High-energy ball-milled (α-Fe$_2$O$_3$)(α-Al$_2$O$_3$) system:
A study on the milling time effects

L.F. Cótica [a], A. Paesano Jr. [a,*], S.C. Zanatta [a],
S.N. de Medeiros [a], J.B.M. da Cunha [b]

[a] *Departamento de Física, Universidade Estadual de Maringá, Av. Colombo 5790,*
Zona 7, 87020-900 Maringá, PR, Brazil
[b] *Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil*

Abstract

The system (α-Fe$_2$O$_3$)$_x$(α-Al$_2$O$_3$)$_{1-x}$ was subjected to high-energy ball-milling, with the milling time varying between 3 and 72 h. The precursor powders, alumina and hematite, were pre-mixed in nominal concentrations $x = 0.10$, 0.25 and milled in a planetary ball-mill, under specific milling conditions. The milled samples were characterized through scanning electron microscopy, X-ray diffraction and Mössbauer spectroscopy. As a result of the above analyses, the formation of two isostructural solid solutions, α-(Fe$_{\Delta y}$Al$_{1-\Delta y}$)$_2$O$_3$ and α-(Fe$_{1-\Delta w}$Al$_{\Delta w}$)$_2$O$_3$, which evolve peculiarly with the milling time, was observed. For samples with $x = 0.10$, α-Fe and the FeAl$_2$O$_4$ compound were identified, in addition to the solid solutions. The presence of the spinel and metallic iron phases is attributed to the abrasion of the vial and balls. For $x = 0.25$ samples, the iron content tends, for increasing milling times, to be equally shared between both solid solutions, verifying the driving force of the process to homogenize the system under milling.
© 2005 Elsevier B.V. All rights reserved.

Keywords: High-energy ball-milling; Mechanochemical synthesis; Nuclear resonances

1. Introduction

The high-energy ball-milling (HEBM) technique has emerged as a non-expensive route to produce non-equilibrium phases in several varied forms, such as nanostructured and amorphous materials, nanocomposites and extended solid solutions [1]. This preparation technique has attracted much attention because it permits the study of metal–metal and oxide–oxide solid solutions, which can be metastably extended [2]. In particular, milled oxides have been extensively investigated mainly focusing their magnetic, ferroelectric and refractory properties [1]. The exploration and understanding of the modifications in the magnetic and electric properties, associated with the structural evolution in the ball-milled oxides, have been the driving force of many efforts conducted in the recent years [3–6].

Among others, the sesquioxide α-Fe$_2$O$_3$ (hematite), which has important magnetic properties, has been extensively studied when individually milled in high-energy ball-mills [3–8]. The hematite crystal structure is isomorphous to alumina (α-Al$_2$O$_3$ = corundum), with a close-packed oxygen lattice and Fe^{3+} cations in octahedral sites. It is a complex magnetic material, being antiferromagnetic (AF) at low-temperatures and undergoing a transition to a weak ferromagnetic state (WF) above the so-called Morin temperature ($T_M \cong 260$ K), because of a spin canting [9]. In addition, the hematite magnetic behaviour is very sensitive to impurities, strain and external fields [10–13]. Taking the great technological and academic importance of the hematite–alumina system into account, as well as its numerous potential applications in electronics, metallurgy

* Corresponding author. Tel.: +55 44 3263 4623; fax: +55 44 3263 4623.
E-mail address: paesano@wnet.com.br (A. Paesano Jr.).

and catalysis of ammonia synthesis [5,14], it is worth exploring and understanding the mechanosynthesis effects provided by HEBM on its physical properties.

In this context, the Mössbauer spectroscopy (MS), being highly sensitive to the hyperfine fields at the probe nuclei, becomes a powerful tool in the study of the ball-milled materials. Indeed, the ^{57}Fe MS, due to its high-energy resolution and detection character of low relaxation time, provides relevant information concerning the identification of the low level iron content phases, being much more sensitive to their identification than the majority of structural characterization techniques. In addition, it offers the possibility to observe magnetic phase transitions through the magnetic hyperfine field (B_{HF}) evolution. Furthermore, MS also allows studying structural and electronic properties through the other hyperfine parameters. Specifically, the isomer shift (δ) provides a direct measurement of the nuclear electronic density, giving important information about the valence state of the excite ion (Fe in ^{57}Fe MS), while the quadruple splitting (QS) permits the study of bounded properties, electronic and molecular structural problems, and possible lattice distorted states, as observed in the ball-milled products.

In some of our previous contributions, we have systematically studied the starting composition, milling velocity and milling medium dependencies on isochronally 24 h high-energy ball-milled α-Fe$_2$O$_3$/α-Al$_2$O$_3$ system [15,16]. The results revealed the formation of an iron-rich (α-(Fe$_{1-\Delta w}$Al$_{\Delta w}$)$_2$O$_3$—magnetically ordered) and an iron-poor (α-(Fe$_{\Delta y}$Al$_{1-\Delta y}$)$_2$O$_3$—magnetically ordered at low-temperatures) solid solutions for most of the initial nominal concentrations and milling conditions. For a stainless-steel milling medium, the relative amounts of those phases were shown to be strongly dependant on the sample's starting concentration and milling energy. We have also verified that lower and upper limits for either the initial concentration or the milling velocity must be obeyed in order to produce an effective mixing and to avoid undesirable iron contamination from the milling medium. Another evidence for contamination, besides the presence of metallic iron in magnetically ordered and non-ordered states, is the appearance of a FeAl$_2$O$_{3+y}$ spinel phase (hercynite), whose formation is attributed to the reaction of metallic iron and alumina and, possibly, with hematite. However, inspite of a considerable body of data obtained in our earlier investigations on the isochronally milled α-Fe$_2$O$_3$/α-Al$_2$O$_3$ system, we did not examine neither the initial nor the final steps for phase formation or iron contamination.

In this context, the aim of this contribution is to analyse the time evolution of reactions and phase transformations induced by the high-energy ball-milling for the hematite–alumina system milled at selected concentrations. The samples were characterized through scanning electron microscopy (SEM), X-ray diffraction and Mössbauer spectroscopy, mainly focusing on identifying and quantifying the phases.

2. Experiment

(α-Fe$_2$O$_3$)$_x$(α-Al$_2$O$_3$)$_{1-x}$ samples were prepared in a Fritsch Pulverisette 6 planetary ball-mill, using a stainless-steel vial charged with stainless-steel balls. Analytical grade α-Fe$_2$O$_3$ and α-Al$_2$O$_3$ pre-mixed powders were used as precursors, which were milled in argon atmosphere without any additives (dry milling) and under closed milling conditions, i.e., the vial was not opened during the milling process. The samples were prepared with nominal compositions of $x = 0.10$ and 0.25, in milling times varying between 3 and 72 h. The ball-to-powder mass ratio (30:1) was kept constant whereas the angular velocity of the supporting disc and vial was changed depending on the nominal concentration (300 rpm for $x = 0.10$; 350 rpm for $x = 0.25$).

The SEM analyses were carried out in a Shimadzu SS-550 electron microscope. The X-ray diffraction (XRD) patterns of the milled products were obtained at room temperature (RT), using a Siemmens D500 X-ray diffractometer operated in Bragg–Brentano geometry, with Cu Kα radiation, in the $20° \leq 2\theta \leq 80°$ range. Mössbauer characterizations were performed in the transmission geometry, using a conventional Mössbauer spectrometer in a constant acceleration mode. The γ-rays were provided by a ^{57}Co(Rh) source and the Mössbauer spectra were analysed with a non-linear least-square routine, with Lorentzian line shapes. Whenever a hyperfine field distribution was necessary in a fit, a histogram was used to represent the frequency of fields. All isomer shift data are given relative to α-Fe throughout this paper.

3. Results and discussion

SEM micrographs for $x = 0.10$ and 0.25 samples milled for 24 h are shown in Fig. 1. The size distribution of agglomerates is similar for both hematite starting concentrations, most of them sizing smaller than 3 µm. However, the $x = 0.10$ powders show rounded shapes whereas the $x = 0.25$ ones reveal protuberances at the surfaces.

XRD patterns for $x = 0.10$ and 0.25 samples, milled for different times, are shown in Figs. 2 and 3, respectively. A progressive broadening of the reflection peaks can be observed in both figures, indicating a continuous decrease in the particles' size and/or an increase in the internal strains with the milling time. In addition, in every diffractogram of the $x = 0.10$ samples, it is possible to identify the major presence of alumina (α-Al$_2$O$_3$—JCPDS no. 10-0173), besides the line for the iron $\langle 1\,1\,0 \rangle$ plane of reflection (JCPDS no. 06-0696). The occurrence of metallic iron may be attributed to the alumina abrasion of the vial and/or balls [16,17]. Peaks of very low intensity for the hematite phase (α-Fe$_2$O$_3$—JCPDS no. 33-0664) can be seen until $t = 12$ h (Fig. 2b); afterwards, this oxide is found to be virtually exhausted.

Diversely, for the $x = 0.25$ samples, the alumina- and hematite-like structures belonging to the precursors oxides