Mechanochemical Reactions in Fe$_2$O$_3$–M (M: Al, Ti)

C. CUADRADO-LABORDE, L. C. DAMONTE and L. MENDOZA-ZÉLIS
Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C.67, 1900, La Plata, Argentina; e-mail: claborde@venus.fisica.unlp.edu.ar

Abstract. The production of metal–ceramic nanodispersion by mechanical milling of powders through the displacement reaction Fe$_2$O$_3$ + M → Fe + M-oxide (with M: Al, Ti) was studied. The reaction progress with milling time was followed by recording the temperature and pressure during the process. The samples were characterized by X-ray diffraction and Mössbauer spectroscopy at the intermediate and final stages. In both cases self-sustained reactions were observed with different activation times. The results confirm that mechanical work at room temperature yields the reduction of hematite by Ti and Al. The final oxides were identified as Ti$_2$O$_3$ and Al$_2$O$_3$, respectively. The dependence of the intermediate and final stages on the milling conditions and the starting composition will be discussed.

Key words: Fe$_2$O$_3$ (hematite), Ti, Al, ball milling, self-sustained reaction, XRD, Mössbauer.

1. Introduction

In the last years there has been a significant development in the study of the so-called nanostructured materials. Cermets (ceramic–metal alloys) are a sub-class of them in which there exist metallic dispersions of nanometer size, embedded in a ceramic matrix. Mechanical alloying has demonstrated to be helpful in the preparation of this kind of composites [1]. One way to produce them is by a solid state reaction, in which a reactive metal reduces the oxide and simultaneously refines the metal in just one step [2, 3].

In some cases the reaction enthalpy is so high that the reaction could proceed in a non-gradual way. This means that there is none or little chemical change in the system until a critical condition is reached after a time interval called the ignition time t_{ig}. Then the system evolves in a violent way, a combustion front is generated and the reaction is completed in a fraction of a second [3]. This kind of process receives the name of self-sustained reactions (SSR). Estimated temperatures during this process indicated that local melting is possible. Experimental evidence of this has been encountered by Transmission Electron Microscopy (TEM) [4] in the mechano-chemical reduction of V$_2$O$_5$ by Al.

In this work we aim to produce cermets by mechanical alloying at room temperature in which the matrix to be produced is a ceramic of the alumina or titanium oxide type and the metals inclusions, iron. In both cases, the reaction enthalpy and the

estimated adiabatic temperature (3962 K and 2986 K, for Al and Ti, respectively) during the process, indicate that these are of the SSR type [2].

2. Experimental

Mechanical alloying was performed in a Restch MM2 vibratory ball mill, in a frequency range between 26 Hz and 36 Hz. The cylinder had a volume of 8 cm^3 with one steel ball of $\varnothing = 12$ mm. The starting materials, Fe_2O_3 (Johnson Matthey Company, 99.99%, -15 mesh), Al (Johnson Matthey Company, 99.5%, -325 mesh) and Ti (Johnson Matthey Company, 99.9%, -15 mesh) were enclosed in the vial under argon atmosphere. The mixture compositions corresponded to one of the following stoichiometric reactions:

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3, \tag{1}$$
$$2Fe_2O_3 + 3Ti \rightarrow 4Fe + 3TiO_2. \tag{2}$$

A 10% excess of reducing agent (Al, Ti) was used in all tests to ensure complete reduction. In the Fe–O–Al system we used a $7:1$ ball to powder weight ratio and $14:1$ in the Fe–O–Ti system.

The temperature during ball milling was monitored using a type K thermocouple located at 1 mm of one of the vial ends. The pressure inside the chamber was also registered with a strain gauge.

The powders were examined using X-ray diffraction (XRD, Phillips diffractometer PW1710, Cu Kα with $\lambda = 0.154184$ nm), and Mössbauer spectroscopy (MS). The MS experiments were done at room temperature using a conventional spectrometer under transmission geometry with ^{57}CoRh radioactive source.

3. Results and discussion

Figure 1 shows the temperature (T) and pressure (P) recorded during the milling runs. The jump in both registers determines the ignition time (t_{ig}) and so the occurrence of SSR in these samples. It is worth noticing some differences in the behavior of both systems. In Fe–O–Al a sharp peak develops in P as well as in T. The absence of any evolved gas allows to assign the P-peak to the gas temperature rise. In this sense, the P register constitutes a much sensitive probe for the sample temperature than the T register itself. In Fe–O–Ti, the P-peak is not so sharp and the T-register just shows a shoulder at t_{ig}, evidencing that the evolved heat is lesser than in the former case. At longer milling times no changes are noticed for Fe–O–Al. Instead, for Fe–O–Ti, a broad peak develops in the P signal, while T remains constant. This pressure variation might be associated with a change in the gas density inside the chamber, probably originated in gas evolving from the sample.
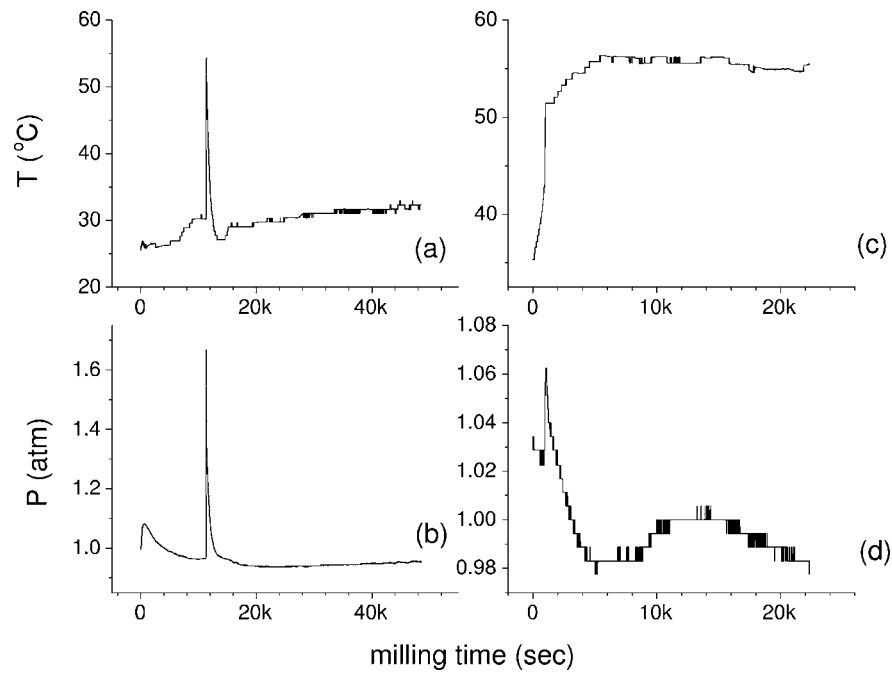
Figure 1. Temperature and pressure recording during the milling for the Fe–O–Al system (a) and (b); Fe–O–Ti system (c) and (d), respectively.
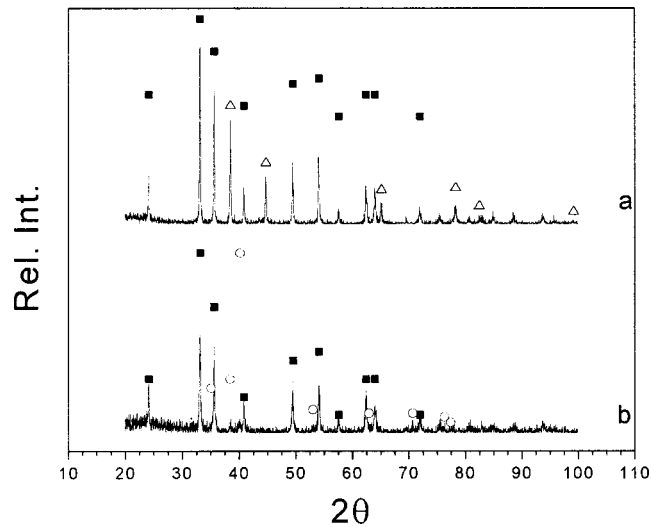

Figure 2. XRD patterns of samples, which have not presented SSR. (a) Fe–O–Al system, (b) Fe–O–Ti system. The symbols represent: Ti (o), Fe$_2$O$_3$ (■), Al (△).

3.1. XRD ANALYSIS

In the Fe–O–Al system, it is clearly observed by XRD (Figure 2(a)), that the reaction has practically not advanced in those samples milled for time periods shorter
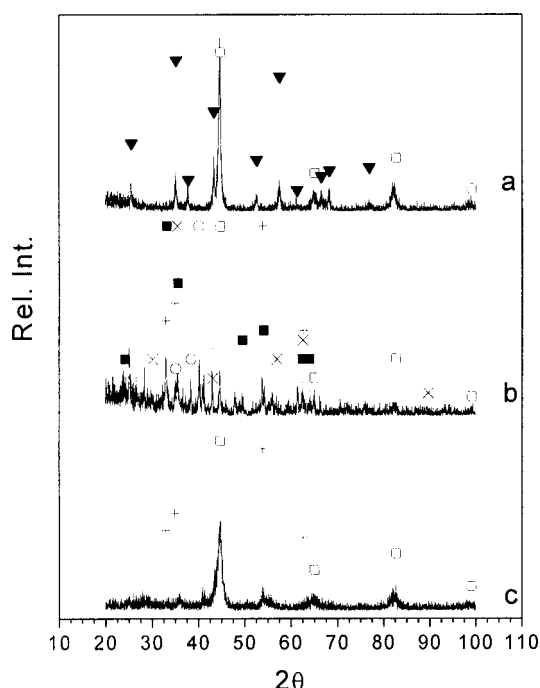
Figure 3. XRD patterns of samples which have presented SSR: (a) Fe–O–Al system, (b) Fe–O–Ti system, immediately after SSR and (c) Fe–O–Ti system, 4 hs after SSR. The symbols represent: Ti (○), Fe_2O_3 (■), Fe (□), Fe_3O_4 (×), Ti_2O_3 (+) and Al_2O_3 (▼).

than t_{ig}. The Fe_2O_3 and Al lines evidence this. The same behavior is observed in the Fe–O–Ti system (Figure 2(b)).

Once the t_{ig} is passed, Fe lines can be observed by XRD in both systems (Figure 3(a) and (b)), indicating that a displacement reaction proceeds. The reduction of hematite by aluminum is very fast, being completed rapidly after the ignition time is reached (Figure 3(a)). In contrast, in the case of titanium the reaction is not complete and the presence of residual Fe_2O_3 strongly depends on the additional milling time. This was studied in a sample in which the milling was interrupted immediately after t_{ig} was reached. A variety of phases: Fe, Fe_2O_3, Fe_3O_4, Ti and Ti_2O_3 (Figure 3(b)) were detected. The presence of Fe_2O_3 and Ti indicated that, in spite of being the SSR detected, the oxide-reduction process had not finished yet. Additional milling drives the system to the final stage of the reaction: Fe and Ti_2O_3 (Figure 3(c)).

The influence of the milling frequency on the process was also investigated. It was found that increasing milling frequencies determines lower ignition times in both systems, without any change in the characterization of the final products. In the Fe–O–Al system it was found that the reaction proceeds only when the hematite grains reach a critical size, calculated with the Scherrer formula from the XRD patterns (using the five principal peaks) to be lower than 25 nm (Figure 4). The
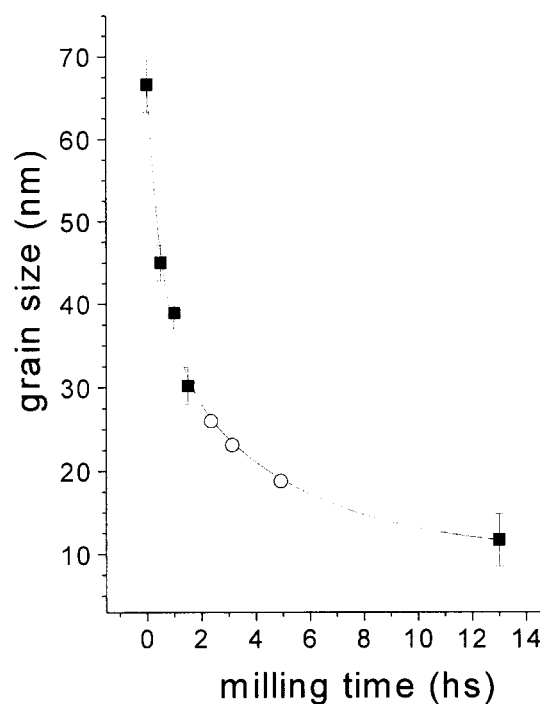
Figure 4. Grain size evolution as a function of the milling time of hematite, in the Fe–O–Al system. Samples which have not presented SSR (■), estimated in those samples which have presented SSR (○).

experimental point located at 13 h of milling time and 12.2 nm of grain size belongs to an off-stoichiometry sample. Then, one possible explanation of the observed behavior is that when the milling intensity is increased, that critical grain size is reached in a shorter time.

The amount of reactants was derived from the stoichiometry of the intended products (Equations (1) and (2)). We investigate the effect of using a starting mixture with a different amount of reducing agent. In the Fe–O–Al system, the SSR does not occurs at all after 13 hs of milling for a sample containing 25% less of Al, as it is evidenced by the XRD pattern (Figure 5(a)). Such deviations from stoichiometry could be considered equivalent to adding an inert material to the reaction mixture. Inert additives form a layer that inhibits diffusion, so SSR is hindered if the composition is far away from exact stoichiometry. This could be an explanation for the absence of SSR in non-stoichiometric samples, even when the hematite grains have reached the critical size. Nevertheless, some systems did not follow this behavior showing shorter activation times at compositions far from stoichiometry [5].

In the Fe–O–Ti system, when the starting mixture was prepared with a 13% excess of reducing agent (Ti), the ignition time (t_{ig} = 795 sec) was shorter than
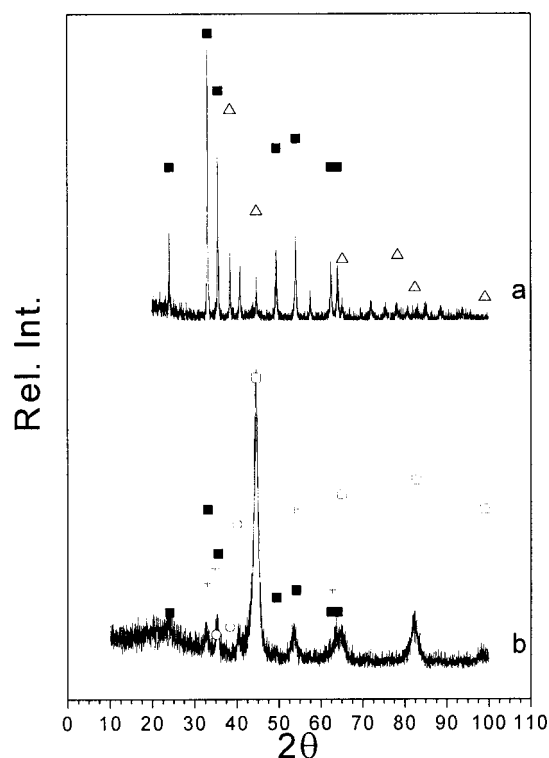
Figure 5. Off-stoichiometry XRD patterns: (a) Fe–O–Al system with −25% Al, (b) Fe–O–Ti system with +13% Ti. The symbols represent: Ti (○), Fe_2O_3 (■), Al (△), Fe (□) and Ti_2O_3 (+).

that observed for stoichiometry (2) ($t_{ig} = 975$ sec). The XRD pattern did not show another differences when it was compared with those samples prepared according Equation (2) (Figure 5(b)). It is interesting to note that this stoichiometry is closer to the final product (Ti_2O_3) than (2), in this way favoring SSR and so presenting a lower ignition time.

3.2. MS ANALYSIS

In the Fe–O–Al system, for samples where the SSR has not been detected due to a low milling time, the spectrum is that of hematite with an additional quadrupole interaction, whose fraction increases with milling time (2–3 at%, Table I; Figure 6(a)). For similar samples in the Fe–O–Ti system, the spectra only show the magnetic interaction characteristic of hematite (Table I; Figure 6(b)).

For increasing milling times, SSR occurs and MS experiments evidences this also. In the Fe–O–Al system (Figure 7(a)), 90% of the MS spectrum may be attributed to Fe nuclei in α-Fe. At least one additional sextet ($B = 30.2_1$ T) is needed to describe this phase indicating the existence of Fe nuclei with non

Table I. Mössbauer parameters for Fe–O–Al and Fe–O–Ti system

System	Sample	f (at.%)	δ (mm/s)	ΔQ (mm/s)	B (T)
Fe–O–Al	Before SSR	98_1	0.363_1	-0.080_1	50.226_6
	(milling time of 30′)	1.9_3	0.18_3	0.66_5	
	After SSR	70_3	0.008_1		32.53_1
	($t_{ign} = 3$ h 8′)	20_2	0.037_6		30.2_1
		7_2	0.9_1	2.4_2	
		2_1	0.18	0.5_1	
	Off-stoichiometry	91_2	0.369_1	-0.077_1	51.72_1
	(−25% Al)	4_2	0		32.3_6
	(milling time of 13 h)	4.8_3	0.16_1	0.53_2	
Fe–O–Ti	Before SSR	100	0.375_1	-0.084_1	52.63_1
	(milling time of 5′)				
	Interrupted	38_2	0.264_3	-0.1778_5	51.71_2
	immediately	26_1	-0.106_3		33.19_2
	after SSR	7_1	-0.15_1	-0.09_3	31.1_1
	($t_{ign} = 17′$)	6_1	0.54_4	-0.04_8	45.8_2
		4_1	0.43_3	-0.53_7	48.7_2
		4_2	0.94_4	1.18_7	
		10_2	0.45_5	1.44_4	
		3.1_7	1.51_3	1.9_6	
	After SSR,	72_2	0.003_1	-0.001_1	33.52_1
	with an additional	13_2	0.03_3	-0.02_3	29.0_3
	milling time of 4 h	10.7_5	-0.098_4		
		3.8_9	1.28_6	1.6_1	
	Off-stoichiometry	89_7	-0.109_3		33.44_2
	(milling time of 5 h)	10_2	0	1.2_1	

f: Area fraction for each component; δ: isomeric shift relative to ^{57}Fe; $\Delta Q = eQV_{zz}(1+\eta^2/3)^{1/2}/4$ and B: magnetic hyperfine field. The subscripts indicate the error in the last number.

magnetic neighbors as expected for a slight dilution of Al in the Fe matrix. Finally, besides the above mentioned quadrupole interaction, another paramagnetic phase associated with hercynite ($FeAl_2O_4$) was observed. This is a normal spinel with Fe (II) on the tetrahedral sites and Al (III) on the octahedral ones. The measured isomeric shift (δ) (Table I) is consistent with a Fe (II) atom in a tetrahedral site (mean δ value: 0.94 mm/sec). The small phase fraction and eventually a small grain size may explain its no detection in the XRD patterns.

For Fe–O–Ti, if milling is stopped immediately after the P-peak is attained, the measured MS pattern is rather complicated (Table I, Figure 7(b)). Approximately 33% of the Fe atoms belong to α-Fe with a slight Ti dilution. As already noted by XRD, there is an important fraction (38% of the spectrum) of hematite in the sam-
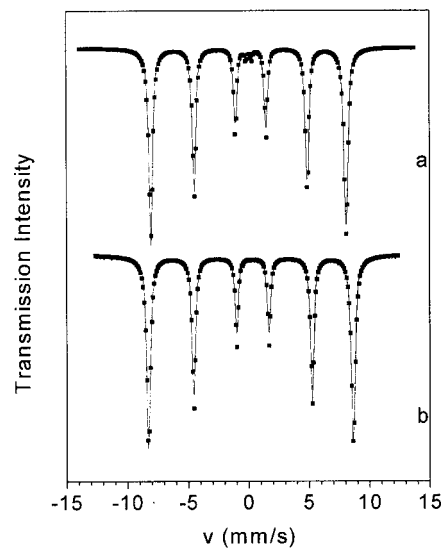
Figure 6. Mössbauer spectra of samples, which have not presented SSR: (a) Fe–O–Al system, (b) Fe–O–Ti system. The symbols represent: experimental data (■), fittings (solid line).
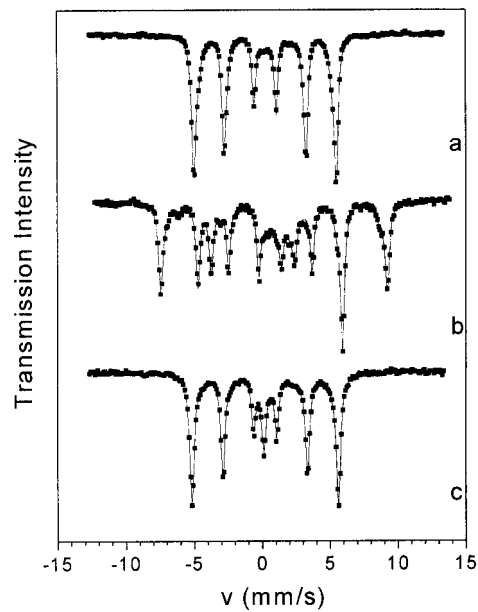

Figure 7. Mössbauer spectra of samples, which have presented SSR: (a) Fe–O–Al system, (b) Fe–O–Ti system (immediately stopped after SSR) and (c) Fe–O–Ti system (4 hr after SSR). The symbols represent: experimental data (■), fittings (solid line).

ple. There is a minor fraction of a third magnetic interaction, possibly due to magnetite (Fe_3O_4), but another iron oxides like maghemite (γ-Fe_2O_3) cannot be discarded. Finally, 17% of Fe atoms are in a paramagnetic phase known as ulvöespinel

(Fe_2TiO_4); three quadrupole hyperfine interactions were proposed to describe this phase. The quadrupole splittings and broad line widths were assumed to originate in a random arrangement of the Fe and Ti ions in the octahedral sites [6, 7].

When an additional milling is carried out (4 hs), no hematite lines were observed (Figure 7(c)), prevailing those of Fe (Table I) with an extra sextet to describe a small dilution of Ti in the matrix. One additional interaction was considered: a single line which was assigned to γ-Fe [8] (11 at.%).

The possibility of deoxidation of hematite by ball milling using Ti like reducing agent was also investigated by Tokumitsu *et al.* [9]. The authors reported the formation of TiO_2 as a final product, the gradual reduction of hematite during milling and the absence of intermediate oxides in this process. In contrast we did not find TiO_2 neither a gradual reduction of hematite. Moreover MS patterns showed the presence of Fe_3O_4 immediately after SSR, possibly like an intermediate stage in the deoxidation path of the hematite. The different milling conditions might be the major cause of these discrepancies.

In agreement with XRD results, no appreciable effect in the MS patterns was observed in those samples milled at different frequencies, for both systems.

Off-stoichiometry generally results in a major complexity of the MS patterns of the milled samples. In the Fe–O–Al system after 13 hs of milling (Figure 8(a), and Table I), the hematite sextet, a quadrupole doublet corresponding to hercynite and a low trace of Fe (4 at.%) were identified. The later could indicate that oxide-reduction reaction proceeds rather slowly in off-stoichiometric samples, at least
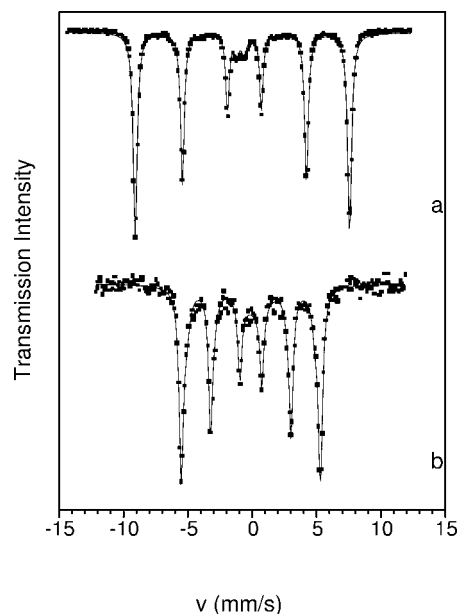

Figure 8. Off-stoichiometry Mössbauer spectra of samples: (a) Fe–O–Al system (−25% of Al), (b) Fe–O–Ti system (+13% of Ti, 5 hs after SSR). The symbols represent: experimental data (■), fittings (solid line).

under the present conditions of milling. The low proportion of Fe is the main reason for its no detection in the XRD pattern (Figure 5(a)).

The spectrum of samples prepared with a 13% Ti excess, in the Fe–O–Ti system, is somewhat different from those obtained under the stoichiometric conditions of Equation (2) (Figure 8(b)). An SSR was detected in the temperature and pressure registers and the spectrum may be fitted with two magnetic interactions assigned to Fe (Ti) and a non identified paramagnetic phase.

4. Conclusions

Mechanically assisted displacement reactions were detected and studied by XRD and MS in the Fe–O–Al and Fe–O–Ti systems. The identified oxides were Al_2O_3, and Ti_2O_3 respectively. Temperature and pressure recordings during milling showed that both systems presents SSR at a characteristic t_{ig}, which is much shorter for the Fe–O–Ti system. Other interesting differences arise between both systems when a characterization of the final products is attempted. While a simple role exchange between Fe and Al seems to occur in Fe–O–Al, giving rise to the intended Fe/alumina dispersion, a complex mixture forms in the case of Fe–O–Ti and the final product does not contain the desired TiO_2. This is probably due to the great complexity of the Ti-O phase diagram between 60–70 at.% Ti with a variety of intermediate oxides, which might favor the formation of lower oxides and would explain the smaller heat effect observed. The further transformation towards the final (undesired) product Ti_2O_3 implies some oxygen excess whose evolution may provoke the observed P variation.

In summary, we have proved that Al oxide/Fe and Ti oxide/Fe cermets could be obtained at room temperature by *in situ* mechanochemical reactions. Subsequent experiments to determine the adequate conditions for the formation TiO_2/Fe dispersions are in course.

References

1. Gaffet, E., Abdellaoui, M. and Malhouroux-Gagget, N., *Materials Transactions, JIM* **36**(2) (1995), 198.
2. Schaffer, G. B. and Mc Cormick, P. G., *Materials Science Forum* **88–90** (1992), 779.
3. Gaffet, E., Bernard, F., Niepce, J. C., Charlot, F., Gras, C., Le Caër, G., Guichard, J. L., Delcroix, P., Mocellin, A. and Tillement, O., *Journal of Material Chemistry* **9** (1999), 305.
4. Mc Cormick, P. G., *Materials Transactions, JIM* **36**(2) (1995), 161.
5. Takacs, L. and Susol, M. A., *Materials Science Forum* **225–227** (1996), 559.
6. Murad, E. and Johnston, J. H., In: G. J. Long (ed.), *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, Vol. 2, Plenum Publishing Corporation, 1987, p. 507.
7. Rossiter, M. J. and Clarke, P. T., *Nature* **207** (1965), 402.
8. Ingalls, R., Van der Woude, F. and Sawatzky, G. A., In: G. K. Shenoy and F. E. Wagner (eds), *Mössbauer Isomer Shifts*, North-Holland Publishing Company, 1978, p. 415.
9. Tokumitsu, K., Nasu, T., Suzuki, K. and Greer, A. L., In: M. D. Baró and S. Suriñach (eds), *Proc. of the Int. Symposium of Mechanically Alloyed, Metastable and Nanocrystalline Materials (ISMANAM)*, Sitges (Barcelona) 1997, Trans Tech Publications LTD, Switzerland, 1998, p. 181.