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Thermochimica Acta 363 (2000) 143–147

thermochimica acta

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Thermal and phase evolution of mechanochemical reactions in the Al–Fe_3O_4 system

P.M. Botta[a,*], E.F. Aglietti[b], J.M. Porto López[a]

[a]Instituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA), CONICET–UNMdP, Av. J.B. Justo 4302, B7608FDQ Mar del Plata, Argentina

[b]Centro de Tecnología de Recursos Minerales y Cerámica (CETMIC), CONICET–CIC–UNLP, Cno. Centenario y 506, 1897 M.B. Gonnet, Argentina

Received 23 May 2000; accepted 11 July 2000

Abstract

The physicochemical and thermal behavior of mechanochemically activated Al–Fe_3O_4 mixtures have been studied. The composition and structural changes undergone in the reaction system have been analyzed by DTA and XRD. Experimental evidence indicates that the nature of the products was dependent on the conditions of mechanochemical and thermal treatments. Under adequate experimental conditions, a self-sustained reaction was triggered, with the production of α-Fe and α-Al_2O_3. By varying the treatment parameters, it was possible, through an alternative reaction path, to obtain different products which show interesting properties in their application as functional materials. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Mechanochemistry; Al–Fe_3O_4; Thermal analysis; Self-sustained reaction

1. Introduction

Mechanochemical synthesis and mechanical activation have been utilized to prepare nanocrystalline powders, nanostructured materials and ferrite magnetic materials. The activation of crystalline solids in high-energy mills results in structural and textural changes which may be used for developing materials [1–3]. These phenomena were initially observed in grinding operations, mainly in impact and attrition milling, through the development of new surfaces and deformations of the crystal lattice of solids. These imperfections have a remarkable effect on the thermal behavior of the solid, including changes in the kinetic parameters of the reactions in which the solid takes part, such as decompositions, oxidations, phase changes, etc. Furthermore, the presence of crystalline defects is a way of storing excess energy, which may result in a diminution of the activation energy of ulterior reactions [4].

Mechanochemical effects are present in activation processes, in which a metal–metal oxide system is made to react in order to obtain new compounds or composites. For these materials, diffusion rates are comparatively high, while diffusion path lengths are reduced. This, coupled with extended interfacial areas, may serve to drive the reaction into a critical ignition condition [5].

It is a well-known fact that the mechanochemical activation of the system Al–Fe_3O_4 produces a violent

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[*] Corresponding author. Tel.: +54-223-481-6600; fax: +54-223-481-0046.
E-mail address: pbotta@fi.mdp.edu.ar (P.M. Botta).

PII: S0040-6031(00)00593-1

exothermal, self-sustained reaction yielding α-Fe and α-Al_2O_3 [6]. However, by controlling adequately the processing variables in the mechanochemical activation and in the final thermal treatment, it is possible to obtain intermediate phases, some of which possess potential applicability as sensors, as in the case of $FeAl_2O_4$ (hercynite) [7].

Taking into account the potential of mechanochemical processing for materials synthesis [8,9], the influence of mechanochemical treatment on the thermal behavior of the system Al–Fe_3O_4 has been studied, with the aim of describing the relationships between the processing variables and the transformations undergone by the reacting solids.

2. Experimental

Magnetite was a concentrate of an iron ore from Sierra Grande, Chubut, Argentina, with $\geq 97.5\%$ Fe_3O_4. Metallic Al was a commercial reagent (99.9% pure). Both reactants had a particle size lower than 44 μm (ASTM sieve No. 325).

For the preparation of the reactant mixtures, both solids were mixed in an Al–Fe_3O_4 molar ratio of 2.67:1, corresponding to the stoichiometry of the reaction

$$3Fe_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Fe \quad (\Delta H^0 = -3021\,\mathrm{kJ})$$

Mechanochemical activations were performed with a planetary laboratory mill Fritsch Pulverisette 7, with vials and balls of Cr steel. The samples were prepared and treated under Ar atmosphere ($P_{O_2} < 1\,\mathrm{Pa}$). The vials were rotated at 1500 rpm, and a ball to powder mass ratio of 20:1 was used. The samples obtained were denominated ME*x*, where *x* is the treatment time in minutes. Differential thermal analyses were performed in a Shimadzu DTA-50H analyzer, with Pt sample holders and α-Al_2O_3 as reference. The analyses were made under flowing Ar atmosphere ($40\,\mathrm{cm^3\,min^{-1}}$), starting the heating program after 20 min of purging with Arat room temperature. Different sample masses and heating rates were used in order to assess the behavior of the system under several heat dissipation conditions. To identify the transformations undergone by the reacting mixture, a Philips PW 1830/00 diffractometer was used, with Mo Kα radiation at 50 kV and 30 mA.

3. Results

The samples, mechanochemically treated for up to 30 min and subsequently analyzed by XRD, did not show any new crystalline phases. The only effect observed was a remarkable diminution in the diffracted intensities and an increase in the full width of half maximum (FWHM) of the diffraction mainly in the case of magnetite. However, with treatment times of 20 and 30 min, deposits of metallic Fe were observed on the walls of the vials, suggesting that the reaction (i) had occurred to a limited extent but this did not extend to the whole solid mass.

With longer treatment times, this reaction took place completely during the mechanochemical activation. The XRD analysis of the sample ME37 revealed the presence of α-Fe and α-Al_2O_3. Longer treatments did not produce any new transformations, but a gradual damage of the crystal structures of the reaction products was observed.

Fig. 1 shows the DTA curves of the samples activated for up to 30 min, using a sample mass of 40 mg and a heating rate of $10^\circ\mathrm{C\,min^{-1}}$. At approximately 600°C, an exotherm was observed, attributed to the oxidation of part of the Al. The intensity of this exotherm was greater for ME0 and ME5, lower for ME10, and not detectable in ME20 and ME30. The assignation of the exotherm to the oxidation of Al was corroborated by DTA measurements in air atmosphere of air. An increase in intensity of the exotherm was more than an order of magnitude was observed, in relation to a sample of pure Al in Ar atmosphere. This

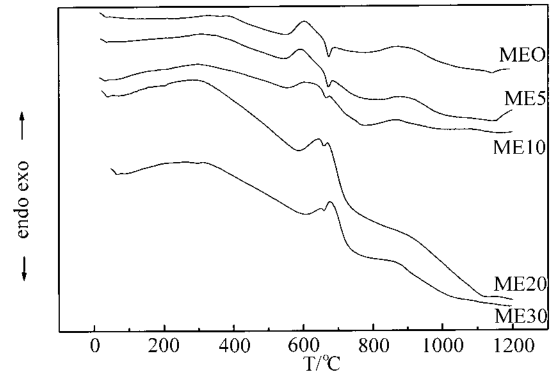

Fig. 1. DTA curves of the activated mixtures ME0–ME30 using a heating rate of $10^\circ\mathrm{C\,min^{-1}}$ and 40 mg of sample.

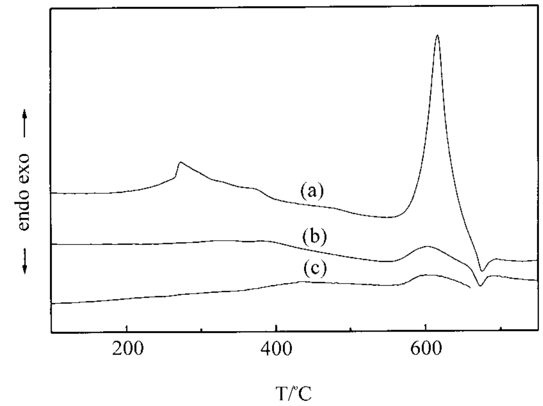

Fig. 2. DTA curves of: (a) ME0 in air atmosphere; (b) ME0 in Ar atmosphere; (c) Al in Ar atmosphere.

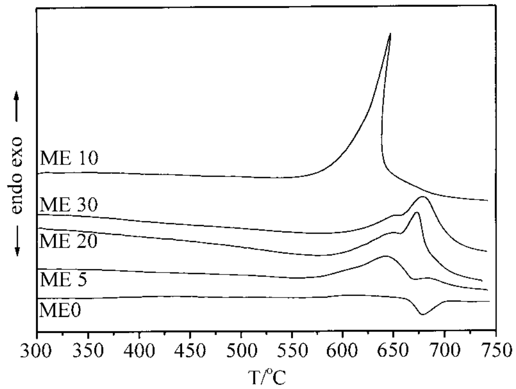

Fig. 3. DTA curves of the activated mixtures ME0–ME30, using a heating rate of 10°C min^{-1} and 100 mg of sample.

last sample showed an exotherm similar to that of ME0 (Fig. 2).

At slightly higher temperatures, an endotherm was superimposed on the exotherm corresponding to the fusion of Al (660°C) and an exotherm (in ME10, ME20 and ME30 only) with increasing intensity for longer treatment times appears. In order to determine the process originating this exotherm, thermal treatments were performed in identical conditions to those in DTA analysis, but just up to 750°C, and the products obtained were analyzed by XRD. The diffractograms showed peaks corresponding to Fe (with intensity increasing with the treatment time), FeO and Fe_2O_3 (in low concentration, which did not vary with treatment time), and Fe_3O_4 (with decreasing intensity).

Fig. 3 shows the DTA up to 750°C of the series ME0–ME30 with a heating rate of 10°C min^{-1}, but with a sample mass of 100 mg. The results were similar to those previously obtained, except for ME10, which has an exotherm centered at 625°C, but far more intense than that obtained with 40 mg of ME10.

Finally, with the objective of studying the effect of the heating rate on the development of the reaction, a series of DTA analysis were made at 20°C min^{-1}, with 100 mg of sample. To make this clear, in this case the thermograms are presented as ΔT vs. time. They have been corrected in order to establish an exact relationship between time and temperature. A very intense exotherm is observed at about 600°C for ME10, ME20 and ME30. This was assigned to reaction (1), since the XRD analyses showed only the diffraction peaks corresponding to α-Fe and α-Al_2O_3. On the other hand, ME0 and ME5 exhibited thermograms similar to those obtained with 40 mg of sample and a heating rate of 10°C min^{-1}. (For the sake of clarity, the diagram corresponding to ME20 has not been included in Fig. 4.)

4. Discussion

As mentioned earlier, for mechanochemical activation equal to or longer than 37 min, reaction (i) proceeded completely. This self-sustaining reaction has been previously reported [6] and is one of the

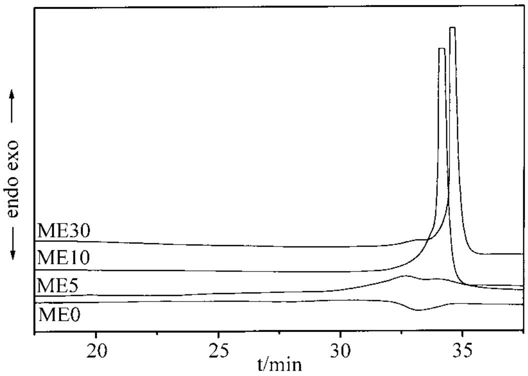

Fig. 4. DTA curves of the activated mixtures ME0–ME30, using a heating rate of 20°C min^{-1} and 100 mg of sample.

reaction used as a synthesis tool in the processes known as self-sustained high-temperature synthesis (SHS) [10,11]. In this case, the ignition of the reaction is produced by a progressive accumulation of energy within the crystal structure (instead of conventional thermal ignition), as a consequence of the mechanical energy supplied to the solid during the treatment. In those samples in which the treatment has not yet produced a complete chemical reaction ($t \leq 30\,\text{min}$), the accumulated energy is barely enough to cause the reaction in limited regions of the solid, and/or to produce a certain concentration of an activated precursor which, under subsequent thermal treatment, will trigger the self-sustained reaction, or will evolve resulting in different products, depending on the thermal treatment parameters employed.

In the DTA runs made with 40 mg of sample and a heating rate of 10°C min^{-1}, none of these samples can react in a self-sustained way. However, ME10, ME20 and ME30 react partially at about 660°C, according to the XRD analysis of these samples heated up to 750°C.

The appearance of the exothermic band at constant temperature for all the reactive mixtures suggests that the mechanochemical treatment produces an activated precursor with a structure which is similar for all the samples in the series. That is, at longer treatment times its concentration is increased, but without a sensible diminution in the activation energy of reaction (1). This behavior is clearly different to that reported for other mechanochemically activated systems [12–14], in which a change in the temperature of this effect is observed according to the intensity of the mechanochemical treatment.

The samples calcined up to 1200°C showed the formation of hercynite in increasing concentration with milling time. This was the only crystalline phase observed for ME20 and ME30. Simultaneously, magnetite and hematite decrease in concentration from ME0 to ME10, and virtually disappear in ME20 and ME30. None of the diffractograms reveals the presence of wüstite (FeO).

The explanation of the observed behavior involves: (1) the oxidation of the Fe produced at 600–700°C by the residual oxygen of the furnace atmosphere, producing hercynite; (2) the reaction of magnetite with Al and/or non-crystalline Al_2O_3, also forming hercynite. The hematite, which was present at 750°C, is reduced and disappears from the samples.

The results of the DTA runs performed at 10°C min^{-1} with 100 mg of sample indicate that ME10 reacts at ≈ 625°C much more completely than ME20 and ME30. This fact, which is different from the results obtained in the previous series, indicates that the heat dissipation capacity of the system is a determining factor in the development of the reaction. ME10 is activated enough to react in thermal conditions in which the dissipation of heat is made difficult. Then, in apparent contradiction with the conclusions from the DTA traces made with smaller samples, ME10 shows a thermal effect greater than the mixtures mechanochemically activated during longer times. This suggests that ME20 and ME30, although contain higher concentrations of activated precursor, suffer the effect of dilution due to the presence of the reaction products [15], formed by the incipient reaction during milling. On the other hand, ME10 contains a concentration of precursor high enough to react, but does not undergo the heat absorption by the reaction products. This dilution effect may be illustrated by Fig. 5, in which the DTA thermograms of ME10 and ME10 diluted with 50% α-Al_2O_3 are shown. Both runs were made using 100 mg of sample and a heating rate of 10°C min^{-1}. It can be seen that, when the sample is diluted, a band is obtained which is less intense and of similar shape to those produced by ME20 and ME30.

Fig. 4 reaffirms the importance of the heat dissipation capacity on the evolution of the reaction mixtures.

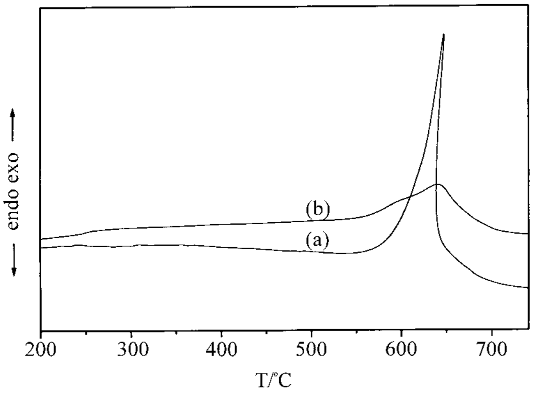

Fig. 5. DTA curves of: (a) ME10; (b) ME10 diluted with α-Al_2O_3 (50:50). In both cases a heating rate of 10°C min^{-1} and 100 mg of sample were used.

The violent reaction occurring for ME10, ME20 and ME30 is a consequence of the heat accumulation within the sample. Under these conditions, reaction (1) occurs as a self-sustained process. However, for ME0 and ME5 these conditions are not sufficient to generate the ignition of the reaction, which occurs only partially because of the low concentrations of activated precursor.

These results reveal that, through an adequate combination of activation time and thermal treatment conditions, it is possible to control the different reaction paths of the system, and consequently the nature and properties of the obtained products. However, it is clear that additional studies are necessary, mainly concerning to structural aspects of the process. The complete understanding of the mechanochemical and thermal effects would be useful to determine the optimal processing conditions for the preparation of functional materials with predetermined properties.

5. Conclusions

1. The mechanochemical treatment produces two clearly different effects:
   - 1.1. Up to 30 min, it decreases the crystallinity of the mixtures and increases their reactivity, with occurrence of incipient reaction in isolated regions of the solids.
   - 1.2. At 37 min of treatment and beyond, reaction (1) is produced as a self-sustained process, with production of α-Fe and α-Al_2O_3.
2. The thermal evolution of the system is critically dependent on its heat dissipation capacity, and then on the conditions in which the heat treatment of the samples is realized.
3. In activated samples, the reaction takes place via an activated precursor, the structure of which is similar along the series of samples. Its concentration increases with activation time. However, the reactivity of the mixture is not invariably higher for longer treatment times, since it is also influenced by the dilution effect from the products of the incipient reaction, formed during milling:
   - 3.1. Using conditions of high heat dissipation rates (40 mg of sample at 10°C min^{-1}), the reactivity is ME30 $>$ ME20 $>$ ME10.
   - 3.2. Using intermediate conditions (100 mg at 20°C min^{-1}), ME10 $>$ ME20 $\approx$ ME30.
   - 3.3. Using low dissipation conditions (100 mg at 20°C min^{-1}), the reaction becomes self-sustained, and ME10 $\approx$ ME20 $\approx$ ME30.
4. Then, through the control of the activation times, and of the thermal treatment conditions (sample mass and heating rate), the production of different materials is possible. Under conditions which favor the heat dissipation, (3.1) and (3.2) of preceding paragraph at 1200°C, the spinel $FeAl_2O_4$ (hercynite) is produced through a process which is favored by the activation of the reaction mixtures. On the other hand, heating the samples in conditions of low heat transfer, (3.3) of preceding paragraph, the production of the composite material Fe–Al_2O_3 is made possible.

Acknowledgements

The authors wish to thank CONICET, CIC and UNMdP for financial support during the realization of this work.

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