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Interaction of compact samples made of pyrophoric iron nanopowders with air

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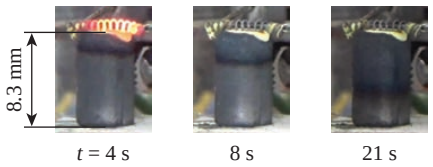
It has been revealed that the maximum temperature of self-heating of a compacted sample prepared from non-passivated iron nanopowder decreases with increasing its relative density, which indicates that the oxidation process is limited by the diffusion supply of oxidant. The passivation method for the compacted samples made of iron nanopowder has been developed.



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Nanopowders of metals are pyrophoric, *i.e.* they are capable of self-igniting upon contact with air due to the high chemical activity and large specific surface area.[1–4] For safety purposes, they are passivated,[3–7] which means covering by a thin protective film on the surfaces of nanoparticles in order to prevent the self-ignition of metal nanopowders. The passivation usually takes a lot of time (dozens of hours), which is a limiting factor for increasing the industrial production of nanopowders. We have previously suggested a model for the passivation of pyrophoric layer of nanopowder and characterized it by analytical and numerical methods.[8]

The passivation processes have been already explored for iron and nickel nanopowders,[9,10] showing the applicability of approaches of classical macroscopic theory of thermal explosion to explain the ignition phenomena for macroscopic objects consisting of iron and nickel nanoparticles. However, for many situations, it is technically impossible or even undesirable to passivate a nanopowder, while technical operations with the nanopowder have to be carried out. Therefore, it is a crucial task to develop new methods for obtaining compact products from nanopowders, which make it possible to maintain the required level of fire and explosion safety and to simultaneously preserve their unique chemical properties during both the processing and manufacturing of nanopowders.

The known data on the features of self-ignition and -heating of compacted samples prepared from non-passivated nanopowders are quite limited. Ignition tests of nanosystems with a particle size of reactants being in the range of 40–80 nm have revealed that their temperature and energy of ignition are considerably lower than those in the mixtures of microparticles (1–100 μm).[11,12] The peculiarities of flame propagation over the tablets made of mixtures of Al/CuO nanopowders (so-called nanothermites) have been investigated upon laser initiation of combustion as dependences on the density.[13] Less dense samples (*e.g.*, 90% porosity) were found to ignite faster, while the velocity of flame propagation within them was an order of magnitude higher than that in denser samples (50% porosity). These results indicated a change in the combustion mechanism upon an increase in the density of compacted sample from a convective mechanism to the diffusion one. Similar measurements[14] were performed with the samples of Al/MoO_3 nanopowders, and the results acquired for the nanothermite were qualitatively the same.

The present work was aimed at the experimental investigation of interaction of compact samples made of non-passivated iron nanopowders with air. The effect of porosity of these compact samples on the dynamics of their self-heating has also been evaluated.

Iron nanopowders prepared according to a chemical metallurgical method were used in this work for experimental studies of ignition and passivation of compact samples.[9,10] The freshly prepared nanopowders were pyrophoric, and the average diameter of their nanoparticles (calculated from the specific surface area of a powder) was 85 nm.†

To confirm the preservation of pyrophoricity of a nanopowder after manipulations in the box, a sample of the powder was poured into a weighing bottle (a ground-glass stopper flask), which was opened after its extraction from the box, and the powder was poured into the air. Then the powder self-ignited and burned brightly, *i.e.* remained pyrophoric during all the preparative operations.

In the first series of experiments, closed weighing bottles after extraction from the box contained the samples remaining under

† Opening vessels with the nanopowders and all the subsequent operations, *viz.* weighing, pressing, and measurements of the sample size, were carried out in a sealed box (hereinafter, 'the box') filled with an inert gas (argon) and equipped with scales, mold and measuring tools, a press, and a lock for changing the powders and samples. The O_2 concentration in the box was monitored by an AKPM-1-02 analyzer. Once the powder vessels were opened and during the samples pressing, the O_2 concentration in the box did not exceed 0.1 vol%. At this O_2 concentration, the nanopowders remained pyrophoric. Cylindrical samples made of iron nanopowders, sized 5 mm in diameter and 7–12 mm in length, and possessing the density of 2.5–4 g cm^{-3} were obtained and examined.

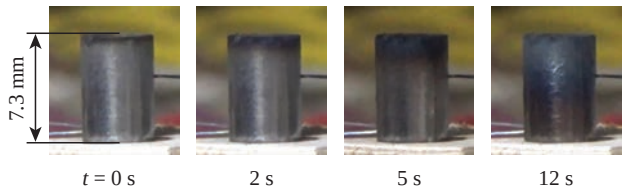

Figure 1 Frames of video filming of the sample during its self-heating.

argon atmosphere until the beginning of experiment (*i.e.*, before the extraction of samples from the weighing bottles). Figure 1 shows the results of video filming of the self-heating process (without any external initiation) of a compacted sample made of pyrophoric iron nanopowder in the air. This type of interaction with air was observed for the all samples in the case of storing the samples under argon atmosphere.

It should be noted that the sample was self-heated non-uniformly, although its self-heating begins simultaneously over the entire surface. This was observed (Figure 2) in both thermocouple measurement (curves *2* and *3*) and infrared video filming (curve *1*) data. As one can see from Figure 2, the warming-up has started simultaneously at different points of the sample, then proceeded at different velocities, and achieved various maximum temperatures during the heating. The infrared video capture data revealed that at almost all the steps of interaction, the maximum temperature was near to the top end of sample. The non-uniformity of sample heating is reasoned by both the best conditions for the oxidant supply at the top end (the bottom end was placed on the gas-inpermeable substrate) and the heat losses into the massive substrate. Another reason for the non-uniformly heating is the non-uniformity of sample density along its height, since the top of sample usually possesses minimum density due to its contact with the punch during the preparation.

Tanking into account the know data,[9] one could expect that the process of interaction of the sample with air is of superficial nature, and consequently, there would be unreacted nanopowder in inner layers of the sample. An analysis of the sample fracture

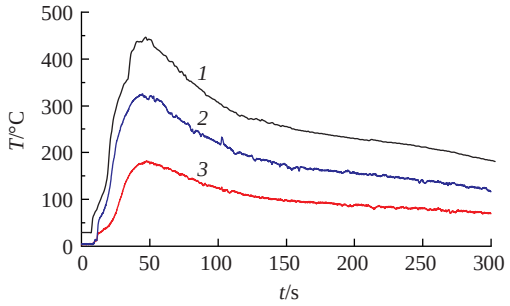

Figure 2 Temperature variation *vs.* time at different points of the sample during its self-heating: data from (*1*) infrared video filming with thermal imager and (*2* and *3*) thermocouple measurements. The thermocouples were located at the distance of (*3*) 1 and (*2*) 4 mm from the bottom end of sample.

The study of heating, ignition and combustion of the samples was carried out under an air atmosphere. The samples were removed from the box and mounted vertically on a boron nitride stand for 3–5 s. Measurements of the time dependence of temperature distribution over a sample surface and the determination of maximum temperature at any given moment were performed using a Flir 60 infrared camera (60 frames per s, 320 × 240 pix, and sensitivity of 8–14 μm). A SONY HDR-CX330 video camera was used to determine the velocity of combustion (the propagation of oxidation reaction along the sample surface). The dynamics of temperature change over the sample surface was also monitored by two rolled thermocouples of 40 μm thickness, tightly touching the lateral surface of sample. The thermocouples were located at the distances of 1 and 4 μm from the lower end of sample.

photos after cooling confirmed this assumption. The thickness of the surface (oxidized) layer was about 0.35 mm.

It should be also noted that according to the thermocouple measurements, a decrease in the relative density of samples from 3.84 to 3.22 g cm^{-3} raises a maximum self-heating temperature from 290 to 385 °C, indicating that the oxidation process is limited by the diffusion supply of the oxidant into the sample. These results are in a qualitative agreement with the conclusions of theoretical analysis,[7] according to which the maximum temperature in the diffusion-controlled wave of conversion θ_{fr} depends on the governing parameters of process according to the following equations:

$$\theta_{fr} = \frac{\eta_{1,k}}{\gamma\nu} \Big/ \left(1 + \frac{\sqrt{2}}{\sqrt{\pi}} \frac{\sqrt{\eta_{1,k}}}{\sqrt{Le\nu}}\right),$$

$$\theta = \frac{E}{RT_0^2}(T - T_0),$$

$$\gamma = \frac{c_c RT_0^2}{EQ} \frac{\rho_c}{\rho_g a_0},$$

$$\eta_1 = \frac{\rho_{c0} - \rho_c}{\rho_{c0}},$$

$$Le = \frac{D_{ef}}{a_c},$$

and $\nu = \bar{\nu}\rho_g a_0/\rho_c$,

where: a_0 and a are the initial and current concentrations of gaseous oxidant, respectively; ρ_{c0} are ρ the initial and current contents of condensed substance in unit volume, respectively; ρ_g is the density of gas phase; c_c is the heat capacity of condensed substance; R is the universal gas constant; E and k_0 are the activation energy and pre-exponential factor of heterogeneous reaction related to unit volume of porous medium, respectively; Q is the thermal effect of heterogeneous reaction related to the unit of oxidant mass, a_c is the thermal diffusivity of condensed phase; D_{ef} is the effective diffusivity of oxidant; $\bar{\nu}$ is the amount of condensed substance reacting with one gram of oxidant. The dimensionless variables and parameters include the following one: θ is the temperature; θ_{in} is the initial temperature of sample equal to the ambient temperature; η is the oxidant conversion depth; η_1 is the condensed substance conversion depth; $\eta_{1,k}$ is the maximum conversion degree of condensed substance; Le is the analogue of Lewis parameter for the oxidant; γ and ν are numerical parameters.

According to the above equations, the temperature in the reaction zone increases with rising the effective diffusion coefficient, whose value grows upon an increase in the porosity of sample.[15]

In another series of experiments, the non-passivated iron nanopowder samples were pressed under argon atmosphere, but the closed weighing bottles containing the samples after the extraction from the box were kept in air until the beginning of experiment. These experiments have demonstrated that the modes of interaction of samples with air after their extraction from the weighing bottles depended on the duration t of exposure of the weighing bottles to air. For instance, the first sample (t < 4 min) behaved similar to the samples from the first experimental series (see above), *viz*. the sample was self-heated along with its colour change (see Figures 1 and 2). The next sample, which was exposed to air for 10 min, was warmed up to 55 °C after its extraction into the air and did not change its colour. The samples exposed to air in the weighing bottle for more than 20 min did not warm up nor change their colour after their extraction from the weighing bottle. Therefore, this time is sufficient for the complete passivation of samples.

To verify the hypothesis about the occurrence of passivation accompanied by the preservation of chemical activity instead of

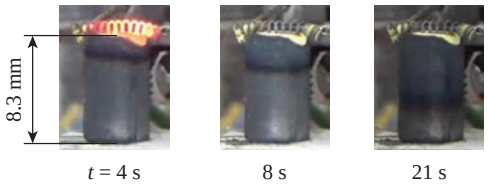

Figure 3 Frames of video filming of the combustion process for the sample, which was exposed to air for more than 20 min (density of 3.07 g cm^{-3}).

complete oxidation of the samples during their contact with air in the weighing bottles, the next series of experiments was performed. The samples that did not warm up after their removal from the weighing bottle were ignited at their top end with a tungsten spiral (Figure 3). This local warming resulted in the combustion wave propagation along the sample. Since the sample surface has changed its colour during the oxidation, the burning velocity was estimated by a frame-by-frame processing of the video filming. According to Figure 3, the combustion wave propagates downward from the top side of sample at an approximately constant velocity. The typical values of combustion velocity were 0.025–0.04 cm s^{-1}.

Similar results were observed in experiments with the passivated iron nanopowders.[9] The local heating with a tungsten spiral caused the propagation of reaction wave over the surface of powder sample. A qualitative agreement of our results with the known data is an additional confirmation of the fact that the passivation of samples has occurred during the exposition of weighing bottles to air.

Note that the infrared filming of dynamics of change in the temperature field of sample during the combustion wave propagation carried out at the same time revealed that the maximum temperature was almost always near to the top end of sample. This result allows us to conclude that the interaction process does not finish inside the combustion wave, and the combustion itself has a surface nature, as was also confirmed by the RFA data.

In summary, it has been demonstrated that the self-heating of a compacted sample made of non-passivated iron nanopowder is not uniform, although it begins simultaneously on the entire surface of sample. The maximum temperature of self-heating was found to decrease with increasing the relative density of samples, which indicates that the oxidation process is limited by the diffusion supply of oxidant. It was revealed that the process of interaction of samples with air possesses a surface nature. The results of theoretical analysis qualitatively agree with the experimental data. The dependence of interaction mode of the samples with air on the duration of exposure of weighing bottles to air was confirmed. The possibility of passivation of compacted iron nanopowder samples was experimentally established.

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