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Temporal characteristics of ignition and combustion of iron nanopowders in the air

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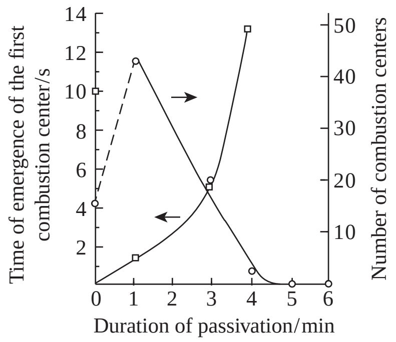
It is shown that both dependencies, namely of a delay of ignition and a quantity of the primary centers of combustion on the time of passivation of iron nanopowders in air, can be used for controlling the passivation. The spatially non-uniform quasi two-dimensional mode of combustion of iron nanopowders is revealed.



Nanophase materials and composites, characterized by ultra-fine grain size, have attracted especially widespread interest in recent years due to their unusual physicochemical properties. These nanosized metallic and explosive powders obtained by chemical methods are usually pyrophoric, *i.e.* are capable of self-ignition in contact with air because of high chemical activity and large specific surface area.[1] To make further processing of nanopowders to products safe, they are usually passivated. The passivation means the creation of a protective thin oxide film on a surface of nanoparticles. This prevents self-ignition at an extraction of metal powders from reactors and provides for the preservation of their unique properties. Until now there are no reliable scientifically grounded methods for the passivation of metallic nanopowders.

The overwhelming number of publications on ignition and combustion of pyrophoric nanopowders is associated with the combustion of aluminum nanopowders. From the literature available, it is possible to conclude that modeling and, accordingly, understanding of the mechanism of combustion of Al nanopowders is still at an initial stage. According to ref. 2, in case of oxidation in a nanoscale, the process is kinetically controlled because of a small diffusive path. However, an oxidation by an oxygen from a gas phase can be either kinetically or diffusionally controlled depending on the Damköhler number. For nanoparticles, the ignition stage always begins with heterogeneous reactions and phase transitions and is observed at rather low temperatures in comparison with the microscale objects.

The models presented in the literature are based on two transfer mechanisms. According to the first one, a driving force of the process is either diffusion or a heterogeneous reaction rate at the possible occurrence of a pressure difference between an Al core covered with an oxide layer, and oxygen out of the core.[3–9] In the second case, a driving force of the process is the double electric layer at the phase boundary between the Al core and the oxide shell.[10–12] The nonlinear model of Cabrera–Motta[12] with a self-consistent potential was used to calculate oxidation reaction rate as a function of temperature and the size of the particles of the oxidized metal.[11] We should note that the macroscopic parameters such as diffusivities, thermal capacities, *etc.* always appear in these calculations. However, it is not a valid assumption for a nanoparticle.

This work was aimed at the experimental establishment of regularities of combustion of thin layers of iron nanoparticles. The dependencies of temporary and critical characteristics of ignition and combustion of iron nanopowders on a passivation time after synthesis are determined for the first time.

For the experimental studies of processes of ignition and passivation we have used iron nanopowders obtained by the method of chemical metallurgy. The main stages of synthesis of metallic nanopowders by this method are sedimentation of metals hydroxides, their drying, reduction, and passivation.[13] The synthesis of iron hydroxide was performed by the heterophaseous interaction of solid metal salt with the solutions

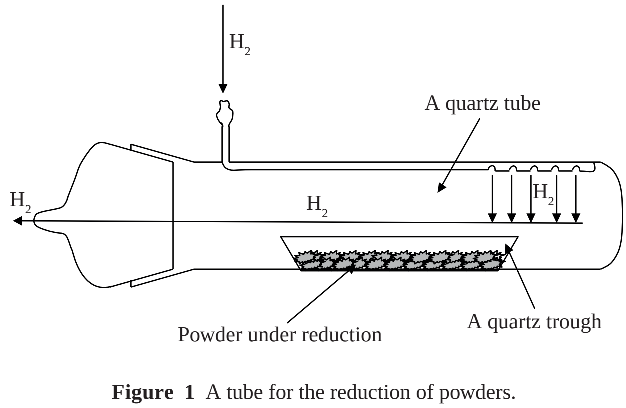


Figure 1 A tube for the reduction of powders.

containing hydroxyl groups at suppression of dissolution of solid salt. After sedimentation of iron hydroxide the product was washed out with water in a Buchner funnel to reach pH 7 and dried in air until dusting. The reactor (Figure 1) with iron hydroxide powder was maintained in the furnace at 400 °C in hydrogen flow for 1 h; then the product was taken out of the furnace and cooled to 20 °C in argon flow. The characteristics of iron nanoparticles were close to those described in ref. 14. For the passivation of the iron nanopowder, which was carried out in the same reactor, 3% by volume of air was added to the argon stream. The time of passivation varied from 0 to 60 min. Then the quartz trough with iron nanopowder was withdrawn from the reactor and placed on a table for high-speed video recording. The process of withdrawal of the trough and placing it on a table took 5 s. A color high-speed video camera Casio Exilim F1 PRO (300–1200 FPS) was used to establish the modes of combustion of iron nanopowder and to control the extent of passivation of nanopowder.

Evidently, the formation of an oxide layer on iron core can be represented by the brutto-reaction:

$$Fe + xO_2 \rightarrow Fe_yO_z.$$

However, the processes of O_2 adsorption and dissociation on the surface should be taken into account as well as consecutive reactions of metallic iron oxidation, namely

$$FeO \rightarrow Fe_2O_3 \rightarrow Fe_3O_4.$$

The detailed mechanism of the passivation has been unknown until now.

The results of high-speed video recording of combustion of 1 mm layer of iron nanopowder (cooled to 0 °C) without passivation and with 4 min passivation in 3% air in Ar are shown in Figure 2(*a*),(*b*). The temperature of 0 °C for nonpassivated powder was chosen to reduce the rate of propagation of the reaction waves. At 20 °C the combustion was already completed in the course of withdrawal of the trough from the reactor. As it is seen from Figure 2 the propagating waves of reaction are spatially non-uniform, *i.e*. the border dividing initial and reacted powder is not a smooth line. Note that under our conditions, the surface of the powder is equally accessible, and the external stream of gas does not occur. An establishment of the driving force, which provides for spatial inhomogeneity of propagation of reaction waves, is therefore quite urgent. For example, the inhomogenities may be caused by gas flows formed around the trough during the reduction process. From this point of view, the existence of primary reaction centers testifies the various chemical activities of various sites of the iron nanopowder surface [Figure 2 (*a*),(*b*)]; this phenomenon can serve as a driving force. On the other hand, the thickness of reacted layer is determined by the diffusion of oxygen through the pores on the sample surface. Therefore, the size of the nanopores[15] is one of the parameters governing the process of the surface reaction wave propagation. Anyway, the nature of inhomogeneous surface wave in the absence of external flows requires further investigations.

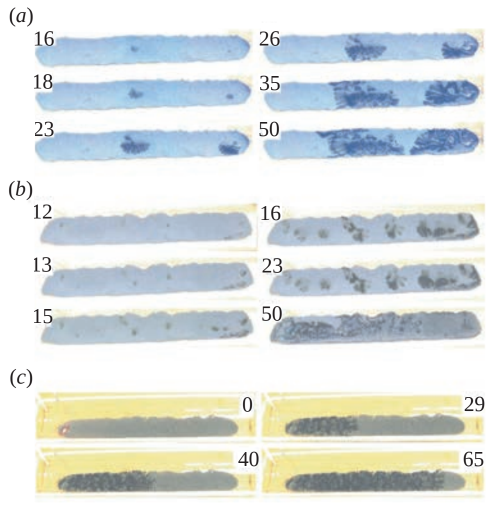


Figure 2 (*a*) The images of the behavior of Fe nanopowder in the air (0 °C) without passivation, 60 FPS. The frame number corresponds to the time (s) after withdrawal of the trough with nanopowder from the reactor. (*b*) The images of the behavior of the iron nanopowder in the air at 20 °C after 4 min of passivation in 3% air in Ar (1 mm layer thickness), 60 FPS. The frame number corresponds to the time (s) after extraction of the trough with nanopowder from the reactor. (*c*) The images of the initiation of surface combustion of Fe nanopowder in air with a heated wire at 20 °C, 30 min passivation in 3% air in Ar (1 mm layer thickness), 60 FPS. The frame number corresponds to the time (s) after the initiation.

Figure 2(*a*),(*b*) shows that the time for the emergence of the first ignition center sharply increases with an increase in the extent of passivation similar to behavior of ignition delays at approach to an ignition limit in gaseous combustion. As it is also clear from Figure 2(*a*),(*b*), the reaction centers occur on a powder surface upon contact with atmospheric air. Then two-dimensional reaction waves propagate from these centers. One can see that the amount of these centers is considerably smaller for the passivated powder [Figure 2(*b*)]. It means that the duration of passivation is directly connected with the quantity of primary centers and the time of their emergence: the higher the extent of powder passivation is, the lower the quantity of the primary centers is observed on contact of the powder with atmospheric air. Note that the existence of the primary reaction centers testifies the various chemical activities of various sites of the surface of both passivated and nonpassivated Fe nanopowder.

The dependences of the time of the emergence of the first ignition center and the quantities of primary ignition centers on passivation duration are presented in Figure 3. It is evident that under our conditions, the phenomenon of occurrence of the primary centers of reaction disappears after about 5 min of passivation, and the surface of iron layer does not change color in the air, *i.e*. the sample surface is completely covered with oxide. The revealed combustion waves on iron nanopowder surfaces are not noticeable in the dark that testifies that reaction proceeds at comparably low temperature.

If the reaction proceeds in a thin layer of nanopowder in the quasi two-dimensional mode, then the bulk of the nanopowder sample should remain combustible. Really, if one extracts the powder from under the oxide layer, which has completely covered the sample, with a thin ceramic pallet and sprays it in the air, the powder would intensively burn with a bright luminescence. Video

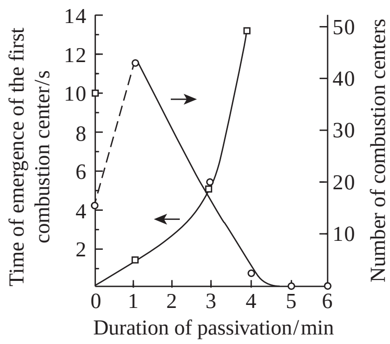


Figure 3 The dependences of the time of emergence of the first ignition centers (squares) and quantities of primary ignition centers (circles) on passivation duration at 20 °C (1 mm layer thickness). The value corresponding to zero time of passivation is obtained at 0 °C. The curves represent the best approximation.

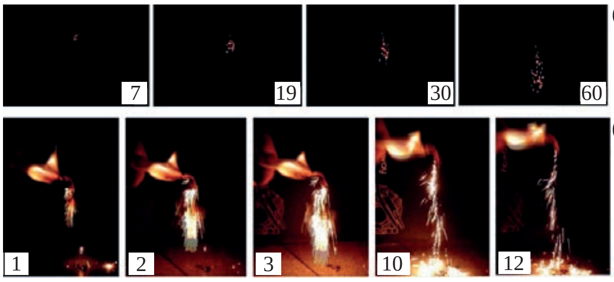


Figure 4 (*a*) The combustion of sprayed nanopowder extracted from under the oxide layer after 4 min passivation in a stream of 3% air in Ar (20 °C) immediately after the end of surface reaction. The frame number is counted from the moment of the end of surface reaction (all surface changes color), 600 FPS. (*b*) The ignition of the passivated iron nanopowder with an external source. The passivation was carried out in a stream of 3% air in Ar (20 °C) within 6 min, 60 FPS.

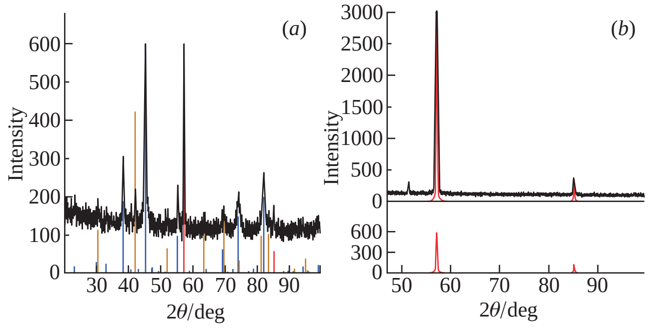


Figure 5 (*a*) The X-ray phase analysis of products of oxidation of non-passivated iron nanopowder after completion of surface reaction, stored in a weighing bottle with the ground-in cover within two weeks. (*b*) The X-ray phase analysis of the passivated iron nanopowder (6 min in the argon stream containing 3% of air) stored in a weighing bottle with the ground-in cover within two weeks.

recording of combustion of the sprayed powder is shown in Figure 4(*a*). This result demonstrates that oxidation process for incompletely passivated nanopowder is diffusionally controlled.

We should remind that the passivation of iron powder for more than 5 min leads to the disappearance of the quasi two-dimensional combustion mode (primary ignition centers do not occur and the surface of the sample does not change color). The powder, extracted by the ceramic pallet from under the oxide layer and sprayed in the air, also does not ignite. However, if one ignites this powder with an external source (for example, places the powder on a paper and ignites it with a match), the powder can burn intensively [Figure 4(*b*)]. One can also ignite the surface layer of the powder with a heated wire. In Figure 2(*c*) the propagation of a quasi two-dimensional surface combustion wave initiated with a heated wire in iron nanopowder after 30 min of passivation (1 mm layer thickness) in the air is presented. After the propagation of this surface combustion wave one can ignite the bulk of the sample on the sheet of paper as it is described above.

It should be noted that the mean value of the reaction front propagation rate both in self-ignited layers (the time of passivation is less than 5 min) and in externally ignited layers (the time of passivation is more than 5 min) is 0.43±0.03 cm s^{-1}. Therefore, the mean value of the two-dimensional reaction wave rate does not depend on the time of the passivation. It indicates that the rate of propagation for combustion wave is determined by thermal diffusivity of the bulk of the sample.

The X-ray phase analysis showed that the nonpassivated sample after combustion contains iron oxides as well as the noticeable amount of metallic iron [Figure 5(*a*)], whereas the nanopowder passivated in a stream of 3% of air in Ar for more than 6 min and stored in a weighing bottle with the ground-in cover within two weeks contains only metallic iron.

We would like to draw an attention to the fact, that the samples of nanopowder thicker than 1 mm require considerably longer passivation time. Thus, the 4-mm thick sample ignites with the delay time about 5 s over the whole volume even after 30 min of passivation; after this time interval the sample is considerably warmed up and its surface changes color nonuniformly. Really, the estimation of the passivation time as $t_P \sim x^2/D$, where D is the oxygen diffusivity and x is the sample thickness (assuming diffusion control), leads to the following conclusion. The minimum time for complete passivation of 4-mm thick iron nanopowder sample $t_{P\,(4\,mm)}$ should be longer by a factor of 16 than $t_{P\,(1\,mm)}$ for 1-mm thick iron nanopowder sample, *i.e*. considerably exceed 30 min.

In short, the results obtained are the following. The non-uniform quasi two-dimensional mode of the combustion of iron nanopowders in the absence of external flows has been revealed for the first time. The method for the estimation of the extent of passivation of Fe nanopowders with the use of a color high-speed video recording has been proposed. It has been experimentally established that both the dependences of a delay of the ignition and quantity of the primary centers of combustion on the time of the passivation can be used for the estimation of the extent of passivation. On the basis of the experimental data for certain samples, the approximate equation for estimation of the minimum time for the complete passivation for the sample of arbitrary thickness has been suggested. It has been demonstrated by the method of X-ray phase analysis that 1-mm thick samples of iron nanopowder treated in a stream of 3% of air in Ar for the time interval more than 6 min contain only metallic iron. Therefore, the suggested method of the passivation is rather effective.

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