



Boron site preference in ternary Ta and Nb boron silicides

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ABSTRACT

X-ray single crystal (XSC) and neutron powder diffraction data (NPD) were used to elucidate boron site preference for five ternary phases. $Ta_3Si_{1-x}B_x$ ($x=0.112(4)$) crystallizes with the Ti_3P -type (space group $P4_2/n$) with B-atoms sharing the 8g site with Si atoms. Ta_5Si_{3-x} ($x=0.03(1)$; Cr_5B_3 -type) crystallizes with space group $I4/mcm$, exhibiting a small amount of vacancies on the 4a site. Both, $Ta_5(Si_{1-x}B_x)_3$, $x=0.568(3)$, and $Nb_5(Si_{1-x}B_x)_3$, $x=0.59(2)$, are part of solid solutions of M_5Si_3 with Cr_5B_3 -type into the ternary M–Si–B systems (M=Nb or Ta) with B replacing Si on the 8h site. The $D8_8$ -phase in the Nb–Si–B system crystallizes with the Ti_5Ga_4 -type revealing the formula $Nb_5Si_3B_{1-x}$ ($x=0.292(3)$) with B partially filling the voids in the 2b site of the Mn_5Si_3 parent type.

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1. Introduction

With good properties at high temperatures, boron-silicides of refractory transition metals (TM) are promising materials for high temperature applications [1], particularly the solid solution phases with stoichiometry $(TM_1, TM_2)_5(Si, B)_3$ exhibit good oxidation resistance, high yield stress and compressive strength and good creep-resistance [2–5]. In some TM–Si–B systems the $(TM)_5(Si, B)_3$ phases are found in equilibrium with the parent metal matrix in the form of a disperse eutectic structure (in-situ metal-matrix composite), providing a good base for the development of high-temperature structural materials. In contrast to the Ta–Si–B system, extended efforts focused on phase equilibria in the Nb–Si–B system [6–10], for which a critical assessment was presented by Korniyenko et al. [11]. A recent thermodynamic modeling of the Nb-rich part of Nb–Si–B system includes a liquidus projection [12]. The ternary compounds or solution phases involved crystallize essentially in three structure types: Cr_5B_3 , W_5Si_3 and Mn_5Si_3 -type, which all three are characteristic for binary transition metal silicides TM_5Si_3 . Depending on the stabilizing influence of boron atoms either in substitutional solutions $(TM)_5(Si, B)_3$ or as interstitials, we observe ternary compounds or extended solid solutions, which, depending on

the temperature, may connect with the corresponding binary structure modification. Modern materials design relies on thermodynamic description of equilibrium as well as non-equilibrium phase relations and solidification paths in multi-component systems. A trustable description is based on reliable thermodynamic stabilities of compounds and solution phases either from calorimetric data or from density functional theory (DFT) calculations. It has been demonstrated in the past that fast DFT calculations can provide ground state energies of compounds and solutions with higher precision than slow calorimetric experiments that suffer from incomplete reactions and/or sample contamination. DFT calculations, however, need precise information on crystal structure data, particularly on crystal symmetry and atom site distribution.

Although compounds and solution phases in both systems {Nb, Ta}–Si–B have been unambiguously identified in the past there is a lack of high precision crystal structure investigations and particularly on the site preference of boron. Due to the low atomic number of B, it is difficult to precisely locate this element besides much heavier atoms such as niobium and particularly tantalum via powder X-ray or synchrotron diffraction techniques. As a task of current investigation, Neutron Powder Diffraction (NPD) has been employed to shed more light on crystal symmetry and particularly on the B/Si site occupation and boron/vacancy distribution for the two compounds of the Nb–Si–B system with Cr_5B_3 and Mn_5Si_3 -type, respectively. The study was complemented by a search for novel compounds in the Ta–Si–B system,

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where two single crystals were extracted from alloys to study via X-ray single crystal (XSC) analyses B/Si site occupation and vacancies in the crystal structures of $Ta_3(Si_{1-x}B_x)$ in comparison with binary Ta_5Si_3-x . By chance also a single crystal of $Ta_3Si_{1-x}B_x$ was found in a ternary alloy, which enabled us to check on the B-incorporation in binary Ta_3Si .

2. Experimental details

Alloys were prepared from metal ingots of Ta, Nb and pieces of Si and B (purity 99.998 and 99.5 mass %, respectively, Alfa Johnson Matthey GmbH, D) by repeated arc melting under argon (weight loss less than 0.1%). The reguli were then annealed in a W-mesh heated furnace under HF-gettered argon at 1800 °C for 6 h in case of the Nb–Si–B alloys and at 1900 °C for 120 h for alloys from the Ta–Si–B system, followed by furnace cooling. 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 $K_{\alpha 1}$ radiation and Ge as internal standard ($a_{Ge}=0.565791$ nm). XRD-Rietveld refinements were performed with the FULLPROF program [13] with the use of its internal tables for atom scattering factors. Annealed samples were polished using standard procedures and were examined by scanning electron microscopy (SEM). Quantitative compositions were determined on a CAMEBAX SX-50 electron-beam probe microanalyzer (WDX) with an electron beam current of about 15 nA. Pure elements served as standards to carry out the deconvolution of overlapping peaks and background subtraction. Finally the X-ray intensities were corrected for ZAF effects using the INCA-Energy 300 software package [14]. Overall composition of the samples derived from EPMA area scans agree with the nominal values within 1.0 at%.

Single crystals of $Ta_3Si_{1-x}B_x$ and $Ta_5(Si_{1-x}B_x)_3$ were isolated via mechanical fragmentation of a specimen with nominal composition $Ta_{65.0}Si_{20.0}B_{15.0}$, which was annealed at 1900 °C for 120 h, whereas the single crystal for Ta_5Si_3 was selected from an as cast sample with nominal composition Ta_5Si_3 . All crystals were inspected on an AXS-GADDS texture goniometer for quality and crystal symmetry prior to X-ray single crystal (XSC) intensity data collection on a four-circle Nonius Kappa diffractometer (CCD area detector and graphite monochromated Mo K_{α} radiation, $\lambda=0.071069$ nm). Orientation matrix and unit cell parameters were derived using the program DENZO [15]. No individual absorption correction was necessary because of the rather regular crystal shape and small dimensions of the investigated specimens. The structures were solved by direct methods and refined with the SHELXS-97 and SHELXL-97 programs [16], respectively.

Two samples with nominal compositions $Nb_{57.0}Si_{10.0}B_{33.0}$ and $Nb_{62.0}Si_{16.0}B_{22.0}$ were prepared from ^{11}B (chemical purity 99.8% with 96% ^{11}B isotopic enrichment) for neutron powder diffraction (NPD) by annealing at 1800 °C for 6 h and were powdered to a grain size below 40 μm in order to reduce preferential orientation effects. Neutron powder diffraction at room temperature was performed at the ORPHEE 14 MW-reactor (CEA-Saclay) using the 3T2 double-axis multi-detector neutron powder diffractometer at a resolution of $\Delta d/d \geq 4 \times 10^{-3}$ ($\lambda_{neutron}=0.12251$ nm) [17]. Further details concerning the experiments are summarized in Table 1(a) and (b). Precise atom parameters, occupation numbers, individual isotropic thermal factors and profile parameters were derived from a least squares full matrix Rietveld refinement routine (FULLPROF program [13] with internal neutron scattering lengths). The various reliability factors calculated are defined in Table 1(a) and (b). Using the DIDODATA program [19] we derived the Voronoi coordination polyhedra for all atom sites in the compounds investigated.

3. Results and discussion

3.1. The crystal structure of $Ta_3(Si_{1-x}B_x)$, $x=0.112(4)$ (Ti_3P -type)

Although the structure of binary Ta_3Si (Ti_3P -type) has already been resolved from X-ray powder diffraction [20], no data on site preference and solubility of B in Ta_3Si have been reported. Therefore, a single crystal was selected from a three-phase sample with nominal composition $Ta_{65.0}Si_{20.0}B_{15.0}$ (at %, annealed at 1900 °C) assuring that the composition determined by EPMA ($Ta_{75.2}Si_{21.3}B_{3.5}$) corresponds to the maximum solubility of B in binary Ta_3Si at this temperature.

Lattice parameters obtained from a single crystal [$a=1.0183(5)$ and $c=0.5169(3)$ nm] were close to those reported in the literature for binary Ta_3Si [$a=1.017$ – 1.0193 and $c=0.516$ – 0.5183 nm] [20–23] indicating a rather low amount of B in solid solution. Systematic extinctions revealed a primitive unit cell with one possible space group symmetry $P4_2/n$ (No. 86). In total, 4 crystallographic sites (all 8g) were obtained, out of which three were fully occupied by Ta and one was a position (M) randomly shared by a mix of 88.8% of Si and 11.2% of B atoms (Table 1(a) and (b)). The refined composition ($Ta_{75.0}Si_{22.2}B_{2.8}$) is close to the EPMA value ($Ta_{75.2}Si_{21.3}B_{3.5}$). With anisotropic displacement parameters, the structure refinement finally converged to $R_{F2}=0.022$ with little residual electron density (2.59 and $-2.38 \times 10^3 e^-/nm^3$). Positional parameters (x, y, z) and interatomic distances obtained in the present study were very close to those obtained for binary Ta_3Si [20–23]. We confirmed the coordination figures for the individual atom sites as hitherto described, however, we found 15 ligands for Ta2 (Fig. 1(a) in contrast to the description in the literature (14 ligands) [24].

3.2. The crystal structure of Ta_5Si_3-x , $x=0.03(1)$ (Cr_5B_3 -type)

Similar to Ta_3Si , the structure of binary Ta_5Si_3 with Cr_5B_3 -type is already known in the literature including a Rietveld refinement of X-ray powder diffraction data [23, 25–28]. In order to provide a set of atom positional parameters of higher precision for Ta_5Si_3 , single crystal X-ray intensity CCD data were collected. Lattice parameters obtained from the single crystal [$a=0.65246(5)$ and $c=1.18853(3)$ nm] are close to those hitherto reported for the binary Ta_5Si_3 -phase ($a=0.6511$ – 0.6519 and $c=1.1873$ – 1.1887 nm [23, 25–28]). Systematic extinctions confirmed a body centered unit cell with three possible space group symmetries, $I4/mcm$, $I-4c2$ and $I4cm$. As structure determination using direct methods in all these space groups revealed practically identical solutions, we describe the structure in the space group with the highest symmetry $I4/mcm$ (No. 140). In total, 4 crystallographic sites were obtained, out of which, Si occupied the 4a and 8h sites whilst sites 4c and 16l were fully occupied by Ta. A small defect was found in the 4a site occupied by Si (see Table 1(a) and (b)). The refined composition ($Ta_{63.1}Si_{36.9}$) was close to the composition ($Ta_{62.6}Si_{37.4}$) obtained from EPMA. With anisotropic displacement parameters, the structure refinement finally converged to $R_{F2}=0.033$ with small residual electron density (7.32 and $-4.88 \times 10^3 e^-/nm^3$). Fig. 1(b) shows the coordination polyhedra for Ta_5Si_3-x , $x=0.03(1)$. The Voronoi analysis excludes the rather long Ta1–Ta1 bond (0.3575 nm) with a very small Voronoi face area (0.10 compared to the maximum area of 4.05) and thus limits the coordination shell for Ta1 to 15 ligands. This is important to mention, because particularly the Ta1–Ta1 bond needs to be included again in the Ta1 polyhedron, when Si is replaced by B in $Ta_5(Si_{1-x}B_x)_3$ (see Section 3.3) and in isostructural $Nb_5(Si_{1-x}B_x)_3$ (see Section 3.4).

3.3. The crystal structure of $Ta_5(Si_{1-x}B_x)_3$, $x=0.568(3)$ (Cr_5B_3 -type)

No details on the site preference of B-atoms within the isotopic solid solution $Ta_5(Si_{1-x}B_x)_3$ have been hitherto reported in the

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