Fe powder was conducted. The ball-to-powder ratio of the milling of Ti and Fe powders were 21.6:1 and 18.6:1, respectively, since the ball set was the same. Both operations were carried out inside the glove box and no visible adherence was observed;

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next, the powders were mixed; and, finally, the mixture was milled for 1 hour in the shaker mill (experiment 4).

Procedure 5 – Instead of metallic Ti powder, titanium hydride (TiH_2) was milled with iron. The intention was to reduce the strong tendency to weld of the titanium powder particles. Experiment 5A and 5B were carried out in the shaker mill (for 5 and 10 hours, respectively), while experiment 5C took place in the planetary mill for 5 hours (ball-to-powder ratio of 50:1). Planetary milling was interrupted every 1 hour for 30 min to allow the cooling of the vial.

For comparison purpose, the mixture of as received powders was milled for 1 hour (experiment 0A) and for 5 hours (experiment 0B and 0C) without any specific procedure to avoid the powder adherence to the vial and balls. Experiments 0A and 0B were conducted at the shaker mill and experiment 0C was carried out in the planetary mill (ball-to powder ratio of 25:1).

RESULTS AND DISCUSSION

The milling yields (loose powder mass percentage) and the details of each milling experiment are shown in Table 1. The results will be analyzed along with the diffraction patterns shown in figures 1 to 4.

The experiments carried out with no concern for powder sticking (0A, 0B, and 0C) show low yields that decrease with the time of milling, as it can be seen from experiments 0A and 0B in the shaker mill. In this type of mill, localized powder sticking on the vial was observed, besides the sticking on the balls, as reported before [1]. Powder sticking in the planetary mill is different as the powder was homogeneously distributed on the vial and balls. Figure 1 shows the powder diffraction patterns from experiments 0B and 0C. TiFe was certainly formed in experiment 0B, which still shows some free titanium and iron. The diffraction pattern from experiment 0C revealed a lower degree of mechanical alloying, despite exhibiting a better yield than experiment 0B. This fact can be attributed to the lower impact energy of the balls in the planetary mill compared to the shaker mill.

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Experiment	Milling			Yield (wt%)	Mill
	Steps	Air Exposure	Time (h)		
0A	0	no	1	58.7	Shaker
0B	0	no	5	14.0	Shaker
0C	5 x 1h	no	5	24.2	Planetary
1	0	no	5	12.6	Shaker
2A	5 x 1h	yes	5	101.3	Shaker
2B	5 x 5h	yes	25	65.0	Shaker
3A	5 x 1h	no	5	6.8	Shaker
3B	5 x 1h	no	5	26.0	Shaker
4	0	no	1	30.2	Shaker
5A	0	no	5	35.0	Shaker
5B	0	no	10	12.9	Shaker
5C	5 x 1h	no	5	93.3	Planetary

Table 1 – Conditions of milling and yields (loose powder mass percentage) from each experiment.

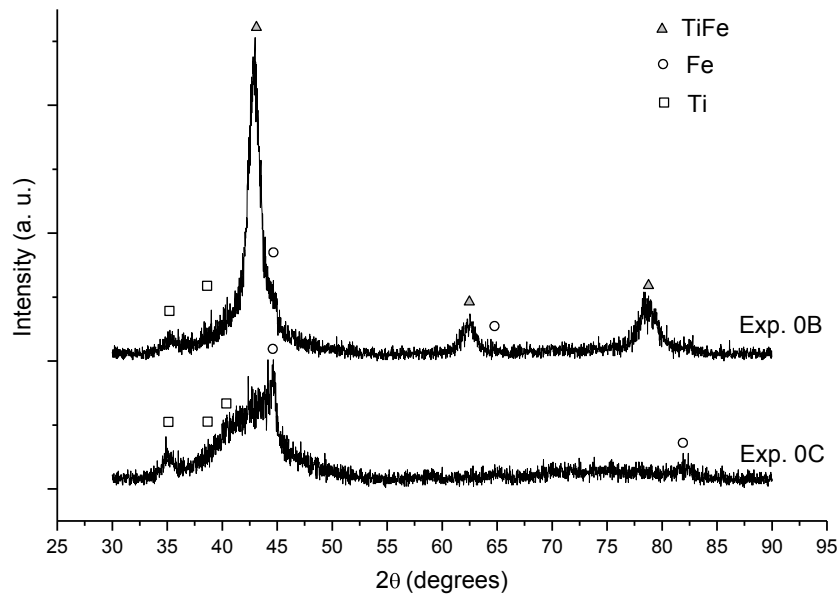


Figure 1 – Powder X-ray diffraction patterns from experiments 0B (shaker mill) and 0C (planetary mill) after 5 hour of milling.

The dirtying operation (procedure 1) was not effective to decrease the powder sticking in shaker milling, as shown by comparing experiment 1 with experiment 0B, which were carried out continuously (no interruptions and openings) for the same milling time (5 h). The XRD pattern of experiment 1 shows very clear lines corresponding to TiFe phase (Fig. 2). As intermediate openings were carried out with air exposure, for the same milling time, there was a huge yield increase (experiment 2A). The value higher than 100 wt% is due to the balls wear. Experiment 2A however exhibits incomplete alloying as the main iron line is still strong. Oxidation should be considered in this experiment, as the strongest TiO peaks can be observed. Yet with openings every 5 h and an extended milling time (experiment 2B – 25h), the yield was not so high (65 wt%) and XRD pattern showed a decrease in intensities, as a result of the increased mechanical deformation. In spite of that, the strongest peak of TiFe phase can be seen along with some peaks of TiO. Air exposure between steps might be the main cause for the increase of yields observed in experiments 2A and 2B, as oxidation may be occurred. Oxides act in this case as a good process control agent against sticking. Oxides or dissolved oxygen are undesirable in this case, since the TiFe compounds are intended for hydrogen storage.

With inversion and rotation carried out in the shaker mill, experiment 3B, which adopted the dirtying operation, gave a superior yield (26 wt%) compared to experiment 3A, where no previous dirtying took place (6.8 wt%). Inversion and rotation decreased localized powder sticking, but not the overall adherence, since the yield of the experiment 0B was 14 wt%. Contrarily to the previous observation (experiments 0B and 1), dirtying procedure was efficient now, indicating that it is good to decrease homogeneous adherence of the powder to the vial and balls but not localized (or heterogeneous) sticking. Localized sticking is attributed by us to an unsymmetrical movement of the vial in the shaker mill, caused by the particularities of the manufacturer's project design of this type of mill (SPEX). We believe that this was the main reason to explain the failure of the dirtying procedure (experiment 1) used before by López-Báez *et al.* [12], despite that these authors have not reported the kind of milling apparatus that they used. XRD pattern from experiment 3B, shown in Fig. 2, is very close to the pattern from experiment 1 and experiment 3A (not shown).

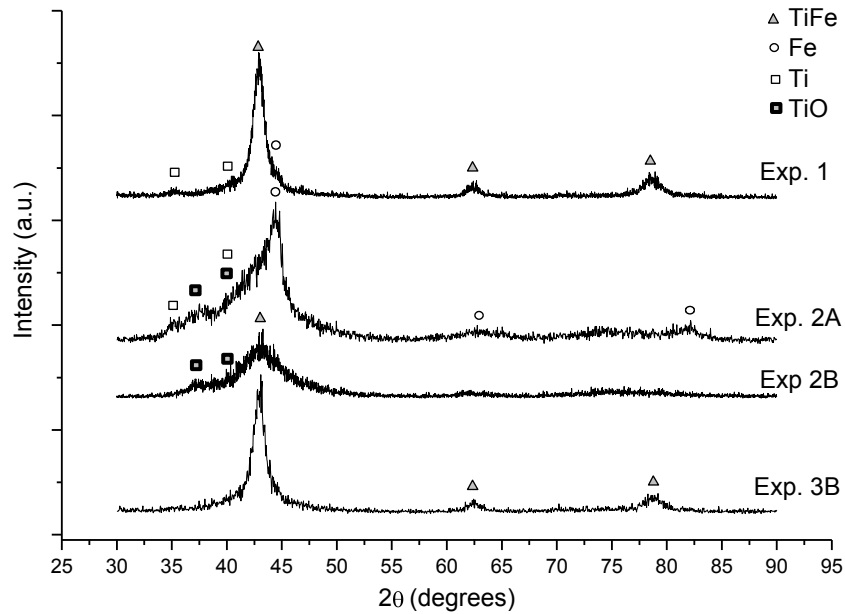


Figure 2 – XRD patterns from experiments that adopted previous dirtying and/or rotation and inversion of the vial (shaker mill).

Surprisingly, the previous hardening of titanium and iron powders, by milling them separately (experiment 4), showed a lower yield (30.2 wt%) than the experiment 0A (58.7 wt %), both milled for 1 hour. As these powders were milled only for 1 hour, XRD pattern (Fig. 3) exhibited peaks of titanium and iron (some peaks remain unidentified and are marked with interrogation symbol).

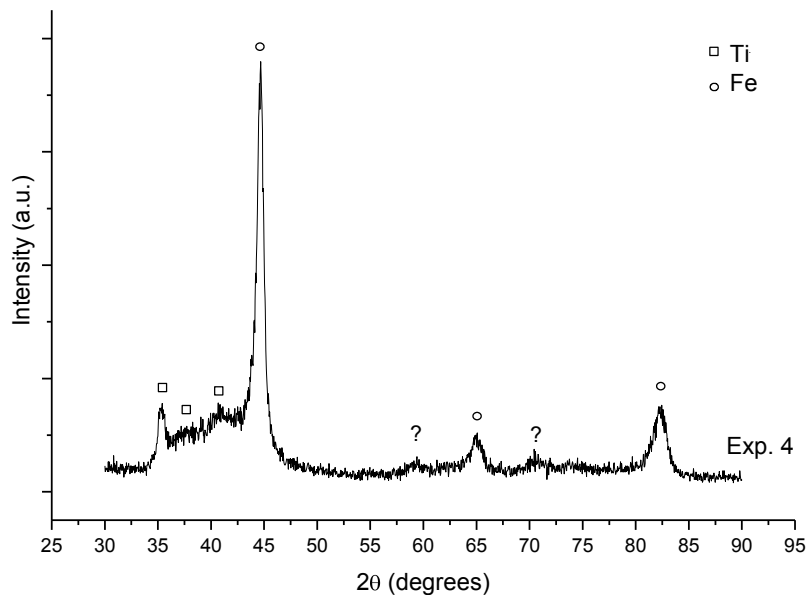


Figure 3 – XRD pattern from experiment 4 (Fe and Ti powders separately milled before the mechanical alloying).

Better yields were obtained by milling TiH_2 and iron powders. Thus, a 35 wt% yield was attained in the shaker mill after 5 hours of continuous milling (experiment 5A). After 10 hours, this yield decreased to 12.9 wt% (experiment 5B). XRD patterns from both experiments show only broad peaks of TiH_2 and Fe (Fig. 4). The strong iron peak that is observed in the pattern from

experiment 5A decreases after 10 hours of milling. No TiFe peaks could be undoubtedly detected. When planetary milling was used (experiment 5C), it is found a very high yield (93.3 wt%). The broadening of the peaks was similar to experiment 5B, but now the TiFe strongest line could be observed between 40 and 45 degree along with the strongest line from TiH₂ at about 35 degree. This fact indicates a superior degree of mechanical alloying, as a higher ball-to-powder weight ratio of 50:1 was used in this case. Annealing treatment is necessary for dehydrating after mechanical alloying, but it was not carried out in this work.

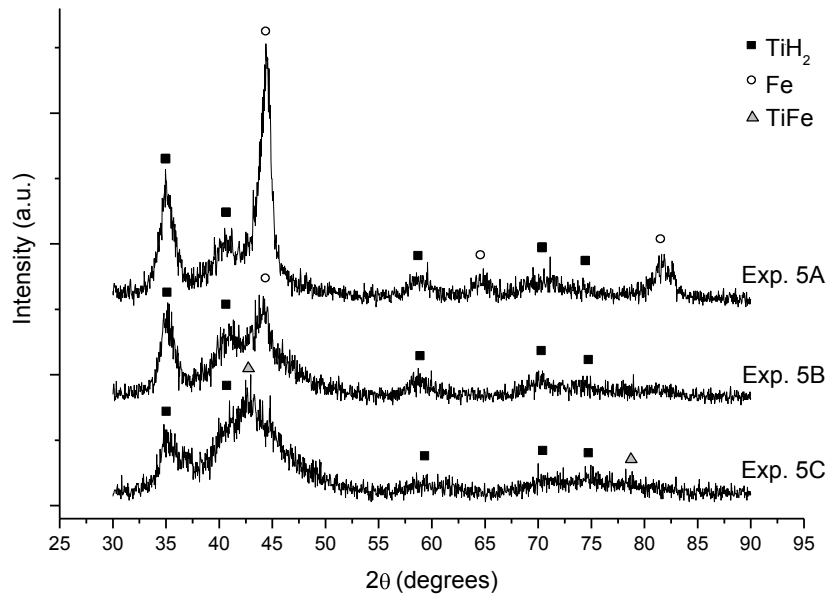


Figure 4 – XRD patterns from experiments starting with TiH₂ and Fe powders.

FINAL COMMENTS

In shaker milling, there is a tendency to occur localized sticking with no preference for a particular position in the top or the bottom of the vial. This behaviour was not observed in the vial used in the planetary mill, where the powder was homogeneously distributed between the vial walls and balls. When inversion and rotation of the vial was implemented, along with the dirtying procedure (experiment 3B), an increased yield was seen (26.0 wt%). This was the best yield obtained in this work with the shaker mill for 5 hours milling that also resulted in the TiFe formation as the major phase.

Stepwise milling should be tested further but with no air exposure between openings (procedure 2).

The previous cold work of the Ti and Fe powders by milling them apart (procedure 4) was not as good as expected, but should be tested for longer times before being regarded as unsuitable.

Milling titanium hydride instead of metallic titanium as starting material (procedure 5), carried out in the planetary mill, is very promising and needs future work to study the effect of extending the milling time and making heat treatments after milling.

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