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The synthesis and properties of nanocrystalline refractory compounds

R A Andrievskii

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Abstract. The methods of synthesis of refractory carbides, borides, nitrides, and oxides in the form of ultradisperse powders, consolidated materials, and films with a grain size less then 100 nm are examined. Information about the properties of nanocrystalline refractory compounds is described systematically and discussed. The bibliography includes 233 references.

I. Introduction

It is believed that one of the most important roles of chemical synthesis is in the establishment and improvement of the properties of modern ceramic, polymeric, and other materials (see, for example, Refs 1 – 5). The dimensional, phase, impurity, morphological, structural, and other features, which to a significant extent determine the physicochemical, physicomechanical, and operational properties of the materials, are in fact established at this stage of the synthesis. The important role of chemical synthesis is also indicated by the following facts: since 1984, the American Materials Science Society has held regular symposia, twice a year, on 'Chemical Methods for the Improvement of Ceramics'; the journals Chemistry of Materials and Journal of Materials Chemistry have been published by the American Chemical Society and the British Royal Society since 1989 and 1991 respectively.

Interest in the methods of synthesis used to create a new class of substances — nanocrystalline materials (NM) the characteristic structural size (grain or subgrain size) of which is less than 100 nm — is understandable. It has been shown for many nanocrystalline materials based on metals and intermetallic compounds (Ni, Pd, Ag, Cu, TiAl, $NbAl_3$, etc.) that a significant change in properties, the nature of which is frequently nonmonotonic, is observed for this grain size.[6-8]

The available review publications mainly describe the properties of the above nanocrystalline materials but are hardly concerned with the problems of refractory compounds (RC). The latter usually include carbides, nitrides, borides, oxides, and other phases with a melting point above 2000 °C.[9] The remarkable properties of these compounds (high hardness and high modulus of elasticity and strength; chemical inertness and low rate of evaporation; a wide range of electrical properties, including superconductivity, etc.) have long attracted to them the attention of a wide range of specialists in the field of the physical chemistry and technology of materials. Recently this interest has intensified in connection with the creation of nanocrystalline materials. The available information about the synthesis and properties of nanocrystalline materials based on refractory compounds is scattered and needs to be surveyed and treated systematically.

The problems of the synthesis of nanocrystalline materials from refractory compounds have several aspects. These are, firstly, the preparation and consolidation of ultradisperse powders and, secondly, the preparation of nanocrystalline films. Apart from these, there are also the characteristic features of the synthesis of amorphous substances which are converted into nanocrystalline materials after crystallisation. Our review is devoted predominantly to nanocrystalline materials in the powder and film form, in both consolidated and discrete states. For this reason, certain questions concerning the complex problem of the consolidation of nanocrystalline materials are also dealt with. So far as we are aware, such an approach had not been used previously although individual data are available in some communications.[10-13]

Clearly, the temperature limit of refractory compounds indicated above is extremely arbitrary and is largely dictated by convenience. According to estimates,[14] there are about 240 two-component refractory compounds for which T_f† > 2000 °C. On the other hand, the number of thoroughly investigated refractory compounds which are used in practice is much smaller. Therefore the subject of our review concerns nanocrystalline refractory compounds such as Si_3N_4, SiC, TiN, TiC, TiB_2, NbC, NbN, WC, Al_2O_3, AlN, ZrO_2, Y_2O_3, MgO, BN, and certain others. It is easily seen that they virtually all form part of the promising group of ceramics popular at present (Advanced Ceramics).

II. Ultradisperse powders and their properties

1. Preparation

The problem of the preparation of ultradisperse powders has long been discussed in publications devoted to ceramics, powder metallurgy, catalysis, and other fields. Various methods for the chemical synthesis of ultradisperse powders of oxygen-free refractory materials, used in ceramics and catalysis, have been

R A Andrievskii Laboratory for Special Inorganic Synthesis, Institute of New Chemical Problems, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-095) 292 65 11.

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† Melting point (Ed. of Translation).

Table 1. Methods of preparation of ultradisperse powders of refractory compounds.

Method	Compound	Ref.
Physical methods		
Vaporisation and condensation		
In an inert gas or a vacuum	MgO, Al_2O_3, SiC;	17, 18
	Al_2O_3, Y_2O_3	19
	ZrO_2	20
in a reactive gas	TiN, ZrN, NbN, AlN, VN, HfN;	21
	ZrO_2, Y_2O_3	20, 22
	Al_2O_3, AlN	23
High energy disruption		
grinding	ZrC, NbC;	24, 25
	Si_3N_4	26, 27
mechanosynthesis	TiC, ZrC, HfC, VC, TaC, WC, SiC, MoC;	28–31
	TiB_2;	32, 33
	TiN, BN, Si_3N_4, AlN, NbN	34–36
detonation treatment	BN;	37, 38
	Al_2O_3, MgO;	39
	SiC, TiC, Al_2O_3	40, 41
Chemical methods		
Synthesis		
plasmochemical	TiN, ZrN, HfN, NbN, Ti(C,N), VN;	10, 42
	AlN, BN, Si_3N_4, TiC, SiC, Si_3N_4 + SiC;	43–51
	Al_2O_3;	52
	TiN + TiB_2	53
laser	Si_3N_4, SiC;	54–56
	TiB_2;	57
	Si_3N_4 + SiC	58
thermal	BN, SiC;	59–61
	SiC;	62
	HfB_2, ZrC;	63
	WC + Co;	64
	$(Mo,W)_2C$;	65
	TiN, ZrN;	66
	ZrO_2;	67
	TiN + TiB_2	68
electrochemical	WC;	69
	ZrO_2;	70
	WB_4, MoB_4	71
in solutions	Mo_2C, W_2C;	72
	TiB_2, SiC	15, 73
Thermal decomposition		
condensed precursors	Si_3N_4, SiC, BN, AlN;	15, 74–76
	ZrO_2, Y_2O_3;	74, 77, 78
	NbN;	79
	Si_3N_4 + SiC	80, 81
gaseous precursors	TiB_2, ZrB_2;	16, 82, 83
	BN	84

analysed in a review.[15] Its authors reduced arbitrarily the wide variety of synthetic methods to four types of reactions — solid-phase, gas-phase, liquid-phase, and reactions of the gas–solid type. Nontraditional methods of synthesis of oxygen-containing and oxygen-free powders such as the sol-gel process, hydrothermal synthesis, pyrolysis of polymers, reactions in nonaqueous solutions, and different versions of the gas-phase synthesis (plasmochemical, laser, etc.) have come to be widely used in recent times.[1,16] One can add to these mechanosynthesis, electrochemical synthesis, self-propagating high-temperature synthesis (SHS), and synthesis in shock waves. The methods of preparation of solid powders of refractory compounds can be divided into two groups — physical and chemical (Table 1). This subdivision is naturally arbitrary because, for example, virtually all the physical methods include an appreciable chemical component and it is indeed frequently difficult to draw a clear-cut boundary between different procedures. Table 1 includes by no means all the examples of the preparation of ultradisperse powders of refractory materials, only the most characteristic being listed. We shall examine certain characteristic features of the methods of preparation of such powders.

a. Vaporisation and condensation

The condensation methods of preparation of clusters and ultradisperse powders have long been known and their theory has been described in many publications (see, for example, Uyeda[18] and Morokhov et al.[85]). There are at least two necessary and sufficient conditions for the condensation of ultradisperse powders — a high supersaturation and the presence in the condensed vapour of the molecules of a neutral gas. An interpretation of the phenomena in the gas-phase condensation, including homogeneous and heterogeneous nucleation, the mechanism of the growth of particles, the influence of impurities, etc., may be found in the sources mentioned above.[18,85]

In relation to nanocrystalline materials, condensation methods have developed after the publication of the communications of Birringer et al.[86] and Siegel and Hahn.[87] They describe the apparatus which makes it possible to combine the condensation process leading to the formation of ultradisperse powders with the vacuum pressing of small specimens (with a diameter up to 10–15 mm and thickens up to 0.2–0.5 mm) at high pressures (up to 3–5 GPa). This made it possible to avoid contamination to a large extent, by excluding contact between the ultradisperse powder and the surrounding medium, which is particularly important in the case of metallic and intermetallic substances. Ultradisperse aluminium, zirconium, yttrium, etc. oxide powders can be obtained in such apparatus by vaporising the oxide targets in a helium vacuum,[19] by the magnetron atomisation of zirconium cathodes in an argon–oxygen medium,[20] and also by forming an ultradisperse yttrium powder with subsequent controlled oxidation.[22] The reactive laser ablation synthesis, designed to obtain spherical Al_2O_3 and AlN particles on evaporation of aluminium, has been described.[23]

Mention should be made of the work of Japanese investigators on the vaporisation of transition metals in a nitrogen or ammonia vacuum (130 Pa) using electron-beam heating[21] and also on the application of the plasma, laser, and arc methods of heating in order to obtain ultradisperse MgO, Al_2O_3, and SiC powders.[17,18]

An advantage of the condensation method is the possibility of obtaining fairly pure ultradisperse powders with an extremely small particle size (with a particle diameter d down to 5–10 nm and less) over a comparatively narrow range of the latter. However, their productivity is low and the energy consumption is considerable. Naturally one has to bear in mind also the possible complications associated with the maintenance of the specific composition, which applies particularly to compounds with a wide range of homogeneity (for example, transition metal carbides and nitrides).

b. High-energy disruption

The usual grinding process is employed comparatively rarely to obtain ultradisperse powders because a grindability limit exists corresponding to the attainment of a kind of equilibrium between the disruption of the particles and their agglomeration.[4] Even when brittle materials are ground, the diameter d is usually not less than 50–100 nm. Furthermore, during grinding the product is contaminated by the material of the spheres and of the lining and also by oxygen. Admittedly, this can be avoided to a large extent by employing special spheres and lining prepared from the same material as the product being ground but the contamination with oxygen of oxygen-free refractory compounds

cannot be prevented. This can be illustrated by the example of the grinding of silicon nitride in a specially lined attrition mill:[26]

	Initial characteristics	4-h grinding	12-h grinding
d/nm	220	95	60
O_2 (mass %)	0.9	2.1	3.9

The characteristics of the preparation of ultradisperse powders of refractory materials by mechanosynthesis have been vigorously investigated recently. This was preceded, starting in the 1970s, by the study of the characteristic features of the so called mechanical alloying — the formation of alloys and intermetallic compounds under the conditions of high-energy grinding. One of the first mentions of the possibility of the synthesis of titanium (TiB_2), molybdenum (MoB), and niobium (NbB_2) borides when the corresponding metallic powder and boron are ground together in a planetary mill can be found in a monograph.[88] The mechanism and characteristics of the mechanosynthesis of refractory materials have been the subject of a lively discussion in the literature.[89-91]. The formation of refractory compounds during grinding is attributed both to the vigorous generation of new active surfaces and intense mixing (which intensifies diffusion processes) and to the exothermic nature of the reactions of the metals with the nonmetallic components (carbon, boron, and nitrogen). Mechanical activation as it were initiates the subsequent development of the self-propagating high-temperature synthesis. In some cases (systems of the Ti–C, Zr–B, and Nb–C type) explosive mechanosynthesis has been noted. This was detected thermographically from the abrupt increase in temperature.[92]

Fig. 1 illustrates the dependence of the nitrogen content in Group IV–VI transition metal nitrides on the duration of mechanosynthesis.[93] The relative disposition of the saturation curves, corresponding to the known differences between the exothermicities of the formation reactions of the nitrides of the test metals, is a characterisic feature. In experiments described by Atsumi et al.,[93] a vibromill of the YAMP-2SND type with a working volume of 1300 cm^3 and a ball charge of 90 : 1 was used; nitrogen was supplied continuously to the reaction space from a 34 litre reservoir. When a mill of the SPEX 8000 type (working volume 90 cm^3, ball charge 13 : 1) was employed, the duration of grinding was reduced severalfold (for example, it was approximately 30 h for TiN with a nearly stoichiometric composition.[35] Electron microscope and X-ray diffraction studies have shown that the particle size of such powders amounts to several nanometers.

Investigators working in the field of mechanosynthesis suggest that this method of preparation of ultradisperse powders can be used on a fairly large scale and is one of the promising procedures for the preparation of nanocrystalline materials.[31] Its advantage consists also in the possibility of obtaining alloyed and composite powders and in the use of nonconditioned raw material. However, the purity and technological properties of the powders obtained in this way have so far been inadequately investigated.

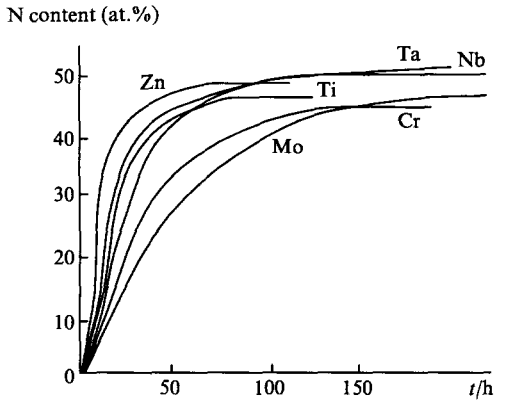


Figure 1. The influence of the duration of grinding on the nitrogen content in the nitrides.[93]

Detonation treatment (synthesis in shock waves and fragmentation) has long been known,[37-41] but, so far as we are aware, there have been few studies of such treatment in relation to nanocrystalline materials. The preparation of ultradisperse powders by the electrical explosion of wires belongs to the class of high-energy disruption methods, but this procedure has not so far been applied to brittle refractory compounds.

c. Synthesis

The chemical methods of the preparation of ultradisperse powders are more universal than the physical methods. Plasmo-chemical synthesis is one of the most popular. Extensive studies on these lines have been carried out in Russia,[10,42] Latvia,[43,44] Ukraine,[45,46] Japan,[18] and other countries.[15,94] The synthesis in a low temperature plasma is carried out at high temperatures, up to $(6-8) \times 10^3$ K, which ensures a high level of supersaturation and high rates of reaction and condensation processes. Examples of the modelling of the thermodynamic equilibrium, the vaporisation and condensation processes, as well as the coagulation of particles in the plasmochemical synthesis of ultradisperse powders of refractory compounds have been described in detail in the literature (see, for example, Refs. 10, 42–46, 95, and 96) and we shall not dwell on them here.

There is, in principle, the possibility of plasmochemical synthesis of virtually all ultradisperse refractory compound powders. Table 1 presents only a proportion of them. In addition, one may point to tungsten, tantalum, niobium, and boron carbide powders.[15,97,98] In order to obtain ultradisperse powders of refractory compounds, both arc plasmatrons[43-47,49,51-53,98] and high-frequency (including UHF) plasma generators[10,42,48] are employed; hybrid apparatus has also been described.[50] Arc plasmatrons are more productive and more readily available, but high- and ultrahigh-frequency devices ensure a higher purity of the products synthesised. Thus an ultradisperse β-SiC powder with a particle size of 5–20 nm and a high purity as regards cationic impurities (99.999%) has been obtained from silane and ethylene in an argon high-frequency plasma.[48] The oxygen content in these powders was ~1%.

It is also significant that plasmochemical technology ensures the preparation of multicomponent ultradisperse refractory compound powders: Si_3N_4+SiC, Ti(N, C), Nb(N, C), $TiN+TiB_2$, Si_3N_4+TiN (MgO, Al_2O_3, Y_2O_3), etc.[10,11,50,53] The manufacture of such powders on a semi-industrial scale has been introduced in a number of countries.

Electric spark dispersion, which combines the discharge-induced metal and alloy fragmentation process in reactive media with the synthesis of carbides and oxides (for example, TiC, SiC, WC, Al_2O_3), is closely related both to plasmochemical synthesis and to high-energy fragmentation.[99,100]

An effective procedure for the stimulation of the gas-phase synthesis involves the use of laser radiation. The optical heating source initiates and maintains the chemical reaction, promoting thereby the uniform 'self-heating' of the molecule, which ensures controlled homogeneous nucleation and rules out the possibility of contamination and of the influence of surfaces. Different versions of the thermochemical effect of laser radiation and the kinetics of these processses have been analysed.[101,102] Detailed studies of the characteristics of the laser synthesis of ultradisperse Si_3N_4, SiC, and TiB_2 powders have been carried out.[54,57] Study of the influence of the radiation intensity, pressure, and flow rate of the gas and its dilution on the dispersity of Si_3N_4 powders, obtained by the reaction

$$3\,SiH_4 + 4\,NH_3 \longrightarrow Si_3N_4\downarrow + 12\,H_2, \qquad (1)$$

showed that an increase in radiation intensity makes the greatest contribution to the decrease in the particle size and to the content of free silicon:

CO_2 laser radiation intensity/W cm^{-2}	760	2×10^4	1×10^5
d/nm	17.6	11.4	9.8
Free silicon (mass %)	35	2	traces

The influence of the intensity is attributed to the increase in the reaction temperature (from ~870 °C to >1020 °C) and to the higher degree of saturation due to the increase in heating [rate] (from 10^6 to 10^8 K s^{-1}), which promotes an increase in the rate of nucleation, a high degree of completion of reaction (1), and a decrease in grain size. In order to improve the process efficiency, two laser sources, arranged opposite one another in such a way that the radiation axes coincide minimising losses thereby, are used; the stream of gas mixture is usually introduced at right angles to the beam. However, so far as we are aware, the laser synthesis of ultradisperse refractory compound powders has not so far gone beyond the limits of laboratory research or the preparation of small experimental batches.

In the concept 'thermal synthesis', we included various processes such as carbothermal reduction of oxides,[59-61,103] carbothermal and borothermal reduction combined with magnesiothermal reduction of oxides,[62,63] including reduction under SHS conditions,[62] direct solid-phase synthesis,[65] thermolysis of zirconium chloride under a NO_2 atmosphere,[67] etc. Whereas in some of the studies[59-61,65,103] comparatively low-temperature conditions were employed and the starting material was highly disperse, which in fact ensured the formation of ultradisperse powders, in others[62,63] the magnesium oxide formed played the role of a coalescence preventing agent. The synthesis of ultradisperse TiN powders in accordance with the scheme

$$\mathrm{Ti} \xrightarrow[400\ ^\circ\mathrm{C}]{\mathrm{NH_4Cl}} \mathrm{TiH_{1.924}} \xrightarrow[>500\ ^\circ\mathrm{C}]{\mathrm{NH_4Cl,\ NH_3}\ (p = 1\ \mathrm{MPa})} \mathrm{TiN}, \qquad (2)$$

has been described.[66]

It has been suggested that ultradisperse TiN and ZrN powders ($d \approx 10$ nm) are formed as a result of the dispersion of the initial metal powders (their particle size is much greater than 150 nm) and their hydrides at a low nitrogenation temperature under pressure; ammonium chloride plays the role of the hydrogen source and activator of the transfer process through the gas phase and to some extent prevents recrystallisation.

The development of a technology for the preparation of nanophase solid-alloy WC + Co compositions using as precursors triethylenediaminecobalt tungstate and tungstic acid or ammonium metatungstate and cobalt chloride $\{Co(en)_3WO_4 + H_2WO_4$ or $[(NH_4)_6(H_2W_{12}O_{40}) \cdot 4\,H_2O] + CoCl_2 \cdot nH_2O$ respectively$\}$ has been reported.[64] These carefully prepared solutions are spray-dried and subjected to low-temperature reduction and carbidisation in a fluidised bed in special reactors, which ensures, on the one hand, a high dispersity, and, on the other, a strict constancy of composition and hence satisfactory physicomechanical properties.

It has been suggested that boron-containing polymers of the type of polyborazole $[B_3N_3H_4]_x$ be used as additives to a titanium powder in order to synthesise nanophase TiN + TiB_2 compositions.[68] Finely disperse Group IV and V transition metal diborides are also synthesised from the oxides with the aid of boron- and carbon-containing precursors of the type decaborane-dicyanopentane, $[-B_{10}H_{12}NC-(CH_2)_5-CN-]_n$.[104]

The familiar sol-gel technology and different versions of the coprecipitation procedure play an appreciable role in the preparation of ultradisperse oxide powders; the synthesis and thermolysis are closely intertwined in this technology.[105,106] The preparation of monodisperse β-SiC powders with spherical particles by the hydrolysis of a mixture of triethoxyphenylsilane and tetraethyl orthosilicate $[C_6H_5Si(OC_2H_5)_3 + Si(OC_2H_5)_4]$ followed by heat treatment under argon at 1500 °C may serve as an example of the synthesis of oxygen-free compounds.[107] Fig. 2 presents the structure of such ~0.6 μm spherical particles. Each particle consists of primary ~40 nm β-SiC nanoparticles. Such agglomeration of particles is undoubtedly useful for the improvement of the technological characteristics, but the properties of the nanocrystalline materials obtained from the conglomerates have to be investigated.

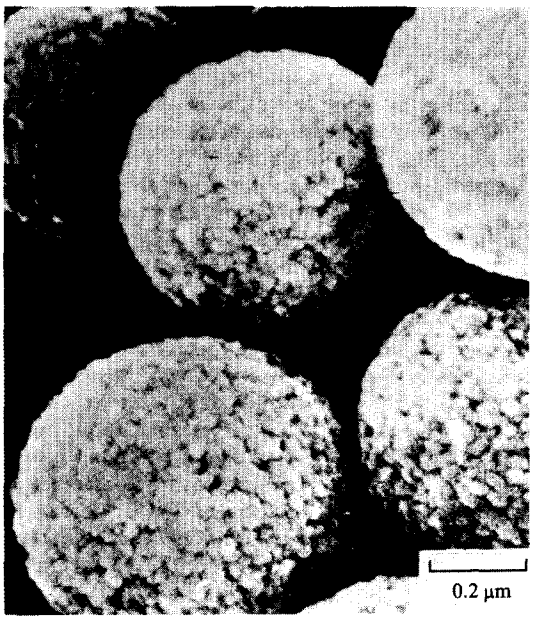


Figure 2. The microstructure of monodisperse β-SiC powders with spherical particles obtained in the sol-gel process[107]

Methods for the hydrothermal synthesis of ultradisperse oxide powders are less common, although some examples of the preparation of such ZrO_2 and Al_2O_3 powders may be found in the literature, for example in Refs. 74, 108, and 109.

An interesting method for the comparatively low-temperature gas-phase synthesis of titanium borides has been described.[73] Vaporising liquid sodium mixed with argon as the carrier gas reduces gaseous titanium boron chloride; the exothermic nature of the reactions ensures the maintenance of combustion conditions and the formation of ultradisperse powders.

The electrochemical synthesis of ultradisperse tungsten carbide and tungsten and molybdenum boride powders in melts and of zirconium oxide powder in aqueous solution has been investigated.[69-71] There is a communication[110] concerning the preparation of ultradisperse AlN powders ($d \sim 25$ nm) by the anodic dissolution of aluminium in a NH_4Br-NH_3 solution at −70 °C without subsequent annealing of the electrolysis products at 1100 °C. The electrochemical method has also been used to synthesise the polymeric precursor $[Al(NH_2)_3NH]_n$, which was subsequently subjected to annealing in ammonia at 600 °C with formation of an ultradisperse AlN powder (particle size ~8 nm).[111]

The liquid-phase synthesis of certain carbides and borides is likewise carried out under low-temperature conditions. Thus an ultradisperse TiB_2 powder may be synthesised by the following reactions:[15,73]

$$\mathrm{TiCl_4(l) + 2\,BCl_3(l) + 10\,Na(s)} \xrightarrow[100-160\ ^\circ\mathrm{C}]{\text{heptane}} \qquad (3)$$

$$\longrightarrow \mathrm{TiB_2(s) + 10\,NaCl(s)},$$

$$TiCl_4(l) + 4\,NaBH_4(l) \longrightarrow \quad (4)$$
$$\longrightarrow Ti(BH_4)_3 \cdot n\,Solv + 4\,NaCl + \tfrac{1}{2}B_2H_6 + \tfrac{1}{2}H_2,$$

$$Ti(BH_4)_3 \cdot n\,Solv \xrightarrow[\sim 215\,^\circ C]{} \quad (5)$$
$$\longrightarrow TiB_2(s) + \tfrac{1}{2}B_2H_6 + \tfrac{1}{2}H_2 + n\,Solv.$$

l = liquid; s = solid.

The powder thus obtained is amorphous to X-rays but after annealing at 900–1000 °C, which is also necessary to distill away sodium chloride, it crystallises. The size of the particles obtained by reaction (3) is ~50 nm,[15] while reactions (4) and (5) afford also larger particles of different morphology.[73] In the last investigation, triglyme was used as the solvent.

d. Thermal decomposition

Many ultradisperse refractory compound powders are prepared by the thermal decomposition (thermolysis) of solid, liquid, and gaseous precursors. We differentiated arbitrarily two varieties, although it is evident that the gas phase plays a role in virtually all cases. It is important to emphasise that, together with traditional precursors of oxide powders such as nitrates, oxalates, sulfates, hydroxides, and other compounds, recently the expansion of research into the refractory compounds of silicon, boron, titanium, and aluminium entailed appreciable use of organometallic polymers of these elements. A new term — preceramic polymers — has come to be widely used. Compounds of this type, used in synthetic procedures, were mentioned above.

Some of these polymers, used for the pyrolysis, are presented in Table 2. For example, polycarbosilane has an average molecular mass of 1200–2000 with a molecular mass distribution of 300–10 000; its softening temperature is in the range 130–180 °C, while fusion begins at 250–330 °C.[115] The pyrolysis temperature is usually ~1300 °C. As shown for ultradisperse Si–C powders, plasma heating (for example, with the aid of a nitrogen arc plasmotron) is preferable to the usual thermal heating.[115] The application of an industrial CO_2 laser for the pyrolysis of liquid silazane $[CH_3SiHNH]_n$, supplied to the reaction zone via a special ultrasonic nozzle in the form of an aerosol, has also been described. The pyrolysis results in the formation of an ultradisperse Si_3N_4 + SiC powder.[81]

Table 2. Organometallic polymers and monomers used as precursors in the preparation of refractory compounds.[112–114]

Precursor		Product
name	formula	
Polycarbosilanes	$\{Si(CH_3)(C_6H_5)-Si(CH_3)_2\}_n$,	SiC
	$\{SiH(CH_3)-CH_2\}_n$	SiC
Polycarbosiloxane	$\{Si(R_2)-O\}_n$, (R = H, alkyl, siloxyl)	SiC
Polysilazanes	$\{Si(R_2)-N(R)\}_n$,	Si_3N_4;
	$\{Si(R_2)-Si(R_2)-N(R)\}_n$, (R = H, alkyl)	Si_3N_4 + SiC
Aluminium amides and polyimides	$[AlR_2(NR_2)]_2$, (R = H, alkyl), $\{Al-NR\}_n$, (R = alkyl)	AlN
Polyborazole	$[B_3N_3H_4]_n$	BN
Polyvinylborazole	$\{C_2H_3(B_3N_3H_5)\}_n$,	BN
Polyvinylpentaborane	$\{C_2H_3(B_5H_8)\}_n$,	B_4C
Poly(titanium imide)	$\{Ti(NR)_2\}_n$, (R = alkyl)	TiN
Titanium tetrakis-(dimethylamide)	$[(CH_3)_2N]_4Ti$	Ti(C,N,O)

Certain features of the reactions occurring in the pyrolysis of preceramic polymers have been studied.[114,116] One should bear in mind that, after the laser or plasma treatment, the products of pyrolysis of preceramic polymers must be subjected to additional annealing for the final stabilisation of the structure and composition. The temperature of such treatment of the SiC, Si_3N_4, and SiC + Si_3N_4 powders is usually 1100–1200 °C, but it sometimes reaches as much as 1400–1600 °C.[81,114,115]

Heat treatment (calcining) invariably forms part of the technological cycles in the technologies of the sol-gel and coprecipitation processes mentioned above. Certain schemes for processes combining hydrolysis, synthesis, and decomposition are presented below.[74]

$$ZrOCl_2 + 2\,H_2O \longrightarrow \underline{ZrO(OH)_2} + 2\,HCl \quad (6)$$
$$\xrightarrow{\text{heat treatment}} ZrO_2$$

$$Zr(C_3H_7O)_4 + Y(C_3H_7O)_3 + 7\,H_2O \longrightarrow \quad (7)$$
$$\longrightarrow \underline{Zr(OH)_4 + Y(OH)_3} + 7\,C_3H_7OH$$
$$\xrightarrow{\text{heat treatment}} (Zr, Y)O_x$$

$$Zr(C_2H_5O)_4 + C_2H_5OH \quad (8)$$
$$\downarrow +\,H_2O$$
$$Zr(OH)_x(C_2H_5O)_{4-x}$$
$$\downarrow +\,H_2O$$
$$\underline{Zr(OH)_4}$$
$$\xrightarrow{\text{heat treatment}} ZrO_2$$

The first two schemes [reactions (6) and (7)] refer to the technologies for hydrolytic coprecipitation, while the last refers to the sol-gel process, where zirconium alkoxide in alcoholic solution is subjected to slow hydrolysis under controlled conditions. The conditions in the hydrolysis, coprecipitation, and heat treatment determine the composition, structure, morphology, and particle size of the ultradisperse powders. Preparation with the aid of oxalate precipitation of the monoclinic and tetragonal forms of the particles of ultradisperse ZrO_2 powders, including Y_2O_3-modified powders, has been described[117].

Fig. 3 presents a thermogravimetric curve for the heat treatment of yttrium hydroxide chloride prepared by sol-gel technology from yttrium trichloride.[77] The temperature of the final heat treatment, attained after 2 h, is 950 °C. A powder with a specific surface at ~20 $m^2\,g^{-1}$ is formed at this temperature.

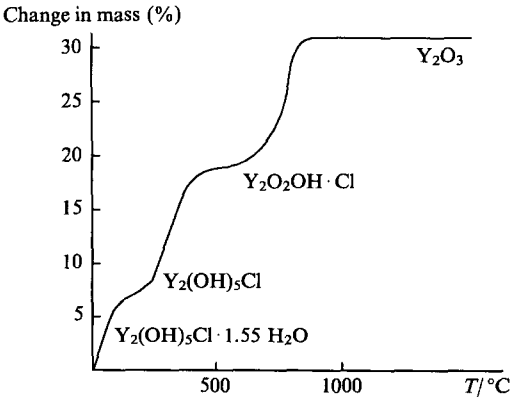


Figure 3. Variation of mass during the heating of an yttrium hydroxide chloride powder.[77]

In recent years, interest has been shown in ultradisperse transition metal boride powders. In this connection, we shall consider the possibility of obtaining them by the thermolysis of highly volatile hydroborates. The latter can dissociate in the range 300–400 °C, which is much lower than the usual temperatures for the preparation of borides. The thermolysis of zirconium tetrakis(tetrahydroborate) $Zr(BH_4)_4$ by a pulse type CO_2 laser has been described;[82] the preparation of powders having the overall composition $ZrB_{3.3-3.7}$, i.e. apparently containing an appreciable amount of free boron, with a specific surface of 40–125 $m^2\ g^{-1}$ has been reported. The thermal decomposition of $Zr(BH_4)_4$ at 300 °C results in the formation of an amorphous $ZrB_{2.76}$ powder, while at 350 °C the product is $ZrB_{3.74}$.[83] Experiments also showed that the excess content of free boron in the borides can be accounted for by the decomposition of the diborane formed.

$$Zr(BH_4)_4 \longrightarrow ZrB_2 + B_2H_6 + 5\,H_2\,. \qquad (9)$$

Indeed analysis of the gas phase showed that the ratio $[H_2]/[B_2H_6]$ is 9 and 12 at 300 and 400 °C respectively. This is appreciably higher than the theoretical value of 5 corresponding to reaction (9). During the annealing of the amorphous powders formed, crystallisation begins at 350 °C and terminates at 1000 °C. Work with transition metal tetrahydroborates requires much caution because they are explosive on contact with air and moisture.

2. Properties

a. Particle size. Morphology and structure

Particle size is one of the most important characteristics of an ultradisperse powder. In order to determine the size and shape of the particles, transmission and scanning electron microscopy (TEM and SEM respectively) is usually employed. Measurement of the specific surface (S) by the method involving the low-temperature adsorption of nitrogen and other gases with subsequent estimation of the so called average particle diameter or the equivalent diameter (d_s) by the familiar formula

$$d_s = \frac{6}{\gamma_t S}, \qquad (10)$$

where γ_t is the theoretical density, is likewise extremely common. Table 3 presents the values of S for certain ultradisperse refractory compound powders as a function of d_s and γ_t. Evidently the range of specific surfaces S extends from several to several hundreds of square metres per gram.

Some information about the particle size (more correctly about the regions corresponding to coherent scattering — blocks) can also be obtained by analysing the broadening of the reflections on the X-ray and neutron diffraction patterns for ultradisperse powders taking into account the possible contribution of lattice deformation. Agreement of the values of d obtained by measuring S and from the X-ray diffraction data for the TiN ultradisperse powder has been observed only for $S > 30\ m^2\ g^{-1}$ ($d < 30$ nm).[118] In the study of ultradisperse ZrN powder, a satisfactory agreement of the results of the determination of d by different methods (TEM, low-temperature adsorption of nitrogen, and neutron diffraction) was noted for particles with $d \approx 20$ nm.[119] For the ZrO_2 ultradisperse powder with a particle size of 8–20 nm, a satisfactory agreement between the values of d measured by different methods has likewise been observed.[120] In the vast majority of cases, it is necessary to resort to several methods of measurement in order to increase the reliability of the information about the particle size of ultradisperse powders because factors such as particle shape, the capacity of the particles for agglomeration, and the presence of lattice distortions cannot be always unambiguously taken into account.

The morphology of ultradisperse powders has been studied in many investigations (see, for example Refs 10, 18, 21, and 121–125). The results of the investigation of Al_2O_3 and SiC powders by high-resolution TEM methods have been reported in a review.[18] Polyhedral (in many cases cubic) forms of particles of carbides and nitrides obtained by plasmochemical synthesis have been frequently noted. Fig. 4 presents electron photomicrographs of TiN particles illustrating the characteristic crystal form of the plasmochemical titanium nitride. A cubic crystal form has also been noted for γ-Al_2O_3 and $TiC_{0.95}$ ultradisperse powders; titanium diboride has a hexagonal form.[123] The nitride powders obtained by the reactive atomisation method has a less distinct crystal habit.[21] NbN particles synthesised by the plasmochemical method had a spherical form.[122] The change in the ammonia concentration in the plasma promoted a transformation of the AlN particles from the spherical to the polygonal form.[45] The ZrB_n particles formed in the thermolysis of zirconium tetrakis-(tetrahydroborate) also have a nearly spherical form.[83] Various morphologies are characteristic of ultradisperse powders synthesised by the electrochemical method.[127] The majority of the particles formed on exposure to high energy influences have an irregular form.

Since the conditions in the preparation of ultradisperse powders are in most cases far from equilibrium, the particle form cannot always be predicted on the basis of any kind of *a priori* postulates. The latter can be based on the crystallographic analysis of Wulf polyhedra taking into account the contribution of the surface energy (see, for example, Refs 5, 85, and 128). Since close-packed structures are known to possess the minimum surface energy, crystal shapes characteristic of face-centred cubic and hexagonal close-packed lattices therefore frequently occur in small particles. Various complicating factors associated with the crystal form of the clusters have been discussed in a review.[128] Processes involving the possible interaction with impurities (for example, oxidation), capable of distorting particular estimates, are also important in relation to ultradisperse powders.

It has been noted in a monograph[85] that the nature of the size distribution of the particles may indicate the condensation mechanism. A logarithmic normal distribution may be a consequence of the coagulation crystallisation of the vapour–liquid–crystal type; on deviation from this relation, the vapour–crystal mechanism (a normal type of distribution) is more probable. Experiments have shown that[124] in the case of ultradisperse tungsten powders, the first version applies, while in the case of titanium there is an appreciable deviation from the logarithmic normal distribution. The coagulation mechanism of the growth of ultradisperse tungsten powders has been confirmed by the

Table 3. The specific surfaces of certain ultradisperse powders of refractory compounds ($m^2\ g^{-1}$).

d_s/nm	B_4C, BN	Si_3N_4, SiC, MgO, AlN	Al_2O_3, TiB_2, TiC	TiN, Y_2O_3	NbN	WC
	(2.3–2.5)	(3.3–3.5)	(4–4.9)	(5.0–5.4)	(8.3)	(15.8)
100	24–26	18–19	12–25	11–12	7	4
50	48–52	36–38	24–25	22–24	14	8
10	240–260	180–190	120–125	110–120	70	40

Note. The theoretical density (g cm^{-3}) is indicated in brackets.

spherical shape of the particles; the noncoagulation crystallisation of TiN is indicated in its turn by the shape of these particles (Fig. 4). However, the logarithmic normal distribution is sometimes accompanied also by a crystalline form of the particles (TiC, TaC, and NbC ultradisperse powders).[121]

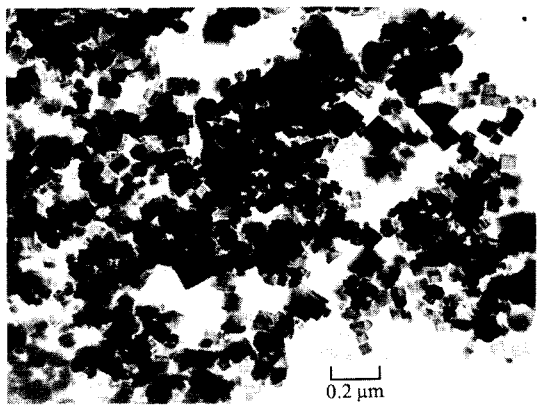


Figure 4. Electron photomicrograph of a plasmochemical ultradisperse TiN powder.[126]

Much attention has been devoted in the literature to the study of the structures of ultradisperse powders by X-ray, neutron, and electron diffraction methods. A detailed description of these results is outside the framework of the present review and we shall therefore quote only the most important of them.

1. Many compounds (Si_3N_4, Al_2O_3, SiC, TiB_2, etc.) may exist in the amorphous state.[19,49,56,76,83]

2. In certain cases (Al_2O_3, ZrO_2), anomalous structures are observed.[85,120]

3.Particle size influences the lattice period and microdeformation (distortions) of the lattice and also the mean square displacement of the atoms.[118,119,125,129,130]

4. The absence of dislocations has been noted in small particles.[118]

The influence of the excess surface free energy on the thermodynamic conditions in phase equilibria has been analysed in a general form in a monograph[85] and in a review.[5] It is evident from general considerations that the phase transition temperatures and the limits of the existence regions of the phases may be different in ultradisperse powders from those in large particles. It has been shown for aluminium oxide that mainly the γ-phase is present in ~30 nm particles, whereas coarser ultradisperse powders ($d \approx 110$ nm) contain also other modifications (ε, β, and θ).[85] Certain structural-morphological features of AlN, Si_3N_4, and Al_2O_3 ultradisperse powders have been analysed in a review.[131]

Table 4 presents data demonstrating the influence of the particle size on the lattice period and the mean square displacements of the atoms in TiN particles.[130] With decrease in d_s, the lattice period diminishes appreciably, while the evolution of the mean square displacements can be less clearly traced. A decrease in the lattice period has been observed also for many small metallic particles[85] and for ZrN particles.[119] This has been attributed to the manifestation of capillary compression. The capillary forces in ultradisperse powders may be appreciable: thus the capillary pressure for ~10 nm particles with a surface tension of ~2 N m^{-1} may be ~1 GPa and this can induce in its turn a deformation of ~10^{-3} nm, which is comparable with the data presented in Table 4.

Two remarks must be made here. Firstly, the capillary compression effect is not always accompanied by a decrease in the lattice constant.[128] Secondly, it has been noted in a review[125] that many results of the investigation of the phase composition and the lattice period of particles of ultradisperse refractory compound powders are to a large extent vitiated by the lack of a detailed specification of the oxygen content in the substances and their nonuniform composition in the region of homogeneity. An attempt has been made to take into account the latter factor to some extent,[130] but the oxygen content in the substances listed in Table 4 was not indicated. Furthermore, both the deviation from stoichiometry and the presence of oxygen affect significantly the lattice period in transition metal carbides and nitrides.[9] Many results of diffraction studies on these ultradisperse powders are distorted by various factors which have not been taken into account. The question of the influence of the refractory compound particle size on the lattice period requires additional study.

Table 4. Certain characteristics of ultradisperse TiN powders.[130]

Composition	$S/m^2\ g^{-1}$	d_s/nm	Lattice period, $10^5\ a$/nm	Overall square atomic displacements $10^4\ a$/nm
$TiN_{0.96\pm0.02}$	39	27	42402 ± 8	98 ± 7
$TiN_{1\pm0.05}$	50.3	22	42381 ± 8	100 ± 20
$TiN_{0.98\pm0.03}$	53.2	21	42384 ± 9	80 ± 20
$TiN_{0.87\pm0.08}$	76.4	14	42371 ± 10	100 ± 10
$TiN_{0.98\pm0.04}$	83.5	13	42367 ± 11	101 ± 5
$TiN_{0.96\pm0.04}$	95.4	11	42354 ± 14	131 ± 2

In conclusion, we emphasise that, although according to TEM and diffraction data the absence of dislocations and microdistortions has been noted in 20–40 nm TiN particles,[118] the question of the defectiveness of ultradisperse refractory compound powder particles requires a more wide-ranging study.

b. The content of impurities and gases. Chemical properties

In terms of the level of impurities and gas content, ultradisperse powders are in most cases inferior to the usual powders let alone single crystals and other highly pure substances. This is associated with, on the one hand, the characteristics of their preparation and, on the other, with their extremely high surface area and the conditions in their storage. Nevertheless, as mentioned previously, it has been possible to synthesise β-SiC which was extremely pure as regards cationic impurities.[48] However, only the use of a special condensation technique[19,20,86,87] creates conditions for the preparation of refractory compound powders with a high purity, including purity as regards oxygen admixtures. However, this method, like, incidentally, others, is not universal.

We shall analyse data on the content of impurities in ultradisperse powders with different dispersities in relation to silicon nitride powders, which have been studied in detail.[132] Analysis of the data in Table 5 permits the following conclusions.

1. There is no correlation whatsoever between the overall chemical composition and the particle size of the powders in the experimental range of values of d_s.

2. The surface of the particles is greatly enriched in oxygen and especially carbon, which is indicated by X-ray photoelectron spectroscopic (XPS) data for a layer 2.3–4.6 nm thick. With the exception of the powder in the R2 batch, the difference between the nitrogen contents on the surface and in the bulk of the particles is not very great—the ratio [N]/[Si] = 0.665 for the stoichiometric Si_3N_4. We may note that the enrichment in carbon of the plasmochemical Si_3N_4 ultradisperse powder (S = 42 $m^2\ g^{-1}$) has been noted also in another study.[133] It is attributed to the formation of carbonate and carboxy-compounds.

The independence of the composition of the particles on their size (Table 5) can be due to the different methods of preparation and storage of the powders. The enrichment of the surface layers in oxygen and carbon is likewise weakly correlated with the overall content of these impurities. Whereas the increased content of oxygen on the surface can be naturally attributed to oxidation, in order to elucidate the causes of the enrichment of the surface in

Table 5. Chemical composition of Si_3N_4 powders of different origin in the bulk phase (I) and on the surface (II) of the particles.[132]

Type of powder	Method of preparation	Composition (mass %)				d_s/nm	[O]/[Si]		[C]/[Si]		[N]/[Si]	
		N	Si	O	C		I	II	I	II	I	II
SNE 10	Decomposition of the diimide	38	60.8	1.0	0.08	125	0.016	0.34	0.001	0.1	0.63	0.54
A 2	Carbothermal synthesis	36.3	60.2	2.5	0.86	110	0.042	0.1	0.014	0.22	0.6	0.64
LC 12	Furnace nitrogenation of silicon	38.5	59.7	1.5	0.17	90	0.025	0.1	0.003	0.3	0.65	0.64
R 2	Nitrogenation of silicon in high-frequency plasma	38.0	58.5	3.1	0.18	60	0.053	0.59	0.003	0.29	0.65	0.41
P 1[a]	Interaction of $SiCl_4$ with NH_3 in high-frequency plasma	38.5	59.6	1.6	0.07	40	0.027	0.26	0.001	0.11	0.65	0.60

[a] Contains 1 (mass %) of chlorine.

carbon it is useful to turn to the results of the study of gas evolution during the vacuum heat treatment of ultradisperse powders.[4, 126, 134]

Fig. 5 illustrates the influence of the heat treatment temperature on the rate of gas evolution from TiN powders with the usual grain size ($d_s \approx 8$ μm) and from the ultradisperse powders ($d_s \approx 0.07$ μm).[126] There are two gas evolution peaks ($T_1 = 250-300$ and $600-700$ °C), carbon monoxide predominating appreciably in the evolving gases. The overall content of the gases correlates with the particle size: the values of S for the usual ultradisperse powder were 0.15 and 16 $m^2\ g^{-1}$, while the total amounts of gases were 1 and 7 $cm^3\ g^{-1}$ respectively under normal conditions. X-Ray photoelectron and Auger spectroscopic studies on these powders showed that the surface layers of the particles contain oxide nitride phases and carbon-containing components, the amount of the latter being appreciably reduced after vacuum annealing. The enrichment of the surface of nitride powders (Si_3N_4 [132, 133] and TiN [126]) in carbon-containing components is associated with the selective adsorption of CO_2 from the ambient medium, but the mechanism of the subsequent formation of CO under these conditions requires additional detailed study. The predominance of carbon monoxide in the gases evolved during vacuum annealing has been noted also in the study of Si_3N_4 powders with different dispersities.[135] Naturally, mainly components with mass numbers of 28 (CO) and 44 (CO_2) are evolved into the gas phase from ultradisperse powders of boron, silicon, and titanium carbides.[134] The possible chemical reactions during the heat treatment of ultradisperse powders of β-sialon ($Si_{6-z}Al_zO_zN_{8-z}$) and, in particular, the formation of ammonia as a result of hydrolysis and its subsequent catalytic decomposition have been discussed.[136]

Thus the distribution of impurities in the particles of ultradisperse powders is usually nonuniform. Different fine effects, associated with the possibility of estimating the surface segregation of atoms in small two-component particles, have been analysed.[85, 137] XPS and Auger spectroscopic methods have proved to be very useful experimentally in this connection. Ultradisperse powders of refractory compounds began to be investigated by XPS methods about twenty years ago. It is necessary to differentiate between the studies[138-141] devoted to these methods. In an early investigation,[139] attention had already been drawn to the different forms in which oxygen exists in an ultradisperse TiN powder (dissolution in the nitride, the formation of individual oxide nitride phases, and adsorption in the form of CO, CO_2, and H_2O on the surface of the particles) and an attempt was made to estimate their amounts. Niobium nitrides and carbide nitrides, silicon nitride and carbide, and other ultradisperse refractory compound powders were also investigated. It was discovered that the F, Cl, Fe, Al, Ca, and Na impurities are present on the surfaces of the SiC and Si_3N_4 powders.[142] The chlorine and sodium impurities may influence significantly the stability of the cubic and tetragonal phases during the annealing of the ultradisperse ZrO_2 powders.[143]

The chemical properties of ultradisperse powders (interaction with acids and alkalis, thermo-oxidative stability, etc.) have also been the subject of study in many investigations (see, for example, the relevant reviews[44, 122, 125]). Comparative study of the decomposition of an ultradisperse TiN powder ($S = 12.4\ m^2\ g^{-1}$) as well as coarser TiN powders, obtained by self-propagating high-temperature synthesis ($S = 0.1\ m^2\ g^{-1}$) in solutions in sulfuric and nitric acids, showed that the absence of an induction period is characteristic of substances with a larger surface area. Their entire surface is involved simultaneously in the reaction, which occurs in dilute acids and at lower temperatures than in the case of coarse-grained powders.[144] The specific rate of decomposition of the ultradisperse TiN powder in sulfuric acid in the concentration range 9.5–12.6 M and in the temperature range 130–150 °C is $(0.4-3.3) \times 10^{-6}$ mol $min^{-1}\ m^{-2}$. The kinetics of the decomposition of the powder in solutions in the $H_2SO_4-H_2O_2$ system have been investigated.[145]

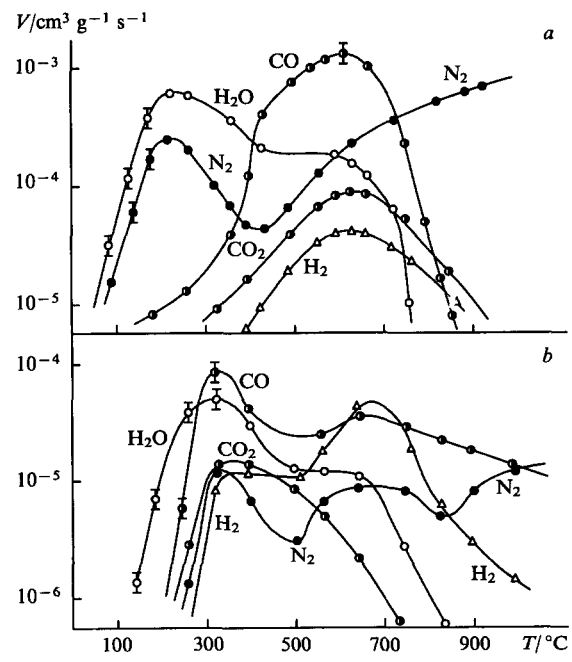


Figure 5. Temperature dependence of the rate of gas evolution from an ultradisperse (*a*) and an ordinary (*b*) TiN powder.[126]

For the temperature of the onset of oxidation of TiN powders, differing in S by five orders of magnitude, the following empirical equation has been proposed:

$$\frac{T}{T_m} = \left(\frac{S}{S_m}\right)^{-n}, \quad (11)$$

where the subscript m refers to the massive material (T_m = 1120 K; S_m = specific surface of ~1 mm particles); n = 0.064.[122]

Many investigators have noted that, when ultradisperse powders are stored in air, hydrolysis takes place. The acid–base properties of the surfaces of ultradisperse powders have been investigated in greatest detail for titanium and silicon nitrides.[146] The position of the zero-charge point in these substances corresponds to a highly acid medium, while the zero electrokinetic potential corresponds to an acid or weakly acid medium. This means that there are uncompensated positive centres. It has been suggested that these comprise coordinated ammonia molecules capable of combining with protons:

$$-NH_3 + H^+ \longrightarrow -NH_4^+ . \quad (12)$$

Contact with water leads to the creation of a weakly alkaline medium and to the appearance of uncompensated negative groups.

The high sensitivity of ultradisperse powders to the ambient medium has given rise to an increased interest in methods for their storage; a hermetically sealed container filled with dry argon is usually employed in practice. Thermochemical methods for the treatment of ultradisperse powders with different reagents, which form a protectic shell on the surface of the particles and prevent both oxidation in air and hydration in water and can be removed on heating, have been analysed.[147] It has been suggested that solutions of organofluorine compounds (epilemmas) in Freon-113 be employed as reagents of this kind.

c. Physicochemical and physical properties

The fraction of surface atoms in particles of ultradisperse powders may reach several tens per cent and this exerts a significant influence on the lattice and electronic properties of the substance. The characteristic correlation size (or the characteristic length of the transfer process) for a particular phenomenon in solids may range from several tenths of a nanometer to several tens of nanometers.[148] Two factors which are largely responsible for the differences between the properties of small particles (d < 10 nm) and massive bodies have been noted. The characteristics of the spectral density of vibrations, anomalies in the heat capacity, and the specific features of electronic states and electrical, thermophysical, optical, and magnetic properties of small particles, mainly metallic particles, have been analysed.[5,85,128,148–150] Questions concerning the thermodynamics of small particles have been discussed in the same studies: the minimum size to which the concepts of 'phase' and 'surface energy' are applicable; the possible transformation in relation to small particles of the familiar Thompson formula for the vapour pressure as a function of the radius of curvature, fusion and other phase transitions in small particles, etc. (see also Refs 151–154). Without dwelling on these topics in detail, we shall only note that there exists little reliable experimental information on the dimensional effect for ultradisperse powders of refractory compounds.

The critical magnetic field (H_{C_2}) increases with decrease in the particle size of transition metal nitrides (NbN, VN, TiN, NbNC).[155,156] The increase in H_{C_2} was ~200% when d changed from ~75 to ~15 nm. Comparative study by XPS and the spectroscopy of characteristic energy losses of a well crystallised hexagonal BN and an ultradisperse BN powder showed that a lower atomic ratio [N]/[B] and a lower concentration of valence electrons per unit volume are characteristic of the latter.[140] A study of the IR spectra of an ultradisperse BN powder with different dispersities (d_s = 5–66 nm), which were regulated by annealing at 800–1800 °C, revealed an appreciable deformation of the basal planes of the lattice of the unannealed small particles, which was also confirmed by X-ray diffraction data.[157]

The band structure of ultradisperse powders of superconducting niobium carbide nitrides (NbC_xN_{1-x}, x = 0.06 to 0.09) was investigated by Auger spectroscopy.[141] It was shown that the effective energies of the hole interaction in the valence band for the metallic and nonmetallic positions are significantly different. Analysis of the IR and fluorescence emission spectra in the ultraviolet region for an ultradisperse powder of amorphous Si_3N_4 led to the conclusion that the width of the forbidden gap is greater for nanoparticles than for massive objects.[158]

III. Consolidated powdered nanocrystalline materials

1. Principal characteristic features of the consolidation of ultradisperse powders

Virtually all the consolidation methods known in powder technology—pressing and sintering, different versions of hot pressing, etc.[4]—are applicable also to ultradisperse powders. However, if one is dealing with the preparation of compact materials with a nanocrystalline structure, i.e. largely with retention of the grain size characteristic of ultradisperse powders, then the usual sintering and hot pressing temperatures are inapplicable because vigorous recrystallisation processes occur. In essence, in the vast majority of cases only high-energy consolidation methods, involving the use of static and dynamic high pressures, electric pulse influences, etc. are suitable for the maintenance of the above conditions.

Certain features of the pressing, sintering, and hot pressing of ultradisperse powders of refractory compounds, including such procedures at high pressures, were described in our earlier communication[13] and here we shall confine ourselves to stating the most important factors. Figs 6 and 7 illustrate the variation of the relative densities of ultradisperse powders of Si_3N_4 and TiN over a wide pressure range.[4,159] Data referring to coarser Si_3N_4 powders are also presented (the experiments were performed under different conditions). It is clearly seen from these results that the susceptibility to compaction on pressing diminishes significantly with decrease in dispersity and that it is impossible to attain or even approach the theoretical density at pressures up to 7–9 GPa. The low susceptibility to compaction of ultradisperse BN, SiC, and Si_3N_4 powders has also been noted in other investigations.[48,160,161]

The low susceptibility to compaction of such powders is associated with a high level of the interparticle friction characteristic of powders with a high surface area.[4] Hence it is understandable why it has not been possible to prepare compact

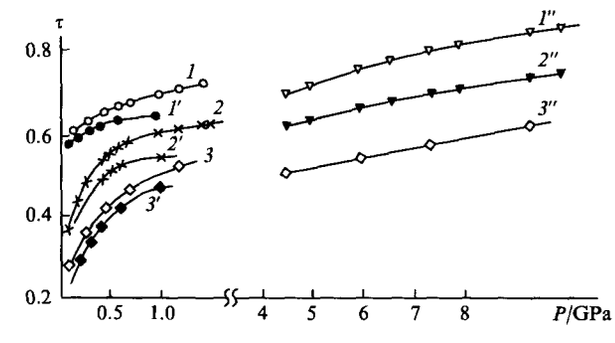


Figure 6. The influence of the pressing pressure on the relative densities (τ) of silicon nitride powders:[4] (*1*)–(*3*) pressing in a hydrostat; (*1'*)–(*3'*) pressing in the usual press-moulds; (*1''*)–(*3''*) pressing in high-pressure apparatus; (*1*), (*1'*), and (*1''*) $d_s \approx 1$ μm; (*2*), (*2'*), and (*2''*) $d_s \approx 0.05$ μm; (*3*), (*3'*), and (*3''*) $d_s \approx 0.017$ μm.

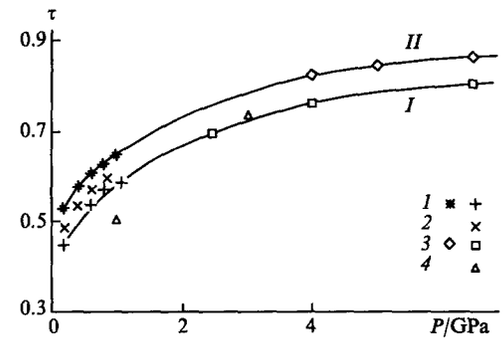


Figure 7. The influence of the pressing pressure on the relative density of an ultradisperse TiN powder:[159] (*I*) $d_s \approx 0.07$ μm; (*II*) $d_s \approx 0.08$ μm; (*1*) usual pressing, specimen diameter 10 mm, height 5 mm; (*2*) ditto, specimen dimensions 15 × 15 × 15 mm; (*3*) pressing at high pressure, specimen diameter 8 mm, height 5 mm; (*4*) magnetopulse pressing, specimen diameter 7 mm, height 15 mm.

specimens from ultradisperse powders obtained by the condensation method:[86,87] the porosity of even metallic pellets in such experiments has rarely been less than 10%. High pressures combined with heating to temperatures not inducing intense crystallisation can lead to appreciable compaction with retention of the nanocrystalline structure.

Unfortunately insufficient data have been accumulated hitherto concerning the preparation of such specimens. As an illustration of the possibilities of hot pressing, we shall quote the results of a study[162] for ultradisperse $ZrO_2-3\%\ Y_2O_3$ powders ($d_s = 40-60$ nm) (Table 6). The sintering and hot pressing temperatures for ultradisperse zirconium oxide powders are low as a consequence of the increased reactivity of these powders, but, despite the short duration of the process, it is impossible to achieve a sufficient compaction and to prevent the growth in grain size at a pressure of 1.6 GPa. By reducing the temperature and by increasing the duration of the sintering ($T = 1050$ °C, $t = 5$ h), it is possible to obtain partially stabilised zirconium dioxide with a relative density of ~99.9% and a grain size of ~85 nm at low heating rates (5 K min^{-1}).[163] Similar data have been obtained in another study.[164] The deagglomeration of ultradisperse powders is also important for active compaction during sintering.[165]

Table 6. Variation of the relative density (τ) and grain size (L) during the sintering and hot pressing of ultradisperse ZrO_2-3 mol % Y_2O_3 powders.

T/°C	Sintering		Hot pressing	
	τ	L/nm	τ	L/nm
1100	0.72	120	0.87	130
1200	0.83	150	0.93	170
1300	0.94	170	0.97	250

Note. In all cases, the pressure was 1.6 GPa and the duration of treatment at the temperatures indicated was 10 s.

Attention should be drawn to possible methods of preparation of nanocrystalline materials from refractory compounds such as dynamic recrystallisation at high pressures[166] and crystallisation from the amorphous state.[167] The temperature conditions, which again should not lead to vigorous growth in grain size, are fundamentally important in both cases. Studies on these lines are only just beginning.[168]

An interesting combination of the pyrolysis of a precursor—polysilazane (Table 2)—with pressing and sintering methods at comparatively low temperatures (1100–1600 °C) made it possible to obtain a Si_3N_4+SiC nanocrystalline composition (overall composition $Si_{1.73}N_{1.56}C_1$) with a relative density of 92%–93%.[169]

2. Properties

Hardness is one of the most thoroughly investigated characteristics of nanocrystalline materials based on refractory compounds. Table 7 shows that the main information about hardness refers to specimens prepared using high dynamic and static pressures. However, even under these conditions it is in many cases impossible to suppress recrystallisation and the grain size increases. An appreciable scatter of the results is characteristic of specimens obtained by explosive methods, which is manifested particularly clearly in the case of ultrahard materials (for comparison, the table includes data for diamond), although other methods also lead to some nonuniformity of the results.

The data[64] obtained for the WC + 10 mass % CO solid alloy, which has been thoroughly investigated, are of great interest. As a result of the application of the thoroughly developed technology for the preparation of ultradisperse powders and their low-temperature consolidation, it has been possible to attain hardness parameters exceeding the corresponding characteristics of standard solid alloys by a factor of 1.5–2.

The overall level of hardness is also affected by the residual porosity, which amounted to several per cent for the majority of the specimens presented in Table 7. According to data of Averback et al.[179] a decrease in τ from 0.94 to 0.89 (i.e. an increase in porosity by 5%) for nanocrystalline titanium oxide leads to a decrease in hardness by more than 30%.

However, even if this fact is taken into account, the hardness of Al_2O_3, SiC, MgO, TiN, ZrO_2, and Si_3N_4 specimens is nevertheless low and does not exceed greatly the hardness of the usual polycrystalline and single crystal refractory compounds or is actually approximately the same.[9] This finding appears strange from at least two points of view. Firstly, measurements have shown that the hardness of nanocrystalline metals and intermetallic compounds (Cu, Ni, Ag, Fe, Pb, TiAl, $NbAl_3$; see, for example, Refs 6–8, 12, and 180–185) can exceed the hardness of the usual polycrystalline materials by a factor of 3–6. Secondly, as will be seen from the consideration below of the refractory compound-based films, the hardness of these substances is appreciably greater than that of the usual massive refractory compounds.

The familiar Hall–Petch relation between hardness (critical splitting shear stress) and grain size:

$$H = H_0 + kL^{-1/2}, \qquad (13)$$

where k and H_0 are constants [L is average grain diameter (Ed. of Translation)], holds for the majority of the nano-crystalline metals and intermetallic compounds mentioned above. Admittedly inversion relations of type (13) (for example, for TiAl [182]) and nonmonotonic relations $H = f(L)$ (for example, for Cu [181] and $NbAl_3$ [183]) are observed fairly frequently. This can be explained by the influence of impurities, residual stresses, sliding along boundaries, etc. One cannot rule out the possibility that the low level of hardness of the materials presented in Table 7 is due to the limited amount of available information: none of the existing publications contain data obtained for a wide range of values of L. It may be that the results in Table 7 were found for an unfavourable range of values of L and that the determination of the purities of the test specimens left something to be desired.

The physicomechanical properties of two-phase nanocrystalline materials based on refractory compounds have been studied.[186–192]. Certain characteristics of percolation effects have been investigated in ultradisperse TiN + AlN, Si_3N_4 + SiC, and ZrO_2 + Ni compositions.[186–189] The critical point for the last system, corresponding to a sharp increase in electrical conductivity of the compositions, is in the range 25 vol.% – 30 vol % Ni,[186] while for the Si_3N_4 + SiC composition it is at the level predicted by percolation theory (~17 vol.% SiC).[187] Special interfaces with a reduced resistance to phonon scattering have been discovered in the TiN + AlN system.[189]

A nonmonotonic variation of the high-temperature and decomposition strengths in the SiC + Si_3N_4 system has been noted.[190] A higher temperature of the degradation of hardness and

Table 7. The hardness (H_v) of nanocrystalline refractory compounds.[13,170]

Compound	Method of consolidation	Characteristics of specimen		H_v/GPa	Ref.
		τ	L/nm		
SiC	Explosive pressing	0.97	60–100	26.4	171
BN	"	0.96	25	43–80	172
Al_2O_3	"	0.94	70	14	173
Si_3N_4	Hot pressing at high pressures	0.99	500	32.4	174
TiN	"	0.95–0.96	200–300	12–18	175
TiN + 30% TiB_2	"	0.95	100–1000	19.1	176
WC + Co	Hot isostatic pressure in the solid phase	1.0	200	19.5	64
ZrO_2	Rapid hot pressing	0.97	250	14	162
MgO	Hot forging	0.99	100–200	8–10	177
Diamond	Explosive pressing	0.91		63–68	178
		0.94		56–65	

of the modulus of elasticity as well as a greater strength compared with aluminium oxide without additives have been observed in the $Al_2O_3 + SiC$ nanocomposites.[191,192] Nanocrystalline ZrO_2–Al_2O_3 specimens are also distinguished by a high decomposition strength and ordinary strength.[193]

The present authors have shown[194] that the use of a plasmochemical ultradisperse Si_3N_4 powder in the $TiB_2 + Si_3N_4$ composition hot-pressed at high pressures is accompanied by a sharp increase in the rate of creep, which may be attributed to the manifestation of superplasticity (Fig. 8). The values of L for these specimens were ~0.5 μm for Si_3N_4 and ~2–4 μm for TiB_2 (the grain size in the usual Si_3N_4 powders was 2–4 μm).

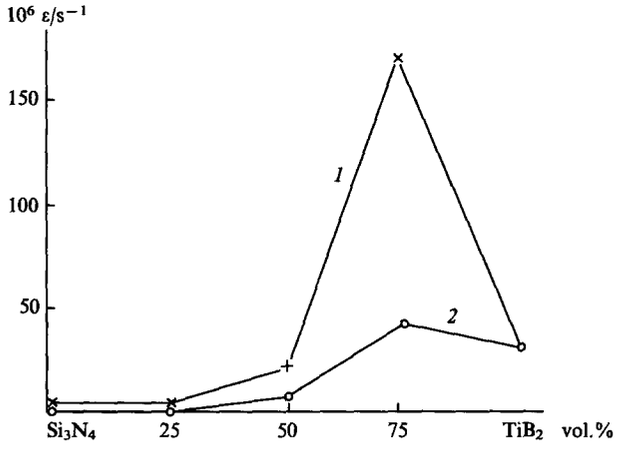


Figure 8. Variation of the rate of creep with the composition of the TiB_2–Si_3N_4 system (T = 1600 °C, tension 20 MPa, t = 30 min):[194] (*1*) Si_3N_4 ($L \approx 0.5$ μm); (*2*) Si_3N_4 ($L \approx 2-4$ μm). The TiB_2 grain size was ~2 μm in both cases.

The superplasticity in the deformation of nanocrystalline sialon at 1500–1600 °C (L = 100–200 nm) has been described.[195] High rates of creep at 1100 °C are also characteristic of zirconium dioxide (L = 100–140 nm), specimens of which (τ = 0.93–0.97) were obtained by the hot forging method.[196]

The optical properties of nanocrystalline silicon nitride obtained by pressing ultradisperse powders at high pressures (up to 5 GPa) and at the temperature of liquid nitrogen with subsequent low-temperature sintering (T = 1400 °C), have been described.[161]

The role of dimensional effects in the establishment of ferromagnetic, ferroelectric, and elastic characteristics on transition from multidomain to single-domain and nanodomain structures has been discussed in a review.[197]

Owing to the presence of an excess surface free energy, specific phase equilibria may be observed in multiphase systems containing ultradisperse particles. Several computational studies, in which the influence of dispersity on the equilibrium in the Zr + C,[198] TiC(TiN) + TiB_2,[12] and TiN + AlN [199] systems was estimated, have been carried out hitherto. Table 8 presents estimates of the influence of dispersity on the eutectic temperature in the TiC + TiB_2 and TiN + TiB_2 systems. These calculations were performed in the simplest regular solution approximations and their results may be regarded as estimates. Nevertheless, they indicate the necessity to take into account the displacement of phase equilibria on passing to multiphase nanocrystalline materials. The desirability of setting up the corresponding experimental studies is likewise quite evident.

Table 8. The influence of the particle size of one of the components in the TiC + TiB_2 and TiN + TiB_2 systems on the eutectic temperature (T_e = 2790 K in the $TiC_{0.9}$ + TiB_2 system, and T_e = 2870 K in the $TiN_{0.9}$ + TiB_2 system).[9,12]

Particle radius/nm	$-\Delta T_e$/K	
	TiC(TiN) + TiB_2	TiB_2 + TiC(TiN)
100	~45	~35
50	~90	~70
10	~450	~350
5	~900	~700

To conclude the description of the properties of consolidated powdered nanocrystalline materials, one should note that the available data are limited, which has a lot to do with the difficulties in the preparation of representative thoroughly authenticated nanocrystalline specimens. As noted in our earlier publications,[13,70] studies concerning titanium dioxide, carried out mainly by American and German investigators, contain somewhat more information (see, for example, Refs 6, 7, 86, 87, and 179). These workers used the condensation method in combination with the preparation of the specimens at high pressures. However, as a consequence of the porosity of the specimens, these data are not always sufficiently representative. Therefore progress in nanocrystalline materials science depends in many respects on the level of the technology for the preparation of test specimens.

IV. Nanocrystalline films

1. Characteristics of the preparation

Available information about films and coatings based on refractory compounds is extremely extensive (see, for example, Refs 200–205) and we shall therefore confine ourselves merely to a description of information on multilayer films as well as films with a specified grain size.

The principal methods for the preparation of refractory compound-based films are presented in Table 9. It is easy to see the similarity between Tables 1 and 9: with a few exceptions, the methods of preparation of ultradisperse powders and films are virtually identical and in many instances differ only in the conditions determining the formation and growth of nuclei in the bulk phase or on the surface. The arbitrary nature of the subdivision of preparative methods into chemical and physical, noted above, applies to an even greater extent to the preparation of films. The existing terms Chemical Vapour Deposition (CVD) and Physical Vapour Deposition (PVD) are mainly of historical significance. In many instances, chemical refractory compound formation reactions are decisive factors in the formation of the structure and properties of films on thermal vaporisation, in atomisation processes, and in the plasma methods. Methods for the modification of the surface such as ion implantation should be added to this list. Plasma (the so called plasma-accelerated or plasma-accompanied processes) and lasers are being used increasingly to activate, for example, processes involving the reduction of halides and the pyrolysis of silazanes and hydroborates.[202,206]

Table 9. The principal methods of preparation of films based on refractory compounds[a].

Method	Compound
Physical	
Thermal vaporisation	
electron beam	Oxides, borides, nitrides
laser	Oxides, nitrides
Ionic atomisation	
ionic-plasma	Nitrides, carbides
magnetron	Nitrides, carbides, borides, oxides
Chemical	
Synthesis	
deposition from gas phase	Nitrides, carbides, borides oxides
Sol–gel technology	Oxides
Thermal decomposition	
condensed precursors	Carbides, oxides, nitrides
gaseous precursors	Borides, oxides

[a] See also Table 1, monographs,[202,204] and a review[203].

The thermal vaporisation methods, used to obtain nanocrystalline films based on refractory compounds, are less universal compared with the plasma and magnetron methods, although they have come to be used to some extent in the formation of oxide films. For example, the preparation of ZrO_2–10 mol.% Y_2O_3 films by the laser pulse vaporisation of metals in a beam of oxygen ions has been described.[207] In the range of deposition temperatures 100–400 °C, the size of crystallites was 10–30 nm.

In the course of the study of wear-resistant instrumental coatings, extensive experimental data have accumulated on the ionic-plasma and magnetron films based on titanium and other transition metal nitrides and carbides (see, for example, Refs 202–204 and 208). Mainly metallic targets, atomised in nitrogen- and carbon-containing media, are used for the preparation, although the magnetron technique in fact makes it unnecessary to resort to reactive methods involving directly refractory compound targets. Such a procedure has been used successfully, for example, in the synthesis of borides. The employment of a relatively low temperature of the support (approximately 200–500 °C) makes it possible to avoid appreciable recrystallisation when physical deposition methods are resorted to, and in many cases a nanocrystalline structure can be formed. Multilayer and two-phase films as well as films with complex alloying are preferable in this respect.[209–212]

The rate of deposition of magnetron films under direct current conditions usually amounts to several tenths of a micrometer per minute; high-frequency devices, which make it possible to atomise dielectric targets, ensure rates approximately an order of magnitude lower. In ionic-plasma devices (of the 'Bulat' type), the rates of deposition are also high, but it is not always possible to avoid the appearance in the films of the so called drop phase as a consequence of the incorporation in the plasma of drops from the fused cathodic crater.

The size of the crystallites in the films obtained by the traditional deposition methods from the gas phase (CVD) is usually several micrometers and a temperature not less than 850–900 °C is then usually developed. Only in the case of multilayer or multiphase films is it possible to achieve nanostructures. In particular, this applies to the TiB_2+TiC composition obtained by deposition at 1000 °C from a $TiCl_4+n\text{-}C_7H_{16}+BCl_3+H_2$ mixture at atmospheric pressure ($L < 100$ nm).[213] The use of the laser technique also makes it possible in many instances to reduce the temperature and to synthesise nanocrystalline films. Thus the formation of silicon carbide films ($L < 50$ nm), deposited from a $Si_2H_8+C_2H_2+Ar$ mixture with exposure to the excimer ArF laser ($T = 518$ K), has been reported; this is the so called photo-CVD process.[214]

Sol-gel technology, involving the preparation of a solution, immersion, drying, and annealing and requiring simple apparatus, is becoming an increasingly popular method of preparation of oxide films (in particular, lead titanates and zirconates as ferroelectric materials). According to Tohye et al.,[215] the physical properties of these films are not inferior to those of magnetron films. The preparation of zirconium oxide films by the sol-gel method has been described.[216]

Thermolysis of organometallic compounds in order to obtain thin films has long attracted the attention of a wide range of investigators (see, for example, Refs 200 and 201). The characteristics of formation of the structure and the properties of thin Al_2O_3 films (~100 nm), arising in the oxidative pyrolysis of aluminium tris(acetylacetonate) $Al(Acac)_3$, have been described.[217] The authors suggest that the molecules of the initial compound in the adsorption layer do not decompose fully and that organic fragments are removed from the upper layers of the film formed. The reason for the instability of the charge in these films is the migration of OH^- and H^+ ions produced by the electrolysis of the water of crystallisation present in the film. Thin ZrO_2 films with Y_2O_3 as the stabilising additive (3–8 mol. %) are obtained by pyrolysing the acetates.[218] The preparation of an ultradisperse Si_3N_4+SiC powder by the thermal decomposition of organosilicon precursors on exposure to a CO_2 laser as well as the formation of films of similar composition have been described.[81] In exactly the same way, the decomposition of Group IV transition metal hydroborates leads to the formation of not only ultradisperse powders but also of films.[82,83]

Comparative results of the analysis of zirconium diboride powders and films, formed in the pyrolysis of the hydroborate $Zr(BH_4)_4$, are presented in Table 10. The characteristic features of the films are evidently crystallinity (the parameters of the structure are close to the tabulated data) and slight deviation from stoichiometry. The powdered deposits are amorphous and contain an appreciable excess of free boron, the origin of which has already been considered in connection with the discussion of reaction (9).

The superstoichiometric content of the nonmetallic component in films is characteristic also of other refractory compounds, for example the nitrides obtained by the ionic-plasma, magnetron, and other methods. Thus zirconium nitride films acquire a superstoichiometric composition at a nitrogen pressure in excess of $\sim 10^{-3}$ Torr under the conditions of high-frequency magnetron atomisation.[219] The appearance of superstoichiometric zirconium

Table 10. Characteristics of films prepared from zirconium diboride powders obtained by the decomposition of zirconium hydroborate.[83]

T/°C	Deposit	[B]/[Zr]	Lattice period/nm		S/m^2 g^{-1}	$[H_2]/[B_2H_6]$ in gas phase
			a	c		
250		No decomposition				
300	Amorphous powder	2.76			27.7	9
	Film	2.03	0.3167	0.3528	–	9
350	Amorphous powder	3.74			26.2	12
	Film	2.15	0.3165	0.3534	–	12

Note. The duration of treatment at the temperatures indicated was 5 h in all cases.

nitride has also been detected in the electron beam vaporisation of zirconium accompanied by bombardment with nitrogen ions having energies in the range 400–700 eV.[220] The mechanism of their formation (the appearance of vacancies in the metallic sublattice, the presence of phases of the Zr_3N_4 type, etc.) is still not entirely clear and is the subject of lively discussion in the literature.

2. Properties

Although the number of publications on the properties of thin films is fairly large, only some of them refer to nanocrystalline refractory compound-based films. Furthermore, not all these data are accompanied by a more or less detailed specification of the size of crystallites in the film. It appears that the study of the characteristic features of the formation and growth of refractory compound films, obtained by many and varied methods (Table 9), is in the initial stage. The overall scheme describing the crystallisation of coatings and films, proposed in the familiar study of Movchan and Demchishin[221] and then amplified by Thornton,[222] should be made significantly more specific in relation to refractory compounds.

For example, there is an interesting approach to the estimation of the stability of polycrystalline thin films obtained by the pyrolysis of zirconium acetate and yttrium nitrate solutions.[218] Heat treatment at 1200 °C is accompanied by the formation of ~25 nm crystallites, but, after annealing at 1400 °C, the continuous film is disrupted and converted into isolated fragments. The latter phenomenon can be described in terms of the hypothesis of the etching of grain boundaries using the energy approach and estimating the critical dihedral angle between the grains. Certain problems of the recrystallisation of thin films, including those based on nitrides, have been examined.[212,223]

Among the properties of films, their hardness has been studied to the greatest extent (as for powdered nanocrystalline materials). It has been demonstrated convincingly in a review[203] that the increased hardness of TiN films can be explained mainly by the small grain size (20–70 nm). Measurement of the hardness of thin films has its characteristic features. It is preferable to use small and even ultrasmall loads (the so called nanoindentation) in order to avoid the influence of the support. Fig. 9 illustrates the influence of the load applied to the indentor on the hardness of Ti–B, Ti–B–N, Ti–B–C, and Ti–B–N–C films obtained by magnetron atomisation (film thickness 3–5 μm; support—solid alloy).[210] Evidently, the hardness remains most stable for loads up to ~0.5 N. The Ti–B–N system has the best parameter. The presence of a phase of the $TiB_{1.6}N_{0.6}$ type has been discovered with the aid of X-ray powder diffraction and Auguer spectroscopy. The hardness of boride films alone is also fairly high, surpassing that of TiB_2 (in the form of the usual polycrystalline material or single crystals) by a factor of approximately 1.5–2. This has also been noted in other investigations.[211,224]

Particularly interesting results have been obtained in the study of multilayer refractory compound-based films.[209,212,225] Fig. 10 illustrates the influence of the number of layers on the hardness of TiN + ZrN, TiN + NbN, and TiN + CrN films (the film thickness was 2 μm in all cases). An appreciable increase in the hardness of

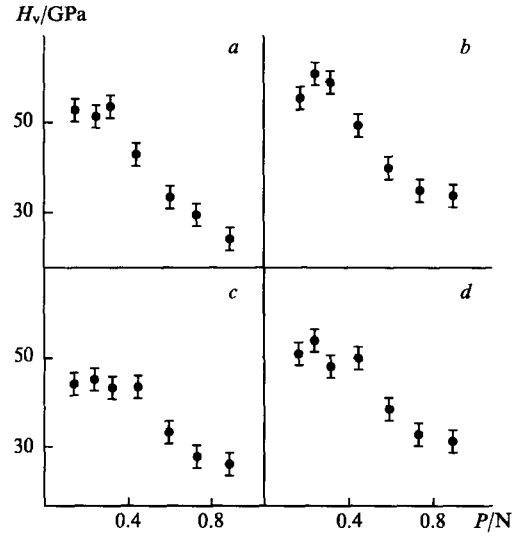


Figure 9. The influence of the load on the hardness of different films: (*a*) Ti–B; (*b*) Ti–B–N; (*c*) Ti–B–C; (*d*) Ti–B–C–N.[210]

the films of the first two systems and its nonmonotonic variation in the TiN–CrN system have been observed. X-Ray powder diffraction revealed the formation of a (Ti,Cr)N solid solution in the latter case, which had not been observed (or had been detected only in the initial stage) for multilayer films of the first two types. Thus the appearance of the solid solution and hence the disappearance of the interfaces with increase in grain size is accompanied by a decrease in the hardness parameters. The strengthening effect due to formation of the solid solution is less significant than the influence of the interfaces on the recrystallisation and the retention of the nanocrystalline structure.

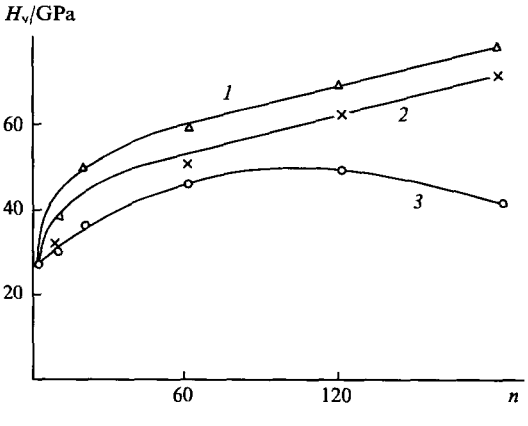


Figure 10. The influence of the number of layers (n) on the hardness of the films:[225] (*1*) TiN–NbN; (*2*) TiN–ZrN; (*3*) TiN–CrN.

Available information about other properties of films based on nanocrystalline refractory compounds is limited to data on the electrical resistance[203] and elastic characteristics[226] of mainly nitride films. In particular, the considerable influence of oxygen on the electrical resistance of TiN, which may vary in the range from 10^4 to ~ 20 $\mu\Omega$ cm, has been noted. In this connection, the precise identification of the role of grain boundaries as one of the factors governing the scattering of carriers (together with structural vacancies, lattice distortions, etc.) is by no means a trivial problem. The deviations from stoichiometry also greatly influence the modulus of elasticity.[226] Several studies using scanning and transmission electron miscroscopy combined with microdiffraction have been devoted to the morphological features and the dislocational structure of W–C–(Co),[227] Ti–N and Ti–B–N,[228] TiN, NbN, VN, and (Ti, Nb)N,[229] TiC + TiB_2,[230] etc. films. However, it is thought that this is only the beginning and systematic studies are still a matter for the future.

V. Conclusion

It is seen from the foregoing that only the first steps have been taken in the study of the properties of nanocrystalline refractory compounds in powder and film form. The amount of information obtained is much smaller than that on nanocrystalline metals.[6–8] It is also smaller than the amount of information available on ultradisperse powders.

The possible applications of nanocrystalline refractory compounds, apart from the materials of the hexanit type based on boron nitride and ultradisperse powders added to the usual powders (see, for example, Refs 231–233), include the technology of the preparation of nanocrystalline WC + Co solid alloys[64] with a high hardness and wear resistance (Table 7) for the manufacture of microtomes and other suitable devices. On the one hand, bearing in mind the high hardness parameters of nanocrystalline metals and intermetallic compounds as well as films, one may hope for the creation of new ultrahard materials based on nanocrystalline refractory compounds. On the other hand, the small grain size of these materials increases significantly their capacity for deformation and the development of ultraplastic compositions based on brittle refractory compounds becomes entirely realistic. The possible temperature of the hot pressing of such materials (1200–1400 °C) is technically entirely acceptable.

Promising applications of nanocrystalline refractory compounds such as preparation of highly selective filters (with fine 5–20 nm filtration apertures) and ion-conducting membranes (in fuel cells and oxygen sensors), the formation of solid-phase junctions between ceramic components, and finally their use for a significant reduction of the sintering temperature have been noted in a review.[165] New possible applications of nanocrystalline refractory compounds in catalysis must be added to the above list.

There is no doubt that the effectiveness of the above materials for particular applied purposes depends significantly on further progress in the study of the methods of preparation of nanocrystalline materials and of the establishment of their properties.

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