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Interaction dynamics between compacted pyrophoric nickel nanopowders and air

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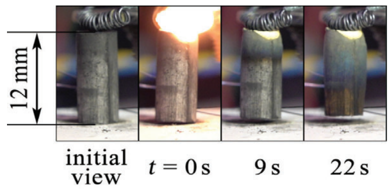
The dynamics of interaction with the air of non-passivated pyrophoric nickel nanopowders pressed into cylindrical compacts has been investigated in detail. A method for preventing self-ignition in the air of compacts made of nickel nanopowder has been experimentally established.



Keywords: pyrophoric nickel nanopowder, passivation, compact samples, critical ignition conditions.

Metal nanopowders are pyrophoric, *i.e.*, they are capable of spontaneously igniting upon contact with air due to their high chemical activity and large specific surface area.[1–4] To ensure the safety of the process of further processing of nanopowders into products, they are passivated.[3–7] Passivation creates a thin protective film on nanoparticle surface; it prevents self-ignition of metal nanopowders since oxygen supply to them is excluded. Usually, passivation lasts for dozens of hours, which is a limiting factor in increasing nanopowder production. Previously, we formulated a model for the passivation of a pyrophoric nanopowder layer, which was analyzed by analytical and numerical methods.[8]

We have already investigated the processes of passivation of iron and nickel nanopowders.[9–11] We have confirmed the applicability of theoretical approaches of the classical macroscopic theory of thermal explosion to explain the phenomena of ignition in macroscopic objects consisting of iron and nickel nanoparticles. However, there are situations when it is technically impossible or undesirable to passivate the nanopowder, although technical operations with the nanopowder have to be carried out. Therefore, an urgent task is to develop new methods for obtaining compact products from nanopowders, which make it possible to ensure the required level of fire and explosion safety in the processing of both nanopowders and products made from them.

The published data on the regularities of self-ignition and self-heating of compacted samples from non-passivated nanopowders are minimal.[12,13] Investigations of nanosystems with reactant particle sizes in the range of 40–80 nm have revealed that ignition temperatures and energies could be significantly lower than in mixtures of ultradispersed powders (1–100 μm). After laser initiation of combustion, the features of flame propagation in tablets of Al/CuO nanopowder mixtures (the so-called nanothermites) have been investigated depending on their density.[14] Less dense samples (90% porosity) were found to ignite faster, and the flame propagation velocity in them was an order of magnitude higher than that in denser samples (50% porosity). These results indicated that with an increase in the compacted sample density, the combustion mechanism changed from a convective mechanism to a diffusion one. Similar measurements[15] were carried out with samples of Al/MoO_3 nanopowders, and the results obtained for this nanothermite were qualitatively the same.

This work aims to an experimental investigation of the interaction of compact samples of non-passivated nickel nanopowder[11,16,17] with air (for details, see Online Supplementary Materials).

To check the retention of the pyrophoric properties of the Ni nanopowder after manipulations in the glove box, we poured part of the powder into a separate weighing bottle, which was removed from the box simultaneously with other samples. After removing it from the weighing bottle, the powder was poured into the air. The powder was ignited and burnt, *i.e.*, after all the preparatory operations, it remained pyrophoric.

In the first series of experiments, closed weighing bottles with samples after being removed from the box were kept in a special container in an argon atmosphere before starting the experiment, *i.e.*, before removing samples from weighing bottles. Figure 1 shows the video filming results of the self-heating process (without external initiation) in the air of a compact made of pyrophoric Ni nanopowder. This type of interaction with air was observed for all samples if the weighing bottles with them were stored in an argon atmosphere.

Comparing the data of thermocouple measurements and infrared video filming with the Flir-60 thermal imager showed

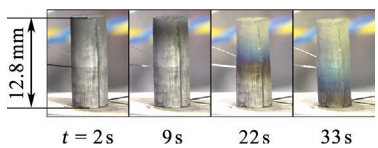


Figure 1 Frames of video filming of the compact sample during its self-heating.

that the sample heating is not uniform, although it starts simultaneously over the entire surface of the sample. Heating, which began simultaneously at different points of the sample, then proceeded at different velocities, and in the process of self-heating, different maximum temperatures were reached. Infrared video filming showed that at almost all stages of interaction with air, the maximum temperature is reached near the upper end of the sample. The reason for the uneven heating of the sample is both the best conditions for supplying the oxidizer at the upper end (the lower end is covered with a gas-tight substrate) and heat loss into the massive substrate. Another reason for the uneven heating is a change in the sample density with height. Note that mounting the sample on the substrate provided the minimum density at the sample top.

Based on the previously obtained results,[11] it could be expected that the interaction of the sample with air is of a surface nature, and, therefore, there is unreacted nanopowder in the inner layers of the sample. An analysis of the sample fracture photos after cooling confirmed this assumption. The oxidized surface layer is about 0.9 mm thick. Inside the oxidized layer, sublayers of different colors can be distinguished.

In another series of experiments, samples of non-passivated Ni nanopowder were also pressed in an argon atmosphere; however, after removing them from the sealed box, the closed weighing bottles with samples were kept in the air. After removing samples from the weighing bottles, the course of their interaction with air was shown experimentally to depend on the air exposure duration *t*. Specifically, the first sample (t < 15 min) behaved similarly to the samples in the first series of experiments; namely, it self-heated and changed its color (see Figures 1 and 2). The next sample, the weighing bottle with which was exposed to air for 15 min, warmed up to 50 °C but did not change its color. Samples in weighing bottles that have been exposed to air for more than 20 min did not warm up and did not change color after being removed from the weighing bottles. Consequently, this time is sufficient for the complete passivation of the samples.

To test the assumption that during air exposure of the weighing bottles, passivation occurred while maintaining the chemical activity rather than complete oxidation of the samples, we carried out the following experiments. Samples that did not heat up when had been removed from the weighing bottles were ignited at the upper end with a tungsten coil (see Figure 2). This local heating caused the combustion wave to propagate along the sample. Since the sample surface changed color during oxidation, the combustion velocity was determined using the video film frame-by-frame processing. According to Figure 2, the combustion wave propagates downward from the upper end of the sample at a nearly constant velocity. Previously, almost similar results were obtained in the combustion of passivated Ni nanopowders.[11] In the reported case, local heating by a coil led to the propagation of a reaction wave over the powder sample surface. The qualitative agreement of our results with the published data[11] is additional evidence that the passivation of compact samples occurred when the weighing bottles were exposed to air.

In our experiments, we recorded the dynamics of temperature field changes in a compact sample during a combustion wave propagation using an infrared camera. Video filming showed that the temperature maximum was near the upper end of the sample throughout the almost entire combustion process. Thus, we can conclude that the combustion process is superficial, and X-ray diffraction (XRD) data confirm this.

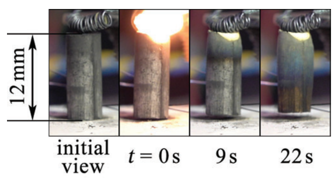


Figure 2 Frames of video filming of the combustion process in the sample exposed to air for more than 20 min (sample density of 1.7 g cm^{-3}).

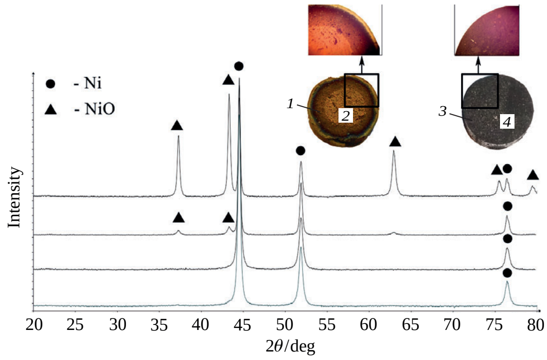


Figure 3 XRD patterns of (*1*) surface layer and (*2*) volume part of the sample (5 mm in diameter) after self-heating as well as of (*3*) surface layer and (*4*) volume part of the passivated sample.

To confirm the surface nature of the interaction during self-heating of non-passivated samples in air, we analyzed the inner and surface regions (1.5 mm thick) of each sample separately (Figure 3). The cross-sectional images of the samples in Figure 3 help understand the sample division into inner and surface regions. The numbers of sample cross-section patterns correspond to the sequence numbers of X-ray diffractograms. The XRD data of the samples after self-heating showed that the content of the NiO phase in the central part of the sample (Figure 3, curve *1*) is negligible, while the surface layer of the sample consists of a mixture of NiO and Ni (Figure 3, curve *2*). These results directly indicate the superficial nature of the interaction of samples with air during self-heating. For passivated samples, according to the XRD data, the NiO phase in the bulk and surface parts of the sample (Figure 3, curves *3* and *4*) is absent. Thus, this fact allows, in this case, considering the volume nature of the passivation process.

In summary, it has been shown that the self-heating of a compacted sample of non-passivated Ni nanopowder is not uniform, although it occurs simultaneously over the entire surface of the sample. It has been demonstrated that the process of interaction of the samples with air is superficial. This fact indicates that the diffusion supply of the oxidant limits the oxidation process. The mode of interaction of compact samples with air was found to depend on the duration of exposure of the weighing bottles to air. The possibility of passivation of nickel nanopowder samples, resulting from slow air intake into weighing bottles exposed to the air, was experimentally established. It was shown that the passivated compact samples made of nickel nanopowder retain high chemical activity; local heating up with a coil leads to the propagation of a reaction wave over the sample surface.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.07.044.

References

1 J. Bouillard, A. Vignes, O. Dufaud, L. Perrin and D. Thomas, *J. Hazard. Mater.*, 2010, **181**, 873.

2 A. Pivkina, P. Ulyanova, Y. Frolov, S. Zavyalov and J. Schoonman, *Propellants, Explos., Pyrotech.*, 2004, **29**, 39.

3 *Nanoparticle Technology Handbook*, eds. M. Hosokawa, M. Naito, K. Nogi and T. Yokoyama, 1st edn., Elsevier Science, Amsterdam, 2007.
4 N. M. Rubtsov, B. S. Seplyarskii and M. I. Alymov, *Ignition and Wave Processes in Combustion of Solids*, Springer International Publishing, 2017.
5 M. Flannery, T. G. Desai, T. Matsoukas, S. Lotfizadeh and M. A. Oehlschlaeger, *J. Nanomater.*, 2015, 682153.
6 M. J. Meziani, C. E. Bunker, F. Lu, H. Li, W. Wang, E. A. Guliants, R. A. Quinn and Y.-P. Sun, *ACS Appl. Mater. Interfaces*, 2009, **1**, 703.
7 *Nanoparticles: Synthesis, Stabilization, Passivation, and Functionalization*, eds. R. Nagarajan and T. A. Hatton, American Chemical Society, Washington, DC, 2008.
8 B. S. Seplyarsky, T. P. Ivleva and M. I. Alymov, *Dokl. Phys. Chem.*, 2018, **478**, 23 (*Dokl. Akad. Nauk*, 2018, **478**, 310).
9 M. I. Alymov, N. M. Rubtsov, B. S. Seplyarskii, V. A. Zelensky and A. B. Ankudinov, *Mendeleev Commun.*, 2017, **27**, 482.
10 M. I. Alymov, B. S. Seplyarskii, S. G. Vadchenko, R. A. Kochetkov, N. M. Rubtsov, N. I. Abzalov and A. B. Ankudinov, *Mendeleev Commun*., 2020, **30**, 380.
11 M. I. Alymov, N. M. Rubtsov, B. S. Seplyarskii, R. A. Kochetkov, V. A. Zelensky and A. B. Ankudinov, *Mendeleev Commun.*, 2017, **27**, 631.
12 S. Dong, P. Hou, H. Cheng, H. Yang and G. Zou, *J. Phys.: Condens. Matter*, 2002, **14**, 11023.
13 E. M. Hunt and M. L. Pantoya, *J. Appl. Phys.*, 2005, **98**, 034909.
14 F. Saceleanu, M. Idir, N. Chaumeix and J. Z. Wen, *Front. Chem.*, 2018, **6,** 465.
15 *Metal Nanopowders: Production, Characterization, and Energetic Applications*, eds. A. Gromov and U. Teipel, Wiley-VCH, Weinheim, 2014.
16 J. G. Dean, *Ind. Eng. Chem.*, 1952, **44**, 985.
17 M. I. Alymov, N. M. Rubtsov, B. S. Seplyarskii, V. A. Zelensky and A. B. Ankudinov, *Mendeleev Commun.*, 2019, **29**, 355.

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