Russian Chemical Reviews **74** (12) 1061 – 1072 (2005) © 2005 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2005v074n12ABEH001202

Nanomaterials based on high-melting carbides, nitrides and borides

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Abstract. Methods for preparation of high-melting carbides, nitrides and borides in the form of ultradisperse powders, nanotubes, nanowires, and nanoporous and compact nanostructured materials are considered. Information concerning the structure, physicochemical and physicomechanical properties and application fields of these objects are presented. Prospects for the use of nanomaterials based on high-melting compounds are discussed. The bibliography includes 161 references.

I. Introduction

Carbides, nitrides and borides of various elements are characterised by high values of melting temperatures, hardness, strength, elasticity, chemical passivity and a broad spectrum of electrical properties. This predetermines the use of these compounds in mechanical engineering, electronics, power engineering, chemical industry and other fields of technology. Recently, interest in high-melting compounds has increased in connection with the design of nanostructured materials (from this point on they are called nanomaterials). Nanostructuring is responsible for significant changes in the physicomechanical, physicochemical and biological properties and, correspondingly, for unique operating characteristics of nanomaterials. A characteristic feature of the structure of nanomaterials is the presence of grains (or phase inclusions and pores) of size less than 100 nm. This limit is not a strong physicochemical or physicomechanical criterion and was chosen conditionally.

The state-of-the-art in the field of research on nanocrystalline high-melting compounds was first analysed [1, 2] by the author of this review a decade ago. It is of interest to revise the situation now. More than thirty review articles reported in the last decade (see, *e.g.*, Refs 3 – 36) indicate that research in the field is topical. They are more or less concerned with problems in nanocrystalline high-melting compounds. However, additional analysis of the data available is required. In this review the emphasis is placed on recent information on the synthesis and properties of nanopowders, compacts and nanofilms based on metal and non-metal carbides, nitrides and borides and their composites; novel species, namely, nanotubes and nanowires are also characterised.

The total number of high-melting carbides, borides and nitrides approaches a hundred (see Ref. 37); however, only a few of them have been well studied. Meeting the condition of nanocrystallinity decreases this number to a total of 15 to 20 binary phases (TiC, ZrC, NbC, WC, VC, TiN, ZrN, NbN, TiB_2, ZrB_2, SiC, B_4C, BN, AlN, Si_3N_4, *etc.*), which will be analysed below. In this review, we left the oxide and intermetallic nanocrystalline high-melting compounds out of consideration. Indeed, a wide variety of compounds in the former group require a separate consideration, while the compounds belonging to the latter group have almost not been studied as yet.

II. Nanopowders.† Nanotubes. Nanowires

1. Silicon carbide and silicon nitride, aluminium nitride, boron carbide and boron nitride

Covalent high-melting materials, such as SiC, Si_3N_4, AlN, B_4C and BN are most often obtained by carbothermal reduction (in particular, in the presence of magnesium),[36, 38, 39] plasma chemical synthesis,[40, 41] pyrolysis of organosilicon and inorganic precursors,[42 – 44] nitridation (including explosion of wires),[45 – 47] sol – gel techniques,[48] self-propagating high-temperature synthesis [36, 49, 50] and laser-assisted synthesis.[51] At present, particular attention is focussed on preparation of complex composite nanopowders of the types Si_3N_4/SiC,[43] TiN/Si_3N_4,[47] AlN/BN (see Ref. 42), *etc.*, and nanopowders with narrow fraction composition (see, *e.g.*, Ref. 51). Various starting compounds for the synthesis of carbides, borides and nitrides and possible strategies of fabrication of silicon carbonitrides and boron nitride have been analysed.[43, 50, 52]

For instance, a Si_3N_4/SiC composite was synthesised from mixtures of the individual compounds necessary for the preparation of SiC and Si_3N_4, from a mixture of polysilane with silicon powder or from a complex compound containing reactive groups, SiH, NH and CH_2CH.[43] Pyrolysis in a nitrogen atmosphere was followed by an X-ray phase analysis (XPA) study, which revealed the formation of composites of desired compositions in all three cases. Monodisperse Si_3N_4/SiC nanopowder was obtained after the Si_3N_4 and carbon (in the form of spherical particles) powders synthesised by heating organosilicon precursors in nitrogen were annealed in argon at 1450 °C.[53] A comparison of different methods of synthesis of BN nanopowder showed that the most

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Received 11 July 2005
Uspekhi Khimii **74** (12) 1163 – 1175 (2005); translated by A M Raevskiy

† Nanopowders (or ultradisperse powders) are powders whose particles are less than 100 nm in size.

efficient method consists of the reduction of B_2O_3 with magnesium in nitrogen atmosphere.[50] MgO particles thus formed play an important role in prevention of the BN [and SiC (see Ref. 39)] particles from further growth; however, the mechanism of the process is still poorly understood. In a general form, combustion in the $B_2O_3-Mg-N_2$ system can be described by the following reaction

$$B_2O_3 + 3\,Mg + N_2 + R = 2\,BN + 3\,MgO + R,$$

where R is the additive precluding the formation of magnesium borides. The semiproduct, BN + MgO, sintered in the course of self-propagating high-temperature synthesis is then chemically dispersed in sulfuric or hydrochloric acid solutions.[50]

β-SiC nanopowder characterised by narrow particle size distribution (15–20 nm) is obtained by laser-assisted synthesis from a silane–acetylene mixture containing diborane (this additive is introduced to form a small amount of boron (~1 mass %), which activates the subsequent sintering of particles).[22,51] For comparison, mention may be made that a conventional SiC nanopowder prepared using this procedure has a much wider particle size distribution (*e.g*, 50 ± 25 nm).[22]

Vapour-phase self-propagating high-temperature synthesis with controllable formation of condensed phases is considered promising for the preparation of nanopowders. However, these reactions, as applied to the synthesis of ultradisperse powders comprising particles of preset size, are still poorly understood.[36]

Often, the synthesis of nanopowders results in X-ray amorphous phases. Analysis of the data listed in Table 1 shows that the temperature affects the phase composition and particle size in the Si_3N_4 powders synthesised from a $SiCl_4 + NH_3$ gaseous mixture in high-frequency plasma. The amorphous phase is quite stable and exists up to ~1500 °C. The particle size increases as a result of grain-coarsening. The results cited [54] can be considered reliable because the grain size was measured using two independent methods, X-ray analysis and transmission electron microscopy (TEM).

Table 1. Change in the phase composition [*c* (vol.%)] and Si_3N_4 particle size (*d* /nm) after annealing.[54]

Phase composition	Before annealing		T = 1350 °C		T = 1500 °C	
	c	*d*	*c*	*d*	*c*	*d*
Amorphous phase	80	30	65	50	20	–
α-Phase	17	35–75	32	50–60	67	95
β-Phase	3	–	3	–	13	95

More complex amorphous high-melting systems such as Si–N–C and Si–N–C–B can be synthesised using organometallic polymers and monomers based on polysilazanes (*e.g*., $-[(Si(Me)R-NH)_n-C(O)NH]-_m$, a polyborazole (of the $[B_3N_3H_4]_n$ type), an oligomer of boron-modified vinylsilazane, *etc*.[55,56] as precursors. Products of thermolysis of these compounds are used for both the preparation of nanopowders (after additional ball milling) and subsequent high-temperature pressure treatment in order to obtain amorphous or nanocrystalline materials.

Information on the synthesis of nanotubes and nanowires of high-melting compounds is scarce at the moment, but the number of studies on the subject is increasing. For instance, the following methods of synthesis of boron nitride nanotubes have been reported: laser ablation (a 1 kW CO_2 laser focussed on a 7.5 mm spot);[57] nitridation of finely disperse boron powder at 1200 °C for 16 h;[58] synthesis involving catalysts (FeB) (see Ref. 59), *etc*. Encapsulation of ZrO_2 and cobalt nanorods inside the BN nanotubes was reported.[60,61] It was pointed out that some methods allow nanotubes to be fabricated in gramme [57] and even kilogramme quantities.[58]

Boron nitride nanowires ~20 nm in diameter and several tens of micrometres long can be formed by the interaction of an $N_2 + NH_3$ vapour mixture with nanoscale iron boride (α-FeB) particles at 1100 °C.[62] At this temperature, aluminium nitride nanowires are synthesised from a mixture of the aluminium and Al_2O_3 powders and carbon nanotubes are obtained, which in this case play the role of not only the reducing agent but also a kind of template that specifies the shape and size of the nanowires.[63] Different methods of synthesis of nanotubes and nanowires (or nanofilaments) based on silicon carbide and silicon nitride have been reported.[64,65] Figure 1 presents the electron micrographs of SiC specimens with different morphologies. Nanowires, nanofilaments, nanoporous materials and SiC nanoparticles were fabricated from a carbonaceous silicon precursor synthesised by the interaction of a phenol-formaldehyde polymer with tetraethoxysilane and treated in a different fashion.[65] However, the stability and reproducibility of the treatment regimes still remain unclear.

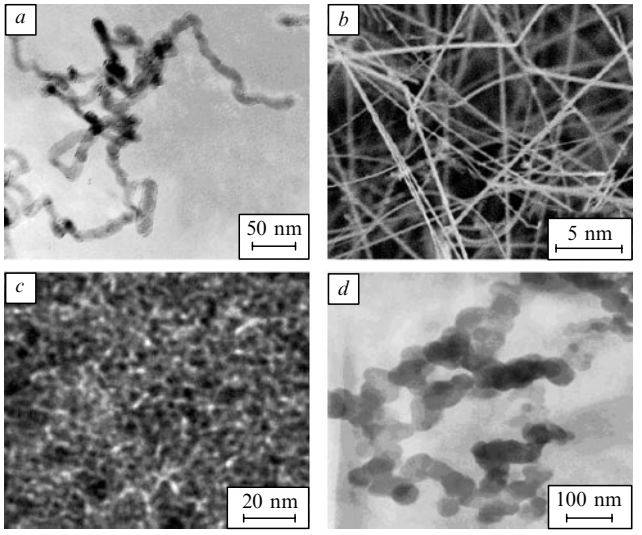


Figure 1. Electron micrographs of carbide silicon specimens with different morphologies:[65]
nanowires (*a*), nanofilaments (*b*), a nanoporous specimen with an average pore size of about 5 nm and a specific surface area of 200 $m^2\,g^{-1}$ (*c*) and nanoparticles (*d*).

2. High-melting transition-metal compounds (WC, TiC, TiN, TiB_2, *etc*.)

Tungsten carbide, as a base for widely used hard alloys, has attracted particular attention of researchers. A method of preparation of WC/Co nanopowders by low-temperature reduction and carbidisation of a mixture of ammonium metatungstate and cobalt chloride in a fluid bed reactor followed by spray drying (this favours good mixing of nanocomponents),[66] which was advertised in a big way in the early 1990s, this did not gain acceptance in industry. This was mainly due to the fact that at present it is impossible to retain the nanostructure in the course of subsequent sintering. Nevertheless, extensive searches for optimum methods of fabrication of WC and WC/Co nanopowders have been carried out with allowance for the general trend towards fabrication of strong, wear-resistant ultrafinely-disperse hard alloys. Doping tungsten carbide with vanadium carbide and with VC–TaC solid solution precludes grain-coarsening in the sintering stage.[67,68] A process involving mechanochemical and plasma chemical syntheses has been reported.[69–74] Micro- and nanopowders of more complex compositions, *e.g*., WC–35% TiC–Co (see Ref. 75) and Ti(C,N)–WC–Ni (see Ref. 76) were prepared by carbothermal reduction and co-milling. It should be kept in mind that nanopowders with particle sizes less

than 100 nm were not obtained by the authors of all the studies cited above;[67–76] often, characterisation of the powders with respect to the impurities and fraction distributions was also incomplete. Usually, the advertising circulars of most of big manufacturers of hard-alloy WC powders [H.C.Starck (Germany), Wolfram BHG (Austria), Dow Chemical Company (USA), *etc.*] indicate a particle size less than 0.2 to 0.3 μm.[68,77,78] Inframat Corporation (IMC, USA) offers the WC and WC–(5%–15%)Co nanopowders characterised by a size 40–80 nm of the carbide grains, which are then agglomerated to form particles with the average size 0.2–0.4 μm.[79] Agglomeration is carried out in order to prepare the charge material to pressing.

Various methods of synthesis of TiN, TiC, TiB_2 nanopowders and related high-melting compounds have been reported. Methods used in addition to the plasma-enhanced and laser-assisted syntheses, carbothermal reduction and conventional ball milling[1,2] mentioned above include self-propagating high-temperature synthesis, mechanochemical synthesis, high-temperature vapour-phase reactions, high-energy ball milling and some others. As in the case of nanopowders of covalent high-melting compounds, the emphasis is placed on the preparation of multicomponent and multicomposition nanoparticles. For instance, nanoparticles of TiN/TiB_2 composite are obtained by high-energy ball milling and mechanochemical synthesis of the starting Ti + TiB_2 mixtures in a nitrogen atmosphere of Ti + BN mixtures in a argon atmosphere.[80–82] A procedure proposed for the preparation of $TiB_2/TiN/Ti(C,N)$ nanocomposites included high-energy ball milling of the starting powders, ($Ti + B_4C$) and (Ti + BN), to give products ($TiC + B_{amorph}$) and ($TiN + B_{amorph}$) and subsequent ball milling of the products to produce TiB_2 following the reaction

$$Ti + B_4C + BN + B_{amorph} \longrightarrow TiC + TiN + TiB_2.$$

The final ball milling step followed by non-isothermal annealing to 1300 °C (at a heating rate of 10 °C/min) produces $TiB_2 + TiN + Ti(C,N)$ nanoparticles of size 30–60 nm, which can be detected by XPA, X-ray analysis and TEM.[83] Methods of synthesis of transition-metal high-melting compounds are characterised in Table 2.

However, in spite of a large number of studies on the synthesis of nanocrystalline high-melting compounds (over 60 publications), in most cases the efficiency of different methods are difficult to compare. The reason is that many important details (impurity content, nanoparticle size distribution, pressing and sintering behaviour of ultradisperse powders, properties of consolidated compacts, *etc.*) are still out of researchers' eyeshot.

3. Selected properties of nanopowders and nanotubes

It should be noted that the particle and crystallite sizes reported in the most representative studies[54,70,74,83,88,91] were obtained by at least two independent methods (*e.g.*, X-ray analysis and TEM). The results of specific surface area measurements and the estimates of the average particle size cannot be considered sufficient without analysing the particle size distribution. This can be explained by the fact that even a small amount of coarse grains can initiate significant grain growth in the course of subsequent sintering and thus favour the disappearance of the nanostructure.

Unfortunately, not all authors of synthetic studies report such characteristics of ultradisperse powders and nanoparticles as the content of impurities (especially, oxygen) and adsorbed gases, interfacial segregations and deviation from stoichiometry. An investigation[99] of WC, NbC, TiC, SiC, Si_3N_4, AlN and TaN nanopowders prepared by plasma chemical synthesis showed that the overall content of oxygen increases as the specific surface area increases, the major contribution to this increase coming from the oxygen-containing gases adsorbed on the surface. Studies of gas evolution in the course of high-vacuum annealing of TiN and Si_3N_4 nanopowders showed that the vapour phase mainly contains CO, nitrogen, water vapour and hydrogen and revealed two gas evolution maxima at ~300 and ~600 °C.[1,4,100] The distribution of impurities and gases across the surface of the Si_3N_4 powder particles has been the subject of a detailed review.[100] The effect of annealing on the content of gases in this nanopowder (average particle size was about 15 nm) before and after annealing at 1200 °C (1 h) can be followed using the data listed below (both gas and water vapour content is given in mass %):

Powder	V/cm^3 g^{-1}	CO	H_2	N_2	H_2O
Starting	625	59	11	21	9
Annealed	89	79	7	10	4

(V is the reduced total volume of the gases).[100]

The quantum-chemical methods suitable for prediction of the adsorption of gases (water vapours, ammonia, *etc.*) on the Si_3N_4 surface have been considered.[101] Changes of the surface charge density in the interaction of ultradisperse Si_3N_4 powder with nitrate solutions were analysed.[102]

The properties of nanotubes, nanowires and nanofilaments of high-melting compounds have become the subject of more and more extensive research (see, *e.g.*, Refs 103–106), but a considerable body of data available require an additional substantiation. Studies on boron nitride hold a leading position; in particular, it was revealed that the bandgap of the BN nanotubes is ~5.5 eV, being independent of the nanotube diameter. As to the elastic characteristics, there are at least two different results for the elastic modulus, $E = 1.22 \pm 0.24$ GPa,[59] which exceeds all the known E values for nanofilaments, and $E = 722$ GPa.[103] Methods of synthesis and the properties of BN, BCN, SiC, AlN, Si_3N_4, TiC and BC_x nanowires have been reviewed.[106]

Table 2. Methods of preparation of high-melting compound nanopowders.

Compound	Nanoparticle size /nm	Method of preparation	Ref.
TiN	5–10	sodium-thermal reduction in nitrogen atmosphere	84
ZrN	30–100	magnesium-thermal reduction in nitrogen atmosphere	85
TiC	–	self-propagating high-temperature synthesis with magnesium additives	86
TaC	30–55	self-propagating high-temperature synthesis in electric field	87
ZrC	< 500 (see [a])	high-energy mechanochemical synthesis	88
TiB_2		vapour-phase synthesis	
	< 15	$TiCl_4 + BCl_4$	89
	15–70	$TiCl_4 + NaBH_4$	90
ZrB_2	15–70	vapour-phase synthesis $ZrCl_4 + NaBH_4$	91
HfB_2	15–70	vapour-phase synthesis $HfCl_4 + NaBH_4$	92
NbB_2	40–50	carbothermal reduction	93
$VC_{0.875}$	~1000 (see [b])	carbothermal reduction with ageing	94, 95
WC	50–200	self-propagating high-temperature synthesis	96
TiC	75	carbothermal reduction involving titania	97
	30–60	as a result of $TiCl_4 + CaC_2$ interaction at 550 °C	98

[a] Particles are comprised of 5-nm nanograins.
[b] Particles are comprised of nanocrystallites of size 400–600 nm and thickness 15–20 nm.

III. Consolidated compacts

1. Consolidation processes: general

Conventional regimes of pressing and sintering of compounds are almost inapplicable to nanopowders.[1,2] No significant densification occurs even in the case of high-pressure pressing (at >1 GPa), because the compactibility appreciably decreases due to the developed surface and strong intergrain friction forces.[107] The residual porosity of the TiN and Si_3N_4 nanopowders pressed at 7–9 GPa exceeded 10%–15%; magnetic-pulse pressing of the TiN powder (particle size 70–80 nm) at pressures to 2–3 GPa also did not lead to significant decrease in porosity.[108,109] At the same time further sintering of powders is usually accompanied by intense grain growth due to recrystallisation occurring at high temperatures. As a result, the nanostructure disappears and the physicochemical and mechanical characteristics are not improved.

At present, there are a number of methods of consolidation of powder nano-objects, which make it possible to prepare materials with the desired nanostructure. These are high-pressure treatment at relatively moderate temperatures,[4,5,110] non-isothermal sintering,[34,111] reactive hot-pressing,[112] arc-discharge (plasma-assisted) sintering,[88,113] short-term liquid-phase sintering,[66] sintering activated by phase transitions [114] and some others. Here, recrystallisation in the course of sintering and, correspondingly, grain growth are precluded due to either lowering the temperature and shortening the duration of sintering under high pressure,[4,5,110] activation of diffusion,[88,112–114] or optimisation of the shrinkage and recrystallisation processes in different temperature intervals.[34,111] Methods combining mechanochemical synthesis and consolidation deserve attention because of considerable promise for preparation of TiB_2/TiN-type nanocomposite materials.[81,112]

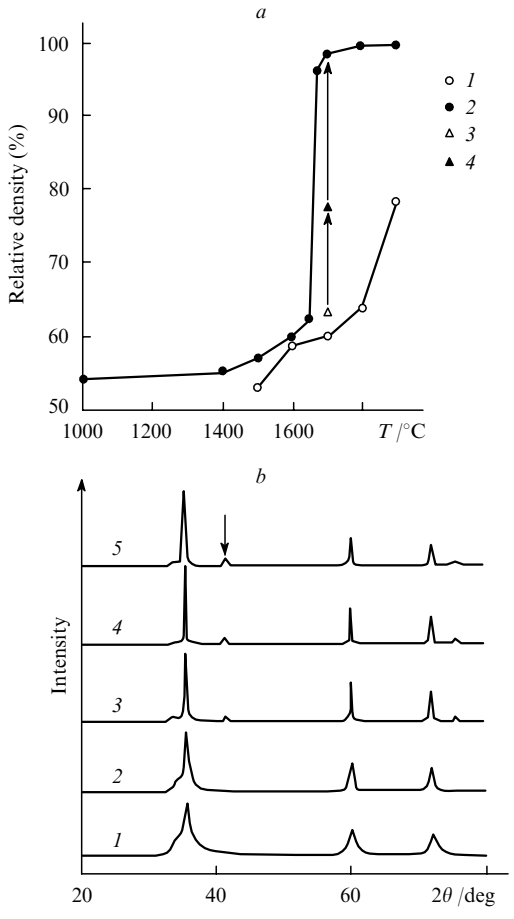


Figure 2. Relative densities of SiC nanopowders plotted *vs.* sintering temperature (*a*) and X-ray diffraction patterns of commercially available SiC powder and specimens sintered at different temperatures (*b*);[114]
(*a*): commercially available SiC powder (*1*); powder obtained by mechanochemical synthesis (*2*); the same powder sintered at 1700 °C for 0 (*3*) and 2 min (*4*). The duration of heating to corresponding sintering temperatures was the same for all specimens. The sintering time of specimens *1* and *2* was 10 min;
(*b*): $T = 1400$ (*1*), 1600 (*2*), 1700 (*3*), 1800°C (*4*); commercially available powder (*5*).

The effect of the disorder–order transition on the sintering of silicon carbide is quite demonstrative.[114] The effect of temperature on the change (in the course of sintering) in the relative density of the SiC nanopowders prepared by mechanochemical synthesis under intense milling (grain size 5 to 10 nm, agglomeration into larger grains of size 100–150 nm) is illustrated by Fig. 2. For comparison, we present the data on the sintering of commercially available SiC nanopowder (grain size of about 30 nm). A dramatic increase in the relative density at $\sim$1700 °C was interpreted as a consequence of structural ordering in the ball milling synthesised SiC, which was confirmed by X-ray analysis data, namely, sharper reflections and the appearance of a peak at $2\theta \sim 40$ °. Besides, an analogy between the X-ray diffraction patterns of the commercially available SiC powder and the carbide sintered at 1800 °C is obvious (see the X-ray diffraction patterns in Fig. 2).

However, in practice the methods listed above always lead to nanomaterials with a grain size of at least about 30 nm and low residual porosity (at least $\sim$2%), which of course affects the physicomechanical and physicochemical properties.

The laws of sintering of WC nanopowders are of particular interest (see, *e.g.*, Refs 66–68, 4–78, 115) because of the wide use of this high-melting compound. It is known that the VC, Cr_3C_2 and TaC additives act as inhibitors of grain growth in sintering of hard alloys. A dilatometric study of shrinkage of conventional WC + 7.8% Co + 0.7% VC powders and nanopowders of the same composition showed that shrinkage of the latter is carried out in the solid phase while that of the coarse-grain powders occurs under conditions of liquid-phase sintering.[115]

A method of synthesis of nanoporous materials based on SiC by reactive sintering of highly disperse silicon–colloidal graphite (Si + 30% C) mixtures at relatively moderate temperatures (1100–1200 °C) has been reported.[116] This technique permits preparation of micro- and nanomaterials with porosities ranging between 50% and 65% and a specific surface area of the order of 30 to 40 $m^2\ g^{-1}$; the calculated effective pore size in the materials is $\sim$20 nm and the maximum pore size is at most 300 nm.

2. Structure and properties

The most widely used methods of studying the structure of nanomaterials include TEM, scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray analysis. High resolution of the electron microscopy methods is necessary for the disclosure of such peculiar features as the presence of very small particles, pores and grains (of size less than 10–20 nm), observation of dislocations and establishment of the structure of interfaces (grain boundaries and phase boundaries) and the character of breakdown of nanostructures (see, *e.g.*, Refs 117–119). Figure 3 presents a high-resolution TEM image of a TiN film.[117] A characteristic strip-like structure can be seen, which corresponds to the atomic planes, and a number of intracrystallite edge dislocations (the possibility for them to exist in the nanomaterials based on high-melting compounds was confirmed by the estimates [117] made with allowance for the concepts developed in another study [120]).

A bright-field electron micrograph of the structure of hot pressed ZrC nanopowders obtained by mechanochemical synthesis (crystallite size is about 5 nm, agglomerate size of nearly 3 μm) and the grain size distribution are shown in Fig. 4.[88] As can be seen, hot pressing at relatively moderate temperatures is accompanied by intense grain growth. The specimens obtained were characterised by an average grain size of nearly 95 nm, which

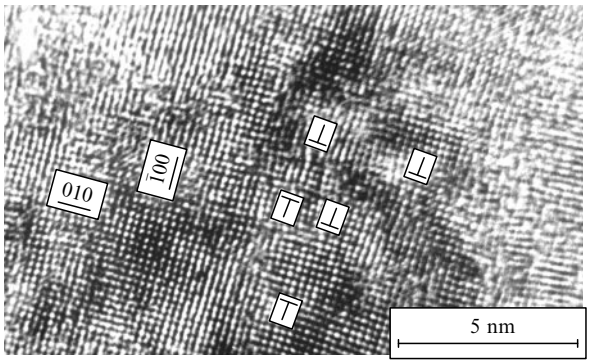


Figure 3. HRTEM image of TiN nanostructure obtained in the direct resolution mode.[117]
Shown are the edge dislocations (⊥).

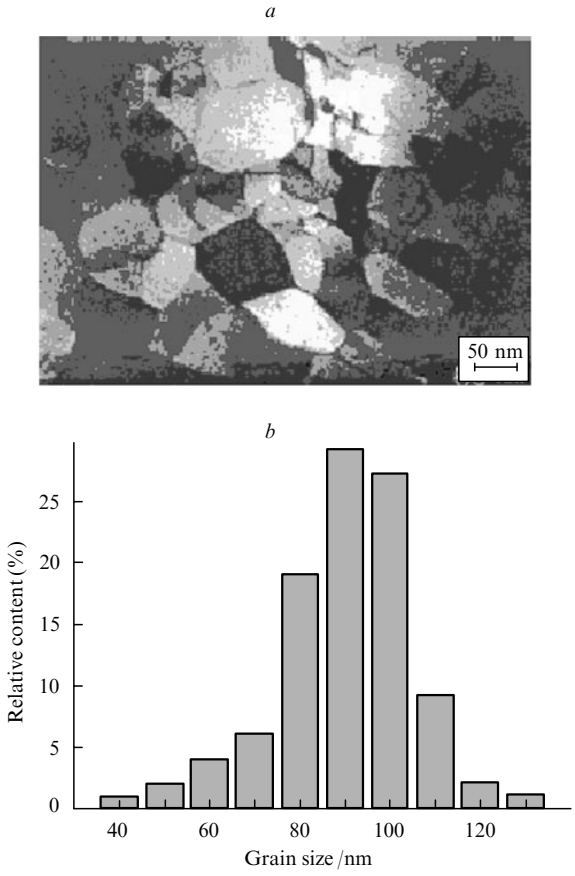


Figure 4. Bright-field electron micrograph of nanocrystalline zirconium carbide obtained by hot pressing at 1300 °C and a pressure of 1.5 GPa (*a*) and the grain size distribution (*b*).[88]

approaches the upper size limit for nanostructures, and a rather broad grain size distribution.

Electron energy dispersive analysis of the TEM and SEM images makes it possible to determine the chemical composition, but the most informative method of investigation of nanomaterials is electron energy loss spectroscopy, which provides information on the interfacial segregations. However, the necessary equipment is available in a few research laboratories and information on impurity segregations on grain boundaries of high-melting compounds is restricted to the data for silicon nitride and to some extent for WC – Co hard alloys.[100, 121]

Hardness is the best studied characteristic of nanomaterials based on high-melting compounds. This can be explained by the availability of measuring instruments and relative ease of specimen preparation. Knowledge of hardness is important in manufactiring of tool materials. Data on the hardness of nanocrystalline high-melting compounds have been the subject of several review articles (see, *e.g.*, Refs 9, 15, 21, 23, 30, 31, 122). These results, as well as the new data [43, 67, 69, 77, 78, 88] showed that the hardnesses of nanocrystalline titanium nitride [110] and tungsten carbide [123] (~30 and ~40 GPa, respectively) are 1.5 – 2 times higher than those of conventional coarse-grained materials only if the specimens were thoroughly prepared and well-characterised. The hardnesses of nanocrystalline SiC,‡ Si_3N_4, ZrC, TiC, *etc.* specimens were comparable with those of polycrystals and single crystals, which can be explained by porosity and poorly developed nanostructures. For instance, the hardness of the ZrC specimens with the morphology shown in Fig. 4 *a* was ~27 GPa,[88] while the corresponding polycrystals and single crystals showed 24 to 26 GPa.[37] Thus, methods of fabrication of certain consolidated nanomaterials based on high-melting compounds are still far from being perfect.

The effect of the relative density on the microhardness and elastic modulus of the specimens prepared from TiN nanopowders of different dispersity can be followed using the data shown in Fig. 5. As can be seen, hardness depends on the porosity and grain size, while the elastic modulus depends only on porosity in this range of grain sizes. From simple estimates it follows that a decrease in the elastic modulus of nanomaterials can be expected at grain sizes less than 10 nm, where the proportion of interfaces (grain boundaries) exceeds 20% of the total volume.

The dependences of hardness (H_V) and elastic modulus on porosity ϑ ($\vartheta = 1-\tau$, where τ is the relative density) have the form

$$H_V = H_{V_c}(1-4.7\,\vartheta) \text{ for } d = 70-80 \text{ nm},$$

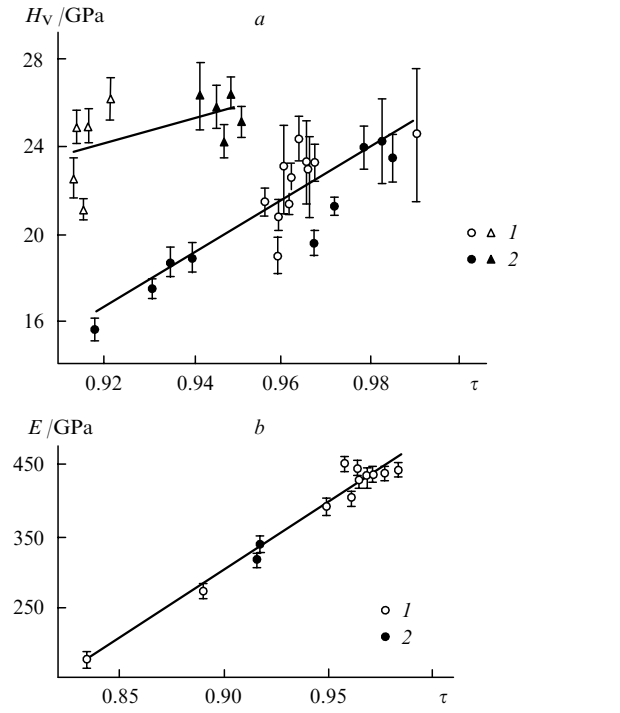


Figure 5. Microhardness (*a*) and elastic modulus (*b*) plotted *vs.* relative density (τ) of TiN nanocrystalline specimens obtained at 4 – 7.7 GPa and T = 1200 – 1400 °C from ultradisperse powders with the particle size 16 – 18 (*1*) and 70 – 80 nm (*2*).[110] The open and solid circles denote the results of two series of experiments.

‡ Even greater hardness, 32 – 41.5 GPa, was reported [124] for superstoichiometric silicon carbide specimens (grain size ~330 nm) obtained at high pressures and high temperatures.

$H_V = H_{V_c}(1-2.1\vartheta)$ for $d = 16-18$ nm,

$E = E_c(1-3.9\vartheta)$,

where H_{V_c} and E_c are the hardness and the elastic modulus for the compacted state ($\vartheta = 0$, $\tau = 1$), which are respectively equal to 26.2 ($d = 70-80$ nm), 28.8 ($d = 16-18$ nm) and 490 GPa (d is the average initial particle size of the TiN nanopowder).

The linear character of the plots shown in Fig. 5 is typical of many powder materials characterised by narrow porosity ranges.[37]

In discussing the properties of nanomaterials one should take into account not only the role of the nanostructure but also the impurity content and the possibility of interfacial impurity segregations; porosity, residual stress, nonequilibrium phases and structural vacancies (deviation from stoichiometry); interface states and many other factors (as applied to hardness, these are, *e.g.*, the measuring technique, load magnitude and surface roughness). Taken altogether, this makes the interpretation of the properties of nanomaterials a complicated task and the results reported should be accompanied by detailed discussion and conclusions should be thoroughly substantiated.§

A fracture toughness study of nanostructured materials based on high-melting compounds revealed an intercrystallite character of crack propagation. This can be confirmed by the micrographs of the TiN fracture surface and the crack (Fig. 6).[10] As can be seen, the fracture occurs at grain boundaries. The intercrystallite character of fractures provides an explanation for the fact that such an important characteristic of brittle single-phase materials as the crack resistance, remains almost unchanged as the grain size decreases.[10]

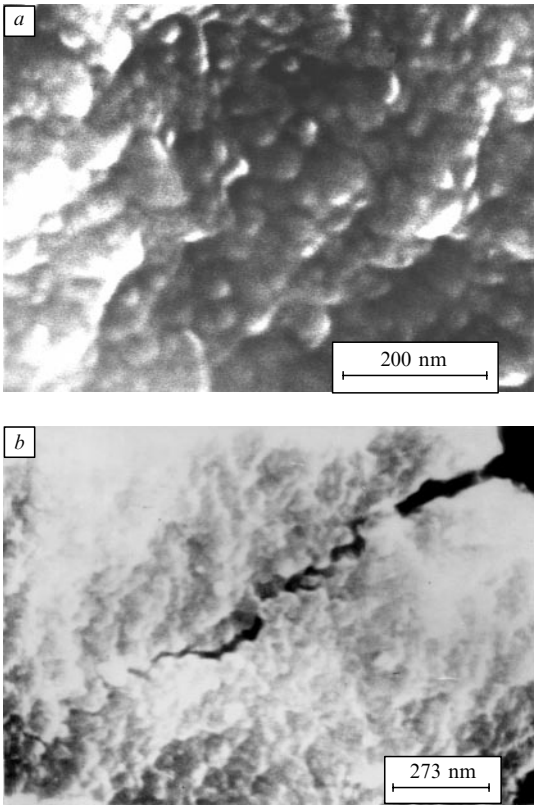


Figure 6. SEM micrographs of the surface of nanocrystalline TiN.[10] Fracture surface (*a*) and crack propagation (*b*).

Information on the high-temperature strength of nanostructured high-melting compounds is scarce. The possibility for superplasticity (high creep rates) to occur in microcrystalline composites of the Si_3N_4/TiB_2 type at 1600 °C was pointed out.[125] At the same time extremely low creep rates were found in Si_3N_4/SiC nanocomposites (see Ref. 126) and in amorphous ternary (Si/C/N) and quaternary (Si/B/C/N) specimens synthesised by pyrolysis of organosilicon polymers.[56]

The effect of the TiN content on the resistivity (ρ) of Si_3N_4/TiN composite (grain size 100–600 nm) is illustrated in Fig. 7.[47] As the TiN concentration in this composite changes, the ρ value changes by nearly fifteen orders of magnitude, from the values characteristic of dielectrics (Si_3N_4) to those typical of metals and metal-like compounds (TiN), the latter being observed at the TiN concentrations of less than 20 vol.%.

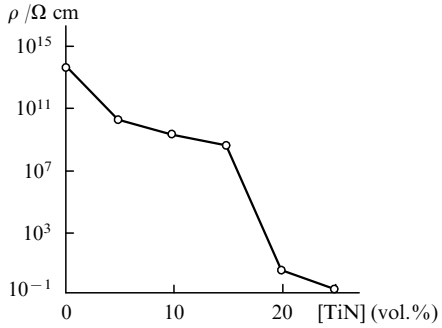


Figure 7. Resistivity of Si_3N_4 – TiN system plotted *vs.* its composition.[47]

Numerous interfaces in nanomaterials produce natural barriers to the motion of charge carriers. Therefore, a decrease in the grain size is accompanied by a decrease in the resistivity and thermal conductivity. A good example of the latter is provided by SiC.[22] At room temperature, the thermal conductivities of nanocrystalline (grain size about 70 nm) and coarse-grained SiC (grain size 3 to 5 μm) specimens differed by a factor of 8. At 1400 °C, only a twofold difference was observed, due to the change in the contribution of phonon–phonon scattering.

Numerous interfaces in nanomaterials can favour enhancement of their radiation stability due to the increase in the number of escape channels of radiation-induced defects and, hence, lower degree of swelling of specimen.[22]

An interesting size effect related to the superconducting properties was found in a number of high-melting compounds. The effect of the particle size of nanopowders on the change in the critical magnetic field in TiN, NbN, VN, Nb (N,C) and V_3Si,[127] which seems to be related to the evolution of the phonon spectrum of nanoparticles, is illustrated in Fig. 8.

However, the physical, mechanical and physicochemical properties of nanomaterials based on high-melting compounds are still poorly understood. Owing to limited quantities of well-characterised specimens, studies of the size effects (*e.g.*, evaluation of the familiar Hall–Petch relation for strength and hardness) are in the early stage of development. Data on the constitutional diagrams of these materials in the nanocrystalline state are almost unavailable. This important information is limited to the old estimates obtained in the simplest regular approximation for the ZrC – C, TiN – AlN, TiN – TiB_2 and TiC – TiB_2 systems.[128–130]

§ For instance, the microhardness values of 60–80 GPa reported [95] for the specimens with ~30% porosity, sintered from vanadium carbide ($VC_{0.875}$) nanopowders at 1700 °C cast some doubt. Extrapolation of these data to zero porosity leads to a microhardness of about 200 GPa, which seems to be unrealistic (the hardness of diamond is ~100 GPa).

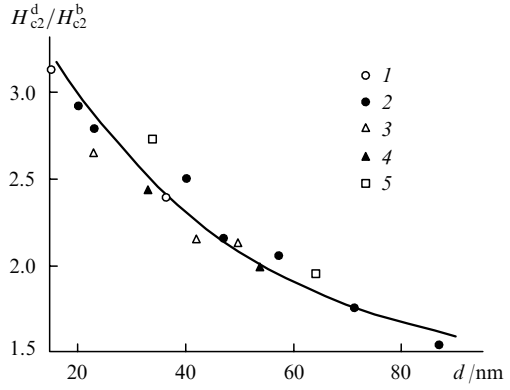


Figure 8. Critical magnetic field plotted *vs.* grain size of high-melting compounds obtained by plasma chemical synthesis.[127]
H_{c2}^{d} is the second critical field strength for nanopowders and H_{c2}^{b} is the same for the coarse-grained specimen.
Nb(N, C) (*1*), TiN (*2*), NbN (*3*), V_3Si (*5*) and VN (*5*).

IV. Nanostructured films

1. Methods of fabrication: general

General information concerning physical and chemical methods of fabrication of films and coatings has been reported in a number of review articles (see, *e.g.*, Refs 1–5, 9, 15, 30, 31). Division of methods into physical and chemical ones is conditional because chemical reactions play a significant role in a number of physical methods (*e.g.*, physical deposition of films) while chemical methods involve many physical phenomena. The most widely used methods of fabrication of nanostructured films belong to the so-called physical deposition techniques, namely, reactive and non-reactive magnetron sputtering (high-frequency and d.c. modes), cathode (or arc-ion) sputtering, laser ablation and ion beam treatment of surface. High-temperature chemical deposition methods are employed more rarely. Coatings several tens of micrometres thick are fabricated using gas-thermal (plasma and detonation) deposition. Therefore, a variety of technological procedures for fabrication of nanostructured films and coatings are available; many of them have found large-scale applications. For instance, very hard multilayered (Ti,Al,Y)N/VN nitride films used as wear-resistant coatings for metal-working instruments are manufactured on large-scale high-vacuum multicathode magnetron sputtering equipment.[30]

The use of an additional magnetic field in the course of deposition permits efficient control of the crystallite sizes and the crystallite size distribution (Table 3).[131, 132] Mention may be made that nanostructured films can have much smaller grain sizes compared to powder compacts. The lattice constant of a titanium nitride film with the NaCl-type structure is ~0.42 nm; the crystallite of size ~2 nm contains only $\sim 5^3 = 125$ unit cells, *i.e.*, such films can be treated as cluster-consolidated materials.[133]

Table 3. Average crystallites size (nm) in nitride/boride films prepared by non-reactive magnetron sputtering with ~400 Œ external magnetic field switched off and on.[131, 132]

Target	Field off	Field on
TiB_2	3.6 ± 1.8	3.3 ± 1.1
75 TiB_2 + 25 TiN	2.3 ± 1.1	not determined
50 TiB_2 + 50 TiN	2.9 ± 1.5	1.8 ± 0.3
25 TiB_2 + 75 TiN	5.9 ± 4.0	6.5 ± 2.5
TiN	29 ± 15	8.8 ± 2.2

2. Investigation of the structure and composition

In addition to the methods of investigation of the structure of powders mentioned above (TEM, SEM, XPA, X-ray analysis and AFM), films are also studied by X-ray photoelectron spectroscopy, Auger electron spectroscopy (AES), Rutherford backscattering spectroscopy, positron annihilation spectroscopy, secondary ion mass spectrometry, local electron diffraction, *etc*.

Table 4 lists the characteristics of some films we have studied.[134] The dark-field TEM image of the structure of the film fabricated in regime IV and the crystallite size distribution are shown in Fig. 9.[133] The size distribution in the case of magnetic field assisted deposition is shifted towards smaller sizes and becomes narrower (see Table 3). Approximate chemical formulae listed in Table 4 were calculated based on the AES data. Table 4 shows that the films deposited can be both superstoichiometric (regimes IV–VI for theTiN-based films) and understoichiometric (regimes I–III for the TiB_2-based films); some films were amorphous after deposition. Considerable attention should be given to high solubility of components in the metallic and non-metallic sublattices. For instance, an equilibrium pseudobinary system TiB_2–TiN is characterised by low mutual solubility of the components at room temperature.[37] However, in the film state the degree of mutual solubility of the boride and nitride becomes high (regimes III–V lead to single-phase composites) due to highly non-equilibrium character of the films deposited.

Thus, the properties of nanostructured films should be analysed with allowance for the possibility of high solubility of metallic and non-metallic components and for the non-stoichiometry of specimens, which is much higher than that of coarse-grained specimens of high-melting compounds. Yet another feature of such films is that their deposition and subsequent cooling to room temperature is accompanied by production of

Table 4. Composition and structures of films (1–3 μm thick) plated in the d.c. regime (I) and in high-frequency regimes (II–X).[134]

Target	Sputtering regime	Approximate formula	Grain size /nm	Type of structure	Lattice constant /nm	
					a	*c*
TiB_2	I	$Ti(B_{0.73}N_{0.2}O_{0.05}C_{0.02})_{1.56}$	4–8	AlB_2	0.3060	0.3201
TiB_2	II	$Ti(B_{0.69}N_{0.24}O_{0.04}C_{0.03})_{1.64}$	3.6 ± 1.8	AlB_2	0.3083	0.3246
TiB_2/25 TiN	III	$Ti(B_{0.56}N_{0.29}O_{0.05}C_{0.1})_{1.32}$	2.3 ± 1.1	AlB_2	0.3005	0.3263
TiB_2/50 TiN	IV	$Ti(B_{0.34}N_{0.49}O_{0.12}C_{0.05})_{1.49}$	2.9 ± 1.5	NaCl	~0.42	
TiB_2/75 TiN	V	not determined	5.9 ± 4.0	NaCl	0.4307	
TiN	VI	$Ti(N_{0.6}O_{0.2}C_{0.2})_{1.58}$	29 ± 15	NaCl	0.4292	
AlN	VII	$Al\ (N_{0.78}O_{0.15}C_{0.07})_{0.98}$	5–10	ZnS	not determined	not determined
AlN/50 TiN	VIII	see [a]	3–10	NaCl	"	
AlN/50 TiB_2	IX	not determined			amorphous film	
AlN/20 SiC/10 TiB_2	X	"			"	

[a] Approximate formula $(Ti_{0.55}Al_{0.37}Fe_{0.08})(N_{0.73}O_{0.11}C_{0.16})_{1.075}$.

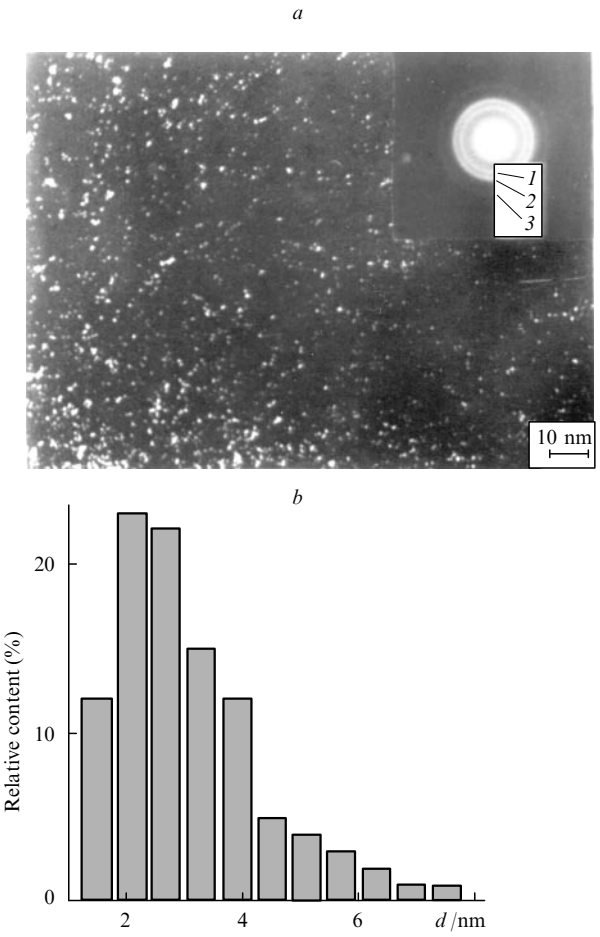


Figure 9. Dark-field TEM image of a Ti(B,N) film (regime IV, see Table 4) (*a*) and the grain size distribution (*b*).[133]
Reflection: 111 (*1*), 200 (*2*) and 220 (*3*).

large residual stress (most often, compressive stress), which can be as high as several GPa;[9] this also affects the film properties.

In the text above we listed not all factors responsible for the properties of nanostructured films of high-melting compounds. But even a brief look at them revealed the need for thorough and comprehensive studies of such films by independent methods. Unfortunately, it does not always happen.

3. Properties of films

Complete information on the hardness, resistivity and elastic characteristics of single- and multilayered films of high-melting carbides, borides and nitrides is available from review articles.[9, 23] These data can be complemented with the following results.

The record hardness values (80 – 100 GPa) were obtained for (Ti, Si)N films fabricated using plasma-assisted chemical deposition.[15] However, these results appeared to be poorly reproducible. This was explained[135] by possible film degradation caused by impurities, in particular, oxygen.

High hardnesses (50 to 70 GPa) of single-layer films based on TiB_2 and B_4C and of multilayered (Ti,Al)N/VN, TiN/TiB_2 and ZrN/ZrB_2 films have been reported (see, *e.g.*, Refs 9, 15, 29, 30, 131 – 138). Earlier,[23, 122] it was pointed out that progress made in the field of fabrication of films of novel ultrahard materials based on nanostructured high-melting compounds is more pronounced compared to fabrication of consolidated powder compacts. This is due to the possibility of forming nanostructures with a crystallite size of less than 10 nm in films.

Layered nanocomposites of the TiC/$C_{amorphous}$ and WC/$C_{amorphous}$ types, characterised by low and stable friction coefficients and high wear resistance, have been developed.[139] These properties are of paramount importance for fabrication of elements of highly efficient friction units used in various fields of technology.

Coatings with a hardness of about 10.6 GPa (under a load of 300 g) were fabricated by gas-thermal (plasma-assisted) deposition of nanopowders of WC – Co hard alloys agglomerated into grains of size 0.3 – 0.5 μm.[140]

High-resolution SEM and AFM studies of the film behaviour revealed two types of deformation, homogeneous and inhomogeneous.[10, 117, 118, 141, 142] The former is mainly observed in films having a columnar structure, *e.g.*, TiN films. Localised inhomogeneous deformation is accompanied by indentation, which is particularly pronounced in the case of TiB_2 films.

As mentioned above, the use of an additional external magnetic field in the course of sputtering[131, 132] permits fabrication of films with different grain size, which enhances the possibilities of studying the size effects in nanomaterials. It is also noteworthy that the magnetic field has a strong effect on the roughness of film surface (roughness appreciably decreases) and affects the properties of not only the nanocrystalline but also amorphous films, which can be seen by taking films of boron carbide based nanomaterials as examples (Table 5).

Table 5. Average crystallite sizes and microhardness values of films of boron carbide based materials with external magnetic field switched off (*I*) and on (*II*).

Target	Average crystallite size /nm		Microhardness H_0 /GPa	
	I	*II*	*I*	*II*
TiB_2	3.6 ± 1.8	3.3 ± 1.1	32 – 39	42 – 48
75% TiB_2/25% B_4C	8.5 ± 4	2.9 ± 0.3	40 – 46	54 – 58
50% TiB_2/50% B_4C	amorphous films		44 – 50	60 – 68
25% TiB_2/75% B_4C	the same		44 – 50	62 – 71
B_4C	"		42 – 50	48 – 56

A study of the galvanomagmetic and electrical properties of TiN films with grain sizes of 29 ± 15 and 8.8 ± 2.2 nm showed that only the charge carrier (electron) mobility and, correspondingly, the conductivity of these films changes, while the charge carrier concentration remains unchanged.[143] These results also indicate a possible absence of large oxygen and carbon segregations at grain boundaries in these films.

A study of high-temperature oxidation of AlN – TiN, AlN – TiB_2 and AlN – SiC – TiB_2 films revealed high thermal stabilities and scale resistances, which exceed those of coarse-grained bulk materials.[144] The results obtained by differential thermal (DTA) and thermogravimetric (TG) analyses at temperatures below 1500°C are presented in Fig. 10. AlN – SiC – TiB_2 films having a self-reinforced nanostructure and aluminium-enriched surface were found to show the highest scale resistance.

Nanostructured boride films and films of some other high-melting compounds are thermally stable up to 1000 – 1100 °C.[26, 132 – 136, 144 – 147] Changes in the microhardness of multilayered TiN/AlN films after annealing in argon atmosphere for 2 h can be followed using the data presented in Fig. 11.[144] As can be seen, films having thinner individual layers are more thermally stable.

An interesting method of improving the thermal stability of multicomponent nanocrystalline high-melting compounds involves the use of spinodal decomposition accompanied by the formation of ultradisperse thermally stable binary structures. The temperature dependences of the microhardness of the coatings based on titanium nitride and zirconium nitride (systems TiN – ZrN and TiN – AlN in amorphous Si_3N_4 matrix) are

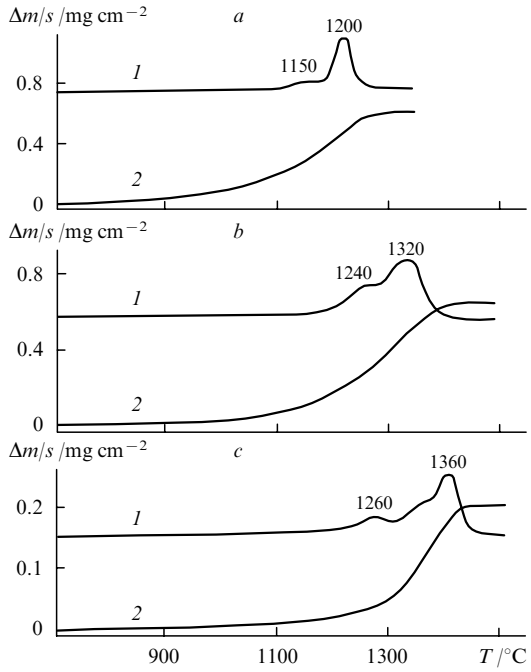


Figure 10. DTA (*1*) and TG (*2*) curves for AlN – TiN (*a*), AlN – TiB_2 (*b*) and AlN – TiB_2 – SiC (*c*) films.[143]

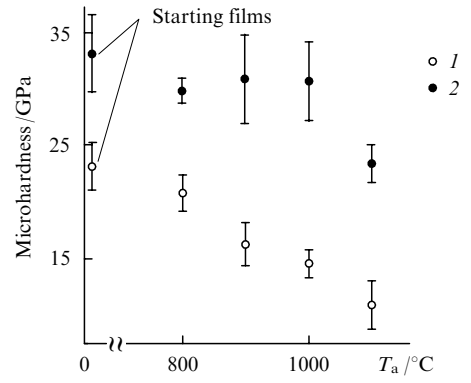


Figure 11. Effect of annealing temperature on microhardness of multilayered TiN/AlN films (overall thickness is 300 nm).[144]
Thickness of individual layers is 16 (*1*) and 2.9 nm (*2*).

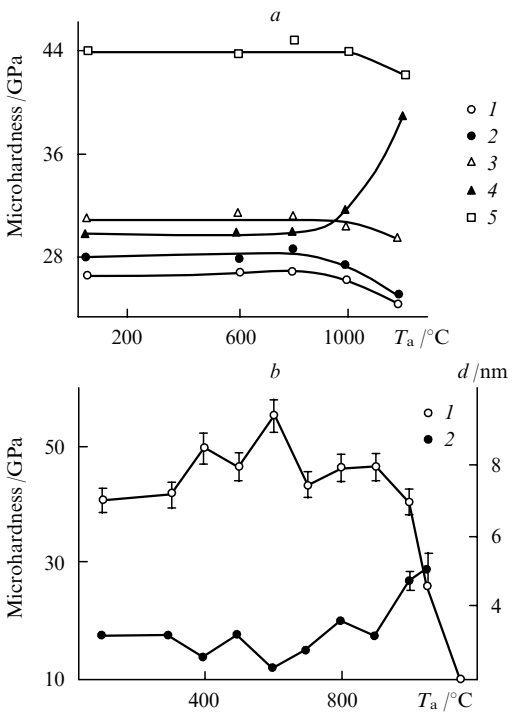


Figure 12. Effect of annealing temperature on microhardness of the coatings based on the TiN – ZrN (*a*) and $(Al_{1-x}Ti_x)N$/a-Si_3N_4 systems (*b*).
(*a*): ZrN (*1*); TiN (*2*); TiN – ZrN, 10 layers (*3*); alloyed films: (Ti,Zr)N (*4*) and TiN – ZrN, 20 layers (*5*);
(*b*): microhardness (*1*), crystallite size (*2*).

shown in Fig. 12. In the former case the hardness of the alloyed (Ti,Zr)N films considerably increases (see Fig. 12 *a*); the corresponding solid solution decomposes into finely disperse phases on heating, which was detected by X-ray analysis.[147] In the latter case the increase in microhardness is not so large (see Fig. 12 *b*); nevertheless, it affects the thermal stabilities of the films based on titanium nitride and aluminium nitride.[135]

The effect of annealing at 900 °C on the composition and structure of films of silicon carbonitride based materials was studied.[148] Using various methods (IR spectroscopy, X-ray photoelectron spectroscopy, X-ray analysis, Raman spectroscopy, *etc.*), the post-annealing changes in the crystallite size and a decrease in the proportion of the amorphous component were revealed.

V. Conclusion

In essence, each type of the nanomaterials (powders, compacts and films) considered in this review deserves a relevant comprehensive analysis. For instance, powders obtained by plasma chemical synthesis have been the subject of a monograph.[149] A joint study makes it possible to compare the results obtained for different types of nanomaterials; however, we had to leave some details out of consideration and only refer to original publications because of limitations on the length of the article. In the text below we present the key results obtained in the last decade in the field under study.

Methods for preparation of nanopowders, nanotubes and nanowires, nanostructured compacts and films of practically important high-melting compounds have been elaborated on a laboratory scale (and in some cases on a large scale). Films have been the best studied and can serve as the basis for fabrication of nanomaterials (grain size of 2 to 3 nm; cluster-consolidated objects) possessing the highest physicomechanical characteristics. It was shown that application of an external magnetic field in the course of film deposition has a strong effect on the film structure and hardness.

The self-propagating high-temperature synthesis and mechanochemical synthesis have found wide use in the preparation of nanopowders. However, a comparison of the cost – performance ratios for different methods of production of ultradisperse powders and disclosure of optimum ones is complicated by the lack of many necessary characteristics.

A number of methods for consolidation of powder nanomaterials have been elaborated, which allow the nanostructure (with a grain size of about 50 nm) to be retained and specimens of low porosity to be obtained. Of particular interest are the methods that combine mechanochemical synthesis and densification of nanopowders. There is a need in comparing the efficiency of these techniques.

The hardness of nanostructured films based on high-melting compounds can compete with that of the classical ultrahard (> 50 GPa) materials. It was shown that the nanostructures of the films based on borides, nitrides and carbides are thermally stable up to 1000 – 1100 °C. Highly wear-resistant, nanostructured, single- and multilayered coatings based on high-melting

compounds (with a hardness of at least 40 – 50 GPa) for tool applications are now produced in the United Kingdom, Germany, Czech Republic and other countries.[30, 31, 135]

A considerable body of information on the structure, physicochemical and physicomechanical properties of nanocrystalline high-melting compounds has been accumulated; selected data on their properties have been reported in a collection of studies.[150] However, there are still many 'blind spots' due to insufficient knowledge of fundamental characteristics of these species (*e.g.*, the electronic structure and constitutional diagrams, the semiconductor and thermodynamic properties, radiation-induced and other types of defects, *etc.*).

Prospects for the design of and research into nanomaterials based on high-melting compounds are associated with both investigation of the nature of the size effects and stability of nanostructures [151] and disclosure of novel (compared to traditional tool and tribotechnical applications) fields of application. For instance, the possibility of using films based on molybdenum and tungsten carbides for electrocatalysis was pointed out;[152, 153] however, by and large the catalytic properties of nanostructured high-melting compounds are poorly studied.

It was shown (see, *e.g.*, Refs 154 – 158) that nanocrystalline films based on high-melting compounds can be used not only as coatings for tool materials but also for biomedical applications and in data storage systems. There is increasing interest in these compounds from specialists working in electronics and nuclear engineering. Particular attention has been given to silicon carbide, silicon nitride and aluminium nitride. Silicon carbide is thought to be quite promising high-temperature semiconductor material for the Schottky diode type devices,[65] while silicon nitride and aluminium nitride are considered as efficient barrier materials. It is of interest to study the possibility of synthesis and the properties of semiconductor heterostructures based on SiC and other high-melting compounds. The high mechanical and dielectric properties of nanocrystalline films based on, *e.g.*, Si_3N_4 are attractive for the design of novel types of microbolometric devices for various measuring systems in transport, in biological studies and in industrial and environmental monitoring. Nanocrystalline silicon carbide is considered as a promising structural material for pressurised water-cooled nuclear reactors and boiling water-cooled reactors. Materials based on SiC can be used as the matrix and shell components and for production of units for the fuel core and the plasma-faced wall of a thermal reactor (see, *e.g.*, Refs 159 – 161).

Clearly, realisation of these promising avenues will require extensive technological and materials science investigations of nanocrystalline structures based on the high-melting compounds described above.

This review has been written with financial support from the NATO (in the framework of the Programme 'Science for Peace', NATO – SfP, Project No. 973529), the Presidium of the Russian Academy of Sciences (in the framework of the Basic Research Programme No. 8) and the Russian Foundation for Basic Research (Project Nos 05-03-32248 and 05-03-07008).

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