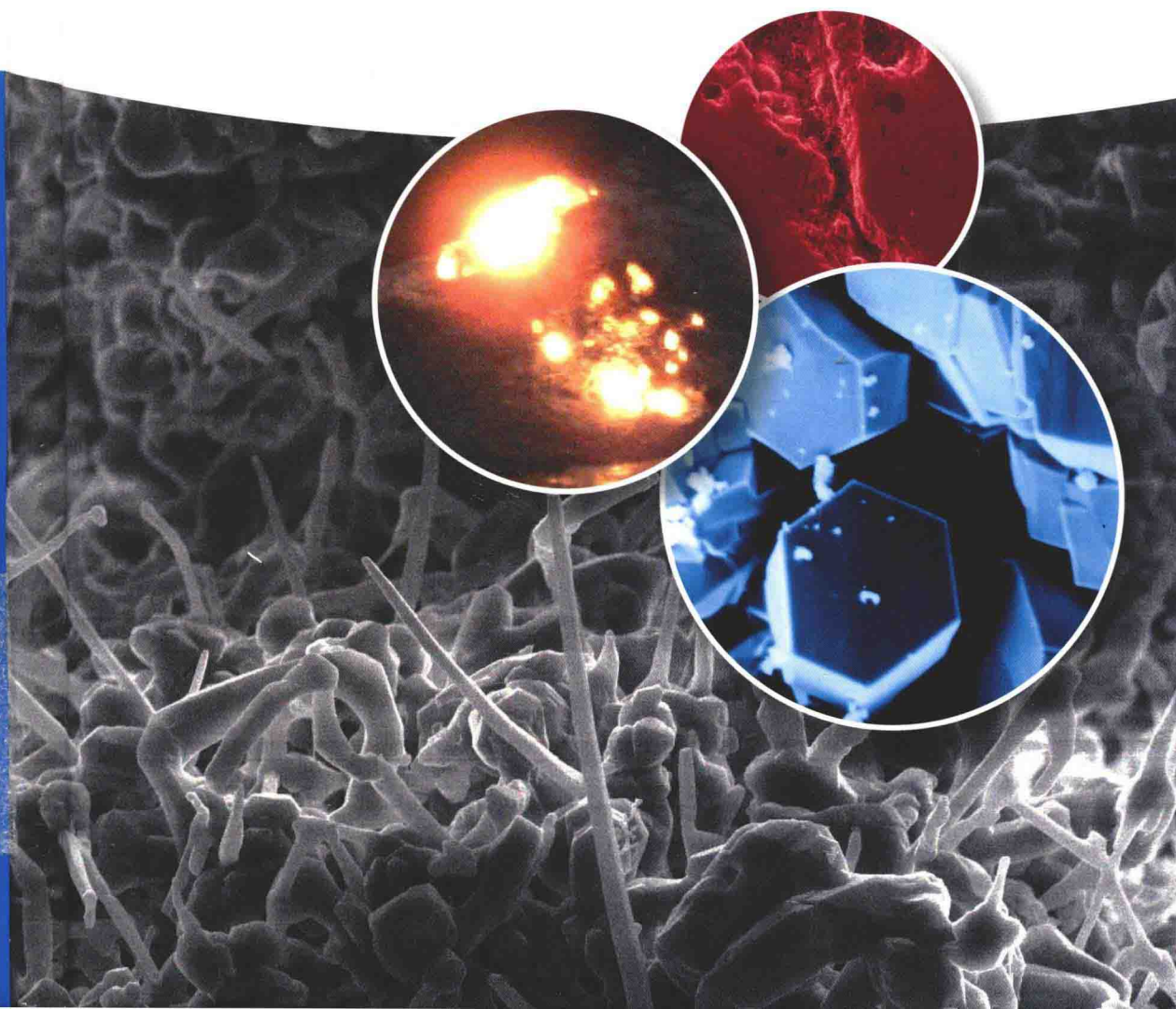


Edited by Alexander Gromov and Ulrich Teipel

Metal Nanopowders

Production, Characterization,
and Energetic Applications



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Foreword

Interest in studying the combustion of metal powders dramatically raised since Russian scientists Kondratyuk and Tsander suggested the use of metals as energetic additives to rocket fuels at the beginning of the twentieth century. Since that time, it is obvious that an increase in the dispersion of flammable substances participating in heterogeneous combustion processes leads to an increase in rate and heat of combustion. The major energy contribution belongs to the process of oxidation, which is also bound up with powder dispersion and purity. Burning of metal nanopowders is accompanied by new physical and chemical laws (such as high reactivity under heating, threshold phenomena, formation of nitrides in air), which allow to fully appreciate the advantages and disadvantages of nanopowders when used in fuel systems.

Widespread use of metal nanopowders is currently hampered by the lack of enough advanced technology for their preparation, certification, and standardization procedures, instability during storage, and subjective factors: the possible toxicity of nanopowders, investment risks, cost of nanotechnologies, and so on. Therefore, the main objective for the authors is to inform a wide readership of fundamental and applied studies on the processes of oxidation and combustion of metal nanopowders.

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Introduction

Stabilization of low-dimension structures, especially nanosized ones, and their use in the heterogeneous chemical reactions as nanopowders allow considering *high specific surface* as an independent thermodynamic parameter along with the temperature, pressure, concentration of reactants, and so on. New characteristics of 2D nanomaterials are well known – the thermal conductivity of graphene ($5000 \text{ W (m K)}^{-1}$) with $1000 \text{ m}^2 \text{ g}^{-1}$ specific surface exceeds those for metals in a factor 10 [1]. The use of the advantages of high specific surface of 3D nanostructures – nanopowders in catalysis, oxidation, and combustion results in high rates of heterogeneous reactions and reduction in activation energies of ignition due to the small size of solid reactants. The laws of classical chemistry and physics are little applicable to the analysis of processes with metal nanopowders. An example of such a system is the burning of the composition nanoAl/nanoMoO₃ at the rate of about 1 km s^{-1} [2].

In USSR, metal ultrafine (in fact, nano-) powders with reproducible properties were first obtained during World War II. In the 1960s and 1970s, numerous works were carried out on metal nanopowder production by electrical explosion of wires [3], evaporation-and-condensation method [4], and the technologies of metal nanopowder application for nuclear synthesis in the USSR and the US. In 1977, the result of these works was published in Morokhov's book [5], where the methods for metal nanopowder production by thermal decomposition of salts were viewed. In Western Europe and the US, the term *nanocrystalline material* appeared and spinned off after the Gleiter's publication in 1980 [6].

Since the discovery by Yu. Kondratyuk and F. Tsander in 1910 [7], the possibilities of powdery metal being used as an additive in energetic materials and as the reagents for self-propagating high-temperature synthesis [8] were intensively studied. Several books (e.g., the work of Pokhil *et al.* [9] and Sammerfield [10]) were published, where the laws of combustion of micron-sized metal powders ($5\div 500 \mu\text{m}$) in high-temperature oxidizing environments were discussed. The study of the laws of combustion of powdered metals was done mainly for Al, Be, Mg, Ti, Zr, and B. The lack of micron-sized metal powders were detected during the first test of metallized fuels in the 1940s: an agglomeration of particles (especially for aluminum and magnesium) in the heating zone of energetic material, a low degree of metal

reaction in the vapor phase (incomplete combustion), significant biphasic loss of a specific impulse (15% or more for the compositions containing 20–25 wt% Al) [9].

In the 1970s, Zeldovich and Leipunsky *et al.* [11] showed one of the approaches to reduce this lack by using low-sized metallic particles for fuels and combustion catalysts, in particular, metal nanopowders. This book summarizes the efforts of several teams over the world to realize those ideas.

The revitalization of the use of metal nanopowders in materials science and engineering became further possible in the 1990s, when the technologies for the large-scale production of those materials became available. Nowadays, tons of rather inexpensive metal nanopowders are produced in several countries for different technological applications, while the problems of their standardization, storage, handling, toxicity, correct application, and so on, are still unsolved.

The idea of this book is also to show the true picture of the properties of metal nanopowders and, correspondingly, their application avenues. The “romantic atmosphere” around nanomaterials and metal nanopowders accordingly should be left in the twentieth century forever. Nanoparticles and, especially, metal nanoparticles are very “capricious” technological raw materials with metastable physical and chemical properties in many cases, because nanometals (in addition to small particle size) show very high reducing properties: nanoCu react similarly to bulk Zn – release the hydrogen from acids, nanoAl show the properties of bulky alkali metals – react with water under room temperature, and so on.

Special scientific and engineering interests represent the new fundamental laws of combustion for the metal nanopowders, analysis of the combustion regimes, and intermediate and final burning products reported in this book. Excited by the experimental works of Ivanov and Tepper [12], scientists worked in the direction of nanometals application in energetic materials intensively during the past decade and the most valuable results are presented in this book.

In conclusion, we want to underline that the study of industrially available metal nanopowders allowed opening previously unknown laws and they will open the significant application prospects in science and technology of the twenty-first century.

Alexander Gromov
Ulrich Teipel

References

1. Seol, J.H., Jo, I., Moore, A.L., Lindsay, L., Aitken, Z.H., Pettes, M.T., Li, X., Yao, Z., Huang, R., Broido, D., Mingo, N., Ruoff, R.S., and Shi, L. (2010) Two-dimensional phonon transport in supported graphene. *Science*, 328 (5975), 213–216.
2. Bockmon, B.S., Pantoya, M.L., Son, S.F., and Asay, B.W. (2003) Burn rate measurements in nanocomposite thermites. Proceedings of the American Institute of Aeronautics and Astronautics Aerospace Sciences Meeting, Paper No. AIAA-2003-0241.
3. Chase, W.G. and Moore, H.K. (eds) (1962) *Exploding Wires*, Plenum Press, New York.
4. Gen, M.Ya. and Miller, A. (1981) A method of metal aerosols production. USSR Patent 814432. No. 11. p. 25.

5. Morokhov, I.D., Trusov, L.I., and Chizhik, S.P. (1977) *Ultradispersed Metal Medium*, Atomizdat, Moscow.
6. Gleiter, H. (1989) Nanocrystalline materials. *Prog. Mater. Sci.*, **33** (4), 223–315.
7. Gilzin, K.A. (1950) *Rocket Engines*, Moscow.
8. Merzhanov, A.G., Yukhvid, V.I., and Borovinskaya, I.P. (1980) Self-propagating high-temperature synthesis of cast refractory inorganic compounds. *Dokl. Akad. Nauk USSR*, **255**, 120.
9. Pokhil, P.F., Belyaev, A.F., Frolov, Y.V., Logachev, V.S., and Korotkov, A.I. (1972) *Combustion of Powdered Metals in Active Media*, Nauka, Moscow.
10. Sammerfield, M. (ed.) (1960) *Solid Propellant Rocket Research*, Academic Press, New York.
11. Zeldovich, Y.B., Leipunsky, O.I., and Librovich, V.B. (1975) *Theory of Non-Stationary Combustion of Powders*, Nauka, Moscow.
12. Ivanov, G.V. and Tepper, F. (1997) “Activated” aluminum as a stored energy source for propellants. *Int. J. Energetic Mater. Chem. Propul.*, **4** (1–6), 636–645.

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