COMPOSITE PARTICLES INTERFACE
AMORPHYSATION AT THE EARLY STAGES OF
MECHANOSYNTHESIS IN Fe₂O₃/Fe/(Ga,Al) POWDERS
MIXTURES

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Mossbauer spectroscopy, X-ray diffraction, Transmission electron microscopy as magnetic measurements have been performed on Fe₂O₃+Fe, Fe₂O₃+Al, Fe₂O₃+Ga, Fe₂O₃+Al+Fe, and Fe₂O₃+Ga+Fe powders mixtures after short intensive mechanical activation during 2’ in high energy planetary mill. Amorphysation at interfaces of composite particles have been observed.

Introduction
Mechanosynthesized composite powder materials used as precursors for different functional materials can satisfy special requirements supporting microstructure and properties achieved at the stages of their preparing [1-5]. According to numerous publications mechanical alloying is very efficient to nanocrystalline state achievement with the aim to generate a composite material in which nonequilibrium and metastable phases are created [2-3]. Interaction of several components in mechanically activated mixtures allows achieve concrete aims such as crystallite disintegration, selective reduction reaction and alteration of its kinetics and mechanism through formation of metastable structures. All in common let to optimize synthesis condition of composite-precursor formation for subsequent material processing.

Intermetallic/ceramic powder composites represent an interesting class of materials for various functional applications [2]. To produce metal/oxide nanocomposites Fe₂O₃ + 2Me = Me₂O₃ + 2Fe-Me (Me – reducing transition metals) mechanosynthesis reaction in powders
termite mixtures have to be realized in a ball mill [2,6]. The final composites are usually of nanoscopic scale and characterized by high surface area and high defect density. We have studied recently mechanically induced solid phase reactions in systems Fe₂O₃/Fe, Fe₂O₃/Al, Fe₂O₃/Ga with different reducing activity of used metals via different mutual concentration and milling time [7-11]. It was carried out that in spite of similarity of Fe-Al, Fe-Ga equilibrium phase formation diagrams [12-13] and structural and magnetic properties of main intermetallics [14], there was some difference in mechanochemical interaction mechanism of these metals with α-Fe₂O₃. Generally it was connected as with different low melting point of Al (660°C) and Ga (29°C) as with the velocity of phase transformation and proceeding reaction through the intermetallics but intermediate ternary oxide structures.

To handle the kinetics of powders reducing we supposed [2, 10] that admixture of pure Fe powder to Fe₂O₃/Al (Fe₂O₃/Ga) mixture should result in some competitive processes that will shift or separate stages of components interaction. Thus in this work mechanoactivation of Fe₂O₃ + Fe, Fe₂O₃ + Al + Fe and Fe₂O₃ + Ga + Fe mixtures with similar elements particle quantities was performed in relation to the Fe₂O₃+Me simple mechanochemical interaction. Phase fine structure and magnetic properties of obtained composites have been studied. As ball-milled iron-containing composite materials structure strongly affected by the local mean composition, defects, strain and average interatomic distance, that certainly influence the chemical bonds and magnetic fields around the iron atoms, Mössbauer spectroscopy was the principal and powerful tool in the study.

**Experimental**

**Sample preparation**

Two sets of powder mixtures high energy ball milling were performed. *I set*: a) pure α- Fe₂O₃; b) (6.4 g) α-Fe₂O₃ + (8 g) Al; c) (6.4 g) Fe₂O₃ + (4 g) Ga; *II set*: d) (6.4 g) α-Fe₂O₃+ (4 g) Fe; e) (6.4 g) α- Fe₂O₃ + (8 g) Al + (4 g) Fe; f) (6.4 g) α-Fe₂O₃ + (4 g) Ga + (2 g) Fe. Weight relations have been chosen taking in account our recent detailed study of phase transformations in series of milled mixtures via time and components relative amount [7-11]. Mechanical milling has been realized with an AGO-2 planetary mill during the same time - 2 minutes.
in vial sealed under Ar. Vial volume was 20 cm$^3$. Steel balls diameters and mass were 5 mm and 200 g, respectively. The speed drum rotation was ~1000 rpm. Initial Fe$_2$O$_3$, Fe, Al and Ga particles mean sizes was about 50-80 µm.

**Experimental methods**

*Mössbauer spectra* were obtained at room temperature using constant acceleration spectrometer with $^{57}$Co(Rh) radiation source. The $^{57}$Fe isomer shifts are given with respect to $\alpha$-Fe at room temperature. Phase composition was determined from the spectra by Univem MS software. *Transmission electron microscopy*. TEM images was performed on LEO 912 AB Omega. *Saturation magnetization* temperature dependence measurements were performed on Curie-balance in applied field of 0.45 T in the temperature range 20-700°C. Remanent magnetization was acquired in magnetic field 0.75T.

**Results and discussion**

Well-pronounced particle sizes decreasing when Fe$_2$O$_3$ milled with Fe have been observed on the TEM pictures comparing to milled Fe$_2$O$_3$ particles (Fig 1a, b). The distributions of particles sizes observed for both milled samples. There are a significantly broader particle sizes distribution to smaller one (up to values of 15-18 nm) for Fe$_2$O$_3$+Fe milled sample.

![Fig.1. TEM pictures of the composite powder particles of 2 min milled Fe$_2$O$_3$ (a) and Fe$_2$O$_3$+Fe (b).](image-url)
Fig. 2. TEM pictures of the composite powder particles Fe$_2$O$_3$+Al+Fe (a) and Fe$_2$O$_3$+Ga+Fe (b) milled during 2 min

Thus, the first, iron powders acts as additional dispersion agent. TEM pictures of agglomerated composite particles in Fe$_2$O$_3$+Al+Fe (Fig. 2a) and Fe$_2$O$_3$+Ga+Fe (Fig. 2b) milled mixtures reflects that aluminium and gallium promote formation of a larger (200-400) nm composite particles with a complicated microstructure. Observed particles consist of ranges with different ordering and inclusions.

Room-temperature Mössbauer spectra for two sets of samples are shown in Fig 3- I samples set and Fig.4 - II samples set. Phase content derived from the spectra are presented in inserted bar and line diagrams. Fe$_2$O$_3$ particles refinement during 2 min milling results in size reducing up to 20 nm [11] and formation of 23% disordered γ-Fe$_2$O$_3$/Fe$_3$O$_4$ layers at their grain boundary(Fig.3(a)).

Fig 3: Mössbauer spectra obtained RT of 2 minutes milled samples: I set:
a) pure α- Fe$_2$O$_3$;
b) (6.4g) α-Fe$_2$O$_3$ + (8g) Al;
c) (6.4g) Fe$_2$O$_3$ + (4g) Ga
2 minutes grinding of $\alpha$-Fe$_2$O$_3$ + Al powder mixture results not only in oxide destruction but partial mechanosynthesis reaction with formation of FeAl intermetallics: spectrum (Fig. 3(b)) consists of $\alpha$-Fe$_2$O$_3$ subspectra, disordered $\gamma$-Fe$_2$O$_3$/Fe$_3$O$_4$ and subspectra of intermetallics Fe$_2$Al$_5$/FeAl – doublet and singlet. $\alpha$-Fe$_2$O$_3$ + Ga powder mixture grinding has a similar results with partial destruction of $\alpha$-Fe$_2$O$_3$ and more significant Fe-Ga intermetallics formation (Fig 3 (c)). In addition the doublet belonging to wustite (Fe$_{1-X}$O) structure appears.

When Fe powder is added in ball-mill process the refinement proceeds more effectively [10], moreover the formation of disordered or even amorphous Fe-based components (black marked on Fig. 4 a, b and c) has been distinguished from all the spectra. This component was derived from experimental spectra by subtraction of well resolved oxide components. This part of spectrum gradually increased with Fe admixture as was observed recently [10] and its Mössbauer spectrum measured at 78 K didn’t reveal hyperfine field dependence as for known iron oxides supporting the absence of superparamagnetic behavior.

The hyperfine field distributions of this component fitted from Mossbauer spectral shape showed wide the range of 200-300 kOe (average hyperfine field value of 250 kOe), which is typical for bcc-Fe-based amorphous oxygen containing surroundings [15]. This component also was fitted by superposition of several sextets with practically equal isomer shifts ($\delta \approx 0.13$ mm/s). Obtained $\delta$ value reflects oxygen occurrence in disordered iron.

As in the case of Fe$_2$O$_3$ + Fe milled sample (Fig.3 (a)) spectrum of Fe$_2$O$_3$ + Al + Fe milled sample (Fig. 3(b)) consists of components belonging to $\alpha$-Fe$_2$O$_3$ particles partial destruction ($\gamma$-Fe$_2$O$_3$/Fe$_3$O$_4$ formation). Small amount of wustite substructure has been also detected. The percent quantity of intensive component (marked by black color) is obviously defined by time of grinding which caused the achieved particles sizes and thick of theirs disordered layer. Hyperfine fields ($H_{\text{eff}}$) distribution analysis of this disordered component reflects different Fe atoms surrounding characteristic for disordered Fe-based component. Besides that the gravity center of hyperfine fields distribution was shifted to the smaller $H_{\text{eff}}$ values in comparison to that in Fe$_2$O$_3$ + Fe sample spectrum. This is evidently explained by aluminum partial substitution in iron-oxygen ferromagnetic amorphous layer.
The hyperfine field distributions of this component fitted from Mossbauer spectral shape showed wide the range of 200-300 kOe (average hyperfine field value of 250 kOe), which is typical for bcc-Fe-based amorphous oxygen containing surroundings [15]. This component also was fitted by superposition. In the case of \( \alpha \)-Fe\(_2\)O\(_3\) + Ga powder mixture grinding with Fe addition the similar results (Fig. 4 (c)) with partial destruction of \( \alpha \)-Fe\(_2\)O\(_3\) and significant Fe-Ga intermetallics also as wustite structure formation were observed. As was noticed recently [16-17] metal-metal interaction during milling of Fe-Al and Fe-Ga mixture of the same compositions reveal particle refinement with intermetalics formation based on easy melting metal. Corresponding spectrum consisted of iron and certain intermetallics.

Estimation of disordered layer thickness on the Fe particles surface with respect to their ordered volume–averaged sizes allows conclude that it doesn’t exceed 3 nm. For these measures X-ray diffraction is insensitive [11]. At the same time this surface layer

![Mössbauer spectra obtained at RT of 2 minutes milled samples: II set:](image)

**Fig. 4.** Mössbauer spectra obtained at RT of 2 minutes milled samples: II set:  
(a) (6.4 g) \( \alpha \)-Fe\(_2\)O\(_3\) + (4 g) Fe;  
(b) (6.4 g) \( \alpha \)-Fe\(_2\)O\(_3\) + (8 g) Al + (4 g) Fe;  
(c) (6.4 g) \( \alpha \)-Fe\(_2\)O\(_3\) + (4 g) Ga + (2 g) Fe
contribution in Mössbauer spectrum integrated over the sample became significant.

Saturation magnetization versus temperature (Ms(T)) curves for mixtures with Fe additions are shown in Fig. 5. Observed Ms(T) dependencies are typical for the multiphase composites behavior, where transformations in oxides at heating are accompanied by amorphous-to-crystalline transformation of amorphous phase. Ms(T) (Fig. 5a) hasn’t reached zero value at Curie temperature \( T_c \) (about 420°C) of amorphous phase. The shoulder on the Ms(T) curve from 420 to 500°C arises mainly due to magnetization of \( Fe_3O_4 \) containing in composite samples as derived from phase analysis. The subsequent two-peaks Ms increase is connected with the crystallization processes of magnetic bcc-Fe phase with large magnetization value.

As seen from the mossbauer spectra Fig.6, heating of milled composite sample up to 500°C (b) supports the ordering process during crystallization: emerging of Fe phase and their grains growth resulted in amorphous phase diminishing. Fe phase and amorphous phase quantity are shown by gray and black colors. As seen from the (Fig. 5) Ms(T) curves for milled \( Fe_2O_3 + Al + Fe \) (Fig. 5b) and \( Fe_2O_3 + Ga + Fe \) (Fig. 5c) powders have not only similar features but some peculiarities.

Wide maximum appearing after 172°C (Fig.5 (b), 5(c)) reveals characteristic phase transformation of wustite to magnetite [15]. In this work the Curie temperature of phase formed at heating is about 540°C what is lower than that of pure magnetite. This is the sequence of Al and
Ga isomorphous substitution. So the wustite phase, determined from the spectra in the case of Al or Ga use, is also substituted Fe$_{1-x}$Al$_x$O (or Fe$_{1-x}$Ga$_x$O). This isomorphous substitution supported by our measurements of remanent magnetization temperature dependence shown in insertion on Fig. (5c).

$T_c$ slightly lower than 420°C, what is clearly seen on thermomagnetic curves of all the samples, relates to formation of Fe-based amorphous phase with oxygen and aluminum (or gallium) surroundings. Ms slow increase at 550-560°C and following temperature dependence is a response of Fe(Al) or Fe(Ga) emerging during amorphous phase heat destruction and grain growth together with oxides transformation at higher temperature.

**Summary**

Mechanochemical interaction in multicomponent powders mixtures reveal formation of composite powder structure consisted of disordered oxides and intermetallics. The excess of iron powder with higher hardness and ductility in interacting substance acts as additional reducing agent for oxide. The observed amorphous phase formation at the iron particles interfaces in milled Fe$_2$O$_3$/Al(or Ga)/Fe powder mixtures is caused by oxygen incorporation into the disordered region of the iron particle in the course of permanent oxide destruction. Disordered phase is diluted by Al(or Ga).

![Fig.6. Mossbauer spectra of Fe$_2$O$_3$+Fe 2’ milled (a) and then heated up to 500°C (b)]
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References