

Mechanochemical Synthesis of Wüstite, Fe_{1-x}O , in High-Energy Apparatuses

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Abstract—It is shown that high-energy milling of $\text{Fe}_2\text{O}_3 + \text{Fe}$ mixtures leads to the formation of nanocrystalline, metastable wüstite Fe_{1-x}O . Its stoichiometry varies systematically with processing time.

INTRODUCTION

Mechanical activation of inorganic materials in high-energy milling apparatuses is of considerable interest as a convenient and simple way of preparing nanocrystalline and amorphous powders and metastable phases [1]. This opens up new possibilities of producing materials with improved properties compared to those prepared by conventional ceramic processing techniques [2]. In particular, the mechanochemical synthesis of wüstite, a compound thermodynamically unstable below $\approx 570^\circ\text{C}$ (eutectoid decomposition temperature), makes it possible to produce, via subsequent thermal decomposition during annealing, a nanocrystalline $\text{Fe}/\text{Fe}_3\text{O}_4$ composite, a promising hard-magnetic material [3, 4]. Varying the annealing temperature, one can tune the microstructure of the resulting composite and, hence, its magnetic characteristics.

Mechanical activation may cause the composition of wüstite (Fe_{1-x}O) to notably deviate from the equilibrium one. In general, the energy delivered to a substance in the course of mechanochemical synthesis in high-energy apparatuses goes, for the most part, into changing its defect structure. The main defect species in wüstite (rock-salt structure) are cation vacancies in octahedral sites and an equivalent amount of holes localized at Fe^{3+} ions. Point defects in wüstite have a tendency to aggregate into small associates in which each Fe^{3+} ion is surrounded by four vacancies. The associates, in turn, form more complex clusters. The stoichiometry of wüstite depends on which type of defect cluster prevails [5]. The formation of Fe_3O_4 and Fe during wüstite decomposition occurs primarily at structural defects. For example, the eutectoid decom-

position of Fe_{1-x}O prepared by the conventional ceramic route is accompanied by the formation of a lamellar $\text{Fe}/\text{Fe}_3\text{O}_4$ composite, which may be due to the existence of a dislocation network in the parent material [6].

In this paper, we describe the synthesis of wüstite, Fe_{1-x}O , via high-energy mechanical activation of $\text{Fe}_2\text{O}_3 + \text{Fe}$ mixtures. Particular attention has been paid to the microstructure and composition of the resultant Fe_{1-x}O and to the possibility of producing an $\text{Fe}/\text{Fe}_3\text{O}_4$ composite via low-temperature decomposition of wüstite.

EXPERIMENTAL

The starting reagents used were Fe and hematite ($\alpha\text{-Fe}_2\text{O}_3$). The latter was prepared via thermal decomposition of $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, followed by annealing in air at 750°C for 2 h. The starting mixture was mechanically activated in air for 10, 20, or 40 min in an AGO-2 planetary mill at $\approx 40\text{g}$, using steel grinding vessels and steel balls ≈ 5 mm in diameter. The $\text{Fe} : \text{Fe}_2\text{O}_3$ molar ratio in the starting mixture corresponded to the reaction



The weight ratio of the sample to ball load was 1 : 30. The grinding vessels were water-cooled to maintain a constant temperature of the process (near room temperature).

To prepare an $\text{Fe}/\text{Fe}_3\text{O}_4$ nanocomposite, the single-phase wüstite powder obtained by milling for 40 min

was annealed in an evacuated silica tube at 200°C for 15 h.

The samples were characterized by x-ray diffraction (XRD) analysis (STADI-P diffractometer, CoK_{α1} radiation), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) (JEOL JEM-2000FXII, 200 kV). The lattice parameter was determined using an FR-552 Guinier–de Wolff focusing camera (CuK_{α1} radiation, Ge internal standard with $a = 5.65074(9)$ Å).

RESULTS AND DISCUSSION

The XRD data for the samples obtained by milling mixtures of Fe and Fe₂O₃ for 10, 20, and 40 min are displayed in Fig. 1. It can be seen that mechanical activation for just 10 min led to complete reduction of Fe₂O₃ and the formation of a mixture of Fe, Fe₃O₄, and Fe_{1-x}O. Phase-pure wüstite was obtained by milling for 40 min. The diffraction peaks from the mechanically activated mixtures were severely broadened, which is attributable to the small size of the coherently scattering domains (CSDs) and the lattice distortions caused by mechanical processing. The table lists the CSD sizes of wüstite, evaluated by the Scherrer formula. The CSD size is ≈10 nm, independent of the milling duration.

SEM results (Fig. 2) indicate that the nanocrystallites resulting from milling form aggregates 0.2 to 2.0 μm in size. After 10 min of mechanical activation, there are both large and small aggregates of spherical particles (Fig. 2a). After milling for 20 min, the aggregates are notably more uniform in size and more densely packed. Increasing the milling duration to 40 min further increases the aggregate size and packing density (Fig. 2c).

TEM examination (Fig. 3) indicates that the aggregates are composed of nanocrystalline particles ≈5–20 nm in average size, in agreement with XRD results.

Our results demonstrate that high-energy milling rapidly reduces the particle size to a level at which no further nucleation or cracking occurs and the particle size remains unchanged. At the same time, the resulting ultrafine particles aggregate rapidly because the system seeks an energetically more favorable state. Thus, during high-energy milling the microstructure evolution is determined by the competition between two processes: disintegration and aggregation of the particles (reduction in particle size and formation of rather large aggregates).

On the whole, the processes induced by mechanical activation of the Fe₂O₃ + Fe mixture can be thought of as follows: In the initial stages of activation, the particle size of Fe₂O₃ and Fe decreases rapidly, and the particles become more uniform in size and form dense aggregates. This leads to the formation of numerous reaction

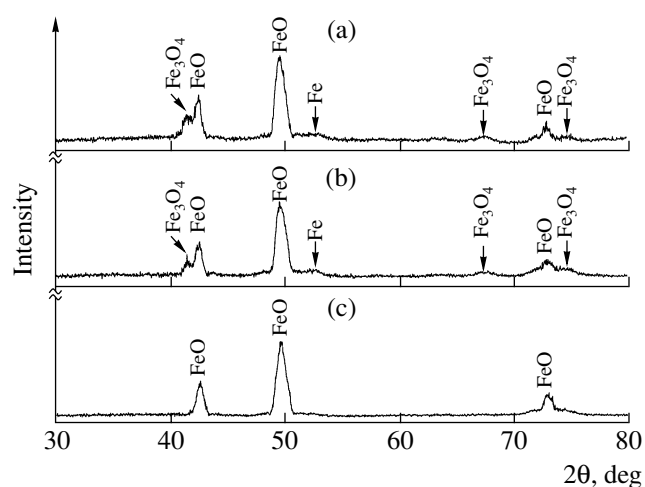


Fig. 1. XRD patterns of the samples obtained by milling a mixture of Fe₂O₃ and Fe for (a) 10, (b) 20, and (c) 40 min.

contacts between Fe₂O₃ and Fe particles, which may lead to chemical interaction because of the relaxation of the supplied mechanical energy, resulting in the formation of the intermediate phase Fe₃O₄ (magnetite) and the final product Fe_{1-x}O (wüstite).

The measured lattice parameter of wüstite as a function of milling time and the composition of the wüstite phase Fe_{1-x}O evaluated by the equation

$$a (\text{Å}) = 3.856 + 0.478(1 - x)$$

are presented in the table.

The composition Fe_{0.96}O obtained by milling for 10 min lies to the left of the low-oxygen phase boundary of wüstite in the T - x phase diagram, which is the result of the nonequilibrium synthesis conditions. Milling for 20 and 40 min leads to the formation of Fe_{0.91}O and Fe_{0.87}O, respectively. Note that, under equilibrium conditions, the former composition coexists with Fe₃O₄ at 750°C, and the latter coexists with Fe₃O₄ at 1100°C. Thus, the formation of oxygen-enriched wüstite is also the consequence of the nonequilibrium oxidation of Fe_{1-x}O in air at room temperature.

To prepare an Fe/Fe₃O₄ nanocomposite, Fe_{0.87}O was decomposed at 200°C in vacuum. As shown by XRD

Effect of mechanical activation time τ_{MA} on the CSD size, lattice parameter, and composition of wüstite

τ_{MA} , min	β , rad	D_{CSD} , nm	a , Å	$1 - x$
10	0.0172	9.8	4.316 (8)	0.96
20	0.0179	9.4	4.289 (7)	0.91
40	0.0174	9.7	4.272 (7)	0.87

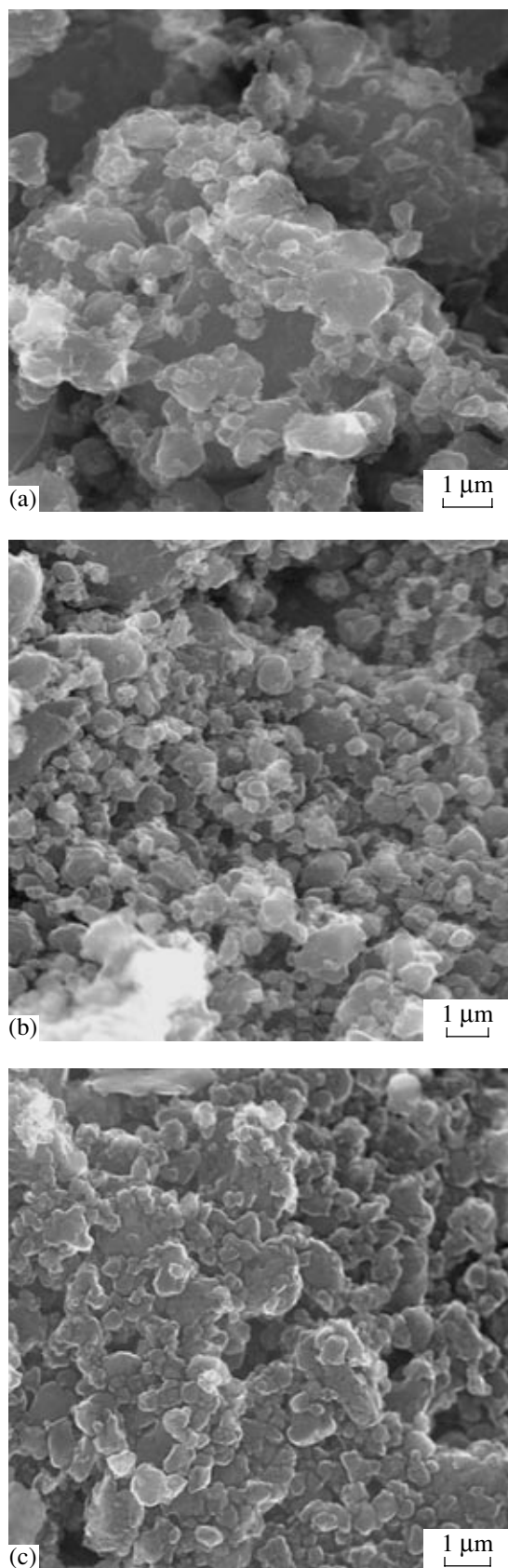


Fig. 2. SEM micrographs of the samples obtained by milling a mixture of Fe_2O_3 and Fe for (a) 10, (b) 20, and (c) 40 min.

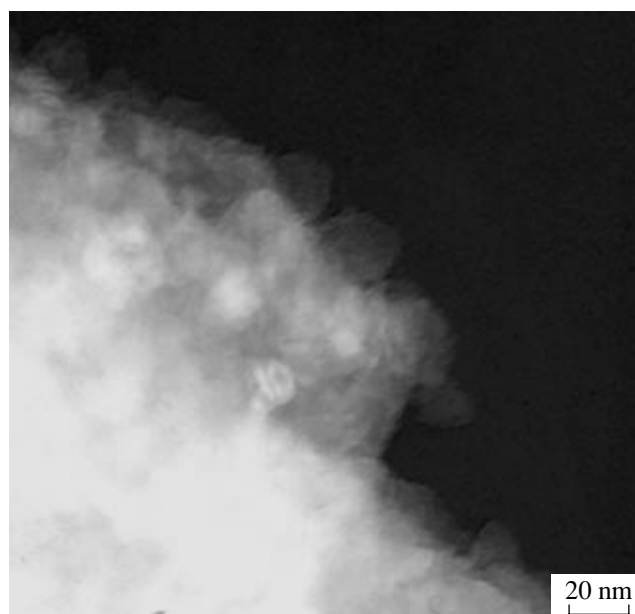


Fig. 3. TEM micrograph of the sample obtained by milling a mixture of Fe_2O_3 and Fe for 40 min.

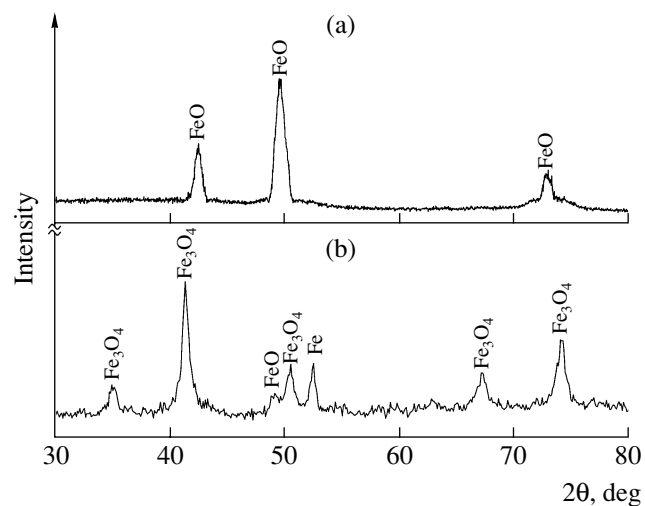
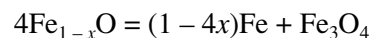


Fig. 4. XRD patterns of the samples obtained (a) by milling a mixture of Fe_2O_3 and Fe for 40 min and (b) subsequent heat treatment in vacuum at 200°C for 15 h.

(Fig. 4), wüstite decomposes almost entirely under these conditions to form a nanocrystalline composite (Fig. 5). It is known that, at moderate temperatures, the stability of wüstite prepared under equilibrium conditions depends on kinetic factors. Thermal decomposition by the reaction



is significant only above 260°C [6]. Thus, wüstite prepared by mechanical activation, i.e., under nonequilib-

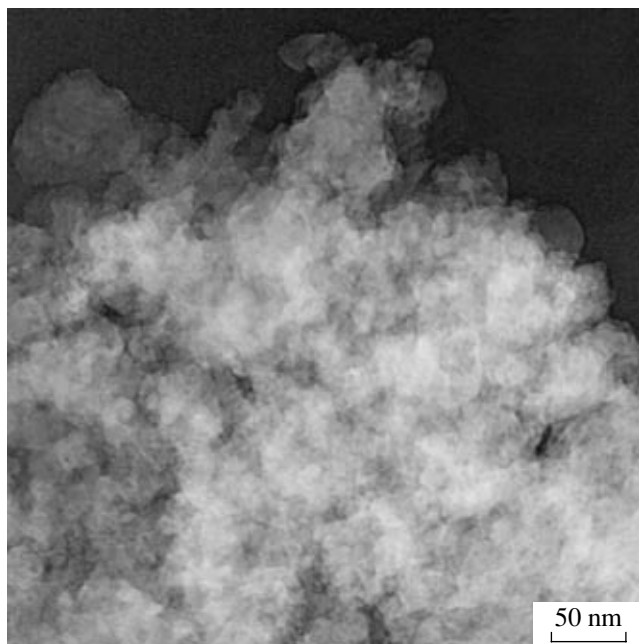


Fig. 5. TEM micrograph of the $\text{Fe}/\text{Fe}_3\text{O}_4$ nanocomposite produced by heat-treating $\text{Fe}_{0.87}\text{O}$ at 200°C .

rium conditions, has a reduced decomposition temperature, in agreement with earlier results [3].

CONCLUSIONS

Our results demonstrate that high-energy milling of $\text{Fe}_2\text{O}_3 + \text{Fe}$ mixtures initially leads to the formation of

nanocrystalline wüstite with a nonequilibrium composition, $\text{Fe}_{0.96}\text{O}$, which oxidizes to $\text{Fe}_{0.87}\text{O}$ during further processing. Thermal decomposition of this material at 200°C in vacuum yields an $\text{Fe}/\text{Fe}_3\text{O}_4$ nanocomposite.

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