The influence of the mode of interaction of compact samples made of nonpassivated iron nanopowders with air on their microstructure

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Abstract. In this work, various modes of interaction (spontaneous ignition or a combustion mode) of compact samples made from nonpassivated iron nanopowders with air are found out. The experiments showed that the modes of interaction of the samples with air after their extraction from a weighing bottle depended on the media (argon or air), in which the weighing bottle was placed before extraction of the samples, as well as on the duration of the exposure of the weighing bottle in the air. It is shown that the process of interaction of the sample with air has a surface character; the inner layer of the sample contains unreacted nanopowder. The microstructure of the transverse fracture of the samples after spontaneous ignition and combustion represents a porous aggregation of agglomerates. Integral energy-dispersive analysis showed a higher content of oxygen in the near-surface layer of the sample about 300÷500 microns thick. The analysis of the microstructure of the fracture of a separate agglomerate showed the presence of a layer with an elevated oxygen content on the surface of the agglomerates. Particles in the agglomerates retain the dimensions of passivated iron nanopowders.

1. Introduction

Nanopowders of metals are pyrophoric, i.e. these are capable of self-ignite on contact with air due to high chemical activity and a large specific surface [1-2]. To make safe further processing of nanopowders to products, they are passivated. Passivation means the synthesis of a thin protective film on the surface of nanoparticles, which prevents self-ignition of metal nanopowders. The processes of passivation of iron and nickel nanopowders were investigated in [3-7].

However, it is obvious that there can also be situations in which the passivation of the nanopowder is technically impossible or undesirable, though technical operations with the nanopowder need to be carried out. Therefore, the relevant task is the development of new methods of obtaining compact products from nanopowders allowing to provide the required fire and explosion safety level in the processing of both nanopowders and their products.

Literary data on the regularities of spontaneous ignition and self-heating of compacted samples obtained from nonpassivated nanopowders are quite limited. In the works [8, 9], a research of ignition of nanosystems with the sizes of particles of reagents in the range of 40-80 nm showed that the temperature and energy of ignition can be much lower than in mixes of micropowders (1-100 microns).
In [10], the features of flame propagation within tablets made of mixes of Al/CuO nanopowders (the so-called nanothermites) depending on the density were investigated at laser initiation of combustion. Similar measurements [11] were carried out with the samples of Al/MoO$_3$ nanopowders; the obtained results were qualitatively similar to the results on Al/CuO nanothermites.

In the work, the interaction of compact samples made of nonpassivated iron nanopowders with the air was experimentally investigated. The main attention was paid to the influence of the interaction mode on the microstructure of the samples after spontaneous ignition and combustion.

2. Experimental

In the work, iron nanopowders obtained by the chemicometallurgical method were used for experimental studies of ignition and passivation of compact samples. The main stages of the synthesis of a metal nanopowder are the metal hydroxide sedimentation, drying and reduction [3-5]. These powders are pyrophoric.

All operations on obtaining compact samples, namely opening the vessels with nanopowders, weighing and pressing them, were carried out in a sealed box (hereinafter - the box) filled with inert gas (argon), equipped with a lock to extract and replace powders and samples. The oxygen concentration in the box did not exceed 0.1 vol.%. Special experiments showed that at such an oxygen concentration, nanopowders remained pyrophoric. Compact cylindrical samples made of iron nanopowder with a diameter of 5 mm, a length of $7 \div 12$ mm and a density of $2.5 \div 4$ g/cm$^3$ were obtained and investigated. After pressing, each sample was placed in a separate weighing bottle.

The weighing bottle with the samples was extracted out of the box via the lock. Cylindrical samples were extracted out of the weighing bottle just before the experiment and set vertically for 3-5 seconds on a boron nitride support. The scheme of the experiment is shown in figure 1. A Flir 60 infrared camera was used for monitoring the time dependence of the temperature within a sample surface and for determination of the maximum temperature at a given time point as well. A SONY HDR-CX330 video camera was used for measuring the combustion velocity (propagation velocity of the oxidation reaction across the surface of the samples). The dynamics of the temperature change on the surface of the sample was also controlled by two tungsten-rhenium thermocouples 40 microns thick, which were tightly touching the lateral surface of the sample.

![Figure 1](image.png)

**Figure 1.** The scheme of the experiment on measurements of the temperature characteristics of samples in air: 1 – weighing bottle with a compact sample after extraction from the box, 2 – boron nitride support, 3 – sample under investigation, 4 – Flir E60 infrared camera, 5 – digital video camera, 6 – tungsten spiral, 7 – computer for processing A/D converter data, 8 – the contact platform with fixed thermocouples, 9 – A/D converter.
The microstructure of the samples after self-ignition and combustion was investigated by the scanning electron microscopy (SEM) method with a Carl Zeiss Ultra Plus microscope. The phase structure of the samples was studied using a DRON-3M diffractometer. The diffractograms were recorded in a mode of step scanning in the range of angles \(2\theta = 30^\circ \div 100^\circ\) with a step 0.2\(^\circ\). The obtained diffractograms were analyzed using the PDF-2 database.

3. Preliminary results
To determine the specific surface and average sizes of the iron nanopowder, the nanopowder was previously passivated. Depending on the passivation time, the specific surface \(S\) of nanopowders determined by the BET method was 9÷9.6 m\(^2\)/g. The average diameter \(d\) of iron particles was calculated according to the following formula \(d = \frac{6}{\rho S}\), where \(\rho\) is the density of iron 8.96 g/cm\(^3\). At \(S = 9.0\) m\(^2\)/g, the diameter of the particles of the iron powder was equal to 85 nm.

4. Results and discussion
In figure 2, the results of video filming of the process of self-heating in air (the external initiation is missing) of a cylindrical sample pressed from a nonpassivated iron nanopowder are presented. After extraction out of the box, the closed weighing bottle with the samples was in the argon atmosphere; then the samples were extracted to air as described above. Such a mode of reaction with air is observed for all samples, if the weighing bottle after extraction out of the box was in argon atmosphere.

![Figure 2. Frames of video filming of a sample during self-heating.](image)

Self-heating of the sample has a non-uniform character, though it begins at the same time within the entire surface of the sample. Infrared video filming showed that the maximum temperature is located near the top end face of the sample practically at all stages of oxidation. The main reason of heterogeneity of a warming up is non-uniformity of the sample density along its height; the top part of the sample always had a minimum density.

In another series of experiments, samples of nonpassivated iron nanopowder were pressed in argon atmosphere, however, after extraction from the box the closed weighing bottle with the samples was placed in air. The experiments showed that the modes of interaction of the samples with the air after they were extracted from the weighing bottle depended on the duration \(t\) of the presence of the weighing bottle in air. The first sample \((t < 4\) min\) showed itself similar to the samples from the first series of experiments. Thus, self-heating of the samples occurred, and they changed their color. The next sample \((t = 10\) min\) was warmed up to only 55 °C and did not change color. The samples, which were in the weighing bottle in air for more than 20 min, showed no temperature rise after extraction and did not change color. To test the hypothesis that passivation with the maintenance of chemical activity occurred while the weighing bottle was in air, the following experiments were performed. The samples, which showed no temperature rise after extraction from the weighing bottle, were ignited from the top end face with a tungsten spiral. This procedure led to the propagation of a combustion wave over the sample. The combustion velocity for a sample density 3.07 g/cm\(^3\) makes \(\approx 0.025\) cm/s.
In the following experiments, the investigation of the microstructure of the transverse fracture of a cylindrical sample after self-heating and cooling was performed. The microstructure of the transverse fracture of a cylindrical sample represents an aggregation of agglomerates of iron nanoparticles. The agglomerates have the form of "crockns" (figure 3), i.e. parts of spheres of irregular form.

The integral energy-dispersive analysis (EDA) from the surface of the fracture showed a higher oxygen content in the near-surface layer (about 300÷500 microns thick) of the sample. When examining the experimental EDA data of, it is necessary to take into account that the transverse fracture of the sample, but not the polished section, was studied. Therefore, the results of EDA have a qualitative character rather than quantitative one; these only provide insights into the magnitude of the oxygen content in various areas of the sample and the distribution of oxygen inside and on the surface of a separate agglomerate. The average content of oxygen in the near-surface area of the sample is 45÷50 atomic percent, and in the central part of the sample it is about 20 atomic percent.

In figure 3 d-c, the microstructure of a fracture of a separate agglomerate in the near-surface area of the sample is presented. In the figure, one can see the existence of a pore-free layer on the surface of the agglomerates ("crust") about 300 nanometers thick. Apparently, the formation of a dense oxide film on the surface of the agglomerates prevents the diffusion of oxygen into the agglomerate and further oxidation of the iron nanopowder as well. The internal part of the agglomerate represents a porous aggregation of iron particles about 100 nanometers in size.

In figure 4 the microstructure of the internal part of the sample is presented. According to a local EDA, the oxygen content on the surface of the agglomerates in the central part of the sample is 15÷20 atomic percent, inside the agglomerates it is about 5 atomic percent. On the surface of the agglomerates of the sample there is no dense "crust", which is characteristic of the near-surface part of the sample. Only a small increase in density to a depth about a single particle is observed. The internal part of the agglomerates does not differ from the similar agglomerates in the near-surface part of the sample.

![Figure 3](image_url)

**Figure 3.** The microstructure of the transverse fracture of the near-surface area of the sample after self-heating and cooling recorded with a different magnification.
Figure 4. The microstructure of the fracture of the internal part of the sample recorded with a different magnification.

Apparently, the pores between the agglomerates serve as the main transport way, by which the air penetrates into the sample, oxidizing incidentally the surface of the agglomerates. The amount of oxygen, which penetrates into the internal part of the sample, is less than into its near-surface part, therefore, the oxidation and passivation of the powder occurs more slowly; these processes do not lead to the formation of dense oxide layers. At the same time, diffusion of oxygen into agglomerates and oxidation of iron nanoparticles occur.

The microstructure of the transverse fracture of the sample, which was ignited from the top end face with a tungsten spiral, is shown in figure 5. Self-heating of this sample after extraction from the weighing bottle was not observed. The near-surface area about 300÷400 microns thick with a higher average content of oxygen (to 45 atomic percent) in comparison with the central part of the sample (about 25 atomic percent of \(O_2\)) can bee seen in the structure of the transverse fracture of the sample.

Within the near-surface area, the agglomerates are covered with the oxide "crust" about 300÷400 nanometers thick (figure 5 d, c). The oxygen content in the "crust" makes about 60 atomic percent, in the agglomerate it makes 15÷30 atomic percent.

Figure 5. The microstructure of the transverse fracture of the near-surface area of the sample after combustion and cooling recorded with a different magnification.

EDA of the microstructure of the internal part of the sample showed that the oxygen content makes 25 atomic percent. The thickness of the sample of the oxidized layer ("crust") does not exceed the size
of the single particle, of which the agglomerates consist, on the surface of the agglomerates of the internal part of the sample.

RFA investigation of the samples after self-heating and ignition showed that in both cases iron oxide Fe$_3$O$_4$ is observed in addition to the iron phase. In the sample in which self-heating was observed, the ratio of the oxide phase is much lower than in the sample after ignition; it correlates with the EDA data obtained using SEM.

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