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Isothermal Section of the V-Si-B System at 1600 °C in the V-VSi_2-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-VSi_2-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 V_3Si, V_5Si_3 (T_1), and V_6Si_5 phases as well as of Si in V_3B_2 and VB phases was noted. Two ternary phases presenting the structures known as T_2 (Cr_5B_3-prototype) and $D8_8$ (Mn_5Si_3-prototype) were observed in both as-cast and heat-treated samples. It is proposed that at 1600 °C the homogeneity range of T_2 extends approximately from 5 at.% to 12 at.% Si at constant vanadium content and the composition of $D8_8$ phase is close to $V_{59.5}Si_{33}B_{7.5}$ (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.[1,2] 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.[3] investigated the stabilization of the $D8_8$ phase (Mn_5Si_3 prototype) in the V-Si-B system phase by B doping the V_5Si_3 (T_1, W_5Si_3 prototype) phase. The authors produced alloys with composition V_5Si_3 + 5% at. B via sintering and arc melting from powders of V (min. 99.86%), Si (min. 99.9%) and B of varied purity grades: min. 83% and min. 96.35%. The $D8_8$ phase was observed in both cases and exhibited the following lattice parameters: $a = 7.19$ Å and $c = 4.90$ Å.

Kudielka et al.[4] studied the phase relations in the V-Si-B system and proposed a partial isothermal section at 1450 °C (Fig. 1) for the near V-V_5Si_3(T_1)-VB region via alloys produced 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 $D8_8$ presents a chemical composition near $V_{59.3}Si_{34.8}B_{5.9}$ (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 V_5Si_3-$V_{(5)}B_{(3)}$ 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-VSi_2-VB region. The results are compared with those from Kudielka et al.[4]

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 $O_{2(g)}$, $H_2O_{(g)}$, and $N_{2(g)}$ 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

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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[5] and DBWS-9807 softwares with crystallographic data from Ref 4, 6, 7 for the expected phases in the samples.

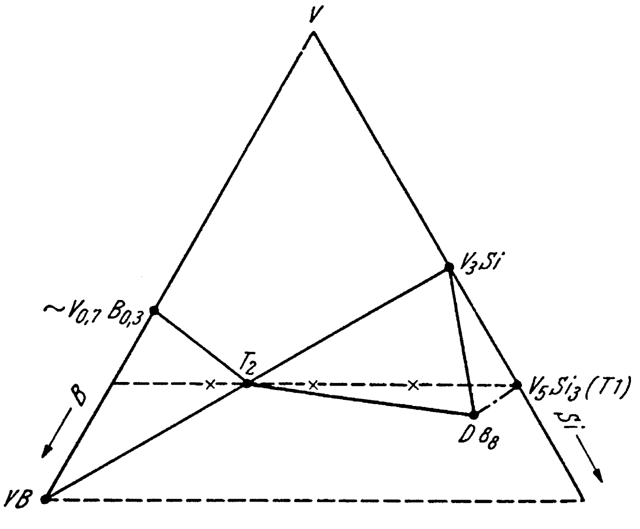

Fig. 1 Isothermal section of the V-Si-B at 1450 °C[4]

3. Results and Discussion

Figure 2 presents the proposed isothermal section at 1600 °C for the V-Si-B system in the V-VSi_2-VB region. The compositions of the investigated alloys are indicated in this figure and given in Table 1.

Alloy #33 ($V_{85}Si_{2.5}B_{12.5}$) showed V_{ss} (ss = solid solution) and V_3B_2 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 V_3B_2 particles embedded in a V_{ss} matrix. Almost the totality of the Si atoms should be present in the V_{ss}, considering the 3.18 at.% Si in V_{ss} and the 0.18 at.% Si in V_3B_2. In the V-Si system, the maximum solubility of silicon in V_{ss} is near 7 at.% Si at 1870 °C.[8] Thus, at 1600 °C the V_3B_2 presents a negligible solubility for Si. In addition, these results indicate the stability of the V_{ss} + V_3B_2 two-phase field at 1600 °C.

Alloy # 12 ($V_{67.5}Si_6B_{26.5}$) showed V_{ss}, VB, and T_2 in the as-cast and V_{ss}, V_3B_2, VB, and T_2 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 V_3B_2 and a significant volume fraction of V_{ss} and T_2 in the heat-treated sample indicate that this alloy is placed in the V_{ss} + V_3B_2 + T_2 three-phase regions at 1600 °C, and that the VB phase was not completely dissolved during heat-treatment. The T_2-phase composition in the heat-treated sample is near $V_{63}Si_5B_{32}$ at.%. Figure 3(b) shows a SEM micrograph of the heat-treated sample; however, it is not possible to distinguish between V_3B_2 and T_2 due to close back-scattering coefficients of these phases.

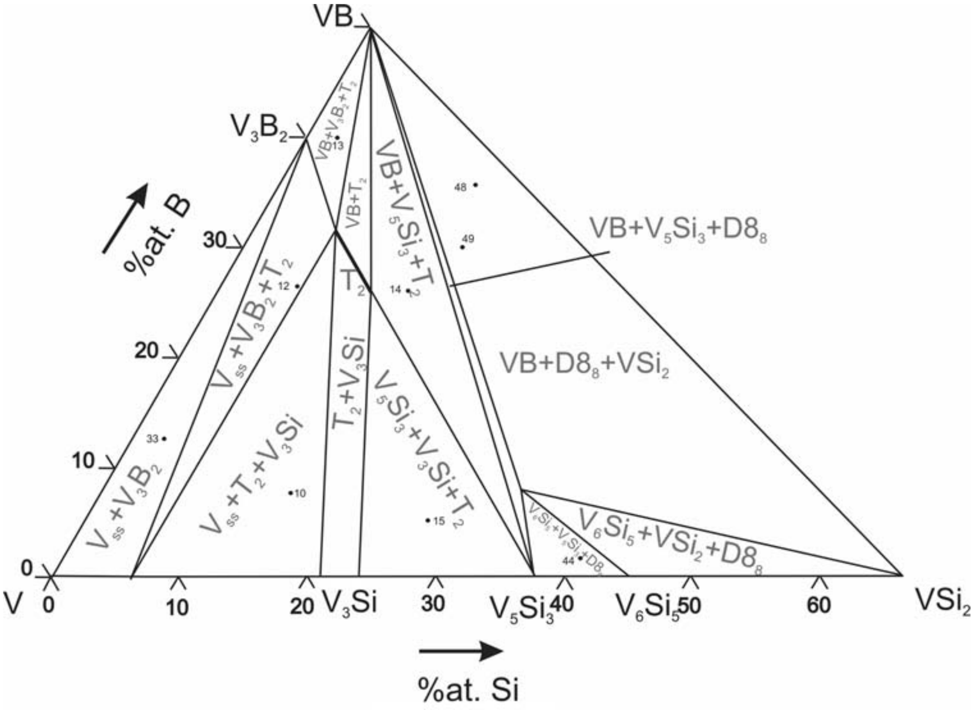

Fig. 2 Isothermal section of the V-Si-B system at 1600 °C in the V-VSi_2-VB region with indication of the alloys produced in this work

Alloy #13 ($V_{57.5}Si_{2.5}B_{40}$) 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.

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

Alloy #	Composition, at.%	Heat-treatment duration, h
10	$V_{77.5}Si_{15}B_{7.5}$	24
12	$V_{67.5}Si_{6}B_{26.5}$	24
13	$V_{57.5}Si_{2.5}B_{40}$	24/72
14	$V_{59}Si_{15}B_{26}$	24
15	$V_{68}Si_{27}B_{5}$	24
33	$V_{85}Si_{2.5}B_{12.5}$	72
44	$V_{55}Si_{40}B_{5}$	24
48	$V_{50}Si_{12.5}B_{37.5}$	72
49	$V_{52.5}Si_{17.5}B_{30}$	72

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

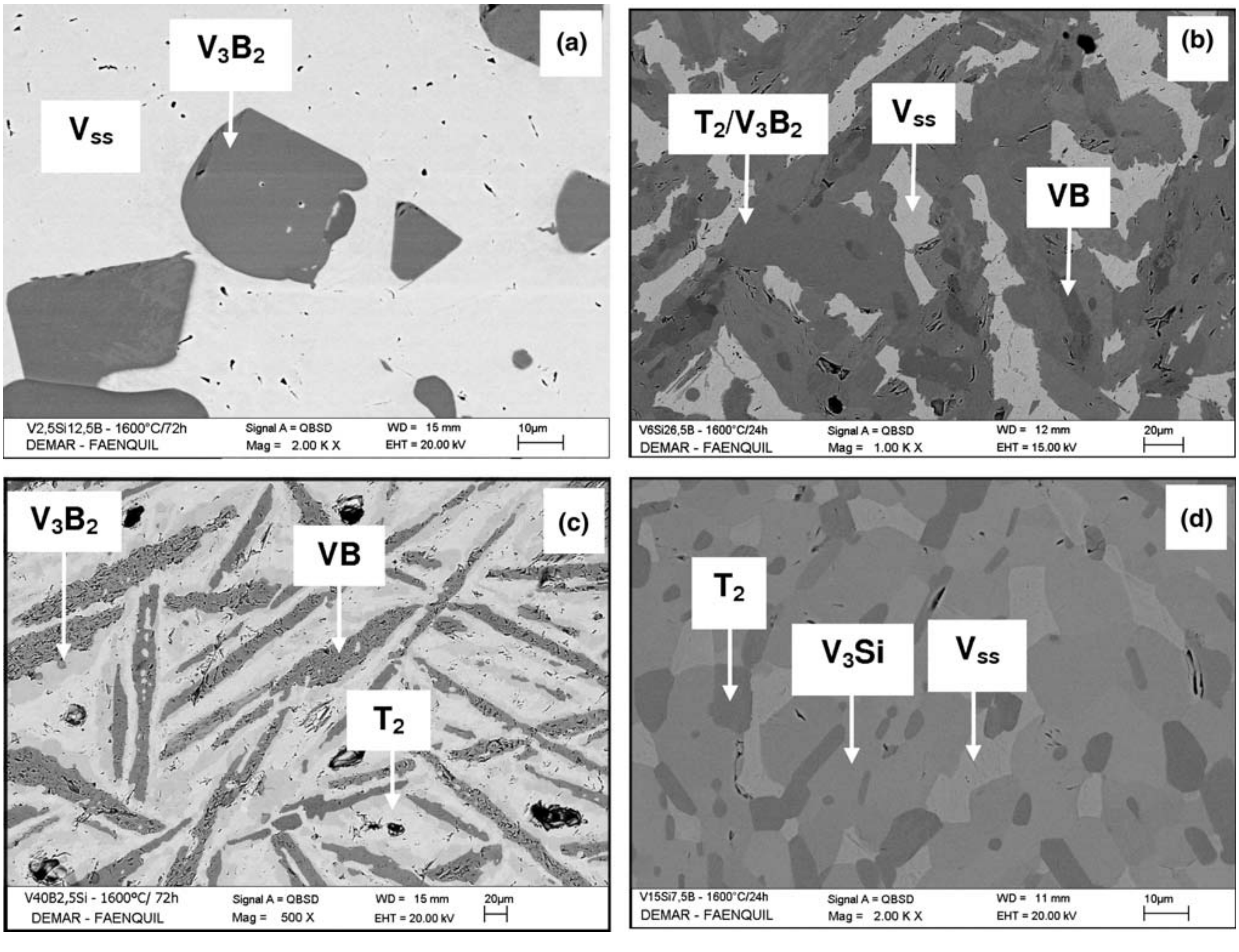

Fig. 3 SEM micrographs (SEM/BSE) of alloys #33 (a), #12 (b), #13 (c) and #10 (d) after heat-treatment at 1600 °C

temperature down to about 1200 °C is quite fast after furnace shut down. It allows us to conclude that alloy #13 lies in the V_3B_2 + VB + T_2 three-phase field and thus the V_3B_2 phase equilibrates with T_2. If this is accepted and considering that alloy #33 lies in V_{ss} + V_3B_2 two-phase field and alloy #10 in the V_{ss} + T_2 + V_3Si three-phase field, as will be discussed below, alloy #12 has to be in the V_{ss} + V_3B_2 + T_2 three-phase field as proposed in Fig. 2. Also, note that in the isothermal section from Kudielka (Fig. 1), the author proposes the equilibrium of T_2 with VB and another boride which should be V_3B_2 based on currently accepted V-B binary system.

Alloy #10 ($V_{77.5}Si_{15}B_{7.5}$) exhibited V_{ss}, V_3Si and T_2 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 V_3Si phase. In order to validate the B content of this phase, identical measurements were carried out in the V_3Si phase from binaries V-Si alloys and the B contents values were very close, allowing the conclusion that the B solubility in V_3Si is negligible. The above discussed results suggest the stability of the V_{ss} + T_2 + V_3Si three-phase field at 1600 °C.

The solubility range of V_3Si 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 T_2 phase composition of alloys #10 and #12 were not significantly different, both being near $V_{63}Si_5B_{32}$ at.%. Considering also that the T_2 lattice parameters in both alloys were close (Table 2), it can be concluded that the T_2 composition of these alloys corresponds to one of the solubility limits of this phase at 1600 °C.

Alloy #15 ($V_{68}Si_{27}B_5$) showed V_3Si, V_5Si_3, and T_2 in the as-cast as well as in the heat-treated (1600 °C) microstructure as shown in Fig. 4(a). The T_2 phase composition is near $V_{63}Si_{12}B_{25}$ (at.%) showing a Si content significantly higher than that of T_2 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 T_2-phase in the Nb-Si-B system,[9,10] but higher than that of T_2 in the Mo-Si-B system.[11] Similar to the V_3Si case, the B content of the V_5Si_3 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 V_5Si_3 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 V_5Si_3 + V_3Si + T_2 three-phase field at 1600 °C.

The lattice parameters of the T_2 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 ($V_{59}Si_{15}B_{26}$) had VB, V_3Si, V_5Si_3 and T_2 in the as-cast microstructure and VB, V_5Si_3, T_2 in the heat-treated microstructure (1600 °C) as shown in Fig. 4(b). This indicates the dissolution of V_3Si phase during heat-treatment and the stability of the VB + V_5Si_3 + T_2 three-phase field at 1600 °C. The T_2 lattice parameters (Table 2) in the VB + T_2 + V_5Si_3 and V_5Si_3 + V_3Si + T_2 three-phase fields are close, which suggest that the compositions of the T_2 phase in alloys #14 and #15 are nearly the same.

Alloy #49 ($V_{52.5}Si_{17.5}B_{30}$) exhibited VB and $D8_8$ in the as-cast and VB, $D8_8$, and VSi_2 in the heat-treated microstructure (1600 °C) as shown in Fig. 4(c), which indicates the stability of the VB + $D8_8$ + VSi_2 three-phase field at 1600 °C.

Alloy #44 ($V_{55}Si_{40}B_5$) exhibited V_5Si_3, V_6Si_5, $D8_8$, and VSi_2 in the as-cast microstructure and V_5Si_3, V_6Si_5, $D8_8$ after heat-treatment at 1600 °C as shown in Fig. 4(d), indicating the dissolution of the VSi_2 phase during heat-treatment. A negligible B solubility in V_6Si_5 was also noted. These results suggest the stability of the V_6Si_5 + V_5Si_3 + $D8_8$ three-phase field at 1600 °C.

From microanalysis measurements in $D8_8$ phase present in the microstructure of heat-treated alloys #44 and #48 a composition near $V_{59.5}Si_{33}B_{7.5}$ (at.%) is proposed for this phase in Fig. 2, a value close to $V_{59.3}Si_{34.8}B_{5.9}$ (at.%) as proposed by Kudielka et al.[4]

The lattice parameters of the VB and V_3B_2 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

	V_{ss}	V_3Si	V_3B_2		T_2		V_5Si_3		$D8_8$		VB		
Phase field/alloy #	***a***	***a***	***a***	***c***	***a***	***c***	***a***	***c***	***a***	***c***	***a***	***b***	***c***
V_{ss} + V_3B_2/33	3.037	…	5.746	3.033	…	…	…	…	…	…	…	…	…
V_{ss} + T_2 + V_3Si/10	3.037	4.746	…	…	5.785	10.779	…	…	…	…	…	…	…
V_5Si_3 + V_3Si + T_2/15	…	4.734	…	…	5.804	10.807	9.441	4.747	…	…	…	…	…
VB + V_5Si_3 + T_2/14	…	…	…	…	5.807	10.810	9.454	4.721	…	…	3.0631	8.0669	2.9769
VB + V_3B_2 + T_2/13	…	…	5.753	3.035	5.789	10.785	…	…	…	…	3.0655	8.0501	2.9809
V_{ss} + V_3B_2 + T_2/12	3.039	…	5.749	3.031	5.785	10.765	…	…	…	…	…	…	…
VB + $D8_8$ + VSi_2/49	…	…	…	…	…	…	…	…	7.181	4.886	3.0660	8.0649	2.9786
[7]	3.0297	4.7272	5.7391	3.0291	5.81	10.79	9.430	4.755	7.135	4.842	3.0603	8.0483	2.9721

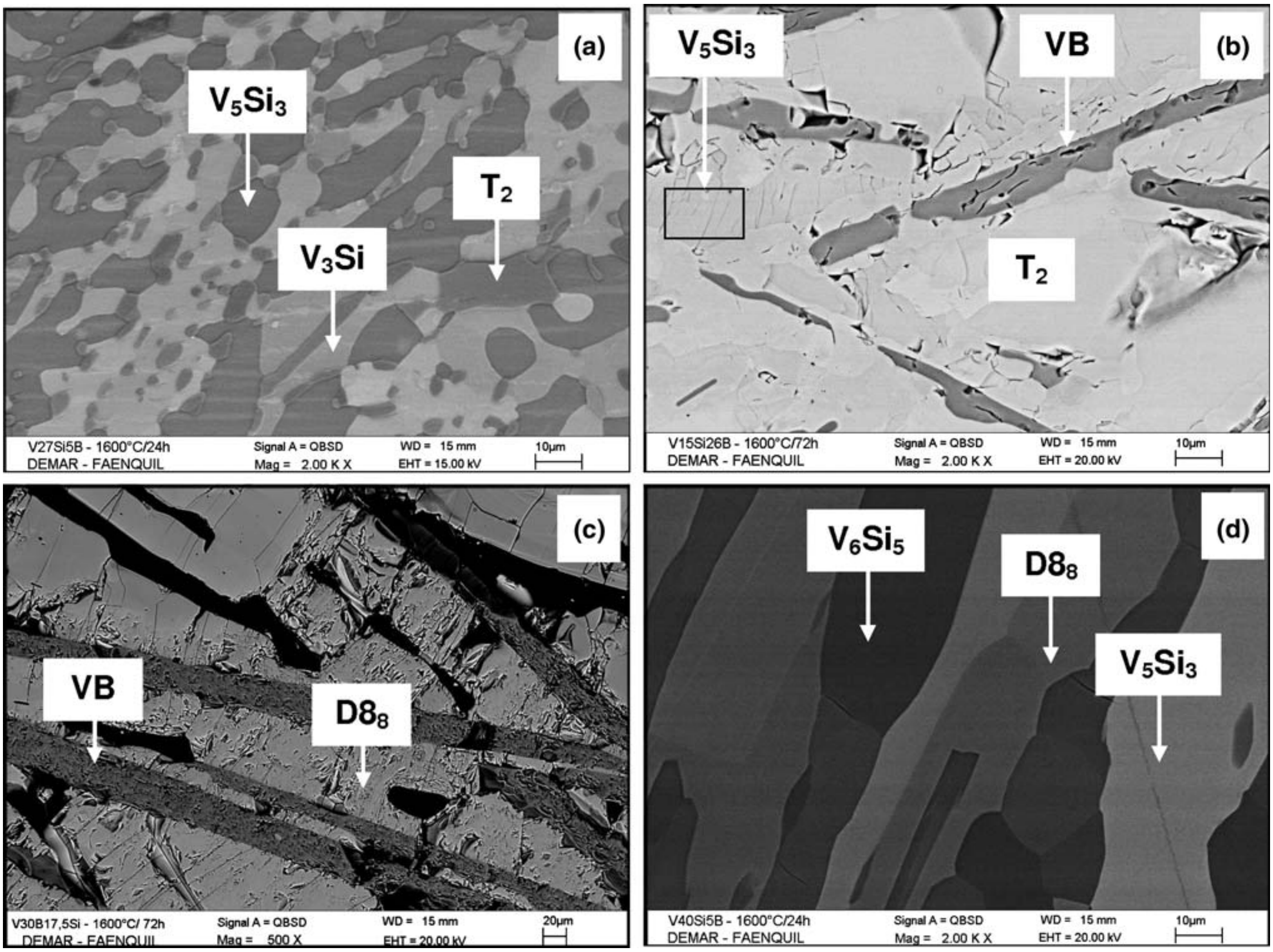

Fig. 4 SEM micrographs (SEM/BSE) of alloys #15 (a), #14 (b), #49 (c) and #44 (d) after heat-treatment at 1600 °C

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-VSi_2-VB region, the stability of the VB + V_5Si_3 + $D8_8$ and V_6Si_5 + VSi_2 + $D8_8$ three-phase fields at 1600 °C are proposed as shown in Fig. 2. Due to the significant solubility range of the V_3Si and T_2 phases, the V_3Si + T_2, and T_2 + 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-T_2 and T_2-V_3Si equilibrium shown by Kudielka et al. were also found in this work but not the $D8_8$-V_3Si and $D8_8$-T_2 two-phase equilibria; Kudielka et al. propose the existence of a binary V-B phase with $V_{70}B_{30}$ (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-VSi_2-VB. The results have confirmed the stability of the ternary T_2 and $D8_8$ phases, with T_2 exhibiting an important solubility range. A negligible B solubility in the silicide phases (V_3Si, V_5Si_3 and V_6Si_5) as well as that of Si in the borides (V_3B_2 and VB) was found.

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