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Phase Equilibria in the Ternary System Titanium–Boron–Carbon: The Sections TiC_y–TiB_2 and B_4C_y–TiB_2

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The phase diagram of the ternary Ti–B–C system has been constructed from 300 to 3500 K, especially for the sections TiC_y–TiB_2 and B_4C_y–TiB_2. The calculation of the energy parameters describing the phase equilibria with the participation of TiB_2 has been carried out in the subregular solutions approximation. The presence of wide homogeneity regions of carbides, $TiC_{0.47}$–$TiC_{1.0}$ and $B_4C_{0.45}$–$B_4C_{1.0}$, has been taken into account. Ordering in nonstoichiometric titanium carbide TiC_y at a temperature below 950 K has been calculated by the order parameters functional method. © 1997 Academic Press

1. INTRODUCTION

Based on a first thermodynamic estimate of the phase diagram proposed by Brewer and Haraldsen (1), a number of experimental studies have been made of the phase equilibria in the ternary Ti–B–C system (2–6).

The currently available and universally accepted phase diagram version for the Ti–B–C ternary system results from a series of critical assessments (7–10). The most complete critical assessment of this system was performed by authors (9) calculating the phase equilibria in the temperature region of 1673 K up to the melting range. The Ti–B–C system involves only binary compounds. No reliable supportive experimental evidence is available for the existence of a Ti_2B_5 boride. A high-temperature phase Ti_2B was claimed to be stable in a narrow temperature interval, between 2100 and 2400 K (11). According to the (12–14), a rhombohedral boride Ti_3B_4 forms up to the temperatures 2400–2500 K. No ternary compounds have been found to exist in the Ti–B–C system. The characteristic isothermal reactions for the Ti–B–C ternary system are compiled in Table 1, including the pseudobinary sections TiB_2–C, TiC_y–TiB_2, and B_4C_y–TiB_2. All available phase diagram versions for the ternary Ti–B–C system have been constructed at a temperature above 1673 K.

As the boron carbide B_4C_y ($0.45 \le y \le 1.00$) and the titanium carbide TiC_y ($0.47 \le y \le 1.00$) possess wide regions of homogeneity, even pseudobinary equilibria with their participation virtually embrace a significant portion of the ternary Ti–B–C system. The main purpose of the present paper is to calculate the phase equilibria of the ternary Ti–B–C system for the TiC_y–TiB_2 and B_4C_y–TiB_2 polythermal sections and also to construct in part of three-dimensional (space) phase diagram of the Ti–B–C system at a temperature from 300 to 3500 K.

2. PATTERN OF CALCULATION AND THE ENERGY PARAMETERS OF THE MODEL

As shown earlier (15, 16), systems involving the participation of nonstoichiometric compounds are inadequately described by the model of regular solutions. In this context, the authors of (15) proposed a method for calculating phase diagrams by means of a subregular solution model taking into account the composition and temperature dependencies of the energy of mixing in different phases. Applying the subregular solutions model permitted the calculation of the phase boundary position in systems formed by carbides of two different transition metals, $M^{(1)}C$–$M^{(2)}C$ (15–19), in oxide–fluoride systems, MeO–Na_3AlF_6 (MeO = Al_2O_3, BeO, SnO_2) (20).

In the general case the free Gibbs energy of the j-phase in a multicomponents system may be represented as

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

with x_i being the concentration of the i-component in the j-phase, $\Delta G_j(x_i = 1, T, p)$ the free energies of the system's components, and $G_j^e(x_i, T, p)$ the free excess energy of mixing. As the phase equilibria in the Ti–B–C system are calculated for constant pressure $p = 1$, the designation of p will henceforth be omitted. Deviation from the ideality in the subregular solution model is given by the quantity $G_j^e = B_j(x_i, T)\prod x_i^{(j)}$, where $B_j(x_i, T)$ is the mutual exchange energy, i.e., an energy parameter that specifies the

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TABLE 1
Comparison of the Literature Data with the Present Calculation Results

			Experimental data[b]					Calculated data (9)				Present calculation[c]			
			Composition (at.%)					Composition (at.%)				Composition (at.%)			
Reaction	Type[a]	Phase	Ti	B	C	T (K)	Ref.	Ti	B	C	T (K)	Ti	B	C	T (K)
$L \Leftrightarrow TiB_2 + TiC_{0.95}$	e_2	L	41.2	37.6	21.2	2973	(5)	—	—	—	—	44.0	26.9	29.1	2950
		TiB_2	—	—	—	⋯		—	—	—	—	33.3	66.7	0	⋯
		$TiC_{0.95}$	50.5	2.7	46.8	⋯		—	—	—	—	50.7	2.0	47.3	⋯
$L \Leftrightarrow TiB_2 + TiC_{0.92}$	e_2	L	44.0	28.7	27.3	2893	(3)	—	—	—	—	44.5	26.9	28.6	2955
		TiB_2	33.7	65.3	1.0	⋯		—	—	—	—	33.9	64.7	1.4	⋯
		$TiC_{0.92}$	51.1	3.4	45.5	⋯		—	—	—	—	51.4	2.6	46.0	⋯
$L \Leftrightarrow TiB_2 + TiC_{0.80}$	e_2 (max)	L	—	—	—	2723	(5)	44.1	33.9	22.0	2916	46.6	27.0	26.4	2961
		TiB_2	—	—	—	⋯		33.3	66.7	0	⋯	34.1	64.5	1.4	⋯
		$TiC_{0.80}$	—	—	—	⋯		54.1	3.2	42.7	⋯	54.4	3.5	42.1	⋯
$L \Leftrightarrow TiB_2 + TiC_{0.68}$	e_2	L	—	—	—	2663	(5)	—	—	—	—	44.5	26.9	28.6	2948
		TiB_2	—	—	—	⋯		—	—	—	—	34.1	64.7	1.2	⋯
		$TiC_{0.68}$	57.3	5.7	37.0	⋯		—	—	—	—	58.4	2.8	38.8	⋯
$L \Leftrightarrow TiB_2 + C$	e_3 (max)	L	23.0	45.0	32.0	2780	(3)	22.2	44.6	33.2	2779	21.8	43.6	34.6	2828
		TiB_2	32.7	65.3	< 2	⋯		33.3	66.7	0	⋯	32.8	65.6	1.6	⋯
		C	< 1	~ 1	> 98	⋯		0	0.7	99.3	⋯	0	0.5	99.5	⋯
$L \Leftrightarrow TiB_2 + B_4C_{1.0}$	e_5	L	7.3	77.1	15.6	2473	(5)	—	—	—	—	9.8	76.1	14.1	2502
		L	8.3	76.7	15.0	2173	(6)	—	—	—	—	⋯	⋯	⋯	⋯
		TiB_2	—	—	—	—		—	—	—	—	33.0	66.8	0.2	⋯
		$B_4C_{1.0}$	—	—	—	—		—	—	—	—	0.4	79.8	19.8	⋯
$L \Leftrightarrow TiB_2 + B_4C_{0.89}$ (or $B_4C_{0.68}$ from (9))	e_5 (max)	L	4.0	80.0	16.0	2583	(3)	7.9	81.1	11.0	2654	9.9	77.3	12.8	2545
		TiB_2	32.7	66.9	0.4	⋯		33.3	66.7	0	⋯	33.0	66.8	0.2	⋯
		$B_4C_{0.89}$	< 1	~ 82	~ 17	⋯		0	85.5	14.5	⋯	0.5	81.6	17.9	⋯
$L \Leftrightarrow TiB_2 + TiC_{1.0} + C$	E_1	L	26.0	36.0	38.0	2673	(3)	28.8	33.5	37.7	2667	28.2	34.4	37.4	2650
		TiB_2	34.0	64.0	< 2	⋯		33.3	66.7	0	⋯	33.3	66.7	0	⋯
		$TiC_{1.0}$	52.0	2.0	26.0	⋯		51.2	0.6	48.2	⋯	49.9	0.6	49.5	⋯
		C	< 1	< 2	> 97	⋯		0	0.3	99.7	⋯	0	0.4	99.6	⋯
$L \Leftrightarrow TiB_2 + B_4C_y + C$ ($y \approx 1.0$)	E_2	L	7.3	64.3	28.4	2513	(3)	9.9	64.1	26.0	2519	9.0	68.4	22.6	2380
		TiB_2	> 33	~ 65	< 2	⋯		33.3	66.7	0	⋯	33.3	66.7	0	⋯
		B_4C_y	< 1	~ 80	> 19	⋯		0	81.4	18.6	⋯	0.5	80.6	18.9	⋯
		C	< 1	~ 3	> 96	⋯		0	2.0	98.0	⋯	0	1.6	98.4	⋯
$L \Leftrightarrow TiB_2 + B_4C_y + B$ ($0.35 \leq y \leq 0.50$)	E_3	L	~ 1.5	~ 97.0	~ 1.5	2289	(3)	1.9	97.9	0.2	2331	1.7	98.1	0.2	2264
		TiB_2	~ 33	~ 66	~ 1	⋯		33.3	66.7	0	⋯	33.3	66.7	0	⋯
		B_4C_y	< 1	> 88	~ 11	⋯		0	91.9	8.1	⋯	0.4	89.6	10.0	⋯
		B	< 1	~ 99	< 1	⋯		0	100.0	0	⋯	0	100.0	0	⋯
$L \Leftrightarrow \beta Ti + TiB + TiC_{0.47}$	E_4	L	92.8	5.0	2.2	1783	(3)	91.2	6.6	2.2	1808	90.7	6.0	3.3	1720
		βTi	> 98	~ 1	~ 1	⋯		97.8	0.1	2.1	⋯	98.1	0.1	1.8	⋯
		TiB	~ 51	> 48	< 1	⋯		50.0	50.0	0	⋯	50.0	50.0	0	⋯
		$TiC_{0.47}$	~ 68	~ 2	~ 30	⋯		68.1	1.7	30.2	⋯	67.3	1.9	30.8	⋯

[a] Reaction type according to (9).

[b] Experimental compositions from (3, 5, 6) modified by A. Gusev; errors of determination of temperature in (3) and (5) are ± 15 and ± 40 K, respectively.

[c] Errors of calculation of composition and temperature are equal to ± 0.5 at.% and ± 50 K, respectively.

interaction of the components in the j-phase and is a function of composition and temperature. In the regular solution model, the mutual exchange energy B_j is a composition and temperature independent constant.

Calculating the phase boundaries requires a knowledge of the mutual exchange energies of all the phases in equilibrium. According to (21), the mutual exchange energy $B_\ell = e_0 + e_p$ of the liquid phase is a sum of the electron interaction parameter, e_0, and the internal pressure parameter, e_p. The mutual exchange energy of the solid phase involves, in addition to the parameters e_0 and e_p, also the parameter of the electron interaction in the solid phase, e_1, and the parameter of elastic crystal lattice distortions, e_2, i.e., $B_s = e_0 + e_p + e_1 + e_2$.

The interaction parameters were calculated in accordance with (15), using the formulas

$$e_0 = \left[\sum_{i=1}^{n} x_i V_i(T)\right] \times \left\{\prod_{i=1}^{n}\left[\left(\frac{E_i}{V_i(T)}\right)^{1/2} - \left(\frac{\sum E_i}{\sum V_i(T)}\right)^{1/2}\right]\right\}^{(2/n)}, \qquad [2]$$

$$e_p = \left[\sum_{i=1}^{n} x_i V_i(T)\right] \times \Bigg\{\sum_{i=1}^{n} \frac{E_i}{V_i(T)}\Bigg)^{1/2} - n\left[\prod_{i=1}^{n}\frac{E_i}{V_i(T)}\right]^{(1/n)}\Bigg\}, \qquad [3]$$

$$e_1 = -\frac{1}{C_n^2}\left[\sum_{i=1}^{n} x_i V_i(T)\right] \times \left\{\sum_{i,k>i}^{\substack{k=n\\ i=n-1}} \left|\frac{\Delta H_i}{V_i(T)} - \frac{\Delta H_k}{V_k(T)}\right|\right\}, \qquad [4]$$

$$e_2 = \frac{1}{3}\left[\sum_{i=1}^{n} x_i \frac{G_i(T)}{V_i(T)}\right] \times \left\{\sum_{i=1}^{n} [V_i(T)]^2 - n\left[\prod_{i=1}^{n} V_i(T)\right]^{(2/n)}\right\}. \qquad [5]$$

In Eqs. [2]–[5] n is the number of components; x_i is the i-component concentration (in mole fractions); $V_i(T) = V_i(300)\,[1 + 3\alpha_i(T - 300)]$ the molar volume of the i-component at temperature T, $V_i(300)$ and α_i the molar volume at 300 K and the mean linear expansion coefficient of the i-component; E_i the atomization energy of the i component (for elements, the atomization energy coincides with the vaporization heat); ΔH_i the melting heat of the i-component, $G_i(T) = G_i(300)\,[1 - \beta_i(T - 300)]$, where $G_i(300)$, $G_i(T)$ stands for the shear moduli of the i-component at 300 K and at temperature T, and β_i the mean shear modulus temperature coefficient of the i-component. Note that the electron interaction parameters e_0 and e_1 are negative; i.e., they describe the bonding part of the interaction energy, whereas the positive parameters e_p and e_2 specify the antiboding part of this energy.

The equilibrium conditions for the phases j_1 and j_2 are determined by combined equations of the form

$$\frac{\partial \Delta G_{j_1}}{\partial x_i} = \frac{\partial \Delta G_{j_2}}{\partial x_i}, \qquad [6]$$

written for all the components of these phases.

The elements or compounds that take part in a particular phase equilibrium may have different crystal structures. This difference should be taken into account when calculating all the interaction parameters by reduction of volumes V_i. To this end, the crystal structure of one of the components participating in the phase equilibrium at hand is chosen as a basis structure and the unit cell parameters of the other components are reduced to that structures. Reduction is performed in such a way that the areas of the surfaces of the reduced and the nonreduced unit cell are identical, while the angles and period ratios of the reduced cell are the same as those in the unit cell of the basis structures. Allowing for this, the reduced unit cell periods and volume $V_i^{\text{red.c.}}$ and the reduced molar volume $V_i^{\text{red.}} = N_A V_i^{\text{red.c.}}/z$ (N_A is the Avogadro number, z the number of formula units in the unit cell) are calculated. If the unit cell of the basis structure has the angles α, β, and γ and the period ratios $a/c = m$ and $b/c = n$, while the surface area of the nonreduced units cell is equal to S, then

$$a_{\text{red.}} = [mnS/(\sin\alpha + m\sin\beta + n\sin\gamma)]^{(1/2)} \qquad [7]$$

and

$$V_i^{\text{red.}} = N_A a_{\text{red.}}^3 \times \sin\alpha \times \sin\beta \times \sin\gamma/mnz. \qquad [8]$$

The choice of the basis crystal structure is arbitrary, for reducing the molar volumes of the components to the same crystal structure ensures the same ratio between $V_i^{\text{red.}}$; i.e., $V_1 : V_2^{\text{red.(1)}} : \ldots : V_n^{\text{red.(1)}} = V_1^{\text{red.(2)}} : V_2 : \ldots : V_n^{\text{red.(2)}} = V_1^{\text{red.}(i)} : V_2^{\text{red.}(i)} : \ldots : V_i : \ldots : V_n^{\text{red.}(i)}$. Hence it is clear that the absolute value of the energy interaction parameters and interaction energy does not depend upon the specific crystal structure to which the molar volumes of the phase components are reduced. Indeed, as Eqs. [2]–[5] tell us, increasing the molar volume V_i of one component by a factor of k or decreasing the molar volume of the other by the same factor yields the same value of energy parameter e.

3. PHASE EQUILIBRIA

For the binary systems Ti–B and B–C, the phase diagrams have been constructed with the use of data (12, 14, 22). The phase diagram of Ti–C has been calculated with allowance for the ordering of a nonstoichiometric titanium carbide, TiC_y, employing the order parameters functional method (15, 23, 24). A detailed description of the Ti–C phase diagram with ordered titanium carbide phases is provided in (25). According to the calculation, ordered phases Ti_2C, Ti_3C_2, and Ti_6C_5 form in the region of homogeneity in titanium carbide TiC_y at a temperature below 930 K over various concentration intervals. Only the disordered TiC_y carbide is in thermodynamic equilibrium at higher temperature.

The liquidus surfaces for the pseudobinaries TiC_y–TiB_2 and B_4C_y–TiB_2 have been calculated by involving the subregular solution model described in Section 2. The energies B_ℓ and B_s and the energy parameters e calculated in accordance with Eqs. [2]–[5] for these pseudobinary systems can be represented by polynomials in the form

$$e = [a_0(y) + a_1(y)T + a_2(y)T^2] + x[b_0(y) + b_1(y)T + b_2(y)T^2]. \qquad [9]$$

For example, the values of the coefficients $a_i(y)$ and $b_i(y)$ of the mutual exchange energies B_ℓ and B_s of the pseudobinary system $(TiC_y)_{1-x}(TiB_2)_x$ are listed in Table 2.

For the general view of the Ti–B–C phase diagram over the temperature range 300–3500 K, refer to Fig. 1. The calculated temperatures of the binary eutectics in the pseudobinary TiC_y–TiB_2 and B_4C_y–TiB_2 systems give a good fit to experimental results (3) and are 100 to 200 K higher than the T_e values reportes in (5, 6). A comparison of the calculated invariances of the Ti–B–C system with the experimental (3, 5, 6) and calculated (9) data is shown in Table 1. In Fig. 2 we show the poythermal pseudobinary sections of $TiC_{0.6}$–TiB_2, $Ti_{0.8}$–TiB_2, $TiC_{1.0}$–TiB_2, and $B_4C_{0.89}(B_{4.5}C)$–TiB_2. The pseudobinary TiC_y–TiB_2 system has a eutectic whose composition and temperature depend on the carbon content of the titanium carbide TiC_y. As the composition of the titanium carbide is varied from $TiC_{0.6}$ to $TiC_{0.8}$ the eutectic temperature T_e increases from 2910 to 2961 K; a further increase in the carbon content of TiC_y decreases T_e toward 2936 K for $TiC_{1.0}$–TiB_2 (Figs. 2a, 2b, 2c; see also Table 1). Note that only $TiC_{0.8}$ carbide melts without a change in composition (congruently); titanium carbides with a different carbon content melt incongruently (with a change in composition). As a result, as the temperature is raised the composition of the titanium carbide, which is in equilibrium with the liquid, changes from $TiC_{0.6}$ to $TiC_{0.7}$ in the $TiC_{0.6}$–TiB_2 section (Fig. 2a); with the temperature being raised from 2936 to 3287 K, the composition of the carbide in equilibrium with the liquid varies in the section of $TiC_{1.0}$–TiB_2 from $TiC_{1.0}$ to $TiC_{0.905}$ (Fig. 2c).

TABLE 2

Coefficients of the Polynomials $\{[a_0(y)+a_1(y)T+a_2(y)T^2]+[b_0(y)+b_1(y)T+b_2(y)T^2]\}$ Approximating the Mutual Exchange Energies B_ℓ and B_s of the Pseudobinary $(TiC_y)_{1-x}(TiB_2)_x$ System

Coefficients	B_ℓ	B_s
$a_0(y)$ (kJ mol^{-1})	$56.49 - 59.68y$	$292.6 - 488.9y + 289.5y^2$
$a_1(y)$ (kJ mol^{-1} K^{-1})	$4.24 - 4.33y$	$-6.63 - 6.68y$
$a_2(y)$ (kJ mol^{-1} K^{-2})	$-0.04 + 0.07y$	$-2.43 - 5.63y + 3.83y^2$
$b_0(y)$ (kJ mol^{-1})	$22.31 - 23.62y$	$32.96 - 54.07y$
$b_1(y)$ (kJ mol^{-1} K^{-1})	$0.86 - 0.86y$	$21.31 - 46.09y + 30.44y^2$
$b_2(y)$ (kJ mol^{-1} K^{-2})	$-0.90 + 0.10y$	$-4.01 + 9.49y - 5.83y$

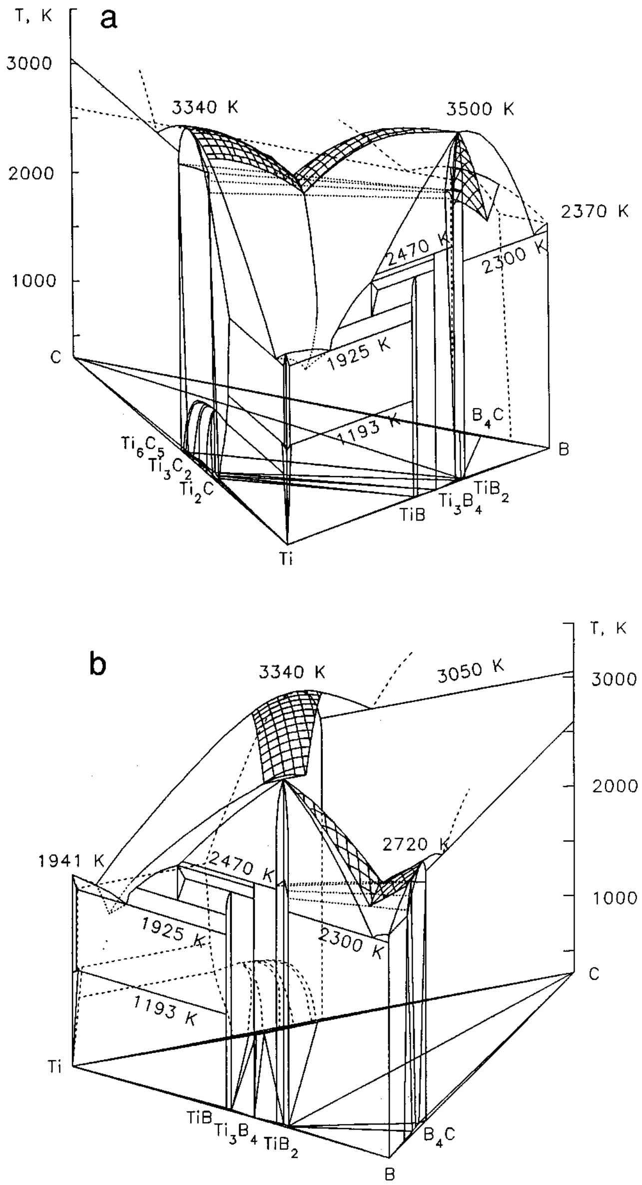

FIG. 1. The phase diagram of the Ti–B–C system over the temperature range 300–3500 K: (a) liquidus surface for the TiC_y–TiB_2 pseudobinary section (Ti_2C, Ti_3C_2, and Ti_6C_5 are the ordered phases of nonstoichiometric titanium carbide TiC_y); (b) liquidus surface for the B_4C_y–TiB_2 pseudobinary section.

The temperature of the eutectic of the pseudobinary system $B_4C_{0.89}$–TiB_2 is 2545 K (Fig. 2d). As the composition of the boron carbide $B_4C_{0.89}$ deviates towards a higher or lower carbon content there is a decrease in the eutectic temperature of the B_4C_y–TiB_2 section.

The isothermal section of the ternary Ti–B–C system at 300 K is shown in Fig. 3. Insertion of even a small (less than 0.8 at.%) amount of boron into a nonstoichiometric titanium carbide leads to disordering of the latter, so the disordered TiC_y carbide is in equilibrium with the titanium

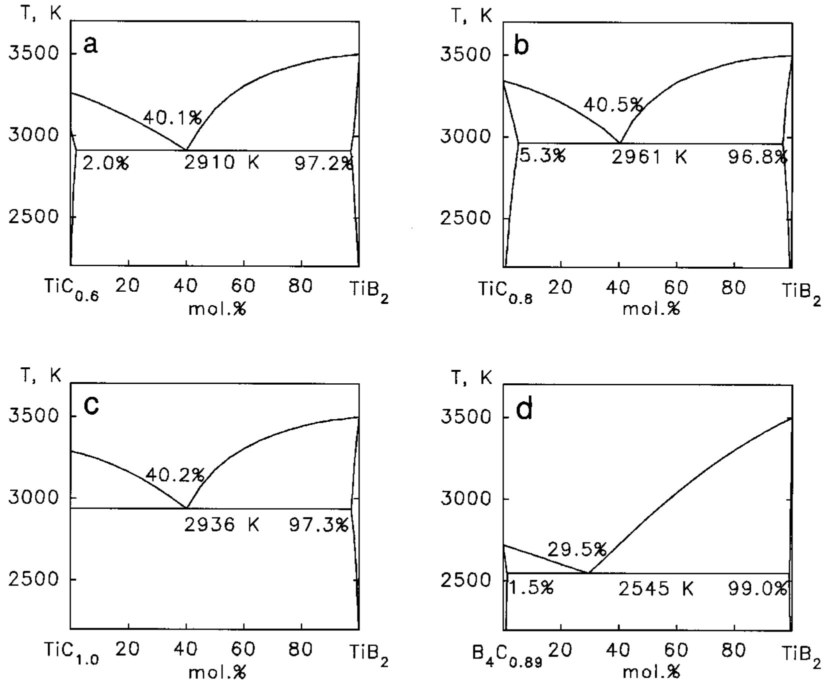

FIG. 2. Polythermal pseudobinary sections: (a) $TiC_{0.6}$–TiB_2; (b) $TiC_{0.8}$–TiB_2; (c) $TiC_{1.0}$–TiB_2; (d) $B_4C_{0.89}(B_{4.5}C)$–TiB_2.

borides TiB, Ti_3B_4, and TiB_2. The titanium boride TiB_2 coexists with not only TiC_y but also carbon C and the boron carbide B_4C. The calculated isothermal section remains virtually unchanged in form up to a temperature of 1900 K. The most dramatic change is associated with the disordering of the low-temperature ordered titanium carbide phases Ti_2C, Ti_3C_2, and Ti_6C_5 at $T \geq 950$ K; therefore, the only compound that remains in the Ti–C system at a higher temperature is nonstoichiometric disordered TiC_y carbide.

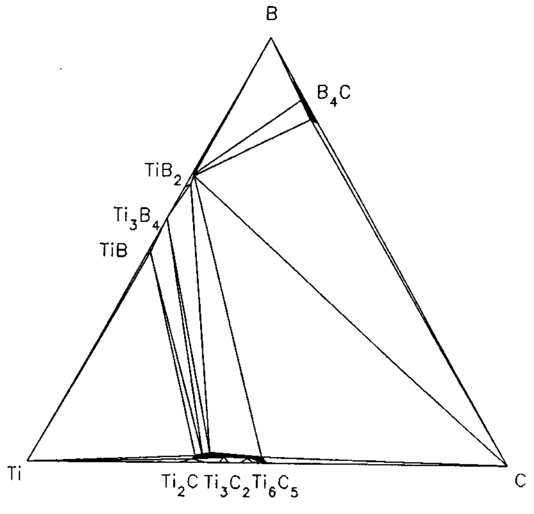

FIG. 3. Isothermal section of the Ti–B–C system at 300 K.

The results of the calculation of the ternary Ti–B–C system are in good agreement with the experimental findings available and testify that the subregular solution model can be applied to calculate and construct phase diagrams of ternary systems containing both stoichiometric and nonstoichiometric compounds.

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