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LECTURE №4

Obtaining high-density materials from nano sized powders of refractory compounds

Both high-density and porous ceramic materials have been widely used in various technologies. The main methods for fabrication of high-density products from conventional powder mixtures are as follows: hot pressing, high-temperature gas-static sealing, slip casting, injection molding. However, in the case of nanopowders, some of these methods do not provide the expected result. Therefore, consolidation of nanodispersed powders is obtained by some other methods that are shown in table. 4.1. These consolidation methods can be divided in two groups, processed with and without molds. In the first case, pressure and temperature are applied to the powder simultaneously. The use of pressure reduces the sintering temperature and the time of high-temperature sintering, which prevent grain growth. In the table 4.2, there are given some methods of high-speed sintering.

Residual porosity above 5% affects the conservation of nanoscale grains. As can be seen from the table 4.2, among a wide range of nanopowders the consolidation methods, the choice may be made dependent on the required theoretical density. Appropriate parameters like temperature, pressure, redox reactions, voltage and current should be chosen for the method. It should be noted that currently in the USA and Japan intensive research is being conducted in the field of consolidation of nanodispersed materials with the electric field activation, the so-called FAST methods (Field Activated Sintering Techniques). Numerous studies have demonstrated the effectiveness of FAST methods in sintering of boron carbide, silicon carbide, molybdenum disilicide, and aluminum oxide.

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Table 4.1. Methods for the consolidation of nanocrystalline powders

Group	Title	An object	Density, %	Grain size, nm
Rigid Matrix Consolidation	Hot pressing, hot isostatic pressing	Ceramic	95	70÷200
	High pressure sintering		4÷98	50÷100
	Electric discharge sintering		95÷97	30÷80
	Shock wave sintering		93÷97	25÷40
Consolidation with preliminary molding	Traditional sintering	Ceramic	99,5	120÷200
	Controlled sintering	Ceramic	98,5÷99	75÷120
	Forging	Ceramic	97÷98,5	150÷180
	Microwave sintering	Ceramic	97÷98,5	150÷180
Free Consolidation	Selective Laser Sintering	Ceramic	90÷99	50÷100
	Rapid Prototyping	Ceramic	85÷98	20÷30

In all available publications, the authors describe the effectiveness of the FAST and SPS (Spark Plasma Sintering) methods. However, some rather contradictory conclusions regarding the processes occurring during sintering by these methods may be questioned, in particular proposal and interpretations of the mechanisms of structure formation. For example, it is suggested that when a pulsed current is applied, plasma is formed between the contacting nanoparticles, and it leads to formation of strong bond between the particles in bulk material. However, there is no convincing evidence for that. It is doubtful that the plasma-forming processes are intensified due to the short-term pulsed current. This proposal has not yet been rebutted, anyway. Another interesting way to consolidate nanopowder materials was found at SuperGriphite (USA). In this pressing method presented in Fig. 4.1, graphite powder is used as the pressing medium through which electric current is passed.

Table 4.2. Modern methods of high-speed sintering of nanopowders

Method of consolidation	Pressure, GPa	Temperature, °C	The final density, %	Heating rate, °C/min	Holding time, s
Hot Isostatic Forging (HIF)	below 1.0	1200÷1500	95	10÷20	120÷300
Hot Isostatic pressing Speed (QHIP)	0.5÷1.0	1500	90	20÷30	60÷300
Field Activated Sintering Technic (FAST)	below 0.06	below 2200	95	20÷30	180÷300
ElectroSintering (ES)	below 0.03	below 3000	5÷100	10÷20	200
High Energy compaction and High Speed Rapid (HEHR)	1.5	3400	95	1÷2	2
Ultra High Pressure Sintering (UPS)	26	2000	95	3÷4	300÷600

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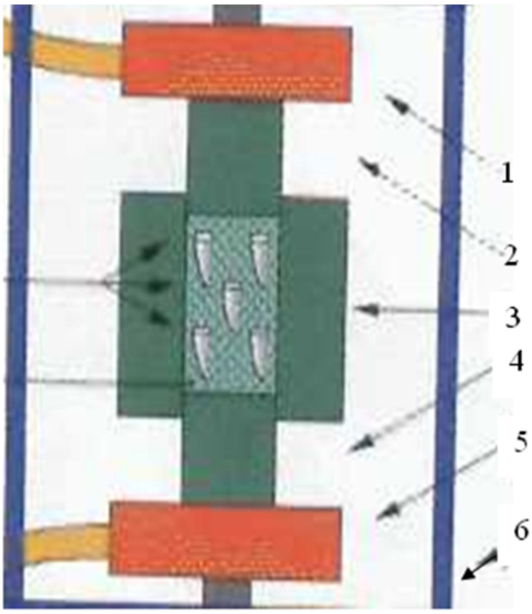

Fig. 4.1. Powder electroconsolidation unit:

1 - upper current lead; 2 - upper punch; 3 - matrix;

4 - lower punch; 5 - lower current lead; 6 - vacuum chamber

The quasi-isostatic pressure is applied at same time as the electrical current of up to 10 A. This method allows to fabricate products of complex shape from pre-sintered, so-called pre-forms, which is the main advantage.

In the technological process of manufacturing products from nanopowders, the most important operation is the molding of high-quality compacts of a given shape. Single-phase nanopowders from often very complex multiphase compositions possess metastability of the structural-phase state, developed specific surface area and, as a result, high surface activity, the ability to agglomerate powders. As a rule, they are characterized by poor formability and compressibility due to the specificity of their physicochemical properties. In particular, they perform high interparticle and wall friction due to the high specific surface, powder agglomeration, and a significant amount of sorbed impurities. Therefore, it is technologically difficult to ensure a uniform density distribution in the compacts even of a simple shape, and to preserve the nanostructure in the compacts during sintering. It is also very important to ensure the chemical purity and the required phase composition of the finished products. In fact, under normal conditions of hot pressing, the last stage of the process is most important, when the compaction

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speed slows down, and in the case of refractory oxides and carbides, the diffusion mechanism is dominating. In crystalline materials, the mechanism of plastic deformation plays a decisive role. Typically, the compaction process during hot pressing takes place in four stages:

- the compaction speed is proportional to the logarithm of the applied pressure and depends on the size of the grains, material reaches about 75% of the theoretical density;

- there is a slip and reordering of the laying of grains, and the material is even more compacted under the pressure;

- in the contact places between the grains, a process of plastic deformation occurs, which usually had started at the second stage. Now, the compaction reaches up to 84% of the theoretical density.

At the final stage, compaction occurs due to diffusion under voltage. The compaction rate is greater than that observed when sintering without pressure, and it depends also on surface energy. Consequently, contribution of plastic deformation is small. According to some researchers, compaction here is a result of diffusion activated by the pressure applied at the last stage. It can be assumed that in the compaction process of nanodispersed powder, sliding along the grain boundaries plays important role. Obviously, the sealing mechanism of hot pressing is complex and for its quantitative assessment it is necessary to conduct separate studies for each material, especially when it comes to refractory compounds such as tungsten monocarbide, silicon carbide, aluminum oxide, etc. In the case of nanoparticles of each of these materials, the processes are, probably, somewhat different. Thus, thorough further studies of the compaction process of nanoparticles during hot pressing are necessary. The vacancies migration issues along the grain boundaries during the hot pressing of nanopowders are also studied insufficiently, while these processes may explain some patterns of sintering. The table 4.3 presents efficiency and productivity of hot pressing methods. It can be seen that the electric current activated methods are the most effective ones.

Table 4.3. Comparative characteristics of some consolidation methods of nanopowders

Process	Sintering temperature, ° C	Product approximate size, m	Pressing Value, MPa	Details with difficult forms	Capital expenses
Electroconsolidation	2500	0,20	70	yes	low
Hot Isostatic Pressing	2000	1,25	300	yes	very high
Ceracon	1500	0,40	400	difficult	medium
Rapid Omnidirectional Compaction	1500	0,40	900	difficult	high

Nanostructured composite materials consist of nanosized particles of two phases. Such a structure provides improvement of not only the main mechanical properties, but also of characteristics such as mechanical workability or high temperature superplasticity like that of metal materials. The most promising direction for the development of composite materials with ceramic matrices is the fabrication of a composition of nano- and microcomposites, as well as materials having a nanocomposite matrix, additionally reinforced with whiskers, microplates and / or dispersed particles. For the fabrication of nanocomposite materials, traditional processes of powder metallurgy and ceramic technology can be used, such as mixing components, molding and subsequent sintering without or with the application of pressure, including hot isostatic pressing (HIP). For example, the strength of corundum ceramics increases almost 3 times as a result of introducing addition of only 5 vol.% SiC nanoparticles in a ceramic matrix. Additional heat treatment in air or in an inert gas environment increases the strength level to 1500 MPa. Due to the introduction of the second phase and the formation of a nanocomposite structure provided an increase in the mechanical properties of materials based on Al_2O_3, MgO and Si_3N_4. In Al_2O_3 / SiC and MgO /SiC materials, silicon carbide particles are located within the grains of the oxide phase. The nature of the destruction of these materials is a completely transcrystalline cleavage in contrast to the mixed inter- and transcrystalline fracture of the matrix material (samples from the matrix). It is possible that transcrystalline destruction is facilitated by fields of tensile residual stresses (more than 1000 MPa) in the matrix around dispersed particles within the grains of the matrix. However, these stresses do not lead to microcracking, since the particle size of SiC is much less than critical. Electron microscopic studies confirmed the formation of a subgrain dislocation structure within Al_2O_3 grains due to the formation of vacancy and dislocation clusters. Annealing of such a material at 1300 °C leads to the development of a substructure, which explains the strength increase. Composite materials have significantly higher strength at elevated temperatures. The transcrystalline nature of fracture in nanocomposite materials persists up to 1000 °C and higher. Dispersed SiC particles in the Al_2O_3-SiC composite material impede the occurrence of grain-boundary slipping and cavity formation within the matrix grains, and also contribute to the inhibition of dislocations during deformation. Mixed and interstructural types of Si_3N_4 / SiC nanocomposites exhibit significant resistance to delayed fracture resulting from subcritical crack growth, since SiC particles located at the boundaries of silicon nitride grains reduce the average crack growth rate through a phase softened at high temperatures, which is formed by sintering additives. The Si_3N_4 / SiC composites therefore retain high strength at 1500 °C. At the same time, Si_3N_4 / SiC nanocomposites exhibit superplasticity at 1600 °C, especially if the α-Si_3N_4 modification can be preserved in the material structure. The composite materials based on Si_3N_4 with an ultrafine structure have increased creep resistance. This effect is due to the fixation of grain boundaries by particles of the second phase (SiC), which impede the process of mutual slipping of grains, as well as by a change in the properties of the grain boundary phase due to the interaction of carbon (in the case of SiC particles) with oxide additives, which are introduced to activate the sintering process. High strength is achieved, and especially crack resistance of ceramic is significant.

In nanostructured materials, effects associated with the polymorphic transformations of zirconia from metastable tetragonal modification to stable monoclinic are used. Such a transformation is initiated by external mechanical loads and leads to irreversible work lost during deformation and destruction of the material. The systems with dispersed ZrO_2 particles, unique materials have been obtained that have a flexural strength above 1500 MPa and fracture toughness K_{1c} above 30. They also have increased resistance to subcritical crack growth and to heat.

The key factor in obtaining finely dispersed particles is the process of mixing and agglomeration of mixtures. In the further process of consolidation, when the

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ligament is removed and the grain begins to grow, growth is inhibited due to the preservation of unstressed grains, since a strong transcrystalline bond remains. Thus, the powder mixing factor strongly affects the further properties of nanocomposites, as well as composites as a whole. Various methods are used in order to improve the processes for preparing mixtures; these are various intensive grinding methods, pyrolysis, sol-gel methods, chemical precipitation (CVD), etc. The Fig. 4.2 shows a diagram of the formation of materials with a fine and dense structure during conventional sintering.

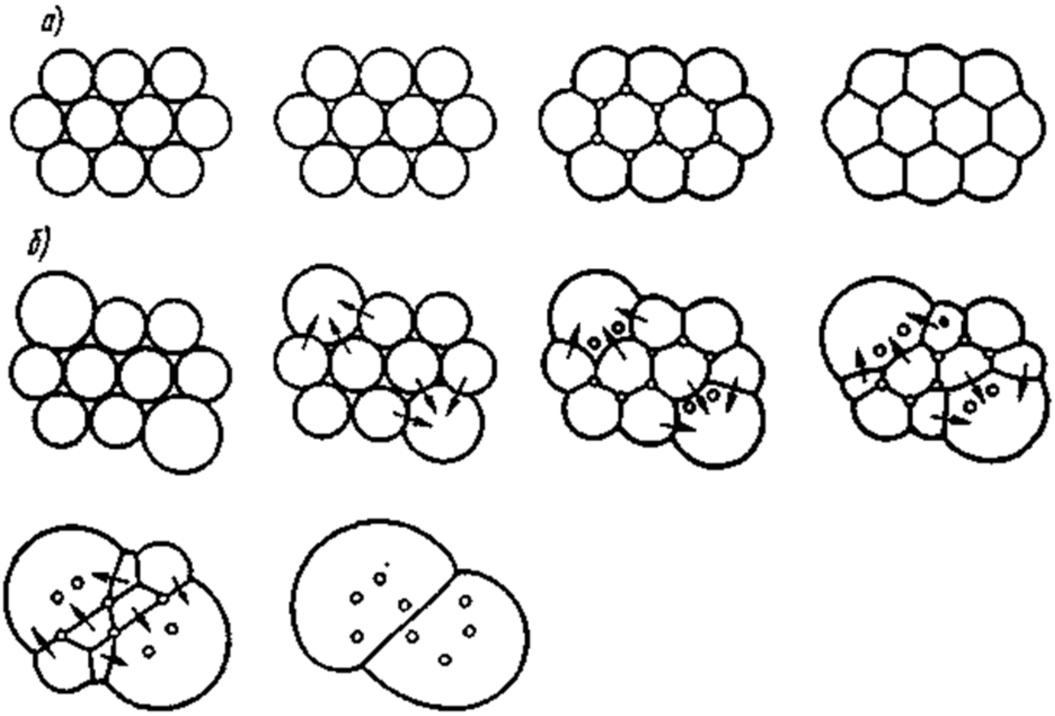

Fig. 4.3. The processes of forming materials with fine and dense structure during sintering:

a - grain boundaries are motionless, pores turn into vacancies and disappear at the grain boundary; b - due to the occurrence of abnormal grain growth, the movement of the boundaries is great and the pores remain inside the material. The arrows in the diagram indicate the direction of movement of the substance.

To obtain materials with a density close to 100% of theoretical one, it must be ensured that:

- the particles are smaller than 1 micron and have no defects;

- the particles should be approximately of the same size and shape.

After mixing, the nanopowder mixture must be molded immediately. To limit the relative movement of particles, additional component is added to the initial material to change the phase composition in the grain boundary region.

Currently, the following types of sintering are used:

- sintering under normal pressure (normal);
- sintering under pressure (hot pressing - no mass production, graphite molds);
- sintering under isostatic pressing (hot isostatic pressing);
- sintering with heating by electric current.

The latter can be divided into two types:

- indirect heating, in particular, induction heating of graphite molds;
- direct heating, when an electric current passes through the sintered powder.

Some problems of sintering occur when heated by electric current. The issue of conductivity of a sintered electric current powder becomes extremely important. If the powder does not conduct an electric current, like alumina, then it is obvious that the current does not pass through the powder, but through the graphite form. Since the electrical resistance of graphite is small, it is necessary to apply a maximum current to heat the graphite form to a required high temperature. In most FAST methods, it is the pulsed electric current, which is a source of presumable short-term plasma formation at the sites of contact of the nanoparticles. However, it should be assumed that the use of an alternating electric field will initiate the creation of Foucault currents in graphite form, which leads to additional heating of the mold and the sintered powder. In addition, alternating current generates an alternating magnetic flux, which, possibly, will allow obtaining more uniform density of sintered powders. In order to reduce the sintering temperature and to obtain a high density of the material, a second component is added that forms the liquid phase during the sintering process. When the formation of a liquid phase is undesirable, a sintering reaction method is used, which allows sintering and solid-phase reactions to be carried out simultaneously. In this case, sintering was carried out not only due to the induction heating of graphite molds, but also due to the exothermic reaction of chromium oxide with an ultrafine aluminum nitride powder obtained by the plasma-chemical method.

The method of obtaining the initial powder is important, since the reaction activity of the powder depends on it in many respects. The choice of powder fabrication

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method is determined not only by physicochemical criteria, but in many cases by economic feasibility. That is why some methods have not gone beyond the scope of the laboratory tests. Existing modern methods of compacting nanodispersed materials with FAST electric fields were applied to a rather narrow range of materials and, although in some cases these methods allow obtaining materials with a high level of physicomechanical properties, many processes associated with the structure formation of aluminum oxide, silicon carbide, boron carbide, titanium carbide, zirconium oxide, cause mixed opinions from researchers. Creation of an effective technology for the production of porous filter elements from submicron alumina powders (Fig. 4.5, Table 4.4) and silicon carbide, development of theoretical and experimental fundamentals of the technology for producing porous, permeable materials from refractory compounds such as aluminum oxide and silicon carbide to obtain products with a given permeability is still a relevant task.

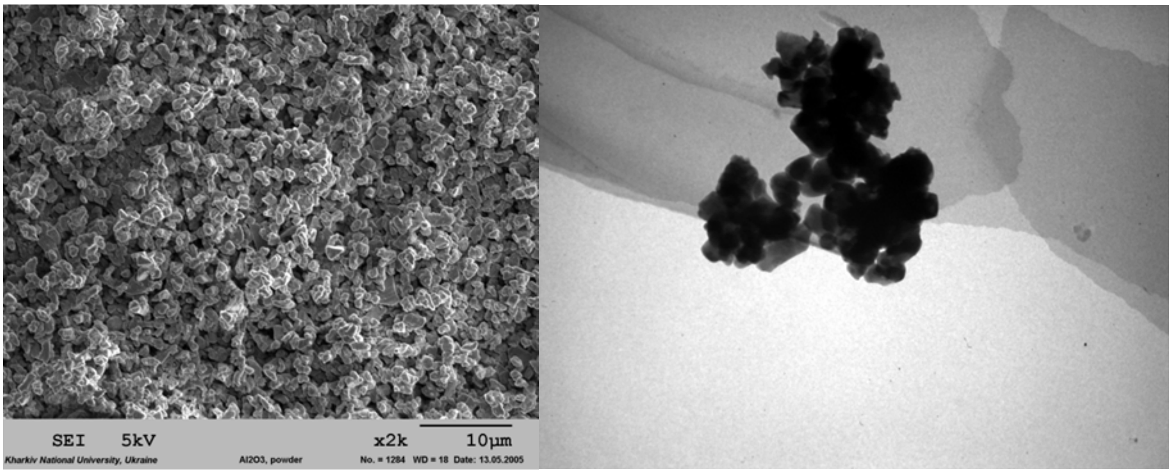

Fig. 4.5. Al_2O_3 powders 600 nm submicron (a) and nanopowder (b) 50 ÷ 80 nm

Table 4.4. Chemical composition of α-Al_2O_3 nanopowder (Infarmat, USA)

Element	Fe	Si	Mg	Cu	Na
Content, wt. %	0.009	0.15	0.001	<0.001	0.008

Alumina powder (Germany, Alcoa World Chemicals) with the following characteristics was used as submicron powders to obtain foamy filters: the average grain size was 0.8 µm, and the specific surface area was 7.5 m^2/g for the powder electroconsolidation unit.

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The design of presses for hot pressing is determined by the method of heating and applying pressure, pressing temperatures, the need to use a protective gas environment or vacuum, and a number of other factors. In the hot pressing process, an electric current is usually used for heating, although the powder or the mold with the powder can be heated in different way before the pressure is applied. When heated by these methods, the outer layers of the samples reach the sintering temperature faster than the inner ones, since the sample is heated externally. To achieve thermal equilibrium, a long time is required, during which compaction from the surface to the middle is possible, which leads to the capture of gases released from the colder inner zone. This process does not allow to obtain high-quality products.

Among the materials used in the fabrication of hot pressing equipment, graphite is most widely used. Graphite is relatively cheap, can be machined well, has a low density, low electrical resistance, high heat resistance and sufficient mechanical strength in a wide range of temperatures. In practice, for the manufacture of molds, graphites MG, MG-1 are used, having compressive strength of 35 ÷ 45 MPa, which allows applying pressure up to about 30 MPa. High-strength graphite, for example MPG-7, can be used at pressures up to 70 MPa (Fig. 4.6).

Fig. 4.6. Graphite mold assembled

The limited use of graphite as molds for hot pressing is due to its low strength, which does not allow the process to be carried out at high pressures, and the ability to reduce certain materials, especially oxides. Graphite also reacts with transition metals, their nitrides and silicides. The method of electroconsolidation has common features with conventional and activated sintering, hot pressing, and at the elemental volume level, with microelectric welding. However, this method has

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some unique features that distinguish it from other methods of powder consolidation. The time dependences of the mechanical and electrical effects and their relationship during electroconsolidation are of great importance. The simplest example of intermittent mechanical action is increasing loading, when the punched electrodes slowly move towards each other. In this case, the final pressing pressure is applied at a temperature above 1400 °C. The main mechanism of compaction of nanodispersed tungsten monocarbide powders is a locally inhomogeneous diffusion-viscous flow with intergranular slippage, limited by grain-boundary diffusion. The second significant driving force of sintering is the energy of imperfections of the crystal lattice. It causes an accelerated exchange of sintered grains.