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Platinum group metal nitrides and carbides: synthesis, properties and simulation

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Abstract. Experimental and theoretical data on new compounds, nitrides and carbides of the platinum group 4d and 5d metals (ruthenium, rhodium, palladium, osmium, iridium, platinum), published over the past five years are summarized. The extreme mechanical properties of platinoid nitrides and carbides, *i.e.*, their high strength and low compressibility, are noted. The prospects of further studies and the scope of application of these compounds are discussed. The bibliography includes 145 references.

I. Introduction

Carbides and nitrides of transition 3d – 5d metals find wide application as the materials for machine-building, nuclear and chemical industries, in the production of structural ceramics, in manufacturing of abrasives, protective coatings, wear-resistant materials, *etc*. The exceptional technological and scientific significance of these materials is determined by the unique combination of their extreme thermal and mechanical properties, radiation and chemical stability, and also by their extraordinary electophysical and magnetic characteristics.[1 – 12]

Thus tantalum and hafnium carbides possess the highest melting points among refractory compounds known, namely, ~3985 and ~3890 °C, respectively.[5] A very important role is played by tungsten carbide [13, 14] as a component of heat-resistant and hard alloys, in the production of wear-resistant coatings and manufacturing of refractory crucibles. Iron carbide Fe_3C (cementite) is the most important component of cast iron and carbon steels.[15, 16] Attention of scientists is also focused on nitrides of the 3d – 5d metals due to the advantageous combination of their electronic, magnetic, optical properties and also due to their low-temperature superconductivity.[1, 4, 9, 12]

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Among the most remarkable features of cubic carbides and nitrides of the Group IV and V 3d – 5d metals (Ti, V, Zr, Nb, Hf) that pertain to a class of so-called strongly non-stoichiometric compounds are their wide homogeneity regions that arise due to considerable (up to 50%) variable concentrations of structural vacancies in their carbon or nitrogen sublattices.[1 – 11, 17, 18]

To date, in addition to binary compounds, multicomponent carbides and nitrides of the 3d – 5d metals were synthesized. They include substitutional solid solutions with variable contents of component atoms of different nature (for example, carbonitrides, oxycarbides, oxycarbonitrides of metals), interstitial solid solutions with impurity atoms localized in the matrix interstices (hydridocarbides), large groups of individual ternary and more complicated carbides and nitrides with a wide diversity of crystallographic types and also various composite materials.[7 – 10, 19 – 24]

A rapidly advancing trend in the production of new carbide and nitride materials with non-trivial sets of functional characteristics is their synthesis in the nanosized state, *i.e.*, as nanopowders or their compacts, nanostructured films, alloys, ceramics, composites, *etc*.[25 – 29] These materials are based on nanoforms (measured < 100 nm) of metal carbides (nitrides) with the variable chemical composition [metal : carbon(nitrogen) ratio]. They can have different morphologies, atomic structures and substantially differ from the corresponding crystalline phases in physicochemical properties. To date, abundant groups of nanocarbides and nanonitrides of the d metals such as molecular clusters, nanocrystals, nanospheres, nanowires, nanotubes, *etc*. were synthesized.

Based on studying equilibrium phase diagrams of M – C (M – N) systems (M is a transition 3d – 5d metal), it was found that the Group III – V metals pertain to carbide- and nitride-forming metals capable of yielding carbide (nitride) phases with considerable content of non-metals (Fig. 1).

Thus yttrium forms a phase the most abundant in carbon, namely, dicarbide YC_2 with $C/M = 2$. In phases based on the Group VI and V metals (Ti, V, Zr, Nb, Hf, Ta), the maximum carbon (nitrogen) content corresponds to the $C(N)/M = 1$ stoichiometry; then with the increase in the d-metal atomic number, the maximum content substan-

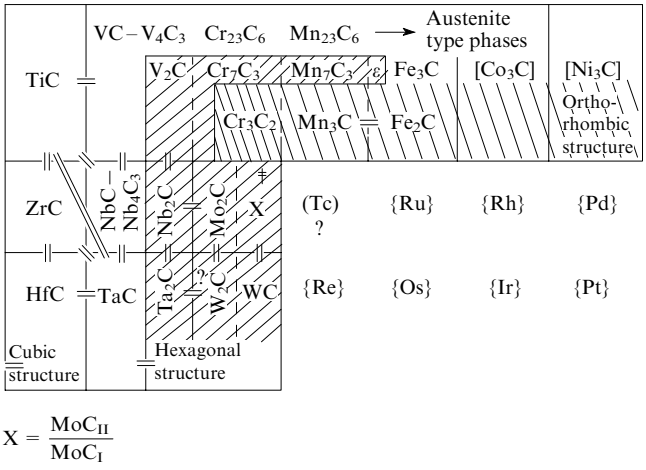


Figure 1. Binary carbides of transition 3d – 5d metals.[1]
Phases with cubic, hexagonal and orthorhombic structures are marked. Phases that form continuous series of solid solutions are connected with double lines. In brackets, unstable carbides are given; in parentheses, metals that form no carbides are shown; the data on the possible existence of technetium carbides are conflicting.

tially decreases. For example, the maximum carbon content in chromium carbides is reached with the Cr_3C_2 phase, whereas for manganese carbides, this is attained at Mn_7C_3 and for cobalt and nickel carbides, this corresponds to $(Co,Ni)_3C$.[1–11]

A special group is formed by 4d and 5d platinum group metals, *i.e.*, Ru, Rh, Pd, Os, Ir and Pt. For a long time, it was assumed (see Fig. 1) that these metals are inert with respect to nitrogen (carbon) and form no stable nitride (carbide) phases.[1–6,8,29,30] The authors of reference books[28,29] restricted themselves to stating that the carbon solubility in these metals is extremely low[29] or noted that liquid Ru, Rh, Pd, Os, Ir and Pt can dissolve certain amounts of carbon and evolve it on cooling in the form of graphite.[30] It was also noted[1] that all platinum group metals are in stable equilibrium with free nitrogen and do not form nitrides.

The situation dramatically changed in 2004 with the appearance of a series of pioneering studies reporting on the successful syntheses (for the most part, at high pressures and temperatures, *i.e.*, $P \approx 60$ GPa, $T \approx 2000$ K) of several binary nitrides and carbides of platinoids, namely, PtN, PtN_2,[31,32] IrN_2, OsN_2,[32,33] RuN_x,[34] PdN_2,[35] PtC.[36] Note that nearly in the same period, synthetic studies were started and theoretical calculations were accomplished that, on the one hand, allowed the synthesis and, on the other hand, theoretically substantiated the possibility of the existence of carbides and nitrides of copper, silver,[37–40] technetium, rhenium[41,42] and also of a large series of platinoid borides.[43–57]

The discovery of a new group of platinoid nitrides and carbides (Table 1) attracted keen attention because some of them (for example, PtN_2, IrN_2, OsN_2 and PdN_2) contain record-breaking amounts of non-metals exceeding that in the majority of 'classical' nitrides and carbides of transition 3d – 5d metals.[1–12] This demands revison of the existing concepts of the mechanism of phase formation in transition metal – nitrogen (carbon) systems.

The combination of properties of platinoid nitrides and carbides and their technological potential attract keen

Table 1. Synthesized and hypothetical carbides and nitrides of platinum group metals.

Nitrides	Carbides	Notes
RuN_{x-1}		synthesized phases
Ru_4N, Ru_3N, Ru_2N, RuN, RuN_2	RuC	hypothetical phases (theoretical calculations)
RhN, RhN_2, RhN_3	–	the same
PdN, PdN_2	PdC	"
OsN_2		synthesized
OsN, OsN_2	OsC	for OsN and OsN_2, hypothetical phases (theoretical calculations); for OsC, early (unconfirmed) data[55,56] pointed to the synthesis of this carbide in the hexagonal WC-type structure
IrN_2		synthesized
IrN, IrN_2, IrN_3	IrC	hypothetical phases (theoretical calculations)
$PtN_{x<1}$, PtN, PtN_2;	$PtC_{x<1}$	synthesized
PtN, PtN_2	PtC	hypothetical phases (theoretical calculations)

attention. Thus even the first experimental and theoretical studies mentioned the exceptionally remarkable mechanical properties of mono- and dinitrides (carbides) of platinoids associated with their high hardness and low compressibility. For example, the experimentally determined bulk modulus (B) for IrN_2 ($\sim$428 GPa)[33] was only 3% lower than that of diamond ($\sim$440 GPa).[57]

This result substantially corrects the views on the possible directions of the quest for new superhard materials. Thus since the bulk modulus is inversely proportional to the molar volume,[58–60] it was believed[57] that the most probable candidates in the search for superhard materials are the phases formed by light atoms (B,C,N,O) with relatively small radii that can form the directed short (covalent) bonds. Indeed, in addition to diamond, the best known superhard materials are cubic boron nitride [κ-BN, $B = 369–392$ GPa (Ref. 61)], β-C_3N_4 [$B = 357–556$ GPa (Ref. 62)], carbides ($B_{13}C_2$, $B_{12}C_3$),[63] boron carbonitrides [z-BC_2N, $B = 403$ GPa (Ref. 64)], several other phases of the B – C – N – O system, *e.g.*, oxide B_6O (Ref. 57, 65 and 66). The obtained results[31–33] suggest that it is the systems with heavy metal atoms surrounded by relatively light atoms (with high coordination numbers) capable of forming directed bonds in the metal sublattice that can be regarded as alternative materials with highly attractive properties.

Indeed, recently, the high bulk moduli (low compressibility, $\beta = 1/B$) were found (or predicted) for certain platinoid nitrides and carbides with different (C,N)/metal ratios, for example, such as RuC ($B = 347$ GPa), PtC ($B = 288$ GPa), PdC ($B = 248$ GPa),[67] OsC ($B = 293–393$ GPa),[68] RhN_3 ($B = 244–311$ GPa).[69] This is why from the viewpoint of practice, it is the quest for new effective materials for hard wear-resistant coatings and films that has given an important impetus for the synthesis of platinoid nitrides and carbides and the studies of their properties. Also note that depending on their composition and structure, platinoid carbides and nitrides can exhibit both the metal- and semiconductor-like conduction; for

some of them (*e.g.*, for OsN_2) low-temperature superconductivity was predicted.[70]

In this review, an attempt was undertaken to generalize the information gathered in recent years (starting from 2004) on the synthesis and properties of new carbides and nitrides of the platinum group 4d and 5d metals, namely, Ru, Rh, Pd, Os, Ir and Pt.

Before embarking on the description of results, we briefly mention the other known types of materials in the platinoid–nitrogen (carbon) system the development of which has been in the focus of recent studies.

One of groups in such systems includes molecular platinoid–(C,N) forms and also nanoforms, *i.e.*, various derivatives of fullerenes or carbon nanotubes in which a platinoid acts as either the 'guest metal' inside hollow carbon frames or is adsorbed (as an atom or in the form of various complexes) on the carbon cage of nanoobjects. The main goal of such studies is the search of new catalytic materials. The synthesis of monolithic palladium carbide nanowires was reported.[71] At the same time, a fairly large number of studies were devoted to thin platinum/carbon films with interesting electrophysical and catalytic characteristics.[72–75]

Another group was formed by multicomponent carbides (nitrides) that simultaneously involve platinoids and(or) transition 3d–5d metals of the Groups III–VI, lanthanides and actinides. The examples are as follows: Pt_2Mo_3N, $PdPtMo_3N$,[76] $Hf_xRu_yN_z$,[77] $Re_xRh_yC_z$,[78] $Ln_5Os_3C_{4-x}$ (Ln = La–Nd, Sm),[79] $Th_2Ru_6C_5$, $Th_{11}Ru_{12}C_{18}$, $ThRu_3C$,[80] $Gd_{3.67}RuC_6$, $Ln_{3.67}OsC_6$ (Ln = La–Nd, Sm),[81] $Ln_{12}Os_5C_{15}$ (Ln = Y, Pr, Nd, Sm, Gd–Tm),[82] $Ln_{10}Ru_{10}C_{19}$ (Ln = Y, Gd–Lu),[83] Gd_2OsC_2,[84] U_2MC_2 (M = Ru, Os, Rh, Ir, Pt),[85] Sc_3MC_4 (M = Ru, Rh, Os, Ir),[86] Pd_2Mo_3N.[87] Their crystallographic data are known,[76–87] but information on their properties is scarce. This group of materials may also include complex composites, the so-called cemented carbides, *e.g.*, WC–Co–Ru, WC–Co–Os, *etc.* that involve carbides of the Group IV–VI 3d–5d metals. Attention of scientists[88] was drawn to the effect of platinoid admixtures to the metallic 'binder' composition on the properties of hard composites. Particularly, it was noted[88] that admixtures of Ru or Os enhance the hardness of WC–Co alloys. However, the discussion of the mentioned groups of materials is beyond the scope of this review.

II. Synthesis of new nitrides and carbides of the platinum group metals

The largest number of experimental studies were so far devoted to the synthesis of materials in the platinoid–nitrogen system and the determination of their composition and structure (see Table 1). Let us consider the main results.

1. Synthesis of platinoid nitrides

The first nitride of a platinum-group metal was synthesized when studying the possibility of a reaction of platinum with nitrogen under high pressures at high temperatures[31] using a laser-heated diamond anvil. Upon reaching a pressure of 45–59 GPa and a temperature of 2000 K, the following reaction was observed by a Raman scattering technique:

$$Pt + N_2 \longrightarrow PtN_x,$$

where the Raman spectra indicated the formation of an ordered crystalline structure in the product.

According to the data from X-ray diffractometry (XRD),[31] the obtained PtN_x phase had the face-centred cubic (fcc) lattice with the parameter $a = 4.8041(2)$ Å. XRD spectra can 'detect' only the metal lattice; hence, the acquired XRD spectrum may correspond to several structural types of binary phases such as NaCl, zinc blende (sphalerite ZnS) and cooperite (PtS). Comparing the theoretical lines of these structures with the experimental Raman spectrum, it was concluded[31] that the synthesized product represented platinum mononitride with the zinc blende structure.

One of the most remarkable results obtained in the above study[31], which had predetermined in many respects the subsequent active studies of platinoid nitrides and carbides, was establishing the bulk modulus of PtN equal to $\sim 372 \pm 5$ GPa, which is 100 GPa higher than for pure platinum. This value turned out to be comparable with the modulus B of a well-known 'superhard' material, namely, cubic boron nitride [369–392 GPa (Ref. 61)].

The further detailed studies[32] of samples in the Pt–N system and in the related Ir–N system prepared at ~ 80 GPa have shown that the synthesized products (Fig. 2) had the $M:N \approx 1:2$ stoichiometry. Based on the results of several spectroscopic methods (Raman, XRD, X-ray photoelectron spectroscopy, Fig. 3), it was concluded that PtN_2 has the pyrite (FeS_2) structure with the lattice parameter $a = 4.8$ Å and includes nitrogen atoms in the form of bonded dimers N_2 with the distance N–N = 1.41 Å; IrN_2 has a structure with lower symmetry.[32]

Using the same method (at pressure > 50 GPa and temperature ~ 2000 K), iridium and osmium nitrides were

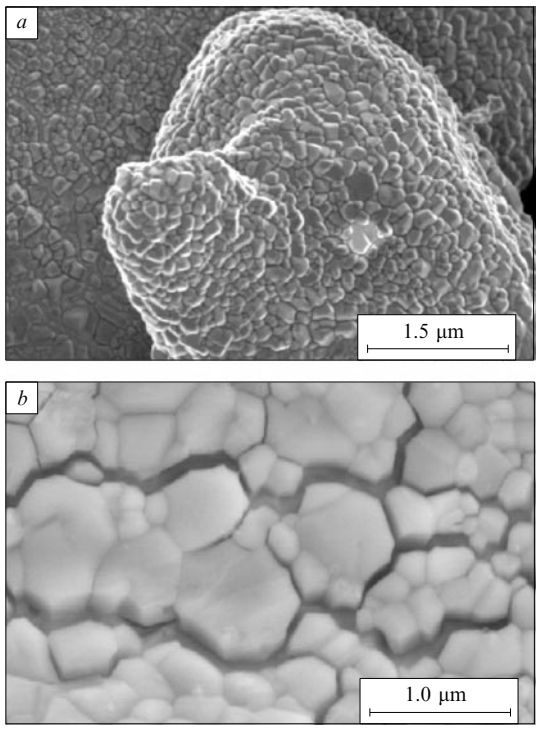


Figure 2. Microimages of samples in the Pt–N (*a*) and Ir–N (*b*) systems.[32]

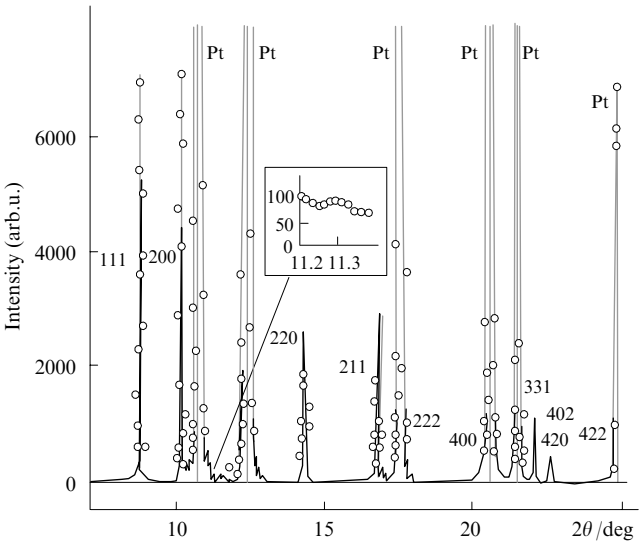


Figure 3. XRD spectra of PtN_2.[32]
Reflection peaks of platinum dinitride are indexed assuming the pyrite structure. Peaks pertaining to the non-reacted platinum structure are shown in grey. A weak peak 210 forbidden for structures with higher symmetry of the fluorite and zinc-blende types is show in the inset.

successfully synthesized.[33] The analysis of microsample composition demonstrated a considerable scatter in stoichiometry, namely, the M : N ratio varied from 1 : 1 to 1 : 3. The XRD analysis performed at $P = 0.1$ MPa has identified the osmium nitride lattice as orthorhombic with unit cell parameters $a = 2.714(2)$, $b = 4.910(5)$ and $c = 4.102(3)$ Å; for iridium nitride, a hexagonal structure with lattice parameters $a = 3.966(4)$ and $c = 6.958(7)$ Å was found. The nitrogen sublattice structure was determined using Raman spectroscopy; according to the obtained data, nitrogen is included in the lattice in the form of bonded dimers N_2, *i.e.*, nitrides have the stoichiometric composition of OsN_2 and IrN_2. An additional argument for this stoichiometry of the synthesized nitrides was obtained[33] when comparing the volumes (as a function of pressure) of osmium and iridium dinitrides with those of their mononitrides and mixtures $(Os,Ir) + N_2$ and $(Os,Ir) + 0.5\,N_2$ (Fig. 4). One of the most important results obtained in the above study[33] was the experimental assessment of very high compression moduli of the synthesized nitrides, namely, 358 (OsN_2) and 428 GPa (IrN_2).

Another study[32] provided additional information on the synthesis of IrN_2 and PdN_2. It was proposed that IrN_2 has the structural type of baddeleyite (ZrO_2). The results of the XRD analysis pointed to the monoclinic symmetry of the PdN_2 lattice. Taking into account the data of Raman spectroscopy, it was concluded that PdN_2 has the structural type of pyrite. It was noted that these materials can be prepared (as films) by the method of ion implantation successfully used in the synthesis of gold nitride films.[89]

It was reported[90] that PtN_x/C films (with the stoichiometry Pt : N = 1 : 2) were synthesized by pyrolysis of a platinum-containing precursor; information on the catalytic activity of this material was given, but structural data were absent.

Ruthenium nitride RuN_x was successfully synthesized[34] using a method of laser ablation of a target (metallic Ru) in a flow of nitrogen; the product was formed as thin films

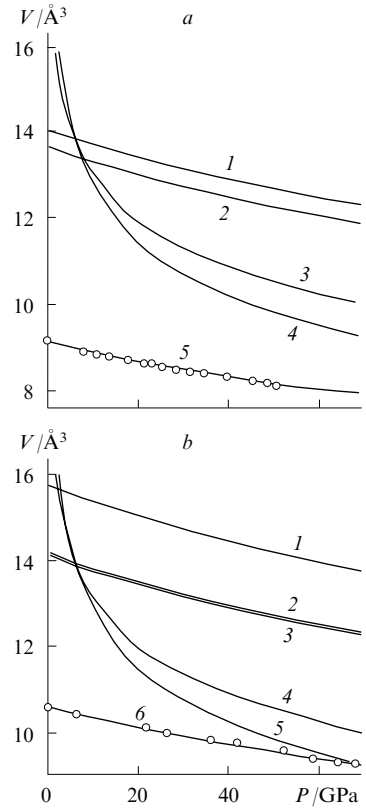


Figure 4. Dependences of the volume (per atom) on the pressure for mono- and dinitrides of osmium (*a*) and iridium (*b*) as compared with the corresponding dependences for the metals and the reactant mixtures.[33]
(*a*): (*1*) Os, (*2*) OsN, (*3*) $Os + 0.5\,N_2$, (*4*) $Os + N_2$, (*5*) OsN_2;
(*b*): (*1*) IrN, (*2*) Ir, (*3*) $IrN_2(R3c)$, (*4*) $Ir + 0.5\,N_2$, (*5*) $Ir + N_2$, (*6*) $IrN_2(P3_232)$. Points correspond to experimental data.

deposited on the silicon substrate. Its composition was analyzed using Auger and X-ray electron spectroscopies, electron energy loss spectroscopy and XRD. It was found that nitrogen is actively sorbed by ruthenium, with the degree of metal saturation with nitrogen being dependent on the N_2 pressure (Fig. 5). At a pressure $P \approx 160$ mTorr, $Ru : N \approx 1 : 1$ stoichiometry of the product was reached. The structure of films with low nitrogen contents was close to amorphous; for $RuN_{x \approx 1}$ compositions, the XRD studies identified the structure to be close to cubic (NaCl type), with the lattice parameter $a = 4.445$ Å. A $RuN_{x \approx 1}$ film remained stable to ~ 100°C and then decomposed with nitrogen evolution; virtually all nitrogen was removed at ~ 200 °C.

The laser ablation method was used for synthesizing platinum nitride PtN_x films;[91] according to their analysis, the obtained products were rather depleted of nitrogen and had the Pt : N = 6 : 1 stoichiometry. This method proved to be efficient[77] in the preparation of a binary nitride $Hf_xRu_yN_z$ ($0 < z < 0.25$), which involved the simultaneous laser ablation of two targets (Hf, Ru) in the $Ar + N_2$ gas mixture. It was established that the film with the maximum nitrogen content has the cubic structure as for RuN_x.

2. Synthesis of platinoid carbides

Information on the synthesis of platinoid carbides is much scarcer as compared with the synthesis of nitrides.

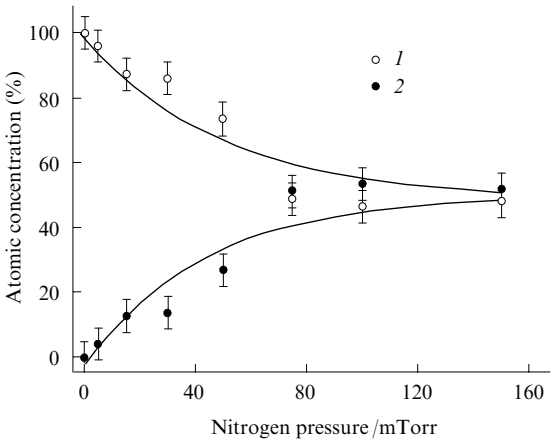


Figure 5. Variations in the RuN_x film atomic composition with the nitrogen pressure.[34]
(*1*) Ru, (*2*) N_2.

Successful synthesis of PtC was carried out[36] using a technique of high pressures and temperatures in a symmetrical diamond anvil with laser heating (Fig. 6). The starting reagent, a homogenized mixture of platinum and carbon powders was placed into an orifice 50 – 100 μm in diameter in a rhenium gasket between two diamond single crystals. The reaction was controlled by an X-ray diffraction technique employing synchrotron radiation.

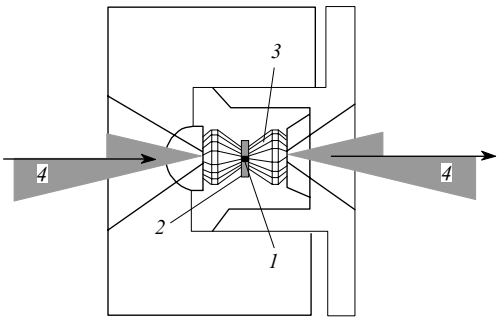


Figure 6. A symmetrical diamond anvil with two-sided laser heating used in the platinum carbide synthesis.[36]
(*1*) Sample (original mixture), (*2*) rhenium gasket, (*3*) diamond single crystals, (*4*) laser-radiation heating. Arrows show the directions of incident and diffracted synchrotron X-ray radiation.

Figure 7 illustrates the obtained results. A sample was subjected to the action of high pressure (up to 70 GPa) at room temperature; the resulting XRD spectrum demonstrated only platinum and carbon lines. Next, the sample was heated to 2600 K and the pressure was increased to 85 GPa; this was accompanied by the appearance of a distinct XRD peak indicating the formation of an individual phase, namely, platinum carbide. On cooling and pressure relief, the PtC lines slightly broadened but remained in the spectrum, *i.e.*, no decomposition of the obtained PtC phase occurred under ambient conditions. In additional experiments, it was confirmed that the PtC phase remains stable at least up to pressures ~121 GPa. According to the obtained data, the new PtC phase is cubic with the lattice parameter $a = 4.814$ Å. Based on the experimental dependence of the unit cell volume on pressure, the bulk

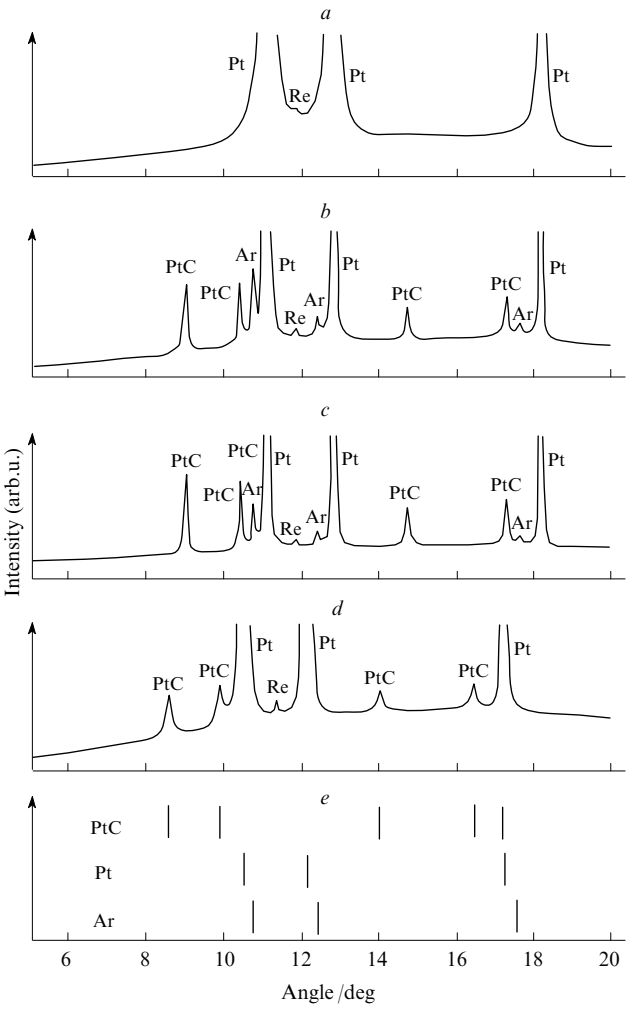


Figure 7. XRD Spectra of a sample representing a mixture of platinum and carbon powders at 70 GPa and 300 K (*a*), 86 GPa and 2600 K (*b*); cooled to 300 K (*c*) and under ambient conditions (*d*), and also the theoretical positions of the PtC, Pt and argon peaks (*e*).[36] Diffraction lines of Pt, Re, Ar (experiments were carried out in an inert atmosphere).

modulus of platinum carbide was determined to be 301 ± 15 GPa.

A method developed[92–94] for synthesizing metal alloys, based on the thermolysis of complex precursors, *e.g.*, binary salts containing platinoid atoms, can become an efficient way of synthesizing platinoid carbides (including more complex compounds, *e.g.*, binary carbides). The use of this method allows one to both strictly preset the compositions of final alloys and vary them.

It was shown that this method can be used to produce binary carbides $Re_{0.67}Rh_{0.33}C_x$ in the synthesis of a Re – Rh alloy from $[Rh(NH_3)_5Cl]ReO_4$ by reduction of the latter in a flow of hydrogen in a furnace (300 °C) followed by thermobaric treatment (1 – 4 GPa, 2000 °C) in a graphite crucible. Based on the results of X-ray examination of the synthesized product, it was concluded that a binary carbide $Re_{0.67}Rh_{0.33}C_x$ (structural type of anti-NiAs) was formed in the graphite crucible as a result of a reaction between the Re – Rh alloy with the heater material. Probably, this method could be used to synthesize other binary carbides of platinum group metals.

As was mentioned above, to date a new group of materials, namely, platinoid nitrides and carbides PtN, PtC, RuN, PtN_2, IrN_2, OsN_2, PdN_2, have been synthesized. The following factors should be taken into account. The majority of mentioned compounds were prepared under extreme conditions (at high pressures and temperatures) and in rather limited amounts. Moreover, on lowering pressure and cooling to room temperature, some of the synthesized phases undergo decomposition. As a result, the use of traditional physicochemical analytical methods in the determination of properties of platinoid nitrides and carbides faces considerable difficulties; hence, many compounds still remain unexplored. Moreover, the possibility of phase formation in the Rh–N, Pd–N, Ru–C, Rh–C, Pd–C, Os–C, Ir–C systems is also not ascertained so far.

In this situation, the methods of theoretical quantum chemical simulation have received wide acceptance in the elucidation of several peculiarities of the electronic structure and chemical bonding for a considerable number of synthesized and hypothetical platinoid nitrides and carbides and also in predicting the structural, mechanical and other properties of these materials.

III. Simulation of the structure and properties of platinoid nitrides and carbides

1. Nitrides

The main problems that attracted attention of researchers who studied the structure and properties of nitrides and carbides of platinoids were the theoretical assessment of the stability of predicted phases (including phase transitions during baric treatment), which is important as regards their possible synthesis, the simulation of certain properties (structural, mechanical, electronic) and the nature of chemical bonds.[95–114] To date, within the framework of quantum chemical simulation, the most thoroughly studied compounds are di- (MN_2) and mononitrides (MN) of platinum group metals (Tables 2 and 3).

In the majority of studies[95–114] considered below, both the thermodynamic and mechanical stabilities of phases were estimated.

The thermodynamic stability was analyzed by invoking two quantities, namely, the cohesion energy (E_{coh}) and the enthalpy of formation (ΔH). The cohesion energy characterizes the effect of energy of crystal 'assembling' from isolated atoms; hence, the E_{coh} value is correlated with the energy of chemical bonds in crystals. For example, E_{coh} of platinum mono- and dinitride is determined as

$$E_{coh}^{PtN} = E_{tot}(PtN) - [E_{tot}(Pt_{at}) + E_{tot}(N_{at})],$$

$$E_{coh}^{PtN_2} = E_{tot}(PtN_2) - [E_{tot}(Pt_{at}) + 2E_{tot}(N_{at})],$$

where $E_{tot}(PtN)$, $E_{tot}(PtN_2)$ are the total energy of PtN and PtN_2 crystals; $E_{tot}(Pt_{at})$ and $E_{tot}(N_{at})$ are the total energies of free (isolated) platinum and nitrogen atoms.

Enthalpies of formation characterize the effect of phase formation from the starting substances. For nitrides, ΔH is usually assessed for their formation from the corresponding metal (the first reactant) and nitrogen in the form of the molecular crystal α-N_2 (Ref. 115) (the second reactant); for carbides, the most stable allotrope, graphite, is usually considered as the second reactant. Then, ΔH for, *e.g.*, PtN_2 and PtC, is calculated as follows:

$$\Delta H^{PtN_2} = E_{tot}(PtN_2) - [E_{tot}(Pt_{met}) + E_{tot}(\alpha\text{-}N_2)],$$

$$\Delta H^{PtC} = E_{tot}(PtC) - [E_{tot}(Pt_{met}) + E_{tot}(C_g)],$$

where $E_{tot}(Pt_{met})$, $E_{tot}(\alpha\text{-}N_2)$ and $E_{tot}(C_g)$ are the total energies of the reactants, *i.e.*, platinum (fcc), α-N_2 crystals and graphite, respectively. In this case, the negative value of ΔH is interpreted as the criterion of phase stability as compared with the mechanical mixture of the starting substances and, *vice versa*, $\Delta H > 0$ points to metastability or instability of the corresponding phase.

Furthermore, the mechanical stability of hypothetical phases is often estimated from the known relationships between elastic coefficients (the proportionality factor between tensors of strains and deformations C_{ij}, where i and j are taken from 1 to 6 in the simplified Voigt scheme) of crystals.[116] Thus for cubic crystals, the criterion of their

Table 2. Calculated unit cell parameters and bulk moduli of platinum-group metal dinitrides.[95–107]

Carbide	Structure	Unit cell parameters /Å			*B* /GPa	Ref.
		a	*b*	*c*		
RuN_2	marcasite (FeS_2)	4.058	4.847	2.665	286	95
RhN_2	the same	3.991	4.803	2.716	–	96
	arsenopyrite (FeAsS)	4.772	4.795	4.807	–	96
OsN_2	marcasite (FeS_2)	4.010	4.827	2.758	343	95
	the same	4.077	4.844	2.621	–	96
		2.685	4.914	4.118	352	98
		4.101	4.889	2.654	413	102
		4.104	4.891	2.663	394	106
	monoclinic ($CoSb_2$)	4.886	4.873	4.913	374	95
	pyrite (FeS_2)	4.839	–	–	383	107
		4.925	–	–	316	99
	fluorite (CaF_2)	4.794	–	–	374	107
		4.819	–	–	361	99
IrN_2	marcasite (FeS_2)	4.025	4.816	2.701	–	96
	arsenopyrite (FeAsS)	4.777	4.822	4.818	–	96
	fluorite (CaF_2)	4.842	–	–	347	97
	monoclinic ($CoSb_2$)	4.807	4.857	4.924	388	100
	arsenopyrite (FeAsS)	4.861	4.907	4.901	373	101
	marcasite (FeS_2)	4.902	4.908	2.754	368	101
	monoclinic ($CoSb_2$)	4.809	4.858	4.848	402	95
	pyrite (FeS_2)	4.781	–	–	366	107
	fluorite (CaF_2)	4.815	–	–	358	107
PtN_2	marcasite (FeS_2)	3.197	4.880	3.779	–	98
	fluorite (CaF_2)	4.992	–	–	295	99
	pyrite (FeS_2)	4.862	–	–	167	99
	the same	4.770	–	–	352	103
	fluorite (CaF_2)	4.912	–	–	290	104
	pyrite (FeS_2)	4.848	–	–	305	105
	the same	4.792	–	–	349	107
	fluorite (CaF_2)	4.886	–	–	300	107

Table 3. Calculated unit cell parameters and bulk moduli for platinum group metal mononitrides.[107–114]

Nitride	Structure	Unit cell parameters /Å		*B* /GPa	Ref.
		a	*c*		
RuN	sphalerite	4.47	—	307	108
RhN	"	4.51	—	268	108
PdN	"	4.62	—	217	108
OsN	cubic (NaCl)	4.287	—	381	107
	sphalerite	4.527	—	323	107
	cubic (NaCl)	4.327	—	333	109
	sphalerite	4.565	—	301	109
	CsCl type	2.698	—	348	109
	wurtzite	2.745	6.653	331	109
	NiAs type	2.777	5.901	369	109
	hexagonal (WC)	2.734	3.105	—	109
IrN	cubic (NaCl)	4.328	—	346	107
	sphalerite	4.573	—	288	107
	cubic (NaCl)	4.396	—	322	109
	sphalerite	4.636	—	284	109
	CsCl type	2.748	—	326	109
	wurtzite	2.847	6.565	253	109
	NiAs type	3.083	5.198	314	109
	hexagonal (WC)	2.833	3.085	—	109
	cubic (NaCl)	4.407	—	284	107
	sphalerite	4.699	—	230	107
	cubic (NaCl)	4.484	—	256	109
	sphalerite	4.776	—	209	109
	CsCl type	2.814	—	254	109
	wurtzite	3.007	6.614	124	109
	NiAs type	3.082	5.552	241	109
	hexagonal (WC)	3.027	2.957	226	109
PtN	cubic (NaCl)	4.407	—	284	110
	sphalerite	4.699	—	230	110
	cooperite (PtS)	3.323	4.579	—	110
	orthorhombic	3.972 (b = 3.977)	6.022	270	110
	sphalerite	4.89	—	192	111
	cubic (NaCl)	4.45	—	232	111
	sphalerite	4.799	—	191	112
	cubic (NaCl)	4.491	—	230	112
	CsCl type	2.818	—	234	112
	wurtzite	3.386	5.529	191	112
	sphalerite	4.805	—	193	113
	cubic (NaCl)	4.504	—	185	113
	sphalerite	4.804		371	114
	cubic (NaCl)	4.5184		431	114

mechanical stability is the fulfilment of the following relationships:

$C_{11} > 0$,

$(C_{11} - C_{12}) > 0$,

$(C_{11} + 2C_{12}) > 0$,

$C_{44} > 0$;

for hexagonal crystals:

$C_{11} > 0$,

$(C_{11} - C_{12}) > 0$,

$C_{44} > 0$,

$(C_{11} + C_{12})C_{33} - 2C_{12}^2 > 0$.

The corresponding criteria for crystals of other symmetry types can be found elsewhere (see, *e.g.*, Ref. 101).

a. Dinitrides (MN_2)

To date, dinitrides MN_2 (M = Ru, Rh, Os, Ir, Pt) were studied in sufficient detail.[95–107, 117–119] Limited experimental data are available for MN_2 crystal structures; hence, in comparing the stability of various possible MN_2 phases and the conditions for their mutual transitions, the methods of computer simulation were extensively used. The calculations were carried out for both cubic phases [fluorite (CaF_2) and pyrite (FeS_2)], and more complicated and low-symmetry structures, namely, monoclinic (the $CoSb_2$ type) and orthorhombic [the arsenopyrite (FeAsS) and marcasite (FeS_2) types] in which nitrogen atoms are localized at distances $R(N-N) = 1.4-1.5$ Å,[95–107, 117–120] *i.e.*, are present in the lattice as N_2 dimers (Fig. 8). Thus it was proposed[95] to consider such compounds as quasimolecular crystals and classify them with the group of metal pernitrides. According to calculations, the dimerization of nitrogen atoms in the MN_2 phase structure is a significant factor of their energy stabilization (see also discussions of several alternative structures[118, 119]).

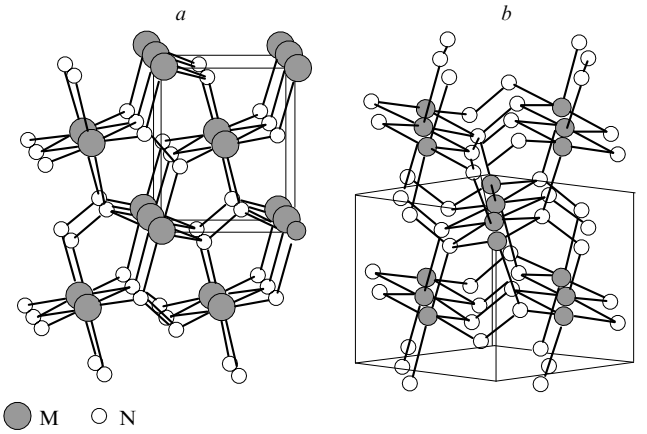


Figure 8. Structures of platinoid dinitrides of the marcasite (*a*) and arsenopyrite types (*b*).[96]

The analysis of the total energy *vs.* unit cell volume dependences (Fig. 9) has shown[95] that for RuN_2 and RhN_2, the marcasite structural type is the most thermodynamically stable; for osmium and iridium dinitrides, the marcasite and $CoSb_2$-type phases are comparative as regards the energy, *i.e.*, phase transitions marcasite $\leftrightarrows$ $CoSb_2$ can occur. Phases with the fluorite and rutile structural types in which direct N—N interactions are absent are the least stable (see Fig. 9).

The role the N—N interactions in N_2 dimers play in the overall system of dinitride interactions can be elucidated by analyzing the data on the orbital overlap population (OOP) for platinum mono- and dinitrides (Fig. 10). It is evident that for PtN_2, the N—N and Pt—N bonds make considerable contributions to the overall system of interatomic interactions in the PtN_2 crystal, whereas for PtN, the N—N interactions are virtually absent. The presence of strong

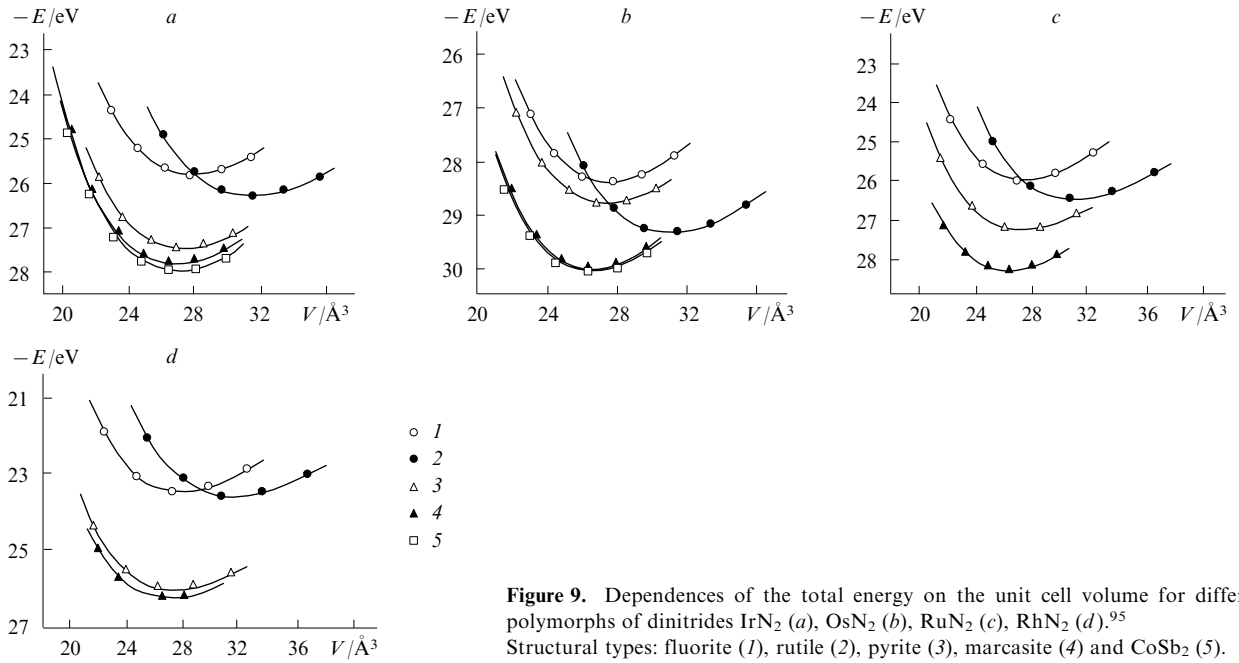


Figure 9. Dependences of the total energy on the unit cell volume for different polymorphs of dinitrides IrN_2 (*a*), OsN_2 (*b*), RuN_2 (*c*), RhN_2 (*d*).[95]
Structural types: fluorite (*1*), rutile (*2*), pyrite (*3*), marcasite (*4*) and $CoSb_2$ (*5*).

N—N bonds was also invoked [105, 117] in explaining the poor compressibility (high bulk moduli) of dinitrides.

Calculations of electronic spectra have shown [95–107, 120] that platinum metal dinitrides can exhibit both metallic and semiconducting properties. As an example, Fig. 11 shows the electronic spectra of OsN_2 with the marcasite and pyrite structures and PtN_2 with the pyrite structure. Here, the feature of metal-like MN_2 phases that distinguishes them from the majority of known nitrides of 3d–5d metals [10] consists of comparable contributions of N2p and Md states to the total density of states on the Fermi level [$N(E_F)$], whereas for the latter nitrides, the $N(E_F)$ composition is largely determined by the 3d–5d metal sublattice states.

As was mentioned, keen attention was paid to mechanical properties of platinoid dinitrides. The applied methods allowed [95–107, 120] the mechanical stability and elastic moduli of different MN_2 phases to be assessed (see Table 2) as well as such important characteristics of crystals as the sound velocity, Debye temperature, molar heat capacity and the coefficient of thermal conductivity. Within the framework of the Voigt–Reuss–Hill approximation widely used [121–125] in describing polycrystalline systems that represent aggregated mixtures of microcrystals with the random mutual orientation, the bulk (*B*), shear (*G*), and Young moduli, the coefficients of compressibility and the Poisson

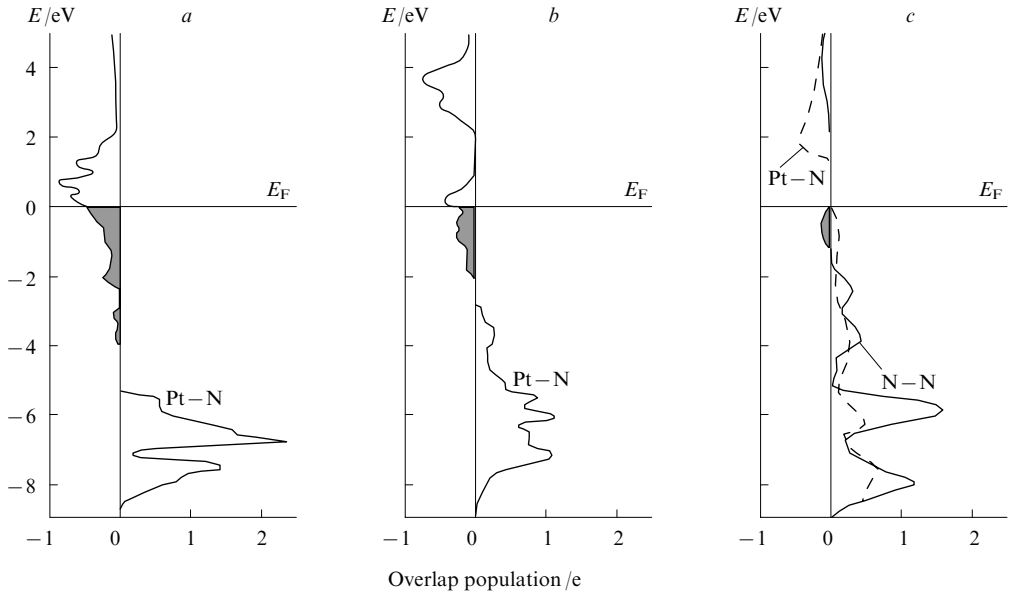


Figure 10. Overlap populations for platinum mono- (*a*, *b*) and dinitrides.[111]
Structural type: sphalerite (*a*), cooperite (*b*), pyrite (*c*). Positive OP correspond to bonding states, negative correspond to antibonding states; dark regions correspond to occupied antibonding states.

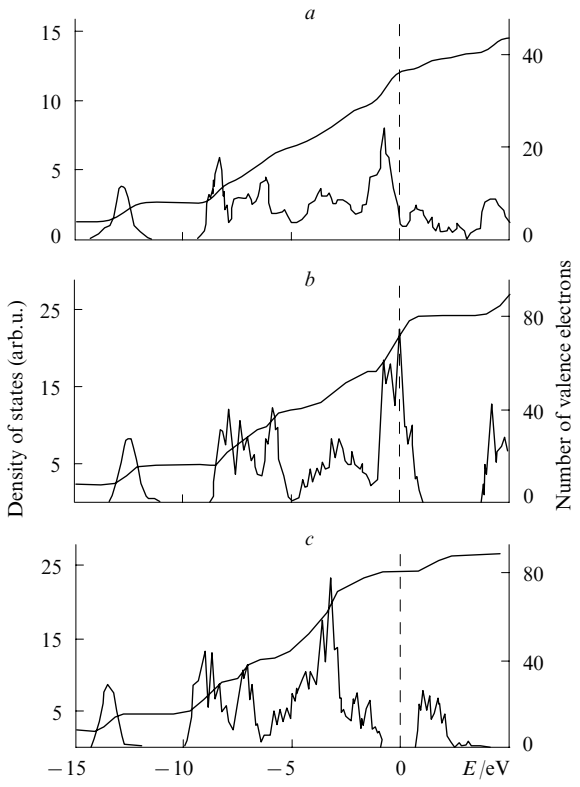


Figure 11. Total electron densities of states for OsN_2 with structural types of marcasite (*a*), pyrite (*b*) and also for PtN_2 with the pyrite structure (*c*).[120]
Vertical line designates the Fermi level.

ratios were estimated for certain polycrystalline MN_2 ceramics.

From the data in Fig. 12, it is evident that the bulk moduli of dinitrides are higher than the shear moduli, *i.e.*, it is the shear modulus that limits the mechanical stability of these phases. Yet another important factor determining the mechanical behaviour of materials is their brittleness. To obtain the brittle–ductile transition criterion, a model has been proposed[126] where the resistance to plastic deformation is assumed to be proportional to the shear modulus times the Burgers vector ***b***. The rupture stress is assumed to be proportional to the elastic modulus times the lattice constant, while the ductility is measured by the B/G quantity. The latter ratio shows how much easier is a brittle fracture compared with a ductile fracture accompanied by plastic strains, *i.e.*, the high B/G ratios correspond to ductile fractures and the low ratios correspond to brittle fractures. Hence, in terms of the model under consideration,[126] it becomes possible to correlate the nature of the dinitride fracture to the platinoid nature and the phase structure.[107]

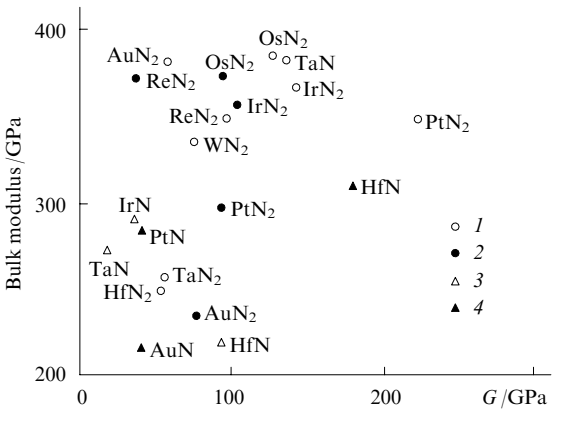


Figure 12. Bulk and shear moduli for certain 5d metal nitrides with the structures of pyrite (*1*), fluorite (*2*), sphalerite (*3*), NaCl type (*4*).[107]

In the majority of studies that discuss the mechanical properties of platinoid dinitrides, their high hardness is suggested. However, considering the known correlations between the moduli B and G, the largest part of these studies[66] dealt with elastic moduli when discussing the hardness of MN_2 phases.

A numerical method was proposed[127] for calculating the hardness (H) of covalent crystals, which included account of such values accessible from quantum chemical calculations as the electron density, the bond distance and the degree of covalence. The evaluation data for a series of covalent compounds[127] were well consistent with the results of experimental studies of microhardness of these crystals [on the Vickers (H_V) or Knoop (H_K) scales]. The method was modified[128] by taking into account yet another parameter, the so-called degree of the metallic nature of bonds

$$f_m = \frac{0.26N(E_F)}{n_e},$$

where n_e is the total number of electrons in the cell; it was applied in assessing the hardness of phases PtN_2 (with the pyrite structure) and OsN_2 (with the marcasite structure). It was found that H amounts to $\sim$27 GPa for OsN_2 and 60 GPa for PtN_2. For comparison, H values of diamond and κ-BN are 96 and 66–63 GPa, respectively.[127]

Vibrational frequencies of PtN_2 with the pyrite structure were calculated[129] and the possibility of the appearance of superconductivity in OsN_2 with the marcasite structure was analyzed.[70] For the latter case, the electron–phonon coupling constant was calculated ($\lambda \approx 0.37$) to be later used in assessing the temperature of the transition to the superconducting state $T_c \approx 1$ K. It was noted[70] that it is the vibrational modes of N_2 dimers that are responsible for the superconducting state and that the value T_c can be substantially elevated by the addition of p-type dopants (*e.g.*, rhenium, for osmium nitride $Os_{1-x}Re_xN_2$). This should provide an increase in $N(E_F)$ and, simultaneously, strengthen the N—N bonds, which would have a beneficial effect on T_c.

b. Mononitrides

Studies on the simulation of the structure and certain properties of platinoid mononitrides were conducted (see Table 3).[107–114] Figure 13 shows the main structural types of mononitrides under consideration, which differ in coordination numbers of atoms. Note that the majority of stable mononitrides (monocarbides) of the Group III–VI 3d–5d metals have structures with the coordination number (CN) 6 (of NaCl and WC types), whereas for certain 3d metals of the Groups VII and VIII, the possibility of the existence of binary phases with CN 4 was supported.[106, 130–133]

Systematic calculations performed for a series of mononitrides of 4d metals with the sphalerite structure[108] and 5d metals (for structures with CN 4, 6 and 8)[107, 109] made it

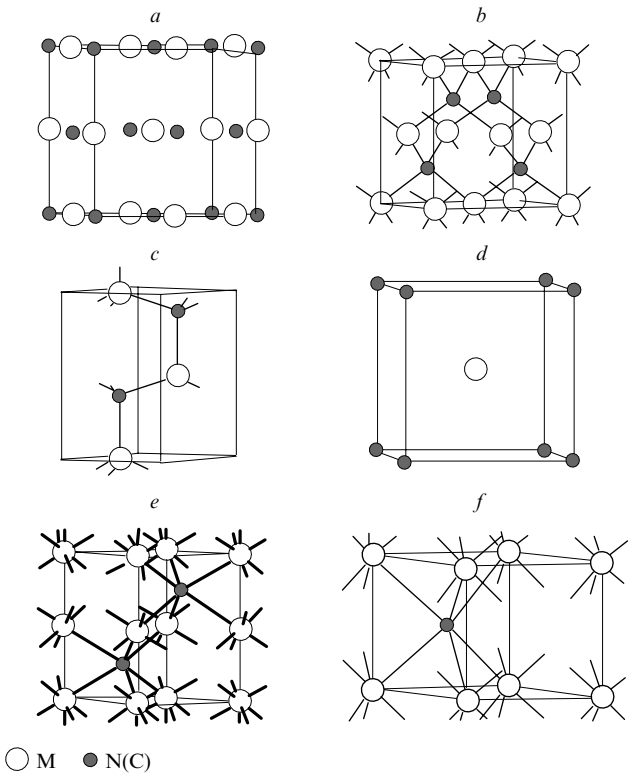


Figure 13. The main studied structural types of platinoid mononitrides (monocarbides) with different coordination numbers of atoms: CN 4 (wurtzite, zinc blende), CN 6 (NaCl, NiAs, WC types) and CN 8 (CsCl).[109]
Structure: (*a*) NaCl type, (*b*) zinc blende type, (*c*) wurtzite type, (*d*) CsCl type, (*e*) NiAs type, (*f*) WC type.

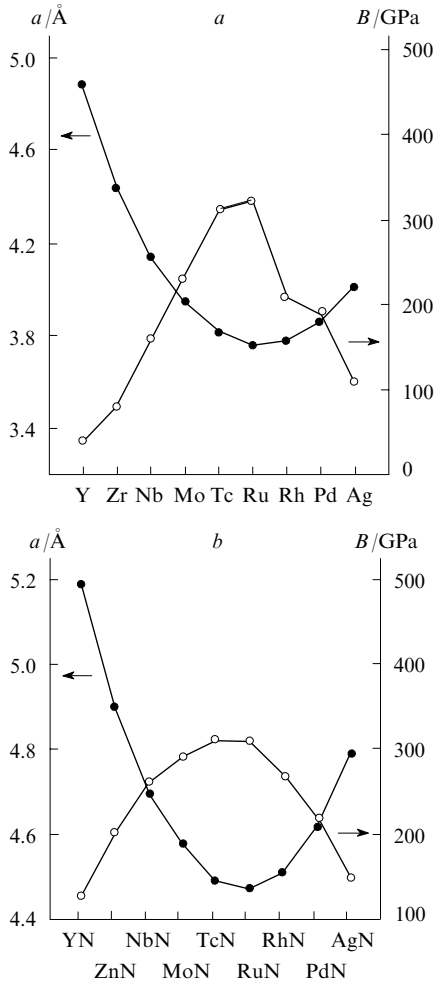


Figure 14. Changes of bulk modulus (*1*) and unit cell parameter (*2*) for 4d metals (*a*) and their sphalerite-like mononitrides (*b*).[108]

possible to reveal the main trends in variations of their structural, mechanical and thermodynamic properties with the metal type. Thus for sphalerite-like nitrides of 4d metals, the dependences of the lattice parameter a and the compression modulus B were non-monotonic, demonstrating minima and maxima for TcN and RuN, respectively, and retraced the corresponding dependences for pure 4d metals (Fig. 14).[108]

Similar dependences were found[109] for mononitrides of 5d metals (Fig. 15), namely, the maximum value of modulus B was predicted for ReN with the NiAs type structure, where B substantially depended on the nitride structural type. An interesting trend was revealed between the variations of energy of the nitride formation and the nature of 5d metal and the structure (see Fig. 15). It is seen that for all platinoid nitrides $\Delta H > 0$, *i.e.*, under ambient conditions, these phases are metastable; moreover, the positive value of ΔH rapidly increases with the increase in the 5d metal number. For OsN, IrN and PtN, the minimum ΔH corresponds to structures such as wurtzite and sphalerite (CN 4), at higher energies, phases with CN 6 are observed; the least probable structure for these nitrides is that of the CsCl type with CN 8. The electronic spectra of OsN, IrN and PtN phases were shown[109] to have the metal-like form, the valence band width correlated with the interatomic distance metal–nitrogen. It was assumed that the destabilization of nitrides of the metals at the end of the 5d row with the increase in the number of valence electrons in the latter may be associated with the progressive population of antibonding states.

Completing this section, the interesting results[111] on the comparative assessment (by the example of platinum nitrides) of enthalpies of formation of mono- and dinitrides with the sphalerite (ZnS), cooperite (PtS), NaCl-type, fluorite (CaF_2) and pyrite structures should be mentioned. The dependences of the enthalpy of formation on the external pressure in Fig. 16 show that at a pressure $P = 0$, all phases are metastable ($\Delta H > 0$), with ΔH increasing in the following series:

PtN_2 (pyrite structure) < PtN_2 (cooperite structure) <

< PtN (ZnS structure) < PtN (NaCl structure) <

< PtN_2 (CaF_2 structure).

As the pressure increased, the energies of formation of the pyrite-like PtN_2 structure and the cooperite-like PtN structure became negative at $P > 10$ and > 40 GPa, respectively. Thus, in the experimental pressure range, platinum dinitride was the most stable phase. This fact can be explained on a qualitative level[111] by analyzing the character of chemical bonds in PtN_2 and PtN (see Fig. 10), namely, the enhanced stability of dinitride is associated with the presence of additional strong nitrogen–nitrogen bonds in N_2 dimers.

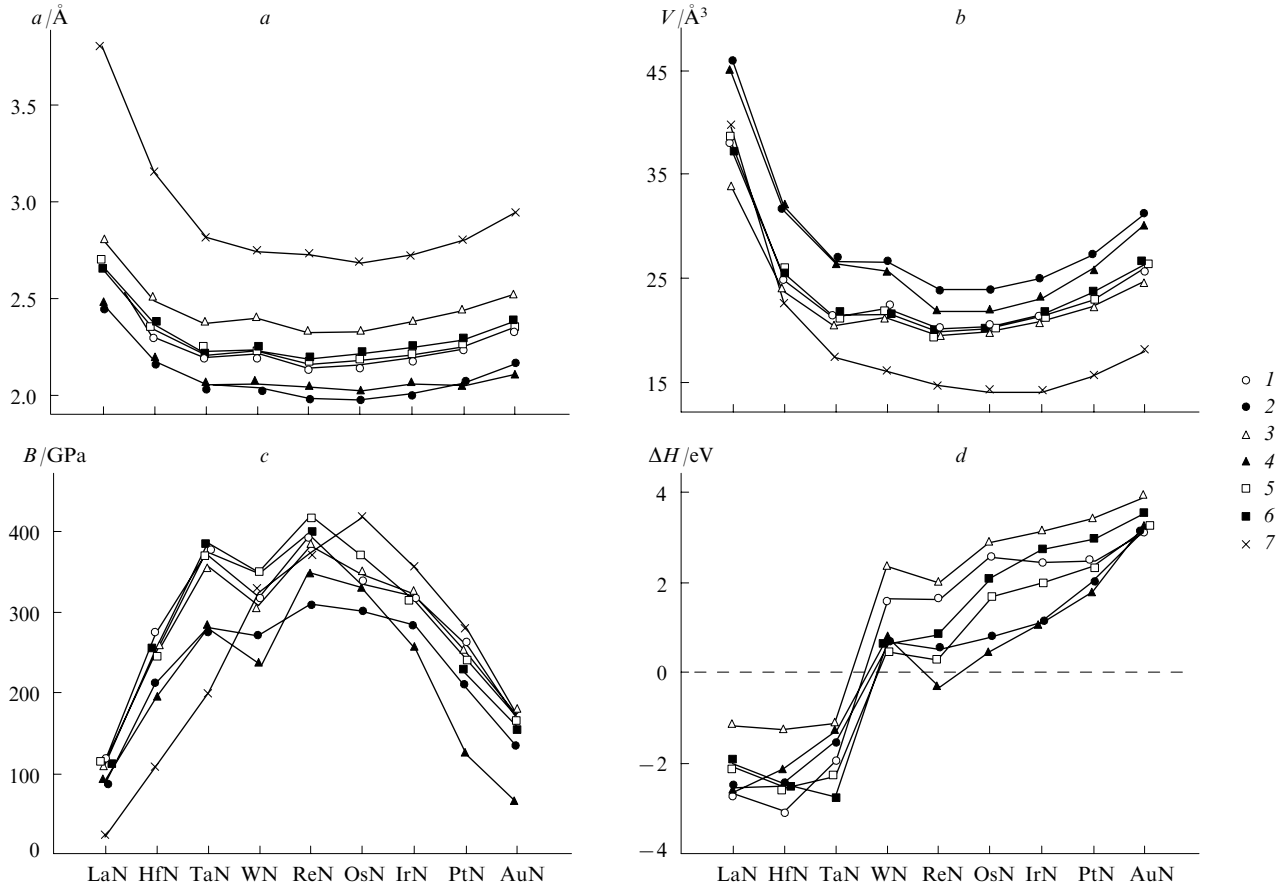


Figure 15. Changes in the unit cell parameter (*a*), cell volume (*b*), bulk modulus (*c*) and energy of formation (*d*) for 5d metals and their mononitrides with different structural types.[109]
Structural types: NaCl (*1*), sphalerite (*2*), CsCl (*3*), wurtzite (*4*), NiAs (*5*), WC (*6*); (*7*) metal.

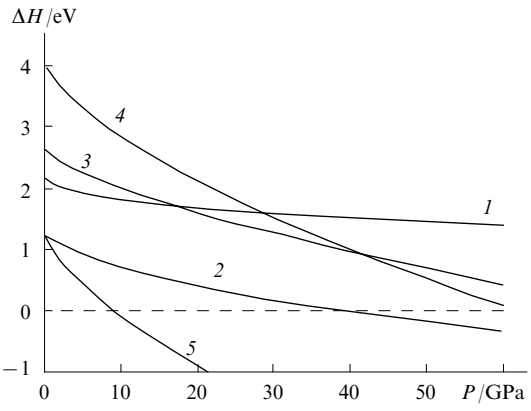


Figure 16. Dependences of enthalpies of formation on the external pressure for PtN phases with the structures of sphalerite (*1*), cooperite (*2*), NaCl type (*3*) and also for PtN_2 phases with the structures of fluorite (*4*) and pyrite (*5*).[111]

c. Trinitrides

The utmost nitrogen-rich hypothetical trinitrides of rhodium[69] and iridium[101] with the cubic structure of the skutterudite type ($CoAs_3$, space group *Im*3) were considered. This structural type is typical of a series of synthesized related phases, namely, IrP_3, $IrAs_3$, $IrSb_3$, CoP_3 and RhP_3.[134, 135] Two types of MN_3 structures, I and II, were analyzed. In both forms, nitrogen atoms were present as diatomic N_2 'molecules'; platinoid atoms were in the octahedral surrounding of nitrogen atoms (MN_6). Structures I and II differed in the conjugation type of MN_6 octahedra (Fig. 17).

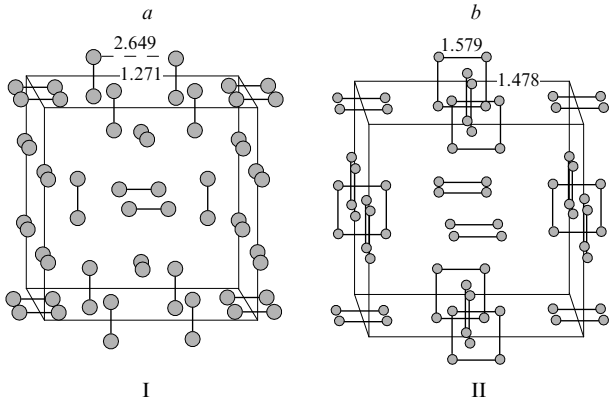


Figure 17. Orientation of N_2 dimers in model structures of the skutterudite type in modifications I (*a*) and II (*b*) (see text) in trinitrides RhN_3 (see Ref. 69) or IrN_3.[101]
Numbers are the distances (in Å) between the nitrogen atoms.

For RhN_3, it was shown [69] that both modification I and modification II were mechanically stable, the RhN_3-I bulk modulus (198 GPa) was smaller as compared with RhN_3-II (277 GPa). The anisotropy factors

$$A = \frac{2C_{44} + C_{12}}{C_{11}}$$

were 0.91 and 1.26 for modifications I and II, respectively, *i.e.*, both materials should exhibit anisotropy of elastic characteristics. The analysis of electronic properties has shown that the conducting properties of both RhN_3-I and RhN_3-II are metallic. The electronic spectra of these compounds revealed considerable overlap of the Rh4d and N2p states, which points to the presence of a covalent Rh—N bond; the ionic bond component was partly associated with the electron polarization in the Rh → N direction (transfer of ~0.25 e to 1 nitrogen atom). The external pressure-induced changes in the ΔH of dinitrides were assessed. It was shown that ΔH was positive at zero external pressure and changed its sign at $P = 2$ and 9 GPa for modifications I and II, respectively. This points to their stabilization under baric treatment conditions; hence, RhN_3-II was less stable at low pressures but at $P > 50$ GPa became more thermodynamically advantageous as compared with RhN_3-I.

The relationships, similar in many aspects, were predicted for analogous modifications of hypothetical iridium trinitride [101] isoelectronic to RhN_3. It was found that the total energy of IrN_3-I is 1.4 eV lower as compared with IrN_3-II. Both modifications were mechanically stable with compression moduli IrN_3-I (263 GPa) < IrN_3-II (358 GPa), where the latter phase turned out to be a semiconductor with the forbidden gap width of ~0.65 eV.

It was demonstrated [101] that IrN_3 is characterized by mixed covalent-ionic interaction with the covalent component due to the directed Ir—N and N—N bonds and the ionic bond associated with the charge transfer (~0.27 e) from iridium to nitrogen. Virtually no Ir—Ir bonds were present. This distinguishes IrN_3 from dinitride IrN_2, because for the latter, the presence of Ir—Ir bond was established. The results of calculations of the ΔH dependence on the external pressure suggest that modifications I and II of iridium trinitride, like RhN_3 modifications, may become thermodynamically stable at $P = 2$ and 11 GPa, respectively; moreover, at $P > 64$ GPa, the modification IrN_3-II should be thermodynamically more stable as compared with IrN_3-I.

d. Subnitrides

No experimental evidence of the synthesis of platinoid subnitrides (M_2N) with the M : N = 2 : 1 stoichiomery was obtained so far. The stability conditions of hypothetical subnitrides Rh_2N and Ir_2N and some of their properties were simulated.[136] It should be mentioned that the experimental data on the synthesis of subnitride of an isoelectronic analogue of rhodium and iridium, *i.e.*, Co_2N, are available.[137, 138] As the structural alternative to Rh_2N and Ir_2N, the antimarcasite (space group *Pnnm*) and antipyrite (space group *Pa*3) structures were considered. Rough estimates have shown that enthalpies of formation of phases Rh_2N and Ir_2N are positive, *i.e.*, these phases (in contrast to Co_2N with $\Delta H < 0$) should be metastable. These phases can be synthesized by the thermobaric method. At the same time, for Rh_2N and Ir_2N, the maximum positive ΔH values were obtained for phases with the antipyrite structure, which points to the higher probability of synthesizing these subnitrides as the phases with the antimarcasite structure.

According to calculations of electronic structures, Rh_2N and Ir_2N are non-magnetic substances that can exhibit metallic properties. Calculated bulk moduli of hypothetical subnitrides are sufficiently high, namely, 254 GPa (Rh_2N, space group *Pnnm*) < 278 GPa (Rh_2N, space group *Pa*3) < 331 GPa (Ir_2N, space group *Pnnm*) < 351 GPa (Ir_2N, space group *Pa*3). Moreover, these materials should be characterized by anisotropy of elastic properties (elastic anisotropy coefficients $A \neq 1$) and brittleness ($B/G = 2.98 - 6.62$, which many times exceeds the critical value $B/G = 1.75$ for plastic systems).

e. Nonstoichiometry

As was mentioned above, the wide homogeneity regions are among the most interesting properties of the known nitrides of the Group III – V 3d – 5d metals. To date, this property of platinoid nitrides remains virtually unexplored. Preliminary results were obtained only for RuN_x (Ref. 34) and PtN_x.[107]

For $RuN_{x<1}$,[34] the calculated electronic structures and enthalpies of formation of phases with the formal compositions Ru_4N, Ru_3N and Ru_2N were found to correspond to the structural types of Fe_4N, ReO_3 and CaF_2, respectively. It was shown that all $RuN_{x<1}$ compositions are metal-like and have positive ΔH (with the exception of nitrogen-deficient Ru_4N). The presence of nitrogen vacancies in the sphalerite-type PtN_x lattice was considered.[107] It was noted that for non-stoichiometric compositions, the criterion of mechanical stability ($C_{11} - C_{12} > 0$) was not met. At the same time, the effect of vacancies on both the conditions of energy stability of a platinum nitride and the changes in its structural and electronic characteristics still remains unexplored.

2. Carbides

In contrast to nitrides discussed above with a large number of already modelled phases in a wide range of $MN_{0.5-3}$ compositions, the studies of the platinoid – carbon system accomplished within the framework of theoretical approaches concentrated so far on stoichiometric monocarbides MC. Table 4 shows the lattice parameters of MC phases with different structural types and also their bulk compression moduli.

Carbides of light platinoids (ruthenium and palladium) were studied only in Ref. 67; for both phases, the cubic structure (NaCl type) was considered. It was noted that an important feature of their electronic spectrum is a considerable overlap of C2p—M4d states, which points to the formation of strong covalent C—M bonds. For RuC, the Fermi level is close to the local minimum of the density of states (Fig. 18); for RhC and PdC, due to the increase in the electron concentration, E_F is shifted up in the energy scale and the antibonding 4d states are occupied. On the qualitative level, it is explained by a decrease in the compression modulus with the increase in the metal number in the Periodic System.

The structural, electronic and mechanical properties of carbides of heavy 5d metals, namely, osmium, iridium and platinum, were studied more thoroughly (see Table 4). The compressibility of OsC and IrC as compared with certain other carbides and diamond was studied.[139] According to Fig. 19, the compressibility of IrC and OsC was lower compared with diamond; however, for OsC, this value

Table 4. Calculated unit cell parameters and compression moduli of platinum-group metal monocarbides.

Carbide	Structure	Unit cell parameters /Å		B/GPa	Ref.
		a (b)	c		
RuC	cubic (NaCl)	4.236 – 4.327	–	313.7 – 379.2	67
PdC	the same	4.340 – 4.433	–	280.2 – 219.2	67
OsC	WC type	–	–	438	44
	FeSi type	–	–	299	44
	OsSi type	–	–	445	44
	WC type	2.897 – 2.925	2.693 – 2.710	–	139
	the same	2.955	2.738	393	68
	sphalerite	4.630	–	292	68
	cubic (NaCl)	4.346	–	–	140
	sphalerite	4.598	–	–	140
	CsCl type	2.686	–	–	140
	FeSi type	5.702 (3.574)	4.124	290	140
	WC type	2.939	2.728	–	140
	Wurtzite	3.245	5.383	–	140
	NiAs type	2.907	5.505	365	140
	CoSn type	5.429	2.771	297	140
	MnP type	5.551 (2.852)	5.323	–	140
	WC type	2.907	2.771	390	141
IrC	the same	–	–	373	44
	FeSi type	–	–	312	44
	OsSi type	–	–	388	44
	WC type	3.012 – 3.024	2.640 – 2.653	–	139
PtC	NaCl type	4.425 – 4.489	–	313.9 – 261.3	67
	WC type	–	–	299	44
	FeSi type	–	–	255	44
	ZnS type	4.687	–	270	142
	NaCl type	4.427	–	339	143
	the same	4.477	–	–	143
	WC type	3.817	6.198	216.9	144
	NiAs type	3.004	5.636	311.6	144
	ZnS type	4.698	–	252.5	144
	PbO type	2.999	5.702	249.4	144
	NaCl type	4.456	–	300.7	144
	sphalerite	4.731	–	235 – 266	145
	cubic (NaCl)	4.490	–	267 – 282	145

exceeded the compressibility of WC. In turn, the Vickers microhardness of iridium carbide (22.7 GPa) was lower compared with tungsten carbide (31.8 GPa). A large series of alternative structures were analyzed [140] for OsC. Based on the comparison of theoretical and experimental [55] crystallographic data, it was concluded [140] that NiAs is the most probable structural type for osmium carbide. According to the results of quantum chemical calculations [144] of energies for PtC modifications (Fig. 20) with different structures (types of NaCl, NiAs, PbO, wurtzite, sphalerite), the sphalerite-like phase is the most stable under ambient conditions, while a phase with the NiAs structure is the most stable at high pressure.

According to the some forecasts, [44, 67, 68, 140 – 145] all platinoid carbides should exhibit metal-like properties and interatomic interactions in them should be of the mixed covalent-ionic-metallic nature. The formation of the ionic–

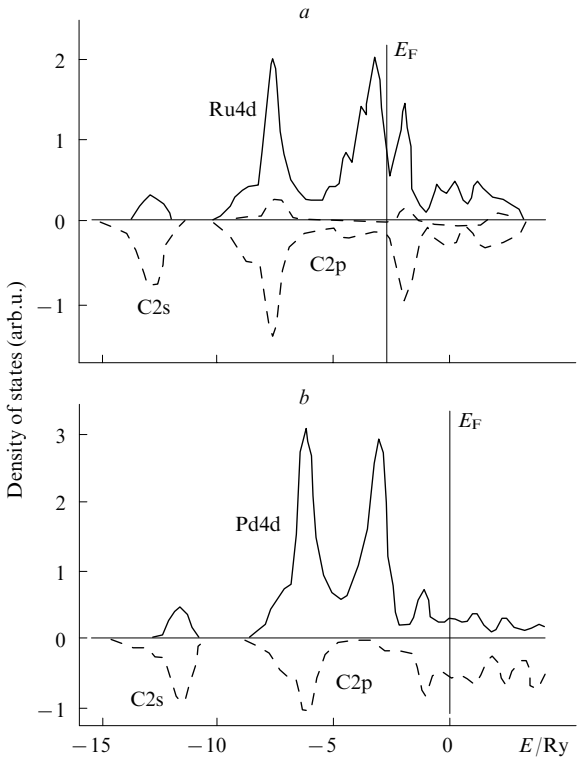


Figure 18. Densities of states of cubic (NaCl type) RuC (*a*) and PdC (*b*).[67]

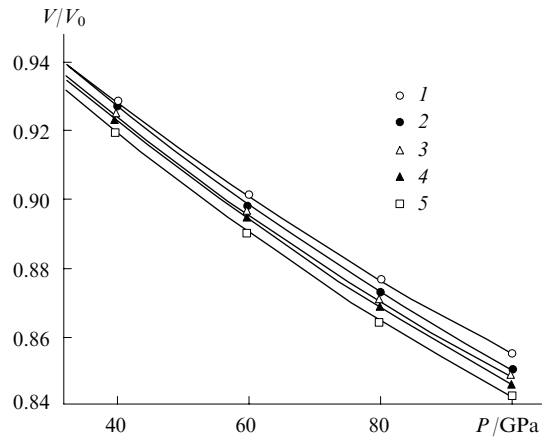


Figure 19. Compressibility of certain carbides as compared with diamond.[139]
(*1*) ReC, (*2*) diamond, (*3*) OsC, (*4*) WC, (*5*) IrC.

bond component (due to the partial charge transfer from platinoid atoms to carbon) is clearly distinguishable in differential maps of charge density $\Delta\rho$ (the difference between the charge densities of a crystal and isolated atoms) in characteristic sections of the osmium carbide crystal (Fig. 21).[141] The positive (negative) $\Delta\rho$ values correspond to the electron density deficiency on both osmium atoms (its excess on carbon atoms) with respect to free atoms.

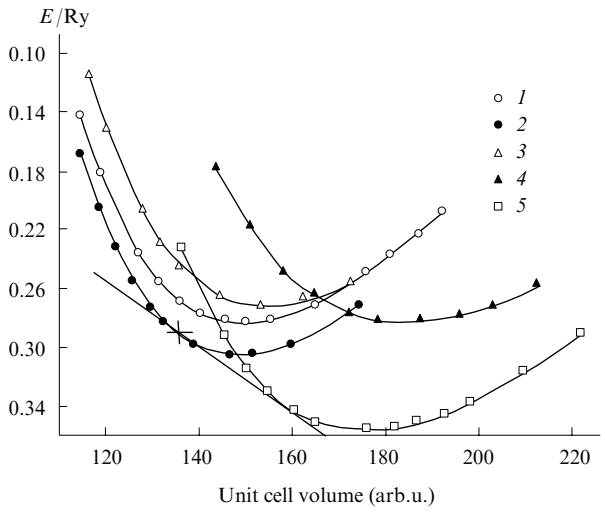


Figure 20. Energy variations as a function of the cell volume for platinum monocarbides with the structural types of NaCl (*1*), NiAs (*2*), PbO (*3*), wurtzite (*4*), sphalerite (*5*).[144]

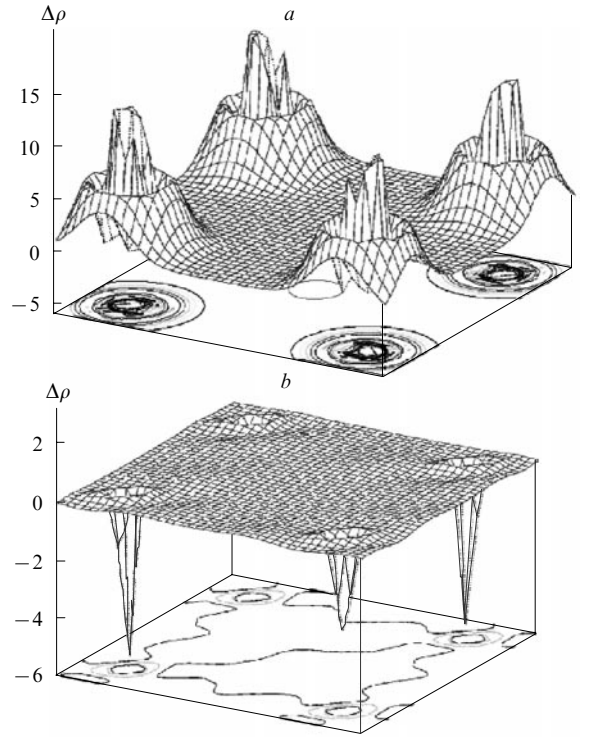


Figure 21. Differential electron density ($\Delta\rho$) distribution maps for OsC in the atomic planes of osmium (*a*) and carbon (*b*), illustrating the partial transfer of charge density in the Os → C direction.[141]

IV. Conclusion

In this review, an attempt was undertaken to generalize the results of the first stage of studies of new compounds, namely, nitrides and carbides of platinum-group metals (Ru, Rh, Pd, Os, Ir and Pt), since their discovery in 2004.[31] The main advances in the present stage are as follows.

A series of crystalline platinoid nitrides and carbides, namely, PtN, PtC, RuN, PtN_2, IrN_2, OsN_2, PdN_2 were synthesized. The use of modern methods of synthesis (high pressures and temperatures, film technologies, and some other) made it possible to obtain binary phases in the systems platinoid – nitrogen (carbon) the existence of which was rejected for a long time. A distinguishing feature of certain new phases (*e.g.*, PtN_2, IrN_2, OsN_2 and PdN_2) is their record-breaking high content of the non-metal exceeding that for the overwhelming majority of previously known nitrides and carbides of transition 3d – 5d metals.

The conditions for the existence of new platinoid nitrides and carbides were experimentally studied as well and their compositions, crystal structures and certain properties, particularly their extreme mechanical properties (enhanced elastic moduli and low compressibility) attracted attention.

The considerable body of information on the structural, mechanical, electronic and certain other properties was obtained using calculation methods of quantum chemistry. The use of these methods also allowed the peculiarities of electronic structure and chemical bonds to be elucidated in a wide series of synthesized and hypothetical nitrides and carbides of platinoids with different structural types and compositions and their stability to be assessed.

However, many problems still remain unsolved. Thus at present no experimental information is available on the phase ratios and the possibility of phase formation in the (Rh,Pd) – N and (Ru,Rh,Pd,Ir) – C systems.

For the new group of phases, many problems already thoroughly elaborated for 'classical' nitrides and carbides of transition 3d – 5d metals remain unclear. These include, first of all, the development of conditions for stabilization of phases (nitrides and carbides) metastable under ambient conditions. The problem of non-stoichiometry and the role of structure vacancies in exerting control over the stability and properties of new binary phases remains virtually unexplored. No information is available on the mutual solubility of platinoid carbides and nitrides and on the possibility of formation of multicomponent solid solutions, for example, carbonitrides of platinoids or double carbides (nitrides) such as $M_xM'_yC(N)$ and also of different composite materials involving them.

From our viewpoint, staging such studies will advance the understanding of the mechanism of phase formation in platinoid – nitrogen (carbon) systems and the development of adequate models for their description; this may also be of considerable importance for the progress in materials science.

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