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Mechanoactivated interaction of hematite and gallium

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ABSTRACT

The aim of this work was to investigate the kinetics of structural transformations during mechanical high energy ball-milling of Fe_2O_3 with Ga in order to reveal the mechanism of the process. The structure of formed intermetallic phases and intermediate oxide compounds were studied by means of Mossbauer spectroscopy, IR spectroscopy and X-ray diffraction. After 8 min of attrition a large part of Fe_2O_3 still remains in mixture. This fact could be explained in view of melted Ga spreading over freshly prepared surfaces during milling process and incorporating into the Fe_2O_3 and intermediate oxides structures.

1. Introduction

Mechanoactivated reducing reactions of iron oxides with metals (e.g. Al, Ti, Fe) in planetary ball-mills are usually used for the production of complex oxide ceramics, dispersion-strengthened with metal nanoparticles [1–4]. For this purpose different elements may be chosen as reducing agents. The basic chemical reaction features are mainly determined by the thermodynamical and kinetics factors such as melting temperature and the interfacial enthalpy for dissolution in Fe.

For the stoichiometric proportions of components hematite/gallium reduction reaction can be written as $Fe_2O_3 + 2Ga = Ga_2O_3 + 2Fe$ ($\Delta H = 480$ kJ/mol). Unlike the $Fe_2O_3 + Al$ reaction, which has been realized by different authors [5–7] for different mill constructions, the reaction features of Fe_2O_3 and Ga have not been studied.

Ga, which is an element of the IIIA group like Al, is an interesting candidate for reducing agent in solid state reaction, not only because Fe–Al and Fe–Ga equilibrium phase diagrams show the same trends in solid solutions concentration and structures of intermetallic phases. But their extremely different melt points (Ga $T = 29.6\,^{\circ}C$, Al $T = 660.2\,^{\circ}C$) might be the key for the drastic change in the kinetics of reduction process. That is why it is important to establish the kinetics features of this reduction process to enable further possible variation of the final composite structure.

It is a well known that temperature of milling bodies can rise by several hundred degrees in high energy activators of the planetary mill type [8]. And under such conditions one can obtain solid solution formation in the grain boundary region even for the immiscible at equilibrium elements, if one of the elements is easy melting [9]. So the same mechanism of reduction by liquid phase might be expected in Fe_2O_3–Ga system, when the reduction is achieved mainly in grain boundary region.

2. Experimental

High energy milling was carried out in a planetary ball-mill AGO-2 under an argon atmosphere during different time intervals from 40 s to 8 min. Vial volume was 20 cm^3. Balls diameters and mass were 5 mm and 200 g, respectively. The mass of every sample was 8.4 g. The ball to powder mass ratio is approximately 20/1. The speed of drum rotation was ∼1000 rpm. Average particle sizes of initial Fe_2O_3 and Ga powders were in the micrometer range. The weight concentration have been chosen as stoichiometric with 3.9 g of Fe_2O_3 and 3.5 g of Ga.

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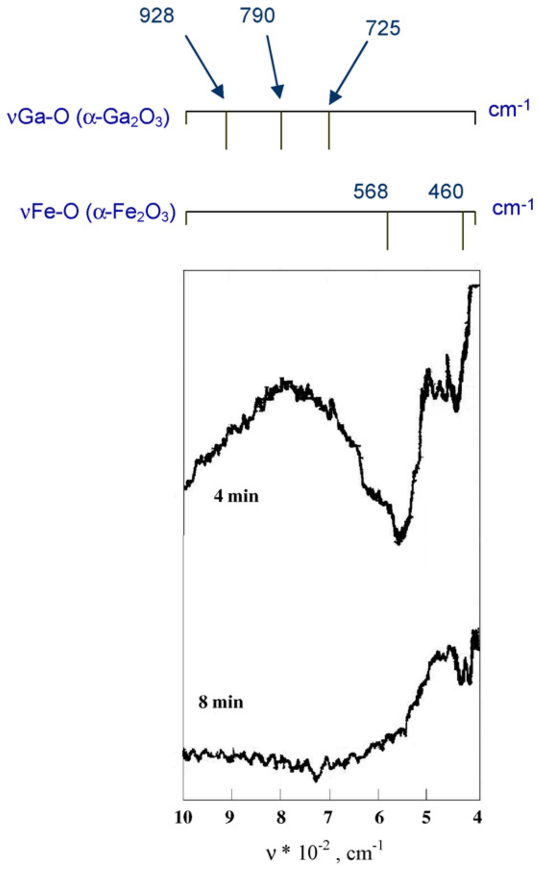


Fig. 1. IR-spectrum of Fe_2O_3 + 2Ga mixture milled during 4 and 8 min.

The as-milled products have been characterized by X-ray diffraction (XRD) on a RIGAKU DX/Max diffractometer using Cu Kα radiation. The mean crystallite size and the value of microstrain were estimated by X-ray line broadening by well-known Williamson–Hall procedure [10]. The detailed quantitative structural analysis of intermetallic phases and intermediate oxide-compounds at different stages of attrition was performed by means of Mossbauer spectroscopy. Mossbauer spectra were obtained at room temperature using a constant acceleration spectrometer with a $^{57}Co(Rh)$ radiation source. Mossbauer spectra have been fitted by means of UNIVEM MS Software. The ^{57}Fe isomer shifts are given with respect to α-Fe at room temperature. To reveal the kinetics of the $Fe_2O_3 \rightarrow Ga_2O_3$ transformation IR-spectroscopy was used, because of its unique ability to determine the presence of Fe–O and Ga–O chemical bonds. The IR absorption spectra were recorded with a Specord-75IR spectrometer.

3. Results and discussion

The obtained IR spectra (Fig. 1) of MA mixtures do not show the formation of Ga_2O_3 up to 4 min. There are two bands near 460 and 568 cm^{-1} associated with Fe_2O_3, but no distinct absorption bands near 725, 790 and 928 cm^{-1} corresponding to gallium oxide. On the contrary after 8 min there are no distinct absorption bands associated with α-Fe_2O_3. All features shift to higher wavenumbers and change significantly in shape in becoming broader. Similar effects have already been reported in [11], where powders have been prepared via a conventional coprecipitation method. Such effects are associated with Fe substitution by Ga in the structure of Fe_2O_3.

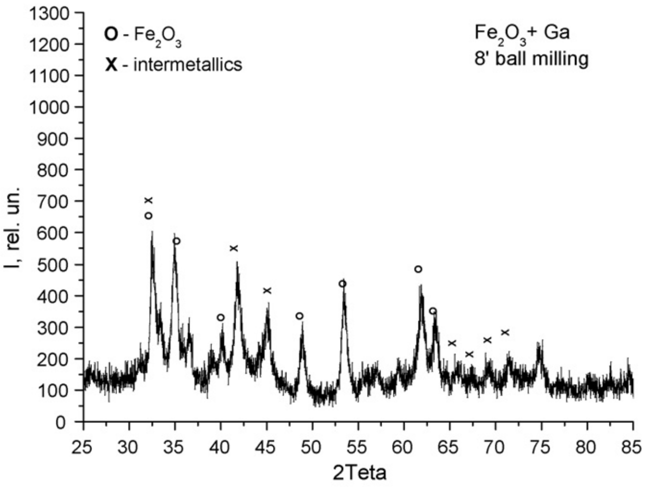


Fig. 2. XRD patterns of the 8-min-milled mixture of Fe_2O_3 with Ga.

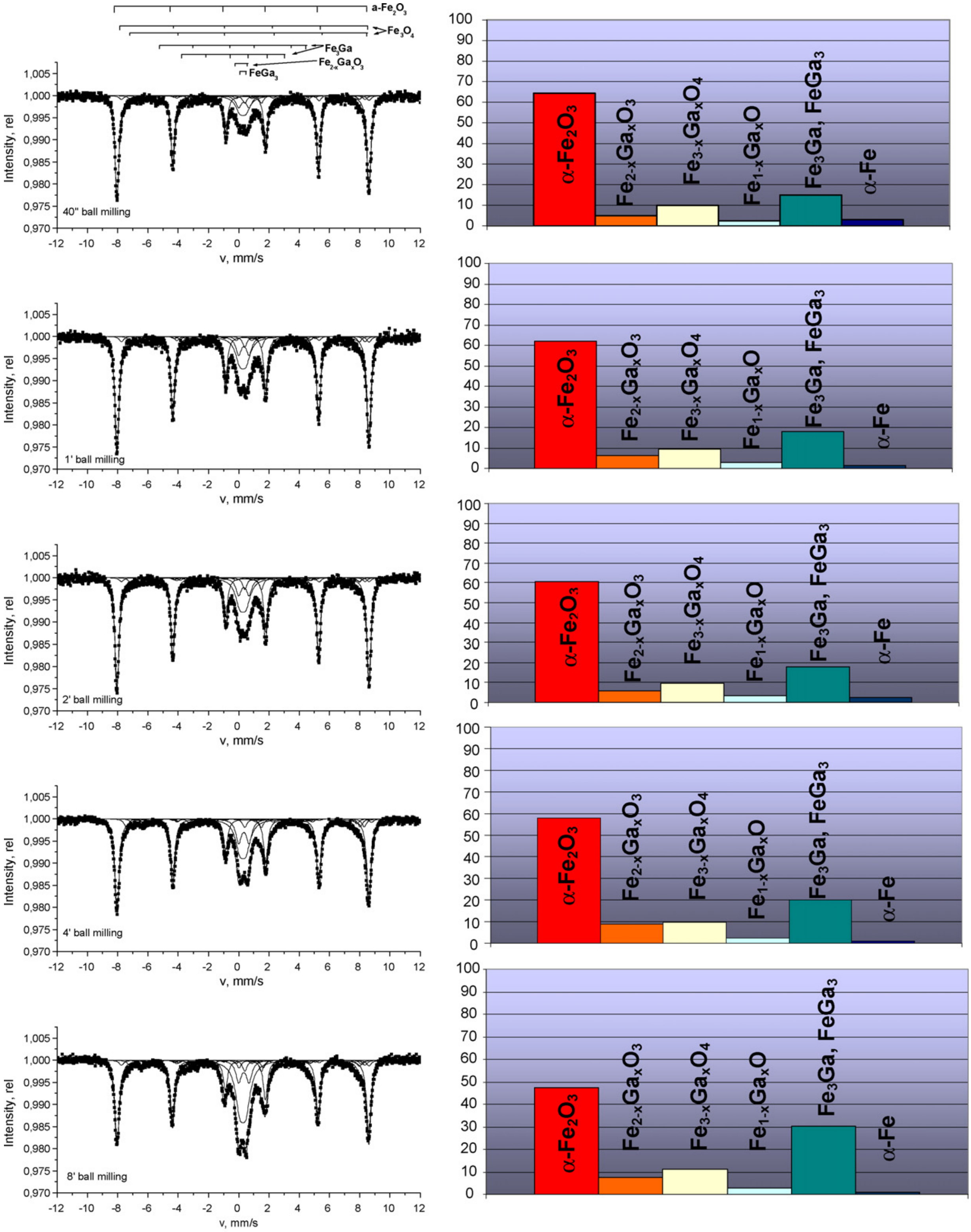
X-ray diffraction pattern (Fig. 2) obtained after 8 min of milling establishes the presence of Fe_3Ga, $FeGa_3$ and unreacted Fe_2O_3. The mean crystallite size and the microstrain estimated by X-ray line broadening brings out that the produced composites contain Fe_2O_3 phase of ~80 nm in size with the microstrain value of $\sim 2.35 \times 10^{-3}$ and intermetallics phases of ~40 nm in size with the microstrain value of $\sim 3.45 \times 10^{-3}$.

The Mossbauer spectra obtained after various milling time at 300 K (Fig. 3) show evolution of mixture microstructures in the course of attrition. The spectra were fitted with superposition of eight sextets and three doublets. Their parameters (isomer shift δ, quadrupole splitting Q, effective hyperfine magnetic field H_{eff} and line width Γ) are shown in Table 1. Sextets are associated with α-Fe_2O_3, α-Fe, number of solid solutions of Ga in spinel Fe_3O_4, and disordered Fe_3Ga. Doublets correspond to solid solutions of Ga in α-Fe_2O_3, disordered $Fe_{1-x}Ga_xO$, and $FeGa_3$.

The quantitative analysis allowed to estimate the kinetic curves of phase evolution (Fig. 4) and to reveal the features of the reduction mechanism. The stages of initial Fe_2O_3 reduction are observed with: $Fe_2O_3 \rightarrow Fe_{2-x}Ga_xO_3 \rightarrow Fe_{3-x}Ga_xO_4 \rightarrow Fe_{1-x}Ga_xO \rightarrow$ *bcc*-Fe. On the other hand, the interaction of reduced *bcc*-Fe with gallium leads to the progressive formation of intermetallics.

Table 1
Values of the isomer shift δ (mm/s), quadrupole splitting Q (mm/s), hyperfine field H_{eff} (kOe) and line width Γ (mm/s) for the fits to the Mossbauer spectra taken at 300 K on samples of the series.

Phase	δ (mm/s)	Q (mm/s)	H_{eff} (kOe)	Γ (mm/s)	Ref.
α-Fe_2O_3	0.37	−0.18	517	0.32	
α-Fe	0	0	330	0.33	
Solid solution of Ga in Fe_3O_4	0.35	−0.10	480	0.36	
	0.60	0.90	445	0.36	
Disordered Fe_3Ga	0.28	−1.09	312	0.36	[12]
	0.18	−0.34	205	0.36	
Solid solutions of Ga in α-Fe_2O_3	0.34	0.69	–	0.45	[13]
Disordered $Fe_{1-x}Ga_xO$	0.95	1.12	–	0.34	
$FeGa_3$	0.28	0.40	–	0.70	[14]



(a) (b)

Fig. 3. Mossbauer spectra (at 300 K) of the mixture of Fe_2O_3 + 2Ga milled during 40 s, 1 min, 2 min, 4 min and 8 min (a) and bar diagrams of the phase as obtained from the analysis of the Mossbauer spectra (b).

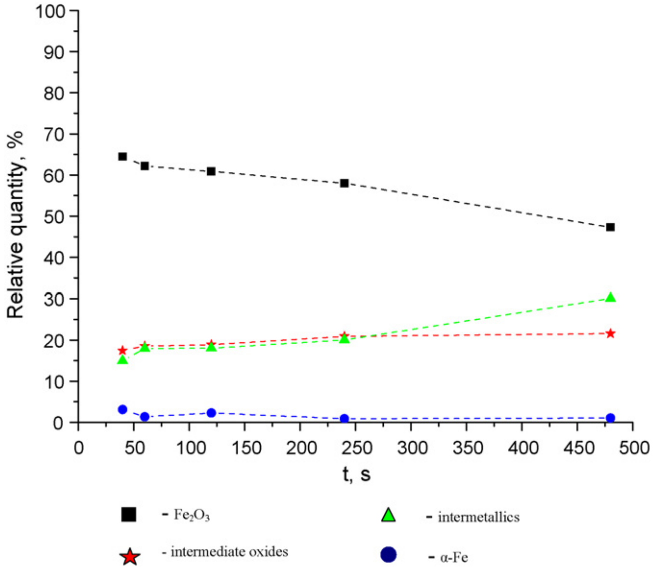


Fig. 4. Kinetics curves for phase evolution.

4. Conclusion

Obtained results allow us to conclude that high energy mechanical activation induces the reduction reaction in Fe_2O_3 + Ga powder mixtures (just like it was in Fe_2O_3 + Al system): reduction of Fe from initial Fe_2O_3 goes through intermediate oxide and intermetallics compounds formation. The difference in rate of reduction in these two systems could be estimated from difference in quantity of formed phases: 34% and 17% of intermediate oxides; 7% and 30% of intermetallics in system with Al and Ga, correspondingly. This drastic difference in kinetics of Fe_2O_3 + Ga system reduction allow us to conclude that spreading of easy-melted Ga over freshly prepared surfaces and its interaction with reduced Fe results in the formation of nanosize-grained FeGa-intermetallics and a number of solid solutions $(Fe, Ga)_2O_3$.

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