Order-disorder transformations and phase equilibria in strongly nonstoichiometric compounds

A I Gusev

DOI: 10 1070/PU2000v043n01ABEH000647

Contents

1.	Introduction	1
2.	Ordering in highly nonstoichiometric interstitial compounds	3
3.	Free energy and equilibrium conditions for ordered phases	5
4.	Equilibrium conditions for nonstoichiometric interstitial compounds	7
	4.1 A model for nonstoichiometric interstitial compounds; 4.2 Basic equations	
5.	Equilibrium phase diagrams of $M - C$ and $M - N$ systems with allowance for ordering	
	of nonstoichiometric carbides and nitrides	9
	5.1 A model equilibrium phase diagram of the $M-X$ system with an ordering nonstoichiometric compound MX_{ν} ;	
	5.2 Phase diagrams of Ti-C, Zr-C, and Hf-C systems; 5.3 Phase diagrams of the V-C, Nb-C, and Ta-C systems;	
	5.4 The Ti – N system	
6.	Phase diagrams of pseudobinary systems	26
7.	Conclusions	34
	References	35

References

Abstract. Data on order-disorder phase transformations in strongly nonstoichiometric carbides and nitrides MX_{μ} (X = C, N) of Group IV and V transition metals at temperatures below 1300-1400 K are reviewed. The order-parameter functional method as applied to atomic and vacancy ordering in strongly nonstoichiometric MX_y compounds and to phase equilibrium calculations for M-X systems is discussed. Phase diagram calculations for the Ti-C, Zr-C, Hf-C, V-C, Nb-C, Ta-C, Ti-N, and Ti-B-C systems (with the inclusion of the ordering of nonstoichiometric carbides and nitrides) and those for pseudobinary carbide $M^{(1)}C - M^{(2)}C$ systems are presented. Heat capacity, electrical resistivity and magnetic susceptibility changes at reversible order-disorder phase transformations in nonstoichiometric carbides are considered.

1. Introduction

The idea of a crystal as a periodic, three-dimensional, and completely ordered ensemble of particles is the physical model of a perfect solid. Real crystals always have defects of various types. The geometric classification of defects takes into account the dimensionality of the distortions of the lattice introduced by the defects. Point (zero-dimensional) defects generate atomic displacements in the crystal, which (in

A I Gusev Institute of Solid-State Chemistry. Ural Branch of the Russian Academy of Sciences ul. Pervomaiskaya 91, 620219 Ekaterinburg, Russian Federation Tel. (7-3432) 49 35 23. Fax (7-3432) 74 44 95 E-mail: gusev@ihim.uran.ru, gusev@chem.ural.ru

Received 27 July 1999 Uspekhi Fizicheskikh Nauk 170 (1) 3-40 (2000) Translated by E Yankovsky; edited by S N Gorin the case of localization near a single defect) concentrate within a volume of microscopic dimensions, rapidly decrease in size, oscillate, and die down in the tenth to twelfth coordination shell, i.e., over distances not exceeding three to four lattice parameters. Vacancies or impurity atoms correspond to such a definition of a point defect. One-dimensional (linear) defects are dislocations, while two-dimensional, or surface, defects are grain boundaries (interfaces), antiphase boundaries in ordered alloys and compounds, stacking faults, etc.

It is point defects that are associated to the greatest extent with nonstoichiometry. The geometric classification of defects implies, indirectly, that point defects are noninteracting. However, the absence of interaction between defects can be directly linked to their low concentration: if the concentration exceeds 0.1 at.%, the defects begin to interact. The effect of point defects on the properties of a crystal is determined by the defect concentration and the character of their distribution in the lattice.

The presence of defects means that an exact stoichiometric composition of crystalline compounds is more an exception than a rule. However, in many compounds the concentration of defects within a broad range of temperatures and pressures is so low that determining it is beyond the limits of modern methods, so that here all deviations from the stoichiometric composition can be ignored.

At T > 0 K, there can be no absolutely defect-free crystals, so that the presence of defects is not by itself an indication of nonstoichiometry. What is essentially an indication is the experimentally observable discrepancy between the chemical composition of a compound and the concentration of the sites of the crystal lattice occupied by the components of the compounds. Nonstoichiometry leads to the emergence of unfilled sites of the crystal lattice, i.e., structural vacancies designated by a symbol . Nonstoichiometry is possible only in crystal substances consisting of two or more components.

In most binary and more complicated compounds, the concentration of defects (vacancies or interstitial atoms) is fairly low and at 300 K does not exceed 0.01 at.%, while the distance between nearest defects is very large and amounts to several microns or even greater [1, 2]. There are, however, compounds in which under ordinary conditions the concentration of such defects as vacancies is very high. Probably the best-known of such compounds is wustite FeO. This compound always contains an excess of oxygen due to the presence of vacancies in the iron sublattice; for example, at 1300 K wustite has the composition $Fe_{0.88}O$. Sizable deviations from stoichiometry accompanied by vacancy formation in the metal sublattice have been detected in the iron and copper sulfides Fe_{0.85}S and Cu_{1.73}S, with a B8-type structure (NiAs). Large deviations from stoichiometry with vacancies in the oxygen sublattice are characteristic of the higher oxides TiO₂, V₂O₅, CeO₂, UO₂, MoO₃, WO₃, etc.

Probably the first who used the term 'structural vacancy' were Andrievskii and Gurov [3]. Later the term was used to describe the defect structure of nonstoichiometric carbides, nitrides, and oxides [4-6]. At present the term has gained wide acceptance in discussing topics related to nonstoichiometric compounds [1, 2, 7-21]. The special features of structural vacancies as defects are in that their concentration is directly linked to the chemical composition of the nonstoichiometric compound; this concentration may be as high as several at.%. In nonstoichiometric compounds the structural vacancies are analogs of atoms, i.e., they are quasiparticles; in their own sublattice they act in the same way as the atoms of this sublattice. In most nonstoichiometric compounds, only one sublattice contains structural vacancies. However, there are nonstoichiometric compounds in which both sublattices have structural vacancies; the concentrations of the structural vacancies in different sublattices may be equal or unequal, depending on the composition of the compound. This duality, i.e., the simultaneous presence of structural vacancies in the metallic and oxygen sublattice, is a characteristic feature of cubic monoxides of titanium and vanadium [22, 23].

As a result of intensive studies of oxides (and later carbides and nitrides) of transition metals it was established that there exist nonstoichiometric phases with broad homogeneity ranges. For instance, according to various data, cubic titanium monoxide TiO_y has a homogeneity region ranging from $TiO_{0.65-0.80}$ to $TiO_{1.25-1.33}$, while cubic titanium carbide TiC_y exists in the range from $TiC_{0.48}$ to $TiC_{1.00}$. In view of the extremely high concentration of vacancies in such phases, the question arises of how the vacancies are distributed over the crystal lattice.

Formally, the vacant sites of the crystal lattice behave as atoms occupying the sites of the same lattice. For this reason the structural vacancies are interpreted not simply as 'holes' in the crystal lattice but as a certain analog of atoms. Structural vacancies diffuse in the lattice in the same way as real atoms do, and the deviation from stoichiometry and the related homogeneity range can be considered as a substitutional solid solution, which can be ordered or disordered. The interpretation of a vacant site as a structural element of a crystal identical to an occupied site [24] emerged in the 1960s and 1970s, when the problems of nonstoichiometry and ordering in oxides, sulfides, and chalcogenides were being actively discussed [25]. Disorder always violates the regularity of the crystal. However, in the case of substitutional solutions, the symmetry of the crystal lattice is conserved even in the presence of disorder. Indeed, for substitutional solutions there is no way that we can know what species of the atom is at a given site **r**; instead we know the probability for an atom of one or another species to occupy the site. In other words, for substitutional solutions there exists a probability lattice with all elements of the crystal's symmetry.

Analysis of the structure of nonstoichiometric compounds made it possible to distinguish between two opposite tendencies, ordering and disordering. The ordered distribution of vacancies has a high probability of existing at low temperatures, while the disordered distribution exists at high temperatures, when the entropy contribution to the free energy of the nonstoichiometric compound is sufficiently large. Completely ordered and completely disordered distributions are the limiting states of the nonstoichiometric compound. As a result of ordering, within the homogeneity region of the nonstoichiometric compound there emerge one or several ordered phases, which can also have homogeneity ranges. The maximum degree of long-range order equal to unity is achieved for ordered phases, whose composition is stoichiometric. Between the chaotic (disordered) distribution of structural vacancies and the presence of long-range order in their arrangement there are intermediate states, including those with short-range order. Thus, nonstoichiometry is closely related to ordering and disordering processes. More than that, the presence of nonstoichiometry is a prerequisite for order or disorder in the distribution of atoms and vacancies in the structure of nonstoichiometric compounds.

Usually we say that a compound is nonstoichiometric if a high concentration of atomic defects is observed even in the absence of impurity atoms. Highly nonstoichiometric compounds are those that contain structural-vacancy type defects and have homogeneity regions within which the vacancy concentration is so high that the vacancies interact. A homogeneity region is one within which the nonstoichiometric compound exists under variations of the composition of this compound for which the type of crystal structure remains unaltered. The combination 'highly nonstoichiometric compound' should be understood as a term. This concept extends to compounds with a stoichiometric composition if the compound 'lies' within the homogeneity region. A similar concept of a 'highly nonstoichiometric phase' was introduced by Anderson [24] while discussing nonstoichiometry in chalcogenides and sulfides, but it did not gain wide acceptance.

The group of highly nonstoichiometric interstitial compounds incorporates carbides, nitrides, and oxides MX_y and M_2X_y (X = C, N, and O) of Group IV and Group V transition metals [26, 27] and related ternary compounds with extended homogeneity ranges. Nonstoichiometry manifests itself most vividly in carbides and nitrides of Group IV and Group V metals. The concentration of structural vacancies \Box in carbides and nitrides can vary within wide limits and reach 30-50 at.% and higher at the lower boundary of the homogeneity range of these compounds. This suggests that the crystal lattice of carbides and nitrides is extremely stable with respect to the formation of structural vacancies.

The compounds that belong to the class of highly nonstoichiometric interstitial compounds are primarily cubic [with the B1-type base structure (NaCl)] and hexagonal [with the L'3-type base structure (W₂C)] carbides, nitrides,

and oxides MX_{ν} and M_2X_{ν} of transition metals [26–29]. In these compounds, the nonmetallic interstitial atoms X (C, N, and O) are located in the octahedral interstices of an fcc or close-packed hexagonal (hcp) crystal lattice formed by the atoms of the transition metal M. Depending on the extent of the deviation from stoichiometry, the interstitial atoms can occupy all octahedral interstices or only some of these interstices, i.e., form atomic groups XM_6 or $\Box M_6$. Ternary compounds also are represented in the group of highly nonstoichiometric compounds. The main element of the structure of these ternary compounds is an ideal or distorted octahedron consisting of six atoms of the transition metal. Partial occupancy of the octahedral interstices is the cause of sufficiently extended homogeneity regions in many ternary compounds, among which are M₅Si₃X with a D8₈-type hexagonal structure (Mn₅Si₃), M₃AlX with an E2₁-type cubic structure (CaTiO₃), M₃Al₂X with an A13-type cubic structure (β -Mn), M₂AlX with a hexagonal structure of the Cr₂AlC type, and others [30]. The difference between the structures of binary and ternary highly nonstoichiometric interstitial compounds is due to the way in which the octahedrons XM₆ are connected. In binary compounds MX_{ν} with a B1-type structure (NaCl), the octahedrons are connected along all twelve edges; in M₅Si₃X, along two faces; in the cubic compounds M₃AlX and M₃Al₂X, at all six vertices; and in the so-called Nowotny phases M2AlX, each octahedron XM₆ is connected to the neighboring octahedrons along six edges.

The history of studies of highly nonstoichiometric carbides and nitrides can arbitrary be divided into three periods. In the first period (from the beginning of the 20th century up to 1940), carbides and nitrides were interpreted as ordinary chemical compounds of stoichiometric composition. Most studies in this period were related to finding the types of crystal structure of the carbides and nitrides obtained in one way or another. By the end of this period, the study of the physical properties of carbides and nitrides began, and massive discrepancies between the results of different investigations of the properties of a single carbide or nitride were revealed. These discrepancies could not be explained by the measurement errors or by differences in the experimental methods. Detailed crystallochemical studies showed that the discrepancies were due to the different content of the interstitial atoms (carbon or nitrogen) in the same compound. It proved that the composition of the carbides and nitrides of Group IV and Group V transition metals can vary within very broad limits while the crystal structure remains unchanged.

The second period in the history of studies of highly nonstoichiometric compounds (1940–1970) was related to investigations of the composition–property dependences. Interest in the compounds in question peaked in the 1960s, when thousands of papers appeared in which researchers studied the effect of composition on the crystal-chemical, thermodynamic, electrical, magnetic, mechanical, and other properties of these substances. The researchers erroneously concluded that there was almost nothing left to study in these compounds.

For a long time after nonstoichiometric compounds were shown to have extended ranges of homogeneity, researchers assumed that nonmetallic interstitial atoms and structural vacancies (unoccupied interstices of the metallic sublattice) are distributed in the lattice at random. However, in 1967 and in later years crystallographic studies revealed that under certain conditions the interstitial atoms and vacancies become redistributed among the sites of the crystal lattice to form various ordered structures. These investigations ushered in the third period of studies, which were actively pursued in 1980s and 1990s and were related to investigations into disorder – order transformations and phase equilibria in highly nonstoichiometric compounds and into the effect of order on the properties of the compounds.

This review discusses the theoretical and experimental results obtained in the last 10 to 15 years in the studies of phase equilibria and disorder-order transformations and their effects on highly nonstoichiometric carbides and nitrides of Group IV and Group V transition metals.

2. Ordering in highly nonstoichiometric interstitial compounds

Atomic ordering considered as a structural disorder-order phase transition is the result of a redistribution of the atoms among the sites of the crystal lattice of a substitutional solid solution. But ordering is possible not only in substitutional solutions. It may also occur in interstitial solutions if the number of interstitial positions exceeds the number of atoms that occupy these positions. In the event of ordering in interstitial solutions, the unoccupied positions and the interstitial atoms act as a substitutional solution of species residing on these positions, while the solvent atoms form the skeleton inside which the interstitial atoms and vacancies become redistributed.

Thus, under certain conditions the presence of structural vacancies in nonstoichiometric compounds may lead to ordering. The nonmetallic interstitial atoms in the disordered compound MX_{ν} are statistically distributed among the sites of the defect (containing structural vacancies) nonmetal sublattice; the random distribution of the interstitial atoms means that the probabilities for any sites of the nonmetal sublattice to become occupied by an interstitial atom X are the same and equal to y (which is the relative content of the interstitial atoms), due to which all the sites of the nonmetal sublattice are crystallographically equivalent. As a result of the ordering that can occur as the temperature lowers, the disordered nonmetal sublattice 'splits' into several sublattices. The sublattices of the ordered phases of the nonstoichiometric compound differ from each other by the probability of occupancy of their sites by interstitial atoms. In the simplest case, the disordered nonmetal sublattice splits into a sublattice of the interstitial atoms and a sublattice of the structural vacancies. Ordering is accompanied by the lowering of the symmetry of the crystal's space group, since part of the symmetry transformations of the disordered nonmetal sublattice that superimpose the occupied sites on the unoccupied is not included in the group of symmetry elements of the ordered compound (because these sites become crystallographically nonequivalent).

A detailed description of the superstructures of nonstoichiometric carbides and nitrides can be found in Refs [2, 14, 17, 28, 29, 31–33]. The main ordered phases are listed in Table 1. These phases have a general formula $M_{2t}X_{2t-1}$, where t = 1, 1.5, 2, 3, and 4. So far, about twenty ordered phases of nonstoichiometric carbides and nitrides have been discovered. However, until recently not one phase diagram of M–C and M–N systems that would allow for ordering of the nonstoichiometric compounds MC_y and MN_y had been built.

		Ordered phase		Ba		
Formula	Honogeneity range or nonmetal content (at.%)	Lattice, structure type	Space group	Formula	Lattice, structure type	References
Ti ₂ C	TiC _{0.52} -TiC _{0.71}	Cubic	Fd3m	TiC _y	fcc, <i>B</i> 1	[34, 35]
Ti ₂ C	$TiC_{0.58} - TiC_{0.63}$	Trigonal	$R\bar{3}m$	TiC_y	fcc, B1	[36, 37]
Ti ₃ C ₂	$TiC_{0.64} - TiC_{0.68}$	Orthorhombic	C2221	TiC_y	fcc, B1	[36, 38]
Ti ₂ C	TiC _{0.49} -TiC _{0.54}	Cubic	Fd3m	TiCy	fcc, <i>B</i> 1	[39]
Ti ₂ C	TiC _{0.55} -TiC _{0.59}	Trigonal	R3m	TiC_v	fcc, B1	[39]
Ti ₃ C ₂	TiC _{0.63} -TiC _{0.67}	Rhombic	C2221	TiCy	fcc, B1	[39]
Ti ₂ C	TiC _{0.47} -TiC _{0.54}			TiC_{y}	fcc, <i>B</i> 1	[26, 40]
Ti ₃ C ₂	TiC _{0.62} -TiC _{0.70}			TiC _v	fcc, B1	[26, 40]
Ti ₆ C ₅	$TiC_{0.80} - TiC_{0.90}$			TiC _v	fcc, B1	[26, 40]
δ' -ZrC _v	39.0-43.0	Trigonal		ZrC_{y}	fcc, B1	[41]
$ZrC_{\nu}(Zr_2C)$	$ZrC_{0.63} - ZrC_{0.74}$	Cubic		ZrC_{v}	fcc, B1	[35]
$ZrC_{0.75}$	$ZrC_{0.69} - ZrC_{0.77}$	Cubic, ThC _{0.76} type		ZrC_{y}	fcc, B1	[42]
Zr ₂ C	$ZrC_{0.47} - ZrC_{0.54}$			ZrC_{y}	fcc. B1	[2, 26, 43 - 46]
Zr_3C_2	$ZrC_{0.60} - ZrC_{0.71}$			ZrC_{v}	fcc. B1	[2, 26, 43 - 46]
Zr_6C_5	$ZrC_{0.76} - ZrC_{0.92}$			ZrC_{y}	fcc. B1	[2, 26, 43 - 46]
Hf ₃ C ₂	$HfC_{0.67} - HfC_{0.72}$			HfC	fcc. $B1$	[2, 26, 46 - 48]
Hf ₆ C ₅	$HfC_{0.77} - HfC_{0.90}$			HfC.	fcc. B1	[2, 26, 46, 47]
β _n -V ₂ C	$\sim 33.0 (VC_{0.5})$	Orthorhombic, ζ-Fe ₂ N type	Phen	V_2C_y	hcp. $L'3$	[41, 49]
$\beta' - V_2 C$	$\sim 33.0 (VC_{0.5})$	Hexagonal	1000	V_2C_y	hcp, L'^3	[41, 49]
V ₄ C ₅	$\sim 45.5 (VC_{0.82})$	Trigonal	$P3_1 P3_2$	VC.	fcc $B1$	[50-53]
V_6C_5	$\sim 45.5 (VC_{0.83})$	Monoclinic	C^{2}	VC.	fcc $B1$	[54 55]
δ'-VC	$\sim 45.5 (VC_{0.83})$	Trigonal	02	VC.	fcc $B1$	[41]
$\delta'' - VC_{m}$	450 - 470	Monoclinic		VC.	fcc $B1$	[41]
$V_{0}C_{7}$	$\sim 46.6 (VC_{0.87})$	Cubic	P4,32	VC.	fcc. $B1$	[51 - 53, 56 - 60]
Nh ₂ C	$\sim 33.3 (NbC_{0.5})$	Orthorhombic type (-Fe ₂ N	Pnma	Nb ₂ C ₂	hen L'^3	[61]
Nb ₂ C	~ 33.3 (NbCo.s)	Hexagonal s-Fe ₂ N type	1 111111	Nb ₂ C _y	hep, L'^3	[61]
Nb ₂ C	$NbC_{0.75} = NbC_{0.84}$	Trigonal V _c C ₅ type [33]	P3, P3,	NbC	fcc $R1$	[67 - 64]
Nb ₆ C ₅	$NbC_{0.75} = NbC_{0.84}$	Monoclinic	C^{2}/m	NbC	fcc B1	[65-70]
Nb ₂ C ₂	$NbC_{0.81} = NbC_{0.88}$	Wohoenne	C2/m	NbC	fcc B1	$\begin{bmatrix} 0 & 7 & 0 \end{bmatrix}$
Nb ₃ C ₂	$NbC_{0.6}$ $NbC_{0.71}$			NbC	fcc B1	[2, 20, 43 - 40]
Tac	~ 33.3 (TaCas)	Trigonal		TacC	hen L^{\prime} 3	[2, 20, 45 40]
TacCe	$T_{a}C_{a} = T_{a}C_{a}$	Incommensurate phase $M_{c}C_{c}$ type		TaC	fcc $R1$	[72 - 76]
TacCe	$TaC_{0.79} - TaC_{0.89}$	medimiensurate phase, m ₆ e ₅ type		TaC_y	fcc B1	[72 - 76]
δ'_{-} Ti ₂ N	$\sim 33.0 - 33.3$	Tetragonal	14, land	TiN	fcc B1	[2, 20, 45, 40] [77 - 81]
Ti-N	$T_{\rm IN}$ $T_{\rm IN}$ $T_{\rm IN}$	Tetragonal	M_1/amd	TIN	fee, B1	[77 - 01]
δ'_{-} Ti ₀ N	$TiN_{0.45} - TiN_{0.50}$	Tetragonal	I_{1}/amd	TiN	fcc, $B1$	[02]
Ti.N	$T_{1}N_{0.50} - T_{1}N_{0.51}$	Tetragonar	1 - 1/ <i>umu</i>	TIN	fee, B1	[35 - 35]
Ti ₂ IN Ti-Ni-	$TIN_{0.52} - TIN_{0.57}$			TINy	fee, B1	[20, 40, 47]
Ti.N.	$TIN_{0.58} - TIN_{0.72}$			TINy	fee B1	[20, 40, 47]
Ti ₆₁ N ₅	$111 v_{0.77} - 111 v_{0.90}$	Orthorhombic		TINy	fcc, B1	[20, 40, 47]
1161N5 V NI	44.7-45.0	Unangenal a Ea Nitura		V N	here $L^{/2}$	[60]
V 2IN	~ 33.3	Hexagonal, E-Fe2N type	D6 22	$V_{21}N_y$	here L'^2	[02]
V 91N4 S' V/NI	~ 33.0	Tetragonal	r 0322	V 91N4 VNI	foo P1	[0/] [41]
$\mathbf{v} - \mathbf{v} \mathbf{n}_y$	44.0-47.0 VN	Tetragonal	DA / mm o		for D1	[41]
V 321N26	$\sim v_{1}v_{0.78}$	Tatragonal	r 42/ MMC	VIN _y NIHNI	for D1	[0/] [00 00]
IND4IN3	\sim 43.0	Tetragonal	14/ <i>mmm</i>	indin _y	ICC, <i>B</i> 1	[88, 89]

Table 1. Ordered phases of highly nonstoichiometric carbides and nitrides of Group IV and Group V transition metals.

Indeed, even the phase diagrams of the M–C and M–N systems that appear in reference books published in 1987–1990 [90–92] usually duplicate the phase diagrams studied 20 to 30 years ago that were built for temperatures above 1300–1500 K [93–95]. No ordering of nonstoichiometric compounds occuring at lower temperatures was reflected in these diagrams. The one exception was the phase diagram of the V–C system [96] in which the boundaries of the ordered phases V₈C₇, V₆C₅, and V₂C were depicted tentatively.

Experimental studies of phase diagrams of transition metals with carbon and nitrogen are extremely involved, since the compounds that are formed have very high melting temperatures (up to 4300 K), interact with the gaseous medium, and evaporate disproportionately. It has proved extremely difficult to attain an equilibrium ordered state of nonstoichiometric compounds at reduced temperatures

(below 1300-1400 K) due to the low diffusion rate. The existing experimental data provide only a general picture of the position of the ordered phases in the phase diagram and are insufficient for building the phase boundaries more accurately. In view of this, the various theoretical methods and models that make it possible to account for atomic ordering are of interest. Most modern theoretical models used in this field [97-104] are based either on the mean-field approximation or the cluster approximation.

The main problem of the statistical theory of atomic ordering is building the thermodynamics of a system consisting of many interacting particles. In the mean-field model and its different variants, this problem is solved, to one extent or another, by replacing the individual interatomic interactions with an interaction averaged over all the atoms. In particular, to describe the structural disorder – order phase transitions in substitutional and interstitial solid solutions, a variant of the mean-field approximation known as the method of static concentration waves [98] has proved its effectiveness. It is based on the idea of the one-particle distribution function $n_v(\mathbf{r})$ describing the distribution of atoms of a given species v among the sites r of the crystal lattice. However, as a result of using a one-particle distribution function the method of static concentration waves ignores multiparticle correlations. More than that, the problem of determining the energy parameters (the mixing energies $V(\mathbf{k})$), which are needed if we want to calculate the configurational energy, is not solved directly in the method of static concentration waves. For this reason, the theoretical approach to finding the superstructures in real systems by employing the method of static concentration waves has yet to be realized. So far the method has not been used to calculate phase diagrams with nonstoichiometric compounds.

In the cluster methods [99-102, 104], the results of the mean-field approximation are improved by applying the same reasoning to a cluster as to a single site of the lattice occupied by an atom of a given species. As a result, local correlations and interactions are taken into account by examining a compact group of atoms in a medium whose properties correspond to the average microscopic state of the substance. In other words, the interactions between the particles inside the cluster are taken into account exactly, while the interactions between the clusters are taken into account approximately, by using an effective field of some sort. To allow for correlations in structural phase transitions, such cluster approximations as the quasichemical approximation [105], the Bethe method [106], and Kikuchi's cluster variation method [99-101] are employed. The most effective is the cluster variation method, but this method has not been used to analyze ordering in such complex objects as nonstoichiometric compounds.

In Refs [2, 14, 107, 108], the order-parameter functional (OPF) method was developed to describe structural disorder-order phase transitions in substitutional solid solutions $A_{\nu}B_{1-\nu}$ and in nonstoichiometric interstitial compounds $MX_{\nu}\square_{1-\nu}$. This method also became known as the thermodynamic model of atomic ordering [109, 110]. Physically, the OPF method is based on the mean-field approximation, but by its formalism the method belongs to the group of cluster methods. However, it differs from cluster methods by its capacity to take into account the symmetry of a crystal with any long-range parameter in detail. In the OPF method, as well in the cluster variation method [99-102], the crystal is described by a set of figures of type s with a configuration i; the sequence $\{s\}$ of special figures necessary to describe a crystal incorporates the base cluster and the overlap figures. The main feature of the OPF method is the representation of the probabilities of different figures (clusters) in terms of the values of the distribution function $n_v(\mathbf{r})$, which directly depends on the long-range order parameters η . The distribution function $n_v(\mathbf{r})$ is the probability of finding the atoms of a given species v at the sites **r** of the ordering lattice. Using the OPF method made it possible to describe not only qualitatively but also quantitatively the first- and second-order phase transitions of the disorder-order type in a number of nonstoichiometric interstitial compounds MXy and solid solutions $A_{\nu}B_{1-\nu}$ and to determine the types of superstructures that are in thermodynamic equilibrium in them [2, 14, 17, 108].

In recent decades the theory of phase transitions has seen the active development of mathematical simulation by the molecular-dynamics and Monte Carlo methods. In particular, the Monte Carlo method was used to analyze the ordering of nonstoichiometric titanium carbide [36, 38]. This is a universal numerical method of solving mathematical problems by simulating random quantities [111]. Before the computer era, it could not find wide application since modeling random quantities is an extremely tedious problem. Today, however, it is used to analyze cooperative phenomena, in which probability plays an important role.

To employ the Monte Carlo method, a fairly small part of the crystal containing a sufficiently large number of atoms (no less than 1000) is separated and is considered as one cell of the periodic lattice out of the set of identical cells. Any equilibrium characteristic of such a system of N particles can be calculated by averaging over the canonical configuration ensemble $g(1, \ldots, N) \sim \exp[-\beta U(1, \ldots, N)]$, where U is the potential energy of the system. Let us assume that in an initial configuration the atoms are at the points $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N$. By the use of a random-number generator the *i*th atom is displaced by a vector $\mathbf{R}'_i - \mathbf{R}_i = \mathbf{\delta}$. The length of the step $|\mathbf{\delta}|$ is chosen arbitrarily in such a way that the entire system can be traversed using a finite number of steps. After each step the change ΔU in the energy of the system is calculated; if $\Delta U \leq 0$, the new configuration is suitable as the next step. The random walks obtained in this manner form a canonical ensemble. Usually, the energy is assumed to be the energy of pairwise (two-particle) interactions. As a result of the sequential procedure, for fixed parameters of particle-particle interactions a certain equilibrium distribution of atoms among the lattice sites sets in the system, a distribution that corresponds to a state with minimum energy. Obviously, the accuracy of the result depends on the number N.

Two main features of the Monte Carlo method follow from the above discussion. The first is that the calculation algorithm is fairly simple and the second, that the calculation error is proportional to $1/\sqrt{N}$.

De Novion et al. [36] and Priem et al. [86] studied ordering in nonstoichiometric titanium and niobium carbides and in titanium nitride. They used the inverse Monte Carlo method and, using neutron-diffraction data on short-range order as the basis, calculated the energy of pairwise interactions in the nonmetal sublattice. A cell measuring $18 \times 17 \times 17 = 5202$ fcc unit cells containing 20808 sites of the nonmetal sublattice was used for simulation.

In the sections that follow we briefly discuss the special features of the description of phase equilibria by the OPF method, generalize the data on phase equilibria in the binary systems M-C and M-N, and give the phase diagrams of these systems that were calculated with allowance for ordering by the OPF and Monte Carlo methods and the phase diagrams of pseudobinary carbide systems calculated in the subregular solution approximation. The construction of phase diagrams is important not only from the theoretical viewpoint but also for practical reasons, since this makes it possible to find the temperature – concentration regions of existence of the disordered and ordered phases, which differ significantly both in structure and in properties [2, 14, 17, 33].

3. Free energy and equilibrium conditions for ordered phases

Let us examine the ordering process in a binary interstitial solid solution $A_y B_{1-y}$ or in a nonstoichiometric compound $MX_y \square_{1-y}$, i.e., ordering in a binary system A-B or $X-\square$.

What is assumed is that ordered phases of the $A_{2t-1}B$ or $M_{2t}X_{2t-1}\Box$ type, where t = 1; 1,5; 2; 3; 4, can be formed in these systems as a result of a disorder – order transition. We will denote the free energies of the disordered phase A_yB_{1-y} (MX_y) and the ordered phase $A_{2t-1}B$ ($M_{2t}X_{2t-1}$) by F(y, 0, T) and $F(y, \eta, T)$, respectively. If we write the dependence of the enthalpy of formation H(y, 0, T) and the nonconfigurational entropy S(y, 0, T) of the disordered crystal ($\eta = 0$) on the crystal's composition y as a power series in y, i.e.,

$$H(y,0,T) = N \sum_{n=0}^{R^{(s)}} y^n H_n(T) ,$$

$$S(y,0,T) = N \sum_{n=0}^{R^{(s)}} y^n S_n(T) ,$$
(1)

then, as shown in the OPF method [108], the free energy *F* of the crystal is described, for any order parameter [from $\eta = 0$ to $\eta = \eta_{\max}(y)$], by the formula

$$F(y,\eta,T) = N \left\{ \sum_{s} \varkappa^{(s)} y^{(s)} \left[F_0(T) + y F_1(T) + \sum_{n=2}^{R^{(s)}} P_0^{(n)(s)}(y,\eta) F_n(T) \right] - T S_c(y,\eta) \right\}.$$
 (2)

Here s is the type of figure (cluster) in the sequence $\{s\}$ of special figures needed to describe ordering by the OPF method, $y^{(s)}$ is the overestimation factor allowing for the overlap of the figures s in the crystal lattice, $\varkappa^{(s)}$ is the factor linking the enthalpy of the crystal and the energy of all figures of the given type s with different configurations, $R^{(s)}$ is the number of sites incorporated in a figure of type s belonging to the ordered lattice, $\hat{P}_0^{(n)(s)}$ is the probability of a complete *n*subfigure formed by $n \leq R^{(s)}$ sites of the figure *s* (all sites of a complete *n*-subfigure are occupied by atoms of the species A (for the solid solution $A_{\nu}B_{1-\nu}$) or the species X [for the nonstoichiometric compound MX_{ν})], and S_c is the configurational (combinatorial) entropy. The probability $P_0^{(n)(s)}$ in (2) is a function of y and η , with the result that for given y and T the variable is the long-range order parameter η , while the model parameters are $F_0(T), F_1(T), \ldots, F_n(T)$.

According to Ref. [14], for a crystal in equilibrium all possible values of the distribution function degenerate to two values, $n_1^{(d)}$ and $n_2^{(d)}$, corresponding to the case where all long-range order parameters are the same: $\eta_1 = \eta_2 = \ldots = \eta_m = \eta$. If the ordering of the solid solution $A_y B_{1-y}$ or the nonstoichiometric compound MX_y leads to the formation of an ordered phase, $A_{2t-1}B$ or $M_{2t}X_{2t-1}$, the degenerate values $n_1^{(d)}$ (the probability of finding an atom of species A at a site of the sublattice B or an interstitial atom X at a site of the vacancy sublattice) and $n_2^{(d)}$ (the probability of finding an atom of species A at a site of the sublattice A or an interstitial atom X at a site of the sublattice formed by the interstitial atoms) are

$$n_1^{(d)} = y - \frac{(2t-1)\eta}{2t}, \quad n_2^{(d)} = y + \frac{\eta}{2t}.$$
 (3)

At $\eta = 0$ we have $n_1^{(d)} = n_2^{(d)} = y$, i.e., these probabilities describe a disordered state. The probability of any figure (cluster) that incorporates several sites of the lattice in which the ordering process takes place can be expressed in terms of the probabilities $n_1^{(d)}$ and $n_2^{(d)}$. Note that $P_0^{(0)(s)} \equiv 0$ and $P_0^{(1)(s)} \equiv y$ [14, 107].

The configurational (combinatorial) entropy of the ordered phase $A_y B_{1-y}$ or $M_{2t} X_{2t-1}$ is given by the following formula:

$$S_{c}(y,\eta) = -\frac{k_{B}}{2t} \left\{ n_{1}^{(d)} \ln n_{1}^{(d)} + (1 - n_{1}^{(d)}) \ln(1 - n_{1}^{(d)}) + (2t - 1) \left[n_{2}^{(d)} \ln n_{2}^{(d)} + (1 - n_{2}^{(d)}) \ln(1 - n_{2}^{(d)}) \right] \right\}.$$
 (4)

Clearly, when $\eta = 0$, equation (4) describes the configurational entropy $S_c(y, 0)$ of the disordered crystal.

With allowance for (1)–(3), the free energy F(y, 0, T) of the disordered ($\eta = 0$) crystal has the form

$$F(y,0,T) = N \left[\sum_{n} y^{n} F_{n}(T) - TS_{c}(y,0) \right].$$
 (5)

The equilibrium of the disordered and ordered phases is described by the following set of equations:

$$\frac{\partial F(y_1, 0, T)}{\partial y_1} = \frac{\partial F(y_2, \eta, T)}{\partial y_2},$$

$$F(y_1, 0, T) - y_1 \frac{\partial F(y_1, 0, T)}{\partial y_1} = F(y_2, \eta, T) - y_2 \frac{\partial F(y_2, \eta, T)}{\partial y_2},$$
(6)

where y_1 and y_2 are the relative contents of the component A (or X) in the disordered and ordered phases, respectively.

According to Ref. [43], after substituting (2), (4), and (5) into the set of equations (6) and combining the result with (3) we arrive at the following conditions for equilibrium of the disordered phase A_yB_{1-y} (or MX_y) and the ordered phase $A_{2t-1}B$ (or $M_{2t}X_{2t-1}$):

$$\begin{split} \sum_{n=0}^{R^{(s)}} y_1^{(n-1)} \big[n + (1-n)y_1 \big] F_n(T) + k_{\rm B} T \ln y_1 \\ &= \sum_s \varkappa^{(s)} y^{(s)} \Big\{ \sum_{n=0}^{R^{(s)}} \Big[P_0^{(n)(s)} + (1-y_2) \frac{\partial P_0^{(n)(s)}}{\partial y_2} \Big] \\ &\times F_n(T) - \eta \sum_{n=0}^{R^{(s)}} \frac{\partial P_0^{(n)(s)}}{\partial \eta} F_n(T) + \frac{k_{\rm B} T}{2t} \\ &\times \Big[\ln n_1^{(d)} + (2t-1) \ln n_2^{(d)} \Big] \Big\}_{\eta=\eta_{\rm equil}}, \end{split}$$

$$\sum_{n=0}^{R^{(s)}} (1-n) y_1^n F_n(T) + k_{\rm B} T \ln(1-y_1) = \sum_s \varkappa^{(s)} y^{(s)} \bigg\{ \sum_{n=0}^{R^{(s)}} \bigg[P_0^{(n)(s)} - y_2 \frac{\partial P_0^{(n)(s)}}{\partial y_2} \bigg] F_n(T) - \eta \sum_{n=0}^{R^{(s)}} \frac{\partial P_0^{(n)(s)}}{\partial \eta} F_n(T) + \frac{k_{\rm B} T}{2t} \bigg[\ln \big(1-n_1^{(d)}\big) + (2t-1) \ln \big(1-n_2^{(d)}\big) \bigg] \bigg\}_{\eta=\eta_{\rm equil}}.$$
(7)

Reasoning in a similar manner, we arrive at the conditions for equilibrium of the two ordered phases of the $A_{2t_i-1}B$ or

 $M_{2t_i}X_{2t_i-1}$ type, where *i* = 1 or 2:

$$\sum_{i=1}^{2} (-1)^{i} \sum_{s} \varkappa^{(s)} y^{(s)} \left\{ \sum_{n=0}^{R^{(s)}} \left[P_{0i}^{(n)(s)} + (1-y_{i}) \frac{\partial P_{0i}^{(n)(s)}}{\partial y_{i}} \right] F_{n}(T) - \eta_{i} \sum_{n=0}^{R^{(s)}} \frac{\partial P_{0i}^{(n)(s)}}{\partial \eta_{i}} F_{n}(T) + \frac{k_{B}T}{2t_{i}} \left[\ln n_{1,i}^{(d)} + (2t_{i} - 1) \ln n_{2,i}^{(d)} \right] \right\}_{\eta_{i} = \eta_{i,\text{equil}}} = 0,$$

$$\sum_{i=1}^{2} (-1)^{i} \sum_{s} \varkappa^{(s)} y^{(s)} \left\{ \sum_{n=0}^{R^{(s)}} \left[P_{0i}^{(n)(s)} - y_{i} \frac{\partial P_{0i}^{(n)(s)}}{\partial y_{i}} \right] F_{n}(T) - \eta_{i} \sum_{n=0}^{R^{(s)}} \frac{\partial P_{0i}^{(n)(s)}}{\partial \eta_{i}} F_{n}(T) + \frac{k_{B}T}{2t_{i}} \left[\ln \left(1 - n_{1,i}^{(d)} \right) + (2t_{i} - 1) \ln \left(1 - n_{2,i}^{(d)} \right) \right] \right\}_{\eta_{i} = \eta_{i,\text{equil}}} = 0.$$
(8)

Here y_i , $P_{0i}^{(n)(s)}$, η_i , t_i , $n_{1,i}^{(d)}$, and $n_{2,i}^{(d)}$ are the quantities corresponding to the ordered phases $A_{2t_i-1}B$ (or $M_{2t_i}X_{2t_i-1}$).

The equilibrium value of the long-range order parameter η_{equil} in the ordered phase $A_{2t-1}B$ (or $M_{2t}X_{2t-1}$) can be found from the condition for the minimum of free energy of this phase, when thermodynamic equilibrium is achieved, i.e., from the condition $\partial F(y, \eta, T)/\partial \eta = 0$. If we allow for (2) and (4), the condition becomes

$$\sum_{s} \varkappa^{(s)} y^{(s)} \left\{ \sum_{n=0}^{R^{(s)}} \frac{\partial P_{0}^{(n)(s)}}{\partial \eta} F_{n}(T) - k_{\rm B} T \frac{(2t-1)}{4t^{2}} \times \ln \left[n_{2}^{(d)} \frac{1-n_{1}^{(d)}}{n_{1}^{(d)} \left(1-n_{2}^{(d)}\right)} \right] \right\}_{\eta=\eta_{\rm equil}} = 0.$$
(9)

Equations (7)–(9) make it possible to calculate equilibrium phase diagrams of binary systems in which ordering is possible. The calculation parameters are the coefficients $F_0(T)$, $F_1(T)$, ..., $F_n(T)$ of the expansion (5) of the free energy of a disordered crystal. Thus, to calculate disorder–order and order–order transformations and equilibrium structural states by the OPF method it is sufficient to know the free energy of the disordered state of the crystal. This quantity can be either specified by the model or found from the experimental thermodynamic data.

4. Equilibrium conditions for nonstoichiometric interstitial compounds

4.1 A model for nonstoichiometric interstitial compounds

The disordered nonstoichiometric monocarbides MC_y and mononitrides MN_y have a *B*1-type structure, in which the nonmetallic interstitial atoms and structural vacancies are statistically distributed over the sites of the nonmetallic facecentered cubic (fcc) sublattice. To give an OPF description of the ordering of nonstoichiometric compounds MX_y with a *B*1-type structure, one must use a sequence $\{s\}$ that incorporates a base figure of type *c* (the base cluster in the form of an octahedron consisting of six sites of the nonmetal sublattice with a metal atom at the center) and overlap figures, which are a figure of type *b* (a bond, i.e., two neighboring sites of the nonmetal sublattice), and a figure of type *a* (a site of the nonmetal sublattice) [2, 14, 17, 107–110]. The base cluster in the form of an octahedron with a metal atom at the center makes it possible to allow for all sites of the crystal lattice; furthermore, the energy $\varepsilon_i^{(c)}$ of the base figure incorporates (implicitly) the energies of the pairwise interactions M–M and M–X, which are the main interactions in nonstoichiometric interstitial compounds.

The results of numerous studies (generalized in Refs [2, 14, 95]), suggest that the energies $\varepsilon_i^{(a)}$ and $\varepsilon_i^{(b)}$ are extremely low compared to ε_{M-M} and ε_{M-X} . This implies that $\varepsilon_i^{(a)}$ and $\varepsilon_i^{(b)}$ are negligible compared to $\varepsilon_i^{(c)}$, with the result that $\varkappa^{(a)} = \varkappa^{(b)} = 0$. As shown in Refs [14, 107], the coefficient $\varkappa^{(c)}$ can be found from the normalization condition $\sum_s \varkappa^{(s)} y^{(s)} = 1$; at $y^{(c)} = 1$ and $\varkappa^{(a)} = \varkappa^{(b)} = 0$, this coefficient is equal to unity. Note that for fcc solid solutions (alloys) only $\varkappa^{(a)} = 0$, while $\varkappa^{(b)} \neq 0$ and $\varkappa^{(c)} \neq 0$.

According to Refs [2, 14], in real binary orderable systems the expansions of the enthalpy of formation (1) and the free energy (5) of disordered nonstoichiometric compounds MX_y or disordered alloys A_yB_{1-y} are limited by second-order terms in concentration y, i.e., $F_{n>2}(T) \equiv 0$. With allowance for this fact and for the values of $\varkappa^{(s)}$ and $\gamma^{(s)}$, we can transform expression (2) for the free energy of nonstoichiometric compounds into the following form [107, 108]:

$$F(y,\eta,T) = F_0(T) + yF_1(T) + P_0^{(2)}F_2(T) - TS_c(y,\eta),$$
(10)

where

$$P_0^{(2)} \equiv P_0^{(2)(c)} = y^2 - \frac{a^{(s)}\eta^2}{4t^2} \,. \tag{11}$$

Clearly, if at $\eta = 0$ we combine (10) and (11), we obtain

$$F(y,0,T) = F_0(T) + yF_1(T) + y^2F_2(T) - TS_c(y,0),$$
(12)

where

$$S_{\rm c}(y,0) = -k_{\rm B} \big[y \ln y + (1-y) \ln(1-y) \big] \,. \tag{13}$$

Equations (10) and (12) imply that the difference $\Delta F = F(y, \eta, T) - F(y, 0, T)$ does not depend on the coefficients $F_0(T)$ and $F_1(T)$ of the linear terms in expansion (5). If expansions (1) that describe the composition dependences of the enthalpy and the nonconfigurational entropy of the disordered compound are linear, i.e.,

$$H(y,0,T) = N[H_0(T) + yH_1(T)],$$

$$S(y,0,T) = N[S_0(T) + yS_1(T)],$$

the free energy has the form

$$F(y,0,T) = N[F_0(T) + yF_1(T) - TS_c(y,0)]$$

Generally $S_c(y, \eta) - S_c(y, 0) < 0$, so that for such a dependence of the free energy we obtain $\Delta F > 0$ and no ordered phase is formed. Thus, within the adopted model approximations, the nonlinear dependence of the free energy F(y, 0, T) (without allowance for the configurational entropy) and the enthalpy of formation H(y, 0, T) is the necessary condition for the ordering of highly nonstoichiometric compounds [2, 14, 17, 108, 112]. According to Ref. [113], the composition

dependence of the free energy (without allowance for the configurational entropy) of a disordered nonstoichiometric compound MX_y is represented by a concave curve; with allowance for (12) this is possible only if $F_2(T) > 0$. Hence, for the disordered nonstoichiometric compounds MX_y in question, whose free energy F(y, 0, T) has the form (12), the energy parameter $F_2(T)$ is always positive, i.e., $F_2(T) > 0$.

The coefficient $a^{(s)}$ in equation (11) depends on the type and structure of the ordered phase and on the shape of the chosen base cluster. Using the concept of superstructural short-range order [114, 115], we can show that for any superstructure

$$a^{(s)} = 1 - 2t + \frac{2t}{R^{(s)}(R^{(s)} - 1)} \sum_{q} R^{(s)}_{q} \sum_{j} z^{(s)}_{jq} m^{(j)}_{21}, \qquad (14)$$

where $R_q^{(s)}$ is the number of sites of the base cluster with the neighbors $\{z_{jq}^{(s)}\}; z_{jq}^{(s)}$ is the number of sites of the base cluster *s* entering into the *j*th coordination shell of an arbitrary site *q* of the same cluster; and $m_{21}^{(j)}$ is the relative number of sites of the nonmetal sublattice occupied by interstitial atoms in the *j*th coordination shell centered at a vacancy. Summation over *q* and *j* in (14) is done within the limits of the base cluster, with $\sum_q R_q^{(s)} = R^{(s)}$ and $\sum_j z_{jq}^{(s)} = (R^{(s)} - 1)$.

4.2 Basic equations

The transformation of the set of equations (7) carried out in Refs [43, 44] with allowance for the model of stoichiometric compounds adopted in Refs [2, 14] made it possible to derive a set of equations describing the equilibrium of the disordered phase MX_{ν} and the ordered phase $M_{2t}X_{2t-1}$:

$$y_{1}(2 - y_{1}) + \frac{k_{B}T}{F_{2}(T)} \ln y_{1} = y_{2}(2 - y_{2}) + \frac{a^{(s)}}{4t^{2}} \eta_{\text{equil}}^{2}$$
$$+ \frac{1}{2t} \frac{k_{B}T}{F_{2}(T)} \left[\ln n_{1}^{(d)} + (2t - 1) \ln n_{2}^{(d)} \right]_{\eta = \eta_{\text{equil}}},$$
$$y_{1}^{2} - \frac{k_{B}T}{F_{2}(T)} \ln(1 - y_{1}) = y_{2}^{2} - \frac{a^{(s)}}{4t^{2}} \eta_{\text{equil}}^{2} - \frac{1}{2t} \frac{k_{B}T}{F_{2}(T)}$$
$$\times \left[\ln \left(1 - n_{1}^{(d)} \right) + (2t - 1) \ln \left(1 - n_{2}^{(d)} \right) \right]_{\eta = \eta_{\text{equil}}}$$

The conditions for the equilibrium of two ordered phases $M_{2t_i}X_{2t_i-1}$ (where i = 1 or 2) are

(15)

$$\sum_{i=1}^{2} (-1)^{i} \left\{ y_{i}(2-y_{i}) + \frac{a_{i}^{(s)}}{4t_{i}^{2}} \eta_{i,\text{ equil}}^{2} + \frac{1}{2t_{i}} \frac{k_{B}T}{F_{2}(T)} \right. \\ \times \left[\ln n_{1,i}^{(d)} + (2t_{i}-1) \ln n_{2,i}^{(d)} \right]_{\eta_{i}=\eta_{i,\text{ equil}}} \right\} = 0,$$

$$\sum_{i=1}^{2} (-1)^{i} \left\{ y_{i}^{2} - \frac{a_{i}^{(s)}}{4t_{i}} \eta_{i,\text{ equil}}^{2} - \frac{1}{2t_{i}} \frac{k_{B}T}{F_{2}(T)} \left[\ln \left(1 - n_{1,i}^{(d)} \right) \right. \\ \left. + (2t_{i}-1) \ln \left(1 - n_{2,i}^{(d)} \right) \right]_{\eta_{i}=\eta_{i,\text{ equil}}} \right\} = 0.$$
(16)

Solving the set of equations (15) and (16) for all binary equilibria that are possible in the ordering compound MX_y , we can find the position of the phase boundaries and build the equilibrium phase diagram.

With allowance for (10) and (11) and for the values of $\varkappa^{(s)}$ and $y^{(s)}$, we can write expression (9) for the equilibrium long-

range order parameter in the following form:

$$\frac{1}{\eta_{\text{equil}}} \ln \left[\frac{n_2^{(d)}(1-n_1^{(d)})}{n_1^{(d)}(1-n_2^{(d)})} \right]_{\eta=\eta_{\text{equil}}} = \frac{2a^{(s)}}{(2t-1)} \frac{F_2(T)}{k_{\text{B}}T} \,. \tag{17}$$

When the disorder – order transition temperature T_{trans} is reached, the free energies of the ordered and disordered phases become equal and $\Delta F = F(y, \eta, T) - F(y, 0, T) = 0$. But when the equilibrium value of η is reached, the free energy $F(y, \eta, T)$ is at its minimum, with the result that $\partial F(y, \eta, T)/\partial \eta = 0$. Combining these facts with (10)–(12), we see [14, 108] that the equilibrium conditions for the disorder – order transition are given by the equations

$$\Delta F(y,\eta,T) = -\frac{a^{(s)}\eta^2 F_2(T)}{4t^2} - T[S_c(y,\eta) - S_c(y,0)] = 0,$$
(18)

$$\frac{\partial F(y,\eta,T)}{\partial \eta} = -\frac{a^{(s)}}{2t^2} \eta F_2(T) - T \frac{\partial S_c(y,\eta)}{\partial \eta} = 0.$$
(19)

Reasoning along similar lines, we find [26] that the conditions for the order – order transition are

$$\Delta F(y, \eta_{\rm l}, \eta_{\rm h}, T) = \left[\frac{a_{\rm h}^{(s)} \eta_{\rm h}^2}{4t_{\rm h}^2} - \frac{a_{\rm l}^{(s)} \eta_{\rm l}^2}{4t_{\rm l}^2} \right] F_2(T) - T \left[S_{\rm c,l}(y, \eta_{\rm l}) - S_{\rm c,h}(y, \eta_{\rm h}) \right] = 0, \quad (20)$$

$$\frac{\partial F(y,\eta_1,T)}{\partial \eta_1} = -\frac{a_1^{(s)}}{2t_1^2} \eta_1 F_2(T) - T \frac{\partial S_{c,l}(y,\eta_1)}{\partial \eta_1} = 0, \quad (21)$$

$$\frac{\partial F(y,\eta_{\rm h},T)}{\partial \eta_{\rm h}} = -\frac{a_{\rm h}^{(s)}}{2t_{\rm h}^2} \eta_{\rm h} F_2(T) - T \frac{\partial S_{\rm c,h}(y,\eta_{\rm h})}{\partial \eta_{\rm h}} = 0, \quad (22)$$

where the subscripts l and h correspond to the low- and hightemperature phases, respectively. The solution of the set of equations (18) and (19) or (20)–(22) yields the equilibrium values of the long-range order parameter at the transition point, η_{trans} , and the transition temperature, T_{trans} . For disorder–order transitions the value of η_{trans} can be found by solving the equation

$$\frac{\eta_{\text{trans}}}{2} \left[\frac{\partial S_{\text{c}}(y,\eta)}{\partial \eta} \right]_{\eta=\eta_{\text{trans}}} - S_{\text{c}}(y,\eta_{\text{trans}}) + S_{\text{c}}(y,0) = 0.$$
(23)

When we are dealing with an order–order transition, the values of the long-range order parameters at transition points, i.e., the values of $\eta_{\text{trans},1}$ and $\eta_{\text{trans},h}$, which correspond to the low- and high-temperature phases, can be found by self-consistently solving the following equations:

The quantity $F_2(T)$, which characterizes the thermodynamic properties of the crystal, does not enter into equations (23) and (24). This means that η_{trans} depends only on the composition of the crystal and the type of superstructure participating in the disorder-order or order-order transition.

As shown in Refs [2, 14, 29, 107–110], the dependence of the maximum value of the long-range order parameter on the composition of the nonstoichiometric compound MX_y in which an ordered phase of the $M_{2t}X_{2t-1}$ type is formed can be expressed as follows:

$$\eta^{\max}(y) = \begin{cases} 2t(1-y), & \text{if } y \ge \frac{2t-1}{2t}, \\ \frac{2ty}{2t-1}, & \text{if } y < \frac{2t-1}{2t}. \end{cases}$$
(25)

By determining η_{trans} from (23) and substituting the result into (19) we arrive at an expression for the disorder-order transition temperature T_{trans} . The order-order transition temperature can be found by determining, via (24), the values of $\eta_{\text{trans},1}$ and $\eta_{\text{trans},h}$ and substituting them into equations (21) or (22), respectively. If the disorder-order or order-order transitions are first-order, the transition temperature is given by the formula

$$T_{\text{trans}} = \frac{2a^{(s)}}{(2t-1)} \frac{F_2(T_{\text{trans}})}{k_{\text{B}}} \eta_{\text{trans}}$$
$$\times \left\{ \ln \left[\frac{n_2^{(d)}(1-n_1^{(d)})}{n_1^{(d)}(1-n_2^{(d)})} \right]_{\eta=\eta_{\text{trans}}} \right\}^{-1}.$$
(26)

Note that the expression in braces is always positive. For order-order transitions, the values of *a*, *t*, and η_{trans} in (26) can correspond to either one of the two ordered phases in equilibrium.

In second-order phase transitions, in which the long-range order parameter varies smoothly from T_{trans} to T as the temperature lowers from $\eta = 0$ to $\eta = \eta_{\text{equil}}$, equation (26) becomes [2]

$$T_{\rm trans} = \frac{2a^{(s)}}{2t - 1} y(1 - y) \frac{F_2(T_{\rm trans})}{k_{\rm B}}, \qquad (27)$$

which is similar to the formula for the transition temperature in the mean-field approximation. We see that in second-order phase transitions the dependence of the ordering temperature on the composition of the compound MX_y or the solid solution A_yB_{1-y} is represented by a symmetric parabola with its maximum at y = 1/2. The entropy jump in order-order or order-disorder transitions of the first order is given [47] by the formula

$$\Delta S_{\text{trans}} = \left[\frac{a_{\text{l}}^{(s)} \eta_{\text{trans},1}^2}{4t_1^2} - \frac{a_{\text{h}}^{(s)} \eta_{\text{trans},h}^2}{4t_h^2} \right] S_2(T_{\text{trans}}) + S_{\text{c}}(y, \eta_{\text{trans},h}) - S(y, \eta_{\text{trans},1}), \qquad (28)$$

where $\eta_{\text{trans},1}$ and $\eta_{\text{trans},h}$ are the equilibrium values of the long-range order parameters at the transition point corresponding to the low- and high-temperature phases, respectively, and $S_2(T) \equiv -\partial F_2(T)/\partial T$. In order-disorder transitions, the high-temperature phase is disordered and $\eta_{\text{trans},h} = 0$ for this phase.

5. Equilibrium phase diagrams of M-Cand M-N systems with allowance for ordering of nonstoichiometric carbides and nitrides

5.1 A model equilibrium phase diagram for the $M\!-\!X$

system with an ordering nonstoichiometric compound MX_{ν} According to the data of Refs [2, 14, 17, 28, 29, 33] and the results of the structural studies generalized in Section 2, from the viewpoint of crystallography, superstructures of the M_2X , M₃X₂, M₄X₃, M₆X₅, and M₈X₇ types can form in nonstoichiometric compounds MX_{ν} with a base B1-type structure. A detailed crystallographic description of these $M_{2t}X_{2t-1}$ superstructures and the distribution functions for the interstitial atoms in such superstructures can be found in Ref. [29]; the values of the coefficients t and $a^{(s)}$ for all the superstructures are listed in Table 2. In Refs [14, 107, 108] it was shown that for the disordered nonstoichiometric compounds MX_{ν} , whose free energy is of the form (12), the energy parameter $F_2(T)$ is positive. Since T_{trans} is always positive, equations (26) and (27) imply that the coefficient $a^{(s)}$ can only be positive. Thus, it is wrong to assume that a trigonal (space group P3m1) M₃X₂ superstructure, for which $a^{(s)} < 0$, can form in an MX_{ν} compound with a base structure of the B1 type. Hence, below, when we mention the ordered phase M_3X_2 , we mean only orthorhombic (space groups Immm and C2221) and monoclinic (space group P2) superstructures of this type.

The general form of the model equilibrium phase diagram of an M-X system with an ordering nonstoichiometric compound MX_y in which all nonmetallic interstitial atoms X are replaced by structural vacancies \Box , i.e., in which y changes from 0 to 1, was found in Ref. [44].

According to the results of the thermodynamic calculations [2, 26, 43, 44] and crystallographic analysis [29], the

Table 2. Structural characteristics of possible ordered phases of highly nonstoichiometric compounds MX_y with a B1-type base structure (NaCl).

Type of ordered phase	Space group	$m_{21}^{(1)}$	$m_{21}^{(2)}$	t	$a^{(s)}$	$\frac{2a^{(s)}}{2t-1}$	
M ₂ X	$R\bar{3}m, Fd3m$	1/2	1	1	0.2	0.4	
	$I4_1/amd$	2/3	1/3	1	0.2	0.4	
	P4/mmm	2/3	0	1	0.067 (1/15)	0.133	
M_3X_2	Immm, P2	5/6	2/3	1.5	0.4	0.4	
	C222 ₁	3/4	1	1.5	0.4	0.4	
	$P\bar{3}m1$	1/2	1	1.5	-0.2	-0.2	
M_4X_3	Pm3m	1	0	2	0,2	0.133	
	I4/mmm	1	1/3	2	0.467 (7/15)	0.311	
M ₆ X ₅	$C2/m, P3_1, C2$	1	1	3	1.0	0.4	
M_8X_7	$Fm\bar{3}m, P4_332$	1	1	4	1.0	0.286	

formation of M_3X_2 , M_4X_3 , M_6X_5 , and M_8X_7 superstructures is a first-order phase transition, while an M_2X -type superstructure can form as a result of a second-order phase transition. Transitions between ordered phases are firstorder.

From (26) and (27) it follows that T_{trans} depends on the coefficient $2a^{(s)}/(2t-1)$. For superstructures of the M₂X type (space groups $R\bar{3}m$, Fd3m, and $I4_1/amd$), M_3X_2 type (space groups Immm, C222₁, and P2), and M₆X₅ type (space groups C2/m, C2, and $P3_1$) this coefficient is the largest (equal to 0.4), while for the tetragonal M_2X (space group P4/mmm) and cubic M₄X₃ (space group Pm3m) superstructures it is the smallest (see Table 2). This implies that for the superstructures of the M_2X (space groups R3m, Fd3m, and $I4_1/amd$), M_3X_2 (space groups Immm, C222₁, and P2), and M_6X_5 (space groups C2/m, $P3_1$, and C2) types, the order-disorder transition temperatures are comparable in value, and in the equilibrium phase diagram these superstructures are stable in close temperature intervals but in distinct concentration intervals. The tetragonal superstructure M_4X_3 (space group *I*4/*mmm*), the cubic superstructure M_8X_7 (space groups Fm3m and P4₃32), and especially the tetragonal superstructure M_2X (space group P4/mmm) and the cubic superstructure M_4X_3 (space group *Pm3m*) can be stable only in the low-temperature region.

The model phase diagram of an orderable nonstoichiometric compound MX_{v} (0 < v < 1) has been calculated and built for temperatures ranging from 300 K to the transition temperature T_{trans} [26, 44]. For nonstoichiometric carbides and nitrides in this temperature range the ratio $k_{\rm B}T/F_2(T)$ is a monotonic increasing function of T. This fact has made it possible to build the phase diagram using the dimensionless reduced temperature $k_{\rm B}T/F_2(T)$ (for the compounds in question the reduced temperature $k_{\rm B}T/F_2(T) = 0.02$ corresponds to roughly 300 K). The calculated phase diagram (Fig. 1) suggests that ordered phases of the M_2X , M_3X_2 , and M₆X₅ types are formed in the process of ordering of the nonstoichiometric compound MXy. There are four twophase regions in the phase diagram: $M_2X + M_3X_2$, $M_3X_2 + M_6X_5$, $M_6X_5 + MX_y$, and $M_3X_2 + MX_y$. Within a concentration interval $0.5236 \le y \le 0.5255$ narrow $(y \equiv X/M)$ at a fixed reduced temperature of $k_{\rm B}T/F_2(T) = 0.09981$ the M₆X₅ phase can form via the peritectoid reaction $M_3X_2 + MX_{\nu} \rightarrow M_6X_5$ (see the inset in Fig. 1). At point 2 of the peritectoid transformation (see the inset in Fig. 1) the curves representing the concentration dependences of the M_3X_2 , MX_{ν} , and M_6X_5 phases have a common tangent, with the minimum of the free energy of the disordered phase MX_y corresponding to a value of y that is larger than those corresponding to the minima of the free energies of the ordered phases M_3X_2 and M_6X_5 .

Even in the low-temperature region (i.e., at values of $k_BT/F_2(T)$ close to 0.02) the values of the parameter η_{equil} of ordered phases of the M₂X type (space group *P4/mnm*) and of the M₄X₃ and M₈X₇ types are small and their free energy is larger than that of other superstructures. For this reason, in equilibrium no ordered phases of types M₂X (space group *P4/mnm*), M₄X₃, and M₈X₇ can emerge in the nonstoichiometric compounds MX_y with a *B*1-type base structure.

Thus, in the process of ordering of a nonstoichiometric compound MX_y , ordered phases of type M_2X , M_3X_2 , and M_6X_5 are formed. Figure 2 depicts the dependence of the parameters η_{trans} and η_{max} on the composition of a non-

Figure 1. Model equilibrium phase diagram of the M-X system built in Ref. [44] with allowance for ordering of interstitial atoms X and structural vacancies \Box in the nonstoichiometric interstitial compound MX_y (MX_y \Box_{1-y}) under the assumption that all nonmetallic interstitial atoms X can be replaced by vacancies \Box . The solid curves represent phase boundaries and the dashed curves, order-order and order-disorder phase transitions of the first order; for the first-order transition MX_y \leftrightarrow M₂X the phase boundary and the phase transition curve coincide. The inset depicts an enlarged area of the ordering region where at a reduced temperature of $k_{\rm B}T/F_2(T) = 0.09981$ a peritectoid transformation M₃X₂ + MX_y \rightarrow M₆X₅ takes place.



Physics-Uspekhi 43 (1)



Figure 2. Equilibrium long-range order parameter at the transition point, η_{trans} (—), and the maximum value of the long-range order parameter, η_{max} (---), versus the composition of the MX_y compound when ordered phases of type M₃X₂ (*I*) and M₆X₅ (*2*) are formed.

0.6

0.4

1.0

0.8

v

0

0.2

stoichiometric compound MX_y when superstructures of type M_3X_2 and M_6X_5 are formed in this compound as a result of a first-order phase transition.



When calculating the ordering process in real nonstoichiometric compounds, one must allow for the boundary conditions of equilibrium. For instance, in the V–C system the upper boundary of the homogeneity range of disordered cubic vanadium carbide VC_y corresponds to VC_{0.875} (for all other carbides and nitrides with a *B*1-type structure the upper boundary of the homogeneity range corresponds to a compound close in composition to, or even coinciding with, $MX_{1.00}$). This boundary effect is the reason why it is only in vanadium carbide that an ordered cubic phase V₈C₇ (space group *P*4₁32 or *P*4₃32) is formed. In other carbides and nitrides, no equilibrium ordered cubic phase of type M₈X₇ is formed.

In real nonstoichiometric compounds MX_y , no complete replacement of nonmetallic atoms by vacancies can occur, since the symmetry of the crystal lattice of the metal M differs from that of the metal sublattice of the nonstoichiometric compound [2, 14]; finally, other compounds can exist (in addition to MX_y) in the M-X system. For instance, Group V transition metals form with carbon and nitrogen not only cubic carbides and nitrides MX_y with a B1-type structure but also M_2X_y compounds with a hexagonal structure. In view of this, when building phase diagrams of real M-X systems, one must calculate, in addition to ordering, the equilibria with the metal M or the compound M_2X_y (M_2X (comp)).

The equilibrium between the metal M and the ordered phase $M_{2t}X_{2t-1}$, i.e., the position of the phase boundary separating the two-phase region $(M + M_{2t}X_{2t-1})$ and the ordered phase $M_{2t}X_{2t-1}$, is described by the following expression [44]:

$$F_{\mathbf{M}}(T) = F_{0}(T) - y^{2}F_{2}(T) + \frac{a^{(s)}}{4t^{2}} \eta_{\text{equil}}^{2}F_{2}(T) + \frac{k_{\mathbf{B}}T}{2t} \left[\ln(1 - n_{1}^{(d)}) + (2t - 1)\ln(1 - n_{2}^{(d)}) \right]_{\eta = \eta_{\text{equil}}},$$
(29)

where $F_{M}(T)$ is the free energy of the metal M.

The equilibrium between the ordered phase $M_{2t}X_{2t-1}$ and the MX_{y_b} compound (here y_b is the maximum relative content of the nonmetallic atoms X at the upper boundary of the homogeneity region) is described by the following equation [26]:

$$F_{\mathbf{MX}_{y_{b}}(\text{comp})}(T) = F_{0}(T) + y_{b}F_{1}(T) + y(2y_{b} - y)F_{2}(T) + \frac{a^{(s)}}{4t^{2}} \eta_{\text{equil}}^{2} F_{2}(T) + \frac{k_{B}T}{2t} \Big\{ \ln \Big[(n_{1}^{(d)})^{y_{b}} (1 - n_{1}^{(d)})^{(1-y_{b})} \Big] + (2t - 1) \ln \Big[(n_{2}^{(d)})^{y_{b}} (1 - n_{2}^{(d)})^{(1-y_{b})} \Big] \Big\}_{\eta = \eta_{\text{equil}}}.$$
 (30)

According to this, the position of the lower boundary of the homogeneity region of the ordered phase $M_{2t}X_{2t-1}$ which is in equilibrium with the compound $M_2X(\text{comp})$ (or $MX_{0.5}(\text{comp})$, i.e., $y_b = 0.5$) can be calculated by the equation

$$D.5F_{M_{2}X(comp)}(T) = F_{0}(T) + 0.5F_{1}(T) + y(1-y)F_{2}(T) + \frac{a^{(s)}}{4t^{2}} \eta^{2}_{equil} F_{2}(T) + \frac{k_{B}T}{4t} \Big\{ \ln \Big[n_{1}^{(d)} \big(1 - n_{1}^{(d)} \big) \Big] + (2t-1) \ln \Big[n_{2}^{(d)} \big(1 - n_{2}^{(d)} \big) \Big] \Big\}_{\eta = \eta_{equil}},$$
(31)

where $F_{M_2X(\text{comp})}$ is the free energy of the lower hexagonal carbide or nitride. In the disordered state, with $\eta = 0$, equations (29) and (31) describe the position of the lower boundary of the homogeneity range of the disordered nonstoichiometric compound MX_y . Thus, these equations make it possible to calculate the equilibrium of the nonstoichiometric compound MX_y , which can be in a state with any value of the long-range order parameter, from η_{max} to 0.

The numerical values of the energy parameters $F_0(T)$, $F_1(T)$, and $F_2(T)$ (Table 3) needed for calculating the phase diagrams were obtained in Refs [2, 26, 43] by expanding the free energy (without allowance for the contribution of the configurational entropy) of the disordered compounds MC_y and MN_y into a power series up to the second order in y; each energy parameter F(T) was represented by a polynomial of the type

$$F(T) = f_0 + f_1 T + f_2 T^2 + f_3 T^{-1} + f_4 T \ln T.$$
(32)

The free energies of the disordered carbides TiC_{y} , ZrC_{y} , HfC_{y} , VC_{y} , NbC_{y} , and TaC_{y} and the disordered nitride TiN_y were found in Refs [2, 26, 43, 52] on the basis of the experimental thermodynamic data taken from Refs [51, 93, 95, 116–122]. The temperature curves representing the dependence of the free energy of the metals α -Ti, β -Ti, α -Zr, β -Zr, and α -Hf and the lower carbides β -Nb₂C, β -V₂C, and α -Ta₂C in equilibrium with nonstoichiometric compounds MX_{v} were also represented by polynomials (32) obtained on the basis of the data of Refs [120-125]. The literature does not contain experimental thermodynamic data characterizing the tetragonal nitride ε -Ti₂N, which has no homogeneity range. Hence, the temperature dependence of the free energy of this nitride was found as a model parameter on the basis of the data on the position on the phase boundary separating TiN_{y} and the two-phase region $(\epsilon - Ti_2N + TiN_{y})$ (these data were taken from Refs [126, 127]). The values of the coefficients $f_0 - f_4$ for all phases taken into account in the calculations of diagrams with allowance for ordering of the nonstoichiometric compounds are listed in Table 3.

5.2 Phase diagrams of Ti-C, Zr-C, and Hf-C systems 5.2.1 The Ti-C system. In this system there is only one compound capable of ordering, cubic titanium carbide TiC_{ν} . At the lower boundary of the homogeneity range, titanium carbide is in equilibrium with metallic α -Ti (when T < 1150 K) or β -Ti (when T > 1150 K). According to Ref. [40], for 1900 K > T > 1000 K the carbide that exists near the lower boundary of the homogeneity region of the disordered phase TiC_{ν} is $TiC_{0.32} - TiC_{0.37}$. Experiments have not yielded the exact position of the lower boundary of the homogeneity range; different estimates yield the composition $TiC_{0.48}$ [93] or TiC_{0.47} at 1900 K [90, 128]. According to Jonsson's calculations [129], this composition at 1900 K is $TiC_{0.52}$. The data of Murray [90], Storms [93], and Jonsson [129] reveal that, as the temperature is lowered, the lower boundary of the homogeneity region of disordered titanium carbide TiC_{ν} shifts in the direction of increasing y, i.e., in the direction of a carbide with a higher content of carbon, at a rate that is somewhat larger than that predicted by the calculations done in Ref. [40].

Figure 3 depicts curves that represent the dependence, at 600 and 1200 K, of the free energy of the disordered and crystallographically possible ordered phases on the carbon content y in titanium carbide. At 600 K, in different concentration ranges, the ordered Ti₂C, Ti₃C₂, and Ti₆C₅

Phase	Free-energy	Coefficient							
	parameters	$f_0,$ kJ mol ⁻¹	$f_1 imes 10^2$, kJ (mol K) ⁻¹	$f_2 imes 10^6,$ kJ (mol K ²) ⁻¹	f_3 , kJ mol ⁻¹	$f_4 imes 10^2$, kJ (mol K) ⁻¹			
TiC _y	F ₀ (298 – 1500 K) F ₁ (298 – 1500 K) F ₂ (298 – 1500 K)	32.61 -327.29 83.36	3.16 7.15 12.77	-9.67 3.09	-3026 3164	-1.20 -0.62 -1.91			
α-Ti	F(298-1150)	-7.02	12.00	-5.28	_	2.20			
β-Τί	<i>F</i> (1150–2000 K)	-6.91	18.05	_	_	-3.14			
ZrC _y	<i>F</i> ₀ (298–1500 K) <i>F</i> ₁ (298–1500 K) <i>F</i> ₂ (298–1500 K)	87.93 -421.72 111.60	-39.28 66.07 0.80	-30.38 40.84 -13.50	-7357 7614	4.46 -9.01			
α-Zr	<i>F</i> (298–1140 K)	-9.93	15.60	-2.34	182	-2.86			
β-Zr	<i>F</i> (1140–2200 K)	-4.90	16.19	_	—	-3.04			
HfC _y	$F_0(298-1500 \text{ K})$ $F_1(298-1500 \text{ K})$ $F_2(298-1500 \text{ K})$	139.03 -487.59 90.18	-83.59 108.80 7.54	-119.49 243.25 -126.54	-11001 12257 	11.17 16.42 			
α-Hf	<i>F</i> (298–2500 K)	-7.58	11.37	-1.09	—	-2.56			
VC _y	$F_0(298 - 2000 \text{ K})$ $F_1(298 - 2000 \text{ K})$ $F_2(298 - 2000 \text{ K})$	97.09 -437.49 211.36	145.0 -86.23 267.21	-11.84 11.75 0	-208 932 0	-26.95 18.29 -42.47			
β -V ₂ C	<i>F</i> (298–1600 K)	-180.96	513.67	-1.70	1290	-83.12			
V_8C_7	<i>F</i> (298–1400 K)	-123.89	274.13	-1.56	608	-43.46			
NbC _y	$F_0(298-1800 \text{ K})$ $F_1(298-1800 \text{ K})$ $F_2(298-1800 \text{ K})$	13.98 -284.99 128.74	6.87 18.89 1.40	-8.00 4.40 	1390 -3186 2246	-1.21 -3.26			
β -Nb ₂ C	<i>F</i> (298–2500 K)	-218.35	38.69	-6.28	429	-6.65			
TaC _y	$F_0(298-1800 \text{ K})$ $F_1(298-1800 \text{ K})$ $F_2(298-1800 \text{ K})$	41.34 -330.78 144.40	17.57 4.12 -0.036	3.04 -10.48 1.80	893 -2325 1500	-3.13 -0.69 			
α-Ta ₂ C	<i>F</i> (298–2500 K)	-220.93	37.26	-6.97	429	-6.65			
TiN _y	<i>F</i> ₀ (298 – 2200 K) <i>F</i> ₁ (298 – 2200 K) <i>F</i> ₂ (298 – 2200 K)	-6.00 -421.42 94.48	20.09 5.76 -2.49	$-8.40 \\ -8.20 \\ 18.80$		-3.02 -0.94			
ϵ -Ti ₂ N	<i>F</i> (500–1350 K)	-1067.24	707.07	306.89	127931	-96.45			

Table 3. Coefficients in the polynomials (32) describing the parameters $F_0(T)$, $F_1(T)$, and $F_2(T)$ of the free energy F(y, 0, T) of disordered nonstoichiometric compounds MX_y , and the free energies F(T) of metals M and lower hexagonal carbides and nitrides M_2X .

phases and disordered titanium carbide TiC_y (with y > 0.94) (curves 2, 3, 4, and 1 in Fig. 3, respectively) may have the lowest free energy. The ordered tetragonal phase Ti₄C₃ (space group *I4/mmm*) and cubic phase Ti₈C₇ have larger free energies (curves 5 and 6 in Fig. 3) and cannot form under equilibrium conditions. The formation of the cubic phase Ti₄C₃ (space group *Pm3m*) and the tetragonal phase Ti₂C (space group *P4/mmm*) at 600 K is impossible at all, since the transition temperatures T_{trans} for these phases lie below 300 K; for this reason the free-energy curves corresponding to these phases are absent in Fig. 3. At 1000 K and higher, only the disordered phase TiC_y can exist over the entire homogeneity region.

The points *I* and *II* in Fig. 3 on the vertical axis (y = 0) correspond to the free energies of α -Ti at 600 K and β -Ti at

1200 K, respectively. The tangent to the free energy F(y, 600 K) passing through the point *I* determines the free energy and width of the two-phase region at the boundary with metallic titanium. Figure 3 shows that at 600 K the two-phase mixture (α -Ti+Ti₂C) dominates at the boundary with metallic titanium.

The low-temperature part of the phase diagram of the Ti-C system (Fig. 4) was calculated by the OPF method [40]; the position of the phase boundaries outside the ordering region is shown in accordance with the data of Murray [90] and Storms [93].

Due to the wide homogeneity range of titanium carbide TiC_y , the Ti_2C , Ti_3C_2 , and Ti_6C_5 phases are formed in the ordering process in thermodynamic equilibrium (see Fig. 4). According to calculations, an ordered Ti_2C phase is formed



Figure 3. Comparison of the free energies of the disordered and possible ordered phases of titanium carbide at 600 and 1200 K: Curves *I* correspond to disordered titanium carbide TiC_y; curves 2-6 correspond to the ordered phases of types Ti₂C (2), Ti₃C₂ (3), Ti₆C₅ (4), Ti₄C₃ (5), and Ti₈C₇ (6); points *I* and *II* correspond to the free energies of α -Ti at 600 K and β -Ti at 1200 K, respectively.



Figure 4. Equilibrium phase diagram of the Ti–C system with allowance for atomic ordering of nonstoichiometric cubic titanium carbide TiC_y. The inset depicts an enlarged area of the ordering region where at a temperature of 963 K the peritectoid transformation $Ti_3C_2 + TiC_y \rightarrow Ti_6C_5$ takes place; the coordinates y = C/Ti of the points 1, 2, and 3 are 0.5236, 0.524, and 0.5255, respectively.

via a second-order phase transition with $T_{\text{trans}} = 920-950$ K. The homogeneity region of Ti₂C is fairly broad (TiC_{0.42} – TiC_{0.56} at 700 K and TiC_{0.40} – TiC_{0.54} at 800 K) and is limited from right and left by two-phase regions (α -Ti+Ti₂C and Ti₂C+Ti₃C₂, respectively). The ordered Ti₃C₂ and Ti₆C₅ phases have homogeneity regions comparable in width (TiC_{0.59} – TiC_{0.71} for Ti₃C₂ and TiC_{0.74} – TiC_{0.87} for Ti₆C₅ at 700 K) and are formed via a first-order phase transition. Order – order transitions in titanium carbide are also first-order phase transitions. The calculated values of T_{trans} , ΔS_{trans} , and the heat of phase transition ΔH_{trans} for all possible order – order and order – disorder first-order phase transitions in titanium carbide are listed in Table 4. On the whole, ordering in titanium carbide TiC_y takes place at T < 1000 K.

Let us compare the calculated phase diagram of the Ti-C system (Fig. 4) with the results of experiments. According to the experimental data, the ordered phases of Ti2C with cubic (space group Fd3m) [34, 35, 130-132] and trigonal (space group $R\bar{3}m$ [36, 37] structures are formed in titanium carbide TiC_v in the range $0.5 \le y \le 0.65$ at T < 1100 K. Reports on the trigonal phase Ti₂C (Ti₆C_{3+x}) with the space group $P3_121$ resulted from an error that was made by Khaenko and Kukol' [133] and was later uncritically repeated by other researchers; we will not go any further into this problem so as not to promote erroneous information. Indeed, if we assume that the base structure is of the B1 type, such a trigonal (space group $P3_121$) phase of type M₂C with lattice parameters $a = b = a_{B1}/\sqrt{2} (a = \{1/2 \ 1/2 \ 0\}_{B1})$ and $c = 3\sqrt{2a_{B1}}$ $(c = \{2 \ 2 \ 2\}_{B1})$ is impossible in principle, since the sites of the metallic and nonmetal sublattices partially coincide.

Analysis of structural experiments [34-38, 130-135] implies that the cubic (space group Fd3m) superstructure of Ti_2C is usually detected in annealed samples of TiC_{ν} with y < 0.55 - 0.56, while trigonal ordering is usually observed in annealed titanium carbide TiC_y with $0.58 \le y \le 0.65$. Note that in a powder diffraction experiment the powder patterns of the cubic (space group *Fd3m*) and trigonal (space group $R\bar{3}m$) ordered phases of Ti₂C contain the same set of superlattice reflections [29] and can be separated if there are noticeable trigonal distortions in the phase with the space group R3m and with allowance for the directions of static atomic displacements. This may be the reason why in earlier works [35, 130-132], where only the cubic model of ordering was discussed [34], even in annealed titanium carbide TiC_{ν} $(y \ge 0.59)$ the observed superlattice reflections were ascribed to the cubic phase Ti₂C. In later papers [36-38, 134, 135], it was shown that the main ordered phase in TiC_v ($y \ge 0.6$) is the trigonal phase Ti₂C.

The ordered phase Ti_3C_2 is assumed to exist in the $TiC_{0.60} - TiC_{0.70}$ range, and there are some experimental indications of this:

(1) the presence of superlattice reflections $(2/3 \ 2/3 \ 0)$ observed by Moisy-Maurice [38] in studies of annealed single-crystal TiC_{0.61} by the method of elastic neutron scattering;

(2) weak superlattice reflections with a diffraction vector $|\mathbf{q}| \approx 2.03$ characteristic of the orthorhombic (space group $C222_1$) phase Ti₃C₂ were observed by Lipatnikov et al. [136] in the X-ray pattern of annealed titanium carbide TiC_{0.70};

(3) diffuse neutron scattering maxima caused by the presence of short-range order in $TiC_{0.76}$ and corresponding in position to the reflections (2/3 2/3 0) were detected by Moisy-Maurice et al. [137]; and

(4) an estimate of the short-range order parameters [36] in single-crystal TiC_{0.64} made on the basis of diffuse neutron scattering data has shown that agreement between theory and experiment is the best when annealed titanium carbide TiC_{0.64} contained two ordered phases, Ti₂C and Ti₃C₂.

The existence of a trigonal ordered phase Ti_2C and an orthorhombic ordered phase Ti_3C_2 also follows from Monte Carlo calculations of de Novion et al. [36] and Priem [138] for the concentration range $TiC_{0.57} - TiC_{0.70}$ (Fig. 5). Landesman et al. [139] found that short-range order and order – disorder transitions in nonstoichiometric carbides and nitrides can be described by using the Ising Hamiltonian for the nonmetal fcc

	Ti_2C-Ti_3	C_2		Ti ₃ C ₂ -Ti	₆ C ₅		Ti ₆ C ₅ -Ti	$Ti_6C_5 - TiC_y$		
У	T _{trans} , K	$\Delta S_{ m trans},$ kJ (mol K) ⁻¹	$\Delta H_{ m trans},$ kJ mol ⁻¹	T _{trans} , K	$\Delta S_{\text{trans}},$ J (mol K) ⁻¹	$\Delta H_{ m trans},$ kJ mol ⁻¹	T _{trans} , K	$\Delta S_{ m trans}, \ { m J} \ ({ m mol} \ { m K})^{-1}$	$\Delta H_{ m trans},$ kJ mol ⁻¹	
0.52	948	0.09	0.08	_	_	_	_	_	_	
0.53	926	0.15	0.14	961	0.003	0.003	962	0.02	0.02	
0.54	893	0.25	0.22	959	0.013	0.013	961	0.03	0.03	
0.55	853	0.28	0.24	956	0.03	0.03	960	0.04	0.04	
0.56	795	0.32	0.25	951	0.05	0.05	959	0.06	0.05	
0.58	460	0.29	0.13	940	0.12	0.12	955	0.10	0.09	
0.60	—	_	_	924	0.19	0.18	949	0.15	0.14	
0.62	—	—	_	902	0.29	0.26	942	0.22	0.21	
0.63	—	—	—	891	0.35	0.31	938	0.26	0.24	
0.64	—	—	—	877	0.41	0.36	934	0.30	0.28	
0.65	—		—	860	0.48	0.42	929	0.35	0.32	
0.66	—		—	841	0.56	0.47	924	0.40	0.37	
0.68	—		—	794	0.74	0.59	912	0.50	0.46	
0.70	_		—	733	0.91	0.66	898	0.62	0.56	
0.72	_	_	—	639	0.99	0.63	882	0.75	0.67	
0.73	_	_	_	566	1.00	0.57	874	0.82	0.72	
0.74	_	_	_	472	0.90	0.42	864	0.90	0.78	
0.75			_	320	0.69	0.22	854	0.97	0.83	
0.76	_	_	_				843	1.05	0.88	
0.78	_	_	_	_			818	1.20	0.98	
0.80		_	_	_	_		789	1.34	1.06	
0.82			_	_	_	_	755	1.46	1.10	
0.83		—	_	_		_	728	1.49	1.08	
0.84	_	_	_	_			713	1.49	1.07	
0.85		_	_	_	_	_	689	1.48	1.02	
0.86			_	_	_	_	662	1.43	0.95	
0.88		—	_	—		_	601	1.27	0.76	
0.90		_	_	_	_		528	1.05	0.55	
0.92	—	_	—		_	_	444	0.82	0.36	
0.94	—	_	—		_	_	348	0.58	0.20	
0.95		_	—		_	_	294	0.46	0.14	

Table 4. Thermodynamic characteristics of order – order and order – disorder phase transition in nonstoichiometric titanium carbide TiC_{y} .

sublattice. In this case the Hamiltonian is determined as the sum of effective energies V_n of the pairwise interactions between the sites of the nonmetal sublattice that are the *n*th



Figure 5. A portion of the phase diagram of the Ti-C system calculated by the Monte Carlo method with allowance for ordering of nonstoichiometric titanium carbide TiC_y in the $TiC_{0.57}-TiC_{0.70}$ range [36, 138].

neighbors. De Novion et al. [36], Priem [138], and Priem et al. [140] calculated the energies V_n of the pairwise interactions in the nonmetal sublattice of the titanium carbides $TiC_{0.76}$ and $TiC_{0.65}$ not only for the nearest (V_1) and next-nearest (V_2) neighbors but also for more distant sites positioned in relation to each other on the third (V_3) and fourth (V_4) coordination shells. The energies of the pairwise interactions were calculated by the following three methods on the basis of the data of Priem et al. [140] gathered in the process of hightemperature experiments on diffuse scattering of neutrons: the mean-field approximation [97, 141, 142], the inverse Monte Carlo method [143], and the cluster variation method [100, 102, 144, 145]. The best agreement with the experimental data was achieved when the phase diagram was calculated by the Monte Carlo method. According to de Novion et al. [36] and Priem et al. [140], the formation of the orthorhombic ordered phase Ti₃C₂ is a first-order phase transition. This conclusion is corroborated by the results of OPF calculations of ordering in TiC_{ν} [40].

A certain difference in the mutual positions of the ordered phases of Ti_2C and Ti_3C_2 in the phase diagrams of the Ti-Csystem calculated by the OPF method [40] (see Fig. 4) and by the Monte Carlo method [36, 138] (see Fig. 5) is due to the following. While in OPF calculations the free energy of the ordering compound is a function of the compound's composition and the long-range order parameters, in Monte Carlo calculations the energies of the interatomic interactions are extracted from the data on short-range order parameters. Obviously, the observed slight differences in the results of calculations can be diminished if in each method the long- and short-range order parameters are taken into account simultaneously. However, in the theory of phase transformations a method by which long- and short-range order parameters would be taken into account simultaneously has yet to be developed.

On the whole, the experimental and theoretical studies [34-38, 130-138, 140] corroborate the results (presented in Ref. [40]) of calculations of the phase diagram of the Ti-Csystem (see Fig. 4). According to these results, at temperatures below 1000 K ordered phases Ti₂C and Ti₃C₂ can form in nonstoichiometric titanium carbide. The existence of an ordered phase Ti₂C at temperatures above 2150 K, as tentatively shown in Enomoto's [128] phase diagram for the Ti-C system, is more than doubtful. According to the calculations done in Ref. [40], an ordered phase Ti₆C₅ can also form in titanium carbide TiC_y with 0.78 < y < 0.88. This phase belongs to the class of ordered phases M₆X₅ that is common for all nonstoichiometric interstitial compounds. Recently, Dzhalabadze et al. [146] detected ordered phase Ti_6C_5 with hexagonal symmetry in thin Ti-C films. The films were prepared by electron-beam sputtering of sintered titanium carbide $TiC_{0.9}$, magnetron sputtering of titanium and carbon, and laser sputtering of titanium and graphite or titanium carbide $TiC_{0.9}$. According to Dzhalabadze et al. [146], the ordered phase Ti₆C₅ corresponds to disordered carbide $TiC_{0.83}$. However, the lattice parameters of the hexagonal ordered phase found by Dzhalabadze et al. [146] correspond to disordered titanium carbide TiC_{ν} with a period $a_0 = 0.4319$ nm of the basic cubic lattice; according to the most reliable data, this period corresponds to the carbide $TiC_{0.68-0.70}$, while for the disordered carbide $TiC_{0.83}$ the value of this period is 0.4326 nm. The understated value of the period of cubic titanium carbide in the film may be due to an admixture of oxygen.

The temperature of the disorder-order transition for the of Ti_3C_2 and Ti_6C_5 phases calculated in Ref. [40] do not exceed 950 K. Note that the phase diagram of the Ti-C system calculated with y < 0.5 contains a broad two-phase region [(α - $Ti + Ti_2C$) at T < 919 K and $(\alpha - Ti + TiC_v)$ at T > 919 K] (see Fig. 4), which is absent in the model phase diagram (see Fig. 1). The presence of this two-phase region is due to the allowance for equilibrium boundary conditions. In nonstoichiometric titanium carbide TiC_{ν} there can be no complete replacement of carbon atoms by structural vacancies, since the symmetries of the crystal lattices of titanium and titanium carbide are different (metallic α -Ti has a hexagonal close-packed structure, while nonstoichiometric titanium carbide TiC_{y} has a B1type cubic structure). As a result, the lower boundary of the homogeneity tange of titanium carbide corresponds (depending on the temperature) to $TiC_{0.4-0.5}$, while at a lower carbon content the two-phase mixture of titanium and titanium carbide is in equilibrium. The model phase diagram (see Fig. 1) was built for the ideal case of complete replacement of interstitial atoms by structural vacancies, which is possible only if the metal and the nonstoichiometric compound are of the same symmetry (in this case there is no two-phase region). The symmetries of the crystal lattices of the transition metal and the nonstoichiometric compound are the same only in the Th-C system at temperatures above 1500 K, and in such a system there is indeed no two-phase region between thorium and thorium carbide.

A recent study of ordering in titanium carbide TiC_y carried out by Lipatnikov et al. [39] is of interest. The

researchers used data on the structure and electrical resistivity of annealed and quenched samples of TiC_{ν} and found that the cubic (space group Fd3m) ordered phase Ti₂C has a homogeneity region extending from TiC_{0.49-0.51} to TiC_{0.54-} 0.55, while the trigonal (space group $R\bar{3}m$) superstructure of Ti_2C is formed in the $TiC_{0.55} - TiC_{0.59}$ range. The $TiC_{0.59} - TiC_{0.59}$ TiC_{0.63} range corresponds to a two-phase region [Ti₂C (space group $R\bar{3}m$) + Ti₃C₂ (space group C222₁)]. The range of existence of the orthorhombic (space group $C222_1$) ordered phase Ti_3C_2 is fairly narrow and does not exceed $TiC_{0.63}$ - $TiC_{0.67}$. The lowest annealing temperature used by Lipatnikov et al. [39] was 770 K. Since as a result of even such lowtemperature annealing of the titanium carbides $TiC_{0.83}$ and $TiC_{0.85}$ no ordered phase of the Ti_6C_5 type was discovered, the researchers assumed that the transition temperature of this phase is below 770 K. The portion of the equilibrium phase diagram of the Ti-C system built by Lipatnikov et al. [39], where the ordering of nonstoichiometric titanium carbide TiC_{ν} takes place, is depicted in Fig. 6.



Figure 6. Low-temperature portion of the equilibrium phase diagram of the Ti–C system [39]. The formation of the orthorhombic ordered phase Ti₃C₂ occurs at 990 ± 10 K as the peritectoid transformation Ti₂C + TiC_y \rightarrow Ti₃C₂; the region of phase equilibria with the participation of the ordered phase Ti₆C₅ is depicted tentatively.

Figure 6 shows that in the range $0.54 \le y \le 0.57$ the following sequential transitions are possible: disordered (space group $Fm\bar{3}m$) titanium carbide $\operatorname{TiC}_{\nu} \overset{900\pm20}{\longleftrightarrow} ^{K}$ cubic (space group $Fd\bar{3}m$) ordered phase $\operatorname{Ti}_{2}C \overset{900\pm20}{\longleftrightarrow} ^{K}$ trigonal (space group R3m) ordered phase Ti₂C. The orthorhombic ordered phase Ti₃C₂ is most likely to form via the peritectoid transformation $Ti_2C + TiC_v \rightarrow Ti_3C_2$ at 990 ± 10 K in the interval $0.61 \le y \le 0.63$. The portion of the phase diagram of the Ti-C system shown in Fig. 6 suggests that the ordered phase Ti₂C with cubic or trigonal symmetry can be observed over a broad composition range of nonstoichiometric titanium carbide, from $TiC_{0.40}$ to $TiC_{0.63}$. However, only the interval $TiC_{0.49-0.50} - TiC_{0.58-0.59}$ constitutes the singlephase range of existence of ordered phase. The range in which the formation of an ordered Ti₆C₅-type phase is possible is depicted tentatively, since experiments have yet to prove that such a range exists. The hysteresis in the temperature dependence of the electrical resistivity (Fig. 7) suggests that the $TiC_y \leftrightarrow Ti_2C$ and $TiC_y \leftrightarrow Ti_3C_2$ transformations are first-order phase transitions with $T_{\text{trans}} = 980 -$ 1000 K [39]. This is in good agreement with the value



Figure 7. Reversible changes in the electrical resistivity ρ of the ordered titanium carbides TiC_{0.54}, TiC_{0.58}, and TiC_{0.62} induced by heating, an order-disorder transition, and cooling.

 $T_{\text{trans}} \approx 1000 \text{ K}$ found for titanium carbide TiC_{0.55} in measurements of electrical resistivity in [147].

Measurements of the heat capacity of the titanium carbides TiC_{0.54}, TiC_{0.58}, and TiC_{0.62} [148] revealed that there is a sharp jump, related to an equilibrium orderdisorder phase transition, at the transition temperature T_{trans} . The peak of heat capacity near T_{trans} is symmetric (Fig. 8) rather than λ -shaped; this symmetry is more characteristic of first-order phase transitions than of secondorder. Moreover, when the sample is cooled, there is a weak hysteresis in the heat capacity, which also supports the idea that the transition is close to a first-order one. According to Ref. [148], the reversible order – disorder transformation Ti_2C (space group Fd3m) \leftrightarrow TiC_{0.54} can be considered to be a weak first-order phase transition with a small latent heat of transition, while the $Ti_3C_2 \leftrightarrow TiC_y$ is an ordinary first-order phase transition. Figure 8 depicts the variations in the enthalpy $H_T^0 - H_{298}^0$ and heat capacity $C_p(T)$ of nonstoichiometric titanium carbide TiC_{0.62} in the vicinity of the phase transition. We see that at the transition temperature T_{trans} there is a jump in the temperature dependence of the enthalpy $H_T^0 - H_{298}^0$. According to Ref. [148], the temperature T_{trans} and the heats ΔH_{trans} of the phase transitions Ti₂C (space group Fd3m) \leftrightarrow TiC_{0.54}, Ti₂C (space group R3m) \leftrightarrow TiC_{0.58}, and Ti_3C_2 (space group $C222_1$) \leftrightarrow $TiC_{0.62}$ are, respectively, 100, 980, and 970 K and 1.5 ± 0.2 , 1.5 ± 0.2 , and 1.8 ± 0.2 kJ mol⁻¹. According to the data of Emel'yanov [149] and Karpov and Kobyakov [150, 151], the temperatures of the disorder-order transitions for the titanium carbides $TiC_{0.49}$, $TiC_{0.55}$, $TiC_{0.60}$, and TiC_{0.63} are somewhat higher and are equal to 1040-1070 K.

Thus, experiments have shown that the ordering of titanium carbide in the intervals $0.52 \le y \le 0.55$, $0.56 \le y \le 0.58$, and $0.62 \le y < 0.68$ at T < 1000 K leads, respectively, to the formation of the cubic (space group *Fd3m*) and trigonal (space group $R\bar{3}m$) ordered phases of Ti₂C and the orthorhombic (space group *C*222₁) ordered phase Ti₃C₂.



Figure 8. Variations in the heat capacity $C_p(T)$ and enthalpy $H_T^0 - H_{298}^0$ of nonstoichiometric titanium carbide TiC_{0.62} in the vicinity of the reversible order – disorder Ti₃C₂ (space group $C222_1$) \leftrightarrow TiC_{0.62} phase transformation with $T_{\text{trans}} = 970 \pm 10$ K and $\Delta H_{\text{trans}} = 1.8 \pm 0.2$ kJ mol⁻¹ [148].

This agrees with the phase diagram of Ti-C (see Fig. 4) calculated in Ref. [40] by the OPF method (note that for Ti_2C -type superstructures the OPF method yields a common range of existence, from $TiC_{0.46}$ to $TiC_{0.58}$, without separation into the cubic and trigonal phases).

The Ti-C system contains, in addition to nonstoichiometric cubic titanium carbide, a Ti₈C₁₂ compound [152]. This compound was discovered in 1992 and was the first compound belonging to a new class of molecular clusters known as metallocarbohedrens. A detailed description of metallocarbohedrens M₈C₁₂ can be found in the review by Eletskiĭ and Smirnov [153]. Ti₈C₁₂ molecules have the almost perfect spherical shape of a slightly distorted pentagonal dodecahedron. The atoms of the metal and carbon are located at the vertices of the dodecahedron, with each titanium atom bonded to three carbon atoms and each carbon atom bonded to the nearest carbon atom and two titanium atoms. The lengths of the Ti-C and C-C bonds in Ti₈C₁₂ differ by roughly 40% and are 1.99 and 1.39 nm, respectively, but the carbon and titanium atoms are located at almost equal distances from the cluster's center. The structure of metallocarbohedrens M8C12 is highly symmetric: its point symmetry group incorporates 24 symmetry elements of the cubic group. In view of the high symmetry of the molecule, metallocarbohedrens are expected to be extremely stable.

Ti₈C₁₂ clusters were obtained by plasmochemical gasphase synthesis combined with laser heating of the metal and the hydrocarbon (methane, ethylene, propylene, benzene, etc.) plasma. The molecular clusters M_8C_{12} (M = Ti, Zr, Hf, V, Nb, and Ta) are formed when a plasma with high hydrocarbon content is heated by high-power laser radiation [152–157], while ordinary plasmochemical synthesis can produce particles of the cubic carbide MC_{ν} . The atoms in metallocarbohedrens M_8C_{12} form strong bonds; e.g., the binding energy per atom of the Ti₈C₁₂ molecule amounts to 6.1-6.7 eV, while for the carbide TiC with a *B*1-type structure this binding energy per atom is only somewhat larger and equal to 7.2 eV [158]. The Ti₈C₁₂ compound is not shown in the phase diagram of the Ti-C system (Fig. 4), since it lies beyond the boundaries of the ordering region under consideration.

5.2.2 The Zr-C system. This system contains only one compound in the nonmetallic sublattice of which ordering can occur, and this is nonstoichiometric zirconium carbide ZrC_{ν} with a broad homogeneity region and a B1-type structure. The phase diagram of the Zr-C system (Fig. 9) closely resembles that of the Ti-C system. Calculations have revealed [2, 43-46] that at temperatures below 1200 K and under conditions of thermodynamic equilibrium, ordered phases Zr₂C, Zr₃C₂, and Zr₆C₅ form in different concentration intervals. The disorder – order $ZrC_y - Zr_2C$ transformation can occur as a second-order phase transition, while all the other transformations, related to the ordering of nonstoichiometric zirconium carbide ($Zr_2C \rightarrow Zr_3C_2$, $Zr_3C_2 \rightarrow Zr_6C_5$, and $Zr_6C_5 \rightarrow ZrC_{\nu}$), are first-order phase transitions. The direct disorder – order $ZrC_y \rightarrow Zr_3C_2$ transformation is possible only in a narrow range of compositions, ZrC_{0.505}- $ZrC_{0.522}$, at T = 1217 K (see Fig. 9). When the carbon content in ZrC_{v} is different, the $Zr_{3}C_{2}$ superstructure can form only as a result of the order-order phase transition $Zr_2C \rightarrow Zr_3C_2$ or $Zr_6C_5 \rightarrow Zr_3C_2$. Note also that in the ordering region of zirconium carbide at T = 1216.7 K and y = 0.524 there is a peritectoid transformation, $Zr_3C_2 + ZrC_v \rightarrow Zr_6C_5$ (see the inset in Fig. 9).

Experiments have revealed the existence in zirconium carbide near the lower boundary of the homogeneity range in the interval $ZrC_{0.63} - ZrC_{0.74}$ of cubic (space group *Fd3m*)



Figure 9. Equilibrium phase diagram of the Zr-C system with allowance for atomic ordering of nonstoichiometric cubic zirconium carbide ZrC_y. The inset depicts an enlarged area of the ordering region where at a temperature of 1216.7 K the peritectoid transformation Zr_3C_2+ $ZrC_y \rightarrow Zr_6C_5$ takes place; the abscissas y = C/Zr of the points *1*, *2*, and *3* are 0.5236, 0.524, and 0.5255, respectively.

[34, 35] and trigonal (space group $R\bar{3}m$) [41] ordered phases, which can be identified as superstructures on the basis of Zr₂C. For zirconium carbide ZrC_{0.63}, the temperature of transition to the cubic (space group Fd3m) ordered phase is 1170 K [35], which is in good agreement with the calculated phase diagram of the Zr-C system (see Fig. 9). Studies of the electrical resistivity of $ZrC_{0.70}$ in the 300 – 1500 K temperature range [42] have shown that at a heating and cooling rate of 2 K per minute there is a weak jump in electrical resistivity at a temperature in the 1330-1350 K range. According to Obata and Nakasawa [42], this jump corresponds to the transition, upon cooling, from the high-temperature disordered state to a low-temperature ordered state; the ordered phase has a cubic structure with a doubled (compared to that of disordered zirconium carbide) lattice parameter. The space group and the type of structure of the ordered zirconium carbide were not determined by Obata and Nakasawa [42]. Lorenzelli and de Dieuleveult [159] suggested that the ordered phase of zirconium carbide has a structure of the ThC_{0.76} type and is formed in the interval $ZrC_{0.69}$ – $ZrC_{0.79}$, and that its stoichiometric composition corresponds to ZrC_{0.75}. The validity of this statement on the strict stoichiometric composition $ZrC_{0.75}$ of the ordered phase is doubtful.

According to de Novion et al. [36] and Lipatnikov et al. [39], in the Ti-C system, which is similar to the Zr-C system, a superstructure of the M_3X_2 is formed. We may, therefore, expect that the ordered phase Zr_3C_2 also forms in the Zr-C system. However, discovering the ordered phases Zr_3C_2 and Zr_6C_5 of the nonstoichiometric carbide ZrC_y (whose existence was predicted theoretically in Refs [43, 44]) requires conducting thorough structural investigations of this compound.

The values of T_{trans} , ΔS_{trans} , and ΔH_{trans} calculated for the first-order phase transitions $\text{Zr}_2\text{C} - \text{Zr}_3\text{C}_2$, $\text{Zr}_3\text{C}_2 - \text{Zr}_6\text{C}_5$, and $\text{Zr}_6\text{C}_5 - \text{Zr}\text{C}_y$, which are related to the ordering of ZrC_y , can be found in Ref. [26]. Note that for zirconium carbide ZrC_y with $y \approx 0.52 - 0.54$ the order-order and order-disorder transition temperatures are approximately 250 K higher than those of similar transitions in titanium carbide; for $y \leq 0.6$ the transition temperatures for ZrC_y are approximately 100 K higher than those for TiC_y. The heats of the order-order and order-disorder transitions in zirconium carbide are, on the average, 20-25 % higher than in titanium carbide.

In 1992, Guo et al. [154] and Wei et al. [155] obtained the compound Zr_8C_{12} in the Zr-C system. This compound has no homogeneity range, belongs to the group of M_8C_{12} metallocarbohedrens, and is similar in structure to the molecular cluster Ti_8C_{12} , which was described in Section 5.2.1 devoted to the Ti-C system.

5.2.3 The Hf-C system. In the disordered state, in the Hf-C system there is only one compound on the basis of which ordering can take place, and that is the nonstoichiometric hafnium carbide HfC_y with a *B*1-type structure (NaCl) and a fairly wide homogeneity range. According to Refs [46, 47], Hf₃C₂ and Hf₆C₅ phases can form in the process of ordering of this hafnium carbide under conditions of thermodynamic equilibrium (Fig. 10). The ordered phase of type M₂C is not formed in hafnium carbide, since the carbon content in such a phase is beyond the lower boundary of the homogeneity region of disordered hafnium carbide HfC_y. According to Refs [2, 14, 28, 160], at the lower boundary of the homogeneity range the composition of hafnium carbide is HfC_{0.54}-

T, K

4000



Liquid

Figure 10. Equilibrium phase diagram of the Hf-C system with allowance for atomic ordering of the nonstoichiometric cubic hafnium carbide HfC_y. The compound Hf₈C₁₂ has no homogeneity range and is not an ordered phase of hafnium carbide HfC_y. The position of the phase boundaries beyond the ordering region at y < 1.2 is depicted in accordance with Rudy's data [94].

HfC_{0.56}, while according to the calculations done in Ref. [47] at 1000 K the lower boundary of the homogeneity range of disordered cubic hafnium carbide corresponds to HfC_{0.54}. The phase diagram of the Hf-C system (see Fig. 10) also contains a new compound Hf₈C₁₂ (which belongs to the

 M_8C_{12} group of metallocarbohedrens) discovered by Guo et al. [154] and Wei et al. [155].

Calculations of the phase diagram of the Hf-C system have shown that the main ordered phase of nonstoichiometric hafnium carbide is the Hf₆C₅ phase with a broad homogeneity region; the Hf₃C₂ phase has a narrower homogeneity range HfC_{0.65}-HfC_{0.70}, is a lower-temperature phase in comparison to Hf₆C₅, and can form only as a result of the sequential transformations HfC_y \rightarrow Hf₆C₅ \rightarrow Hf₃C₂ (see Fig. 10). The formation of the Hf₃C₂ and Hf₆C₅ phases occurs as a first-order phase transition and is accompanied by a thermal effect ΔH_{trans} . The values of T_{trans} , ΔS_{trans} , and ΔH_{trans} for the phase transformations associated with ordering of the nonstoichiometric cubic hafnium carbide HfC_y are listed in Table 5.

Figure 10 shows that the ordered phases of hafnium carbide form below 800 K. When T < 800 K, the diffusion rate is low and experimentally it is extremely difficult to achieve an equilibrium ordered state in the Hf - C system via prolonged annealing. It seems logical to assume that the prolonged absence of experimental data on ordering of hafnium carbide in the literature is an indication that achieving an equilibrium disordered state is difficult and that studying the structure of ordered phases by X-ray and neutron diffraction is virtually impossible. Indeed, in X-ray experiments the relative intensity of possible superlattice reflections is very low because of the large difference in the scattering amplitudes for hafnium and carbon atoms; in neutron-diffraction experiments the high absorption of neutrons by massive hafnium nuclei leads to a substantial drop in the overall intensity of the diffraction spectrum, with the result that it is almost impossible to determine the superlattice reflections. Note that studying the distribution of atoms in the crystal lattice of HfC_{ν} by NMR methods is also impossible, since the most abundant isotopes of hafnium,

Table 5. Thermodynamic characteristics of order – order and order – disorder phase transition in nonstoichiometric hafnium carbide HfC_y .

у	$Hf_3C_2\!-\!Hf_6C_5$			$Hf_6C_5 - HfC_y$		
	T _{trans} , Κ	$\Delta S_{\text{trans}},$ J (mol K) ⁻¹	$\Delta H_{\rm trans},$ kJ mol ⁻¹	T _{trans} , K	$\Delta S_{\text{trans}},$ J (mol K) ⁻¹	$\Delta H_{\rm trans},$ kJ mol ⁻¹
0.62	_	_	_	805	0.44	0.36
0.63	—	—	—	803	0.52	0.42
0.64	775	0.77	0.59	801	0.60	0.48
0.65	767	0.89	0.68	799	0.69	0.55
0.66	758	1.02	0.77	797	0.78	0.62
0.68	734	1.28	0.94	792	0.98	0.77
0.70	700	1.46	1.02	785	1.19	0.94
0.72	641	1.47	0.94	778	1.42	1.11
0.73	589	1.37	0.81	774	1.54	1.19
0.74	511	1.11	0.57	769	1.67	1.28
0.75	363	0.73	0.26	764	1.9	1.37
0.76	_	_	_	759	1.91	1.45
0.78	_	_	_	747	2.14	1.60
0.80	_	_	_	731	2.33	1.70
0.82	_	_	_	712	2.44	1.73
0.83	_	_	_	697	2.42	1.69
0.84	_	_	_	688	2.40	1.65
0.85	_	_	_	673	2.31	1.55
0.86	_	_	_	656	2.18	1.43
0.88	_	_	_	614	1.81	1.11
0.90	_	_	_	559	1.38	0.77
0.92	_	_	_	486	0.98	0.47
0.94	_	_	_	392	0.63	0.25
0.95	_	—	_	335	0.49	0.17

January, 2000

¹⁸⁰Hf, ¹⁷⁶Hf, and ¹⁷⁴Hf, and carbon, ¹²C, have nuclei with zero spin, or zero magnetic moments.

It is only recently that the first experimental study of ordering in hafnium carbide HfC_{ν} by the magnetic susceptibility method took place [48, 161, 162]. The results in Ref. [161] suggest that the Hf₃C₂-type phase is formed within a range of compositions that is wider than that calculated in Refs [46, 47]: from HfC_v (with 0.62 < v < 0.71) to HfC_{0.78}, while the range of existence of the Hf₆C₅ phase is no wider than 0.80 < y < 0.87. The results of Ref. [161] do not allow the determination of whether the formation of the Hf_3C_2 phase involves the formation of an intermediate phase, Hf_6C_5 , or whether the process begins directly from HfC_{ν} , since the temperature interval between two successive measurements of χ is too large and the accuracy of measuring χ is too low to fix an intermediate phase with a temperature range of existence no wider than 30-50 K [from approximately 760 to 806 K (see Fig. 10)]. The temperatures, measured by Zyryanova et al. [48, 161, 162], of the equilibrium disorder-order transition HfCy-Hf3C2 for HfC0.71 and HfC_{0.78} are 870-980 K and 970-1000 K, respectively. This is approximately 100-110 K and 220-230 K higher than the disorder – order transition temperatures for $HfC_{0.71}$ and HfC_{0.78} calculated in Ref. [46].

The study of the magnetic susceptibility of nonstoichiometric hafnium carbide HfC_y and the calculation of shortrange order parameters [48, 161] corroborate the formation of ordered phases of the Hf_3C_2 and Hf_6C_5 types. According to the data of Zyryanova et al. [48, 161, 162], the main ordered phase of hafnium carbide is Hf_3C_2 , which forms as a result of a first-order phase transition.

5.3 Phase diagrams of the V-C, Nb-C, and Ta-C systems

5.3.1 The V – C system. This is one of the best-studied systems. However, as far as ordering is concerned, the phase diagram of this system established by Carlson et al. [96] repeats the estimates made by Billingham et al. [55], while Huang [163] did not discuss ordering at all, with the result that the phenomenon was not reflected in the V-C diagram. The main difficulty in building the phase diagram of the V-Csystem consists in the fact that the upper boundary of the homogeneity range of disordered cubic vanadium carbide VC_{ν} is represented by the carbide $VC_{0.875}$ rather than the compound MC_{1.0} of stoichiometric composition (as is the case with other transition metals). The unusual position of the upper boundary of the homogeneity range of the carbide VC_{ν} explains a boundary effect that manifests itself in the formation of an ordered phase of the M₈C₇ type, which does not exist in other carbides.

New experimental data [51, 52] on the temperatures and heats of the phase transformations $V_6C_5 \leftrightarrow VC_y$ and $V_8C_7 \leftrightarrow VC_y$ made it possible [164, 165] to take into account the ordering of the carbide VC_y in the phase diagram of the V-C system.

Phase equilibria in the region of ordering of the nonstoichiometric cubic vanadium carbide VC_y were calculated by the OPF method [2].

The first variant of these calculations assumed that the ordered phase V_8C_7 has no homogeneity range. Indeed, single-phase samples with a cubic superstructure V_8C_7 form only within the composition range $VC_{0.87-0.875}$, while at a lower carbon content (0.83 < y < 0.875) samples with the ordered phase V_8C_7 always contain the V_6C_5 phase, which

has a broad homogeneity range [5, 52, 58, 166]. Moreover, according to the data of Volkova and Gel'd [121], Emmons and Williams [167], and Shacklette and Williams [168], the temperature of the $V_8C_7 \leftrightarrow VC_y$ transition is virtually independent (within experimental errors) of the composition of the carbide VC_y . To allow for the specific features of the ordered phase V_8C_7 (VC_{0.875}), which has no homogeneity range, the free energy of this phase was written not in the standard form (12) but in the form

$$F_{V_{8}C_{7}(VC_{0,875})}(T) = F(T) - TS_{c} + \frac{\Delta H_{trans}}{T_{trans}}(T - T_{trans}), (33)$$

where $F(T) = F_0(T) + xF_1(T) + x^2F_2(T)$ at x = 0.875 (the parameters $F_0(T)$, $F_1(T)$, and $F_2(T)$ are the same as for the disordered carbide VC_y), $S_c = 3.132 \times 10^{-3}$ kJ mol⁻¹ is the configurational entropy of the carbide VC_{0.875}, and $\Delta H_{\text{trans}} = 3$ kJ mol⁻¹ and $T_{\text{trans}} = 1380$ K are the heat and temperature of the V₈C₇ \rightarrow VC_{0.875} transition estimated on the basis of the experimental data of Lipatnikov et al. [51, 52], Volkova and Gel'd [121], and Emmons and Williams [167].

The phase boundary that separates the homogeneity region of the disordered carbide VC_y and the two-phase region $VC_y + V_8C_7$ was found by solving the equation

$$F_{V_{8}C_{7}(VC_{0,875})}(T) = F(y,0,T) - (y - y_{b})\frac{\partial F(y,0,T)}{\partial y},$$
(34)

where $y_b = 0.875$, and

$$F(y, 0, T) - (y - y_b) \frac{\partial F(y, 0, T)}{\partial y}$$

= $F_0(T) + y_b F_1(T) + y(2y_b - y)F_2(T)$
+ $k_B T \left[\ln(1 - y) + y_b \ln \frac{y}{1 - y} \right].$ (35)

Similarly, the position of the phase boundary that separates the homogeneity region of the ordered phase $V_{2t}C_{2t-1}$ (V₆C₅) and the two-phase region $V_{2t}C_{2t-1} + V_8C_7$ is described by the equation

$$F_{V_8C_7(VC_{0,875})}(T) = F(y,\eta,T) - (y-y_b) \frac{\partial F(y,\eta,T)}{\partial y},$$
(36)

where $y_{\rm b} = 0.875$, and

$$F(y, \eta, T) - (y - y_{b}) \frac{\partial F(y, \eta, T)}{\partial y}$$

= $F_{0}(T) + y_{b}F_{1}(T) + y(2y_{b} - y)F_{2}(T)$
+ $\frac{a^{(s)}}{4t^{2}} \eta_{\text{equil}}^{2} F_{2}(T) + \frac{k_{B}T}{2t} \{ \ln \left[n_{1}^{y_{b}} (1 - n_{1})^{1 - y_{b}} \right]$
+ $(2t - 1) \ln \left[n_{2}^{y_{b}} (1 - n_{2})^{1 - y_{b}} \right] \}.$ (37)

Here, the quantities n_1 , n_2 , η_{equil} , t, and $a^{(s)}$ refer to the phase $V_{2t}C_{2t-1}$ (V₆C₅).

Phase equilibria with the participation of the lower hexagonal carbide β -V₂C (V₂C_y) were calculated without taking the homogeneity range of this carbide into account, i.e., at a fixed carbon content y = 0.5. The calculations were done by equation (31).

The phase diagram of the V-C system is depicted in Fig. 11. The calculations done in Ref. [165] show that there

T, K

4000

3500

3000

2500

2000

1500

1000

T, K

1500

1400

1300



150 K

1485 k

 $V_2C_v + V_6$

1155 K

 V_2C_y

 V_3C_2

 V_4C_3

380 K

 $VC_v + C$

1360 K

1331 K

 $V_8C_7 + C$

640 K

 $V_6C_5 + V_8C_7$

 $iq + V_2C$

925 K

 $V + V_2 C_1$

 $\sim 1600 \, \overline{K}$

 $V + \alpha - V_2 C$

 V_2C_1



right P(1) Equilibrium phase diagram of the V=C system [105] with allowance for atomic ordering of the nonstoichiometric cubic vanadium carbide VC_y (the phase boundaries beyond the ordering region are given in accordance with the data of Carlson et al. [96] and Smith [172], and the position of the ζ-V₄C_{3-x} phase is given according to the data of Wiesenberger et al. [170]): V₈C₇, V₆C₅, and V₃C₂ are the ordered phases of the cubic vanadium carbide VC_y; and α-V₂C is the ordered phase of the lower hexagonal vanadium carbide V₂C_y (β-V₂C). Inset (a) depicts an enlarged area of the ordering region near the upper boundary of the homogeneity range of VC_y (calculations were carried out under the assumption that the V₈C₇ phase has no homogeneity range). Inset (b) depicts an enlarged area of the ordering region of VC_y calculated under the assumption that the V₈C₇ phase has a narrow homogeneity range.

are three ordered phases, vis., V_3C_2 , V_6C_5 , and V_8C_7 , that can form because of ordering of the nonstoichiometric cubic carbide VC_y in different temperature and concentration ranges.

The main ordered phase of vanadium carbide is V_6C_5 , which forms below 1485 K, and at 1100 K has a homogeneity region extending from $VC_{0.745}$ to $VC_{0.831}$. This phase can also be observed in two-phase regions, in view of which it exists in almost the entire homogeneity region of VC_{y} (see Fig. 11). The ordered phase V_8C_7 forms at a lower temperature, 1380 K, and at 1330 K can be observed together with the V₆C₅ phase in the two-phase region extending from $VC_{0.83}$ to $VC_{0.875}$, which is in good agreement with the experimental data of Arbuzov et al. [58], Emmons and Williams [167], and Hiraga [169]. As the temperature lowers, the two-phase region $V_6C_5 + V_8C_7$ where the ordered phase V8C7 exists narrows. The ordered phases V_6C_5 and V_8C_7 form a eutectic with $T_e = 1331$ K and $y_e = 0.852$; this result is very close to the estimate made by Athanassiadis et al. [59], according to which $T_{\rm e} \approx 1300$ K and $y_e \approx 0.852$. The calculations also imply that under equilibrium conditions in vanadium carbide there can form, via the peritectoid reaction $V_2C_{\nu} + V_6C_5 \rightarrow V_3C_2$, an ordered phase V_3C_2 with a narrow homogeneity range (from $VC_{0.667}$ to $VC_{0.710}$ at 800 K); no experimental evidence of this has been found so far. According to the calculations, the range of existence of the ordered phase V_3C_2 is close to the concentration range within which the orthorhombic phase ζ - V_4C_{3-x} is actually observed. In the calculations of the ordering of the carbide VC_y the existence of the ζ - V_4C_{3-x} phase was ignored, since the thermodynamic characteristics of this phase are unknown. If the free energy of the ζ -phase at T < 1150 K is smaller than that of the ordered phase V_3C_2 only tentatively.

The position of the ζ -V₄C_{3-x} phase is given in accordance with the most recent experimental data of Wiesenberger et al. [170]; earlier, the range of existence of this phase was depicted only tentatively. The phase contains 37.9% carbon and has a very narrow (about 0.4 at.% C) homogeneity range, VC_{0.605} – VC_{0.615}. The lowest temperature at which the presence of this phase was ever recorded after a 78-annealing was 1540 K [170]. This is close to the calculated maximum temperature of the disorder – order transition VC_y – V₆C₅, which is equal to 1485 K and is assumed to be the lower temperature limit of existence of the ζ -V₄C_{3-x} phase. The temperature of the peritectoid decomposition of the ζ phase upon heating is 2150 K.

In the homogeneity region of the lower carbide V_2C_{ν} $(\beta$ -V₂C) an ordered orthorhombic phase α -V₂C is formed [171]. The exact ordering temperature is unknown; according to Carlson et al. [96] and Smith [172], it is below 1870 K. So far no structural phase transition α -V₂C \rightarrow V₂C_v (β -V₂C) has been detected at temperatures as high as 1300 K in measurements of the magnetic susceptibility of the ordered carbide α - V_2C in the 300–1300 K temperature range [173]. With allowance for the results of Refs [172, 173], the temperature of the α -V₂C \rightarrow V₂C_{ν} (β -V₂C) order – disorder phase transition can be tentatively set at roughly 1600 K in the phase diagram of the V-C system (see Fig. 11). In 1992, a new compound, V₈C₁₂, was found in the V-C system [154]. This compound is not depicted in the phase diagram of the V-C system, since it occupies a position beyond the composition range in question.

The phase diagram of the V-C system clearly shows (see Fig. 11) that the disorder-order phase transitions in the vanadium carbide VC_{y} are of the first order. Such a conclusion was drawn by Lipatnikov et al. [51, 52], who studied the variation of the heat capacity of the $VC_{0.79}$, $VC_{0.83}$, and $VC_{0.87}$ carbides upon heating and cooling; a typical temperature dependence of the heat capacity is shown in Fig. 12. Indeed, the presence in the temperature dependence $C_p(T)$ of the VC_{0.79}, VC_{0.83}, and VC_{0.87} carbides of jumps in the region of reversible disorder-order transitions and the fact that the peaks are symmetric rather than λ shaped (see Fig. 12) suggest that the $V_6C_5 \leftrightarrow VC_{\nu}$ and $V_8C_7 \leftrightarrow VC_{0.875}$ transformations are first-order phase transitions. Moreover, there is a weak hysteresis in the heat capacity (see Fig. 12), which indicates the proximity to a first-order phase transition.

The calculated values of T_{trans} , ΔS_{trans} , and ΔH_{trans} for the phase transformations related to ordering in the nonstoichiometric vanadium carbide VC_y are listed in Table 6. For the sake of comparison, the experimental data of Lipatnikov et al. [51, 52] on T_{trans} and ΔH_{trans} are also listed. For VC_{0.79}, the calculated temperature T_{trans} and heat ΔH_{trans} of the V₆C₅ \rightarrow VC_{0.79} transition are 1450 K and 2.84 kJ mol⁻¹,



Figure 12. Variations in the heat capacity C_p of annealed vanadium carbide VC_{0.87} for heating (1) and cooling (2). The symmetric shape of the peaks and the hysteresis of heat capacity in the vicinity of the order – disorder transition temperature suggest that the phase transition is first-order [52].

respectively; the experimental value of ΔH_{trans} (see Table 6) is somewhat smaller since, according to the calorimetric measurements of Lipatnikov et al. [51], a small fraction of the ζ -V₄C_{3-x} phase is formed in VC_{0.79}.

An additional model calculation was carried out to establish the shape of the phase diagram of the V–C system for the case where the V_8C_7 phase has a narrow homogeneity range. In this variant of the calculations the free energy of ordering of the V_8C_7 phase was represented in the form

$$F_{V_8C_7(VC_{0.875})}(T) = F(T) - TS_c$$

+
$$\frac{\Delta H_{trans}(y)}{T_{trans}(y)} \left[T - T_{trans}^{max}(a + by + cy^2)\right], \quad (38)$$

where $F(T) = F_0(T) + xF_1(T) + x^2F_2(T)$ at x = 0.875 (the parameters $F_0(T)$, $F_1(T)$, and $F_2(T)$ are the same as for the

disordered carbide VC_y); $S_c = 3.132 \times 10^{-3}$ kJ mol⁻¹ is the configurational entropy of the carbide VC_{0.875}; $\Delta H_{\text{trans}}(y)/T_{\text{trans}}(y) \equiv \Delta S_{\text{trans}} = 2.174$ J (mol K)⁻¹, $T_{\text{trans}}^{\text{max}} = 1380$ K is maximum temperature of the V₈C₇ \rightarrow VC_y transition corresponding to the carbide VC_{0.875}; a = 40.7455, b = -93.367, and c = 54.793.

The phase boundaries of the two-phase region $VC_y + V_8C_7$ in the case where the V_8C_7 phase has a homogeneity region were found by solving the equations

$$y_1^2 F_2(T) - k_B T (1 - y_1) = y_2^2 F_2(T) - k_B T \ln(1 - y_2) - \Delta S_{\text{trans}} \left[T - (a - cy_2^2) T_{\text{trans}}^{\text{max}} \right], y_1(2 - y_1) F_2(T) + k_B T \ln y_1 = y_2(2 - y_2) F_2(T) + k_B T \ln y_2 + \Delta S_{\text{trans}} \left[T - (a + b + 2cy_2 - cy_2^2) T_{\text{trans}}^{\text{max}} \right].$$
(39)

Similarly, the phase boundaries of the $V_6C_5 + V_8C_7$ twophase region in the case where the V_8C_7 phase has a homogeneity range were found by solving the equations

$$y_{1}^{2}F_{2}(t) - \frac{a^{(3)}}{4t^{2}} \eta_{\text{equil}}^{2}F_{2}(T) - \frac{k_{\text{B}}T}{2t} \left[\ln(1-n_{1}^{(d)}) + (2t-1)\ln(1-n_{2}^{(d)})\right]_{\eta=\eta_{\text{equil}}} = y_{2}^{2}F_{2}(T) - k_{\text{B}}T\ln(1-y_{2}) - \Delta S_{\text{trans}}\left[T - (a-cy_{2}^{2})T_{\text{trans}}^{\text{max}}\right],$$

$$y_{1}(2-y_{1})F_{2}(T) + \frac{a^{(s)}}{4t^{2}} \eta_{\text{equil}}^{2}F_{2}(T) + \frac{k_{\text{B}}T}{2t} \left[\ln n_{1}^{(d)} + (2t-1)\ln n_{2}^{(d)}\right]_{\eta=\eta_{\text{equil}}} = y_{2}(2-y_{2})F_{2}(T) + k_{\text{B}}T\ln y_{2} + \Delta S_{\text{trans}}\left[T - (a+b+2cy_{2}-cy_{2}^{2})T_{\text{trans}}^{\text{max}}\right].$$

(40)

Table 6. Temperatures T_{trans} (K), entropies (J (mol K)⁻¹), and heats ΔS_{trans} (kJ mol⁻¹) of the order-order and order-disorder phase transitions in nonstoichiometric vanadium carbide VC_y.

у	V ₃ C ₂ -V ₆ C ₅ (theory [52, 165])		$V_6C_5 - VC_y$					$V_8C_7 - VC_y$					
	T _{trans}	$\Delta S_{ m trans}$	$\Delta H_{\mathrm{trans}}$	T _{trans}		ΔS_{trans}	$\Delta H_{\rm trans}$		T _{trans}		$\Delta S_{\rm trans}$	$\Delta H_{ m trans}$	
_			Theory [52, 165]	Experi- ment [51, 52]	(theory [52, 165])	Theory [52, 165]	Experiment [51, 52]	Theory [52, 165]	Experi- ment [51, 52]	(theory [52, 165])	Theory [52, 165]	Experiment [51, 52]	
0.73	1138	1.38	1.57		_	_	_	_					_
0.74	993	1.17	1.16	_	_	_	_	_	_	_	_		
0.75	728	0.82	0.60	_		_					_		_
0.76		_	_	_			_				_		_
0.77		_	_	1481		1.75	2.59				_		_
0.78		_	_	1466		1.85	2.72				_		_
0.79	_	_	_	1450	1430 ± 5	1.96	2.84	2.16 ± 0.1	_		_		
0.80	_	_	_	1433		2.05	2.94				_		_
0.81		_	_	1413		2.13	3.01				_		_
0.82	_	_	_	1391	_	2.19	3.04		_		_		
0.83	_	_	_	1366	1442 ± 5	2.21	3.02	$1.26\pm0.1*$	_	1334 ± 5	_		$0.70\pm0.1*$
0.84		_	_	1338		2.20	2.95				_		_
0.85		_	_	1307		2.15	2.81				_		_
0.86		_	_	1272		2.06	2.62				_		_
0.87	_	_	_	_		_				1355 ± 5	_		2.30 ± 0.1
0.875	_	_			_	_	_	_	1380	—	2.17	3.00	_

*For transformations in the carbide VC_{0.83} initiated by cooling, Lipatnikov et al. [51] gives the value of the overall thermal effect $\Delta H_{trans} = 2.11 \text{ kJ}$ mol⁻¹. This thermal effect incorporates the thermal effects of two transformations: VC_{0.83} \rightarrow V₆C₅ ($\Delta H_{trans} \approx 1.37 \text{ kJ} \text{ mol}^{-1}$), and VC_{0.83} \rightarrow V₈C₇ ($\Delta H_{trans} \approx 0.75 \text{ kJ} \text{ mol}^{-1}$).

Here the quantities n_1 , n_2 , t, η_{equil} , and $a^{(s)}$ refer to the ordered phase V₆C₅.

The portion of the phase diagram of the V-C system calculated with allowance for the existence of a homogeneity range of the V_8C_7 phase is depicted in inset (b) in Fig. 11. According to the calculations, the homogeneity range of the V₈C₇ phase is very narrow: its maximum width is from $VC_{0.852}$ to $VC_{0.875}$ at 1340 K. As the temperature drops below 1340 K, the homogeneity range of the V₈C₇ phase narrows even more. The V₆C₅ and V₈C₇ phases form a eutectic at 1340 K with $y_e \approx 0.8476$. The two-phase region $V_6C_5 + V_8C_7$, which exists at T < 1340 K, is almost twice as narrow as in the first variant of the calculation. In all other respects, however, the phase diagram of the V-C system is the same. The final solution of the problem of whether the V8C7 phase has a homogeneity range requires very thorough experimental investigations of the structure of vanadium carbide in the narrow composition range $VC_{0.85} - VC_{0.875}$.

On the whole, the calculations have shown that three phases are formed as a result of ordering of vanadium carbide: a monoclinic or trigonal ordered phase V_6C_5 with a homogeneity range $VC_{0.75}-VC_{0.83}$ (at 1100 K); a cubic ordered phase V_8C_7 , which may exist together with the V_6C_5 phase in the two-phase region; and an ordered phase V_3C_2 , which is formed below 1150 K and has a very narrow homogeneity range. The temperatures of the $V_6C_5 \leftrightarrow VC_y$ and $V_8C_7 \leftrightarrow VC_{0.875}$ transformations are 1400–1450 K and 1360–1380 K, respectively.

5.3.2 The Nb-C system. The first variant of the phase diagram of the Nb-C system in which the ordered phase Nb₆C₅ was depicted tentatively was suggested by Smith et al. [174]. A more exact and correct phase diagram of the Nb-C system was built in Refs [26, 27] on the basis of the calculations done in Ref. [43].

The Nb-C system contains not only the cubic carbide NbC_y with an extended homogeneity range but also a lower hexagonal carbide β -Nb₂C with a narrow homogeneity range, whose presence was ignored in the calculations done in Refs [43-46]. The calculated phase diagram of the Nb-C system in which ordering of the nonstoichiometric niobium carbide NbC_y is observed is depicted in Fig. 13; the position of the phase boundary beyond the ordering range is depicted in accordance with the data of Rudy [94] and Storms et al. [175].

As Fig. 13 shows, below 900 K under conditions of thermodynamic equilibrium there exists an ordered phase, Nb₃C₂, with a very narrow homogeneity region (0.67 < y < 0.71 at 400 K). There are still no experimental indications of the existence of an ordered M₃C₂-type phase in niobium carbide. It is extremely difficult to detect this low-temperature phase since below 900 K the diffusion mobility of the atoms is low, and achieving a thermodynamically equilibrium structural state requires prolonged annealing of the NbC_y sample; moreover, the composition of the non-stoichiometric carbide NbC_y must correspond exactly to the concentration range of existence of the superstructure Nb₃C₂.

The main ordered phase of niobium carbide is the Nb₆C₅ phase, which forms as a result of a disorder – order transition below 1594 K and has a sufficiently wide range of existence: at T = 800 K the ordered phase Nb₆C₅ has a homogeneity region $0.80 \le y \le 0.88$. The results of calculations for the Nb₆C₅ phase are in good agreement with the experimental data described in Refs [54, 63, 67–69, 176]. The T_{trans} temperature for the carbide NbC_{0.63} measured in the



Figure 13. Equilibrium phase diagram of the Nb – C system with allowance for atomic ordering of the nonstoichiometric cubic niobium carbide NbC_y (Nb₃C₂ and Nb₆C₅ are ordered phases of NbC_y). The position of the rhombohedral phase ζ -Nb₄C₃, which is not an ordered phase of NbC_y, is depicted in accordance with the data of Wiesenberger et al. [170].

experiments is 1304 K [67–69]. When the temperature is above 800 K, the calculated range of existence of the Nb₆C₅ superstructure is somewhat larger than the one obtained in experiments [14, 63, 67–69]. The ordered phase Nb₆C₅ was also observed by Lewis et al. [62], Christensen [64], Rempel' et al. [65, 66], and Khaenko and Sivak [70].

The transformation of the disordered phase NbC_{y} into the ordered phase Nb₆C₅ at the transition temperature T_{trans} is accompanied by a jump in the long-range order parameter η from 0 to η_{trans} , which is an indication that the disorderorder transition is of the first order. As the temperature decreases from T_{trans} to absolute zero, the long-range order parameter of the carbide gradually increases from η_{trans} , and at 300 K it almost reaches $\eta_{\max}(y)$ (Fig. 14). At the temperatures of the Nb₃C₂-Nb₆C₅ and Nb₆C₅-NbC_{ν} transitions, the temperature dependence of the free energy, F(T), exhibits a break, while the temperature dependence of the enthalpy and entropy exhibits pronounced jumps characteristic of first-order phase transitions. The calculated values of T_{trans} , ΔS_{trans} , and ΔH_{trans} for the phase transformations related to the ordering of the nonstoichiometric cubic niobium carbide NbC_{ν} are listed in Table 7.

The calculated values of the transition temperatures are in good agreement with the values of T_{trans} found experimentally by differential thermal analysis [65, 67]. For NbC_{0.81} and NbC_{0.83}, the calculated temperatures of the Nb₆C₅-NbC_y transition are 1375 and 1288 K, respectively; the experimental values of T_{trans} are 1258 ± 10 and 1304 ± 10 K, respectively. According to Venables and Meyerhoff [176] and Dy and Williams [177], the experimental values of T_{trans} for the order-disorder transition Nb₆C₅-NbC_{0.83} are 1298 ± 25 and 1303 ± 50 K, respectively. The neutron-diffraction



Figure 14. Abrupt change in the temperature dependence of the long-range order parameter η in the course of formation of the ordered phase Nb₆C₅ in niobium carbide NbC_{γ} [14].

study conducted by Landesman [178] has shown that for NbC_{0.83} the temperatures T_{trans} of the order-disorder and disorder-order transformations are 1298 ± 5 and 1273 ± 10 K, respectively. Niobium carbide NbC_y is the first nonstoichiometric compound in which disorder-order transformations were detected [179] by measuring the magnetic susceptibility (Fig. 15).

The phase diagram of the Nb–C system (see Fig. 13) depicts, with the use of the data of Wiesenberger et al. [170], the position of the ζ -Nb₄C_{3-x} phase existing at temperatures from 1600 to 1850 K. The homogeneity range of the ζ -Nb₄C_{3-x} phase extends from 40.1 to 40.7 at.% C. The rhombohedral carbide ζ -Nb₄C₃ [180] is not an ordered phase of the nonstoichiometric niobium carbide NbC_y. Note that the calculated concentration range of existence of the ordered phase Nb₃C₂ is close to the concentration range in which the ζ -Nb₄C_{3-x} phase is actually observed. In the calculations of the ordering of NbC_y the existence of the ζ -Nb₄C_{3-x} phase was ignored, since the thermodynamic characteristics of this phase are unknown.

Wei et al. [157] used plasmochemical gas-phase synthesis combined with laser heating to synthesize an entirely new



Figure 15. Effect of ordering on the magnetic susceptibility χ of niobium carbide NbC_{0.83} [179]: O, disordered state; \bullet , ordered state; and \bullet , transient state. The sudden irreversible drop in χ at 1120 K is a consequence of the transition from a nonequilibrium quenched disordered state to an equilibrium ordered state. The abrupt reversible change in χ at $T \approx 1300$ K corresponds to a reversible order-disorder transformation.

compound, Nb₈C₁₂, in the Nb–C system (similar synthesis was carried out in the Ti–C, Zr–C, and Hf–C systems). This compound is a molecular cluster and belongs to the group of metallocarbohedrens M_8C_{12} . It is stable below 1500 K; in the phase diagram of the Nb–C system given in Fig. 13 this compound is not shown, since it exists at y = C/Nb > 1.2.

As noted earlier, the disordered state of highly nonstoichiometric carbides can easily be preserved as a metastable state at temperatures below T_{trans} . The analysis of the difference $\Delta C_p(T)$ of the heat capacities of a nonstoichiometric compound in the equilibrium nonstoichiometric state and the quenched nonequilibrium disordered states [181, 182] has shown that $\Delta C_p(T)$ may change sign upon temperature

Table 7. Thermodynamic characteristics of order – order and order – disorder phase transition in the nonstoichiometric niobium carbide NbC_y and nonstoichiometric tantalum carbide TaC_y .

у	Nb ₃ C ₂ -Nb	₆ C ₅	Nb ₆ C ₅ -NbC _y				$Ta_6C_5 - TaC_y$		
	T _{trans} , Κ	$\Delta S_{ m trans},$ J (mol K) ⁻¹	$\Delta H_{\rm trans},$ kJ mol ⁻¹	T _{trans} , K	$\Delta S_{ m trans},$ J (mol K) ⁻¹	$\Delta H_{ m trans},$ kJ mol ⁻¹	T _{trans} , Κ	$\Delta S_{ m trans},$ J (mol K) ⁻¹	$\Delta H_{\rm trans},$ kJ mol ⁻¹
0.74	761	0.81	0.62	_	_	_			_
0.75	505	0.67	0.34	1575	0.70	1.10	_	_	_
0.76	_			1547	0.76	1.17		_	_
0.78	_			1485	0.88	1.31		_	_
0.80	_			1415	1.01	1.42	1399	1.10	1.54
0.82	—			1333	1.11	1.48	1325	1.22	1.61
0.83	—		—	1272	1.16	1.47	1270	1.26	1.60
0.84	—		—	1239	1.17	1.45	1239	1.28	1.58
0.85	—		—	1186	1.18	1.40	1190	1.28	1.52
0.86	—		—	1129	1.16	1.31	1137	1.26	1.43
0.88	—		—	1004	1.07	1.07	1020	1.15	1.17
0.90	—		—	864	0.92	0.79	887	0.98	0.87
0.92	—			711	0.75	0.53	738	0.79	0.58
0.94	_	_		549	0.56	0.31	576	0.58	0.34
0.95	—	—	_	463	0.47	0.22	489	0.49	0.24

variations. Figure 16 depicts the calculated [2, 181] temperature curves $\Delta C_p(T)$ for the equilibrium ordered and quenched disordered carbide NbC_{0.85} (at $T < T_{\text{trans}} = 1186$ K) and for the equilibrium ordered carbide of the same composition at $T > T_{\text{trans}}$. At 300 K, the difference $\Delta C_p > 0$, but, as the temperature grows, the difference decreases, and at 900 K < $T < T_{\text{trans}}$ it is already negative. Clearly, at T_{trans} the heat capacity undergoes a discontinuity, which is an indication that the order – disorder phase transition is of the first order.



Figure 16. Heat capacity of nonstoichiometric niobium carbide NbC_{0.85} in the equilibrium ordered state (——) and in the nonequilibrium disordered state (– –) at $T < T_{\text{trans}} = 1186$ K and in the equilibrium disordered state at $T > T_{\text{trans}}$ [2, 182].

5.3.3 The Ta – C system. Nonstoichiometric tantalum carbide TaC_y is complex object for experimental studies of ordering, with the result that building the phase diagram of the Ta – C system with allowance for ordering of the carbide TaC_y done in Refs [43–46] by theoretical means has attracted much attention. In addition to the cubic carbide TaC_y, which has a wide homogeneity range, the Ta – C system contains a lower hexagonal carbide α -Ta₂C_y with a narrow homogeneity range. Since the literature contains only the thermodynamic characteristics for the stoichiometric composition of the lower tantalum carbide, i.e., for α -Ta₂C_y, equation (31) was used to calculate the phase equilibria involving this compound.

Earlier we noted that, generally speaking, ordered phases of types M₂X, M₃X₂, M₄X₃, M₆X₅, and M₈X₇ may form (from the crystallographic viewpoint) in a nonstoichiometric compound MX_{ν} . To determine the ordered phases that can actually form in tantalum carbide TaC_{ν} , the free energies of disordered tantalum carbide TaC_{y} and the possible ordered phases Ta₂C, Ta₃C₂, Ta₄C₃, Ta₆C₅, and Ta₈C₇ (Fig. 17) were calculated at 700 and 1600 K using equations (3), (4), (10)-(13), and (17). The ordered phase Ta_4C_3 cannot exist at 700 K, since in the interval $0.5 \le y \le 1.0$ its transition temperature $T_{\text{trans}} < 600$ K. At 700 K, the ordered phases Ta₂C, Ta₃C₂, and Ta₆C₅ and the disordered carbide TaC_y (with y > 0.96) have the smallest free energy in different concentration ranges. The free energy of the possible ordered phase Ta₈C₇ is larger than the free energies of the other ordered phases in the entire interval $0.5 \le y \le 1.0$. Above 1430 K only the disordered phase can exist over the entire homogeneity region.



Figure 17. Comparison of the free energies of the disordered and possible ordered phases of tantalum carbide at 700 and 1600 K: curve *I* corresponds to the disordered carbide TaC_y , curve 2 to the ordered Ta_2C type phase, curve 3 to the ordered Ta_3C_2 type phase, curve 4 to the ordered Ta_8C_7 type phase, and curve 5 to the ordered Ta_6C_5 type phase; the points *I* and *II* correspond to the free energy $0.5F_{\alpha-Ta_2C}$ at 700 and 1600 K, respectively.

The points *I* and *II* on the vertical axis (at y = 0.5) in Fig. 17 correspond to the free energies $0.5F_{\alpha-Ta_2C}$ at 700 and 1600 K, respectively. At 700 K the tangent to the free energy F(y, 700 K) passing through point *I* determines the width of the possible two-phase region (α -Ta₂C + Ta_{2t}C_{2t-1} or α -Ta₂C + TaC_y) and the free energy of the two-phase mixture. Clearly, at 700 K the two-phase mixture (α -Ta₂C + Ta₆C₅) has the lowest free energy, with the result that no ordered phases of type Ta₂C or Ta₃C₂ can exist.

The equilibrium phase diagram of the Ta-C system calculated with allowance for atomic ordering of nonstoichiometric cubic tantalum carbide TaC_{ν} is depicted in Fig. 18. The position of the phase boundary beyond the ordering range is given according to Storms [93]. The position of the rhombohedral phase ζ -Ta₄C_{3-x} [180] is depicted according to Wiesenberger et al. [170]. This ζ phase is not an ordered phase of the carbide TaC_y , has a narrow homogeneity range (carbon content ranges from 38.2 to 39.0 at.%), and is formed below 2450 K [170]. The free energy of ζ -Ta₄C_{3-x} is unknown, so that in calculations of the phase diagram of the Ta-C system the existence of this phase is ignored. Not so long ago Guo et al. [154] and Wei et al. [155] synthesized a new compound Ta_8C_{12} in the Ta-C system. This compound is a molecular cluster and belongs to the group of metallocarbohedrens M_8C_{12} (M = Ti, Zr, Hf, V, Nb, Ta, and Cr). The relative carbon content in the Ta_8C_{12} compound (y = 1.5) is beyond the limits of the part of the diagram considered here and, therefore, is not shown in the phase diagram of the Ta-C system given in Fig. 18.

Figure 18 shows that the only ordered phase of nonstoichiometric tantalum carbide is the Ta₆C₅ phase. It has a narrower homogeneity region than the similar ordered phase Nb₆C₅. Venables and Meyerhoff [176] studied the carbide TaC_{0.83} by the electron-diffraction method and detected a diffuse band whose geometry corresponds to ordering of a phase of the M₆C₅ type with a very small order parameter. Rempel et al. [74–76] and Lipatnikov et al. [183] used the neutron-diffraction method to do the most thorough investigation, which was actually the first of this type, of the structure of the ordered tantalum carbide. Their studies



Figure 18. Equilibrium phase diagram of the Ta – C system with allowance for atomic ordering of nonstoichiometric cubic tantalum carbide TaC_y [76]. The position of the rhombohedral phase ζ -Ta₄C₃ is depicted in accordance with the data of Wiesenberger et al. [170]; this phase is not an ordered phase of the carbide TaC_y and is formed below 2450 K.

showed that as a result of prolonged slow cooling of the nonstoichiometric tantalum carbide TaC_y from 1600 to 750 K there was formed an incommensurate ordered phase with properties close to those of the known superstructures of the M₆C₅ type. The studies of magnetic susceptibility conducted by Lipatnikov et al. [72, 73] also corroborated the fact of formation in tantalum carbide of an ordered M₆C₅-type phase; for the carbides TaC_{0.83} and TaC_{0.85}, the values of T_{trans} of the Ta₆C₅-TaC_y transition found from magnetic-susceptibility measurements are 1110 and 1130 K, respectively.

The calculated values of T_{trans} , ΔS_{trans} , and ΔH_{trans} for the phase transformations related to the ordering of the non-stoichiometric cubic tantalum carbide TaC_y are listed in Table 7.

Measurements of the heat capacity of the nonstoichiometric tantalum carbide in the temperature range of 80– 300 K showed that the ordered carbides have a greater heat capacity than the disordered carbides with the same carbon content [181, 182]. Figure 19 depicts the variations of the free energy *F*, the enthalpy *H*, the entropy *S*, and the heat capacity of the tantalum carbide TaC_{0.83} near the temperature of the order-disorder Ta₆C₅-TaC_{0.83} transition. At the transition temperature $T_{\text{trans}} = 1284$ K, the free energy undergoes a break, the temperatures curves of the enthalpy and entropy exhibit jumps, and the temperature curve of the heat capacity has a discontinuity, which is characteristic of first-order phase transitions.

5.4 The Ti–N system

There are two stable compounds in the Ti–N system, the nonstoichiometric titanium nitride TiN_y with a *B*1-type base structure (NaCl), which has a wide homogeneity range (from



Figure 19. Variations of the free energy *F*, the entropy *S*, the enthalpy *H*, and the heat capacity C_p of nonstoichiometric tantalum carbide TaC_{0.83} in the course of the order – disorder transition at $T_{\text{trans}} = 1284$ K [2, 182].

TiN_{0.38} to TiN_{1.00} at $T \ge 1350$ K), and the lower tetragonal (space group $P4_2/mnm$) titanium nitride ϵ -Ti₂N, which has almost no homogeneity range and is not an interstitial compound. The E-Ti2N nitride exists only below 1300-1350 K [126]. Lengauer and Ettmayer [184] found that ε-Ti₂N forms at the boundary of two phases, α -Ti and TiN_v, with no direct phase transformation of the nonstoichiometric cubic titanium nitride $TiN_{0.50}$ into the ϵ -Ti₂N phase being possible. Lengauer and Ettmayer [185-188] discovered two new (probably metastable) high-temperature phases in the Ti-N system: η -Ti₃N_{2-x} and ζ -Ti₄N_{3-x}. Both are trigonal (rhombohedral), have a space group $R\bar{3}m$, and exist within narrow temperature ranges, 1335 - 1374 K and 1344 - 1570 K. respectively [187]. The ζ -Ti₄N_{3-x} phase is isostructural to the ζ carbides of vanadium, niobium, and tantalum. It should particularly be noted that the η -Ti₃N_{2-x} and ζ -Ti₄N_{3-x} phases have no homogeneity ranges and are not ordered phases of the cubic titanium nitride TiN_{ν} .

Calculations have revealed (see Ref. [47]) that in the ordering of TiN_{ν} the ordered Ti₂N, Ti₃N₂, and Ti₆N₅ phases form in different temperature and concentration ranges (Fig. 20). The positions of the phase boundaries beyond the ordering range are shown in accordance with the data of Wriedt and Murray [126], and the positions of the η -Ti₃N_{2-x} and ζ -Ti₄N_{3-x} phases are shown in accordance with the data of Lengauer and Ettmayer [184, 185, 187]. The ordered phase Ti₂N has a narrow homogeneity range (TiN_{0.51}-TiN_{0.53} at 1000 K and $TiN_{0.52}$ – $TiN_{0.57}$ at 800 K); to the left and right of the Ti₂N phase, there are two-phase regions ε -Ti₂N + Ti₂N and $Ti_2N + Ti_3N_2$, respectively. The direct disorder-order $TiN_v - Ti_2N$ transition is possible only for the nitride $TiN_{0.51}$, and the temperature of the $TiN_{0.51} - Ti_2N$ transition is about 1068 K. The ordered Ti₂N phase with a higher nitrogen content, y > 0.51, forms as the temperature lowers as a result of the following sequence of transformations: $TiN_{0.511-0.524} \rightarrow$



Figure 20. Equilibrium phase diagram of the Ti–N system with allowance for atomic ordering of nonstoichiometric cubic titanium nitride TiN_y. The inset depicts an enlarged area of the ordering region where at a temperature of 1073.4 K the peritectoid transformation Ti₃N₂ + TiN_y \rightarrow Ti₆N₅ takes place; the coordinates y = N/Ti of the points 1, 2, and 3 are 0.5236, 0.524, and 0.5255, respectively. The hightemperature trigonal phases η -Ti₃N_{2-x} and ζ -Ti₄N_{3-x} are not ordered phases of the nonstoichiometric titanium carbide TiN_y and are stable at T > 1300 K.

Ti₃N₂ \rightarrow Ti₂N and TiN_{0.525-0.570}Ti₆N₅ \rightarrow Ti₃N₂ \rightarrow Ti₂N. According to the results of calculations, the main ordered phase that can be formed in the cubic titanium nitride TiN_y is the Ti₆N₅ phase, which is formed as a result of the direct first-order disorder – order phase transition TiN_y – Ti₆N₅. We also note that in the ordering range of the nonstoichiometric titanium nitride TiN_y there is a peritectoid transformation, Ti₃N₂ + TiN_y \rightarrow Ti₆N₅ at T = 1073.4 K and y = 0.524 (see the inset in Fig. 20). The TiN_y – Ti₂N transformation is a second-order phase transition, while all the other disorder – order corder phase transitions are of the first order. The values of T_{trans} , ΔS_{trans} , and ΔH_{trans} for the disorder – order can be found in Ref. [26].

The fact of the formation of the ordered tetragonal (space group $I4_1/amd$ phase Ti₂N (δ' -TiN_{0.50}) in the nitride TiN_v was established in the experiments of Lobier and Marcon [78] and later corroborated by Nagakura and Kusunoki [79], Christensen et al. [81], and Alamo and de Novion [189]. According to Alamo and de Novion [189], the temperature of the transition $Ti_2N-TiN_{0.50}$ is 1070–1140 K and this phase transition is of the first order. According to Etchessahar et al. [85], the ordered phase Ti₂N has no homogeneity region and its composition corresponds, in nitrogen content, to $TiN_{0.51}$; the transition from the disordered cubic nitride TiN_{y} to the ordered phase $Ti_{2}N$ takes place within the range $TiN_{0.5}-TiN_{0.6}$ at 1070 \pm 10 K. Below this temperature (at roughly 1000-1070 K) to the left and right of the ordered phase with the composition $TiN_{0.51}$ there are two-phase regions ϵ -Ti₂N + Ti₂N and Ti₂N + TiN_y, respectively. According to the data of Lengauer and Ettmayer [84] on thermal decomposition, the ordered phase Ti₂N exists at temperatures no higher than 1140-1180 K.

The results of calculations (see Refs [40, 47]) of the phase diagram of the Ti-N system imply that the ordered phase Ti₂N has a small homogeneity region and that the presence of the two-phase region $Ti_2N + TiN_v$ at 1000 K is possible only if there is no way in which an equilibrium state can be reached in which there are two more ordered phases of titanium nitride, Ti₃N₂ and Ti₆N₅. The ordered phase Ti₆N₅ has yet to be observed in experiments. However, the formation of the superstructure Ti₆N₅ also follows from the results of calculations of Priem et al. [86, 138] done by the Monte Carlo and cluster variation methods (Fig. 21). According to Priem [138], the temperature of the transition $Ti_6N_5 - TiN_{0.83}$ is roughly 560 K; probably, this value of T_{trans} is understated. Interestingly, in their calculations of the phase diagram of the Ti-Nsystem, Priem et al. [86, 138] arrived at a structure of the ordered phase Ti₆N₅ in which the arrangement of atoms is identical to that of the monoclinic (space group C2/m) superstructure Nb₆C₅ [65-69].



Figure 21. Portion of the phase diagram of the Ti – N system calculated by the Monte Carlo method with allowance for ordering of the nonstoichiometric titanium nitride TiN_y in the TiN_{0.80} – TiN_{0.87} range [86, 138]

6. Phase diagrams of pseudobinary systems

An important feature of highly nonstoichiometric compounds is that they form solid solutions by mutual substitution of atoms of the metal or the nonmetal or both simultaneously. The degree of mutual solubility of nonstoichiometric compounds varies within broad limits and depends on the features of their crystalline and electronic structure and on external conditions. The distribution of the mutually substituting components in the lattice of solid solutions can be either statistical or ordered.

Atomic ordering in the crystal lattice of a solid is an isobaric process, so that the common approach in the thermodynamic analysis of ordering is to use the free energy F. Indeed, for solids the pressure p = 0. In this case the internal (configurational) energy E of the lattice coincides with the enthalpy H of the crystal, since H = E + pV = E (pV = 0 at p = 0), and the isobaric potential (Gibbs free energy G) coincides with the free energy F, since

G = F + pV = F. The Gibbs free energy is used directly in the thermodynamic analysis of equilibria with allowance for possible changes in the aggregate state, e.g., melting or solidification.

Experimental investigations of the phase diagrams of pseudobinary systems formed by nonstoichiometric compounds are extremely difficult. It is almost impossible to find by experimental means the position of the liquidus line in a system formed by compounds with melting points of 3000 K and higher or to find in such a system a latent solid-phase decomposition region. At the same time, calculations make it possible to establish the shape of the phase diagram to a sufficient degree of accuracy if the dependence on temperature and composition of the parameters describing the interaction in the system is known. Systems based on nonstoichiometric compounds do not obey the models of ideal or regular solutions. For this reason, a model of subregular solutions [190-193], which takes into account the dependence on temperature and composition of the interchange energies in the different phases, was proposed in order to calculate the phase diagrams of such systems.

With the pressure remaining constant, the Gibbs free energy of the *j*th phase in a multicomponent system can be written as follows:

$$\Delta G_j(\{x_i\}, T) = \sum_i x_i \Delta G_j(x_i = 1, T) + RT \sum_i x_i \ln x_i + G_j^{e}(\{x_i\}, T), \qquad (41)$$

where x_i is the concentration of the *i*th component in the *j*th phase, ΔG_j ($x_i = 1, T$) are the free energies of the components of the system, and $G_j^e(\{x_i\}, T)$ is the excess free energy of mixing for the *j*th phase. The conditions of phase equilibrium are invariant on adding to the free energy of mixing

$$\Delta G_j^{\text{mix}} = \sum_i x_i \Delta G_j(x_i = 1, T) + RT \sum_i x_i \ln x_i$$

any linear function of the composition, with the result that phase equilibria can be described by a relation linking the free energies of mixing of the phases in equilibrium.

The extent to which a system differs from an ideal one is determined by the value of the excess free energy of mixing $G_i^{e} = B_j(\{x_i\}, T) \prod x_i^{(j)}$, where $B_j(\{x_i\}, T)$ is the energy of interchange in the *j*th phase, i.e., an energy parameter that characterizes the interaction of the components in the *j*th phase and is a function of composition and temperature. In a binary system A - B the interchange energy is assumed to be the difference of energies of pairwise interactions of unlike (ϵ_{AB}) and like $(\epsilon_{AA}$ and $\epsilon_{BB})$ atoms, i.e., the quantity $B = N_{\rm A}[\varepsilon_{\rm AB} - (\varepsilon_{\rm AA} + \varepsilon_{\rm BB})/2]$. In the ideal solution model, the interchange energy $B_i = 0$, with the result that the excess free energy of mixing of an ideal solution, G_i^e , is zero. In the regular solution model, the interchange energy $B_i = \text{const}$, i.e., is a finite constant and does not depend on temperature and composition. In accordance with this fact, when the regular solution model is used, the excess free energy of mixing of a binary solid solution is given by the relationship $G_i^e = x_A x_B B_i$. Finally, in the more complicated model of subregular solutions, the interchange energy B_i depends on the temperature and composition of the solid solutions, so that for a binary solution the excess free energy of mixing has the form $G_i^e = x_A x_B B_j(x_A, x_B, T)$.

To calculate the phase boundaries in the subregular solution model, one must know the interchange energies of all the phases in equilibrium. According to Kaufman and Bernstein [194], the interchange energy of the liquid phase, $B_l = e_0 + e_p$, is the sum of the electron interaction parameter e_0 and the internal pressure parameter e_p ; the interchange energy of the solid phase also includes (in addition to e_0 and e_p) the parameter of electron interaction in the solid phase, e_1 , and the parameter of elastic distortions of the crystal lattice, e_2 , i.e., $B_s = e_0 + e_p + e_1 + e_2$.

In the subregular solution model [192], when calculating the interaction parameters in pseudobinary carbide systems, the quantity that characterizes the strength of the interatomic bonds is assumed to be the atomization energy (enthalpy) E^{at} , i.e., the energy required to separate the compound into individual atoms and to take these atoms to distances at which their separation is infinite (in other words, the energy spent on transferring the compound from the standard state to an atomic gas). For the nonstoichiometric compound MX_y, the atomization energy $E^{at}(y) = \Delta H^0_{s,M} + y \Delta H^0_{s,X} \Delta H_{f,298}^0(y)$ [195–197], where ΔH_s^0 are the evaporation heats of the components, and $\Delta H^0_{f,298}(y)$ is the enthalpy of formation of the compound MX_y . According to Refs [198-200], in this case the internal pressure parameter e_p with allowance for variations in the system's volumes due to changes in temperature and composition can be written as follows:

$$e_p = \left[\sum_{i=1}^n x_i V_i(T)\right] \left\{\sum_{i=1}^n \frac{E_i^{\text{at}}}{V_i(T)} - n \left[\prod_{i=1}^n \frac{E_i^{\text{at}}}{V_i(T)}\right]^{1/n}\right\}.$$
(42)

The internal pressure parameter in the liquid phase, e_p , is related to the difference in the cohesion energies of the atoms in the components of the liquid solution and to the difference in the molar volumes (or atomic volumes in the case of elements) of these components. The parameter is always positive and characterizes the degree of immiscibility of the solution's components in the liquid state.

The electron interaction parameter for the liquid phase, e_0 , is defined as follows:

$$e_{0} = \left[\sum_{i=1}^{n} x_{i} V_{i}(T)\right] \left\{\prod_{i=1}^{n} \left[\left(\frac{E_{i}^{\text{at}}}{V_{i}(T)}\right)^{1/2} - \left(\frac{\sum E_{i}^{\text{at}}}{\sum V_{i}(T)}\right)^{1/2}\right]\right\}^{2/n}.$$
(43)

Clearly, in two-component systems (binary or pseudobinary) the parameter e_0 is always negative.

In addition to e_0 and e_p , the interchange energy of the solid phase contains the electron interaction parameter e_1 and the elastic distortion parameter e_2 . In liquids there are no elastic distortions, thus the only quantity that can be directly related to a solid–liquid transition is the parameter e_1 , which is negative (just as the parameter e_0 is). The electron interaction parameters e_0 and e_1 reflect the phenomenon of charge redistribution between unlike atoms and the Coulomb interaction of the atoms. The parameter e_1 can be calculated by the formula

$$e_{1} = -\frac{1}{C_{n}^{2}} \left[\sum_{i=1}^{n} x_{i} V_{i}(T) \right] \left\{ \sum_{i,k>1}^{k=n,i=n-1} \left| \frac{\Delta H_{i}}{V_{i}(T)} - \frac{\Delta H_{k}}{V_{k}(T)} \right| \right\}.$$
(44)

The parameter of elastic distortion of the crystal lattice, e_2 , characterizes the deformation of the lattice of the solid solution and the stresses generated in this solution by the difference in molar volumes and elasticity moduli of the components of the solid solution. The parameter e_2 usually introduces the largest positive contribution to the overall energy of the system and is, therefore, responsible for solidsolution decomposition. The parameter e_2 can be calculated by the formula

$$e_{2} = \frac{1}{3} \left[\sum_{i=1}^{n} x_{i} \frac{G_{i}(T)}{V_{i}(T)} \right] \left\{ \sum_{i=1}^{n} \left[V_{i}(T) \right]^{2} - n \left[\prod_{i=1}^{n} V_{i}(T) \right]^{2/n} \right\}.$$
(45)

In equations (42)–(45), x_i is the concentration of the *i*th component (in molar fractions); *n* is the number of components in the phase; $V_i(T) = V_i(300)[1 + 3\alpha_i(T - 300)]$ is the molar (or atomic for elements) volume of the *i*th component at the temperature *T*; the quantities $V_i(300)$ and α_i are the molar volume of the *i*th component at 300 K and the average linear thermal expansion coefficient of the *i*th component (for elements, the atomization energy coincides with the heat of evaporation); ΔH_i is the heat of melting of the *i*th component; and $G_i(T) = G_i(300)[1 - \beta_i(T - 300)]$ and $G_i(300)$ are shear moduli of the *i*th component at the temperatures *T* and 300 K, respectively, with β_i being the average temperature coefficient of the *i*th component.

The electron interaction parameters e_0 and e_1 are negative and describe the bonding part of the interchange energy, while the positive parameters e_p and e_2 describe the antibonding part of this energy. Depending on the ratio of the bonding and antibonding parameters, the interchange energy may be positive, zero (in the case of ideal solutions), or negative. In turn, the interchange energies that differ in sign and absolute value result in different types of phase diagrams, e.g., phase diagrams with complete mutual solubility of the components in the liquid and solid states, diagrams with phase-separation (solution-decomposition) regions in the liquid or solid states, and diagrams with a eutectic.

The conditions for the equilibrium of the phases j_1 and j_2 are described by an ordinary set of equations of the type

$$\frac{\partial \Delta G_{j_1}}{\partial x_i} = \frac{\partial \Delta G_{j_2}}{\partial x_i} \tag{46}$$

written for all components of these phases. Let us examine these conditions in relation to a two-component system.

In the subregular solution model, the free energy (41) for a two-component system becomes

$$\Delta G_j(x, T) = (1 - x_j) \Delta G_j(0, T) + x_j \Delta G_j(1, T) + RT [x_j \ln x_j + (1 - x_j) \ln(1 - x_j)] + \Delta G_i^e(x, T),$$
(47)

where x_j is the concentration of the second component in the *j*th phase, $\Delta G_j(0, T)$ and $\Delta G_j(1, T)$ are the free energies of the initial components of the system, and $\Delta G_j^e(x, T) = x_j(1 - x_j)B_j(x, T)$ is the excess mixing energy of the *j*th phase. In the particular case of equilibrium of the solid and liquid phases with the free energies (47), the equilibrium conditions (46) can be written, after performing certain transformations, in the form of equations for

calculating the positions of the liquidus and solidus lines:

$$\begin{aligned} RT \ln(1-x_{\rm l}) + x_{\rm l}^2 B_{\rm l}(x_{\rm l},T) - x_{\rm l}^2(1-x_{\rm l}) \frac{\partial B_{\rm l}(x_{\rm l},T)}{\partial x_{\rm l}} \\ &= RT \ln(1-x_{\rm s}) + x_{\rm s}^2 B_{\rm s}(x_{\rm s},T) \\ &- x_{\rm s}^2(1-x_{\rm s}) \frac{\partial B_{\rm s}(x_{\rm s},T)}{\partial x_{\rm s}} + \Delta H_1 \frac{T-T_1}{T_1} , \end{aligned}$$
$$\begin{aligned} RT \ln x_{\rm l} + (1-x_{\rm l})^2 B_{\rm l}(x_{\rm l},T) + x_{\rm l}(1-x_{\rm l})^2 \frac{\partial B_{\rm l}(x_{\rm l},T)}{\partial x_{\rm l}} \\ &= RT \ln x_{\rm s} + (1-x_{\rm s})^2 B_{\rm s}(x_{\rm s},T) \\ &+ x_{\rm s}(1-x_{\rm s})^2 \frac{\partial B_{\rm s}(x_{\rm s},T)}{\partial x_{\rm s}} + \Delta H_2 \frac{T-T_2}{T_2} , \end{aligned}$$
(48a)

where x_1 and x_s are the concentrations of the second component in the liquid and solid phases, respectively.

To describe the decomposition of solid solutions in the subregular approximation, it is assumed that in the diffusiondecomposition process the transition from one phase to the other is a second-order phase transition without a jump in entropy and that the phases that form as result of decomposition with concentrations x_1 and x_2 of the second component have equal interchange energies: $B_1(x_1, T) = B_2(x_2, T) = B_s(x, T)$. In this case the system of equations (48a) becomes

$$RT \ln(1 - x_1) + x_1^2 B_s - x_1^2 (1 - x_1) \frac{\partial B_s}{\partial x_1}$$

= $RT \ln(1 - x_2) + x_2^2 B_s - x_2^2 (1 - x_2) \frac{\partial B_s}{\partial x_2}$,
 $RT \ln x_1 + (1 - x_1)^2 B_s + x_1 (1 - x_1)^2 \frac{\partial B_s}{\partial x_1}$
= $RT \ln x_2 + (1 - x_2)^2 B_s + x_2 (1 - x_2)^2 \frac{\partial B_s}{\partial x_2}$. (48b)

The various features of the description of the decomposition of binary solid solutions in the subregular solution model have been studied in Refs [201, 202]. Let us examine a system with a concentration x of the second component in the solid phase. According to Refs [2, 190], in systems based on nonstoichiometric compounds the interchange energy is given by the formula $B(x_i) = B_0 + xB_1$. Adding this fact to the subregular solution model yields an expression for the excess free energy of mixing in the solid phase in the form $G^e = x(1-x)(B_0 + xB_1)$, with the result that the free energy of mixing in the solid phase, G(x), is given by the formula

$$G(x) = x(1-x)(B_0 + xB_1) + RT [x \ln x + (1-x)\ln(1-x)].$$
(49)

In a theoretical analysis of the dependence of the free energy of the solid phase on the values of the parameters B_0 and B_1 , it is more convenient to use (49) in the form

$$G^{*}(x) = x(1-x)(b_{0}+xb_{1}) + T_{r}[x \ln x + (1-x)\ln(1-x)], \qquad (50)$$

where $G^*(x) = G(x)/RT^*$, $b_0 = B_0/RT^*$, $b_1 = B_1/RT^*$, and $T_r = T/T^*$ are dimensionless quantities.

Figure 22 demonstrates how the concentration dependence of the free energy of mixing, $G^*(x)$, of the solid phase



Figure 22. Isotherms of the free energy of mixing, $G^*(x) = G(x)/RT^*$, of a binary system in the subregular solution model at fixed values of the parameters $b_0 = 1$ and $b_1 = 0.2$. The isotherms are built for the temperature $T_r = T/T^*$ varying from 0.3 to 0.8. For the sake of comparison, the solid curve depicts $G^*(x)$ calculated at $T_r = 0.4$ in the regular solution approximation ($b_1 \equiv 0$) [202].

changes with temperature at fixed values of the parameters b_0 and b_1 . At sufficiently high temperatures ($T_r > 0.6$) the freeenergy curve has one minimum, which corresponds to a single-phase state of the pseudobinary system, i.e., unlimited mutual solubility of the components. The fact that when $T_{\rm r} < 0.6$ the curve $G^*(x)$ acquires a second minimum means that in this temperature range the homogeneous solid solution decomposes into two phases of different compositions. As Fig. 22 shows, in the subregular solution model $(b_1 \neq 0)$ the curves $G^*(x)$ are asymmetric, while in the regular solution approximation $(b_1 \equiv 0)$ the curves $G^*(x)$ are symmetric with respect to x = 0.5. Note that the symmetry of the concentration curves for the free energy of mixing, $G^*(x)$, also determines the symmetry of the boundaries of the decomposition region in the phase diagram, which is far from the real situation and points to the limited applicability of the regular solution approximation.

The conditions for equilibrium of phases 1 and 2 into which the solid solution decomposes are given by two equations: $\partial G_1(x)/\partial x = 0$ and $\partial G_2(x)/\partial x = 0$. Allowing for the fact that $B(x_i) = B_0 + xB_1$ and subjecting these equations or equations (48) to standard transformations, we arrive at the following conditions for equilibrium:

$$RT \ln(1 - x_1) + x_1^2(B_0 + x_1B_1) - x_1^2(1 - x_1)B_1$$

= $RT \ln(1 - x_2) + x_2^2(B_0 + x_2B_1) - x_2^2(1 - x_2)B_1$,
$$RT \ln x_1 + (1 - x_1)^2(B_0 + x_1B_1) + x_1(1 - x_1)^2B_1$$

= $RT \ln x_2 + (1 - x_2)^2(B_0 + x_2B_1) + x_2(1 - x_2)^2B_1$,
(51)

where x_1 and x_2 are the concentrations of the second component in phases 1 and 2 into which the solid solution decomposes. By solving the set of equations (51) we can determine the position of the boundary of the decomposition region. The results of model calculations with different b_0 -to- b_1 ratios show that these boundaries are asymmetric, with the top of the dome shifted to the left or right depending on the value of the b_0 -to- b_1 ratio (Fig. 23): $x_{\text{max}} < 0.5$ if $b_0/b_1 < 0$, and $x_{\text{max}} > 0.5$ if $b_0/b_1 > 0$ (x_{max} is the composition of the solid solution corresponding to the top of the decomposition dome).



Figure 23. Position of the decomposition regions in the phase diagram of a binary system for $b_0 = 1$ and different values of the parameter b_1 . (•) shift of the position of the top of the dome caused by variations in b_0/b_1 from -1/3 to +1 (or within $-3 \le b_1 \le 1$ and $b_0 = 1$). For the sake of comparison, the boundaries of the decomposition region calculated in the regular solution approximation (∇) at $b_0 = 1$ and $b_1 \equiv 0$ (or at $b_0/b_1 \equiv 0$) are depicted [201, 202].

The conditions for critical miscibility reduce to the second and third composition derivatives of the free energy of mixing being equal to zero:

$$\frac{\partial G^2(x)}{\partial x^2} = 0, \qquad \frac{\partial G^3(x)}{\partial x^3} = 0, \qquad (52)$$

which yields the maximum temperature of decomposition of the solid solution, i.e., the immiscibility temperature T_{decomp}^{max} above which the components form unbounded solid solutions and below which an immiscibility region emerges. The same equations make it possible to determine the composition of the solid solution corresponding to the top of the decomposition dome, x_{max} . Solving the set of equations (52) combined with (49), we obtain

$$T_{\text{decomp}}^{\max} = 6B_1 x_{\max}^2 \frac{(1 - x_{\max})^2}{(2x_{\max} - 1)R},$$
(53)

$$x_{\max} = \frac{1}{9} \left\{ 4 - \frac{B_0}{B_1} \pm \left[7 + \frac{B_0}{B_1} + \left(\frac{B_0}{B_1} \right)^2 \right]^{1/2} \right\}.$$
 (54)

The physically meaningful solutions of equations (53) and (54) are those for which $T_{\text{decomp}}^{\text{max}} \ge 0$ and $1 \ge x_{\text{max}} \ge 0$.

Analysis of equations (53) and (54) suggests that

$$T_{\text{decomp}}^{\max} \ge 0 \text{ at}$$

$$\begin{cases}
0 \le x_{\text{max}} < 0.5, \quad B_1 < 0 \text{ and} \\
x_{\text{max}} = \frac{1}{9} \left\{ 4 - \frac{B_0}{B_1} - \left[7 + \frac{B_0}{B_1} + \left(\frac{B_0}{B_1}\right)^2\right]^{1/2} \right\}, \\
0.5 < x_{\text{max}} \le 1.0, \quad B_1 > 0 \text{ and} \\
x_{\text{max}} = \frac{1}{9} \left\{ 4 - \frac{B_0}{B_1} + \left[7 + \frac{B_0}{B_1} + \left(\frac{B_0}{B_1}\right)^2\right]^{1/2} \right\}.
\end{cases}$$
(55)

Analysis of equation (54) shows that the limiting values of x_{max} equal to 1 and 0 are attained at $B_0/B_1 = -2$ and $B_0/B_1 = 1$, respectively (note that $B_0/B_1 \equiv b_0/b_1$). The limiting values $x_{\text{max}} = 0$ (for $B_1 < 0$) and $x_{\text{max}} = 1$ (for $B_1 > 0$) correspond to $T_{\text{decomp}}^{\text{max}} \equiv 0$, i.e., the decomposition region degenerates. As $B_0/B_1 \rightarrow \pm \infty$, the value of x_{max} asymptotically tends to 0.5 (Fig. 24). Clearly, $B_0/B_1 \rightarrow \pm \infty$ if $B_1 = 0$ at the limit, which is equivalent to the regular solution approximation with $x_{\text{max}} \equiv 0.5$. Thus, the regular solution model with $B_1 = 0$.



Figure 24. Composition of the solid solution corresponding to the top of the decomposition dome, x_{max} , as a function of the parameter ratio $b_0/b_1 \equiv B_0/B_1$: the upper branch corresponds to b_1 positive ($b_1 > 0$) and the lower branch, to b_1 negative ($b_1 < 0$) [202].

The dependence of the maximum temperature of decomposition of the solid solution, $T_r^{max} = T_{decomp}^{max}/T^*$, on x_{max} is depicted in Fig. 25. Three regions are clearly visible in the diagram. The left region corresponds to $b_0 < 0$, $b_1 < 0$ and $b_0/b_1 > 0$ (the left branch in Fig. 25 corresponds to $b_0 = -1$, while b_1 varies from -7 to -1). In this case, the value of x_{max} varies from 0 to $(4 - \sqrt{7})/9 \approx 0.150$. The value $x_{max} = 0.150$ is asymptotically attained as $b_0/b_1 \rightarrow 0$, i.e., at $b_0 = 0$. The middle branch of the T_r^{max} vs. x_{max} dependence corresponds to $b_0 > 0$, while the parameter b_1 may be either positive or negative (in Fig. 25 this branch corresponds to $b_0 = 1$, while b_1 varies from -3 to +3). Analysis shows that at $b_0 = \text{const} > 0$ and all other things being equal the smallest value $T_{decomp}^{max} = -8B_1/9R \equiv 4B_0/9R$ is attained when $B_1 < 0$ and $B_0/B_1 \equiv b_0/b_1 = -2$, which corresponds to $x_{max} = 1/3$. For the middle branch, $(4 - \sqrt{7})/9 < x_{max} < (4 + \sqrt{7})/9$; the



Figure 25. Maximum temperature of decomposition of the solid solution, $T_r^{max} = T_{decomp}^{max}/T^*$, as a function of x_{max} : the left branch corresponds to $b_0 < 0$ and $b_1 < 0$, with $0 \le x_{max} < 0.150$; the middle branch corresponds to $b_0 > 0$ and the parameter b_1 assuming any positive or negative value, with $0.150 < x_{max} < 0.738$; and the right branch corresponds to $b_0 < 0$ and $b_1 > 0$, with $0.738 < x_{max} \le 1$ [201, 202].

limiting values of x_{max} , equal to 0.150 and $(4 + \sqrt{7})/9 \approx 0.738$, are asymptotically attained when $b_0 = 0$ and $b_1 < 0$ or when $b_0 = 0$ and $b_1 > 0$. Finally, the right branch of the T_r^{max} vs. x_{max} dependence corresponds to $b_0 < 0$ and $b_1 > 0$, i.e., $b_0/b_1 < 0$ (in Fig. 25 this branch corresponds to $b_0 = -1$, while b_1 varies from 4.5 to 0.5).

The elements or compounds forming one or another phase can have different crystal structures. This difference must be taken into account in calculations of all interaction parameters by reducing the volumes. To this end the crystal structure of one of the components participating in the phase equilibrium in question is chosen as the base structure, and the parameters of the unit cells of the other components are reduced to this structure. This reduction is done in such a way that the surface areas of the reduced and unreduced unit cells are the same and the angles and the axial ratios in the reduced cell are the same as in the unit cell of the base structure. Bearing all this in mind, we can calculate the lattice parameters and the unit cell volume $V_i^{\text{red.c}}$ of the reduced unit cell and the reduced molar volume $V_i^{\text{red}} = N_A V_i^{\text{red.c}}/z$, which is needed to calculate the energy parameters e_p , e_0 , e_1 , and e_2 (here z is the number of formula units in a unit cell). If a unit cell of the base structure has angles α , β , and γ , the axial ratios are such that a/c = m and b/c = n, and the surface area of the unreduced unit cell is S, we have

$$a_{\rm red} = \left(\frac{mnS}{\sin\alpha + m\sin\beta + n\sin\gamma}\right)^{1/2}$$
(56)

and

$$V_i^{\text{red}} = \frac{N_A a_{\text{red}}^3 \sin \alpha \sin \beta \sin \gamma}{mnz} \,. \tag{57}$$

Selection of the base crystal structure is arbitrary, since the reduction of the molar volumes of the components to any one crystal structure ensures the same ratio of the reduced volumes V_i^{red} , i.e.,

$$V_1: V_2^{\text{red}(1)}: \dots: V_n^{\text{red}(1)} = V_1^{\text{red}(2)}: V_2: \dots: V_n^{\text{red}(2)} = \dots$$
$$\dots = V_1^{\text{red}(i)}: V_2^{\text{red}(i)}: \dots: V_i: \dots: V_n^{\text{red}(i)}.$$

Clearly, the absolute values of the interaction energy parameters and the interchange energies do not depend on the choice of the specific crystal structure to which the molar volumes of the phase components are reduced. Indeed, from equations (42)-(45) it follows that a *k*-fold increase in the molar volume of one component leads to the same value of the energy parameter *e* as a *k*-fold decrease in the molar volume of the other component.

The above method was used in Refs [190-193, 203] to determine the interaction energy parameters and the interchange energies of 15 pseudobinary carbide systems formed by carbides of titanium, zirconium, hafnium, vanadium, niobium, and tantalum. The data on the lattice parameters, atomization energies, heats of melting, melting points, thermal expansion coefficients, and shear moduli of these compounds, needed for the calculations, are given in Refs [190, 202, 203]. Figures 26–28 depict the phase diagrams of the pseudobinary carbide systems calculated in Refs [190– 193, 201–203]. The monocarbides of titanium, zirconium, hafnium, vanadium, niobium, and tantalum have the same *B*1-type crystal structure, so that no reduction of volumes was carried out in calculations of the energy parameters.

The results of calculations of the phase diagrams corroborated the limited solid solubility in the VC_{0.88}–ZrC and VC_{0.88}–HfC systems and the formation of continuous series of solid solutions in the following systems: TiC–ZrC, TiC–HfC, TiC–NbC, TiC–TaC, ZrC–HfC, ZrC–NbC, ZrC–TaC, HfC–TaC, VC_{0.88}–TiC, VC_{0.88}–NbC, VC_{0.88}–TaC, NbC–HfC, and NbC–TaC. The calculated positions of the phase boundaries are in sufficient agreement with the experimental data of Kieffer et al. [204, 205] (see Fig. 26). The phase diagrams of 10 pseudobinary carbide systems (see Figs 27 and 28) were calculated in Refs [190 – 193, 203] for the first time; phase diagrams of these systems based on experimental data have yet to be built.

The shape of the calculated phase diagrams (see Fig. 26) agrees with the idea of a gradual transition from continuous solid solutions to systems with limited solubility in the solid state and a eutectic. The size factor strongly affects mutual solubility: the VC_{0.88} – TaC system is close to an ideal system due to the proximity of the atomic radii of the mutually substituting metals, while the VC_{0.88} – HfC system exhibits a very small limited solubility due to the large difference between the atomic radii of vanadium and hafnium.



Figure 26. Phase diagrams of the pseudobinary carbide systems TiC-HfC, TiC-ZrC, $VC_{0.88}-ZrC$, $VC_{0.88}-TaC$, $VC_{0.88}-NbC$, and $VC_{0.88}-HfC$ (the solid curves are the results of calculations in Refs [190, 193, 203], and the dashed curves are the results of calculations in Refs [204, 205]).



Figure 27. Phase diagrams of the pseudobinary carbide systems ZrC-TaC, ZrC-NbC, HfC-TaC, NbC-HfC, $VC_{0.88}-TiC$, and TiC-NbC (the results of calculations in Refs [190, 192, 193]).

Analysis of phase equilibria made it possible to establish the presence of latent decomposition regions in the solid state in TiC-ZrC, TiC-HfC, VC_{0.88}-NbC, and VC_{0.88}-TaC (see Fig. 26) and in ZrC–TaC, ZrC–NbC, HfC–TaC, VC_{0.88}–TiC, NbC–HfC, and TiC–NbC (see Fig. 27). The tops of the decomposition domes in these systems correspond to the



Figure 28. Phase diagrams of the pseudobinary carbide systems ZrC-HfC, NbC-TaC, and TiC-TaC with solubilities close to ideal (the results of calculations in Refs [190, 191, 193]).

following temperatures: 2281, 2075, 1773, 1581, 1212, 843, 1161, 488, 821, and 316 K. In 1979, Fedorov and Andrievskii [206] estimated the critical temperatures corresponding to the tops of latent decomposition regions in the solid state for some pseudobinary systems. To estimate T_{decomp} of solid solutions formed by stoichiometric carbides MC_{1.0}, the researchers used a relationship similar to that used in calculating the decomposition temperature of binary metallic alloys. According to Fedorov and Andrievskii [206], the temperatures T_{decomp} for the TiC-ZrC, TiC-HfC, TiC-NbC, ZrC-NbC, and NbC-TaC systems are 2530, 2150, 1140, 1260, and 760 K, respectively. The results on T_{decomp} cited in Refs [190-193] and in Ref. [206] are close (to within calculation errors) for the TiC-ZrC and TiC-HfC systems. The values of T_{decomp} given in Ref. [206] for the TiC-NbC, ZrC-NbC, and NbC-TaC systems are probably overstated. The reason for this may be the fact that Fedorov and Andrievskii [206] took into account only the difference in the heats of formation, while in Refs [190-193] the molar volumes and their variation with temperature and some other characteristics of the carbides were also taken into account.

The ZrC-HfC, NbC-TaC, and TiC-TaC systems exhibit no decomposition ranges and the solid solutions are stable from 300 K up to the melting points (see Fig. 28).

The results of experiments conducted by Umanskii and Myuller [207, 208] (see also Ref. [209]), who studied shortrange order in solid solutions of the TiC-NbC, TiC-TaC, and VC_{0.88}-NbC systems by X-ray diffuse scattering, agree with those of the calculations of the phase diagrams of these systems. According to [207, 208, 209], the $Ti_{0.5}Nb_{0.5}C$ and Ti_{0.5}Ta_{0.5}C solid solutions quenched from 2200 K have a negative short-range order parameter in the first coordination shell of the metal sublattice ($\alpha_1 = -0.06$), i.e., at this temperature the solid solutions do not tend to decompose. On the contrary, in the $V_{0.5}Nb_{0.5}C$ solid solution quenched from 2100 K, the parameter α_1 is positive ($\alpha_1 = 0.01$), which suggests that such solid solutions tend to decompose. Indeed, from the calculated phase diagram of $VC_{0.88}$ – NbC it follows that decomposition in this system begins at 1773 K (see Fig. 26).

In their experimental studies of phase equilibria in the ZrC-TaC and VC-NbC systems, Shurin et al. [210, 211] noted that the calculations done in Refs [191, 192, 203] in terms of the subregular solution model provide precise predictions of the shape of the phase diagrams of these carbide systems.

The calculations done in Ref. [191] revealed no maximum in the melting point of the solid solutions of the ZrC-TaCand HfC-TaC systems formed by carbides with almost stoichiometric composition. This agrees with the results of Andrievskiĭ et al. [196], who found that the melting point of these solid solutions is elevated because they are depleted of carbon, since carbon easily evaporates at high temperatures. In other words, a melting-point maximum is observed in solid solutions of nonstoichiometric carbides, whereas the solid solutions of stoichiometric carbides exhibit no such maxima.

The subregular solution model was used to calculate the phase boundaries not only in pseudobinary carbide systems but also in oxide-fluoride systems such as $MO-Na_3AlF_6$ ($MO = Al_2O_3$, BeO, SnO₂) [212] and in the ternary Ti-B-C system [198-200, 213].

The schematic calculated phase diagrams of the Ti-B-C system in the 300-3500 K temperature range and the liquidus surfaces for the pseudobinary equilibria TiC_v-TiB_2 and

 B_4C_y -TiB₂ of this system are depicted in Fig. 29 [198–200, 213]. The phase diagram of the binary system Ti-C was calculated, with allowance for ordering in nonstoichiometric titanium carbide TiC_y, by the OPF method, and the pseudobinary equilibria (including TiC_y – TiB₂ and B_4C_y – TiB₂) were calculated by the subregular solution model. In calculations of the equilibria with allowance for compounds with different crystal structures, reduced molar volumes were used (see Refs [198–200]).

The composition and temperature of the eutectic of the pseudobinary $\text{TiC}_y - \text{TiB}_2$ system depend on the carbon content in TiC_y . As the carbon content changes from $\text{TiC}_{0.6}$ to $\text{TiC}_{0.8}$, the eutectic temperature T_e increases from 2910 to 2961 K; a further increase in carbon content in TiC_y leads to a drop in T_e to 2936 K in the $\text{TiC}_{1.0} - \text{TiB}_2$ section (Fig. 30). The eutectic contains 40.1, 40.5, and 40.2 mol.% of TiB₂ for the



Figure 29. Spatial phase diagram of the ternary system Ti-B-C in the temperature range of 300-3500 K [198-200, 213]: (a) view of the liquidus surface in the region of pseudobinary $TiC_y - TiB_2$ equilibrium (Ti₂C, Ti₃C₂, and Ti₆C₅ are ordered phases of nonstoichiometric titanium carbide TiC); (b) view of the liquidus surface in the region of pseudobinary $B_4C_y - TiB_2$ equilibrium.



Figure 30. Vertical pseudobinary sections of the ternary system Ti-B-C [199, 200]: (a) $TiC_{0.6}-TiB_2$, (b) $TiC_{0.8}-TiB_2$, (c) $TiC_{1.0}-TiB_2$, and (d) $B_4C_{0.89}$ ($B_{4.5}C$) $-TiB_2$.

TiC_{0.6}-TiB₂, TiC_{0.8}-TiB₂, and TiC_{1.0}-TiB₂ sections, respectively. Note that it is only the carbide TiC_{0.6} that melts without changes in its composition (congruently); the titanium carbides with other carbon contents melt incongruently, i.e., with changes in their composition. The result of this is that in the TiC_{0.6}-TiB₂ section, the composition of the titanium carbide in equilibrium with the liquid changes, as the temperature increases, from TiC_{0.6} to TiC_{0.7} (Fig. 30a). In the TiC_{1.0}-TiB₂ section, the composition of the titanium carbide in equilibrium with the liquid changes, as the temperature increases from 2936 to 3287 K, from TiC_{1.0} to TiC_{0.905} (Fig. 30c).

The eutectic temperature of the pseudobinary system $B_4C_{0.89}$ ($B_{4.5}C$) – TiB₂ is 2545 K, and the eutectic contains 29.5 mol.% TiB₂ (Fig. 30d). When the carbon content in the boron carbide $B_4C_{0.89}$ increases or decreases, the eutectic temperature of the pseudobinary section B_4C_y – TiB₂ drops. The values of the calculated temperatures of the binary eutectics of the TiC_y – TiB₂ and B_4C_y – TiB₂ systems are in good agreement with Rudy's experimental data [94] and are 100–200 K higher than the value of T_e reported by Ordan'yan et al. [214] and Portnoĭ et al. [215].

According to Refs [198–200], the temperature of the ternary eutectic β -Ti + TiB + TiC_y is 1720 ± 20 K, which is close to the values of Rudy [94] (1783 K) and Duschanek et al. [216] (1808 K). The temperatures of the ternary eutectics TiB₂+TiC_{1.0}+C and TiB₂+B₄C_y+C are 2650 ± 50 K and 2380 ± 50 K, respectively. Finally, T_e of the ternary eutectic TiB₂+TiC_{1.0}+C is 2673 K according to Rudy [94] or 2667 K according to Duschanek et al [216], while T_e of the ternary eutectic TiB₂+B₄C_y+C is 2513 K [94] or 2519 K [216].

Introduction of even a small amount (less than 1 at.%) of boron into nonstoichiometric titanium carbide leads to the disordering of the carbide. Hence, the titanium borides TiB, Ti₃B₄, and TiB₂ are in equilibrium with the disordered carbide TiC_y. The titanium boride TiB₂ coexists not only with titanium carbide TiC_y but also with carbon C and the boron carbide B₄C. According to Refs [198, 200], the isothermal sections of the ternary system Ti-B-C retain an almost unaltered shape from 300 K up to 1900 K; the most important changes are related to the disordering of the low-temperature ordered phases Ti_2C , Ti_3C_2 , and Ti_6C_5 of the carbide TiC_y above 950 K.

The results of the calculations of phase equilibria in the ternary system Ti - B - C (see Refs [198 – 200]) are in good agreement with the experimental data of Duschanek et al. [216], Schouler M et al. [217], and Villars et al. [218] and corroborate the usefulness of the subregular solution model in calculating and building phase diagrams of binary, pseudobinary, and ternary systems containing both stoichiometric and nonstoichiometric compounds.

7. Conclusions

The calculation of the phase diagrams of the binary systems M-C (M = Ti, Zr, Hf, V, Nb, and Ta) and Ti-N [26, 40, 43–47, 76] with highly nonstoichiometric ordering compounds is the main result of employing the OPF method. Indeed, until recently the literature contained no equilibrium phase diagrams for these systems within a broad temperature range from 300 K to the melting point. Bearing this in mind, we focused in this review on the results of theoretical and experimental studies of phase equilibria, since the data on short- and long-range order in nonstoichiometric compounds and on the structure and properties of the ordered phases of these compounds have already been generalized in many reviews (see Refs [28, 29, 31, 33, 36]) and monographs (see Refs [1, 2, 14, 17]).

The results suggest that the OPF method can be used in calculating the phase diagrams in model and real systems with atomic ordering. Theoretical analysis has shown that, from the viewpoint of thermodynamics, in nonstoichiometric carbides and nitrides MX_{ν} with a *B*1-type base structures, M₂X, M₃X₂, and M₆X₅-type superstructures can form; which superstructure actually forms in the ordering of a specific nonstoichiometric compound depends on the width of the homogeneity region of the compound MX_{ν} and on which phases this compound is in equilibrium with. M₄X₃ and M₈X₇-type superstructures cannot form in nonstoichiometric cubic carbides and nitrides MX_{y} , with the exception of the carbide VC_{ν} , in which the ordered phase V_8C_7 forms because of a boundary effect: in disordered vanadium carbide the upper boundary of the homogeneity range corresponds to the carbide MC_v with y = 0.88 instead of y = 1.00 (as is the case in other nonstoichiometric interstitial compounds MX_{ν}). Recently, the formation of the V₈C₇ phase was used to obtain vanadium carbide in the nanocrystalline state [219]. Grain refinement in vanadium carbide took place due to the sudden increase in the unit cell volume in the $VC_{y} - V_{8}C_{7}$ disorder – order transition.

The lowest temperatures of transition to an ordered state belong to the nonstoichiometric carbides of hafnium, titanium, and zirconium, HfC_y, TiC_y, and ZrC_y. This means that producing M^(IV)C_y carbides of Group IV transition metals is more difficult than producing carbides of vanadium, niobium, and tantalum since, with the same carbon content, the annealing temperatures sufficient for ordering the M^(IV)C_y carbides are 300–700 K lower than those required for ordering of M^(V)C_y carbides. As a result, the diffusion mobility of carbon atoms in the M^(IV)C_y carbides is much lower than in the M^(V)C_y carbides. An important factor that affects the diffusion mobility of interstitial atoms is the atomic mass of the metal atoms, since an increase in the atomic mass of the metal leads to a decrease in the diffusion rate of the nonmetal atoms. If the transition temperature and the atomic mass of the metal are taken into account simultaneously, there are grounds to believe that among the nonstoichiometric carbides the most complicated for ordering is hafnium carbide HfC_{ν} , since the time of annealing this carbide at temperatures no higher than 750 K is several thousand hours. More than that, as noted in Section 5.2, it is extremely difficult to determine through measurements whether hafnium carbide is ordered. It is also very difficult to achieve ordering in the carbides of tantalum and zirconium, TaC_{ν} and ZrC_{ν} .

On the whole, the predominantly correct values that were calculated for the main thermodynamic characteristics of order-disorder and order-order phase transitions in the nonstoichiometric compounds considered in this review confirm the correctness of the main ideas of the OPF method and the approximations used in the method. The results of the theoretical analysis and the calculations suggest that this method can be used to describe both qualitatively and quantitatively the ordering process in solid substitutional and interstitial solutions and in nonstoichiometric compounds.

A remark is in order. The variant of the OPF method used in Refs [2, 14, 26, 44] ensures that only the long-range parameters and the correlations caused by these parameters (or superstructural short-range order [114, 115]) are taken into account simultaneously. However, in addition to correlations caused by long-range order, ordered phases contain short-range correlations, which do not disappear at the order-disorder transition temperature but prevail in the disordered phase within a temperature range above $T_{\rm trans}$, gradually decreasing as the temperature grows. This implies that the position of the phase boundaries in the calculated phase diagrams can be determined more accurately if one fully accounts for the short-range order of the ordered and disordered phases. Thus, further improvements of the OPF method are possible if we fully take into account short-range order effects.

The results of calculations of the phase diagrams of pseudobinary carbide systems in the subregular solution model agree with experimental data and justify the use of this model in calculating the phase diagrams of other pseudobinary systems with total or partial substitution of the atoms.

Financial support for this work was provided by the Russian Foundation for Basic Research (project no. 98-03-32856a).

References

- 1. Gusev A I, Rempel' A A Termodinamika Strukturnykh Vakansii v Nestekhiometrichestikh Fazakh Vnedreniya (Thermodynamics of Structural Vacancies in Nonstoichiometric Interstitial Phases) (Sverdlovsk: Ural. Nauchn. Tsentr, Akad. Nauk SSSR, 1987)
- Gusev A I Fizicheskaya Khimiya Nestekhiometricheskikh Tugoplavkikh Soedinenii (Physical Chemistry of Nonstoichiometric Compounds) (Moscow: Nauka, 1991)
- 3. Andrievskii R A, Gurov K P Fiz. Met. Metalloved. 26 818 (1968)
- Korobeĭnikova A V, Fadeeva V I, Reznitskiĭ L A Zh. Strukt. Khim. 4. 17 860 (1976)
- 5. Gusev A I et al. Izv. Akad. Nauk. SSSR, Neorg. Mater. 13 1910 (1977)
- Gusev A I Zh. Fiz. Khim. 53 1379 (1979) 6
- Gusev A I Teplofiz. Vys. Temp. 17 1232 (1979) 7.

- Gillot B, Bouton F J. Solid State Chem. 32 (3) 303 (1980) 8.
- 9 Gusev A I Zh. Fiz. Khim. 57 1382 (1983)
- 10. Gubanov V A et al. J. Phys. Chem. Solids 45 719 (1984)
- Gusev A I Phys. Status Solidi A 85 (1) 159 (1984) 11
- 12. Gusev A I et al. Usp. Khim. 55 2067 (1986) [Russ. Chem. Reviews 55 1175 (1986)]
- 13. Novikov D L, Ivanovsky A L, Gubanov V A Philos. Mag. B 63 1409 (1991)
- 14. Gusev A I, Rempel' A A Strukturnye Fazovye Perekhody v Nestekhiometrticheskikh Soedineniyakh (Structural Phase Transitions in Nonstoichiometric Compounds) (Moscow: Nauka, 1988)
- 15. Ivanchenko B I et al. Metallofizika 12 (1) 14 (1990)
- 16. Tsurekawa S, Yoshinaga H J. Jpn. Inst. Met. 56 (2) 133 (1992)
- Rempel' A A Effekty Uporyadocheniya v Nestekhiometricheskikh 17. Soedineniyakh Vnedreniya (Ordering Effects in Nonstoichiometric Interstitial Compounds) (Ekaterinburg: Nauka, 1992)
- 18. Puska M J et al. Phys. Rev. B 49 10947 (1994)
- Brauer G et al. J. Phys.: Condens. Matter 7 9091 (1995) 19
- 20. Il'yasov V V, Nikiforov I Ya Fiz. Tverd. Tela (St. Petersburg) 39 1064 (1997) [Phys. Solid State 39 955 (1997)]
- Ogawa T et al. J. Alloys and Compounds 271-273 347 (1998) 21
- 22. Andersson S et al. Acta Chem. Scand. 11 1641 (1957)
- 23 Westman S, Nordmark C Acta Chem. Scand. 14 (6) 465 (1960)
- 24. Anderson J S, in Problems of Nonstoichiometry (Ed. A Rabenau) (Amsterdam: North-Holland, 1970) p. 11
- 25. Problems of Nonstoichiometry (Ed. A Rabenau) (Amsterdam: North-Holland, 1970)
- 26. Gusev A I, Rempel A A Phys. Status Solidi A 163 (2) 273 (1997)
- 27. Gusev A I, Rempel A A, in Materials Science of Carbides, Nitrides and Borides (Eds Y G Gogotsi, R A Andrievski) (Dordrecht: Kluwer Acad. Publ., 1999) p. 47
- Gusev A I Phys. Status Solidi B 156 11 (1989); 163 17 (1991) 28.
- Gusev A I, Rempel A A Phys. Status Solidi A 135 15 (1993) 29.
- 30. Gusev A I Usp. Khim. 65 (5) 407 (1996)
- 31. De Novion C H, Landesman J P Pure and Appl. Chem. 57 (10) 1391 (1985)
- Gusev A I, Rempel A A J. Phys. C 20 5011 (1987) 32
- 33. Rempel' A A Usp. Fiz. Nauk 166 33 (1996) [Phys. Usp. 39 31 (1996)]
- 34 Goretzki H Phys. Status Solidi 20 K141 (1967)
- Karimov I et al. Izv. Akad. Nauk. Uzb. SSR, Ser. Fiz.-Mat. Nauk (4) 35. 81 (1979)
- 36. De Novion C H et al., in The Physics and Chemistry of Carbides, Nitrides and Borides (Ed. R Freer) (Dordrecht: Kluwer Acad. Publ., 1990) p. 329
- 37. Lorenzelli N et al. Solid State Commun. 59 765 (1986)
- Moisy-Maurice V Structure Atomique des Carbures Non-Stoechio-38 metriques de Metaux de Transition (Rapport CEA-R-5127) (Gif-sur-Yvette (France): Commissariat a l'Energie Atomique, 1981)
- 39. Lipatnikov V N, Zueva L V, Gusev A I, Kottar A Fiz. Tverd. Tela (St. Petersburg) 40 1322 (1998) [Phys. Solid State 40 1211 (1998)]
- 40. Gusev A I, Rempel' A A Dokl. Ross. Akad. Nauk 332 717 (1993)
- 41. Khaenko B V Izv. Akad. Nauk SSSR, Neorg. Mater. 15 1952 (1979)
- 42 Obata N, Nakasawa N J. Nucl. Mater. 60 (1) 39 (1976)
- Gusev A I Dokl. Akad. Nauk SSSR 313 887 (1990) [Sov. Phys. Dokl. 43. 35 615 (1990)]
- 44. Gusev A I Fiz. Tverd. Tela (Leningrad) 32 2752 (1990) [Sov. Phys. Solid State 32 1595 (1990)]
- 45. Gusev A I, Rempel' A A Zh. Fiz. Khim. 65 625 (1991) [Russ. J. Phys. Chem. 65 330 (1991)]
- Gusev A I, Rempel A A J. Phys. Chem. Solids 55 (3) 299 (1994) 46.
- Gusev A I Dokl. Akad. Nauk SSSR 322 918 (1992) [Sov. Phys. Dokl. 47. 37 84 (1992)]
- 48. Zyryanova A N, Nazarova S Z, Gusev A I Dokl. Ross. Akad. Nauk 359 (3) 348 (1998) [Dokl. Phys. Chem. 359 91 (1998)]
- 49. Khaenko B V Poroshk. Metall. (1) 71 (1978) [Sov. Powder Metall. Met. Ceram. 17 55 (1978)]
- Venables J D, Kahn D, Lye R G Philos. Mag. 18 177 (1968) 50.
- 51. Lipatnikov B N et al. J. Alloys and Compounds 261 192 (1997)
- Lipatnikov B N et al. J. Phys.: Condens. Matter 11 163 (1999) 52.
- Lipatnikov V N, Gusev A I, Ettmeier P, Lengauer W Fiz. Tverd. 53.
- Tela (St. Petersburg) 41 529 (1999) [Phys. Solid State 41 474 (1999)] 54. Billingham J, Bell P S, Lewis M H Acta Crystallogr. A 28 602 (1972)
- 55 Billingham J, Bell P S, Lewis M H Philos. Mag. 25 661 (1972)

56. De Novion C H, Lorenzell N, Costa P C. R. Acad. Sci. (Ser.) B 263 775 (1966)

- 57. Alyamovskii S I et al. Zh. Neorg. Khim. 13 895 (1968)
- 58. Arbuzov M P et al. Ukr. Fiz. Zh. (Russ. Ed.) 22 (2) 291 (1977)
- Athanassiadis T, Lorenzelli N, de Novion C H *Ann. Chim.* (France) 12 (2) 129 (1987)
- 60. Rafaja D et al. J. Alloys and Compounds 269 60 (1998)
- 61. Rudy E, Brukl C E J. Am. Ceram. Soc. 50 (5) 265 (1967)
- Lewis M H, Billingham J, Bell P S, in *Solid State Chemistry: Proc. of* 5th Intern. Mater. Res. Symp. (NBS Special Publ. 364) (Berkeley, Calif.: NBS Publ., 1972) p. 1084
- 63. Landesman J P et al. J. Phys. C 18 809 (1985)
- 64. Christensen A N Acta Chem. Scand. A 39 803 (1985)
- Rempel' A A, Gusev A I Uporyadochenie v Nestekhiometricheskom Monokarbide Niobiya (Ordering in Nonstoichiometric Niobium Monocarbide) (Sverdlovsk: Ural'skiĭ Nauchn. Tsentr AN SSSR, 1983)
- Rempel' A A, Gusev A I, Zubkov V G, Shveikin G P Dokl. Akad. Nauk SSSR 275 883 (1984) [Sov. Phys. Dokl. 29 257 (1984)]
- Gusev A I, Rempel' A A Fiz. Tverd. Tela (Leningrad) 26 3622 (1984) [Sov. Phys. Solid State 26 2178 (1984)]
- Rempel' A A, Gusev A I Kristallografiya **30** 1112 (1985) [Sov. Phys. Crystallogr. **30** 648 (1985)]
- 69. Gusev A I, Rempel A A Phys. Status Solidi A 93 71 (1986)
- Khaenko B V, Sivak O P Kristallografiya 35 1110 (1990) [Sov. Phys. Crystallogr. 35 653 (1990)]
- 71. Bowman A L et al. Acta Crystallogr. 19 (1) 6 (1965)
- Lipatnikov V N, Rempel' A A, Gusev A I Zh. Neorg. Khim. 33 1860 (1988) [Russ. J. Inorganic Chem. 33 1058 (1988)]
- Gusev A I, Rempel A A, Lipatnikov V N Phys. Status Solidi A 106 459 (1988)
- Rempel' A A, Lipatnikov V N, Gusev A I Dokl. Akad. Nauk SSSR 310 878 (1990) [Sov. Phys. Dokl. 35 103 (1990)]
- Gusev A I, Rempel' A A, Lipatnikov V N Fiz. Tverd. Tela (Leningrad) 33 2298 (1991) [Sov. Phys. Solid State 33 1295 (1991)]
- Gusev A I, Rempel A A, Lipatnikov V N J. Phys.: Condens. Matter 8 8277 (1996)
- 77. Holmberg B Acta Chem. Scand. 16 1245 (1962)
- 78. Lobier C, Marcon J P C. R. Acad. Sci. Ser. C 268 1132 (1969)
- 79. Nagakura S, Kusunoki T J. Appl. Crystallogr. 10 (1) 52 (1977)
- Arbuzov M P, Golub S Ya, Khaenko B V Izv. Akad. Nauk SSSR, Neorg. Mater. 13 1779 (1977)
- Christensen A N, Alamo A, Landesman J P Acta Crystallogr. C 41 1009 (1985)
- Khidirov I, Karimov I, Em V T Dokl. Akad. Nauk Uzb. SSR (1) 21 (1980)
- 83. Sundararaman D et al. Trans. Jpn. Inst. Met. 24 (7) 510 (1983)
- 84. Lengauer W, Ettmayer P High Temp. High Pressure 19 (6) 673 (1987); 22 (1) 13 (1990)
- 85. Etchessahar E et al. J. Less-Common Met. 167 (2) 261 (1991)
- 86. Priem T et al. J. Phys. (Paris) **50** 2217 (1989)
- 87. Onozuka T Trans. Jpn. Inst. Met. 23 (6) 315 (1982)
- 88. Terao N Jpn. J. Appl. Phys. 4 (5) 353 (1965)
- Chervyakov A Yu, Somenkov V A, Umanskii Ya S Izv. Vyssh. Uchebn. Zaved., Ser. Tsvetn. Metall. No. 5 140 (1971)
- Murray J L, in *Phase Diagrams of Binary Titanium Alloys* (Ed. J L Murray) (Metals Park, Ohio, USA: ASM Int. Publ., 1987)
- Andrievskii R A, Spivak I I Prochnost' Tugoplavkikh Soedinenii i Materialov na Ikh Osnove (Strength of Refractory Compounds and of Materials Based on Them) (Chelyabinsk: Metallurgiya, 1989)
- Binary Alloys Phase Diagrams (Eds T B Massalski, H Okamoto, P R Subrmanian, L Kacprzak) (Metals Park, Ohio, USA: ASM Int. Publ., 1990)
- Storms E K The Refractory Carbides (New York: Academic Press, 1967)
- Rudy E Compendium of Phase Diagram Data. Final Tech. Report AFML TR-65-2 Part V (Wright-Patterson Air Force Base) (Metals Park, Ohio, USA: Metals and Ceramics Division, Air Force Materials Laboratory, 1969)
- 95. Toth L E *Transition Metal Carbides and Nitrides* (New York: Academic Press, 1971)
- Carlson O N, Ghaneya A N, Smith J F Bull. Alloy Phase Diagrams 6 (1) 115 (1985)

- 97. Krivoglaz M A, Smirnov A A The Theory of Order-Disorder in Alloys (Amsterdam: Elsevier, 1965)
- Khachaturian A G Theory of Structural Transformations in Solids (New York: Wiley, 1983)
- 99. Kikuchi R Phys. Rev. 81 988 (1951)
- 100. Kurata M, Kikuchi R, Watari T J. Chem. Phys. 21 434 (1953)
- 101. Kikuchi R, Brush S G J. Chem. Phys. 47 195 (1967)
- 102. Hijmans J, de Boer J Physica 21 (6) 471 (1955)
- 103. Vaks V G, Zinenko V I, Schneider V E Usp. Fiz. Nauk 141 629 (1983) [Sov. Phys. Usp. 26 1059 (1983)]
- 104. Golosov V S Izv Vyssh. Uchebn. Zaved., Ser. Fiz. (8) 64 (1976)
- Fowler R H, Guggenheim E A Statistical Thermodynamics (Cambridge: University Press, 1939)
- 106. Bethe H A Proc. R. Soc. London Ser. A 150 552 (1935)
- Gusev A I, Rempel A A Phys. Status Solidi B 131 43 (1985); 140 335 (1987)
- 108. Gusev A I Philos. Mag. B 60 307 (1989)
- 109. Gusev A I, Rempel' A A Zh. Fiz. Khim. 60 1349 (1986)
- 110. Rempel' A A, Gusev A I Zh. Fiz. Khim. 60 1353 (1986)
- 111. Sobol' I M A Primer for the Monte Carlo Method (Boca Raton: CRC Press, 1994)
- 112. Gusev A I, Rempel' A A, Lipatnikov V N Zh. Fiz. Khim. 61 916 (1987)
- 113. Gusev A I Dokl. Akad. Nauk SSSR 311 631 (1990)
- 114. Rempel' A A, Gusev A I Fiz. Tverd. Tela (Leningrad) 32 16 (1990) [Sov. Phys. Solid State 32 8 (1990)]
- 115. Rempel A A, Gusev A I Phys. Status Solidi B 160 389 (1990)
- Bolgar A S, Turchanin A G, Fesenko V V Termodinamicheskie Svoistva Karbidov (Thermodynamic Properties of Carbides) (Kiev: Naukova Dumka, 1973)
- Bolgar A S, Litvinenko V F *Termodinamicheskie Svoĭstva Nitridov* (Thermodynamic Properties of Nitrides) (Kiev: Naukova Dumka, 1980)
- 118. Kornilov A N et al. J. Chem. Thermodyn. 9 629 (1977)
- 119. Nazarova S Z, Gusev A I Stekhiometricheskie Tverdye Rastvory Karbidov Niobiya i Tantala i Ikh Svoĭstva (Stoichiometric Solid Solutions of Niobium and Tantalum Carbides and Their Properties) (Sverdlovsk: Ural. Nauchn. Tsentr, Akad. Nauk SSSR, 1987)
- 120. Barin I Thermochemical Data of Pure Substances Third ed. (Weinheim: VCH, 1995)
- 121. Volkova N M, Gel'd P V, in *Khimiya Soedinenii Redkikh Tugoplav-kikh Elementov* (Chemistry of Compounds of Rare Refractory Elements) (Proc. of the Institute of Chemistry of the Ural Branch of the USSR Academy of Sciences, No. 14 pp. 51–46) (Sverdlovsk: Ural Branch of the USSR Academy of Sciences, 1967)
- 122. Turchanin A G et al. Izv. Akad. Nauk SSSR, Neorg. Mater. 10 1619 (1974)
- 123. Wicks C E, Block F E Thermodynamic Properties of 65 Elements, Their Oxides, Halides, Carbides and Nitrides (US Bureau of Mines, Bulletin 605) (Washington: US Government Printing Office, 1963)
- Voĭtovich R F *Tugoplavkie Soedineniya: Termodinamicheskie Kharakteristiki* (Thermodynamic Characteristics of Refractory Compounds) (Kiev: Naukova Dumka, 1971)
- Termodinamicheskie Svoĭstva Individualnykh Veshchestv (Thermodynamic Properties of Individual Substances) (Moscow: Nauka, 1979, Vol. II, Pt. 2; 1982, Vol. IV, Pt. 2)
- 126. Wriedt H A, Murray J L Bull. Alloy Phase Diagrams 8 (4) 378 (1987)
- 127. Othani H, Hillert M CALPHAD 14 (3) 289 (1990)
- 128. Enomoto M J. Phase Equilibria 17 (2) 237 (1996)
- Jonsson S *PhD Thesis* (Stockholm (Sweden): Royal Institute of Technology, 1992)
- 130. Arbuzov M P et al. Ukr. Fiz. Zh. (Russ. Edn) 19 497 (1974)
- 131. Em V T et al. Kristallografiya 20 320 (1975) [Sov. Phys. Crystallogr. 20 198 (1975)]
- Remeev A Sh, Karimov I A Izv. Akad. Nauk Uzb. SSR, Ser. Fiz.– Mat. Nauk (2) 87 (1986)
- Khaenko B V, Kukol V V Kristallografiya 34 1513 (1989) [Sov. Phys. Crystallogr. 34 965 (1989)]
- 134. Khaenko B V et al. Poroshk. Metall. (6) 63 (1990)
- 135. Moisy-Maurice V et al. Acta Metall. 30 1769 (1982)
- Lipatnikov V N, Rempel A A, Gusev A I Intern. J. Refract. Metals and Hard Mater. 15 (1-3) 61 (1997)
- 137. Moisy-Maurice V et al. Solid State Commun. 39 661 (1981)

- 138. Priem T Etude de L'ordre a Courte Distance Dans les Carbures et Nitrures Nonstoechio-Metriques de Metaux de Transition par Diffusion Diffuse de Neutrons (Rapport CEA-R-5499) (Gif-sur-Yvette (France): Commissariat a l'Energie Atomique, 1989)
- 139. Landesman J P et al. J. Phys. (Paris) 46 1001 (1985)
- 140. Priem T et al. Physica B 156/157 47 (1989)
- 141. Clapp P C, Moss S C Phys. Rev. 142 418 (1966)
- 142. Fletcher R, Powell M J D Comput. J. 6 (2) 163 (1963)
- 143. Livet F Acta Metall. 35 2915 (1987)
- 144. Kikuchi R J. Phys. Colloq. 38 C7-307 (1977)
- 145. Finel A "Contribution a l'etude des effets d'ordre dans le cadre do modele d'Ising: etats de base et diagrammes de phase", PhD Thesis (Paris (France): Universite Pierre et Marie Curie, 1987)
- Dzhalabadze N V, Eristavi B G, Maĭsuradze N I, Kuteliya E R Fiz. Met. Metalloved. 86 (1) 85 (1998) [Phys. Met. Metallogr. 86 (1) 59 (1998)
- 147. Emel'yanov A N Fiz. Tverd. Tela (St. Petersburg) 38 3678 (1996) [Phys. Solid State 38 2003 (1996)]
- Lipatnikov V N, Gusev A I Pis'ma Zh. Eksp. Teor. Fiz. 69 631 (1999) [JETP Lett. 69 669 (1999)]
- 149. Emel'yanov A N Teplofiz. Vys. Temp. 28 269 (1990)
- Karpov A V, Kobyakov V P Izv. Ross. Acad. Nauk, Neorg. Mater. 31 655 (1995)
- 151. Karpov A V, Kobyakov V P Teplofiz. Vys. Temp. 34 965 (1996)
- 152. Guo B C, Kerns K P, Castleman A W Science 255 1411 (1992)
- Eletskii A V, Smirnov B M Usp. Fiz. Nauk 165 977 (1995) [Phys. Usp. 38 935 (1995)]
- 154. Guo B C et al. Science 256 515 (1992)
- 155. Wei S et al. J. Phys. Chem. 96 4166 (1992)
- 156. Pilgrim J S, Duncan M A J. Am. Chem. Soc. 115 6958 (1993)
- 157. Wei S et al. J. Am. Chem. Soc. 116 4475 (1994)
- 158. Guo B C, Castleman A W Adv. Met. Semicond. Clusters 2 137 (1994)
- 159. Lorenzelli R, de Dieuleveult I J. Nucl. Mater. 29 349 (1969)
- 160. Gusev A I Phys. Status Solidi A 111 443 (1989)
- Zyryanova A N, Gusev A I Zh. Fiz. Khim. 72 2234 (1998) [Russ. J. Phys. Chem. 72 2034 (1998)]
- 162. Gusev A I, Zyryanova A N Pis'ma Zh. Eksp. Teor. Fiz. 69 296 (1999) [JETP Lett. 69 324 (1999)]
- 163. Huang W Z. Metallkd. 82 174 (1991)
- 164. Gusev A I Dokl. Ross. Akad. Nauk 365 644 (1999) [Dokl. Phys. Chem. 365 107 (1999)]
- 165. Gusev A I Zh. Fiz. Khim. 74 595 (2000)
- Volkova N M, Gel'd P V, Alyamovskiĭ S I Zh. Neorg. Khim. 10 1758 (1965)
- 167. Emmons G H, Williams W S J. Mater. Sci. 18 2589 (1983)
- 168. Shacklette L W, Williams W S Phys. Rev. B 7 5041 (1973)
- 169. Hiraga K Philos. Mag. 27 1301 (1973)
- 170. Wiesenberger H, Lengauer W, Ettmayer P Acta Mater. 46 651 (1998)
- 171. Yvon K, Rieger W, Nowotny H Monatsh. Chem. 97 689 (1966)
- Smith J F, in *Phase Diagrams of Binary Vanadium Alloys* (Ed. J F Smith) (Metals Park, Ohio, USA: ASM Intern. Publ., 1989) p. 33
- Lipatnikov V N, Gusev A I, in Abstr. 5th All-Union Conference on Chemistry, Technology, and Applications of Vanadium Compounds (Chusovoĭ, 1987) Pt. 1 (Sverdlovsk: Ural. Nauchn. Tsentr, Akad. Nauk SSSR, 1987) p. 166
- 174. Smith J F, Carlson O N, de Avillez R R J. Nucl. Mater. 148 (1) 1 (1987)
- 175. Storms E K, Calken B, Yencha A *High-Temp. Sci.* **1** (4) 430 (1969)
- Venables J D, Meyerhoff M H, in *Solid State Chemistry: Proc. of 5th* Intern. Mater. Res. Symp. (NBS Special Publ. 364) (Berkeley, Calif.: NBS Publ., 1972) p. 583
- 177. Dy L C, Williams W S J. Appl. Phys. 53 8915 (1982)
- Landesman J P Etude de la Stabilite de Phases Ordonnees dans les Carbures et Nitrures Sous-Stoechiometriques de Metaux de Transition (Rapport CEA-R-5342) (Gif-sur-Yvette (France): Commissariat a l'Energie Atomique, 1986)
- 179. Gusev A I, Rempel A A Phys. Status Solidi A 84 527 (1984)
- 180. Yvon K, Pathe E Acta Crystallogr. B 26 149 (1970)
- 181. Gusev A I, Rempel' A A, Lipatnikov V N Zh. Fiz. Khim. 64 2343 (1990) [Russ. J. Phys. Chem. 64 1265 (1990)]
- Gusev A I, Rempel A A, Lipatnikov V N Phys. Status Solidi B 194 467 (1996)

- Lipatnikov V N, Rempel A A, Gusev A I, in Collected Abstr. of Intern. Conf. "Advanced Methods in X-ray and Neutron Structure Analysis of Materials" (Praha (Czechoslovakia), 1990) p. 95
- 184. Lengauer W, Ettmayer P Rev. Chim. Miner. 24 707 (1987)
- 185. Lengauer W, Ettmayer P Mater. Sci. Eng., A 105/106 257 (1988)
- 186. Lengauer W J. Solid State Chem. 91 (2) 279 (1991)
- 187. Lengauer W Acta Metall. Mater. **39** 2985 (1991)
- 188. Lengauer W, Ettmayer P J. Phase Equilibria 14 (1) 162 (1993)
- Alamo A, de Novion C H, in 7th Intern. Conf. Solid Compounds of Transition Elements (Grenoble (France), 1982) Paper II A1
- 190. Gusev A I Izv. Akad. Nauk SSSR, Neorg. Mater. 20 1132 (1984)
- 191. Gusev A I Zh. Neorg. Khim. 59 579 (1985)
- 192. Gusev A I Raschety i Eksperimental'nye Metody Postroeniya Diagramm Sostoyaniya (Calculations and Experimental Methods Used in Constructing Phase Diagrams) (Moscow: Nauka, 1985) p. 42
- Gusev A I, in VIII Intern. Pulvermet. Tagung Bd. 3 (Dresden (GDR): Zentralinstitut Festkörperphysik und Werkstofforschung, 1985) Vortrage. S. 169
- Kaufman L, Bernstein H Computer Calculation of Phase Diagrams (New York: Academic Press, 1970)
- 195. Ormont B F Dokl. Akad. Nauk SSSR 106 687 (1956)
- Andrievskii R A, Lanin A G, Rymashevskii G A Prochnost' Tugoplavkikh Soedinenii (Strength of Refractory Compounds) (Moscow: Metallurgiya, 1974)
- Gusev A I, Zyryanova A N Dokl. Ross. Akad. Nauk 354 493 (1997);
 Zh. Fiz. Khim. 72 793 (1998) [J. Phys. Chem. 72 692 (1998)]
- 198. Gusev A I Dokl. Ross. Akad. Nauk 350 209 (1996)
- 199. Gusev A I Zh. Fiz. Khim. 71 1177 (1997) [J. Phys. Chem. 71 1049 (1997)]
- 200. Gusev A I J. Solid State Chem. 133 (1) 205 (1997)
- 201. Rempel' S V, Gusev A I Dokl. Ross. Akad. Nauk 367 (1) 85 (1999) [Dokl. Phys. Chem. 367 187 (1999)]
- 202. Rempel' S V, Rempel' A A, Gusev A I Zh. Fiz. Khim. 74 482 (2000) [J. Phys. Chem. 74 341 (2000)]
- 203. Rempel' A A, Gusev A I, Shveikin G P Zh. Fiz. Khim. 58 2163 (1984)
- 204. Kieffer R J. Inst. Metals 97 (6) 164 (1969)
- 205. Kieffer R et al. Monatsh. Chem. 99 1020 (1968)
- Fedorov E M, Andrievskiĭ R A Izv. Akad. Nauk SSSR, Neorg. Mater. 15 454 (1979)
- 207. Umanskiĭ Ya S, Myuller A S Izv. Vyssh. Uchebn. Zaved., Ser. Chern. Metallurgiya (7) 130 (1969)
- Umanskiĭ Ya S, Myuller A S Izv. Vyssh. Uchebn. Zaved., Ser. Chern. Metallurgiya (1) 128 (1970)
- Iveronova V I, Katsnel'son A A Blizhnii Poryadok v Tverdykh Rastvorakh (Short-Range Order in Solid Solutions) (Moscow: Nauka, 1977)
- 210. Shurin A K et al. Poroshk. Metall. (1) 56 (1987)
- 211. Shurin A K et al. Poroshk. Metall. (8) 67 (1987)
- 212. Milova G D, Gusev A I Rasplavy (5) 79 (1991)
- Gusev A I, in Proc. of the ISBB'96 12th Intern. Symp. on Boron, Borides and Related Compounds (25-30 August 1996, Baden, Austria) (Wien (Austria): Universiträt Wien, 1996) p. 23
- 214. Ordan'yan S S, Unrod V I, Avgustinnik A I Poroshk. Metall. (9) 40 (1975)
- Portnoĭ K I, Samsonov G V, Frolova K I Zh. Prikl. Khim. 33 577 (1960)
- 216. Duschanek H, Rogl P, Lukas H L J. Phase Equilibria 16 (1) 46 (1995)
- 217. Schouler M, Dicarroir M, Bernard C *Rev. Int. Hautes Temp. Refr.* **20** (4) 261 (1983)
- Villars P, Prince A, Okamoto H, in *Handbook of Ternary Alloy Phase Diagrams* Vol. 5 (Metals Park, Ohio, USA: ASM Publication, 1995) p. 5373
- 219. Rempel' A A, Gusev A I Pis'ma Zh. Eksp. Teor. Fiz. 69 436 (1999) [JETP Lett. 69 472 (1999)]