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Isothermal Section of the V-Si-B System at 1600 °C in the V-VSi₂-VB Region

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In recent years, the Me-Si-B (Me-metal) ternary systems have received considerable attention aiming at the development of high-temperature structural materials. Assuming that any real application of these materials will rely on multicomponent alloys, as is the case of Ni-base superalloys, phase equilibria data of these systems become very important. In this work, results are reported on phase equilibria in the V-Si-B system, and are summarized in the form of an isothermal section at 1600 °C for the V-VSi₂-VB region. Several alloys of different compositions were prepared via arc melting and then heat-treated at 1600 °C under high vacuum. All the materials in both as-cast and heat-treated conditions were characterized through x-ray diffraction, scanning electron microscopy, and selected alloys via wavelength dispersive spectroscopy. A negligible solubility of B in the V₃Si, V₅Si₃ (T₁), and V₆Si₅ phases as well as of Si in V₃B₂ and VB phases was noted. Two ternary phases presenting the structures known as T₂ (Cr₅B₃-prototype) and D₈₈ (Mn₅Si₃-prototype) were observed in both as-cast and heat-treated samples. It is proposed that at 1600 °C the homogeneity range of T₂ extends approximately from 5 at.% to 12 at.% Si at constant vanadium content and the composition of D₈₈ phase is close to V₅₉₅Si₃₃B₇₅ (at.%).

Keywords: borosilicides, isothermal section, phase diagram, V-Si-B system

1. Introduction

Me-Si-B (Me-metal) alloys have been considered for high demanding structural applications at high temperature and, so far, most of the research has been carried out in the Mo-Si-B system. However, considering the balance of properties an ideal alloy must present, it is very likely that a multicomponent material has to be found and in this way, phase equilibria information in related systems has to be known.

Nowotny et al. investigated the stabilization of the D₈₈ phase (Mn₅Si₃ prototype) in the V-Si-B system phase by B doping the V₅Si₃ (T₁, W₅Si₃ prototype) phase. The authors produced alloys with composition V₅Si₃ + 5% at. B via sintering and arc melting from powders of V (min. 99.86%), Si (min. 99.9%) and B (min. 96.35%) and sintered at 1450 °C for 24 h under argon. In Fig. 1, the phase identified as D₈₈ presents a chemical composition near V₅₉₅Si₃₃B₇₅ (at.%) and the alloys studied by the authors are marked with an “x” letter, with B and Si contents varying in the proportion 3:1, 1:1, and 1:3 along the V₅Si₃-V(5)B(3) line.

In this work, the phase relations in the V-Si-B system have been evaluated through the determination of an isothermal section at 1600 °C in the V-VSi₂-VB region. The results are compared with those from Kudielka et al.

2. Experimental Procedure

The V-Si-B alloys were produced from V (min. 99.75%), Si (min. 99.998%) and B (min. 99.5%) via non-consumable tungsten electrode arc melting under argon in a water-cooled copper hearth. Several melting steps were carried out to produce chemically homogeneous ingots. Before each melting step a Ti-getter was melted to remove residual O₂(g), H₂O(g), and N₂(g) from the furnace atmosphere. To produce thermodynamically equilibrated samples, heat treatments were carried out at 1600 °C for 24/72 h under high vacuum (10⁻⁶ mbar). At the end of the experiments, the samples were furnace cooled to room temperature.

All the alloys in the as-cast and heat-treated conditions were characterized via x-ray diffraction (XRD, Cu-Kα) and scanning electron microscopy (SEM/back-scattered electron mode). The V, Si, and B contents of phases in selected
samples were determined via wave-length dispersive spectroscopy (WDS) using pure element standards and a LiF crystal for V (Kα line), a PET crystal for Si (Kα line) and a LSM-200 crystal for B (Kα line). The analyses were performed at 10 kV and 10 nA.

The XRD diffractograms were evaluated using the PowderCell and DBWS-9807 softwares with crystallographic data from Ref 4, 6, 7 for the expected phases in the samples.

### 3. Results and Discussion

Figure 2 presents the proposed isothermal section at 1600 °C for the V-Si-B system in the V-VSi2-VB region. The compositions of the investigated alloys are indicated in this figure and given in Table 1.

Alloy #33 (V85Si2.5B12.5) showed Vss (ss = solid solution) and V3B2 in the as-cast as well as in the heat-treated (1600 °C) microstructure. Figure 3(a) shows a SEM micrograph of the heat-treated sample displaying V3B2 particles embedded in a Vss matrix. Almost the totality of the Si atoms should be present in the Vss, considering the 3.18 at.% Si in Vss and the 0.18 at.% Si in V3B2. In the V-Si system, the maximum solubility of silicon in Vss is near 7 at.% Si at 1870 °C. Thus, at 1600 °C the V3B2 presents a negligible solubility for Si. In addition, these results indicate the stability of the Vss + V3B2 two-phase field at 1600 °C.

Alloy #12 (V67.5Si6B26.5) showed Vss, VB, and T2 in the as-cast and Vss, V3B2, VB, and T2 in the heat-treated (1600 °C) microstructures. The presence of four phases suggests that thermodynamic equilibrium conditions were not reached during heat-treatment. However, the formation of V3B2 and a significant volume fraction of Vss and T2 in the heat-treated sample indicate that this alloy is placed in the Vss + V3B2 + T2 three-phase regions at 1600 °C, and that the VB phase was not completely dissolved during heat-treatment. The T2-phase composition in the heat-treated sample is near V63Si5B32 at.%. Figure 3(b) shows a SEM micrograph of the heat-treated sample; however, it is not possible to distinguish between V3B2 and T2 due to close back-scattering coefficients of these phases.

![Fig. 1 Isothermal section of the V-Si-B at 1450 °C](image1)

![Fig. 2 Isothermal section of the V-Si-B system at 1600 °C in the V-VSi2-VB region with indication of the alloys produced in this work](image2)
Alloy #13 ($V_{57.2}Si_{2.5}B_{40}$) exhibited $V_{ss}$, VB and $T_2$ in the as-cast and VB, $V_3B_2$ and $T_2$ in the heat-treated (1600 °C) microstructures. Thus, the $V_{ss}$ phase was dissolved and the $V_3B_2$ phase formed during heat-treatment. The Si atoms present in the $V_{ss}$ phase of the as-cast sample were used in the $T_2$ formation during heat-treatment considering the low contents of Si in the $V_3B_2$ (0.17 at.% Si) and VB (0.22 at.% Si) phases. Figure 3(c) shows a SEM micrograph of this alloy where in this case it was possible to distinguish between $T_2$ and $V_3B_2$ phases in spite of their low contrast. These results show the stability of the VB + $V_3B_2$ + $T_2$ three-phase field at 1600 °C.

It could be argued that the $V_3B_2$ phase was formed in the previous alloys during cooling of the samples to room temperature. If it was the case, instead of the $V_{ss} + V_3B_2 + T_2$ and VB + $V_3B_2$ + $T_2$ three-phase fields proposed, the two-three phase fields could be $V_{ss} + V_3B_2 + VB$ and $V_{ss} + VB + T_2$. Considering this possibility, the $V_3B_2$ phase could not equilibrate with $T_2$ and alloy #13 could not present $V_3B_2$. However, alloy #13 clearly showed the total dissolution of the $V_{ss}$ phase and the formation of significant amount of $V_3B_2$, apparently through a peritectoid-like reaction involving $V_{ss}$ and VB which were present in the as-cast microstructure together with $T_2$. In addition, such an amount of $V_3B_2$ could not have been formed in solid state during cooling, considering that diffusion in such a system is sluggish and the drop in

Table 1 Composition of alloy used for the determination of the isothermal section at 1600 °C and heat-treatment durations

<table>
<thead>
<tr>
<th>Alloy #</th>
<th>Composition, at.%</th>
<th>Heat-treatment duration, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$V_{77.5}Si_{15}B_{7.5}$</td>
<td>24</td>
</tr>
<tr>
<td>12</td>
<td>$V_{67.5}Si_{26.5}B_{6}$</td>
<td>24</td>
</tr>
<tr>
<td>13</td>
<td>$V_{57.5}Si_{32}B_{40}$</td>
<td>24</td>
</tr>
<tr>
<td>14</td>
<td>$V_{50}Si_{15}B_{6}$</td>
<td>24</td>
</tr>
<tr>
<td>15</td>
<td>$V_{48}Si_{17}B_{8}$</td>
<td>24</td>
</tr>
<tr>
<td>33</td>
<td>$V_{52}Si_{13}B_{8.5}$</td>
<td>72</td>
</tr>
<tr>
<td>44</td>
<td>$V_{50}Si_{12}B_{2}$</td>
<td>24</td>
</tr>
<tr>
<td>48</td>
<td>$V_{50}Si_{15}B_{30}$</td>
<td>72</td>
</tr>
<tr>
<td>49</td>
<td>$V_{52}Si_{17.5}B_{30}$</td>
<td>72</td>
</tr>
</tbody>
</table>

Fig. 3 SEM micrographs (SEM/BSE) of alloys #33 (a), #12 (b), #13 (c) and #10 (d) after heat-treatment at 1600 °C.
temperature down to about 1200 °C is quite fast after furnace shut down. It allows us to conclude that alloy #13 lies in the V3B2 + VB + T2 three-phase field and thus the V3B2 phase equilibrates with T2. If this is accepted and considering that alloy #33 lies in Vss + V3Si2-B two-phase field and alloy #10 in the Vss + T2 + V3Si three-phase field, as will be discussed below, alloy #12 has to be in the Vss + V3B2 + T2 three-phase field as proposed in Fig. 2. Also, note that in the isothermal section from Kudielka et al. (Fig. 1), the author proposes the equilibrium of T2 with VB and another boride which should be V3B2 based on currently accepted V-B binary system.

Alloy #10 (V77.5Si15B7.5) exhibited Vss, V3Si and T2 in the as-cast as well as in the heat-treated (1600 °C) microstructure, which is shown in Fig. 3(d). WDS measurements of the heat-treated sample indicated approximately 2.00 at.% B in the V3Si phase. In order to validate the B content of this phase, identical measurements were carried out in the VSi phase from binaries V-Si alloys and the B contents were very close, allowing the conclusion that the B solubility in VSi is negligible. The above discussed results suggest the stability of the Vss + T2 + VSi3 three-phase field at 1600 °C.

The solubility range of VSi at 1600 °C from equilibrated V-Si binary alloys was reevaluated in this work and found to vary in the 21-25 at.% Si range, in close agreement with data from the literature.\[8\]

The T2 phase composition of alloys #10 and #12 were not significantly different, both being near V6Si5B32 at.% Si. Considering also that the T2 lattice parameters in both alloys were close (Table 2), it can be concluded that the T2 composition of these alloys corresponds to one of the solubility limits of this phase at 1600 °C.

Alloy #15 (V68Si27B5) showed V3Si, V5Si3, and T2 in the as-cast as well as in the heat-treated (1600 °C) microstructure as shown in Fig. 4(a). The T2 phase composition is near V6Si5B32 at.% showing a Si content significantly higher than that of T2 phase present in alloys #10 and #12 (~5 at.% Si) and therefore indicates an important solubility range of this phase at 1600 °C. This solubility range is smaller than that of the T2-phase in the Nb-Si-B system,[9,10] but higher than that of T2 in the Mo-Si-B system.[11] Similar to the V3Si case, the B content of the V5Si3 phase was found to be near 3 at.%; however, measurements carried out in this phase from equilibrated binary V-Si alloys gave approximately the same B contents and therefore the B solubility in V5Si3 should also be negligible. This finding is also supported by the lattice parameter data shown in Table 2. Anyhow, these results suggest the stability of the V5Si3 + V3Si + T2 three-phase field at 1600 °C.

The lattice parameters of the T2 phase (Table 2) varied in the a = 5.785-5.807 Å and c = 10.765-10.807 Å range. The “a” and “c” parameters increase for higher Si contents which is analogous to that of this phase in the Nb-Si-B system.[10] These results strengthen the proposal that this phase has a significant solubility range at 1600 °C, as mentioned earlier.

Alloy #14 (V59Si13B26) had VB, V3Si, V5Si3, and T2 in the as-cast microstructure and VB, V5Si3, T2 in the heat-treated microstructure (1600 °C) as shown in Fig. 4(b). This indicates the dissolution of V3Si phase during heat-treatment and the stability of the VB + V5Si3 + T2 three-phase field at 1600 °C. The T2 lattice parameters (Table 2) in the VB + T2 + V5Si3 and V5Si3 + V3Si + T2 three-phase fields are close, which suggest that the compositions of the T2 phase in alloys #14 and #15 are nearly the same.

Alloy #49 (V52Si17.5B30) exhibited VB and D88 in the as-cast and VB, D88, and VS12 in the heat-treated microstructure (1600 °C) as shown in Fig. 4(c), which indicates the stability of the VB + D88 + VS12 three-phase field at 1600 °C.

Alloy #44 (V55Si14B31) exhibited V2Si3, V6Si5, D88, and VS12 in the as-cast microstructure and V2Si3, V6Si5, D88 after heat-treatment at 1600 °C as shown in Fig. 4(d), indicating the dissolution of the V2Si3 phase during heat-treatment. A negligible B solubility in VS12 was also noted. These results suggest the stability of the V6Si5 + V3Si3 + D88 three-phase field at 1600 °C.

From microanalysis measurements in D88 phase present in the microstructure of heat-treated alloys #44 and #48 a composition near V59.5Si34.8B5.9 (at.% Si) is proposed for this phase in Fig. 2, a value close to V59.3Si34.8B5.9 (at.% B) as proposed by Kudielka et al.[4]

The lattice parameters of the VB and V3B2 phases (Table 2) in the investigated alloys did not vary significantly and were near the values reported by Villars and Calvert[7] for this phase in V-B binary alloys, confirming the

### Table 2 Lattice parameters (Å) of phases present in heat-treated (1600 °C) V-Si-B alloys

<table>
<thead>
<tr>
<th>Phase field/allloy #</th>
<th>Vss</th>
<th>V3B2</th>
<th>V3Si</th>
<th>T2</th>
<th>V5Si3</th>
<th>D88</th>
<th>VB</th>
</tr>
</thead>
<tbody>
<tr>
<td>V3B2 + V3Si3</td>
<td>3.037</td>
<td>5.746</td>
<td>3.033</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V3B2 + V3Si10</td>
<td>3.037</td>
<td>4.746</td>
<td>3.033</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V3Si + V3Si15</td>
<td>3.039</td>
<td>5.749</td>
<td>3.031</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V3Si + V3Si15 + T2/5</td>
<td>3.039</td>
<td>5.749</td>
<td>3.031</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V5Si3 + V3Si + T2/14</td>
<td>3.039</td>
<td>5.749</td>
<td>3.031</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V5Si3 + T2 + V3Si3</td>
<td>3.039</td>
<td>5.749</td>
<td>3.031</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V3Si + T2 + V3Si3</td>
<td>3.039</td>
<td>5.749</td>
<td>3.031</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[7]

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stoichiometric nature of these phases and their low solubility for Si.

Based on all previous results and in order to complete the phase relations in the V-VSi₂-VB region, the stability of the VB + V₅Si₃ + D₈⁸ and V₆Si₅ + VSi₂ + D₈⁸ three-phase fields at 1600 °C are proposed as shown in Fig. 2. Due to the significant solubility range of the V₃Si and T₂ phases, the V₃Si + T₂, and T₂ + VB two-phase fields are broad at 1600 °C.

Comparing the present results with those from Kudielka et al. [4] it is possible to state that the VB-T₂ and T₂-V₃Si equilibrium shown by Kudielka et al. were also found in this work but not the D₈⁸-V₃Si and D₈⁸-T₂ two-phase equilibria; Kudielka et al. propose the existence of a binary V-B phase with V₇₀B₃₀ (at.%) stoichiometry which does not exist in the V-B system at 1600 °C.

4. Summary

In this work, the V-Si-B system has been investigated with respect to the phase relations at 1600 °C in the region delimited by V-VSi₂-VB. The results have confirmed the stability of the ternary T₂ and D₈⁸ phases, with T₂ exhibiting an important solubility range. A negligible B solubility in the silicide phases (V₃Si, V₅Si₃, and V₆Si₅) as well as that of Si in the borides (V₃B₂ and VB) was found.

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Section I: Basic and Applied Research


