High Temperature FeB-type Phases in the Systems Ta-{Ti,Zr,Hf}-B

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Novel FeB-type phases have been evaluated in the systems Ta-{Ti,Zr,Hf}-B either from as cast or arc treated samples by x-ray powder and single crystal diffraction as well as electron probe microanalysis. In each of the three systems the formation of the FeB-type phase suggests a high temperature stabilization of a binary group IV metal monoboride with FeB-type. This holds true for Ti and Hf, while for Zr the single crystal study of (Ta,Zr)B proves that it is a true ternary phase, as no stable monoboride exists in the binary Zr-B system. EPMA analyses reveal that the FeB-type phases Ta{Ti,Zr,Hf}B are formed by substitution of Ta in TaB by rather small amounts of group IV elements (~ 3 at.% of Zr, ~ 7 at.% Hf, and ~ 10 at.% Ti).

Keywords crystal structure, microstructure, refractory materials, x-ray analysis

1. Introduction

Monoborides of transition metals (T) constitute a unique group of crystal structures with characteristic infinite boron zig-zag chains compatible with covalent single bonds at a distance of $0.165 \text{ nm} < d_{\text{B-B}} < 0.190 \text{ nm}$ and a bond angle of $\sim 115^\circ$.^[1] As the boron atoms are coordinated by trigonal metal prisms, which share two of their rectangular faces, the crystal structures consist of infinite rows of metal prisms. The structure types of FeB, CrB (also described as TℓI-type) and α MoB are the most widely found binary monoborides.^[1,2] As shown in Fig. 1, simple geometrical relationships exist, which shift blocks of FeB- into CrB-type^[3] or blocks of CrB-type into α MoB-type.^[4] Due to these geometrically defined shift operations, randomly appearing shifts reduce the intensities of certain x-ray powder reflections in for instance a powder spectrum recorded on fine FeB powders synthe-

sized at 650°C (for details see Ref 5). A random stacking of CrB- and FeB-type units may freeze as an orthorhombic low temperature modification of FeB ($< 650^\circ\text{C}$).^[6] From near-neighbor diagrams it became obvious that the monoborides follow strong metal-boron interactions.^[7]

Simple shifts of structure slabs usually do not involve large transformation energies—thus most binary metal monoborides exhibit low and high temperature modifications for which a graphical distribution is shown in Fig. 2. Whereas the FeB-type involves the electropositive metals Ti, Hf as well as the 3d-metals Mn, Fe, Co, we see a gradual decrease in stability towards CrB and MoB variants moving towards the more electronegative metals. It is interesting to note that the monoborides of the Cr, Mo, W group exhibit a CrB-type high temperature modification and a low-temperature α MoB-type, but we so far only know the CrB-type for the neighbouring V, Nb, Ta group. The group of platinum metals sees a set of structures which are prone to defect sublattices such as {Ru, Os, Ir}B (WC-type = AlB_2 -type with ordered B-defect), RhB and PtB_{1-x} (NiAs-type derivatives) etc. (for details see Ref 1,2 and references therein).

Adding to binary transition metal borides a second transition metal component to form a ternary monoboride $\text{Ti}_{1-x}\text{TII}_x\text{B}$ (TI and TII are transition metals) usually leads to extended solid solutions eventually stabilizing one of the other monoboride structures or a novel arrangement such as the NbCoB_2 -type, which is an ordered combination of FeB- and CrB-type units.^[1] From the unsymmetrical distribution of the binary monoboride structure types among the transition metals, it appeared of interest to investigate the most refractory metal-boron combinations such as {Ti,Zr,Hf}-Ta-B. The corresponding phase equilibria have hitherto been determined at moderate temperatures (see Fig. 3) and, for the sections TaB-{Ti,Zr,Hf}B, have revealed extended solution phases of Ti,Zr,Hf in TaB and Ta in TiB.^[8-10] It should be noted here that HfB (FeB-type) was not considered for the equilibria at 1400°C ,^[10] although earlier studies have documented its existence and peritectic decomposition at 2218°C .^[11-13] ZrB with NaCl-type is

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$$V_{\text{FeB}} = V_{\text{CrB}} \Leftrightarrow a_{\text{FeB}} \times b_{\text{FeB}} \times c_{\text{FeB}} = a_{\text{CrB}} \times b_{\text{CrB}} \times c_{\text{CrB}}$$

$$a_{\text{FeB}} = \frac{2 \times a_{\text{CrB}} \times b_{\text{CrB}}}{\sqrt{a_{\text{CrB}}^2 + b_{\text{CrB}}^2}}; \quad b_{\text{FeB}} = c_{\text{CrB}}; \quad c_{\text{FeB}} = \frac{1}{2} \sqrt{a_{\text{CrB}}^2 + b_{\text{CrB}}^2}$$

(a)

Fig. 1 (a) Upper panel, left: projection of the FeB structure along its b-axis; upper panel, right: shift of three slabs of the FeB-type atom arrangement along $\frac{1}{2}c$ creating the atom arrangement of the CrB-type. Metal atoms in blue; boron atoms in red. The unit cells of FeB and CrB (both orthorhombic) are outlined with bold frames. (b) Lower panel, top: the structures of CrB and of αMoB , both projected along the a-axis; lower panel, bottom: schematic arrangement of CrB-type slabs; every second CrB slab is shifted by $\frac{1}{2}a + \frac{1}{2}c$ and creates the atom arrangement of αMoB . Random stacking faults may appear creating diffuse x-ray reflections (Color figure online)

impurity (C,N,O) stabilized, but the degree of thermodynamic stability of the ZrB-phase with FeB-type has been evaluated.^[14] With an estimated heat of formation of $\Delta H_f^0 \sim -84$ kJ/(g.at.ZrB) it was shown that ZrB with FeB-

type can only be stable below 590 °C with respect to αZr and ZrB_2 .^[14]

A preliminary check of arc melted monoboride alloys $\text{Ta}_{1-x}\{\text{Ti,Zr,Hf}\}_x\text{B}$ ($x \sim 0.2$) interestingly revealed in all

three cases a major phase fraction of an FeB-type compound (i) either supporting a stabilization of the group-IV FeB-type phase, or (ii) a novel ternary phase separated from both

Fig. 2 Distribution of monoboride structure types among binary transition metal borides

metal binaries. In any case the extended CrB-type phase solutions $Ta_{1-x}\{Zr,Hf\}_xB$ (up to $x \sim 0.6$) claimed in the literature^[9,10] (for details see Fig. 3) are not seen at subsolidus temperatures. Therefore this paper will address the formation of ternary FeB-type monoborides in the afore mentioned combinations at elevated temperatures.

2. Experimental Details

Alloys $Ta_{1-x}T_xB$ ($x = 0.32$ for $T = Ti$; $x = 0.2, 0.22$ for Hf and $x = 0.2, 0.3$ for Zr) were prepared from metal ingots of Ti, Zr, Hf (purity 99.9 mass%), Ta-foil (99.9%) and pieces of crystallized B (purity 99.5 mass%), all from Alfa Johnson Matthey GmbH, Germany, by repeated arc melting under argon. B-pieces—although wrapped in the corresponding

Fig. 3 Phase relations in isothermal sections as shown in the literature for the ternary diagrams Ti-Ta-B (1250 °C),^[8] Zr-Ta-B (1500 °C),^[9] and Hf-Ta-B (1400 °C).^[10] The small circles represent the composition of samples investigated in this work

mass of Ta-foil—tend to shatter under the arc and were replenished in several meltings so that overall weight losses were kept below 1%, however, the Ta:T ratio after synthesis was always within 0.1% of the nominal values (as monitored by EPMA—see below). With a melting temperature of TaB at 3090 ± 15 °C,^[13,15] subsolidus temperatures of the alloys near TaB are significantly higher than temperatures available for annealing in W-mesh furnaces. Therefore some reguli have been “heat-treated” directly after arc melting at subsolidus temperatures for 5 min running the arc at slightly lower energy than needed for melting. In the following, these alloys are labeled as “low-arc” samples.

Lattice parameters and standard deviations were determined by least squares refinements of room temperature x-ray powder diffraction (XRD) data obtained from a Guinier-Huber image plate employing monochromatic Cu K α_1

radiation and Ge as internal standard ($a_{\text{Ge}} = 0.565791$ nm). XRD-Rietveld refinements were performed with the FULLPROF program^[16] with the use of its internal tables for atom scattering factors.

All samples were polished using standard procedures. Microstructures/phase distributions were examined by scanning electron microscopy. For composition analyses, electron probe microanalysis (EPMA) measurements (point measurements and scans) were performed on a Zeiss Supra 55 VP scanning electron microscope, operated at 20 kV and ~60 μA employing energy dispersive x-ray (EDX) analysis for determining the metal ratios Ta:{Ti,Zr,Hf}. Pure elements served as standards.

Single crystals of Ta $_{1-x}$ Zr $_x$ B were isolated via mechanical fragmentation of an arc melted specimen with nominal composition Ta $_{0.80}$ Zr $_{0.20}$ B. X-ray single crystal diffraction (XSCD) data were collected at room temperature on a

Table 1 Lattice parameters (from XRD) and corresponding EPMA data for the phases in Ta $_{1-x}$ T $_x$ B alloys, T = Ti,Zr,Hf

Composition/code	PC [#]	Phase(structure type)	Lattice parameters, nm			EPMA, at.% (± 0.5)			Mass%
			a	b	c	T	Ta	B ^S	
TaB	Arc	TaB (CrB)	0.32795(2)	0.8671(2)	0.31552(1)	...	49.0	51.0	100
Ta $_{0.8}$ Zr $_{0.2}$ B	Arc*	(Ta,Zr)B (FeB)	0.6207(10)	0.3174(2)	0.4749(8)	3.8	46.2	50	73
		(Ta,Zr)B (FeB)	0.6153(11)	0.31648(5)	0.4674(7)	12.0	38.0	50	26
		Ta(Zr) (W)	...	...	...	92.5	7.5	...	1
		(Ta,Zr)B (FeB)	0.6134(25)	0.31689(9)	0.4839(73)	3.2	46.8	50	35
Ta $_{0.8}$ Zr $_{0.2}$ B #1	Arc (1)*	(Ta,Zr)B (FeB)	0.6162(3)	0.31627(5)	0.4704(1)	7.1	42.9	50	63
		Ta(Zr) (W)	...	...	...	73.5	26.5	...	2
		(Ta,Zr)B (FeB)	0.6147(1)	0.31638(5)	0.46754(3)	3.4	46.6	50	43
		(Ta,Zr)B (CrB)	0.32865(7)	0.8687(11)	0.31659(3)	4.5	45.5	50	42
Ta $_{0.8}$ Zr $_{0.2}$ B #2	Arc (2)*	Ta(Zr) (W)	...	...	...	18.7	81.3	...	15
		(Ta,Zr)B (FeB)	0.6162 (2)	0.31616(1)	0.4717(2)	8.5	41.5	50	38
		(Ta,Zr)B (FeB)	0.6258 (1)	0.31647(1)	0.46861(3)	6.1	43.9	50	58
		Ta(Zr) (W)	...	...	...	89.9	10.1	...	4
Ta $_{0.8}$ Hf $_{0.2}$ B	Arc	(Ta,Hf)B (FeB)	0.6188 (4)	0.31576(1)	0.4711(3)	9.6	40.4	50	74
		(Ta,Hf)B (FeB)	0.6148(17)	0.3170 (1)	0.4646(45)	5.8	44.2	50	26
Ta $_{0.78}$ Hf $_{0.22}$ B	Arc	(Ta,Hf)B (FeB)	0.61800(7)	0.31577(2)	0.47025(4)	8.6	41.4	50	58
		(Ta,Hf)B (FeB)	0.6168(2)	0.31593(3)	0.4693(2)	7.2	42.8	50	23
		Ta(Hf) (W)	0.3376(1)	...	...	41.3	58.7	...	19
		(Ta,Ti) $_3$ B $_4$ (own)	0.30961(3)	0.32768(3)	1.3921(5)	11.4	28.8	59.9	23
Ta $_{0.68}$ Ti $_{0.32}$ B #1	Slow cooled	(Ta,Ti)B (CrB)	0.32645(1)	0.86517(1)	0.31387(1)	9.3	40.7	50	4
		(Ta,Ti)B (FeB)	0.6121(4)	0.31166(4)	0.4646(1)	12.8	37.2	50	46
		(Ta,Ti)B (FeB)	0.6158(2)	0.31163(3)	0.4685(1)	11.0	39.0	50	13
		(Ta,Ti)B $_2$ (AlB $_2$)	0.30509(3)	...	0.32412(5)	13.4	19.7	66.9	13
		Ta(Ti) (W)	...	...	...	...	...	...	<1
		(Ta,Ti) $_3$ B $_4$ (own)	0.3099(2)	0.3277(2)	1.396(5)	10.3	34.6	55.1	9
		(Ta,Ti)B (CrB)	0.32761(3)	0.8729(5)	0.31253(2)	9.3	40.7	50	7
		(Ta,Ti)B (FeB)	0.61222(8)	0.31216(1)	0.46469(4)	12.8	37.2	50	72
Ta $_{0.68}$ Ti $_{0.32}$ B #2	Low arc	(Ta,Ti)B $_2$ (AlB $_2$)	...	...	...	15.4	17.0	67.7	5
		Ta(Ti) (W)	0.3288(8)	...	...	...	...	...	7

[#] PC stands for processing conditions

^S For all transition metal monoborides, the B content is assumed to be 50 at. %

* Same nominal composition prepared in different batches

Broker APEXII diffractometer equipped with a CCD area detector and an Incoatec Microfocus Source I μ S (30 W, multilayer mirror, Mo K α). Several sets of phi- and omega-scans with 2.0° scan width were measured at a crystal-detector distance of 3 cm (full sphere; 2° < 2 θ < 81°). The crystal structures were solved applying direct methods (program SHELXS-97) and refined against F² (SHELXL-97-2)^[17] within the program WinGX.^[18] The crystal structures were all standardized with the program Structure Tidy.^[19] Further details concerning the experiments are given in Table 1.

3. Results and Discussion

3.1 Formation of FeB-type Compounds in the Systems Ta-(Ti,Zr,Hf)-B

Table 1 summarizes the results of the combined evaluation of x-ray lattice parameters and EPMA-compositions of the phases in the ternary alloys investigated. X-ray powder patterns in most cases document the existence of three-phases: (i) a CrB-type phase (presumably linking to a solid solution extending from binary TaB, (ii) an FeB-type phase (which defines the ternary T-substituted phase) and (iii) in smaller amounts a softer matrix phase with W-type structure (consistent with the binary Ta-T solid solutions). EPMA line-scans over the large monoboride dendrites in the microstructures revealed significant coring effects in the solidification process, which is also obvious from the corresponding x-ray powder patterns: central and peripheral areas of the dendrites (or small dendrites) give rise to broadened x-ray intensity peaks. Furthermore primary dendrites and secondary precipitates in solidification produce identical x-ray intensity patterns (FeB-type) but with slightly different lattice parameters (doubling of peaks). Although derived from non-equilibrium alloys—some slowly cooled in the arc, some “quenched” (equivalent to cooling in the argon filled arc melter by removing the arc) from high temperature, the spread of lattice parameters and corresponding compositions of the FeB-type phase in each alloy can be taken as a sign for the extent of a phase region in the phase diagram.

For the binary Ta-B system, EPMA data as well as Rietveld refinement of an as cast alloy with composition of Ta₅₀B₅₀ (in at.%) clearly document CrB-type as the only phase constituent. Whereas FeB-type solid solutions for T = Ti,Zr,Hf comprise the compositions Ta_{1-x}Ti_xB for 0.22 < x < 0.26 and Ta_{1-x}Zr_xB for 0.06 < x < 0.24; the dendrites of Ta_{1-x}Hf_xB indicate a composition range for 0.12 < x < 0.20 (see Fig. 4). From the three transition elements zirconium is unique, as hitherto there has been no binary FeB-type compound ZrB experimentally observed.^[13,20] Therefore FeB-type Ta_{1-x}Zr_xB is a truly ternary phase, whilst the solutions Ta_{1-x}Ti_xB for T = Ti,Hf may be considered as a simple stabilization of binary FeB-type phases TiB ($T_m = 2190 \pm 25$ °C),^[12,13] and HfB ($T_m = 2100 \pm 20$ °C)^[12,13] to higher temperatures via Ta/T-substitution. A similar situation is met for the homologous

Fig. 4 Compositional dependence of lattice parameters and ranges of existence (indicated by arrows) of the FeB-type phases Ta_{1-x}{Ti,Zr,Hf}_xB

section Nb_{1-x}Ti_xB for which large ternary mutual solid solubilities in the corresponding CrB- and FeB-type phases extend far into the ternary and which at 2650 ± 15 °C are separated by a small two-phase region of about 5 at.% metal.^[21]

3.1.1 The Ta-Ti-B System. Two samples in the Ta-Ti-B system with nominal composition Ta_{0.68}Ti_{0.32}B were subjected to two different processing conditions: slow cooling by gradually reducing the power of the arc (#1) and arc treatment at low power (#2). Microstructure analyses of both samples (see Fig. 5a, b) show a significant segregation, where in one side the overall composition shifts towards the B-rich side, thus contains B-rich binary (Ta,Ti)-B phases such as (Ta,Ti)₃B₄ and (Ta,Ti)₂B₃. The other part of the samples shows only monoboride phase(s). This observation was also confirmed by analysis of XRD patterns via Rietveld refinements, which document B-rich binary (Ta,Ti)-B phases and monoborides with FeB/CrB-type.

Sample #1 (see Fig. 5a) shows significant coring effects in the B-poor side, which is not visible in sample #2 (Fig. 5b). Note that the different contrast in sample #2 is due to grain orientation effects. The slowly cooled sample shows two FeB-type phases, (Ta,Ti)B, with very close Bragg positions. On the other hand the XRD pattern of sample #2 does not reveal any doubling of FeB-type peaks, and the pattern could be satisfactorily refined with only one FeB-type phase (see Table 2). Despite XRD shows a small quantity of (Ta,Ti)B with CrB-type (~8 wt.%), it was not possible to distinguish the CrB-type from the FeB-type by phase composition, i.e. from the Ta/Ti ratio as EDX measurement showed rather similar values. Nevertheless, we can differentiate three groups of data (only two in sample #2), one with a highest Ta/Ti ratio (4.4), and two sets with a lower Ta/Ti ratio (3.5 and 2.9) (see Table 1 for details). In

Fig. 5 (a) XRD pattern and micrographs of Ta_{0.68}Ti_{0.32}B #1 (slowly cooled) samples. (b) XRD pattern and micrographs of Ta_{0.68}Ti_{0.32}B #2 (low arc power treated) sample

Fig. 6 (a) XRD pattern and micrographs of $\text{Ta}_{0.80}\text{Zr}_{0.20}\text{B}$ #1 sample. (b) XRD pattern and micrographs of $\text{Ta}_{0.80}\text{Zr}_{0.20}\text{B}$ #2 sample

such a case, however, we can assume that the monoboride with the highest Ta/Ti ratio belongs to the CrB-type, which represent the end of solid solution $(\text{Ta,Ti})\text{B}$ with CrB-type, whereas those with lower Ta/Ti ratio represents the end of the $(\text{Ta,Ti})\text{B}$ solid solution with FeB-type.

3.1.2 The Ta-Zr-B System. Formation of the FeB-type phase $(\text{Ta,Zr})\text{B}$ in the Ta-Zr-B system has been investigated with four samples: three with nominal composition

$\text{Ta}_{0.80}\text{Zr}_{0.20}\text{B}$ and one with $\text{Ta}_{0.70}\text{Zr}_{0.30}\text{B}$. In most cases samples look homogeneous except for $\text{Ta}_{0.70}\text{Zr}_{0.30}\text{B}$ where some parts contain a larger amount of (Ta,Zr) phase with W-type. In all cases $(\text{Ta,Zr})\text{B}$ with FeB-type is the major constituent.

Figure 6a, b shows the XRD patterns and micrographs of two $\text{Ta}_{0.80}\text{Zr}_{0.20}\text{B}$ samples with different phase constituents. Sample #1 (Fig. 6a) shows only two FeB-type phases

Table 2 Structural data for (Ta,Ti)B from Rietveld refinement (Guinier-Huber Image Plate, Cu K α 8° ≤ 2 Θ ≤ 100°); standardized with program *Structure Tidy*^[19]

Parameter/compound	Ta _{1-x} Ti _x B, x = 0.25
Structure type	FeB
Space group type (No.)	<i>Pnma</i> (62)
<i>a</i> (nm)	0.61222(8)
<i>b</i> (nm)	0.31216(1)
<i>c</i> (nm)	0.46469(4)
Reflections in refinement	61
Number of variables	16
R _F = F _o - F _c /F _o	0.0217
R _I = I _o - I _c /I _o	0.0314
R _{WP} = [w _i y _{oi} - y _{ci} ² /w _i y _{oi} ²] ^{1/2}	0.113
R _P = y _{oi} - y _{ci} / y _{oi}	0.10
R _c = [(N - P + C)/w _i y _{oi} ²] ^{1/2}	0.0272
χ^2 = (R _{WP} /R _c) ²	17.25
M in 4c (x, 1/4, z); occ.	x = 0.1758(1); z = 0.6239(1); 0.75(1) Ta + 0.25 Ti
B _{iso} (10 ² nm ²)	0.56
B in 4c (x, 1/4, z); occ.	x = 0.037(1); z = 0.111(2); 1.00(-)
B _{iso} (10 ² nm ²)	0.54

(Ta,Zr)B in combination with smaller amounts of (Ta,Zr) matrix (W-type), with a high amount of Zr solved in the (Ta,Zr) matrix (> 70 at.% Zr). This situation is also observed in the sample with higher amount of Zr (Ta_{0.7}Zr_{0.3}B). On the other hand sample #2 (Fig. 6b) shows almost equal amounts of FeB- and CrB-type phases (Ta,Zr)B. In this sample the (Ta,Zr) matrix shows more Ta (~80 at.% Ta) than Zr. The difference in the phase constitutions may arise from a somewhat lower B content in sample #2. Note that in both samples the difference in the Ta:Zr ratio for the monoborides between different grains is not greater than 5 at.%. Similar to the Ta-Ti-B system, one can assume that the monoboride with the higher Ta:Zr ratio corresponds to the CrB-type.

3.1.3 The Ta-Hf-B System. Two samples with nominal composition Ta_{0.80}Hf_{0.20}B and Ta_{0.78}Hf_{0.22}B reveal only (Ta,Hf)B monoborides with FeB-type. Both samples exhibit coring and secondary precipitation, which results in broadening and doubling of XRD reflections. The doubling can be identified easily in the Ta_{0.80}Hf_{0.20}B sample (Fig. 7a), whilst for Ta_{0.78}Hf_{0.22}B the reflections between the two FeB-type phases (Ta,Hf)B closely overlap (see Fig. 7b). This phenomenon is also confirmed by EPMA measurements, which show significant differences in the Ta:Hf ratio measured throughout the sample Ta_{0.80}Hf_{0.20}B (~5 at.%) whilst the difference for alloy Ta_{0.78}Hf_{0.22}B is less than 2 at.%. These differences are seen in EPMA line scans across large grains with coring effect, whereas small grains reveal large grains.

3.2 The Crystal Structure of Ta_{0.76}Zr_{0.24}B with FeB-type

In order to prove the FeB-type structure, a single crystal (SC) was chosen from the system Ta-Zr-B. The crystal was broken from an arc melted specimen with nominal composition Ta_{0.8}Zr_{0.2}B, for which EPMA revealed a composition

Ta₃₈Zr₁₂B₅₀ (in at.% $\equiv$ Ta_{0.76}Zr_{0.24}B) for rather homogeneous crystallites of ~25 μ m diameter, suitable for x-ray structure analysis. An FeB-type compound in this system will thus constitute a truly ternary phase, as a stable monoboride phase was hitherto experimentally not recorded in the high purity binary Zr-B phase diagram. The “ZrB”-phase with NaCl-type, which is occasionally listed in structure and phase diagram compilations, was shown to be a (C,N,O)-stabilized phase (for a detailed discussion see Ref 14.).

Analyses of the x-ray single crystal intensity data, particularly of the systematic extinctions (observed for $0kl$, $k + l = 2n + 1$ and $hk0$ for $h = 2n + 1$), prompted an orthorhombic unit cell ($a = 0.617526(11)$ nm, $b = 0.316427(5)$, $c = 0.469934(9)$ nm) consistent with space group symmetry *Pnma* (No. 62), which, as the highest symmetric one, was chosen for further structure analysis. Direct methods delivered a structure solution with metal atoms in site 4c. The boron atoms were unambiguously located via a difference Fourier synthesis in a further 4c-site. A free variable on the Ta/Zr ratio yields only a slightly lower Zr content than that determined by EPMA. With only one 4c-site for the metal atoms, no ordering among Ta/Zr atoms is possible and no evidence exists from the x-ray diffraction spectra for supercell reflections. A final refinement (with Ta/Zr ratio inserted from EPMA) inferring anisotropic atom displacement parameters (ADP's) in general but isotropic ADP's for the boron site converged to an R-value R_{F2} = 0.0165 with Fourier ripples in the electron density of less than 3.2 e⁻/Å³ at 0.09 nm from B. The value of the isotropic ADP of boron atoms confirms full occupancy of the B-site corresponding to a B-defect free monoboride. The parameters derived from refinement for Ta_{0.76}Zr_{0.24}B are listed in Table 3 including interatomic distances. A search for the structure type in Pearson's Crystal Data^[1] and in ICSD (Fachinformationszentrum Karlsruhe)^[22] involving also the Wyckoff sequence c^2 ,

Fig. 7 (a) XRD pattern and micrographs of $\text{Ta}_{0.80}\text{Hf}_{0.20}\text{B}$ sample. (b) XRD pattern and micrographs of $\text{Ta}_{0.78}\text{Hf}_{0.22}\text{B}$ sample

prompted isotypism with the (undisturbed) structure of FeB in its high temperature form.

Interatomic distances in Table 3 show that boron-boron distances, $d_{\text{B-B}} = 0.188$ nm, in $\text{Ta}_{0.78}\text{Zr}_{0.22}\text{B}$ appear somewhat increased with respect to the boron chain in binary FeB with significantly smaller metal (Fe) atoms: $d_{\text{B-B}} = 0.1785$ nm (from x-ray SC data;^[23] or $d_{\text{B-B}} = 0.1783$ nm, from unpolarized neutron diffraction SC data^[24]). Bonds from B to the six Ta/Zr atoms within the

trigonal prisms are rather homogeneous, $0.240 \text{ nm} < d_{\text{B-Ta/Zr}} < 0.243 \text{ nm}$, and are close to the sum of radii ($R_{\text{Ta}} = 0.1467 \text{ nm}$, $R_{\text{Zr}} = 0.1602$, $R_{\text{B}} = 0.088 \text{ nm}$ ^[25]) documenting a strong metal-boron interaction. The characteristic feature of compounds with the FeB-type structure (see Fig. 1, 8) is the infinite boron zig-zag chain (along the b -axis) with a bond distance range of $0.165 \text{ nm} < d_{\text{B-B}} < 0.190 \text{ nm}$, and with bond angles of $\phi_{\text{B-B-B}} \sim 115^\circ$.^[2] As each boron atom is close to the centre of a triangular

Table 3 X-ray single crystal data[#] for Ta_{0.76}Zr_{0.24}B (FeB-type; space group *Pnma*) at RT (anisotropic displacement parameters U_{ij} in [10⁻² nm²])

Parameter/compound	Ta _{0.76} Zr _{0.24} B
Phase composition (EPMA, at.%) [*]	Ta ₃₈ Zr ₁₂ B ₅₀
Composition from refinement (at.%)	Ta ₃₈ Zr ₁₂ B ₅₀
<i>a</i> [nm]	0.617256(11)
<i>b</i> [nm]	0.316427(5)
<i>c</i> [nm]	0.469934(9)
θ range (deg)	2.7 < 2θ < 80.74
Mosaicity	0.54
Number of variables	10
Reflections in refinement	282 ≥ 4r(F _o) of 319
R _{F2} = F _o ² - F _c ² /F _o ²	0.0165
wR2	0.0451
R _{int}	0.053
GOF	1.203
Extinction (Zachariasen)	0.007(1)
Residual density e ⁻ /Å ³ ; max; min	3.21; -3.14
Atom positions	
0.76(4) Ta + 0.24 Zr in 4c (x, ¼, z)	x = 0.17579(3); z = 0.62342(5)
U ₁₁ ; U ₂₂ ; U ₃₃ ; U ₂₃ = U ₁₂ = 0; U ₁₃	0.0021(1); 0.0026(1); 0.0019(1); 0.0002(1)
B in 4c (x, ¼, z); occ.	x = 0.0315 (9); z = 0.1004(13); 1.00(-)
U _{iso}	0.0055(9)

Interatomic distances, nm; Standard deviation < 0.0001

Atom 1	Atom 2	Distance, nm
B	2 B	0.1883
	2 Ta/Zr	0.2404
	2 Ta/Zr	0.2412
	Ta/Zr	0.2413
	Ta/Zr	0.2434
	Ta/Zr	0.2614
	Ta/Zr	0.2614
Ta/Zr	2 B	0.2404
	2 B	0.2412
	B	0.2413
	B	0.2434
	B	0.2614
	2 Ta/Zr	0.2925
	4 Ta/Zr	0.2977
	2 Ta/Zr	0.3164
	2 Ta/Zr	0.3307

[#] Standardized with program *Structure Tidy*^[19]

^{*} The highest Zr/Ta ratio (after EPMA) for the sample from where the single crystal was selected

Bonding angle in boron zig-zag chain: φ_{B-B-B} = 114.3°

metal prism, infinite columns of those prisms connected along their rectangular faces follow the direction of the boron chains. One of the rectangular faces of the triangular metal prism is capped by a metal atom linking adjacent columns of prisms. With d_{B-Ta/Zr} = 0.2614 nm the distance to the capping metal atom is only slightly longer than those to the prism-forming Ta/Zr atoms. Due to strong covalent boron-boron bonds, boron defects in the metal borides with CrB-type, MoB-type and FeB-type are rare (see Ref 2).

4. Conclusions

The existence of novel high temperature FeB-type phases Ta{Ti,Zr,Hf}B have been confirmed either from as cast or arc treated samples by x-ray powder and single crystal diffraction and electron probe microanalysis. In most cases the FeB-type monoboride is the major constituent, which suggests that this phase is the high temperature stabilization

Fig. 8 Connectivity of mono-capped triangular prisms of Ta/Zr-atoms in $\text{Ta}_{0.8}\text{Zr}_{0.2}\text{B}$ sharing triangular faces. Each mono-capped metal prism is centered by a boron atom: $[\text{Ta}(\text{Zr})_7]\text{B}$ forming infinite -B-B-B- chains running parallel to the b-axis inferring also infinite chains of Ta/Zr-prisms sharing their rectangular faces. Ta/Zr-atoms in blue are presented with ADPs from single crystal refinement, isotropic B-atoms (ADP from SC refinement) are red (Color figure online)

of a binary group IV metal monoboride. This holds true for Ti and Hf, while for Zr the evaluation proves that $(\text{Ta},\text{Zr})\text{B}$ with FeB-type is a true ternary phase, as no stable FeB-type monoboride has been documented in the binary Zr-B system. An x-ray single crystal study of $\text{Ta}_{0.78}\text{Zr}_{0.22}\text{B}$ unambiguously proved isotypism of the crystal structure with the FeB-type. EPMA evaluations show that the novel FeB-type phases $\text{Ta}_{1-x}\{\text{Ti},\text{Zr},\text{Hf}\}_x\text{B}$ form via substitution of Ta in TaB by small amounts of group IV elements (~ 3 at.% of Zr, ~ 7 at.% Hf, and ~ 10 at.% Ti).

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