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Projekt pt.: **„Zintegrowany Program UTHRad.”**, POWR.03.05.00-00-Z105/17
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Course title: Materials Engineering and Application

Lector: Dr. Prof. Edwin Gevorkyan

Ukraine State University of Railway Transport
Kharkov, Ukraine

LECTURE №2

1. The use of nanopowders

All currently produced nanomaterials are divided into four groups: metal and silicon oxides, complex oxides (consisting of two or more metals), pure metal powders and mixtures. Metal oxides make up at least 80% of all produced nanopowders. Pure metal nanopowders constitute a significant and increasing proportion of the total production volume. Complex oxides and mixtures are produced in limited quantities, but it is expected that the need for them will increase in the long term.

Silicon and metal oxides. Three nanopowders, **SiO_2**, **TiO_2** and **Al_2O_3** make up about 80% of all oxide powders. In short:

SiO_2. Silicon dioxide, or silica, is the nanopowder most widely produced in the world. Silicon dioxide finds various applications in electronics and optics, is also widely used in the manufacturing industry as an abrasive, paint and plastic filler, coating and primer for building materials, and also as a water-repellent coatings.

TiO_2. Titanium dioxide is mainly used in the manufacturing industry for the production of paints, protective coatings, abrasives and polishing, this material plays an important role in optics as a photocatalyst and a coating of lenses to inhibit ultraviolet radiation. Titanium dioxide is increasingly used for ecological purposes, for example, in wastewater treatment, in air filters, etc. In addition, it is used in the production of building materials, cosmetics, plastics, printing inks, glass and mirrors. It finds its application also in defense industry, e.g. for the destruction of missile chemical warheads.

Al_2O_3. Aluminum oxide, or alumina, is mainly used in the manufacturing industry as an abrasive, for inkjet cleaning, grinding and polishing, especially in electronics and optics. In addition, it is used for air purification, as a catalyst, in structural ceramics and for the production of capacitors.

The remaining 20% of production is mainly accounted for by the following seven nanopowders - oxides of iron, zinc, cerium, zirconium, yttrium, copper and magnesium. Large number of other important nanopowders are produced in smaller quantities.

Nd_2O_3. The neodymium oxide, used exclusively in electronics and optics, is applied in ceramic capacitors, in phosphors for color TVs, carbon arc electrodes and for vacuum deposition. It also finds limited use in high temperature glazes and glass pigments.

Eu_2O_3.The europium oxide, used almost exclusively in electronics and optics, is used in phosphors for color TVs and X-ray screens, for vacuum deposition, and in graphite rods in nuclear reactors.

Dy_2O_3. The dysprosium oxide is an important oxide for electronics and optics, it is used for the production of optical magnetic memory, as well as in halogen and metal halide lamps. It is also used as a dopant in iron-yttrium and aluminum-yttrium garnet, and also to control material in nuclear reactor.

Pure metal powders. Almost all of the solid metal elements are commercially available as pure metal nanopowders. The industrial application of many of them requires further processing. The costs of producing homogeneous metal powders with a high degree of purity are significantly higher than the costs of metal oxides fabrication. Five nanopowders - iron, aluminum, copper, nickel and titanium - are the leaders in terms of production volume. Precious metals and silicon powders are produced in small volumes. Many applications require a low concentration, but as area of their use expands, their global production must grow.

Ag. The metallic silver is widely used in many industries. It used to be used in electrical contacts and conductive pastes in electronics. The antibacterial and antiviral properties of silver have made it attractive for use in cosmetology and pharmaceuticals, as well as in the textile industry, in cleaning pads, dentistry and as sanitary coatings, in air filters and as a catalyst.

Au. The gold accounts for only a small fraction of the total global production of nanopowders per year, it is widely used in electronics as a coating for wire contacts, electroplating and protection against infrared radiation. In the field of energy and ecology, gold is used in chemical batteries and as a catalyst. Recently, gold has been used in medicine as DNA markers.

Pt. The platinum nanopowder is mainly used in electronics and as a catalyst. It plays an important role in fuel cells, automobile parts, oil refining, medicine and fiberglass manufacturing.

Si. The silicon nanopowder is widely used in electronics as the main component of semiconductors, microcircuits, and solar cells. It also plays an important role in metallurgy as a hardener of iron and alloys, as well as an additive to increase heat resistance. In addition, it is used in ceramics, welding rods, pyrotechnics, artillery, cement and abrasives.

Mixtures and complex oxides. Complex oxides, such as antimony-tin oxide and indium tin oxide, make up a small fraction of the world production volume. In contrast to metal oxides and powders of pure metals and silicon, just a small amount of complex oxides is produced. Mixtures are more diverse, although they are highly specialized.

Sb_2O_3 / SnO_2. These powders are used exclusively in electronics and optics, antimony-tin oxide is an important component of displays due to its antistatic effect, and the ability to absorb the infrared part of the spectrum and light transmission.

In_2O_3 / SnO_2. These powders are used as an important component of modern displays. This oxide is used mainly to create a conductive and transparent coating.

Si_3N_4. The silicon nitride finds its applications in the manufacturing of turbines, engine parts, heat-resistant and heat-insulating materials, as well as heat and corrosion-resistant clamps.

$BaTiO_3$. The barium titanate is a commercially significant additive used in electronics for the production of storage devices, dielectric amplifiers and ferroelectric ceramics.

C. Carbon in form of **nanodiamonds** is used exclusively in the machining industry, usually for wear-resistant coatings of polishing and cutting tools and drills, as well as lubricating coatings. Nanodiamonds contribute to increase of corrosion resistance when they are added to steel. A semiconductors manufacturing consumes only a small fraction of the volume of nanodiamonds produced in the world.

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WC-Co. The tungsten carbide-cobalt nanopowder is used for cutting tools and wear resistive material.

2. The powder consolidation methods

One of the effective methods for producing high-density bulk materials is hot pressing. This process consists of sintering powders under the simultaneously applied high pressure and temperature. For the first time this method was introduced by P.G. Sobolevsky in 1826 to obtain platinum. In the hot pressing, regardless of the degree of plasticity of the material, each temperature corresponds to the minimal pressure, at which practically non-porous bulk product can be obtained in a short time. The hot pressing can reduce significantly the heating, with holding and cooling times compared to free sintering. The maximum density during normal sintering is reached after two hours exposure, while during hot pressing after 5 ÷ 10 minutes. By hot pressing it is possible to obtain products with a high and evenly distributed density without warping. This is practically the only method for producing almost non-porous products without introducing activating additives into the initial powder. This method is used widely for poorly pressed and poorly sintered compositions based on refractory oxygen-free compounds (borides, carbides, nitrides, oxides, silicides). The hot pressing method among the other advantages has perspective to save a chemical composition of the pressed substance, reduction of furnace equipment and less sensitivity to the technological properties of powders. Unlike in conventional sintering processess, special preparation of the powder is not necessary.

3. Basic theory of the hot pressing compaction process

A theoretical analysis of the processes occurring during the hot pressing of porous bodies is presented in many works. The phenomenological theory of sintering was first proposed by Mackenzie and Shuttleworth. They examined the viscous and plastic flow of a mass containing uniformly distributed closed pores. Using the model of Mackenzie and Shuttleworth, and equating the energy released when the pore surface decreases and the energy dissipated during the flow, an equation was proposed for quantifying the rate of material compaction during hot pressing:

$$\left(\frac{d\mu}{dt}\right)_{HP} = \left(\frac{d\mu}{dt}\right)_{S} + \frac{3}{4}\cdot\frac{P}{\eta}\cdot(1-\mu) \tag{1}$$

where

$\left(\frac{d\mu}{dt}\right)_{S}$ – is the conventional sintering compaction speed.

The hot pressing experimental confirmation of this dependence is given in works on hot pressing of quartz and alkaline glass, i.e., for materials with Newtonian viscosity, but varying in time. The shear viscosity of compact alumina was determined, which was Pa • s at 1300 ºC and Pa • s at 1600 ºC.

An analysis of experimental data on the study of the hot pressing of carbides and borides using theoretical dependencies combining the equation of the viscous volumetric flow of a porous body with the equations of the nonlinear steady creep of porous crystalline bodies demonstrated that the process of compaction of refractory compounds and metals is controlled by unsteady creep combined with the mutual sliding of particles powder relative to each other at the initial stage, and steady creep on subsequent, longer stages of hot pressing.

4. The process of compaction an experimental laws

Cermets are composite materials containing ceramic and metal. They are fabricated mainly with hot pressing process out of powders and nanopowders. Many studies are devoted to the production of cobalt hard alloys, tungsten-free hard alloys based on nickel and cermets based on niobium. It is proposed, based on the constancy of mass, shrinkage, final density and height of the sample, to determine the current relative density as follows:

$$\mu = \frac{d_t \cdot h_t}{(h_t + \Delta h)\cdot d_\infty} \tag{2}$$

For some studied mixtures, the relative density dependencies on time, pressure, and temperature are identical to those shown in Fig.2. Typically, for the metal phase regardless of the composition (Co, Ni - Mo, Nb), increasing temperature, pressure, time, and the amount of the metal component, causes increase of the resulting density. Moreover, the compaction rate decreases with time.

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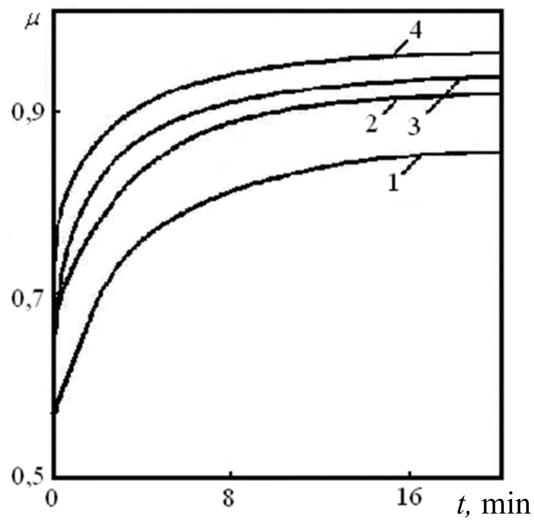

Fig. 2 The relative density μ versus time of hot pressing for Nb - 80 ZrB_2 powders under pressure (T=2000 °C) at different pressures:

1 - 5.6 MPa; 2 - 11.4 MPa; 3 - 14.3 MPa; 4 - 18.4 MPa

Particularly sharp decrease in the compaction rate is observed in the first 2–3 minutes, which is due to the large porosity of the pressed material at the initial stage of the hot pressing process. During compaction process, which is a decrease in porosity, the bulk viscosity of the porous body increases, and the rate of volumetric deformation slows down. Compared to kinetic curves of density changes during hot pressing of pure refractory compounds during cermet pressing, the same density is achieved at significantly lower pressing temperatures and pressures.

Comparison of the properties of cermets obtained by hot pressing method and conventional sintering is presented in Table 2.2. It is seen that the hardness, density and coercive force of hot-pressed hard alloys are higher than that of sintered ones, while the strength characteristics are practically at the same level. The Curie point for hard alloys obtained by hot pressing, is 1223 K with a tungsten content in cobalt of 7%; for alloys obtained by conventional sintering, is 1233 K and 7.8%, respectively. An increase in the hardness and coercive force of the hot pressed hard alloys is apparently associated with a refinement of the structure and a decrease in the tungsten content in the cobalt phase in comparison with alloys sintered in the conventional process.

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Table 1

The properties of sintered (S) and hot-pressed (HP) cermets

Cermet type and content	d_V, g/см^3		*HRA*		б $_b$, MPa		I $_c$, A/m	
	HP	S	HP	S	HP	S	HP	S
BK6 (WC-6%Co)	15 -	14,9 14,8	90,5 -	89,0 88,5	1568 -	1617 1422	1194 -	995 -
BK15 (WC-15% Co)	14 -	- 14,0	88,5 -	- 86,0	- -	- 1765	8800 -	- -
TH-20 (TiC-20% Ni)	5,3 -	- 5,6	91,0 -	- 91,0	- -	- 1120	8080 -	- -
THM-30 (TiC-Ni-Mo)	5,6	-	90,0	-	1225	-	4140	-
KHT-1 (TiC-1%Ni-1%C)	5,6	-	86,0	-	-	-	4400	-
KXH-15 (CrC_2-15%Ni-)	6,6	-	92,0	-	-	-	8000	-

The properties of samples made out of tungsten-free carbide THM-30 obtained by hot pressing practically do not differ from the properties of the alloy obtained by conventional pressing and sintering, namely: relative density [g/cm^3], hardness [HRA], strength [MPa], and coercive force [A/m]. The wear resistance of the alloy at the equal of wear resistance of the hard alloy BK15. An increase in the coercive force of samples hot-pressed with increasing temperatures, is explained by a decrease in grains of the carbide phase as a result of intensification of the dissolution of Mo and Mo_2C in carbide phase.