An X-ray Diffraction and Mössbauer Spectroscopy Study of the Reaction between Hematite and Aluminum Activated by Ball Milling

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The reaction between hematite and aluminum in presence of allumina as diluent activated by Ball Milling powder mixtures in different energetic conditions has been investigated. To this purpose, the powders at different milling times have been characterized by X-ray Diffraction and Mössbauer Spectroscopy. A self-substained combustion reaction was observed when the strongest energetic conditions of milling were adopted. The intermediate products of the reaction also depend on the energetic conditions: the formation of hercynite is favoured by the use of strong energetic conditions while the formation of an Fe-Al alloy was observed when a low energy per single hit is transferred to the powders.

1. Introduction

Ball Milling (BM) is a solid processing technique which has shown to be able to produce a variety of new materials starting from powder mixtures, through repeated welding, fracturing and rewelding of powder particles. The intimate mixing at atomic level which occurs favours the interdiffusion of the starting components and promotes the formation of the reaction products [1, 2]. Displacement reactions between a metal oxide and a more reactive metal, which are frequently highly exothermic, can be induced by BM [3–14]; an example is the reaction between hematite and aluminum [4–6]. Thermite reactions are typically activated by Self-propagating High-temperature Synthesis (SHS) [15].

Recently, the aluminothermic reaction of Fe_2O_3 in presence of Al_2O_3 induced by SHS and BM both under argon atmosphere or under air has been investigated [16]. It was concluded that a similar reaction path in SHS and BM under argon atmosphere could be postulated, even if the two preparation procedures are quite different. In particular, SHS involves the formation of a melt from which the products crystallize, while BM proceeds through a solid state reaction, and no melting take place. The products of SHS and BM under air are, on the contrary, quite different because SHS, being very fast, is scarcely influenced by the reaction atmosphere while BM under air gives rise to a progressive reoxidation of the products.

The energy involved in BM can be modulated by properly choosing the process parameters, like milling mechanics, diameter of balls and ball/power weight ratio.

In order to study the influence of milling energy on the reaction between Fe_2O_3 and Al in presence of Al_2O_3, BM under argon atmosphere has been extended to different energetic conditions by varying the ball diameter and the ball/powder weight ratio.

2. Experimental Procedure

Hematite (Aldrich Chemical Company Inc., purity >99%, av. particle size <5 μm) and aluminum (Aldrich Chemical Company Inc., purity 99%, av. particle size 200 mesh) in stoichiometric ratio according to the reaction $Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$, and 25% wt of alumina (Aldrich Chemical Company Inc., purity 99.8%, av. particle size <10 μm) were used in powder form as received.

Ball milling experiments were performed in a Spex 8000 vibratory mill. 5 g of the mixture were milled under 3 different experimental conditions, summarized in Table 1, which correspond to 3 different energy levels. In all sets the mixture was sealed in a 80 ml stainless steel vial with balls of the same material. Sealing was performed in a glove box filled with argon (<10 ppm O_2,

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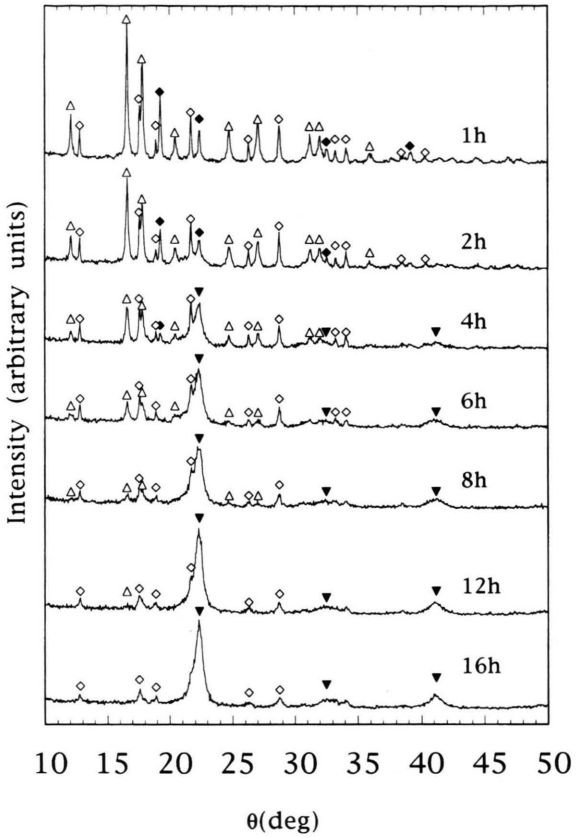


Fig. 1. X-ray diffraction spectra at selected milling times for Set 1.

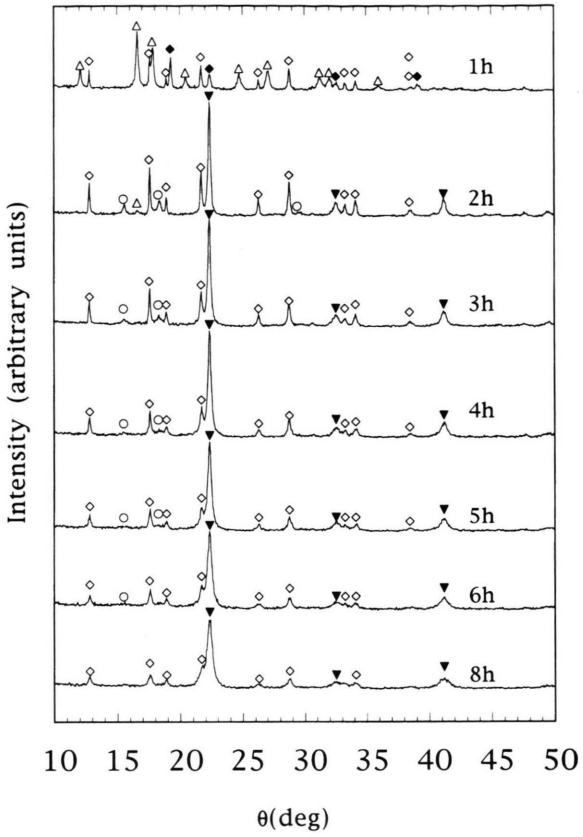


Fig. 2. X-ray diffraction spectra at selected milling times for Set 2.

Table 1. Milling conditions.

Set	Ball/Powder Weight ratio	Diameter of Balls	Number of Balls
1	10:1	4 mm	200
2	10:1	8 mm + 10 mm	8 + 8
3	5:1	8 mm + 10 mm	4 + 4

<10 ppm H_2O). In order to prevent an excessive overheating of the vial, the experiments were carried out alternating milling and rest periods at 5 min intervals.

The effect of milling was monitored by X-ray diffraction (XRD) performed on small portions of the powders, sampled at different milling times in a glove box filled with argon.

XRD spectra were recorded using CuK_α radiation on a θ-θ Seifert X3000 diffractometer equipped with a graphite monochromator on the diffracted beam.

The Mössbauer absorption spectra were obtained in a standard transmission geometry, using a source of ^{57}Co in rhodium (37 MBq). A calibration was performed using a 25 μm thick natural α-Fe foil; the isomer shift values are referred to α-Fe.

The measurements were carried out at room temperature on powder samples contained in a Plexiglas holder. The iron surface density for all of the samples ranges from 26.5 and 29.5 mg/cm^3.

The absorption spectra of the samples were analysed by fitting the data by curves of Lorentzian shape.

3. Results

In Figs. 1, 2, and 3 the XRD spectra are reported for set 1, 2, and 3 at selected milling times.

In the spectra of Set 1 a slow evolution of the system with milling time is discernible. After 1 h milling all

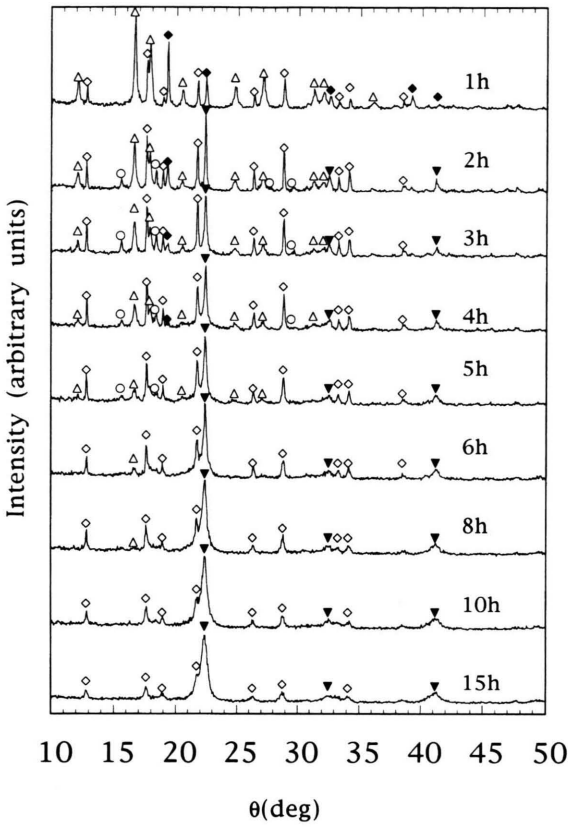


Fig. 3. X-ray diffraction spectra at selected milling times for Set 3.

peaks are due to the starting phases, i.e. hematite, aluminum and corundum. As milling proceeds, the intensity of the Fe_2O_3 and Al peaks slowly decreases while α-Fe peaks appear and the grow and broaden. No peaks due to any intermediate phase are detected in any of the milling stages.

The evolution of the XRD spectra of Set 2 with milling time is, on the contrary, very fast between 1 and 2 h milling. After 1 h milling the spectrum is very similar to that of Set 1 but after 2 h milling the Fe_2O_3 and Al peaks have already disappeared; at the same time sharp peaks due to a α-Fe are present, and some peaks due to $FeAl_2O_4$ (hercynite) are also evident together with the already present Al_2O_3 peaks. The evolution after this stage is much slower. In particular, the hercynite peaks show the strongest intensity at 2 h milling, and then their intensity slowly decreases until they completely disappear after 6 h milling.

In the spectra of Set 3, peaks due to hercynite ($FeAl_2O_4$) and α-Fe begin to appear after 2 h while the intensity of the Fe_2O_3 and Al peaks decreases. Hercynite peaks slightly grow until 3 h milling time and then this phase begins to disappear together with Fe_2O_3 and Al, while the intensity of α-Fe peaks keeps increasing. After 4 h milling Al peaks are no more detectable, those due to hercynite disappear after 6 h milling while Fe_2O_3 peaks are detectable until 8–10 h milling.

Table 2. Mössbauer parameters as obtained by fitting the spectra of the samples. Shown are the isomer shift δ, quadrupole splitting Δ, magnetic field $\boldsymbol{B}$, half width at half maximum of the peaks $\Gamma_1/2$ and $\Gamma_2/2$, and absorption of each phase (Area).

Sample	Phase	δ mm/s	Δ mm/s	$\boldsymbol{B}$ T	$\Gamma_1/2$ mm/s	$\Gamma_2/2$ mm/s	Area %
Set 1	α-Fe	0.00		33.3	0.18		57
	$FeAl_2O_4$	1.14	1.37		0.51	0.54	5
	Fe clusters	–0.11			0.27		5
	Fe-Al alloy	0.01		29.9	0.60		33
Set 2	α-Fe	0.00		33.4	0.17		74
	$FeAl_2O_4$	1.05	1.74		0.36	0.39	5
	Fe clusters	–0.09			0.18		4
	Fe-Al alloy	0.02		30.4	0.65		17
Set 3	α-Fe	0.00		33.2	0.22		82
	$FeAl_2O_4$	1.07	1.77		0.45	0.55	14
	Fe clusters	–0.11			0.27		4

In Fig. 4, the Mössbauer spectra of the samples of Set 1 at selected times are reported, while Figs. 5 and 6 show the spectra of Set 2 and 3, respectively. Continuous lines in the figures are obtained by fitting the experimental data by means of Lorentzian curves. The resulting evolution of the absorption area of each phase during the milling is given in Fig. 7 for the three sets. Table 2 reports the results of the least squares fits of the spectra of the samples. The values of the isomer shift (δ) relative to α-Fe, quadrupole splitting (Δ), internal magnetic field (B), half width at half maximum of the peaks ($\Gamma_1/2$ and $\Gamma_2/2$) and absorption of each phase (Area) are reported.

In Set 1, the spectrum after 2 h still shows a prevalence of hematite, that is completely reduced only after 12 h milling. α-Fe is clearly visible after 4 h, and its content increases up to a maximum of 57% at 16 h. In this case, a component attributed at an Fe-Al alloy is quite important. After 4 h it becomes quite stable, with its content ranging between 32% and a maximum of 39% at 6 h milling. A small quantity of hercynite was observed (a maximum of 8% after 4 h, 5% in the final sample) but this phase is formed in a non stoichiometric form; we have tried to fit it with a asymmetric doublet component, which can be used when polyphasic spectra are present.

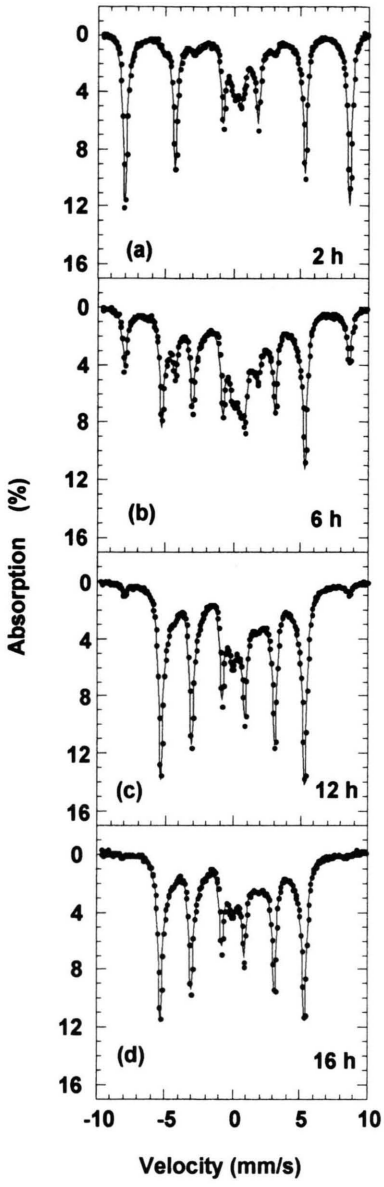


Fig. 4. Mössbauer absorption spectra at selected milling times for Set 1. Experimental data are reported as dots, the fit as solid line.

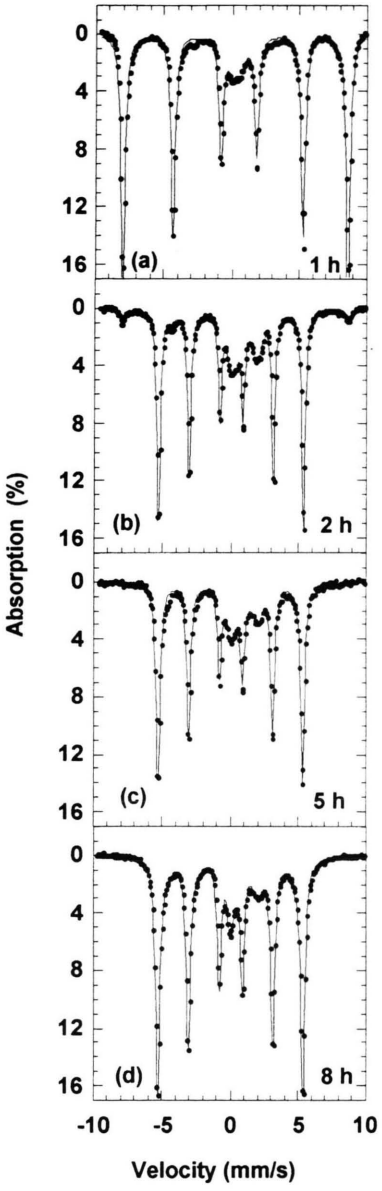


Fig. 5. Mössbauer absorption spectra at selected milling times for Set 2. Experimental data are reported as dots, the fit as solid line.

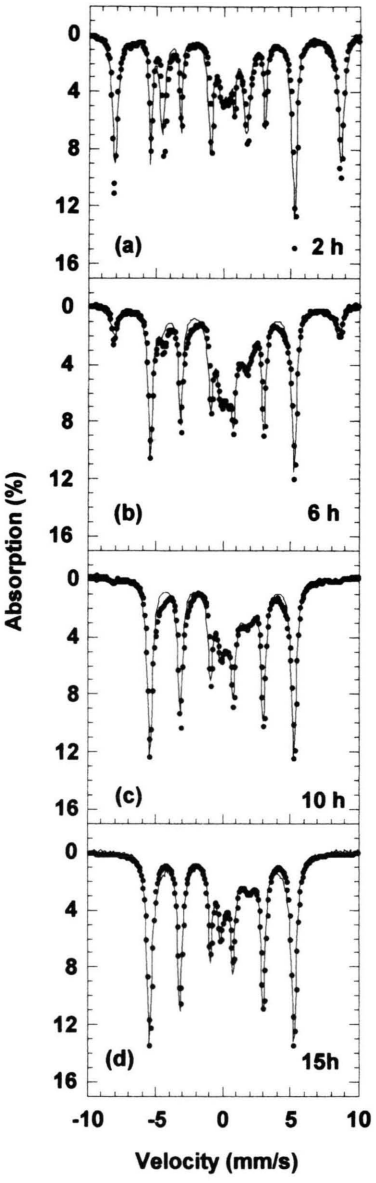
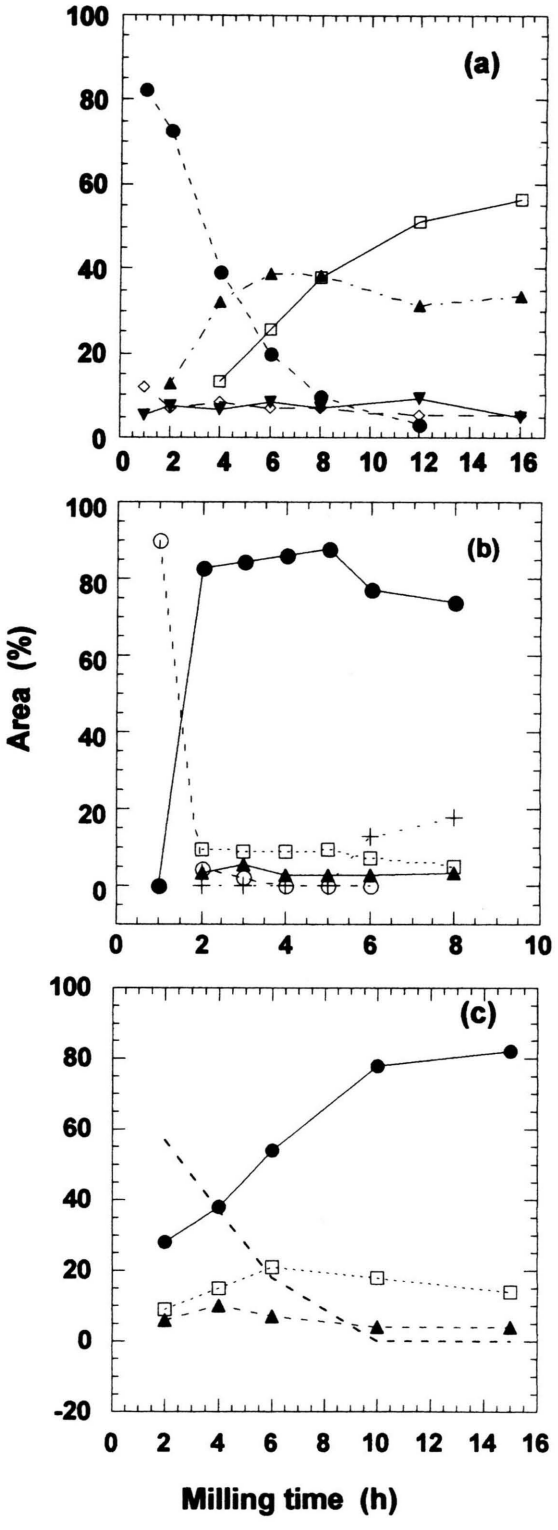


Fig. 6. Mössbauer absorption spectra at selected milling times for Set 3. Experimental data are reported as dots, the fit as solid line.

In Set 2, after 1 h milling the pattern of the spectrum shows the presence of the starting hematite; other phases are not completely discernible. After 2 h milling almost all the hematite component has been reduced to α-Fe (83%); the sample also shows a 10% contents of stoichiometric hercynite and a little single-line component with isomer shift –0.1 mm/s, ascribed to clusters of iron atoms with a size of few nanometers. The hercynite components were fitted by two symmetric Lorentzian quadrupole doublets. Hematite completely disappears after 4 hours milling. The α-Fe content increases until it reaches a maximum (88%) after 5 h. The hercynite content is unchanged around 9% until 5 h, when it starts decreasing down to 5% after 8 h. After 6 h, the presence of



a magnetic sextet component with field intensity around 30 T, attributed to an Fe-Al alloy, can be seen.

In Set 3, 28% of iron is present as α-Fe after 2 h milling, and then the content increases up to 82% after 15 h. The starting hematite disappears at 10 h milling. The hercynite component reaches the maximum of absorption (21%) after 6 h and then decreases to the final 14%. Even in this case, a percentage of Fe clusters is present; it reaches a maximum (10%) at 4 h milling. The Fe-Al alloy does not emerge in any of the milling stages.

4. Discussion

The reaction between aluminum and hematite in presence of allumina is influenced by the ball milling conditions. The strong energetic conditions in Set 2, where a large ball/powder weight ratio and large balls where used, give rise to a very fast evolution between 1 and 2 hours milling. During this stage, at about 1.5 h milling a significant increase of the temperature of the vial was observed, showing that a self-substained combustion reaction similar to a SHS reaction develops. Such a self-substained reaction takes place in spite of the presence of the alumina as diluting agent in the starting powder mixture which should suppress combustion [17]; but it does not succeed completely because of the strong energetic conditions of milling. Actually, the self-substained reaction is not complete, and after 2 h milling the reaction proceeds slowly towards the formation of the final products; in fact, the amount of Al_2O_3 and its diluting effect increases while the Fe_2O_3 and Al content decreases, so that self-substained combustion can non longer continue. The violent evolution of the reaction during the first milling hours has been confirmed by the formation of stoichiometric hercynite, as observed in the SHS reaction of similar mixtures [16].

When the energy level of the BM conditions is lowered, the self-substained combustion reaction does not take place. In Set 3, where the ball/powder weight ratio is decreased from 10/1 to 5/1 while the ball diameters are kept the same, the reaction is slower but the same products form during milling. The formation of non-stoichiometric hercynite was evidenced both by X-ray diffraction and Mössbauer spectroscopy.

Fig. 7. Phase analysis from Mössbauer spectra as per cent of the total spectral area at different milling times for Set 1 (a), Set 2 (b), and Set 3 (c). The used markers are: open circles for hematite, full circles for α-Fe, squares for hercynite, triangles for Fe clusters and crosses for Fe-Al alloy.

Set 1 is characterized by a much smaller energy for single hit than the other two sets because balls of smaller diameter were used but, at the same time, the number of hits is highly increased due to the number of balls which were used in order to keep the ball/powder weight ratio equal to 10/1. In this case the formation of non stoichiometric hercynite was only evidenced by Mössbauer results because its amount is evidently below the detection limit od X-ray diffraction. The Mössbauer results also pointed out the formation from the first stages of the ball milling of an Fe-Al alloy, observed by other authors [6]. From the shift of the magnetic field with respect to that of α-Fe, the amount of Al in the alloy can be extimated to be around 15 at. % [18]. The formation of a small amount of Fe-Al alloy was also observed in Set 2 in the final milling stages. It seems that the formation of hercynite is favoured by the use of strong energetic conditions, while a low energy per single hit favours the formation of Fe-Al alloy.

In all sets, hercynite is the only intermediate compound containing Fe(II) which forms during milling. The formation of Fe_3O_4 (magnetite) and FeO (wuestite), which was observed in the SHS reaction of similar reaction mixtures [16] and in the reaction between Fe_2O_3 and Si induced by ball milling [10], was not evidenced. This was probably due to the excess of Al_2O_3 present in the starting powder mixture.

5. Conclusion

The reaction between Fe_2O_3 and Al in presence of Al_2O_3 activated by ball milling is influenced by the milling conditions. A self-substained combustion reaction was observed with the strongest energetic milling conditions. The intermediate products of the reaction also depend on the energetic conditions: the formation of hercynite is favoured under strong energetic conditions while a low energy per single hit favours the formation of Fe-Al alloy.

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[1] C. C. Koch, in Material Science and Technology: A Comprehensive Treatment, ed. by R. W. Cahn, P. Haasen, and E. J. Kramer, VCH Verlagsgesellschaft, Weinheim 1991, Vol 5, Chapt. 5.
[2] F. H. Froes and J. J. de Barbadillo, Structural Application of Mechanical Alloying, ASM International, Metals Park Ohio 1993.
[3] G. B. Schaffer and P. G. Cormack, Metall. Trans **A21**, 2789 (1990).
[4] P. Matteazzi and G. L. Le Caer, Hyperfine Interact. **68**, 177 (1991).
[5] D. Basset, P. Matteazzi, and F. Miani, Mater. Sci Eng. **A168**, 149 (1993).
[6] D. Basset, P. Matteazzi, F. Miani, and G. L. Le Caer, Hyperfine Interact. **95**, 2235 (1994).
[7] L. Takacs, Mater. Lett. **13**, 119 (1992).
[8] L. Takacs, Nanostr. Mater **2**, 241 (1993).
[9] L. Takacs and M. Pardavi-Horvath, J. Appl. Phys. **75**, 5864 (1994).
[10] A. Corrias, G. Ennas, G. Paschina, G. Piccaluga, and D. Zedda, Mater. Sci. Forum, **195**, 25 (1995).
[11] G. Concas, F. Congiu, A. Corrias, C. Muntoni, G. Paschina, and D. Zedda, Z. Naturforsch. **51a**, 915 (1996).
[12] A. Corrias, G. Paschina, P. Sirigu, and D. Zedda, Mater. Sci. Forum, **235–238**, 199 (1997).
[13] A. Corrias, G. Ennas, A. Musinu, G. Paschina, and D. Zedda, J. Mater. Res. **12**, 2767 (1997).
[14] A. Corrias, G. Paschina, and P. Sirigu, J. Non-Cryst. Solids, in press.
[15] R. Orrù, B. Simoncini, P. F. Virdis, and G. Cao, Metall. Sci. Tech. **14**, 69 (1996).
[16] G. Cao, G. Concas, A. Corrias, R. Orrù, G. Paschina, B. Simoncini, and G. Spano, Z. Naturforsch. **52a**, 539 (1997).
[17] L. Takacs, Appl. Phys. Lett **69**, 436 (1996).
[18] M. B. Stearns, Phys. Rev. **147**, 439 (1966).