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IN MEMORY OF VALERY SKOROKHOD

DEVELOPMENT OF SINTERING THEORY AT THE FRANTSEVICH INSTITUTE FOR PROBLEMS OF MATERIALS SCIENCE UNDER THE NATIONAL ACADEMY OF SCIENCES OF UKRAINE

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On 1 July 2017, Valery Skorokhod, a brilliant scientist, an originator of the modern science of materials, Editor-in-Chief of Powder Metallurgy, Director of the Frantsevich Institute for Problems of Materials Science from 2002 to 2015, and Academician of the National Academy of Sciences of Ukraine, passed away. Valery Skorokhod devoted all his active life to studying the properties of materials and developing the scientific foundations of their formation. The modern materials science is a synthesis of knowledge based on very different scientific concepts. One can rarely find an expert who would have mastered this knowledge to the extent Valery Skorokhod did. The range of Skorokhod's scientific interests was extremely diverse and included virtually all aspects relating to the behavior of materials and associated effects. Despite his busy activities, Valery Skorokhod found time to conduct his own research in seemingly distant areas of science. When Valery Skorokhod departed from life, several studies performed on his own and in collaboration with his colleagues were in their final stage. The Editorial Board of Powder Metallurgy offers some of them to the readers.

Keywords: *modern science of materials, scientific foundations of materials formation, sintering theory.*

Sintering plays a decisive role in the consolidation of raw powder materials; in particular, in the production of many semi-finished parts in metallurgical and other processes, such as powder metallurgy and ceramic technology. Sintering commonly accompanies the majority of solid-phase chemical reactions that occur in fine mixtures of solids when heated.

As a process operation, sintering has a clear purpose, which is to impart desired mechanical, physical, and physicochemical properties to materials produced from compact or bulk powders. Sintering can also be regarded as a spontaneous kinetic process in which a disperse system (in particular, a powder compact) approaches equilibrium. There are various reasons why a powder conglomerate can deviate from equilibrium: concentration heterogeneity,

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crystal lattice microdistortions, developed intergranular boundaries and their imperfection, and networked three-dimensional and two-dimensional macrodefects, such as pores, fissures, and imperfect contacts between particles. The last reason is due to the excess free surface energy. It is considered the main driving force of sintering.

Interest in the physical explanation and theoretical description of the sintering process was manifested in the first postwar years. In 1945–1947, the fundamental papers of Frenkel, Pines, and Ivensen were published in a row. They addressed the sintering phenomenon from three different positions: viscous flow of solids, diffusion of vacancies, and phenomenological kinetics. These papers pioneered both description of the problem and methodological approaches to its solution, and actually raised more questions than answered the inquiries of experts in the field of powder metallurgy and ceramic technology.

Nevertheless, the year of 1949 was marked by a real breakthrough in the phenomenological theory and physics of sintering. It was this year, as well as subsequent 1950, that saw the experimental and theoretical studies of Kuczynski, Schaler, Mackenzie, Herring, et al., which later became classical and formed a solid basis for modern ideas about driving forces and high-temperature thermal activation mechanisms of sintering as an irreversible kinetic process. These studies placed the physics of sintering on a par with the physics of phase transformations and the physics of high-temperature strength.

A further stage in the development of experimental capabilities for the diffusion theory of sintering and the improvement of its mathematical tools for describing the behavior of pores in polycrystals is associated with Kharkov physicists, Pines, Geguzin, Lifshitz, and Slezov, as well as American scientists, Kuczynski, Coble, and others. The intermediate results of this stage were summed up by Pines in *Essays on Metal Physics* (1961) and Geguzin in *Macroscopic Defects in Metals* (1962), and the final ones were set forth by Geguzin in his classical monograph *Physics of Sintering* (1967) and remarkable popular scientific essay *Why and How Voids Disappear* (1976). The diffusion theory of sintering, including the concept of diffusion linear creep allowing for grain-boundary diffusion and diffusion-controlled mechanism of collective recrystallization, thus became complete and final.

In the meantime, numerous and fairly systematic technological studies of the isothermal and nonisothermal kinetics of sintering for compacts from real, in particular, superfine metal and oxide powders, continued in parallel with the physical studies and gave rise to extensive experimental material that did not fit into the diffusion theory and even contradicted it in some cases. This made powder metallurgy and ceramic technology experts to be content for many years with the phenomenological description of sintering kinetics using parameters determined from the same experiments without attempting to impart any physical meaning to them.

At the Institute for Metal Ceramics and Superalloys, Academy of Sciences of the Ukrainian Soviet Republic, systematic studies of solid-phase sintering began in the department of Ivan Fedorchenko in 1955. Fedorchenko himself was the first in the USSR to defend a doctoral thesis entirely devoted to the sintering of metallic powders in 1951. His first postgraduate students at the Institute for Metal Ceramics and Superalloys, Raichenko and Andrievsky, were requested to study sintering experimentally as self- and heterodiffusion processes in single- and two-component powder systems. Raichenko managed to describe quantitatively the kinetics of diffusion-controlled alloy formation in the sintering of systems with complete mutual solubility, including the diffusion swelling phenomenon caused by unequal partial diffusion coefficients of the components. He used a three-dimensional model of a heterogeneous body with periodic microstructure to effectively apply the mathematical theory of diffusion, in particular, the Fourier series. Andrievsky experimentally showed the presence of a threshold when external load was applied to a porous body being sintered, which allowed a conclusion that there was no plastic flow in pressureless sintering. It should be noted that the hypothesis assuming the predominant role of nonlinear creep induced by capillary pressure in a porous body in the sintering mechanism was actively discussed in those years in the national (Meerson) and foreign literature (Mackenzie and Shuttleworth). Frenkel also assumed that there was plastic flow in sintering. Therefore, the results obtained by Andrievsky were of fundamental importance.

I became a postgraduate student of Academician Fedorchenko a little later. It was planned that my thesis would be devoted to the sintering of two-phase systems with noninteracting phases such as W–Cu. However, it was actually needed to solve very general problems, in particular, those on the effect of initial porosity on the densification kinetics and on the major flow mechanism during sintering of, first of all, single-phase porous bodies. I managed to essentially generalize Mackenzie's results and develop a rheological theory of sintering, in which the temperature-, substructure-, and time-dependent shear viscosity coefficient of a respective metal in nonporous state appeared as an experimentally determined parameter. At the same time, a hydrodynamic version of the theory of elasticity was widely used to elaborate the ideas of Frenkel and Mackenzie. In particular, Mackenzie's consistent field method was generalized to solve the problem of calculating the isotropic elastic moduli of a multiphase statistical mixture of solid particles (1961). Therefore, a fairly general phenomenological theory to describe the deformation of porous materials under both external loads and Laplacian capillary forces was developed. In fact, it was also a closed physical theory for pressureless sintering and pressure sintering of powders produced from materials with a constant Newtonian viscosity coefficient (glass) at a given temperature. However, study on the kinetics of isothermal sintering of fine metallic powders revealed a number of essential features that could not be explained within the theory of viscous flow for real crystalline bodies with defects and interfaces (Nabarro–Herring–Lifshitz–Coble). In particular, it turned out that the technological genesis of a powder made of the same substance and having the same particle size had a huge influence on the kinetic constants of shrinkage process during sintering. This influence was studied in detail and described by Ivensen. It was also confirmed in the experimental work of Skorokhod and Ranneva (1963). In search of a physical explanation for the influence of initial powder structure on the flow processes during sintering, Skorokhod and Khrienko conducted detailed X-ray analysis of nickel powders that had approximately the same particle size but were produced by different methods (carbonyl decomposition and oxide reduction) in the initial state and after annealing at different temperatures. Active part in these efforts was also taken by a colleague of Professor Ristic, Dragan Uskokovic from Belgrade (later Professor and Director of the Institute of Technical Sciences, Serbian Academy of Sciences and Arts). The results of these efforts served as the basis for my doctoral thesis, which was defended in 1968. Yakov Geguzin was one the opponents at the defense event. In 1972, Skorokhod's monograph *Rheological Fundamentals of the Theory of Sintering* was published, making the Kiev school of sintering the leader in this area.

Later on, the link between sintering and high-temperature superplastic flow of sintered materials with ultrafine crystal structure was theoretically justified and experimentally confirmed using Ashby's model (Skorokhod, Litvinenko).

In the 1970s, intensive experimental studies focusing on the production and structurization of highly active metallic powders continued at the department for physics of sintering and hardening of sintered materials. The research team mastered various physicochemical methods of activating and intensifying the metal reduction from oxides to obtain superfine metallic powders, and examined the structure of intermediate and final reaction products (Panichkina, Uvarova, Yuri Solonin, Khrienko, Konchakovskaya, Grintsov). Technological regimes for the production of refractory metal powders by oxide reduction were found and justified; they showed the greatest activity in the densification and diffusion-controlled formation of alloys in the sintering process. The effect of small activating additives (Ni, Pd) on the densification kinetics, collective recrystallization, and diffusion-controlled formation of alloys in the sintering of refractory metal powders (W, Mo, Re) (Panichkina, Shnaiderman) was studied almost in parallel. The *Fine Powders of Refractory Metals* monograph (1979) of Skorokhod, Panichkina, Yuri Solonin, and Uvarova became the definite result of these studies. One of the generic conclusions drawn in the monograph was that structural factors, such as dislocation and grain boundary processes of mass transfer, played the main role in the kinetics of active and activated sintering of metallic powders. This implies that the slowdown in the densification rate under isothermal sintering is primarily due to reduction in the concentration of defects, including the total length of the grain (subgrain) boundaries in powder particles. However, the change in kinetic coefficients, shear viscosity in this case, was not the only cause behind the slowdown of densification process. The point is that free surface energy of a disperse system, such as a superfine powder, can decrease both when the porosity reduces and when the powder particles and, consequently, pores coarsen. In the former case, the volume derivative of surface energy represents Laplace capillary pressure, being the driving force of densification. In the latter case, this derivative may be close to zero. The average pore size can increase because of surface mass transfer processes, i.e., surface self-diffusion or gas-phase transport. Nevertheless, local shrinkage, described way back by Balshin, becomes the main reason for significant pore growth in the active densification process. These considerations led to systematic studies on the dynamics of pore growth in the sintering of superfine powders, especially in the early stages of the process. For disperse systems with open porosity, such studies could involve porosity measurement or a simpler method of gas/liquid displacement (first gas bubble). The greatest merit in the systematic conduct of such experiments on a wide range of sintering systems belongs to Getman. The local densification in the sintering process was later clearly modeled in exquisite computer experiments by Kadushnikov and colleagues (1991).

The concept according to which the densification of a powder conglomerate and the formation of a porous and grain structure in sintered materials were regarded as a single structurization process was the ideological outcome of all the above studies. Sintering was addressed exactly from these positions by Skorokhod and Sergei Solonin in *Physical and Metallurgical Fundamentals of Powder Sintering* (1984), which proved to be well timed and highly sought by experts. Noteworthy is the importance of Sergei Solonin's studies, in particular, those intended to establish the correlation of densification processes in the sintering of two-component systems with the corresponding phase diagrams to form a complete and intelligible system of views on this complex process, which was adequately reflected in the monograph.

As noted above, in department 18 that I headed, the sintering processes were always studied along with the kinetics of other physicochemical processes in disperse systems, such as topochemical reactions, diffusion-controlled alloy formation, coalescence, etc. The fruitfulness of this approach to the study of disperse systems is now beyond question, but its implementation requires concerted actions of skilled experts in various areas. Fortunately, department 18 managed to establish the required interaction; its results are reflected by Skorokhod, Yuri Solonin, and Uvarova in *Chemical, Diffusion, and Rheological Processes in the Technology of Powder Materials* (1990) and Skorokhod, Uvarova, and Ragulya in *Physicochemical Kinetics in Nanostructured Systems* (2001). In recent years, these studies have successfully continued both in our department (Vasylkiv) and in the departments headed by Yuri Solonin, Uvarova, and Ragulya.

The optimized sintering of nanosized powders of metals, oxides, and nonoxide refractory compounds should be separately noted. The sintering of such systems is specific in that it is needed to balance the densification and grain growth kinetics so that the final polycrystalline material is practically nonporous but remains nanocrystalline. This problem was successfully solved for conventional ceramics, though mainly empirically, by the famous American ceramist H. Palmour III. The solution was based on rate-controlled sintering. Ragulya and I succeeded in developing the fundamentals for the theory of nonisothermal sintering of nanosized systems, which allowed us to reasonably design and implement optimum sintering regimes for a given program of variable heating rates to produce nanocrystalline ceramics without applying high pressures.

It should be noted that the macroscopic theory of linear and nonlinear flow of porous bodies with simultaneous action of Laplace and external forces was substantially developed in the papers of Mikhail Stern and Eugene Olevsky, my former postgraduate and doctoral student (now professor at the San Diego State University, USA).

In conclusion, I would like to note that the study of sintering when external nonmechanical (electric, magnetic) fields are applied has become a new stage in the theoretical description and simulation and full-scale experiments. The varieties of processes such as electric discharge (spark plasma) and microwave sintering attract the greatest attention for their versatility and technological flexibility. Encouraging advances have already been made by Panichkina and Getman in collaboration with the Institute of Applied Physics of the Russian Academy of Sciences in Nizhny Novgorod in studying the kinetic features of microwave sintering and their manifestation in the structure of sintered materials. Of course, new, understudied phenomena in the experiment raise more questions than give answers to those posed by production engineers. Nevertheless, the physical understanding of these phenomena already inspires hope that microwave sintering would be mastered and applied in ceramic technology.

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