Tungsten Carbides and W–C Phase Diagram

A. S. Kurlov and A. I. Gusev

Institute of Solid-State Chemistry, Ural Division, Russian Academy of Sciences, Pervomaiskaya ul. 91, Yekaterinburg, 620219 Russia e-mail: gusev@ihim.uran.ru Received May 17, 2005; in final form, September 8, 2005

Abstract—The crystal structures of the tungsten monocarbide δ -WC and the disordered lower carbide β -W₂C are studied. Using magnetic susceptibility measurements, the hexagonal carbide δ -WC is shown to be stable from 300 to 1200 K. The sequence of phase transformations associated with β -W₂C ordering is analyzed. The temperature and composition stability limits of the cubic carbide γ -WC_{1-x} are evaluated, and the first data are presented on the variation of its lattice parameter with composition. An optimized W–C phase diagram is proposed which takes into account detailed structural and phase-equilibrium data for tungsten carbides.

DOI: 10.1134/S0020168506020051

INTRODUCTION

Group IV-VI transition metal carbides offer the highest melting points and hardness values among known compounds [1-3]. Owing to this, they are widely used in the production of structural and tool materials capable of working at high temperatures, in aggressive environments, and under high loads. The hardness of WC is sufficiently stable and decreases relatively little compared to other carbides as the temperature is raised from 300 to 1200-1300 K. In addition, WC has a factor of 1.5-2 higher elastic modulus and a factor of 1.5–2 smaller thermal expansion coefficient in comparison with other transition metal carbides. It is this combination of properties and their thermal stability which underlie the wide use of WC in the production of wear-resistant hard alloys, which are basic components of all tool materials. The first synthesis of tungsten carbide was reported by Moissan in 1893 [4], and commercial-scale production of WC-based hard alloys began just 20-25 years after the discovery of WC and continues to this day. The practical importance of the W-C system has led to intense studies of the W-C phase diagram and the structure and properties of tungsten carbides.

The compounds existing in the W–C system are W_2C and WC. Both compounds have several polymorphic modifications, stable in different temperature and composition ranges. Although only a limited number of groups have studied phase equilibria in the W–C system, some of the data available in the literature are inconsistent and even mutually exclusive. Moreover, different designations were sometimes used for the same phase, which added confusion to phase-diagram data.

This led us to study the crystal structure and some properties of tungsten carbides with the aim of more accurately assessing the phase equilibria in the W–C system.

EXPERIMENTAL

The structure of tungsten carbides was investigated by x-ray diffraction (XRD) (Cu $K_{\alpha_{1,2}}$ radiation, $2\theta = 10^{\circ}-140^{\circ}$, step-scan mode with a step size $\Delta(2\theta) = 0.03^{\circ}$ and a counting time of 2 s per data point).

Magnetic susceptibility χ was measured by the Faraday method on a Domenicalli balance in a vacuum of 10^{-3} Pa and magnetic fields of 576, 640, and 704 kA/m at temperatures from 300 to 1200 K.

RESULTS AND DISCUSSION

The major phase in the W–C system is the higher tungsten carbide δ -WC (WC). Its XRD pattern is displayed in Fig. 1. According to our results, WC has a hexagonal structure (sp. gr. $P\bar{6}m2 = D_{3h}^1$) with lattice parameters a = 0.2906 nm and c = 0.28375 nm. Both the W and C atoms in WC form simple hexagonal sublattices. The carbon atoms sit in the center position of trigonal-prismatic interstices in the tungsten sublattice. Below 1300 K, δ -WC has no homogeneity range. The present results agree well with earlier data [3, 5–8]. Conclusive experimental evidence that the hexagonal carbide δ -WC exhibits no deviations from stoichiometry has been recently reported by Rempel *et al.* [9]: their positron annihilation results indicate that δ -WC in a normal state contains no carbon vacancies.

Our magnetic susceptibility measurements demonstrate that WC is a weak paramagnet (Fig. 2) with $\chi(300) \approx 0.058 \times 10^{-6} \text{ cm}^3/\text{g}$. This agrees with the report by Klemm and Schüth [10] that the 293-K sus-



Fig. 1. XRD patterns of the hexagonal tungsten monocarbide δ -WC (WC_{1.0}) (sp. gr. *P*6 *m*2, *a* = 0.2906 nm, *c* = 0.28375 nm) and the hexagonal lower tungsten carbide β -W₂C (WC_{0.48}) (sp. gr. *P*6₃/*mmc*, *a* = 0.2996 nm, *c* = 0.4724 nm) with disordered carbon and vacancy distributions.

ceptibility of WC is about 0.07×10^{-6} cm³/g. As the temperature is raised from 300 to 1250 K, the susceptibility of WC increases steadily, exhibiting Pauli-paramagnetic behavior, $\chi(T) = \chi(0) + BT^2$, with $\chi(0) \approx 0.0565 \times 10^{-6}$ cm³/g and $B \approx 1.3 \times 10^{-14}$ cm³/(g K²). The absence of anomalies in $\chi(T)$ implies that, in the range 300–1200 K, the electronic structure of WC remains unchanged, and hexagonal WC undergoes no phase transformations. This agrees with earlier reports [5–8] that hexagonal WC is stable between 300 and 3030–3050 K.

The lower tungsten carbide β -W₂C (W₂C) was initially believed to be stable from 300 K to its melting point. It was shown, however, later that, below 1523 K, W₂C does not exist in thermodynamic equilibrium, undergoing solid-state decomposition. Lander and Germer [11] reported the synthesis of cubic W₂C with a = 0.416 nm via deposition from tungsten hexacarbonyl vapor. Using a spark discharge between WC electrodes immersed in oil, Lautz and Schneider [12] obtained a cubic carbide with a = 0.425 nm and tentatively identified it as W₂C.

According to current views, the lower tungsten carbide W₂C exists in three polymorphs—low-temperature (β "), intermediate (β '), and high-temperature (β) which were also designated α -, β -, and γ -W₂C, respectively [5, 7]. In the three W₂C polymorphs, the W atoms form an hcp sublattice in which half of the octahedral interstices are occupied by carbon atoms. Depending on the arrangement of carbon atoms, W_2C may be disordered (at high temperatures) or ordered (at low temperatures).

The XRD pattern of the high-temperature phase β -W₂C of the lower carbide WC_{0.48} is displayed in Fig. 1. WC_{0.48} has a hexagonal structure (sp. gr. $P6_3/mmc = D_{6h}^4$) of the L'3 type with a disordered arrangement of carbon atoms and vacancies. Its lattice



Fig. 2. Magnetic susceptibility of hexagonal WC as a function of temperature.



Fig. 3. XRD patterns of the lower carbides β-W₂C, β'-W₂C, and β"-W₂C. The only differences are observed at low 2θ angles. The intensity of the (110)_{ortho} and (111)_{ortho} reflections, characteristic of the orthorhombic carbide β'-W₂C, and that of the (001)_{C6} reflection, characteristic of β"-W₂C (*C*6 structure), are at the background level, less than 0.5% of the intensity of the strongest reflection (101)_{L'3}, (101)_{C6}, or (121)_{ortho}.

parameters are a = 0.2996 nm and c = 0.4724 nm. In an ideal unit cell of the lower carbide β -W₂C, the two W atoms sit in positions 2c (1/3 2/3 1/4 and 2/3 1/3 3/4) and the C atom occupies positions 2a (0 0 0 and 0 0 1/2) at random. The partially occupied (half of the sites), disordered carbon layers are stacked along the *c* axis. According to earlier reports [5–7], the disordered hexagonal phase β -W₂C has a homogeneity range from WC_{0.34} to WC_{0.52} and is stable in the range from 2670–2720 K to its melting point (3000–3050 K).

The XRD patterns of the high-temperature $(\beta-W_2C)$, intermediate $(\beta'-W_2C)$, and low-temperature $(\beta''-W_2C)$ phases differ very little because these phases have the same hexagonal tungsten sublattice, whereas the atomic scattering factor of carbon is many times lower than that of tungsten. For this reason, changes in the arrangement of carbon atoms in W_2C are only detectable at low diffraction angles (Fig. 3). This led us to critically evaluate the diffraction data available in the literature before discussing the structures of $\beta'-W_2C$ and $\beta''-W_2C$.

The β' -W₂C phase possesses orthorhombic symmetry, even though it has an hcp tungsten sublattice, just as the high-temperature phase β -W₂C. The structure of the orthorhombic phase β' -W₂C can be assigned to the PbO₂ structure type (sp. gr. *Pbcn* = D_{2h}^{14}). Rudy and Windisch [5] assumed that β' -W₂C is similar in struc-



Fig. 4. Arrangement of carbon atoms in the structure of the lower carbides β -W₂C, β '-W₂C, and β "-W₂C (the carbon planes are normal to the *c* axis of the parent, disordered structure of the *L*'3 type; W atoms are not shown): (a) *L*'3 type (random arrangement of the carbon atoms and vacancies), (b) ζ -Fe₂N type (ordered arrangement of the carbon atoms and vacancies in each carbon plane of β '-W₂C, (c) *C*6 type (ordered arrangement of the carbon atoms and vacancies in alternating carbon and vacancy planes of β "-W₂C); (*I*) interstitial positions occupied at random by carbon atoms with a site occupancy of 1/2, (2) carbon atoms, (*3*) carbon vacancies.

ture to the ordered molybdenum carbide Mo_2C (ζ -Fe₂N type) [13], but they failed to accurately determine the atomic position coordinates of W in the structure of β' -W₂C. Our analysis of the arrangement of atoms in the orthorhombic unit cell, derived from the hexagonal cell of the L'3 structure, and calculation of the XRD pattern for β' -W₂C with the ζ -Fe₂N structure (Fig. 3) indicate that the atoms in the orthorhombic unit cell have the following position coordinates: W in 8d (1/4 \simeq 1/8 $\approx 1/2$) and C in 4c (0 $\approx 3/8$ 1/4). The β' -W₂C phase with the ζ -Fe₂N structure (Fig. 4b) has an ordered carbon sublattice, in contrast to the high-temperature hexagonal phase β -W₂C (Fig. 4a). The orthorhombic phase β' -W₂C has a homogeneity range from WC_{0.34} to WC_{0.49} and exists in the temperature range from 2370 to 2670-2750 K [5]. It cannot be ruled out however that β -W₂C and $\beta'-W_2C$ are in fact the same, hexagonal phase (sp. gr. $P6_3/mmc$) with a disordered carbon sublattice.

The low-temperature phase β "-W₂C has a hexagonal structure of the C6 type (sp. gr. $P\bar{3}m1 = D_{3d}^3$) [14]. The carbon atoms and vacancies in this phase are arranged in the form of ordered layers perpendicular to the *c* axis. The carbon planes are sandwiched between A and B tungsten layers, and the vacancy planes, between B and A tungsten layers (Fig. 4c). In an ideal structure of β "-W₂C, the two W atoms sit in position 2*d* (1/3 2/3 *z* and 2/3 1/3 –*z*, with *z* = 0.25), the C atom sits in position 1a(000), and the vacancy is located in position 1b (0 0 1/2). Actually, the c-axis spacing between tungsten layers separated by a vacancy layer is slightly narrower than that between tungsten layers separated by a carbon layer, and z slightly exceeds 0.25. Comparison with the structure of the disordered carbide β -W₂C indicates that ordering splits position 2a, occupied at random by C atoms with a site occupancy of 1/2, into positions 1a and 1b, one of which is fully occupied by carbon, and the other is vacant. At ≈ 2300 K, the homogeneity range of $\beta"\text{-}W_2C$ extends from $WC_{0.34}$ to $WC_{0.48}$. With decreasing temperature, the homogeneity range narrows down, to the extent that, at 1523 K, there is no homogeneity range, and the composition of this phase is $WC_{0.48}$ [5, 15]. Below 1523 K, the lower carbide β "-W₂C decomposes into W and the higher carbide δ -WC. The ordering-induced changes in the arrangement of the carbon atoms and vacancies in the lower carbide W₂C are illustrated in Fig. 4.

In the composition range between the lower tungsten carbide β -W₂C and the higher carbide δ -WC, there exists the cubic phase γ -WC_{1-x} (also designated β -WC [8], α -WC_{1-x} [7], or simply WC_{1-x}). This phase was first described in [11, 12, 16] and was assumed initially to be yet another polymorph of the lower carbide W₂C. Given, however, that all of the octahedral interstices in its hcp tungsten sublattice can be occupied by carbon atoms, resulting in the stoichiometry γ -WC_{1.0}, it is more correct to consider it a cubic polymorph of the higher tungsten carbide WC. Data on the temperature and composition stability limits of the cubic carbide γ -WC_{1-x} are the most contradictory.

 γ -WC_{1-x} has the *B*1 structure (sp. gr. $Fm\bar{3}m = O_h^5$), typical of nonstoichiometric Group IV and V transition metal carbides and nitrides with the general formula MX_v. Goldschmidt and Brand [16] obtained cubic tungsten carbide by spark processing of W foil. Evidence for the existence of cubic tungsten carbide was also reported by Sara [8]. Ronsheim et al. [17] identified γ -WC_{1-x} with the B1 structure among the products of the arc plasma (Ar-CH₄) synthesis of tungsten carbide from W powder. The reaction product contained 74 to 96% cubic tungsten carbide ranging in particle size from 2 to 16 nm. The chemical composition of the cubic phase γ -WC_{1-x} synthesized in [17] was not reported. In studies by Willens et al. [18, 19], concerned with the superconducting transition temperatures of cubic MoC, WC, and carbide solid solutions, cubic tungsten carbide was obtained by rapid quenching from the liquid state. According to Willens and Buehler [18], the stoichiometric cubic carbide γ -WC_{1.0} has a relatively high $T_{\rm c}$ of 10 K, whereas the $T_{\rm c}$ of $WC_{0.85}$ is 9 K. Note that the superconducting transition temperatures of the hexagonal carbides β -W₂C and δ -WC, 3.6 and 0.3 K, respectively [18], are substantially lower than the T_c of γ - W_{1-x} . Krainer and Robitsch [20] found the cubic carbide γ -WC_{1-x} on the surface of spark-processed, melted samples of δ -WC and WC–Co hard alloys. Given the processes that were successfully used to prepare cubic tungsten carbide [8, 16–20], it seems likely that Lander and Germer [11] and Lautz and Schneider [12] also obtained the cubic phase γ -WC_{1-x} rather than the lower carbide W₂C with a cubic structure.

Single-phase γ -WC_{1-x} exists in the composition range $WC_{0.58}$ to $WC_{0.65}$ at temperatures above 2790– 2810 K [6, 7, 15]. Moreover, γ -WC_{1-x} may exist in equilibrium with β -W₂C or δ -WC. According to studies of cubic tungsten carbide containing 51.0 at % C [7], the DTA curve obtained during cooling of the melt from \approx 3270 K shows peaks at \approx 2990 and \approx 2200 K, which are due to the eutectic transformation $L \Leftrightarrow$ γ -WC_{1-x} + δ -WC and eutectoid decomposition γ -WC_{1-x} $\Leftrightarrow \beta$ -W₂C + δ -WC. It follows from the results reported by Rudy and Hoffman [7] that the cubic phase γ -WC_{1-x} forms rather readily from the melt, but the direct solid-state transformation δ -WC $\Leftrightarrow \gamma$ -WC_{1-x} is hindered and requires that the temperature be varied slowly near the transformation temperature $T_{\rm tr}$. Another possibility is that the temperature stability range of the cubic carbide is very narrow.

Sara [8] investigated in detail the phase equilibria in the W-C system with the participation of the cubic phase γ -WC_{1-x}. Microstructural examination of samples with 45 at % carbon quenched in the solid state from 2988-3023 K or liquid-quenched from 3043-3063 K revealed the presence of the cubic tungsten carbide γ -WC_{1-x}. According to Sara [8], the tungsten-rich phase boundary of the cubic carbide γ -WC_{1-x} is $WC_{0.59}$, independent of temperature, whereas its carbon-rich phase boundary shifts to higher carbon contents with increasing temperature and may reach the composition $WC_{1.00}$. On the whole, according to his results the cubic tungsten carbide γ -WC_{1-x} has a broader homogeneity range at temperatures from 3030 to 3055 K, from $WC_{0.59}$ to $WC_{0.98-1.00}$, than was reported by Rudy et al. [6, 7, 15]. Additional evidence that the carbon-rich phase boundary of γ -WC_{1-x} reaches the stoichiometric composition $WC_{1.0}$ is the high superconducting transition temperature of this compound reported by Willens *et al.* [18, 19]: $T_c = 10$ K.

According to Goldschmidt and Brand [16], the lattice parameter of γ -WC_{1-x} is $a_{B1} \approx 0.427$ nm. The lattice parameter of cubic WC_{0.82} was reported to be 0.4215 nm [8]. Ronsheim *et al.* [17] found the lattice parameter of cubic tungsten carbide of unknown composition to be 0.4229 nm. According to Krainer and Robitsch [20], a near-stoichiometric cubic tungsten carbide has a = 0.4248 nm. The lattice parameters of cubic WC_{1.0} and WC_{0.85} were reported to be 0.4266 and 0.4252 nm, respectively [18]. In a sample containing, in addition to cubic tungsten carbide, the lower carbide



Fig. 5. Lattice parameter a_{B1} as a function of carbon content for the cubic tungsten carbide γ -WC_{1-x} $\equiv \gamma$ -WC_y (B1 structure) in its homogeneity range. The dashed line represents the best fit to the data reported in [7, 15, 18–21]: $a_{B1}(y) =$ 0.4015 + 0.0481y – 0.0236y² [nm].

 W_2C and a large amount of free carbon, the lattice parameter of the cubic phase was 0.4240 nm [18]. Under the assumption that the lattice parameter of the cubic carbide γ -WC_{1-x} is a linear function of carbon content, $a_{B1} = 0.424$ nm corresponds to the composition WC_{0.71-0.72}. Rudy *et al.* [7, 15] determined the lattice parameter of cubic WC_{0.61} to be 0.4220 nm. Extrapolating this value, Krainer and Robitsch [21] obtained a =0.4265 nm for a defect-free cubic tungsten carbide. As seen in Fig. 5, the most consistent data on the lattice parameter of the cubic carbide γ -WC_{1-x} were reported in [7, 15, 18–21]. Those data demonstrate that a_{B1} increases with carbon content and are well represented by $a_{B1}(y) = 0.4015 + 0.0481y - 0.0236y^2$ [nm].

Thus, among tungsten carbides, only the hexagonal phase WC (δ -WC) has an insignificant homogeneity range, whereas the three polymorphs of the lower carbide W₂C and the cubic carbide γ -WC_{1-x} have rather broad homogeneity ranges.

The broad homogeneity range of the cubic carbide γ -WC_{1-x} [8], extending to the composition WC_{1.0}, fits well with the results reported in [16–20]. At the same time, according to the W–C phase diagram reported by Sara [8] the stoichiometric cubic carbide WC_{1.0} exists only at \approx 3058 K, and the phase boundary of γ -WC_{1-x} for $(1-x) \rightarrow 1$ is such that, as the temperature is lowered from 3058 to 3028 K, WC_{1.0} must undergo two consecutive transformations, peritectic and then peritectoid, which appears unlikely. Moreover, one of the phase-equilibrium lines in that phase diagram is drawn



Fig. 6. Phase diagram of the W-C system.

Phase		Composition			u	Structure type
designation in Fig. 6	designation in earlier reports	range, at % C	Lattice parameters, nm	Sp. gr.	Pearso symbo	and symmetry
W	W	0–1.0	<i>a</i> = 0.3165	$Im\bar{3}m(O_{\rm h}^9)$	cI2	A2 (W type), fcc
β -W ₂ C	γ-W ₂ C [5, 7]	≈25.5–34.0	<i>a</i> = 0.3002, <i>c</i> = 0.475–0.476 [15]	$P6_3/mmc(D_{6h}^4)$	hP3	<i>L</i> '3 (W ₂ C type), hexagonal
β' -W ₂ C	β-W ₂ C [5, 7]	≈29.5-33.0	a = 0.4728, b = 0.6009, c = 0.5193 [5]	$Pbcn(D_{2h}^{14})$	-	$PbO_2 \text{ or } Mo_2C (\zeta - Fe_2N)$ type, orthorhombic
β "-W ₂ C	α -W ₂ C [5, 7]	≈29.5-32.5	a = 0.2985, c = 0.4717 (WC _{0.41}) [15]	$P\bar{3}m1(D_{3d}^3)$	hP3	<i>C</i> 6 (CdI ₂ type), hexagonal
			a = 0.3001, c = 0.4728 (WC _{0.50}) [15]			
γ -WC _{1-x}	α -WC _{1-x} [7]	≃37.0–39.5 [7]	$a = 0.4266 (WC_{1.0}),$	$Fm\bar{3}m(O_{\rm h}^5)$	cF8	B1 (NaCl type), cubic
	β-WC [8, 17]	≃37.1–50.0 [8]	$a = 0.4252 (WC_{0.85}) [18]$			
δ-WC	WC [7]	≃5 0	a = 0.2906,	$P\bar{6}m2(D_{3h}^1)$	hP2	$B_{\rm h}$ (WC type), hexagonal
	α-WC [8]		c = 0.2837 [15]			-
С	С	100	a = 0.142, c = 0.339	$P6_{3}/mmc(D_{6h}^{4})$	hP4	A9 (C, graphite), hexagonal

Table 1. Structural data for phases existing in the W–C system above 1300 K

Table 2. Special points in the phase diagram of the W–C system (Fig. 6) at T > 1300 K

Reaction	at % C in the phases involved			Т, К	Reaction type	
$L \Leftrightarrow W$	0	0	_	3755 ± 5	Melting	
$L \Leftrightarrow \beta - W_2 C$	≃30.6	≃30.6	_	3058 ± 10	Congruent melting	
$L + C \Leftrightarrow \gamma - WC_{1-x}$	≃42.0	100.0	50.0	3058 ± 5	Peritectic	
$L \Leftrightarrow W + \beta - W_2 C$	≃23.5	≃1.2	≃25.5	2988 ± 5	Eutectic	
$L \Leftrightarrow \beta - W_2 C + \gamma - W C_{1-x}$	≃37.0	≃34.3	≃37.8	3028 ± 5	Eutectic	
γ -WC _{1-x} $\Leftrightarrow \delta$ -WC	≃49.3	≃49.3	_	3008 ± 5	Polymorphic transformation	
γ -WC _{1-x} $\Leftrightarrow \delta$ -WC + C	50.0	≃49.8	100.0	2993 ± 5	Eutectoid decomposition	
γ -WC _{1-x} $\Leftrightarrow \beta$ -W ₂ C + δ -WC	≃38.2	≃34.0	≃49.5	2798 ± 5	Eutectoid decomposition	
$\beta\text{-}W_2C \Leftrightarrow W + \beta'\text{-}W_2C$	≃28.6	≃0.7	≃29.7	2673 ± 10	Eutectoid decomposition	
$\beta\text{-}W_2C \Leftrightarrow \beta\text{'}\text{-}W_2C$	≃31.6	≃31.6	_	2768 ± 10	Disorder-order transformation	
$\beta \text{-} W_2 C \Leftrightarrow \beta' \text{-} W_2 C + \delta \text{-} W C$	≃33.5	≃32.8	≃49.8	2657 ± 10	Eutectoid decomposition	
$\beta'-W_2C \Leftrightarrow \beta''-W_2C$	30.0-32.5	30.0-32.5	_	2370 ± 15	Order-order transformation	
β "-W ₂ C \Leftrightarrow W + δ -WC	≃32.6	0	50.0	1523 ± 5	Eutectoid decomposition	

improperly: the horizontal representing the invariant eutectic transformation $L \Leftrightarrow \beta$ -W₂C + γ -WC_{1-x} gradually passes into a monovariant curve, which is physically impossible and incorrect from the viewpoint of geometrical thermodynamics. Such a phase equilibrium would be possible if the point common to the eutectic horizontal and monovariant curve were singu-

lar (inflection point). This, however, would reduce the temperature range of the two-phase field $L + \gamma$ -WC_{1-x} and would raise its lower boundary, which is at variance with the DTA and microstructural analysis results reported by Sara [8]. The inconsistencies in question can be eliminated by assuming that the cubic carbide WC_{1.0} has at least a narrow temperature stability range

and that the two consecutive phase transformations occur at different compositions.

Figure 6 shows the W–C phase diagram which takes into account the temperature stability range of the cubic carbide $WC_{1,0}$, the experimental data reported in [5–8, 15–20], and the present results. Table 1 summarizes structural data for the phases of the W–C system. Near the composition $WC_{1,0}$ (Fig. 6), reducing the temperature from 3058 to 2993 K leads first to the peritectic formation of the cubic tungsten carbide, $L + C \Leftrightarrow$ γ -WC_{1-x}, and then to the cubic–hexagonal phase transformation, γ -WC_{1-x} $\Leftrightarrow \delta$ -WC. The temperature of the eutectoid decomposition γ -WC_{1-x} $\Leftrightarrow \delta$ -WC + C (2993 K) was inferred from the DTA data reported by Rudy and Hoffman [7] for a carbide sample containing 51 at % C. It is clear from Fig. 6 that, even though the temperature stability range of γ -WC_{1-x} is rather narrow, the stoichiometric cubic carbide $WC_{1,0}$ can be liquid-quenched. This correlates with the results reported by Willens et al. [18, 19]. The phase diagram in Fig. 6 provides a consistent picture of phase equilibria in the W-C system, which agrees with earlier reports. The special points in the phase diagram of the W-C system (Fig. 6) at T > 1300 K are listed in Table 2.

Note that the structural data for tungsten carbides (especially for those expected to be ordered-vacancy compounds) are only tentative. To refine the structure of nonstoichiometric tungsten carbides to the point of determining the positions of carbon atoms and vacancies, neutron or synchrotron x-ray diffraction studies are needed.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 06-03-32047.

REFERENCES

- 1. Gusev, A.I. and Rempel, A.A., *Nestekhiometriya, besporyadok i poryadok v tverdom tele* (Nonstoichiometry, Disorder, and Order in Solids), Yekaterinburg: Ural. Otd. Ross. Akad. Nauk, 2001.
- Gusev, A.I., Rempel, A.A., and Magerl, A.J., Disorder and Order in Strongly Nonstoichiometric Compounds: Transition Metal Carbides, Nitrides, and Oxides, Berlin: Springer, 2001.
- Storms, E.K., *The Refractory Carbides*, New York: Academic, 1967. Translated under the title *Tugoplavkie karbidy*, Moscow: Atomizdat, 1970.
- Moissan, H., Préparation au four électrique de quelques métaux réfractaires: tungstène, molybdène, vanadium, *Compt. Rend.*, 1893, vol. 116, pp. 1225–1227.
- Rudy, E. and Windisch, S., Evidence to Zeta Fe₂N-Type Sublattice Order in W₂C at Intermediate Temperatures, *J. Am. Ceram. Soc.*, 1967, vol. 50, no. 5, pp. 272–273.

- Rudy, E., Compendium of Phase Diagram Data. Ternary Phase Equilibria in Transition Metal–Boron–Carbon– Silicon Systems, *Report AFML TR-65-2*, Wright–Patterson Air Force Base (Ohio), 1969.
- Rudy, E. and Hoffman, J.R., Phasengleichgewichte im Bereich der kubischen Karbidphase im System Wolfram–Kohlenstoff, *Planseeber. Pulvermetall.*, 1967, vol. 15, no. 3, pp. 174–178.
- Sara, R.V., Phase Equilibrium in the System Tungsten– Carbon, J. Am. Ceram. Soc., 1965, vol. 48, no. 5, pp. 251–257.
- Rempel, A.A., Würschum, R., and Schaefer, H.-E., Atomic Defects in Hexagonal Tungsten Carbide Studied by Positron Annihilation, *Phys. Rev. B: Condens. Matter*, 2000, vol. 61, no. 9, pp. 5945–5948.
- Klemm, W. and Schüth, W., Magnetochemische Untersuchungen: 3. Über den Magnetismus einiger Carbide und Nitride, Z. Anorg. Allg. Chem., 1931, vol. 201, no. 1, pp. 24–31.
- Lander, J.J. and Germer, L.H., Plating Molybdenum, Tungsten, and Chromium by Thermal Decomposition of Their Carbonyls, *Trans. AIME*, 1948, vol. 175, pp. 661–691.
- Lautz, G. and Schneider, D., Über die Supraleitung in den Wolframkarbiden W₂C und WC, Z. Naturforsch., A, 1961, vol. 16, no. 12, pp. 1368–1372.
- 13. Parthe, E. and Sadagopan, V., The Structure of Dimolybdenum Carbide by Neutron Diffraction Technique, *Acta Crystallogr.*, 1963, vol. 16, no. 3, pp. 202–205.
- Butorina, L.N. and Pinsker, Z.G., Electron Diffraction Study of W₂C, *Kristallografiya*, 1960, vol. 5, no. 4, pp. 585–588.
- Rudy, E., Windisch, S., and Hoffman, J.R., W–C System: Supplemental Information on the Mo–C System. Ternary Phase Equilibria in Transition Metal–Boron– Carbon–Silicon Systems (Part I. Related Binary Systems, vol. VI), *Report AFML-TR-65-2*, Wright–Patterson Air Force Base (Ohio), 1966, pp. 1–50.
- Goldschmidt, H.J. and Brand, J.A., The Tungsten-Rich Region of the System Tungsten–Carbon, *J. Less-Common Met.*, 1963, vol. 5, no. 2, pp. 181–194.
- 17. Ronsheim, P., Toth, L.E., Mazza, A., et al., Direct Current Arc-Plasma Synthesis of Tungsten Carbides, J. Mater. Sci., 1981, vol. 16, no. 10, pp. 2665–2674.
- Willens, R.H. and Buehler, E., The Superconductivity of the Monocarbides of Tungsten and Molybdenum, *Appl. Phys. Lett.*, 1965, vol. 7, no. 1, pp. 25–26.
- Willens, R.H., Buehler, E., and Matthias, B.T., Superconductivity of the Transition-Metal Carbides, *Phys. Rev.*, 1967, vol. 159, no. 2, pp. 327–330.
- Krainer, E. and Robitsch, J., Röntgenographischer Nachweis des kubischen Wolframkarbides in funkenerosiv bearbeiteten Hartmetallen und in reinen Wolframschmelkarbiden, *Planseeber: Pulvermetall.*, 1967, vol. 15, no. 1, pp. 46–56.
- 21. Krainer, E. and Robitsch, J., Zur Frage des kubischen Wolframkarbids, *Planseeber. Pulvermetall.*, 1967, vol. 15, no. 3, pp. 179–180.