

15. HISTORY AND SOME PROGRAMS OF ULTRADISPERSED MATERIALS DEVELOPMENT IN RUSSIA

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The preparation and study of ultradispersed materials (UDM) was ongoing for about 50 years behind closed doors in the USSR (Krouglov 1994). Ten scientists (I.D. Morokhov, I.K. Kykoin, V.N. Lapovok, et al.) were awarded the Lenin Prize for their successful application of metallic ultrafine powders and high-porous filters in uranium problems. A diffusion method of isotope division has been improved, but UDM research only reached experimental and theoretical prominence some 30 years later (Morokhov 1977). In addition to salt decomposition, a utilization of gas evaporation (and condensation), plasma-chemical, electrowire explosion, and other physical and chemical methods essentially expands the assortment of UDM (Morokhov 1977; Morokhov 1981; Ziskin 1959).

Over the last two decades, a new direction has appeared in investigations at the frontier between atomic-molecular, solid state physics and chemistry, material science and metallurgy: the physics and chemistry of ultradispersed systems (UDS). The ultradispersed state of solids or liquids was formerly determined specifically by physical factors. When the size of condensed matter, morphological elements (small particles, crystallites) becomes comparable to a critical physical length such as an electron mean free path, the size of a magnetic domain, or the extent of a defect, then various interesting phenomena may be observed. To this class of materials were assigned thin films, thin whiskers, fine powders, highly porous materials, etc., and their different ensembles. Nanocrystals (NCs) may be called "compact UDM" by this definition (Gleiter 1992). UDMs have significant energy due to their large surfaces, and they are usually prepared under extreme conditions (high temperatures, rapid processes) so that they are nonequilibrium systems.

To develop this field of science, the section on "Ultra Dispersed Systems" in the Academy of Science USSR was organized in 1979. It drove the Russian scientists' investigations, and three All Soviet Union Conferences on the "Physics and Chemistry of Ultra Dispersed Systems" were carried out in 1984 (Zvenigorod), 1989 (Riga), and 1993 (Tomsk) (Physics 1987; Physics 1989; Physics 1993). Many metals, alloys, and compounds in the ultra dispersed state were investigated, and experimental and theoretical data about their structure and property peculiarities were discovered by different methods (Physics 1987; Physics 1989; Physics 1993; Alymov 1995).

By generalizing all theoretical and experimental results, one can suggest a model of UDMs' atomic arrangement that illustrates the possibility of a transition from a crystalline to an amorphous state through an ultra dispersed one (Fig. 15.1) (Petrunin 1991). Inhomogeneous distortion of a small particle provokes an atomic density distribution that is different from its crystalline and amorphous distributions (Fig. 15.2). For very long distances, (more than 100 Å), particles present a crystalline atomic ordering; for very short distances, (less than 10 Å), they take on an amorphous quality; but for middle distances (10-100 Å) the state seems to be UDM. So the UDM atomic structure is peculiar, midway between a crystalline and an amorphous state. The reasons for the UDM atomic structure's peculiarity are its significant surface energy, the small size of its crystallites, and the extreme conditions of its preparation.

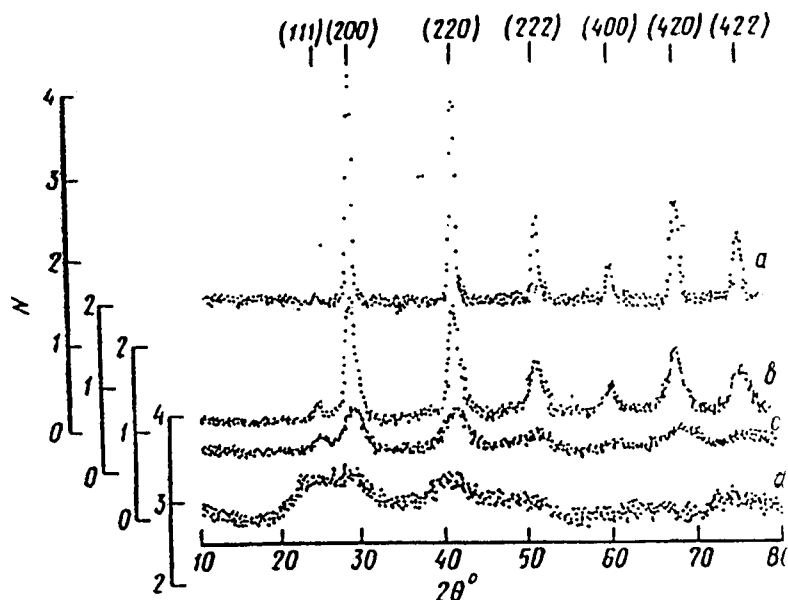


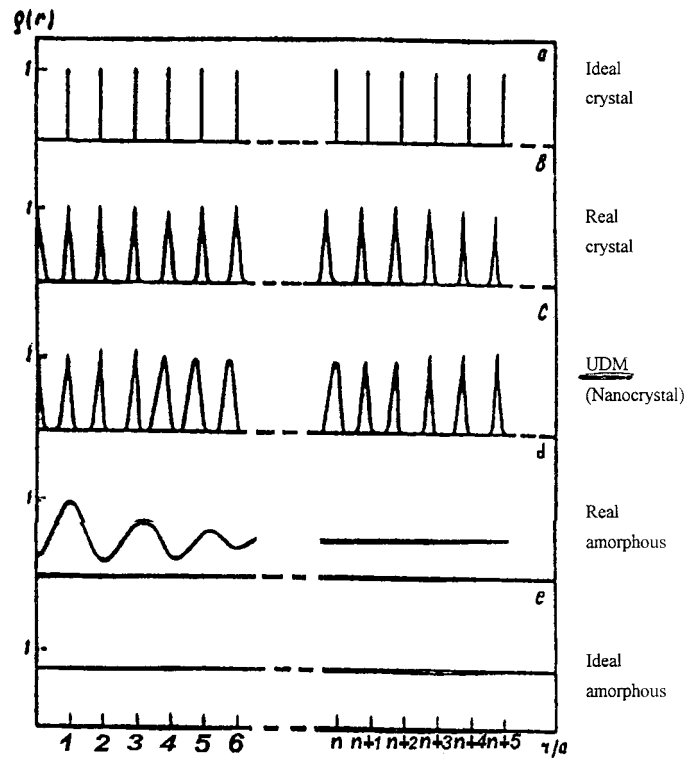
Fig. 15.1. Neutron diffraction patterns of ultradispersed powders NbN, prepared at different temperatures: a—5270 K, b—1270 K, c—1070 K, d—770 K.

Investigators have directed most of their attention toward the mechanical properties of UDM (Morokhov 1977; Alymov 1995). Compressing crystallite (or grain) size with dislocations or with disclinations causes the hardness to increase. And simultaneously the developed boundaries reduce the net viscosity. That is why UDM can combine high hardness and superplasticity.

The thermal properties are changed at the transfer from the usual crystalline to the ultra dispersed state mainly by a specific phonon spectrum (Morokhov 1981). Additional surface atoms' vibrations become considerable from one side. And the small size of the crystallites limits them from the second side. The role of these factors changes in different materials, but their thermocapacity increases and melting and sintering temperatures decrease for the most part.

The other properties of UDM are interesting as well. Metals with very small crystallites can be semiconductor-like; ferro- and antiferromagnetic materials transfer to superparamagnetic ones; and superconductive materials to insulators.

In order to realize the remarkably wide possibilities for highly efficient new materials and for the simultaneous preservation and development of the present scientific, technological, and industrial potential, the Russian Ministry of Atomic Energy in 1996 established a special program for obtaining, studying the properties of, and applying UDM (Gryaznov 1992). This program will work out some new ways for obtaining UDM and bringing to pilot-commercial production earlier developed methods (evaporation-condensation, plasmochemical, etc.) for obtaining a wide assortment of UDM: metals, alloys, and compounds as well as compacted UDM (nanomaterials). The integrated technique of characterization by present-day physical methods will be developed including X-ray, electron- and neutron scattering, nuclear gamma-resonance, positron annihilation, and others.



Size of Ordering Field: $100a \leq L < \infty$ crystal state
 $10a \leq L \leq 100a$ middle state (UDM)
 $a \leq L \leq 10a$ amorphous state

Fig. 15.2. Atomic density in various material structures.

The main goal of the program is to develop and bring items based on UDM to production. For example, one aim is to launch the production of motor oil with a UDM additive for a motor-car engine that will allow one to reclaim the surface of worn out friction pairs and to increase their usefulness by a factor of 1.5-2.0.

The production of magnetohard and magnetosoft ferrites made of UDM will enable the Russian electronics industry to eliminate the deficiency caused by the reduction of supplies from Commonwealth of Independent States (CIS) [former FSU] countries. Piezoelectric ceramics made of UDM will find applications not only in Russia but also in the United States, South Korea, and other countries. Hard ceramic UDM (oxides, carbides, and diamonds) will be used for making filters, cases for different articles, gauges, and dies for obtaining electric wires from non-ferrous and ferrous metals. Putting UDM on the surface of cutting tools will help to decrease the aging of such widely used tools as face milling cutters, rough heads, bushings for saws, etc. High-porous intermetallic UDM will be utilized as filter elements, and thermal tubes that have a high resistance to corrosion and might be used at temperatures up to 800°C.

The program contains several projects of interest to atomic power engineering itself. The program is a refinement of the technology used at nuclear power plants for refining fuel elements from uranium and plutonium oxide UDM mixed at the atomic level. The program also offers much promise for the absorption of materials on the basis of rare-earth metals UDM. Such materials can be more resistant to radiation and more efficient than those used at present.

Notice should be taken of high-porosity beryllium. Items made of this material are lightweight and have other unique properties that may be useful in X-ray equipment. Beryllium UDM may eventually become the material for thermonuclear reactor targets' shells as well.

Realization of this Ministry of Atomic Energy program will give rise to the formation of a market with new science-intensive and high technology production. Saturation of this market is not expected in the near future, and therefore, Russian enterprises that are being converted now have a real chance "to dictate what is in fashion" for the market.

Editor's note: The following material was taken from the viewgraphs used in Professor Petrunin's presentation.

Some Historical Stages of Ultra Dispersed (Nano-) Material (UDM) Research in Russia (USSR)

- 1949 - First thin powders (100 nm) were received
- 1958 - Lenin Prize for successful application (I.D. Morochov, I.K. Kykoin, V.N. Lapovok, ...)
- 1971 - Gas evaporation method was developed (M.Y. Gen)
- 1976 - First open paper about UDM physical properties peculiarities (L.I. Trusov, V.F. Petrunin)
- 1979 - Section "Ultra Dispersed Systems" was organized in the Academy of Science Council
- 1981 - Determination of the Ultra Dispersed State by physical criteria
- 1984 - First All Soviet Union Conference "Physics and Chemistry of Ultra Dispersed Systems"
- 1989 - Second All Soviet Union Conference "Physics and Chemistry of Ultra Dispersed Systems"
- 1993 - Third (Russian) Conference "Physics and Chemistry of Ultra Dispersed Systems"
- 1994 - Education Ministry program for investigating UDM properties was started
- 1995 - State Science and Technology Komitet Program of New Perspective Materials Investigations
- 1996 - Atomic Energy Industry (AEI) Program "Preparation and Study of Properties and Applications of UDM"
- 1997 - Federal National Technology of Russia Program
- 1998-9 - Fourth Russian Conference "Physics and Chemistry of Ultra Dispersed Systems"

Examples of UDM Applications Being Worked out by the Atomic Energy Industry (AEI) Program*Restoration Additives for Motor Oil (UDP: Fe, Cu, ...)*

Goals: decreasing friction; restoration of working surfaces; increasing resources 1.5 to 2 times

Strong Ceramic Manufactured Goods

Goals: mechanical protection of neutron counter; calibers, fillers for electric wire production

High Light Manufactured Goods (UDP: Be)

Goals: X-ray equipment details; shells for thermal nuclear reactor (with U.S.A.?)

*Soft and Solid Magnetic Ferrites, Piezoelectric Ceramic Materials for the Electronics Industry**Highly Porous Filters*

for water, technical liquids, oil products, cleaning

*Solid Coatings for Instruments (UDP: Diamond)**Some Nuclear Reactor Construction***References**Alymov, M.I. and O.N. Leontieva. 1995. *Nanostructured Mater.* 6:393.Gleiter, H. 1992. *Nanostructured Mater.* 1:1.Gryaznov, G.M. and V.F. Petrunin. 1996. *Conversion in Machine of Russia* 1:24.Krouglov A.K. 1994. *How atomic industry has been created in USSR* (in Russian). Moscow, CSII atominform, 181-190.Morokhov I.D., L.I. Trusov, and S.P. Chizhyk. 1977. *Ultradispersed metallic media* (in Russian). Moscow, Atomizdat, 263.Morokhov I.D., V.I. Petinov, L.I. Trusov, and V.F. Petrunin. 1981. Structure and properties of ultradispersed metallic particles. *Sov.Phys.Usp.* 24:295-316.V.F. Petrunin and J. Mendeleev. 1991. *Chem. Soc.* (in Russian) 7:146.*Physics and chemistry of ultra dispersed systems.* Proceedings of 1st All Soviet Union Conference. 1984. Zvenigorod, Moscow reg. (in Russian). Moscow, Nauka, 1987.*Physics and chemistry of ultra dispersed systems.* Proceedings of 2nd All Soviet Union Conference. 1989. Riga, (in Russian). Riga, INCh. Latv.*Physics and chemistry of ultra dispersed systems.* Proceedings of 3rd All Russian Conference. 1993. Tomsk (in Russian). Tomsk, TPI.Ziskin, Gen. M.Y., M.S., and Yu.I. Petrov. 1959. *Doclady Acad.Sci. USSR* 127:366-368.

