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Passivation of iron nanoparticles at subzero temperatures

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**Experimental evidence has been provided that Fe nano-
particles do not ignite in dry air at a temperature lower than
–25 °C; however, passivation with air occurs to make the
particles stable at room temperature.**
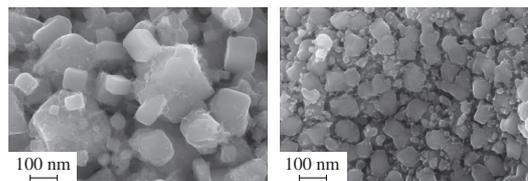
Nanotechnology incorporates methods for the synthesis of materials with nanometer structure sizes and nanometer-size objects. The transition to a nanocrystalline state, in which the characteristic geometrical sizes of a substance structure are commensurable with a characteristic scale of some physical phenomenon, leads to drastic changes in the properties of the substance.[1] As the surface to volume ratio of arbitrary objects rises with decreasing size, the surface of nanosized structures becomes increasingly important for their properties. Additionally, quantum mechanical effects come into play, and they can be exploited in advanced functional devices[2,3] (*e.g.*, quantum dots in light-emitting diodes).

Nanoscale zerovalent iron nanopowder is a nanomaterial extensively applied to groundwater and wastewater treatment. At nanoscales, the specific surface area of iron nanopowder increases drastically; hence, the surface reactivity of iron nanoparticles becomes about 30-fold higher than that of 325 mesh iron powder.[4] Despite its high potential for environmental applications, there is limited knowledge about the fundamental properties of iron nanopowders, particularly, its structure and surface composition.[5] However, the nanopowders of metals, in particular, iron nanopowders, are pyrophoric immediately after synthesis, *i.e.*, they are capable of self-igniting in contact with air because of high chemical activity and a large specific surface area. To make safe the further processing of nanopowders to products, the powders are passivated. The passivation means the creation of a protective thin oxide film on the surface of nanoparticles, which prevents their self-ignition.

Previously,[6,7] we synthesized nanoscaled (20–100 nm) iron powders by the reduction of 1 mm layer of iron(III) hydroxide in a hydrogen flow at 400 °C followed by passivation in a flow of 3% air + Ar for 6–60 min. The passivated iron nanoparticles could be stored without significant oxidation for five months.[6] It was found[7] that the dependences of the delay period of ignition and the quantity of primary centers of combustion on the passivation time of iron nanopowders with air could be used for controlling passivation. The spatially nonuniform surface mode of combustion of iron nanopowders was revealed, *i.e.*, the fronts of oxidation propagated on a sample surface from primary combustion centers. It was also shown that the delay period of

ignition of nonpassivated Fe nanoparticles markedly increased (from ~0.3 to 4.2 s) with decreasing the temperature from 20 to 0 °C. Therefore, we suggested that, upon attainment a certain value of subzero temperature at some instant of passivation, the rate of heat release in a reaction of Fe nanoparticles with O_2 can be lower than heat losses into reactor walls; thus, Fe nanoparticles would not ignite in dry air; however, passivation would occur.

The aim of this work was to develop a new highly effective method of passivation to provide the demanded safety level of the processing of nanopowders with preservation of their unique properties. The method is based on Fe nanoparticle passivation at subzero temperatures; certain properties of passivated nanoparticles have been examined.

Iron nanopowders were obtained by a chemical metallurgy method including the synthesis of metal hydroxides by alkali treatment of metal salts, the sedimentation and drying of hydroxides and their reduction.[6,7]

Figure 1 shows the time dependence of sample heating during passivation combined with video filming at initial temperatures of –35 and –14 °C.[†] The warming up at –14 °C makes up 140 °C; in this case, the appearance of the sample markedly changes.

[†] The reactor (Figure S1, see Online Supplementary Materials) with a sample of iron hydroxide powder in a quartz trough 1 mm thick was maintained in a furnace at 400 °C in a hydrogen flow for 1 h; then, the reactor was extracted from the furnace and cooled to room temperature in an Ar flow. The quartz trough was equipped with a chromel–alumel thermocouple (0.3 mm) placed in the nanopowder. Further, the reactor was placed in an external bath of a HAAKE-Q cryostat and cooled (0 to –35 °C) in an argon flow using ethanol as a cooling agent. Upon reaching the necessary subzero temperature, the Ar flow was replaced by a flow of dry air. To obtain dry air, it was passed through a 0.6 m column of solid KOH and then the coil of a flexible tubing placed in the cooled bath of the cryostat. The detected heating of the thermocouple after replacing flows indicated the beginning of ignition. At temperatures $T_0 > 0$ °C, the warming up was independently controlled with a Fluke 62 pyrometer. The time delay of ignition was estimated as a time between replacing flows and a maximum warming up (when a sharp increase in the temperature was detected, see Figure 1). A Casio Exilim F1 PRO color high-speed video camera (60 frames per second) was used to detect the combustion of iron nanopowder. If ignition occurred, the sample surface
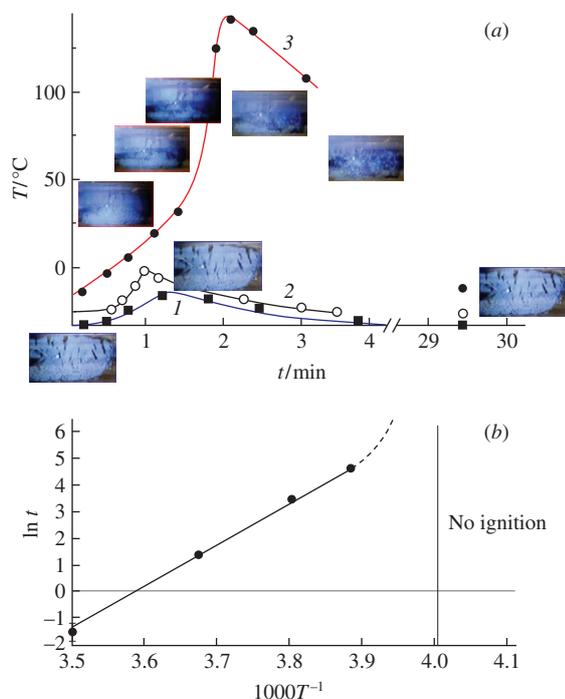
Figure 1 (*a*) The time dependence of warming up during passivation combined with video filming at (*1*) –35 °C, (*2*) –25 °C and (*3*) –14 °C. The time of the frame recording corresponds to the coordinate of its center on the *x* axis. 60 frames s⁻¹. Zero time corresponds to the moment of replacing Ar flow with the dry air flow. (*b*) Dependence of the logarithm of the delay time of nanopowder ignition on reciprocal temperature in a range of 20 to –14 °C.

The warming up at –35 °C makes up ~20 °C, the warming up at –25 °C makes up ~23 °C; in both cases, the samples do not change its appearance at all. The comparably small warming up values at $T_0 < -25$ °C are probably due to heat release in Fe oxidation reactions leading to the formation of a thin protective oxide film on the surface of the nanoparticles. It is evident that the ignition does not occur at –25 °C; therefore, at a certain moment of passivation, the rate of heat release becomes smaller than heat losses,[8–11] *i.e.* the critical condition of a thermal ignition is not attained. Thus, we have shown that the classical macroscopic theory of thermal explosion is quite applicable to nano-objects. The fact is of obvious interest. It turns out that one can reasonably use macroscopic parameters in calculations even if the research object is a set of nanoparticles. This question demands further investigations.

Note that the warming up at 20 °C reaches 300 °C and a surface mode of combustion of iron nanopowder occurs.[7] Thus, the lower the initial temperature, the smaller the warming up; in addition, at an initial subzero (–14 °C) temperature, a surface mode of combustion is missing [Figure 1(*a*)]. The reaction proceeded without a pronounced front of chemical conversion: the oxidation occurred over the whole surface. It means that combustion modes at room temperature and –14 °C differ qualitatively.

changed its appearance (the initial temperatures of 0 to –14 °C). If the ignition was missing in 30 min, the air flow was replaced with the argon flow and the reactor was heated up to room temperature. Then, the quartz trough with the passivated iron nanopowder was extracted from the reactor.

The phase structure of the samples was studied on a Diffray-401 X-ray diffractometer with a coordinate-sensitive detector. The microstructure of the powders was examined using a Zeiss Ultra Plus field emission ultra-high resolution scanning electron microscope equipped with an INCA 350 Oxford Instruments X-ray microanalysis console with a resolution of 2 nm.

In accordance with the theory of thermal ignition,[8,9] the logarithm of the delay time of ignition of nanopowder *vs.* reciprocal temperature was plotted [Figure 1(*b*)]. This dependence is almost linear over a range of 20 to –14 °C. The effective activation energy of ignition was ~7.5 kcal mol⁻¹, *i.e.*, the oxidation of iron nanopowder is a weakly activated reaction in this range. Such a low activation energy is characteristic of surface processes.[10]

However, no ignition was observed below –25 °C. It is natural to expect that the formation of an oxide layer on the surface of nanoparticles can be represented by the overall reaction Fe + xO₂ → Fe$_y$O$_z$; however, the detailed mechanism of passivation remains unknown.

In experiments with the ignition of nanopowder (over an initial temperature range of 20 to –14 °C), X-ray phase analysis showed that the nonpassivated samples after combustion contain iron oxides and a noticeable amount of metallic iron, whereas the sample of nanopowder passivated in the dry air for >30 min at –35 °C contained only metallic iron (Figure 2). Note that the oxide content of the sample after combustion markedly decreased with a decrease in the initial temperature.

Figure 1(*a*) shows that the passivation process at $T_0 < -25$ °C was complete in 4–5 min after the start of air supply, if we consider that the time of completion of passivation corresponds to cooling the sample down to the initial temperature. In that case (in 5 min, according to the reading of the thermocouple), the air flow was replaced with the argon flow and the reactor was heated to room temperature. Then, the quartz trough with the passivated iron nanopowder was extracted from the reactor. The X-ray method for the sample processed at –35 °C and passivated in the dry air for 5 min till the warming-up came to an end, and the temperature of the sample became equal to initial one, detected only iron.

Figure 3 depicts the SEM images of the nanopowders passivated at 20 and –35 °C. Such a noticeable distinction between the sizes of the nanoparticles synthesized at 20 and –35 °C is due to the fact that the velocities of processes of coalescence at diffusive migration of the adsorbed atoms considerably increase with the temperature of the environment.[12] Indeed, since the processes of aggregation and coalescence of Fe nanoparticles slow down at lower temperatures, the mean size of iron nanoparticles passivated at –35 °C is less than that for particles passivated at 20 °C (35–85 nm[7]).

Thus, we have experimentally established that, at a certain subzero temperature, Fe nanoparticles do not ignite in dry air; however, passivation occurs and provides the stability of nano-
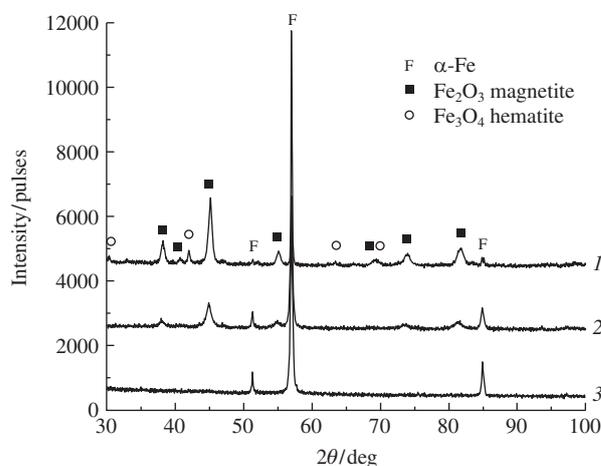

Figure 2 X-ray phase analysis of the oxidation products of nonpassivated iron nanopowder in air after completion of surface reaction (*1*) at an initial temperature of 20 °C,[4] (*2*) at –14 °C with dry air and (*3*) after treatment with dry air for 30 min at –35 °C and further heating up to 20 °C.
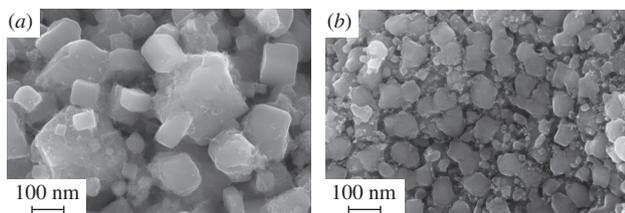
Figure 3 Micrographs of the iron nanopowders passivated (*a*) at 20 °C for 10 min in a flow of 3% air + Ar and (*b*) at –35 °C for 5 min in a flow of dry air.

particles at room temperature. The combustion modes at room and subzero temperatures differ qualitatively. Both the oxide content of the iron nanopowder sample after combustion and the maximum warming up decrease with decreasing the initial temperature. The sample of iron nanoparticles passivated in dry air at –35 °C contained only iron. According to the SEM data, passivation at subzero temperatures prevents the agglomeration and coalescence of Fe nanoparticles. It has been demonstrated for the first time that the classical macroscopic theory of thermal explosion is quite applicable to nanosized objects.

Online Supplementary Materials
Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.09.017.

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