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To cite this version:


HAL Id: jpa-00230792
https://hal.archives-ouvertes.fr/jpa-00230792
Submitted on 1 Jan 1990

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MECHANICAL ALLOYING OF THE Fe-Zr SYSTEM IN DIFFERENT MILLING CONDITIONS

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Abstract - Iron-zirconium powders have been Mechanically Alloyed (MA) by ball milling the pure elements. The Fe\textsubscript{2}Zr composition, corresponding to a stable intermetallic compound, has been investigated in different milling conditions, and the MA process was monitored via x-ray diffraction. Different reaction paths, tending towards amorphous or intermetallic phase formation, have been detected in the different milling conditions. The experimental findings are evidently correlated to the different ways by which energy is transferred from the milling tools to the alloying powder. Theoretical-empirical correlations between the input energy and the end products have been established.

1 - INTRODUCTION

Ball milling has proved to be an easy tool for synthetizing amorphous phases /1-4/ as well as intermetallic compounds /5-8/. The end products of the milling process strongly depend on the milling conditions. It has been pointed out, indeed, that using different ball mills /9,10/ or different conditions with the same ball mill /11/ can give markedly different outcomes. This is not surprising if we think that by ball milling we realize an energy transfer from the milling tools to the milled powder and that changing the operative conditions will obviously affect the energy transfer.

In the present paper we present an empirical correlation between the milling conditions adopted and the products obtained by the process.

The Fe\textsubscript{2}Zr system is well suited for the present purpose. Previous investigation has shown the possibility of preparing amorphous powder alloys in a wide concentration range /4/. Furthermore amorphous alloys with high Fe content (more than 60% at. Fe) exhibit a crystallisation temperature of about 680°C /12/. Thus the effect of a slight warming up of the milling device can be reasonable neglected and the process outcomes will only be influenced by the energy transfer.
2 - EXPERIMENTAL

Pure iron (99.999% from Carlo Erba) and zirconium (99:9% Ventron FmmbH) powders were mixed to the average Fe\textsubscript{2}Zr composition. The Mechanical Alloying process was carried out in a conventional planetary ball mill (from Fritsch, model Pulverisette P5). Four 250 cc tempered steel vials were contemporarily used in a given experiment. To avoid oxidation the vials were sealed under pure Argon.

In order to prevent an excessive warming during milling 15 minutes of milling were followed by 30 minutes of rest and compress air was forced into the mill both during milling and rest times. The weight ratio balls to powder was kept constant to the value of ten while the absolute weight of the powder used (PW) was varied from 5 to 90 grams. 10 mm diameter balls of the same steel of the vials were employed.

From time to time the vials were open and sampling performed to monitoring the MA process. X ray diffraction patterns of the samples were recorded by automatic Seifert PAD IV and GSD diffractometers. A sufficient wide angular range (10-40 28 degrees), in which fall both iron and zirconium main Bragg reflections, was covered using Mo K\textsubscript{\alpha} radiation (\( \lambda = 0.07107 \) nm).

3 - ANALYSIS OF THE RESULTS

The products obtained by milling iron-zirconium mixtures with different charges of the vials are significantly different and we have identified several typical situations to occur during the milling process. We will refer to them as:

- Line broadening. The main effect of the milling process is only a broadening of the x-ray lines of the starting iron and zirconium components.

- Formation of an amorphous phase. Disappearance of the initial x-ray lines and appearence of a rather symmetric broad halo centred at 18.6 28 degrees, in agreement with previous results (13), has been assumed as formation of a "true" amorphous phase.

- Formation of an amorphous intermetallic-like phase. The broad halo grows highly asymmetric around 19.2 28 degrees, where the main reflection of the Fe\textsubscript{2}Zr cubic intermetallic phase is expected to occur (ASTM 18-666). Clear evidence of the Fe\textsubscript{2}Zr intermetallic phase formation has been detected in some cases and indicated accordingly.

Intermediate situations have been properly classified, whenever possible, otherwise the dominant situation has been assumed.

Figures 1-6 show the diffraction patterns of the iron-zirconium system at different milling times and for the different charges of the vials investigated in the present work (PW = 90, 60, 30, 20, 15 and 5 grams). The following mean features can be outlined looking to figures 1 to 6.

For the maximum degree of filling of the vial (fig. 1, PW = 90, weight of the ball 900 g) 225 balls have been used and the vial resulted almost filled up. In this situation the movement of the balls during milling is highly hindered and, experimentally, only after 24 hours of milling an amorphous halo is evident in the x-ray patterns.

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Going to a lower degree of filling (PW = 60, 30 figs. 2, 3) results in a increased amorphisation rate. Disappearance of Bragg lines is completed between 14 and 24 hours for PW = 60 and at about 14 hours for PW = 30. In all cases the amorphous halos are centred at 18.6 28 degrees and are symmetric. This is the situation we have called formation of a "true" amorphous phase.
Fig. 1-6  X-ray diffraction patterns of the composition Fe:Zr=2:1 at various milling times for different grams of powder charge (PW from 90 to 5 grams). Each pattern has been classified by a symbol indicating (see text): O line broadening; ▲ formation of an amorphous phase; ▼ formation of the intermetallic Fe$_2$Zr or of an amorphous intermetallic-like phase. Mixed symbols are self-explaining.
At $PW = 20$ (fig.4) the amorphisation rate does not change significantly but the growth of the amorphous halo is now shifted towards 19 20 degrees. The phenomenon is clearer at $PW = 15$ and $PW = 5$ (fig.5 and 6). For $PW = 5$, clear evidence of the (311) main peak of the Fe$_2$Zr phase is detected at 5 and 9 hours.

For both $PW = 15$ and $PW = 5$, the broad amorphous halos are asymmetric and the maxima lie on the expected position of the main peak of the intermetallic phase. This is the situation we have called formation of an "amorphous intermetallic-like" phase.

4 - DISCUSSION

By simply varying the degree of filling of the vial, we have obtained different end products. The energy transfer realized should therefore have been different and hence different reactions have been promoted. The various kinds of reactions that can take place in the milling process are related to: (a) the level of energy obtained during a single collision event; (b) the total energy transferred to the powder.

The level of energy, that is the "quantum" energy transferred to the powder during a collision, can be correlated to the activation energies of the different reactions that can occur. At an higher activation energy of a given reaction a more energetic milling condition should correspond. The preferred pathway taking place in the solid state depends on the activation energies (and hence on the milling conditions) since thermodynamic considerations only will ever favor the formation of a stable crystalline phase.

As far as we know one example is given in literature about the influence of different levels of energy transfer, in rigorously controlled conditions, on the final products. Ni$_x$Zr$_{1-x}$ mixtures have been investigated by Eckert et al. /11/ at different rotation speeds in a Pulsiverset.le (P5) ball mill. They noticed that in order to form Ni - Zr intermetallic compounds an higher energy (i.e. higher rotation speed) was required than the one needed to form an amorphous phase.

We have the same evidence in the present investigation. Formation of the Fe$_2$Zr intermetallic phase (or amorphous intermetallic-like phase) has been detected when the highest energetic conditions were used as we will see in the following.

The energy transferred during a collision event should be proportional to the kinetic energy acquired by one ball:

$$E_b = \frac{1}{2} m_b V_b^2$$  \hspace{1cm} (1)

being $m_b$ the mass of the ball and $V_b$ the velocity of a ball inside a vial launched, at a given moment, against the opposite wall by a given composition of inertial forces of the mill apparatus (see fig.7). The $E_b$ energy of a single ball can be properly evaluated by kinematic considerations /14/. In a real experiment, however, we are dealing with a finite number, $N_b$, of balls that hinder each other so that the kinetic energy must be modified by an empirical factor, $\phi_b$, able to account for the degree of filling of the vial. In order to obtain a simple analytical expression for $\phi_b$, we have found convenient to express it as a function of two parameters $n_v$ and $n_s$:

$$n_v = \frac{N_b}{N_b,v}$$

$$n_s = \frac{N_b}{N_b,s}$$

where $N_b,v$ is the number of balls that can be contained in a simple cubic arrangement in the vial and
Fig. 7 - Scheme of Fritsch Pulverisette (P5) ball mill. \( \omega_p \) and \( \omega_w \) are the non-independent angular velocities of the ball mill plate and of the vials respectively. \( V_b \) is the velocity of one ball leaving the wall.

where now \( N_{bs} \), is the number of balls needed to cover, in a simple cubic arrangement, one third of the inner surface wall. We will assume that the \( \varphi_b \) factor must fulfill the following conditions:

a) when the vial is completely filled \( (n_v = 1) \) no movement at all is possible and \( \varphi_b = 0 \);

b) on the opposite \( \varphi_b = 1 \) for \( n_v = 0 \) (i.e. vial empty or, in real cases, one or very few balls);

c) \( \varphi_b \) near to \( 1 \) (e.g. 0.95) for \( n_s = 1 \) (this assumption means that until one third of the inner surface wall is not covered, the reciprocal hindering of the ball is negligible).

According to these assumptions a simple form for \( \varphi_b \) is given by

\[
\varphi_b = (1 - n_v^\varepsilon) \quad (2)
\]

where \( \varepsilon \) is a parameter depending on the ball diameter that can be evaluated by condition (c)

\[
0.95 = (1 - (N_{bs}/N_{bv})^\varepsilon)
\]

which gives \( \varepsilon = 1.624 \) for a ball diameter of 10 mm used in the present experiments. Fig. 8 shows the occupancy factor versus \( n_v \).

According to the previous considerations, in a real experiment containing a given number of balls, \( N_b \), equation (1) must therefore be modified so that the energy transfer contribution of a single ball becomes:

\[
E_b = \frac{1}{2} m_b V_b^2 \varphi_b \quad (3)
\]

where we assume that to a constant rotation speed of the planetary mill a constant velocity \( V_b \) of launch of the balls corresponds.

With the above assumption the total energy \( E_t \) transferred from the mill to the system is proportional to the number of balls multiplied by the energy of one ball

\[
E_t = KN_b E_b
\]

where \( K \) is constant for any given rotation speed and takes into account the frequency of launches [14]. We can rearrange the expression as

\[
E_t^* = \frac{E_t}{t/KPW} = \varphi_b N_b \frac{t}{PW} \quad (4)
\]
where \( t \) is the milling time and \( \text{PW} \) the weight of the powder. If we now represent the experimental findings by plotting \( \varepsilon_t^* \) versus \( \varepsilon_t \) we obtain the "energy map" shown in fig. 9.

\[ \text{Fig.8} - \text{Occupancy factor, } \varphi_b, \text{ versus } n_v \text{ (see text).} \]

\[ \text{Fig.9} - \text{Energy map showing } E_b^*(\text{Eq. } 2) \text{ versus } E_t^*(\text{Eq. } 4). \text{ Each horizontal line is proportional to the level of energy release during a collision event in each experimental milling condition and is labelled by the } \text{PW identifying parameter (\text{PW} = \text{weight of the powder}). On each line seven symbols (see figure 1) are reported for the times: 3, 5, 7, 9, 14, 24 and 34 hours of milling. The level } E_b^* \text{ represents the level above or below which intermetallics or "true" amorphous phase are formed (see text). A, B, C regions define conditions where only line broadening (A), amorphous phase (B) and amorphous intermetallic-like phase (C) formation are preminent. Regions AB and AC define self-explained mixed situations. } \]

\( * \text{ note: the map includes more patterns than those reported on figures 1-6). } \]

(*) note: the map includes more patterns than those reported on figures 1-6).
The resulting map clearly defines different regions where predominancy of a given product can be established. The most interesting point is the individual of $E^*$ value, marked on figure 9 as $E^*$, above which true amorphous phase is no more obtainable and only intermetallic Fe$_2$Zr or amorphous intermetallic-like are detected. Below $E^*$ the amorphous phase can be obtained in shorter or longer milling time depending on the $E^*$ level.

With a few of exceptions, probably related to the intrinsic experimental uncertainty of sampling, all the experiments performed can be fairly well framed into the energy map. Conversely the energy map can be used to define the experimental conditions to be employed in order to obtain a given final product.

We want to point out that to derive the previous "hit model" equations, we have done the severe assumption that energy only released by collisions between balls and walls. Further the energy release concerns the balls, the hited region walls and the powder, while the energy transfer we are interested in is the one from the balls to the powder trapped during collisions which is obviously only a fraction of the total energy release considered in the model. In spite of these limitations, the model based on collisions is able to correlate, in a coherent picture, the experimental milling conditions and the end products.

REFERENCES