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On the Ternary System Hafnium–Boron–Carbon

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Phase equilibria in the Hf–B–C system were calculated by thermodynamic modeling. The liquid phase was described as a substitutional solution using the Redlich–Kister formalism for the excess Gibbs energy and a reaction scheme was constructed for the entire ternary system. With respect to the increasing technological interest in dense ceramic parts HfB_2–"B_4C" with various degrees of $^{10}B/^{11}B$ enrichment as nuclear reactor control or moderator substances, we focus in this paper on the phase relations pertinent to the fabrication of HfB_2–"B_4C" ceramic material. © 2000 Academic Press

Key Words: **ternary system Hf–B–C; thermodynamic calculation; phase relations; isopleths Hf–"B_4C" and HfB_2–"B_4C."**

INTRODUCTION

The demand for dense ceramic parts of hafnium diboride and boroncarbide with various degrees of $^{10}B/^{11}B$ enrichment as nuclear reactor control or moderator substances has recently triggered increasing interest in the detailed knowledge of proper phase relations and melting temperatures in the system Hf–B–C. Based on a recent critical assessment and thermodynamic calculation of the phase equilibria in the Hf–B–C system by the authors (1) in the temperature range of 1400°C up to the melting range employing the ThermoCalc program system, we provide a detailed analysis on the phase relations involved in the fabrication processes of HfB_2–"B_4C" ceramic material which usually follow two major routes: (a) high-temperature hot pressing of fine powder grades of HfB_2 and "B_4C" or (b) reaction sintering starting from powders of "B_4C" and elemental hafnium plus boron.

Although several compilations of the most relevant data on the topology of the Hf–B–C system were published (2–5), the thermodynamic calculation (1) is essentially based on the experimental investigation by Rudy (6) of the entire constitutional system (isothermal section at 1400°C, three isopleths HfB_2–C, HfB_2–$HfC_{0.9}$, HfB_2–$B_{4.5}C$, and liquidus projection) assisted by independent studies of the isopleths HfB_2–C (7), HfB_2–HfC_{1-x} (8), and HfB_2–"B_4C" (9).

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BINARY SYSTEMS

Critical assessments of experimental data and corresponding thermodynamic calculations are available for all three binary boundary systems: B–C (10), Hf–B (11), and Hf–C (12). A partial phase diagram Hf–C was calculated (13) employing the order parameter functional method and essentially concerns (hypothetical) ordered superlattice phases at low temperatures (below ~520°C), Hf_3C_2 and Hf_6C_5, deriving from NaCl-type HfC_{1-x}. Data of the binary phase diagram are summarized in Table 1.

EXPERIMENTAL DATA ON THE TERNARY SYSTEM Hf–B–C

Phase equilibria at temperatures below 1800°C are characterized by the absence of ternary compounds and rather small mutual solid solubilities of the binary boride and carbide phases (6–9, 14). However, for the (B, C)-deficient solution $Hf(C, B)_{1-x}$ a maximum boron exchange of about 12 at% B was observed at a carbon deficiency of about 7 at% at 3140°C (6). The low B-solubility in HfC_{1-x} at 1400°C of about 2.5 at% B results in precipitation of HfB_2 on cooling which could not be suppressed at cooling rates lower than 100 K/s (6). Similar to boron containing TiC_{1-x} this effect may serve as a precipitation hardening of the hafnium monocarbide solution.

The phase relations obtained from the isothermal sections at 1400°C (6) and 1500°C (14) in combination with the experimental isopleths derived for HfB_2–C (6, 7), HfB_2–$HfC_{0.9}$ (6, 8) and HfB_2–"B_4C" (6, 9), all revealing eutectic pseudobinary behavior, as a consequence result in compatibility of HfB_2 + "B_4C" but incompatibility of the join Hf + "B_4C." Agreement exists on the experimental findings for the HfB_2–"B_4C" pseudobinary section between (6) (68 ± 4 mol% $B_{4.5}C$, originally given as 78 mol% $B_{0.817}C_{0.183}$ at 2330 ± 25°C) and the reinvestigation (9) (78 mol% "B_4C" at 2380 ± 30°C). These results have consequences for the fabrication of ceramic parts

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HfB$_2$ + "B$_4$C", where densification of powder mixtures HfB$_2$ + "B$_4$C" in the hot press may be achieved only at rather high subeutectic temperatures approaching 2300°C or via additions in form of densification aids operating at lower temperatures.

Microhardness measurements on samples in the isopleth HfB$_2$–"B$_4$C" near the eutectic composition were found to reveal values well below the linear combination of the binary compounds and to be strongly dependent on the eutectic crystallization conditions. Microhardness for the HfB$_2$–"B$_4$C" eutectic was reported to be 32 to 33 GPa (9).

THERMODYNAMIC CALCULATION OF THE TERNARY PHASE DIAGRAM

Details of the thermodynamic calculation of the ternary Hf–B–C system employing the ThermoCalc computer program (15) and the sublattice concept (16) were presented earlier (1). Here we shall only give the essential informations on the sublattices used in the modeling: liquid–(B, C, Hf)$_1$, βB–(B)$_{93}$(B, C)$_{12}$, graphite–(B, C)$_1$, ßHf–(Hf)$_1$(B, C, Va)$_3$, αHf–(Hf)$_1$(B, C, Va)$_{0.5}$, "B$_4$C"–(B$_{12}$, B$_{11}$C)$_1$(B$_2$, C$_2$B, B$_2$C, C)$_1$, HfC$_{1-x}$–(Hf)$_1$(B, C, Va)$_1$, HfB–(Hf)$_1$(B)$_1$ and HfB$_2$–(Hf)$_1$(B)$_2$. Referring to the Stable Element Reference (SER), the Gibbs energies of all phases are described relative to the enthalpies of the pure elements in their states stable at 298.15 K and 0.101325 MPa taken from (17).

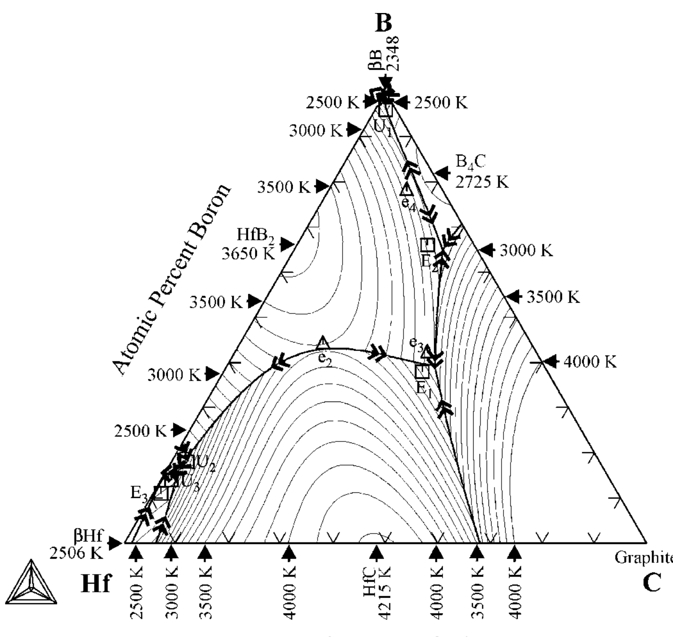

FIG. 1. Hf–B–C calculated liquids projection at 100 K intervals with experimental data from (6) (△ maximum in liquid trough, □ four-phase equilibrium); the symbols e_1, E_1, etc., and their corresponding temperature and concentration refer to Table 2.

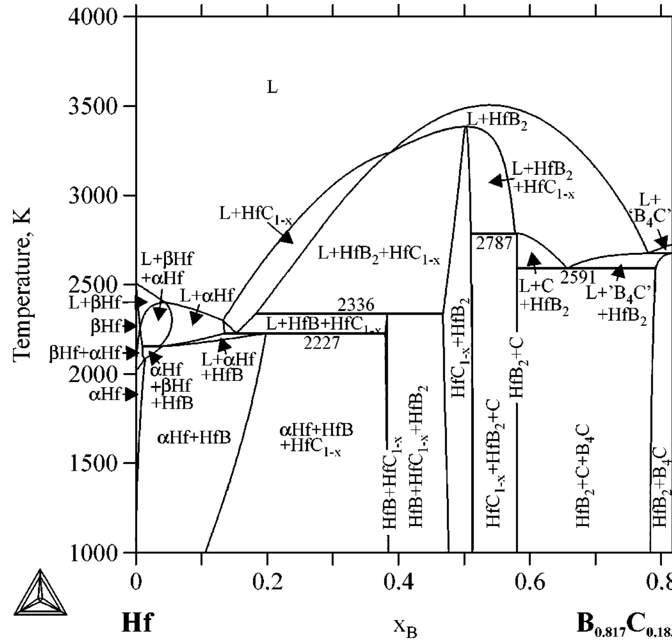

FIG. 2. Calculated isopleth from Hf to B$_{0.817}$C$_{0.183}$.

The assessed thermodynamic parameters of the Hf–B–C system are deposited with the *Journal of Solid State Chemistry* and may be obtained from the authors on request. The calculated liquidus surface is shown in Fig. 1, vertical sections in Figs. 2 to 4.

As seen from a comparison in Table 2, the calculation is in good agreement with the experimental observation. A

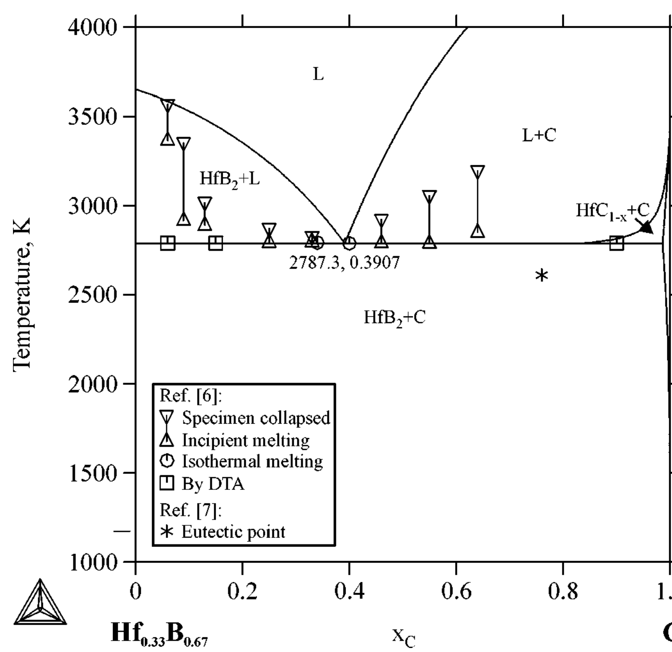

FIG. 3. Calculated isopleth "HfB$_2$–C" with experimental data from (6, 7).

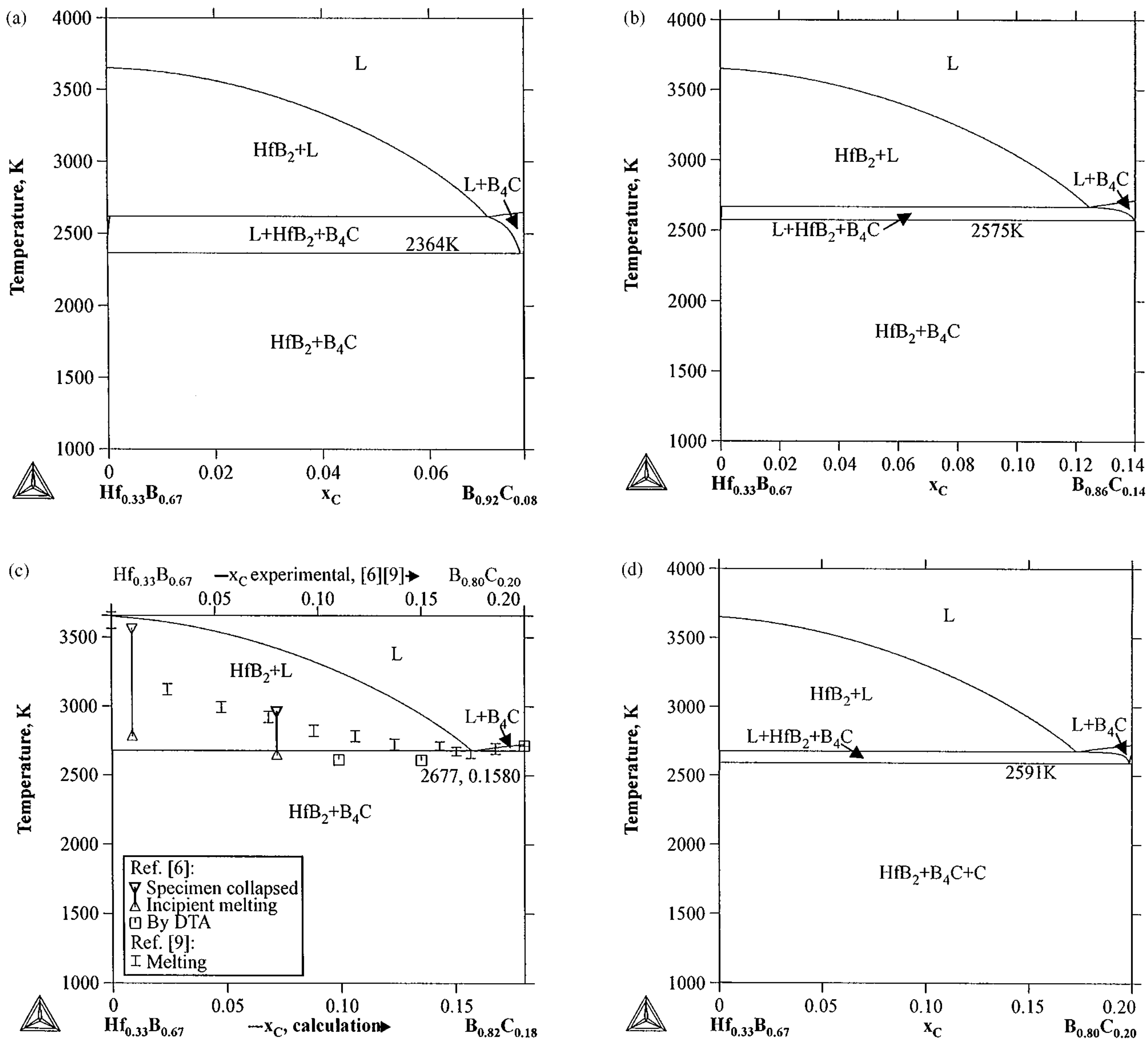

FIG. 4. Calculated isopleths "HfB_2–B_4C": (a) section HfB_2–$B_{0.92}C_{0.08}$, (b) section HfB_2–$B_{0.86}C_{0.14}$, (c) section HfB_2–$B_{0.82}C_{0.18}$, (d) section HfB_2–$B_{0.80}C_{0.20}$.

complete reaction scheme for the ternary Hf–B–C system is given in Fig. 5.

PHASE EQUILIBRIA INVOLVING "B_4C"

Table 2 compares the experimental compositions of the phases at the four-phase isothermal reactions (6) with the thermodynamic calculation. In the very boron-rich region the thermodynamic calculation favors a transition-type reaction at 2091°C, L + "B_4C" $\Leftrightarrow \beta$B + HfB_2, rather than a ternary eutectic at 1950°C, L $\Leftrightarrow \beta$B + "B_4C" + HfB_2, as reported by Rudy (6). This discrepancy essentially results from the latest assessment of the B–C system (10), revealing a peritectic reaction L + "B_4C" $\Leftrightarrow \beta$B at 2103°C rather than a eutectic L $\Leftrightarrow \beta$B + "B_4C" at 2080°C as believed earlier (6). The experimentally reported (6) sudden drop of more than 100°C and within less than 2 at% from the binary reaction isotherms into the ternary eutectic (at 1950°C) therefore seems unlikely and as a consequence cannot be obtained from thermodynamic modeling.

With the absence of a homogeneous binary range for HfB_2 as well as of any significant solubility of Hf in "B_4C"

TABLE 1
Calculated Data for the Binary Phase Diagrams B–C, Hf–B, and Hf–C

Reaction	Composition of respective phases,			Temperature, K (°C)	Reaction type
B–C system from [96Kas]		at% C			
L ⇔ "B_4C"	18.3	18.3	—	2725(2452)	Congruent
L ⇔ "B_4C" + C	29.3	19.5	97.7	2663(2390)	Eutectic
L + "B_4C" ⇔ βB	0.57	9.86	1.43	2376(2103)	Peritectic
L ⇔ βB	0	0	—	2348(2075)	Melting
Hf–B system from [97Bit1]		at% B			
L ⇔ HfB_2	66.7	66.7	—	3650(3377)	Congruent
L ⇔ βHf	0	0	—	2506(2233)	Melting
L + HfB_2 ⇔ HfB	22	66.7	50	2377(2104)	Peritectic
L ⇔ βB	100	100	—	2348(2075)	Melting
L ⇔ HfB_2 + βB	99	66.7	100	2338(2065)	Eutectic
L ⇔ βHf + HfB	15	1.1	50	2154(1881)	Eutectic
βHf + HfB ⇔ αHf	0.7	50	1.5	2064(1791)	Peritectoid
βHf ⇔ αHf	0	0	—	2016(1743)	Allotropic
Hf–C system from [97Bit2]		at% C			
L ⇔ HfC_{1-x}	48.4	48.4	—	4215(3942)	Congruent
L ⇔ HfC_{1-x} + C	68	49.9	100	3446(3173)	Eutectic
L + HfC_{1-x} ⇔ αHf	6.02	33.5	14	2649(2376)	Peritectic
L ⇔ βHf	0	0	—	2506(2233)	Melting
L ⇔ βHf + αHf	1.37	0.5	2.93	2480(2207)	Eutectic
βHf ⇔ αHf	0	0	—	2016(1743)	Allotropic

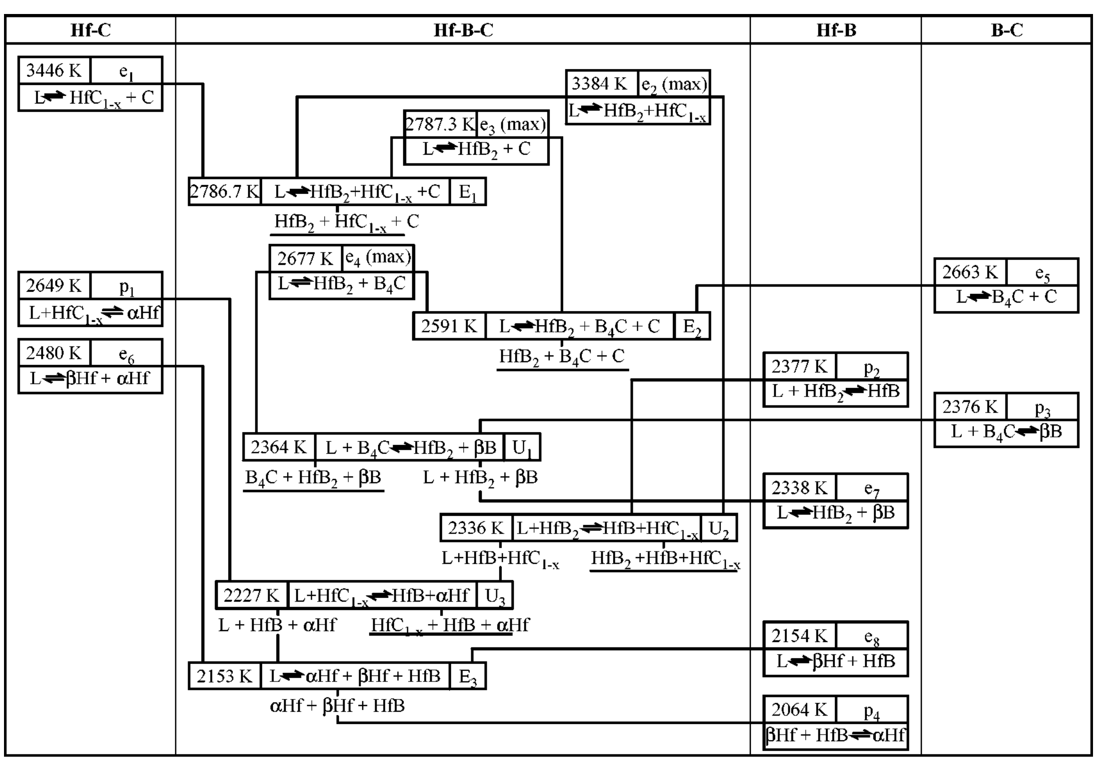

FIG. 5. Calculated reaction scheme for the Hf–B–C system.

TABLE 2
Isothermal Reactions in the Hf–B–C System: Comparison of Experimental Data from (6) with Calculated Data

		Experimental data				Calculated data				
		Composition (at%)				Composition (at%)				
Reaction	Phase	Hf	B	C	Temperature, K (°C)	Hf	B	C	Temperature, K (°C)	Reaction type
$L \rightleftharpoons HfB_2 + HfC_{1-x}$	L	40	44	16	3413(3140)	40.78	42.94	16.28	3384 (3111)	e_2(max)
	HfB_2	~34	>64	<2		33.33	66.67	0.00		
	HfC_{1-x}	~55	~12	~33		50.48	12.00	37.52		
$L \rightleftharpoons HfB_2 + C$	L	21	42	37	2788(2515)	20.18	40.75	39.07	2787.3 (2514.2)	e_3(max)
	HfB_2	>33	>64	<3		33.33	66.67	0.00		
	C	<1	~2	>97		0.00	0.95	99.05		
$L \rightleftharpoons HfB_2 + HfC_{1-x} + C$	L	24	38	38	2753(2480)	20.95	39.31	39.74	2786.7 (2513.6)	E_1
	HfB_2	~33	>64	<3		33.33	66.67	0.00		
	HfC_{1-x}	~51	~5	~44		50.05	4.35	45.60		
	C	<1	~2	>97		0.00	0.90	99.10		
$L \rightleftharpoons HfB_2$ + "B_4C"	L	~7	~78	~15	2603(2330)	4.20	80.00	15.80	2677 (2404)	e_4(max)
	HfB_2	~33	>65	<2		33.33	66.67	0.00		
	"B_4C"	<1	~81	>18		0.00	81.94	18.06		
$L \rightleftharpoons HfB_2$ + "B_4C" + C	L	~9	~66	~25	2533(2260)	6.64	64.88	28.48	2591 (2318)	E_2
	HfB_2	~33	>64	<3		33.33	66.67	0.00		
	"B_4C"	<1	~80	>19		0.00	80.43	19.57		
	C	<1	~2	>97		0.00	2.09	97.91		
L + "B_4C" $\rightleftharpoons HfB_2 + \beta B$	L	—	—	—	—	1.11	98.39	0.50	2364 (2091)	U_1
	"B_4C"	—	—	—		0.00	90.15	9.85		
	HfB_2	—	—	—		33.33	66.67	0.00		
	βB	—	—	—		0.00	98.58	1.42		
$L \rightleftharpoons HfB_2$ + "B_4C" + βB	L	~2	~96	~2	2223(1950)	—	—	—	—	
	HfB_2	~33	>66	<1		—	—	—		
	"B_4C"	<1	~89	>10		—	—	—		
	βB	<1	~98	<1		—	—	—		
$L + HfB_2 \rightleftharpoons HfB + HfC_{1-x}$	L	~79	~18	~3	2323(2050)	78.60	18.86	2.54	2336 (2063)	U_2
	HfB_2	~34	>64	<2		33.33	66.67	0.00		
	HfB	~50	>49	<1		50.00	50.00	0.00		
	HfC_{1-x}	~60	~9	~31		61.22	7.75	31.03		
$L + HfC_{1-x} \rightleftharpoons HfB + \alpha Hf$	L	~84	~14	~2	2213(1940)	82.05	15.62	2.33	2227 (1954)	U_3
	HfC_{1-x}	~62	~6	~32		62.75	6.50	30.75		
	HfB	~51	>48	<1		50.00	50.00	0.00		
	αHf	~90	~1	~9		92.27	0.45	7.28		
$L \rightleftharpoons \alpha Hf + \beta Hf + HfB$	L	~87.5	~11	~1.5	2123(1850)	85.01	14.92	0.07	2153 (1880)	E_3
	αHf	~96	~1	~3		97.74	1.30	1.96		
	βHf	>97.5	~1.5	<1		99.00	0.96	0.04		
	HfB	~50	49	<1		50.00	50.00	0.00		

and of "B_4C" in HfB_2, the maximum eutectic melting in the pseudobinary system HfB_2 + "B_4C" (experimentally observed at 2330°C, calculated at 2404°C, 2677 K) occurs on the tie line connecting HfB_2 with "B_4C" (at $B_{82}C_{18}$) via the maximum pseudoeutectic point. Samples with compositions deviating from this tie-line, either slightly richer in boron or poorer in boron, will in any case reveal a decrease in melting temperature toward the four-phase reaction isotherms: L + "B_4C" $\Leftrightarrow$ ßB + HfB_2, at 2091°C (2364 K, for boron-rich grades) or L $\Leftrightarrow$ "B_4C" + HfB_2 + C, at 2318°C (2591 K, for boron-poor grades). This feature of the phase diagram is seen from the isothermal section at 2350°C (2623 K; Fig. 6 and Table 2) and may explain the scatter in the experimental melting temperatures of samples with nominal compositions between HfB_2 and the range of concentrations for "B_4C" [6, 9]. The significantly lower melting temperatures of all those alloys deviating in composition from the maximum pseudoeutectic join HfB_2–$B_{82}C_{18}$ may provoke the use of additions of boron or carbon as system-intrinsic densification aids for short-term liquid phase sinter reactions in order to obtain dense ceramic parts "B_4C" + HfB_2 either in pressureless or pressure-assisted sinter techniques.

The alternative route to obtain dense ceramic parts "B_4C" + HfB_2 may start from the elemental powder blends or from proper powder blends Hf + B + B_4C.

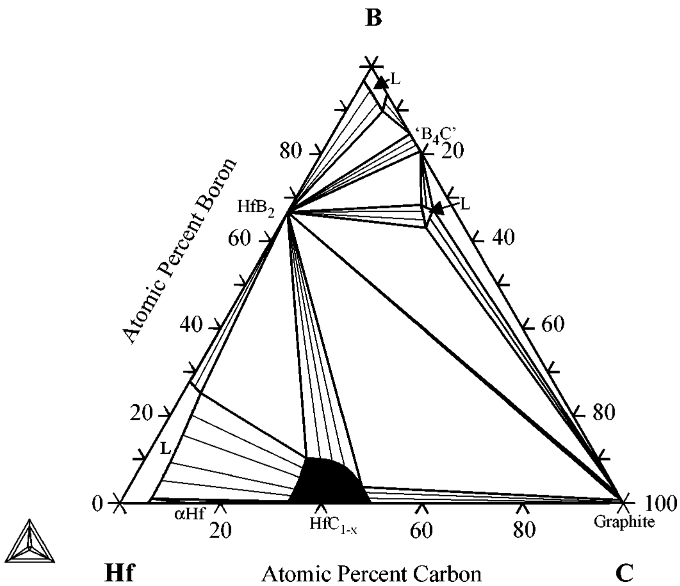

FIG. 6. Hf–B–C calculated isothermal section at 2623 K (2350°C).

According to the liquidus surface in Fig. 1 and the isopleth Hf + "B_4C" in Fig. 2, reactions in the latter case will run through low laying binary and ternary reaction isotherms involving densifying liquids: $L \Leftrightarrow Hf + HfB$ at 1881°C, $L \Leftrightarrow \beta B + HfB_2$, at 2065°C, L + "$B_4C$" $\Leftrightarrow \beta B$ at 2103°C, $L + HfB_2 \Leftrightarrow HfB$ at 2104°C, and L + "B_4C" $\Leftrightarrow (\beta B) + HfB_2$, at 2091°C. Thus for complete reaction via diffusion, a final reaction temperature close to 2100°C may still be essential.

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