Defect structure of the T2 phase in the Cr–Si–B system: an SXRD/DFT study

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Abstract

The defect structure of the Cr\textsubscript{5}(B, Si)\textsubscript{3} (T2) phase was systematically investigated using X-ray diffraction experiments with synchrotron radiation (SXRD) and first-principles electronic-structure calculations within the scope of the Density Functional Theory (DFT). An excellent agreement was obtained between experiments and theoretical calculations, revealing that Si occupies preferably the 4\textsubscript{a} sublattice of the structure, due to the presence of weak B bonds, making the defect structure a key factor for its stabilization. The results of this work provide crucial information to support a better description of this phase in alloys with Si and B, as the T2 phase is known to occur in many important ternary systems.

Keywords: X-ray diffraction (XRD), Density Functional Theory (DFT), Refractory metals, Crystal defects, Intermetallic compounds.

In a global technological endeavor perspective, it is very meaningful to improve the efficiency in generating and utilizing energy in a broad range of applications in the industry. This development process necessarily demands the search for new materials and processing routes capable of stabilizing mechanical and thermal properties during long time periods under high temperatures. One of the main classes of materials for high temperature applications is based on multicomponent systems containing refractory metals (RM) such as Nb and Mo, often modified with Si and B [1–7], originating the so-called RM-silicides composites. However, these alloys are known to exhibit moderate resistance to oxidation/corrosion at elevated temperatures. If modification of the alloy chemistry is not effective to enhance the oxidation behavior at high temperatures during long working life cycle, the deposition of protective coatings is required to ensure the integrity of parts during service [8–10]. Coatings developed in the past for this class of materials are based on silicide compounds that are able to form a silica protective layer during exposure [8, 11, 12]. Additions of boron to the silicides is of particular interest leading to the modification of the silica layer by lowering its viscosity which can help to heal cracks that may form because of stress induced by thermal cycling. Then, knowledge of phase diagrams and crystal structures associated with intermetallic phases present in RM–Si–B systems is very important to develop new compositions for alloys and coatings.

Among the key systems in this material class, the Cr–Si–B is a promising candidate especially in the Cr-rich region [13–15]. Despite its potential in a plethora of applications, there is a lack of experimental and theoretical attempts in the literature. This system presents a phase, usually denoted by T2 (which is a ternary extension of Cr\textsubscript{5}B\textsubscript{3} with silicon substitution to boron), along the section with constant Cr content at x\textsubscript{Cr}=0.625, with very scarce information regarding its defect structure and enthalpy of formation.

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Figure 1: Structure visualization and crystallographic information on the Cr$_5$B$_2$Si$_1$ (T2) compound [24] with the proposed thermodynamic model based on the present results. Silicon appear in the 4$a$ sublattice for visualization purposes.

| Stoichiometry | Cr$_5$B$_{3-x}$Si$_x$ |
|--------------|----------------------|
| Prototype    | Cr$_5$B$_3$          |
| Space group  | $I4/mcm$ (140)       |
| Pearson symbol | tI32               |
| Wyckoff positions | Cr$_1$ = 16$l$   |
|               | B$_2$, Si$_2$ = 4$a$ |
| Proposed model | (Cr)$_5$ (B, Si)$_2$ (B, Si) |

The aim of the present work, therefore, is to determine the defect structure of the Cr$_5$(B, Si)$_3$ T2 compound using synchrotron X-ray diffraction (SXRD) measurements and Density Functional Theory (DFT) calculations in order to improve the reliability of Cr–Si–B thermodynamic databases. In the following discussion, we demonstrate that Si atoms, in fact, have a site-preference for one of the sublattices of the Cr$_5$B$_3$ phase, in contrast to what was proposed in the last optimization [14], calling for a new, appropriate thermodynamic reassessment of the Cr–Si–B system. In addition, our work provides relevant information to support a better description of related phases, as the T2 phase is known to occur in many important ternary systems, including the Nb/Mo/W/Ta/Ti/V–Si–B systems [16–23].

The crystal structure [25] and crystallographic informations of the Cr$_5$B$_3$ compound are presented in Fig. 1. The Cr atoms occupy the 16$l$ and 4$c$ sites, while B occupies the 8$h$ and 4$a$ Wyckoff positions. As described by Joubert et al. [26], these structures present five main layers: $z = 0$, with both the 4$c$ (Cr) and 8$h$ (B) atoms; $z = 1/8$, with only the 16$l$ (Cr); $z = 1/4$, with the 4$a$ (B); $z = 3/8$, with another layer of 16$l$ (Cr); and $z = 1/2$, similar to $z = 0$. The remaining atoms are positioned according to the tetragonal body-centered symmetry.

A few samples, with different compositions, were prepared along the relevant section ($x_{Cr} = 0.625$) of the Cr–Si–B system. However, it is particularly important for the present work the sample with nominal composition Cr$_{0.625}$Si$_{0.2}$B$_{0.175}$. It was obtained by arc melting of high-purity elements, Cr (min. 99.99 wt%), Si (min. 99.99 wt%) and B (min 99.5 wt%), in a water-cooled copper crucible under pure argon (min 99.995%) atmosphere. After the melting process, the mass losses were lower than 1.3%. To achieve thermodynamic equilibrium, the samples were encapsulated in quartz tubes under vacuum and heat-treated at 1400°C for 96h, in an atmosphere with constant flow of analytical argon (99.99%). As-cast and heat-treated samples were characterized at room temperature through Scanning Electron Microscopy/Back-Scattered Electron Images (SEM/BSE) and SXRD. SEM/BSE micrographs were obtained from flat and polished specimens and SXRD experiments were carried out in high resolution mode using a multiple axes Huber diffractometer located at the Brazilian Synchrotron Light Laboratory (LNLS). Powder samples sieved to below 53 µm were placed in a cylindrical support with 5 mm
As cast. Heat treated at 1400°C for 96h.

**Figure 2:** Micrographs of the Cr$_{0.625}$Si$_{0.2}$B$_{0.175}$ sample, showing (a) the presence of CrB and Cr$_5$Si$_3$ precipitates in a Cr$_5$B$_3$ matrix in the as-cast state, and (b) the microstructure after heat treatment at 1400°C for 96h, with a two-phase microstructure constituted by Cr$_5$Si$_3$ and Cr$_5$B$_3$.

Figs. 2a-b presents a comparison of the as-cast and heat-treated Cr$_{0.625}$Si$_{0.2}$B$_{0.175}$ samples. Clearly, during the heat treatment, the primary precipitate, CrB, is consumed in order to form larger amounts of the T1 and T2 phases, as predicted by the thermodynamic database of Villela [14]. Thus, the heat treatment at 1400°C for 96h leads the system very close to the thermodynamic equilibrium state. Fig. 3 shows the XRD pattern of the as-cast and heat-treated samples. All peaks were identified with the Cr$_5$B$_3$, Cr$_5$Si$_3$, and CrB phases, as expected. Nowotny and Wittmann [13] proposed the existence of a D8$_8$ ternary phase at 1300°C, which was contested in the experimental investigations performed by Villela [14] and Chad [15] at 1200°C, based on the fact that the graphite crucible and the low purity boron (96.5 at%) used in the older work (Ref. [13]) are suspected to stabilize the ternary phase. The present results reinforce the suggestion that the real equilibrium is the Cr$_5$B$_3$–Cr$_5$Si$_3$–CrB tie-triangle, showing, also at 1400°C, that the D8$_8$ phase is not stable.

The Rietveld refinement was done in the Cr$_{0.625}$B$_{0.175}$Si$_{0.2}$ sample and the resulted adjustment can be seen in Fig. 3. It should be noted that the composition of silicon and boron was free to vary in both compositions of the 4a and 8h sublattices, which leads to a more reliable result regarding the real position of both elements in the sublattices of the T2 structure. Table 1 presents, in the last row, the experimental result for the occupancy of Si in the two T2 sublattices, which can be clearly seen that silicon preferably occupies the 4a sublattice, with only a small fraction going to the 8h position.

In order to be able to compare the experimental analysis of the T2 compound with ab-initio calculations, the most important step is to choose structures that are representative and that simulate the different possible substitutional defects in the compound. To begin with, microanalysis experiments by Ref. [14] indicated that Si dissolves in this boride by replacing the B atoms, keeping the chromium content constant. Therefore, the calculated structures reported in this work considered only the substitution of B by Si in the 4a and 8h sublattices. In addition, since the extrapolation of the Cr–Si–B system by Ref. [14] at 1400°C suggests a solubility of approximately 9% at. Si in the T2 phase, the proposed substitutions, shown in Table 1, were limited to unit-cell size, with $x_{Si}$ up to 18.75%, varying not
Figure 3: Synchrotron x-ray diffraction pattern of the Cr$_{0.625}$Si$_{0.2}$B$_{0.175}$ sample heat-treated at 1400°C for 96 hours, showing the calculated intensities differences, using the Rietveld refinement, considering Si in the 4$a$ and 8$h$ sublattices. The T2 unit cell is shown as an inset.

only the sublattice occupied by Si, but also its relative content. The DFT [32, 33] calculations were then performed with the Quantum Espresso code [34]. The Generalized Gradient Approximation (GGA) was used for the exchange and correlation (XC) functional with the Perdew-Burke-Ernzerhof (PBE) parametrization [35]. A plane wave cutoff energy of 190 Ry was used for all calculations, with a 14x14x7 Monkhorst-Pack grid [36]. All structures were fully relaxed, maintaining the body-centered tetragonal symmetry.

Fig. 4a-b presents the experimental and ab-initio comparison of the lattice parameters $a$ and $c$ obtained in the present work as a function of the amount of Si and site occupancy. The maximum difference between the results is approximately 2%, which may be explained by the XC functional, since the GGA functionals tend to overestimate the forces between atoms, leading to a decrease in the lattice parameter [37]. This difference can be duly noticed in Figs. 4a-b for both lattice parameters in the case of the Si-free compound (with only one exception for $a$), when compared to the experimental data [38–40].

Fig. 5 shows the calculated formation energies for all calculated T2 structures, given by the difference between the total energy of this structure and the total energies of the most stable phases of the pure elements at 0 K:

$$
\Delta_f E_{\text{Cr}_5\text{Si}_{3-x}\text{B}_x} = E_{\text{Cr}_5\text{Si}_{3-x}\text{B}_x} - \frac{5}{8}E_{\text{A}_2-\text{Cr}} - \frac{3 - x}{8}E_{\text{A}_4-\text{Si}} - \frac{x}{8}E_{\text{R}12-\text{B}}.
$$

(1)

The value of $-41.4$ kJ/mol for the binary Cr$_5$B$_3$ compound is very close to those reported by other
Table 1: Ab-initio and experimental results for the formation energy at 0 K (kJ/mol of atoms) and lattice parameters (nm) for the different T2 compounds, depending on the site occupancy and composition.

|                | Cr$_{20}$B$_{12}$ | Cr$_{20}$B$_{10}$Si$_2$ | Cr$_{20}$B$_{8}$Si$_4$ | Cr$_{20}$B$_{6}$Si$_6$ | Cr$_{0.625}$B$_{0.175}$Si$_{0.2}$ (exp.) |
|----------------|-------------------|------------------------|-----------------------|------------------------|------------------------------------------|
| 4a occ.        | 4B                | 4B                     | 4B                    | 4Si                    | ——                                       |
| 8h occ.        | 8B                | 6B/2Si                 | 8B                    | 4B/4Si                 | 8B                                      |
| $\chi_{Si}$    | 0                 | 0.0625                 | 0.0625                | 0.125                  | 0.125                                    |
| $\Delta_fH$    | −41.37            | −28.15                 | −39.13                | −15.76                 | −38.05                                   |
| $\alpha$       | 1.002             | 1.056                  | 0.552                 | 0.569                  | 0.562                                    |
| $\sigma$       | 0.541             | 0.556                  | 0.552                 | 0.569                  | 0.574                                    |
| $\Delta_fH$    | −41.37            | −28.15                 | −39.13                | −15.76                 | −38.05                                   |
| $\alpha$       | 1.002             | 1.056                  | 0.552                 | 0.569                  | 0.574                                    |
| $\sigma$       | 0.541             | 0.556                  | 0.552                 | 0.569                  | 0.574                                    |
| Si occupancy 4a (atom) | ——                | ——                     | ——                    | ——                     | 2.96(2)                                   |
| Si occupancy 8h (atom) | ——                | ——                     | ——                    | ——                     | 0.29(5)                                   |

Figure 4: Comparison between the lattice parameters $a$ (a) and $c$ (b) obtained by the DFT calculations of selected structures with the experimental parameters obtained by Rietveld refinement of SXRD measurements and results from the literature [38–40].

ab-initio [41] and CALPHAD extrapolations [42, 43] studies. A significant difference of 11 and 22 kJ/mol can be observed at the composition 6.25 and 12.5% at. Si, respectively, on the 4a and 8h positions. This result is a clear evidence that the Si atoms have a preference to occupy the 4a positions in this structure, since the enthalpy of formation of the configurations in which silicon occupies the 4a sublattice is more negative than the configuration that silicon occupies the 8h. In addition, by adding 2 atoms of Si in the 8h sublattice with the 4a fully occupied by Si (at $x_{Si} = 0.1875$), there is an increase of approximately 8 kJ/mol when compared to only the 4a site occupied by Si, being one more indication that Si preferentially fills the 4a.

Other studies that discuss the defect structure of the T2 compounds, as the V$_5$Si$_3$ in the V–Si–B system [18] and the Nb$_5$Si$_3$ in the Nb–Si–B system [26], arrived at the conclusion that B tends to form dumbbell features in the 8h position. In addition, as observed in B$_{14}$Ga$_3$Ni$_{27}$ [44] and Nb$_2$OsB$_2$ [45] compounds, for instance, boron atoms have an energetic preference to form short bonds, with interatomic distances varying from 1.40 to 1.90Å, and can be organized, preferentially, in linear or zigzag infinite chains. In the present work, the calculated structures have B bonds in the 8h sublattices ranging from 1.68 to 1.82Å, which are within the expected range discussed above. Meanwhile, Si will preferably occupy the 4a sublattice because the boron atoms in these positions are weakly bonded, with first neighbors distances of approximately 3.86Å.
In conclusion, the defect structure of the T2 Cr$_5$(B,Si)$_3$ compound was successfully determined. Synchrotron X-ray diffraction experiments showed that there is a better adjustment when considering the solubility of silicon in the 4$a$, instead of the 8$h$ sublattice position. In addition, first-principles DFT calculations identified a significant energy difference in the calculated T2 structure with silicon in different positions and sublattice distributions, also pointing to a preferred substitution in the 4$a$ Wyckoff position. However, although there has been reported a significant preference for the position of the elements, the sublattice model for a thermodynamic database must be compatible with the other systems that present this phase. Therefore, contrary to what has been previously reported, the thermodynamic model for the T2 phase in the Cr–Si–B ternary system should be given by (Cr)$_5$(B,Si)$_2$(B,Si)$_1$, as seen in Table 1. More importantly, for the compatibility of thermodynamic descriptions [46], a similar site preference is expected in other, relevant systems in which the T2 phase is known to be stable [16–18].

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