

# Investigation of oxidation process of mechanically activated ultrafine iron powders

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**Abstract.** The oxidation of mechanically activated ultrafine iron powders was studied using X-ray powder diffraction and thermogravimetric analyzes. The powders with average particles size of 100 nm were made by the electric explosion of wire, and were subjected to mechanical activation in planetary ball mill for 15 and 40 minutes. It was shown that a certain amount of FeO phase is formed during mechanical activation of ultrafine iron powders. According to thermogravimetric analysis, the oxidation process of non-milled ultrafine iron powders is a complex process and occurs in three stages. The preliminary mechanical activation of powders considerably changes the nature of the iron powders oxidation, leads to increasing in the temperature of oxidation onset and shifts the reaction to higher temperatures. For the milled powders, the oxidation is more simple process and occurs in a single step.

## 1. Introduction

Iron powders are widely used in powder metallurgy for catalysts and other magnetic fluids producing [1]. With the development of nanotechnology, the various methods of ultrafine metal powders producing have been developed. These methods include a technique based on an electrical wire explosion [2-4]. Ultrafine iron powders obtained from this technology are differ from micropowders by their characteristics, primarily, ultrafine powders have high reactivity.

In the works [5-8], the strongly influence of the structure and particle size on the oxidation rate of ultrafine iron powders was shown, that leads to decrease in temperature and an increase in initial rate of the oxidation process. It was also shown that the oxidation of the iron powder is a complicated mechanism; the oxidation occurs through the formation of intermediate products [9], and depends on particle size, temperature, and partial pressure of oxygen in the gas phase, the rate of heating of the powder.

It is known that the mechanical activation in high-energy ball mill is one way of preparing of powder material in a highly dispersed state with disordered structure [10, 11]. It should be assumed that a change in the character of the oxidation of nanopowders, subjected to preliminary mechanical activation in a planetary mill, occurs.

Thus, using X-ray powder diffraction and thermogravimetric analyzes, the effect of mechanical activation on the oxidation of ultrafine iron powders obtained electro-explosion method are investigated. It should be noted that the thermogravimetric analysis is a popular method to study the oxidation processes in materials [12, 13].

## 2. Experimental

Ultrafine iron powders were made by the electric explosion of wire (EEW) in argon using the technique detailed in [14-16]. The powder was stored in hexane to prevent oxidation during shipping



and storage. From Brunauer-Emmett-Teller (BET) surface area, the average particles size was calculated (Table 1) and value was equal 100 nm.

The powder was dry milled in air using an AGO-2S planetary ball mill with stainless steel balls and vials. The powder to ball mass ratio was 1:1. The powder was milled according to different regimes, and was divided into three parts: the initial non-milled powder (sample A) and the powders are mechanically activated for 15 (sample B) and 40 minutes (sample C).

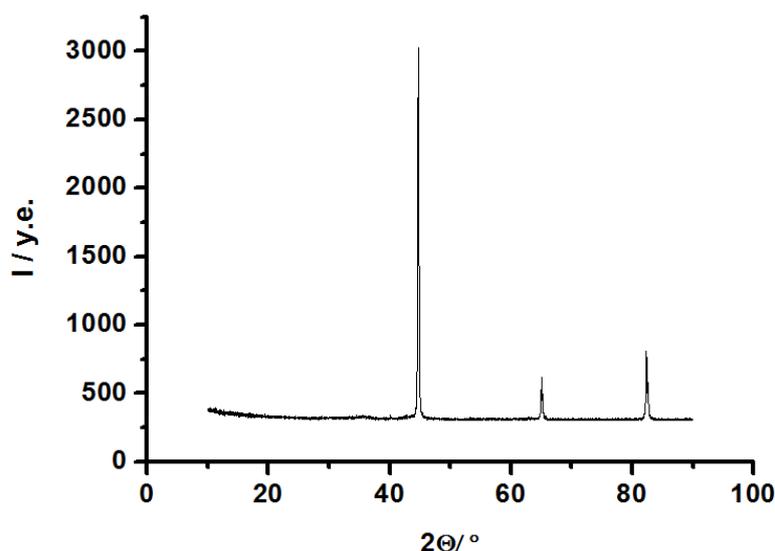
The powder oxidation was studied by thermogravimetric analysis, which performed using a STA 449C Jupiter (Netzsch-Geratebau GmbH, Germany) instrument. Samples with a mass of ~10 mg were placed in the alumina crucibles and heated up to 800°C with programmed heating rate of 10 C/min. Both TG and DSC baselines were corrected by subtraction of predetermined baselines run under identical conditions except for the absence of sample. All oxidation experiments were performed under atmospheric pressure conditions using air as the oxidant. The gas flow rate was controlled at 20 mL/min. The Netzsch Proteus software packages were used for data analysis.

Phase composition of the initial powders and oxidation products were determined by XRD phase analysis using ARL X'TRA diffractometer with  $\text{CuK}_\alpha$  radiation. The Powder Cell 2.4 software was used for a full-profile analysis of XRD patterns.

### 3. Results and Discussion

Figure 1, 2, 3 show the X-ray diffraction patterns for initial ultrafine iron powder (Figure 1) and milled powders during 15 min (Figure 2), 40 min (Figure 3). For the initial powder, all observed reflections belong to the phase of a pure  $\alpha$ -Fe. For the mechanically activated powders, a decrease in the intensities and an increase in the half-width of superstructure reflections for  $\alpha$ -Fe were observed with increase of the duration of mechanical activation. This clearly indicates that the crystallite size has been decreased with the increase of the milling time. The crystallite size of all samples was calculated using Debye-Scherrer formula and is shown in Table 1.

According to XRD-data shown in Table 1, a monoxide of iron (FeO) is produced as a result of oxidation of iron powder during mechanical activation; and the concentration of FeO increases with the increase of the milling time.



**Figure 1.** XRD pattern recorded from the non-milled ultrafine iron powder

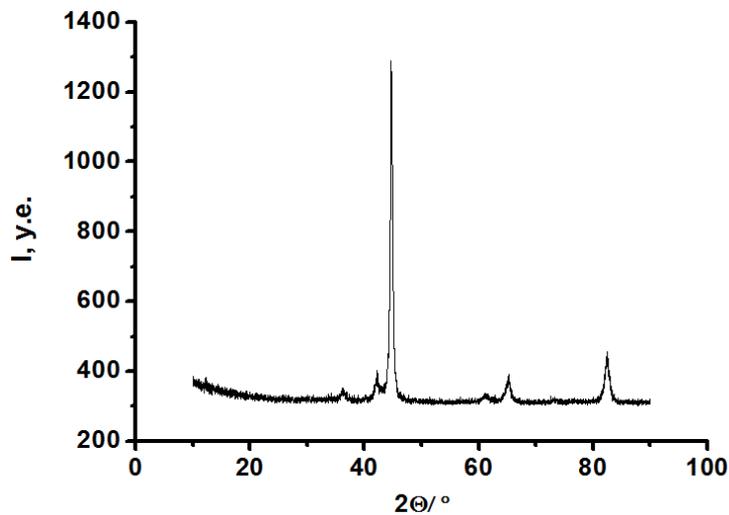


Figure 2. XRD pattern for 15 min milled ultrafine iron powder

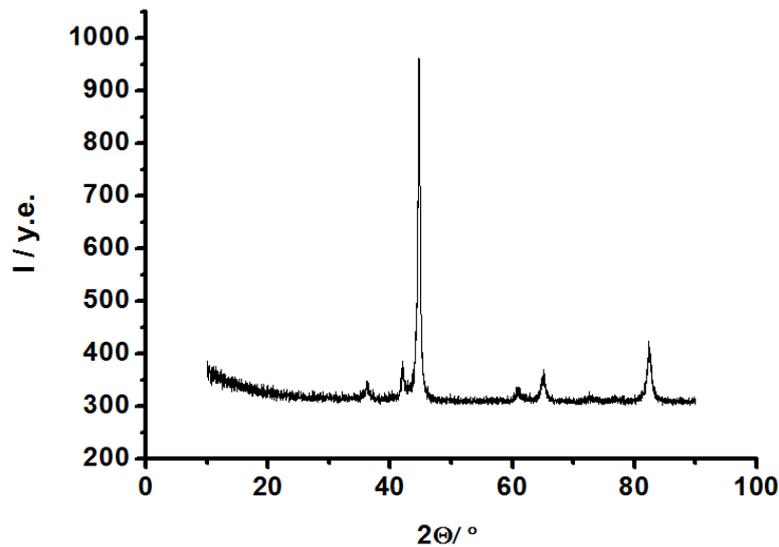
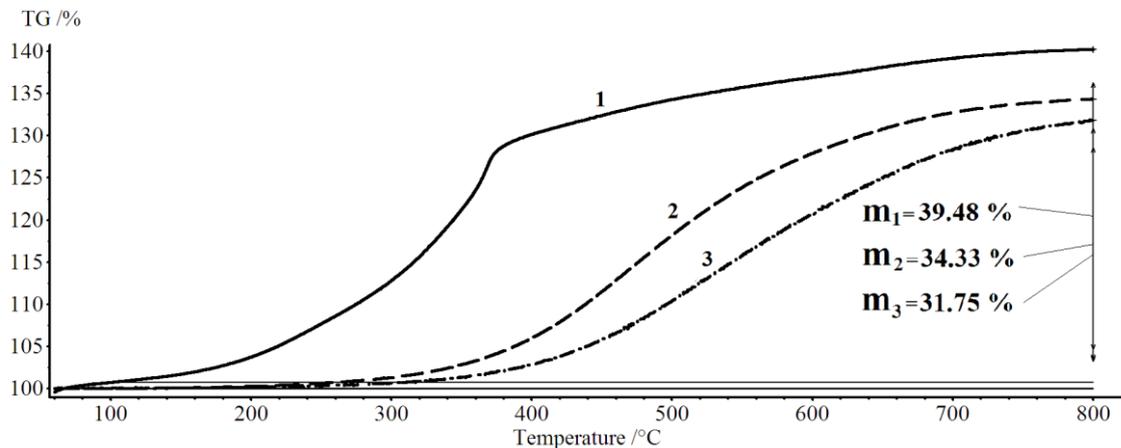


Figure 3. XRD pattern for 40 min milled ultrafine iron powder

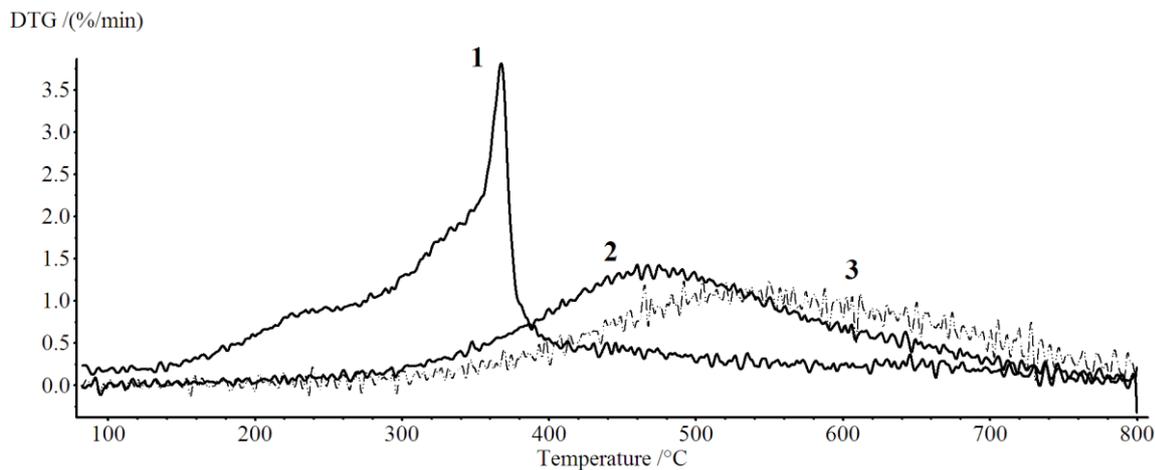
Table 1. The results of XRD analysis

Sample	Phase composition (%)		Average particle size (nm)
	$\alpha$ -Fe	FeO	
A	100	-	100
B	81.5	18.5	100
C	77.3	22.7	49

Figure 4 shows the TG curves obtained during the heating of iron powders. Derivative thermogravimetric curves (DTG) are shown in Figure 5. For all samples, the mass increasing is observed up to 800°C, and the mass change values were 39.48 % for sample A, 34.33 % for sample B, and 31.75% for sample C.

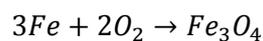
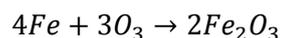


**Figure 4.** TG curves for sample A (curve 1), sample B (curve 2), and sample C (curve 3)

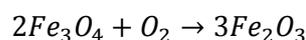


**Figure 5.** DTG curves for sample A (curve 1), sample B (curve 2), and sample C (curve 3)

For initial powder, the mass change in the end of reaction is close to the theoretical value, which correspond to the reaction  $4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$ . In this case, the DTG curve (Figure 5, curve 1) indicates a three-step oxidation process. Obviously, the mechanism of the oxidation reaction for initial  $\alpha$ -Fe is complex and changes during the reaction. It was shown in [7], the first step is the oxidation of the iron with simultaneously production of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  according to the following equation:



In the second stage, magnetite is oxidized to hematite to the following equation:



Different nature of oxidation is observed for mechanically activated samples. Start oxidation is shifted to higher temperatures, and one-step process of oxidation takes place. Thus, mass gain decreases with increasing of milling time that is consistent with the results of XRD analysis, which indicates the presence of partially oxidized iron powder.

#### 4. Conclusion

The processes of oxidation of ultrafine iron powders mechanically activated in a planetary ball mill for 15 and 40 minutes were investigated. It was shown that the mechanism of oxidation for initial powder is complex and changes during the reaction. For the milled ultrafine powders, a monoxide of iron is produced as a result of oxidation of iron powder during mechanical activation; and the concentration of FeO increases with the increase of the milling time. In this case, the oxidation processes are simpler and occur in one stage for both milled iron oxides. However, oxidation starts at a higher temperature compared with the non-milled powder. The data, which were obtained for the oxidation processes, can be used to simulate the processes of oxidation and calculate the kinetic parameters of oxidation.

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