



Phase Equilibria in the V-Rich Region of the V-Si-B System at 1400 °C

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Submitted: 11 August 2024 / in revised form: 18 January 2025 / Accepted: 29 January 2025 / Published online: 12 February 2025
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Abstract The phase equilibria in the V-rich region of the V-Si-B system, including the V_8SiB_4 phase, have been experimentally investigated. Eleven alloys with key compositions were produced by arc-melting or levitation-melting. The samples were then annealed at 1400 °C for 100/200/300 h under high vacuum condition. The as-cast and heat-treated alloys were investigated by scanning electron microscopy, electron backscatter diffraction, energy-dispersive x-ray spectroscopy and x-ray diffraction. The isothermal section at 1400 °C of the V-rich V-Si-B system was determined and compared with the one at 1600 °C. The determined isothermal section can be applied to the design of V-Si-B alloys.

Keywords energy dispersive spectrometry (EDS) · experimental phase equilibria · isothermal section · metallic alloys · ternary phase diagram · x-ray analysis

1 Introduction

Most high-temperature mechanical properties, e.g., high-temperature strength and creep resistance, can be correlated with the melting temperature of respective metals or alloys. Thus, similar to molybdenum-,^[1–3] niobium-^[4] and platinum-based alloys,^[5] vanadium-based alloys are promising candidates for high-temperature structural applications due to the high melting temperature of vanadium and a comparatively low density. V-Si-B alloys are one of the most promising vanadium-based alloys because the addition of Si and B can improve the oxidation resistance by facilitating the formation of a protective silica layer primarily through the intermetallic phases such as V_3Si , V_5Si_3 and V_5SiB_2 .^[6,7]

For alloy design and development, the phase diagram is one of the most important tools. The isothermal section of the V-Si-B system was first investigated at 1450 °C by Kudielka et al.^[8] using X-ray diffraction (XRD) in 1957. Three alloys, which are located along V_5B_3 - V_5Si_3 (Fig. 1), were produced via sintering at 1450 °C for 24 h under argon using powders of V (min. 99.86%), Si (min. 99.9%) and B (min. 96.35%).^[8] Based on XRD, two three-phase phase fields were identified,^[8] namely $\sim V_{0.7}B_{0.3}$ -VB- V_5SiB_2 and V_5SiB_2 - V_3Si -D8₈ (Fig. 1). The composition of $\sim V_{0.7}B_{0.3}$ phase, which was an unknown phase in 1957 for Kudielka et al.^[8] was roughly estimated as 30 at.% B. One year later (in 1958), the crystal structure of the $\sim V_{0.7}B_{0.3}$ phase was determined by Nowotny and

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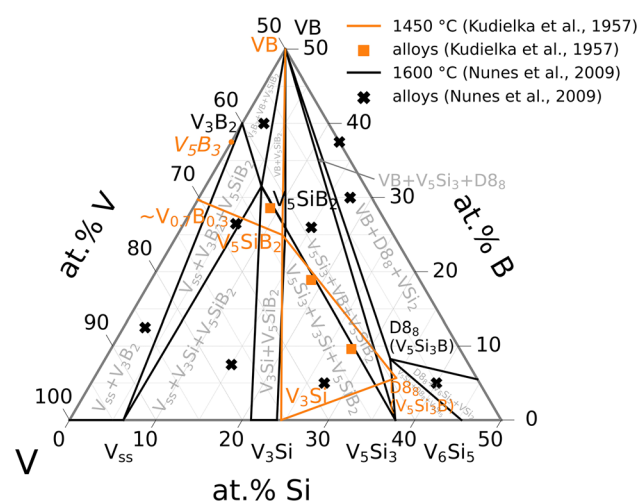


Fig. 1 The partial isothermal section of the V-Si-B system at 1450 °C proposed by Kudielka et al. [8] in comparison to that at 1600 °C proposed by Nunes et al. [9]

Wittmann,^[10] indicating that the $\sim V_{0.7}B_{0.3}$ phase actually was V_3B_2 . Regarding the $D8_8$ phase, the defect enthalpies of formation of $D8_8$ - V_5Si_3 unit cell, which were calculated using density functional theory (DFT),^[11] indicate that the B atoms should interstitially be located at 2b sites. Because “ $D8_8$ ” is also a Strukturbericht designation, the $D8_8$ phase is referred to as the V_5Si_3B phase in the following.

The latest systematic experimental investigation of the isothermal section of the V-Si-B system was carried out by Nunes et al. [9] at 1600 °C in 2009. They produced the samples via arc-melting under argon followed by heat treatment at 1600 °C for 24 h and 72 h under high vacuum (10^{-9} bar) using V (min. 99.75%), Si (min. 99.998%) and B (min. 99.95%). The samples were furnace cooled to room temperature at the end of the heat treatment. The composition of each phase in the samples investigated by Nunes et al. [9] (marked by “x” in Fig. 1) was measured by wavelength dispersive x-ray spectroscopy (WDS) using pure element standards. Based on the WDS results, the isothermal section of the V-Si-B system at 1600 °C in the V-VB- VSi_2 region of the V-Si-B system was proposed and is partially shown in Fig. 1. The observed binary V-Si and V-B phases (Fig. 1) are consistent with the investigated phase diagrams of V-Si [12–14] and V-B.^[15] The B solubility in V_{ss} , V_3Si and V_5Si_3 was found to be negligible, as was the Si solubility in V_3B_2 and VB.^[9] Furthermore, the stabilities of the two ternary phases at 1600 °C, i.e., V_5Si_3B and V_5SiB_2 , were confirmed, and a solubility range of the V_5SiB_2 phase was reported.^[9]

Based on the isothermal section of the V-Si-B system at 1600 °C presented by Nunes et al. [9], V-9Si-13B (if not stated otherwise, all alloy compositions are given in at.% in this work) was chosen for a powder metallurgical (PM) processing route by Krüger et al. [7,16]. The PM processed V-9Si-13B, consisting of a continuous V_{ss} matrix with embedded intermetallic phases V_3Si and V_5SiB_2 , showed great potential for high-temperature structural applications at around 900 °C.^[7,16]

Recently, we have observed a new ternary phase, V_8SiB_4 ,^[17] in the alloy V-5Si-9B annealed at 1400 °C. The new ternary phase has nearly the same composition as the V_5SiB_2 phase in the V_{ss} - V_3B_2 - V_5SiB_2 phase field at 1600 °C but a different crystal structure.^[17] The presence of the new ternary phase at 1400 °C indicates that there is indeed a difference between the isothermal sections of the V-rich V-Si-B system at 1400 °C and 1600 °C. In this work we have experimentally investigated the phase equilibria in the V-rich region of the V-Si-B system at 1400 °C. The microstructures were observed before and after different annealing times. The phase compositions and crystal structures were identified.

2 Experimental Methods

For producing samples, the raw materials (ChemPUR, Karlsruhe, Germany) were carefully weighed in the form of high-purity elemental turnings of V (99.7 wt.%) and granules of Si (99.99 wt.%) and B (99.0 wt.%) according to the nominal compositions of alloys listed in Table 1. The selection of alloy composition is based on the isothermal section of the V-Si-B system at 1600 °C (Fig. 1) [9] and the phase composition of V_{ss} in the V-Si system at 1400 °C.^[14] For each of the investigated V-Si-B alloy compositions having a B content less than 30 at.%, a 15 g button was produced by remelting five times in a conventional arc-melter under flowing argon gas, while for each of the investigated compositions having a B content greater than 30 at.%, a 10 g button was produced by remelting three times in a conventional arc-melter and then two times in a levitation melter under argon gas. A negligible weight loss (< 1 wt.%) indicates that the compositions after melting are very close to the nominal compositions. For confirmation, inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 7600, Thermo Fisher Scientific, USA) was performed and the measured chemical compositions of the investigated

Table 1 The nominal and chemical compositions of the alloys investigated in this work and the corresponding heat treatment duration at 1400 °C

No.	Nominal composition, at. %	Actual chemical composition (according to ICP-OES), at. %	Heat treatment duration at 1400 °C, h
#1	V-2Si-12B	V-2.1Si-11.5B	0 (as-cast)
			100
			200
#2	V-3Si-17B	V-2.9Si-17.6B	0 (as-cast)
			200
			300
#3	V-5Si-5B	V-5.2Si-4.7B	0 (as-cast)
			100
			200
#4	V-16.5Si-3.5B	V-16.7Si-3.5B	0 (as-cast)
			100
			200
#5	V-18.5Si-6.5B	V-17.9Si-6.1B	0 (as-cast)
			100
			200
#6	V-1Si-40B	V-1.0Si-42.0B	0 (as-cast)
			200
			300
#7	V-3Si-38B	V-2.8Si-38.7B	0 (as-cast)
			100
			200
#8	V-7Si-33B	V-7.2Si-33.7B	0 (as-cast)
			200
			300
#9	V-20Si-6.5B	V-20.4Si-6.3B	0 (as-cast)
			100
			300
#10	V-26Si-3B	V-25.5Si-3.4B	0 (as-cast)
			100
			200
#11	V-20Si-20B	V-22.2Si-17.1B	0 (as-cast)
			200
			300

alloys are shown in Table 1. Combustion analysis (Leco CS600, LECO, USA) was used to determine the carbon (C) content of the alloys. The as-cast buttons were cut in half by electrical discharge machining (EDM). One half was used to investigate the as-cast microstructure, while the other half was heat-treated at 1400 °C for 100 h under high vacuum (1.5×10^{-5} mbar) and furnace cooled within 3 h below 200 °C. The annealing at 1400 °C for 100 h was

repeated 2 or 3 times. The heat treatment times of the investigated alloys are listed in Table 1.

For metallographic preparation, the samples were cold-mounted (Expoy 2000, Cloeren Technology, Wegberg, Germany), and subsequently ground with SiC papers down to 2000 grit. The polishing was conducted with 15 µm, 6 µm, 3 µm and 1 µm diamond suspension, and finished with colloidal silica.

X-ray diffraction (XRD) measurements were performed on the polished bulk samples at room temperature using a diffractometer EMPYREAN (Malvern Panalytical, UK) or a diffractometer D8 ADVANCE (Bruker, USA) to identify the crystal structures of the phases. The lattice parameters of the phases were determined using the software GSAS-II^[18] and the Pawley refinement,^[19] in which the intensities of the calculated diffraction peaks do not depend on the atomic kinds and positions in the crystal structure. Except for the V_8SiB_4 phase, whose crystal structure was taken from recent work,^[17] the corresponding crystal structures used for the XRD were taken from the Inorganic Crystal Structure Database (ICSD)^[20] with the collection code 241937,^[21] 87328,^[22] 652506,^[23] 652505,^[23] 88317,^[24] 44490^[8] and 615658^[25] for V_{ss} , V_3Si , tetragonal V_5Si_3 , hexagonal V_5Si_3 , V_3B_2 , VB and V_5SiB_2 phases, respectively.

A Zeiss Merlin (Zeiss Microscopy, Oberkochen, Germany) scanning electron microscope (SEM) was used to observe the microstructures using the backscattered electron (BSE) mode. Furthermore, electron backscatter diffraction (EBSD, Oxford Instruments, UK) with a scanning step size smaller than 0.6 μm for the as-cast samples and smaller than 1 μm for the heat-treated samples was used to identify the phases by matching the backscatter Kikuchi patterns to the crystal structures of V_{ss} , V_3Si , V_5Si_3 , V_3B_2 , VB and V_5SiB_2 and obtain the phase mapping. Due to the similar crystal structure of the V_5SiB_2 and V_8SiB_4 phases, the V_5SiB_2 phase suggested by EBSD can be identified as the V_8SiB_4 phase in the EBSD phase mapping when the V_8SiB_4 phase was suggested by Energy-dispersive X-ray spectroscopy (EDS, X-Max 150, Oxford Instruments, UK) and XRD. In the case of coexistence of V_5SiB_2 and V_8SiB_4 phases, the crystal structures of both phases were used for matching the backscatter Kikuchi patterns.

After confirming the homogeneity of elemental distribution in every single phase using EDS mapping, EDS point measurements were performed to quantitatively determine the chemical compositions of phases. The AZtec software (Oxford Instruments, UK) was used to calculate the element amount in weight percent. Pure V, Si, and B were used as standard materials for the calibration of EDS. It should be noted that the quantitative detection of B using EDS is challenging because of the low electron density of B atoms (5 electrons per atom^[26]), but can be achieved since no peak overlap with the V or Si EDS spectra exists (in contrast to the Mo M_{α} -line of 0.193 keV and the B K_{α} -

line of 0.183 keV^[27]). Furthermore, the B content of the B-containing phases investigated in this work is sufficiently high to be detected.

The phase area fraction was determined by EBSD, while the phase volume fraction was determined using the phase compositions and the phase molar volumes measured by EDS and XRD, respectively. For a three-phase alloy, using the measured composition of each phase j , c_j^{Si} and c_j^B in at.%, the phase molar fraction of each phase f_j can be calculated by solving the following set of equations:

$$\begin{cases} \sum_j f_j = 1 \\ \sum_j f_j c_j^{Si} = c_{alloy}^{Si} \\ \sum_j f_j c_j^B = c_{alloy}^B \end{cases} \quad (\text{Eq 1})$$

where c_{alloy}^{Si} and c_{alloy}^B are the alloy compositions in at.%. For a three-phase alloy, the nominal alloy compositions (Table 2) were used in Eq 1. By contrast, for a two-phase alloy, the alloy composition, which fulfills the set of Eq 1 and is the closest to the nominal alloy composition, was used to calculate the phase molar fractions. The calculated phase molar fractions can be converted to the phase volume fractions using the phase molar volumes determined by XRD.

3 Results and Discussion

The microstructural evolution upon annealing at 1400 °C of the alloys investigated is presented in section 3.1. The evolution of phase area or volume fraction with increasing annealing time was used to confirm the equilibrium state of the alloys studied in this work. Then the isothermal section of the V-Si-B system at 1400 °C is proposed in section 3.2. To estimate the accuracy of the EDS analysis, the measured compositions of binary phases were compared to those reported in the binary V-Si and V-B systems in section 3.3.

3.1 Evolution of Microstructure and Phase Composition in Each Phase Field

3.1.1 Phase Field of V_{ss} - V_3B_2

The microstructure of the as-cast alloy V-2Si-12B consists of the V_3B_2 primary phase having a polygonal shape and the V_{ss} - V_3B_2 eutectic (Fig. 2a). After annealing at 1400 °C

Table 2 Lattice parameters (Å) of phases in the as-cast and heat-treated (1400 °C) V – Si – B alloys

No.	Alloy	Heat treatment time, h	$V_{ss}, Im\bar{3}m$			VB, $P4/mbm$			$V_3Si, Pm\bar{3}n$			$V_5Si_3, I4/mcm$			$V_5Si_3, P6_3/mcm$			$V_5SiB_2, I4/mcm$			$V_8SiB_4, I4/mcm$		
			a	b	c	a	b	c	a	a	c	a	a	c	a	a	c	a	a	c	a	a	c
#1	V-2Si-12B	0 (as-cast)	3.026
		100	3.029
		200	3.026
#2	V-3Si-17B	0 (as-cast)	3.022
		200	3.025
		300	3.023	5.768	16.796	...
#3	V-5Si-5B	0 (as-cast)	3.022	5.769	16.791	...
		100	3.023	4.737	5.765	16.793	...
		200	3.027	4.739	5.769	16.799	...
#4	V-16.5Si-3.5B	0 (as-cast)	3.026	4.736	5.767	10.737	...
		100	3.026	4.740	5.768	16.793	...
		200	3.026	4.739	5.769	16.799	...
#5	V-18.5Si-6.5B	0 (as-cast)	3.024	4.730	5.785	10.772	...
		100	4.736	5.786	10.766	16.781
		200	4.736	5.781	10.776	16.770
#6	V-1Si-40B	0 (as-cast)	3.027	3.061	8.047	2.971
		200	3.040*	3.060	8.046	2.977	5.768	16.799	...
		300	3.051*	3.061	8.048	2.971	5.766	16.818	...
#7	V-3Si-38B	0 (as-cast)	3.028	3.062	8.049	2.973	5.775	10.744	16.813*
		100	...	3.062	8.051	2.969	4.739*	5.786	10.799	16.793
		200	...	3.062	8.047	2.971	4.736*	5.787	10.761	16.786
#8	V-7Si-33B	0 (as-cast)	3.033*	3.058	8.055	2.974	4.737	5.786	10.770	...
		200	3.049*	3.061	8.049	2.971	4.734	5.786	10.772	...
		300	3.050*	3.060	8.040	2.973	4.732	5.786	10.774	...
#9	V-20Si-6.5B	0 (as-cast)	4.730	5.784	10.772	...
		100	4.731	5.785	10.770	...
		300	4.730	5.787	10.776	...
#10	V-26Si-3B	0 (as-cast)	4.726	9.417	4.752	5.798	10.793	...
		100	4.728	9.420	4.750	7.143*	4.868*	5.798	10.798	...
		200	4.728	9.420	4.750	7.142*	4.865*	5.798	10.796	...
#11	V-20Si-20B	0 (as-cast)	...	3.058	8.055	2.971	4.726	9.412	4.727	5.795	10.786	...
		200	...	3.062	8.050	2.971	4.727	9.423	4.757	7.147	4.872	5.798	10.793	...
		300	...	3.060	8.052	2.974	9.422	4.738	5.797	10.791	...

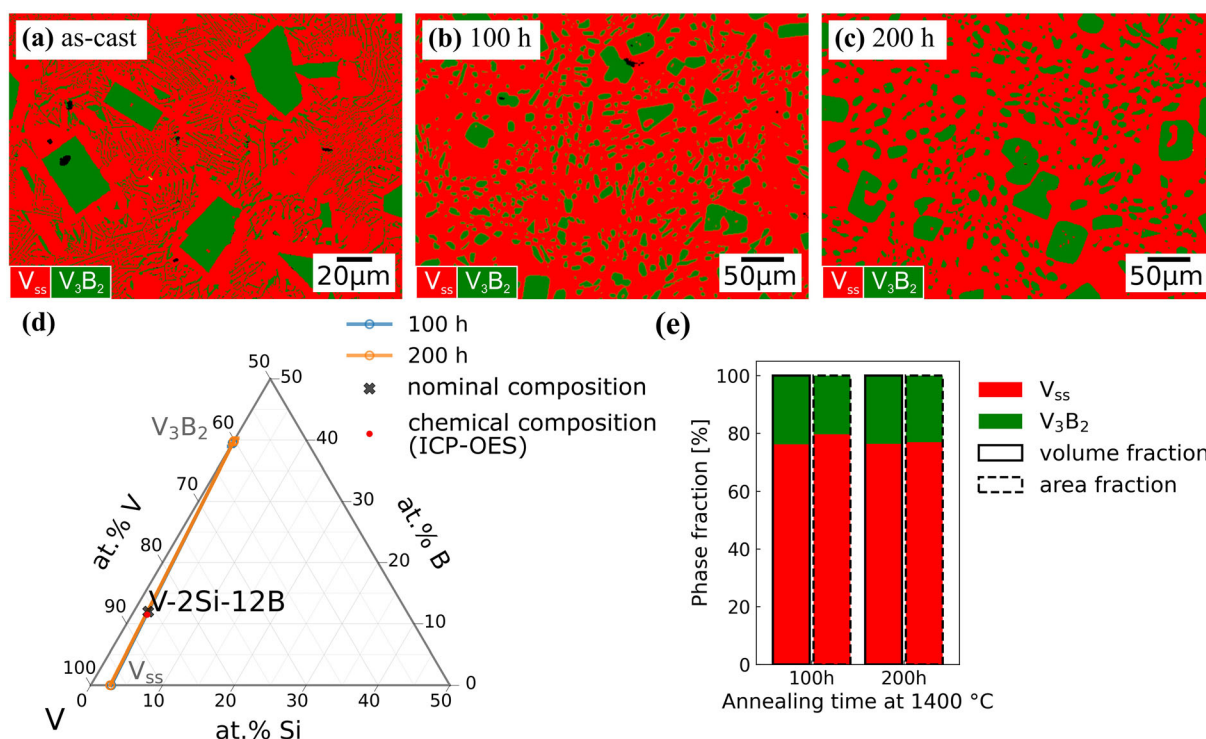


Fig. 2 Experimental microstructures (EBSD phase mappings) of alloy V-2Si-12B in the (a) as-cast condition and after annealing for (b) 100 h and (c) 200 h. (d) The phase compositions measured by EDS (marked with open circles), where the error bars are plotted along the

for 100 h, the corners of the polygon-shaped V_3B_2 phase were rounded, while the V_{ss} - V_3B_2 eutectic was replaced by the globular V_3B_2 phase distributed in the V_{ss} phase (Fig. 2b). The microstructure after heat treatment at 1400 °C for 200 h is similar to the microstructure after 100 h (Fig. 2c). In agreement with the observed microstructures, the XRD results show that there are two phases present after annealing, i.e., the V_{ss} phase and the V_3B_2 phase (Table 2). The EDS results of the annealed alloys V-2Si-12B (Table 3) are plotted in a ternary diagram (Fig. 2d), where the compositional position of alloy V-2Si-12B is located on the line connecting the V_{ss} phase and the V_3B_2 phase. The change of each phase volume or area fraction does not depend on the annealing time (Fig. 2e). Therefore, after 100 h, the alloy V-2Si-12B must have reached the equilibrium state at 1400 °C, which confirms the V_{ss} - V_3B_2 phase field.

3.1.2 Phase Field of V_{ss} - V_3B_2 - V_8SiB_4

In the as-cast alloy V-3Si-17B, the VB primary phase is surrounded by the V_3B_2 phase, and the V_{ss} - V_3B_2 eutectic was observed (Fig. 3a). After 200 h of annealing at 1400 °C, the VB primary phase was no longer observed (Fig. 3b), which indicates the transformation of the VB

fixed B and Si contents for the standard deviations exceeding 0.3 at.% Si and B. (e) The evolution of phase volume and area fractions showing that the equilibrium state at 1400 °C was reached after 100 h

primary phase into the V_{ss} and V_3B_2 phases. The V_{ss} - V_3B_2 eutectic was replaced by the globular V_3B_2 phase and the newly formed V_8SiB_4 phase (Fig. 3b). The observed microstructure agrees well with the XRD results (Table 2). When the annealing time was increased to 300 h, no microstructural changes were observed (Fig. 3c). Correspondingly, the phase compositions measured by EDS after 200 h are almost identical to those after 300 h (Table 3 or Fig. 3d). The volume or area fraction of each phase did not change with increasing annealing time (Fig. 3e). Thus, it can be confirmed that 200 h is sufficient for the alloy V-3Si-17B to reach the equilibrium state at 1400 °C. The annealed alloys V-3Si-17B were used to determine the phase field of V_{ss} - V_3B_2 - V_8SiB_4 .

3.1.3 Phase Field of V_{ss} - V_3Si - V_8SiB_4

Comparing the microstructures of the as-cast and annealed (1400 °C/100 h) alloy V-5Si-5B (Fig. 4a and b), it can be seen that the dendritic V_{ss} primary phase and the V_{ss} - V_3B_2 and the V_{ss} - V_5SiB_2 eutectics had vanished after annealing. In agreement with the observed annealed microstructures, the XRD results show that the annealed alloys consist of V_{ss} , V_3Si and V_8SiB_4 phases (Table 2). The newly formed V_8SiB_4 phases may have been transformed from the

Table 3 Composition of phases (at.%) measured by EDS in the heat-treated (1400 °C) V-Si-B alloys

No.	Alloy	Heat treatment time, h	V _{ss}		VB		V ₃ Si		V ₃ B ₂		V ₅ Si ₃		V ₅ SiB ₂		V ₈ SiB ₄	
			Si	B	Si	B	Si	B	Si	B	Si	B	Si	B	Si	B
#1	V-2Si-12B	100	2.8 ± 0.1	0	0	39.5 ± 0.5
		200	2.7 ± 0.1	0	0	39.8 ± 0.5
#2	V-3Si-17B	200	3.8 ± 0.1	0	0	40.1 ± 0.5	6.4 ± 0.1	31.3 ± 0.7	...
		300	3.8 ± 0.1	0	0	39.3 ± 0.6	6.6 ± 0.2	29.7 ± 0.8	...
#3	V-5Si-5B	100	4.1 ± 0.1	0	18.9 ± 0.1	0	6.5 ± 0.2	30.8 ± 1.2	...
		200	3.9 ± 0.1	0	18.9 ± 0.1	0	6.6 ± 0.2	30.3 ± 0.5	...
#4	V-16.5Si-3.5B	100	4.1 ± 0.1	0	19.4 ± 0.3	0	6.5 ± 0.2	31.4 ± 0.8	...
		200	3.3 ± 0.3	0	19.2 ± 0.2	0	6.6 ± 0.2	30.5 ± 1.1	...
#5	V-18.5Si-6.5B	100	20.1 ± 0.3	0	11.5 ± 0.3	22.9 ± 1.5	6.9 ± 0.3	30.0 ± 1.9
		200	19.8 ± 0.1	0	11.1 ± 0.3	24.5 ± 1.1	6.6 ± 0.1	31.0 ± 0.6
#6	V-1Si-40B	200	0	49.8 ± 0.5	0	39.6 ± 0.9	6.6 ± 0.3	30.6 ± 1.0	...
		300	0	50.1 ± 0.5	0	40.1 ± 0.5	6.5 ± 0.1	31.2 ± 0.7	...
#7	V-3Si-38B	100	1.7 ± 0.6	0	0	50.3 ± 0.6	20.9 ± 0.2	0	0	40.4 ± 0.7	10.9 ± 0.2	25.2 ± 1.1	6.6 ± 0.4	31.7 ± 1.1
		200	0	49.8 ± 0.3	0	40.7 ± 0.7	10.8 ± 0.2	25.8 ± 0.8	6.6 ± 0.1	31.9 ± 0.6
#8	V-7Si-33B	200	0	50.5 ± 0.4	22.8 ± 0.2	0	0	40.5 ± 1.0	11.1 ± 0.3	25.3 ± 1.0
		300	0	50.6 ± 0.4	23.2 ± 0.1	0	0	40.7 ± 0.7	11.1 ± 0.3	25.7 ± 0.8	6.7 ± 0.2	31.8 ± 0.6
#9	V-20Si-6.5B	100	21.5 ± 0.1	0	11.3 ± 0.4	25.3 ± 1.0
		300	21.8 ± 0.1	0	11.1 ± 0.2	25.5 ± 0.9
#10	V-26Si-3B	100	23.5 ± 0.1	0	35.2 ± 0.2	0	12.1 ± 0.1	23.9 ± 0.8
		200	23.6 ± 0.1	0	35.2 ± 0.1	0	12.4 ± 0.2	22.3 ± 1.0
#11	V-20Si-20B	200	0	50.8 ± 0.7	35.6 ± 0.2	0	12.0 ± 0.2	24.4 ± 0.8
		300	0	49.9 ± 0.6	35.4 ± 0.2	0	12.0 ± 0.2	24.6 ± 0.8

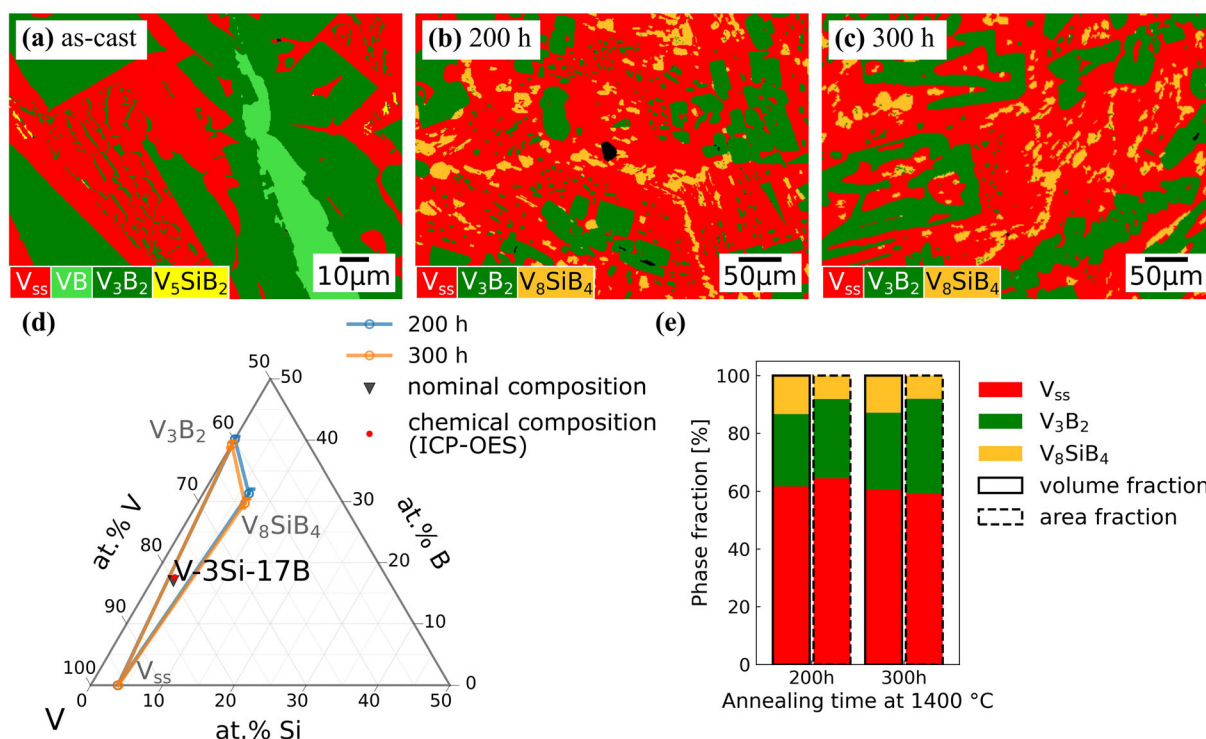


Fig. 3 Experimental microstructures (EBSD phase mappings) of alloy V-3Si-17B in the (a) as-cast condition and after annealing for (b) 200 h and (c) 300 h. (d) The phase compositions measured by EDS (marked with open circles), where the error bars are plotted

V₅SiB₂ phase in the as-cast state. After 100 h of annealing at 1400 °C, the alloy V-5Si-5B is close to the phase equilibrium because an additional 100 h of annealing did not change the phase compositions (Table 3 or Fig. 4d) or the volume and area fractions of each phase (Fig. 4e). Furthermore, as shown in Fig. 4(d), V-5Si-5B is located close to the line connecting the V_{ss} and V₈SiB₄ phases, but the V₃Si phase can still be observed after annealing, which suggests that the alloy is close to the V_{ss}-V₈SiB₄ phase region.

In the as-cast alloy V-16.5Si-3.5B, the V₃Si primary phase, the coarse V₅SiB₂ phase and the V_{ss}-V₅SiB₂ eutectic were observed (Fig. 5a). After annealing at 1400 °C for 100 h, discontinuous regions consisting of the V_{ss} and V₈SiB₄ phases were observed in the V₃Si matrix phase (Fig. 5b). The coexistence of the V_{ss}, V₃Si and V₈SiB₄ phases after the heat treatment was confirmed by XRD (Table 2). Like alloy V-5Si-5B, alloy V-16.5Si-3.5B is also located within the three-phase field of V_{ss}-V₃Si-V₈SiB₄ (Fig. 5d). The difference between these two alloys is, however, that the most abundant phase in the annealed

alloy V-3Si-17B is the V_{ss} phase, while in the annealed alloy V-16.5Si-3.5B it is the V₃Si phase. Similarly, the phase equilibrium must be reached in alloy V-16.5Si-3.5B annealed at 1400 °C after 100 h according to the evolution of phase volume and area fractions (Fig. 5e), where the changes from 100 h to 200 h are negligible. Thus, the annealed alloys V-5Si-5B and V-16.5Si-3.5B were used to determine the phase field of V_{ss}-V₃Si-V₈SiB₄.

3.1.4 Phase Field of V₃Si-V₈SiB₄-V₅SiB₂

In the as-cast alloy V-18.5Si-6.5B, the V₃Si-V₅SiB₂ and V_{ss}-V₅SiB₂ eutectics were observed (Fig. 6a). After annealing at 1400 °C for 100 h, the V_{ss} phase had almost disappeared, while the V₈SiB₄ phase had formed close to the V₅SiB₂ phase within a V₃Si matrix (Fig. 6b). An additional 100 h annealing did not change the microstructure significantly (Fig. 6c), although the V_{ss} phase, which has a negligible area fraction (Fig. 6e) and cannot be detected by XRD (Table 2), was detected by EBSD. Thus, the annealed alloys V-18.5Si-6.5B must be very close to

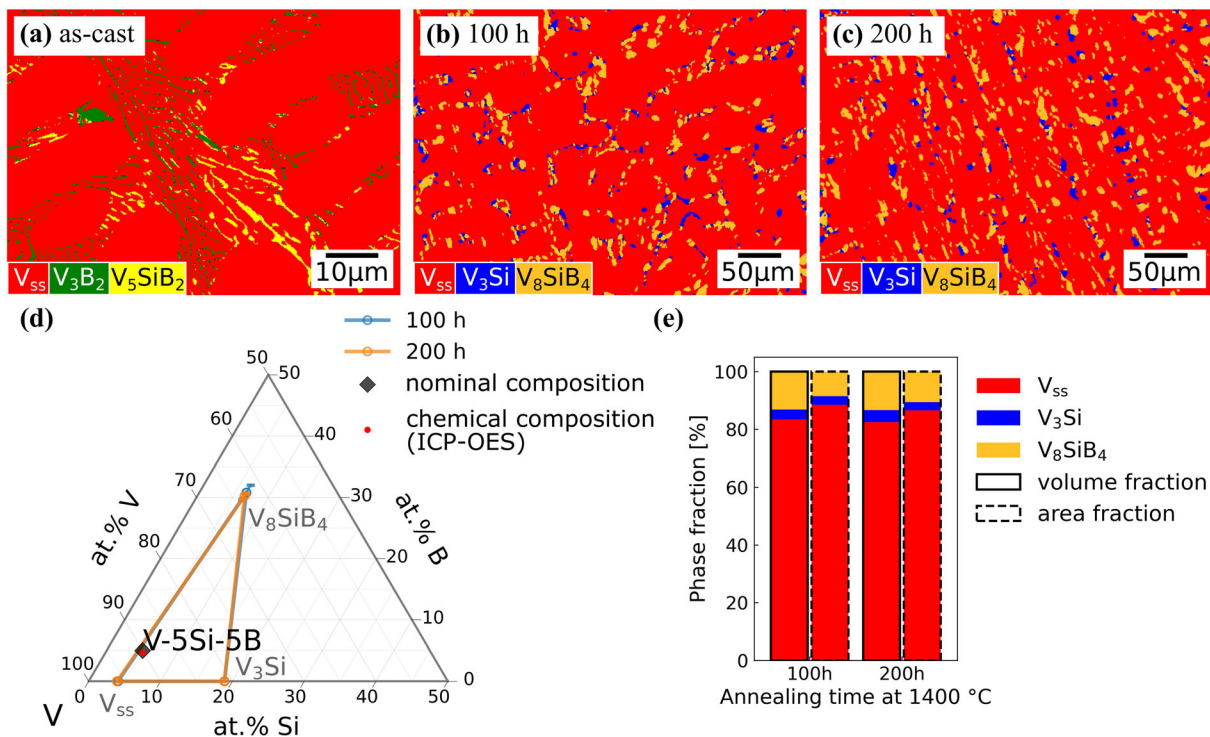


Fig. 4 Experimental microstructures (EBSD phase mappings) of alloy V-5Si-5B in the (a) as-cast condition and after annealing for (b) 100 h and (c) 200 h. (d) The phase compositions measured by EDS (marked with open circles), where the error bars are plotted along the fixed B and Si contents for the standard deviations

the equilibrium state between V_3Si , V_8SiB_4 and V_5SiB_2 phases. The measured phase compositions (Table 3 or Fig. 6d) were used to determine the phase field of V_3Si - V_8SiB_4 - V_5SiB_2 .

3.1.5 Phase Field of V_3Si - V_5SiB_2

The as-cast alloy V-20Si-6.5B consists of the continuous V_3Si phase, the coarse V_5SiB_2 phase and the V_{ss} - V_5SiB_2 eutectic (Fig. 7a). The continuous V_3Si phase should be the primary phase according to the reported liquidus projection.^[28,29] After annealing at 1400 °C for 100 h and 300 h, the V_{ss} phase had disappeared and the V_5SiB_2 phase had been distributed within a V_3Si matrix (Fig. 7b and c). The observed microstructures agree well with the XRD results (Table 2). Furthermore, the phase compositions of V_3Si and V_5SiB_2 were measured by EDS and the corresponding results (Table 3) are plotted in Fig. 7(d), where the compositional position of alloy V-20Si-6.5B is located close to the line connecting the average phase compositions of V_3Si

exceeding 0.3 at.% Si and B. (e) The evolution of phase volume and area fractions showing that the equilibrium state at 1400 °C was reached after 100 h

and V_5SiB_2 . As the annealing time was increased from 100 h to 300 h, no significant change in phase volume and area fraction (Fig. 7e) was detected, indicating that the equilibrium state must have been reached after 100 h. Thus, the annealed alloys V-20Si-6.5B confirm the existence of V_3Si - V_5SiB_2 phase field at 1400 °C.

3.1.6 Phase Field of V_3Si - V_5SiB_2 - V_5Si_3

According to the XRD results (Table 2), the V_3Si , tetragonal V_5Si_3 and V_5SiB_2 phases exist in the as-cast alloy V-26Si-3B. However, the EBSD results (Fig. 8a) show some unexpected phases, the hexagonal V_5Si_3 and V_2C phases with negligible volume fractions in the as-cast state. In the annealed alloys V-26Si-3B, the V_3Si , tetragonal and hexagonal V_5Si_3 and V_5SiB_2 phases were observed (Fig. 8b and c). The hexagonal V_5Si_3 phase shown in EBSD phase mappings was detected by combining the EBSD and EDS mapping, because the EBSD method cannot distinguish between the hexagonal V_5Si_3 ^[23,30] and

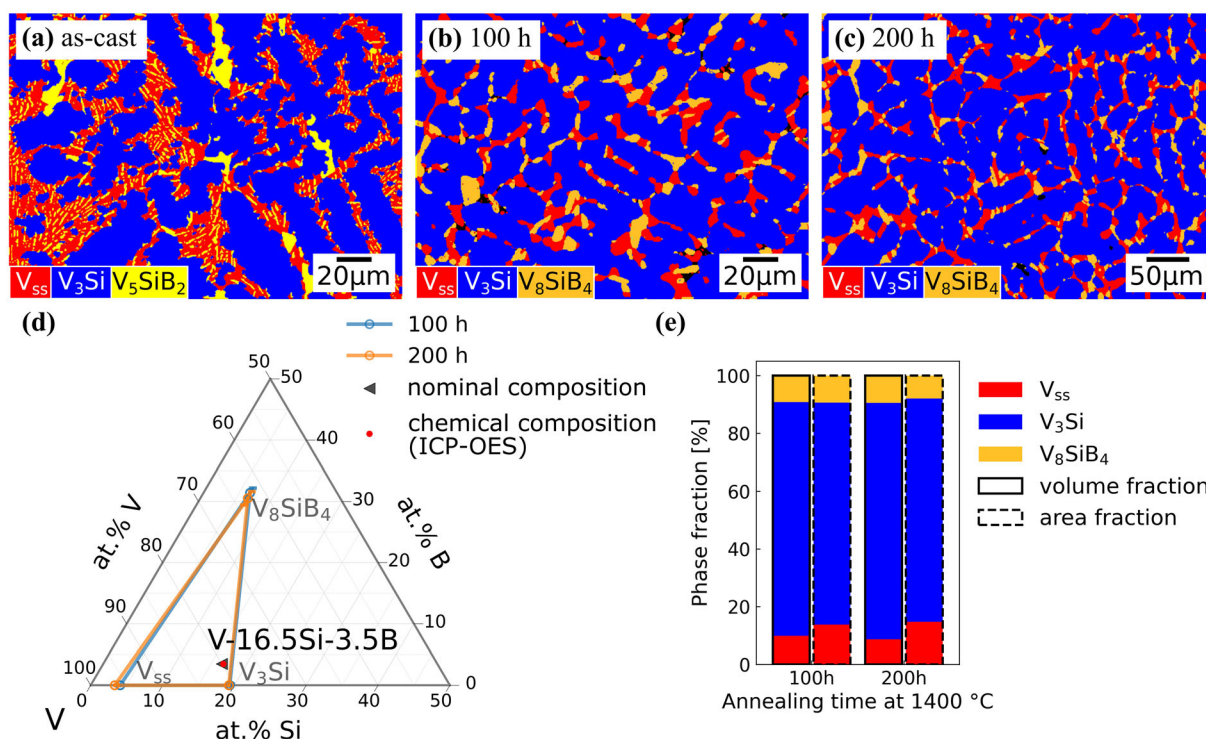


Fig. 5 Experimental microstructures (EBSD phase mappings) of alloy V-16.5Si-3.5B in the (a) as-cast condition and after annealing for (b) 100 h and (c) 200 h. (d) The phase compositions measured by EDS (marked with open circles), where the error bars are plotted

V₅Si₃B^[8,9] phases due to their similar crystal structures and lattice parameters. Fortunately, the EDS elemental mappings can indeed help to distinguish these two phases due to their different compositions (Fig. 8d and e). In agreement with EBSD and EDS, XRD detected both the tetragonal and hexagonal V₅Si₃ phases after the heat treatment (Table 2).

According to the investigation of the V-Si-B system at 1450 °C^[8] and 1600 °C,^[9] the V₅Si₃ phase should have a tetragonal crystal structure (*I4/mcm*). However, a hexagonal V₅Si₃ phase (*P6₃/mcm*) can be stabilized by a small amount of carbon (0.1–0.2 wt.%).^[23] Thus, the existence of a hexagonal V₅Si₃ phase could be an indicator of a small amount of carbon contamination, which could originate from the raw materials or the fabrication process and was confirmed by the combustion analysis of carbon (0.013 ± 0.004 wt.%) for the as-cast alloy. This finding agrees well with the occurrence of the V₂C phase suggested by EBSD in the as-cast alloy (Fig. 8a).

The phase compositions of the V₃Si, tetragonal V₅Si₃ and V₅SiB₂, measured by EDS in the annealed alloys

along the fixed B and Si contents for the standard deviations exceeding 0.3 at.% Si and B. (e) The evolution of phase volume and area fractions showing that the equilibrium state at 1400 °C was reached after 100 h

V-26Si-3B (Table 3), are shown in a ternary diagram (Fig. 8f) and were used to calculate the phase volume fractions. The calculated volume fraction or the measured area fraction of each phase remained almost constant in alloy V-26Si-3B annealed at 1400 °C when the annealing time was increased from 100 h to 200 h (Fig. 8g). Thus, alloy V-26Si-3B must have reached the equilibrium state at 1400 °C after 100 h. Since the volume fractions of the hexagonal V₅Si₃ phase are much smaller than those of the other three phases in the annealed alloys (Fig. 8g), the compositions of the other three phases are very close to the phase equilibrium of the V₃Si-V₅Si₃-V₅SiB₂ phase field. Thus, the annealed alloys V-26Si-3B were used to determine the phase field of V₃Si-V₅Si₃-V₅SiB₂.

3.1.7 Phase Field of VB-V₃B₂-V₈SiB₄

The microstructure of the as-cast alloy V-1Si-40B (Fig. 9a) indicates that the VB primary phase was followed by the formation of the V₃B₂ phase, and the formation of the V_{ss}-V₃B₂ and V_{ss}-V₅SiB₂ eutectics in agreement with the

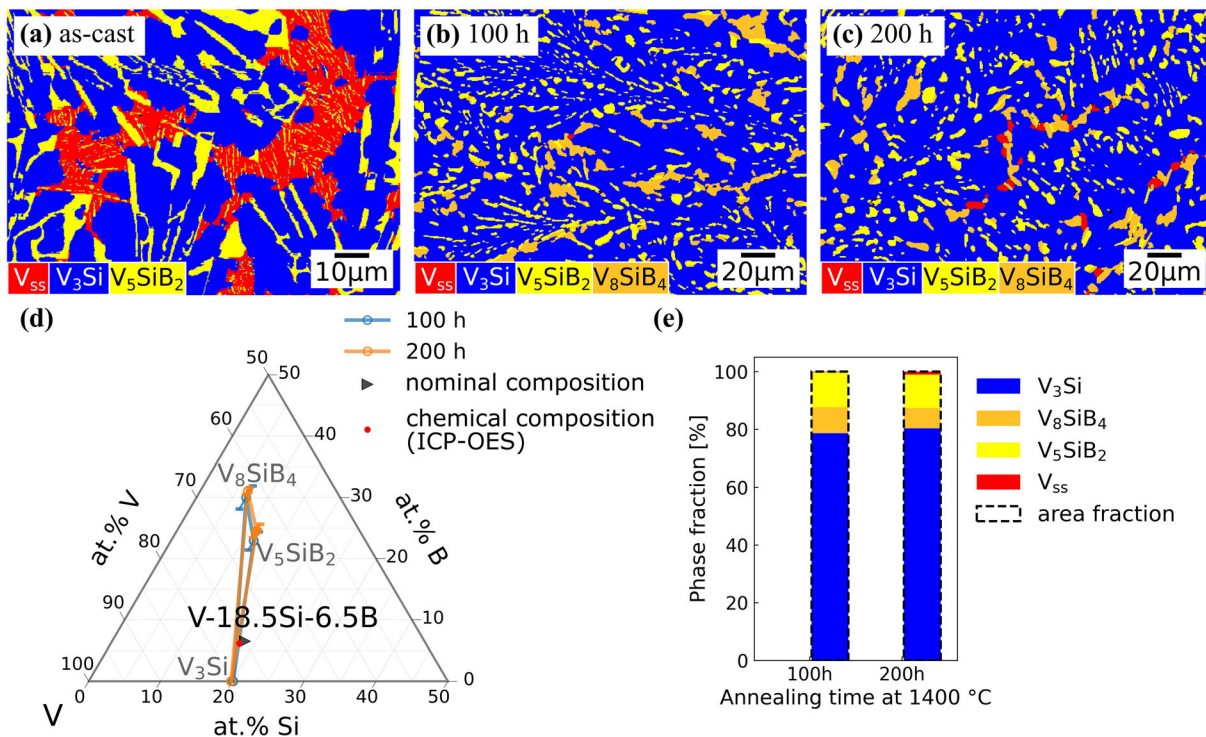


Fig. 6 Experimental microstructures (EBSD phase mappings) of alloy V-18.5Si-6.5B in the (a) as-cast condition and after annealing for (b) 100 h and (c) 200 h. (d) The phase compositions measured by EDS (marked with open circles), where the error bars are plotted

reported liquidus projection.^[28,29] Annealing at 1400 °C for 200 h caused the V_3B_2 phase adjacent to the VB phase to grow and separate the VB phase from the newly formed V_8SiB_4 phase (Fig. 9b). As the annealing time increased, the V_{ss} phase further dissolved (Fig. 9c). Consistent with the observed microstructures (Fig. 9b and c), the XRD results suggest a negligible volume or area fraction for the V_{ss} phase in the annealed alloys (Table 2). Neglecting the presence of the V_{ss} phase, the measured phase compositions (Table 3 or Fig. 9d) were used to calculate the evolution of the phase volume fractions (Fig. 9e), which can indicate that the phase equilibria after 300 h annealing was almost reached. Thus, the alloy V-1Si-40B annealed at 1400 °C for 300 h was used to determine the phase field of VB- V_3B_2 - V_8SiB_4 in this work.

3.1.8 Phase Field of VB- V_5SiB_2 - V_5Si_3

The as-cast alloy V-20Si-20B consists of the VB primary phase, the tetragonal V_5Si_3 phase, the V_5SiB_2 phase and the V_3Si - V_5SiB_2 eutectic (Fig. 10a). After annealing at 1400 °C for 200 h, the V_3Si phase had disappeared, while

along the fixed B and Si contents for the standard deviations exceeding 0.3 at.% Si and B. (e) The evolution of phase area fractions showing that the equilibrium state at 1400 °C was almost reached after 100 h

the V_5SiB_2 phase had formed separating the VB phase from the other phases (Fig. 10b).

Similar to the annealed alloys V-26Si-3B, not only the tetragonal V_5Si_3 phase, but also the hexagonal V_5Si_3 phase were identified by combining the EBSD phase mappings and the B elemental mappings in the annealed alloys V-20Si-20B (Fig. 10b–e). As mentioned for the annealed alloys V-26Si-3B, the presence of the hexagonal V_5Si_3 phase may indicate a small amount of carbon contamination in the alloys V-20Si-20B, which was also confirmed by the combustion analysis of carbon (0.034 wt.%, here only one measurement was performed) for the as-cast alloy. Thus, carbon, in negligible amounts, stabilized an additional hexagonal V_5Si_3 phase in the phase fields containing the tetragonal V_5Si_3 phase, namely VB- V_5SiB_2 - V_5Si_3 and V_3Si - V_5SiB_2 - V_5Si_3 . However, it did not influence the other equilibrium phase fields investigated in this work.

Neglecting the hexagonal V_5Si_3 phase, the calculated evolution of phase volume fractions in the annealed alloys V-20Si-20B can indicate the phase equilibrium state after the annealing at 1400 °C for 200 h (Fig. 10g). By contrast, the area fraction of the VB phase had decreased

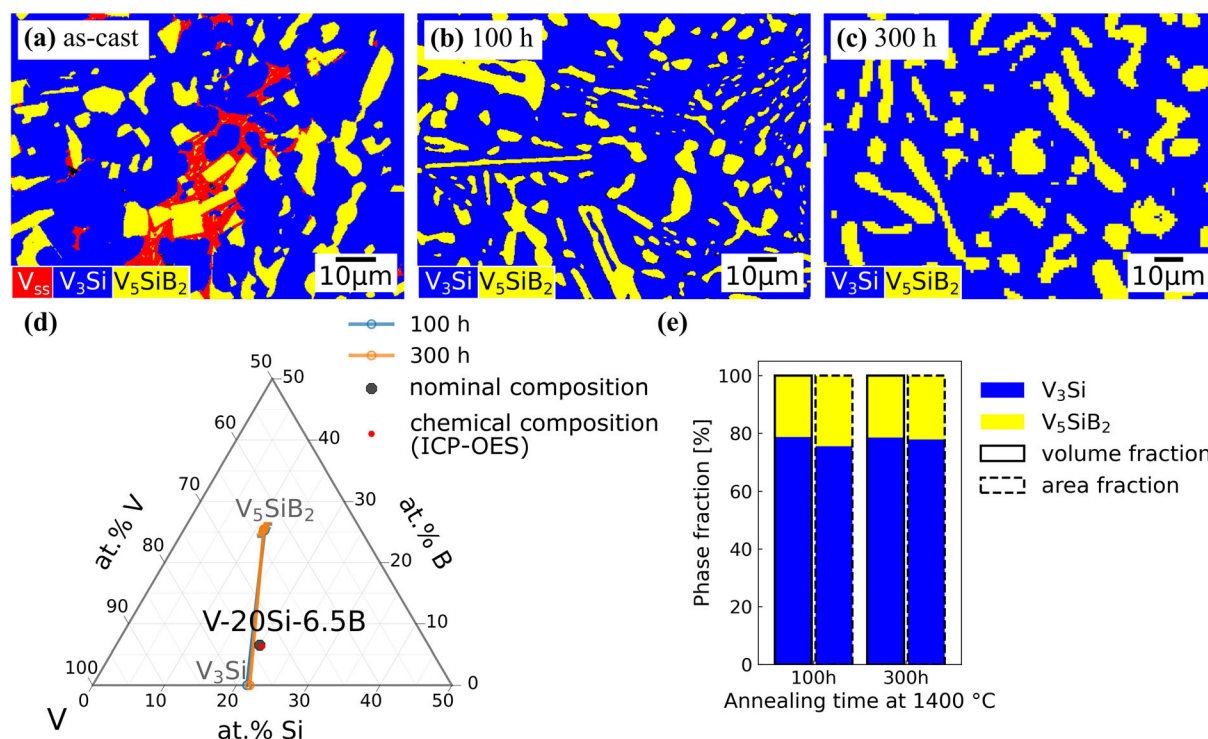


Fig. 7 Experimental microstructures (EBSD phase mappings) of alloy V-20Si-6.5B in the (a) as-cast condition and after annealing for (b) 100 h and (c) 300 h. (d) The phase compositions measured by EDS (marked with open circles), where the error bars are plotted

significantly from 200 h to 300 h, while the area fraction of the V₅SiB₂ phase had increased (Fig. 10g). However, this observation might be related to the insufficient area scanned by EBSD (Fig. 10b and c). As in the annealed alloys V-26Si-3B, the negligible hexagonal V₅Si₃ phase in the annealed alloys V-20Si-20B has no significant effect on the phase equilibrium of the VB-V₅SiB₂-V₅Si₃ phase field, and therefore the measured compositions of the VB, V₅SiB₂ and V₅Si₃ phases (Table 3) were used to determine the phase field of VB-V₅SiB₂-V₅Si₃.

3.1.9 Phase Field of VB-V₈SiB₄-V₅SiB₂

According to the microstructure of the as-cast alloy V-7Si-33B (Fig. 11a) and the reported liquidus projection,^[28,29] the solidification sequence in the as-cast alloy V-7Si-33B should be the VB primary phase, the V₅SiB₂ phase, the V₅SiB₂-V₃Si and V_{ss}-V₅SiB₂ eutectics. The presence of the V₃B₂ and V₈SiB₄ phases suggested by EBSD (Fig. 11a) in the as-cast state cannot be confirmed by XRD (Table 2) due to their negligible phase fractions. After annealing at

1400 °C for 200 h and 300 h, the V_{ss} phase and the eutectics had disappeared, while the V₃B₂ phase had precipitated along the boundaries between the VB and V₅SiB₂ phases (Fig. 11b and c). Meanwhile, small globular V₈SiB₄ phase was observed mostly near the boundaries between the V₃B₂ and V₅SiB₂ phases. The residual V₃Si phase is surrounded by the V₅SiB₂ phase (Fig. 11b and c). Thus, the annealed alloys V-7Si-33B located in the phase field of VB-V₈SiB₄-V₅SiB₂ (Fig. 11d) had not reached the equilibrium state. However, the VB, V₅SiB₂, V₈SiB₄ phases observed after annealing still agree with the existence of the corresponding three-phase field of these phases as a consequence of the existence of the VB-V₃B₂-V₈SiB₄, V₃Si-V₈SiB₄-V₅SiB₂, V₃Si-V₅SiB₂ and VB-V₅SiB₂-V₅Si₃ phase fields, which were confirmed above.

1400 °C for 200 h and 300 h, the V_{ss} phase and the eutectics had disappeared, while the V₃B₂ phase had precipitated along the boundaries between the VB and V₅SiB₂ phases (Fig. 11b and c). Meanwhile, small globular V₈SiB₄ phase was observed mostly near the boundaries between the V₃B₂ and V₅SiB₂ phases. The residual V₃Si phase is surrounded by the V₅SiB₂ phase (Fig. 11b and c). Thus, the annealed alloys V-7Si-33B located in the phase field of VB-V₈SiB₄-V₅SiB₂ (Fig. 11d) had not reached the equilibrium state. However, the VB, V₅SiB₂, V₈SiB₄ phases observed after annealing still agree with the existence of the corresponding three-phase field of these phases as a consequence of the existence of the VB-V₃B₂-V₈SiB₄, V₃Si-V₈SiB₄-V₅SiB₂, V₃Si-V₅SiB₂ and VB-V₅SiB₂-V₅Si₃ phase fields, which were confirmed above.

The formation of the V₃B₂ phase in the annealed alloys V-7Si-33B (Fig. 11b and c) can indicate that it is difficult to reach equilibrium in the phase field of VB-V₈SiB₄-V₅SiB₂ because of the reaction and diffusion kinetics. To estimate the phase field of VB-V₈SiB₄-V₅SiB₂, the VB-V₈SiB₄ phase field was assumed as a coexistence line in

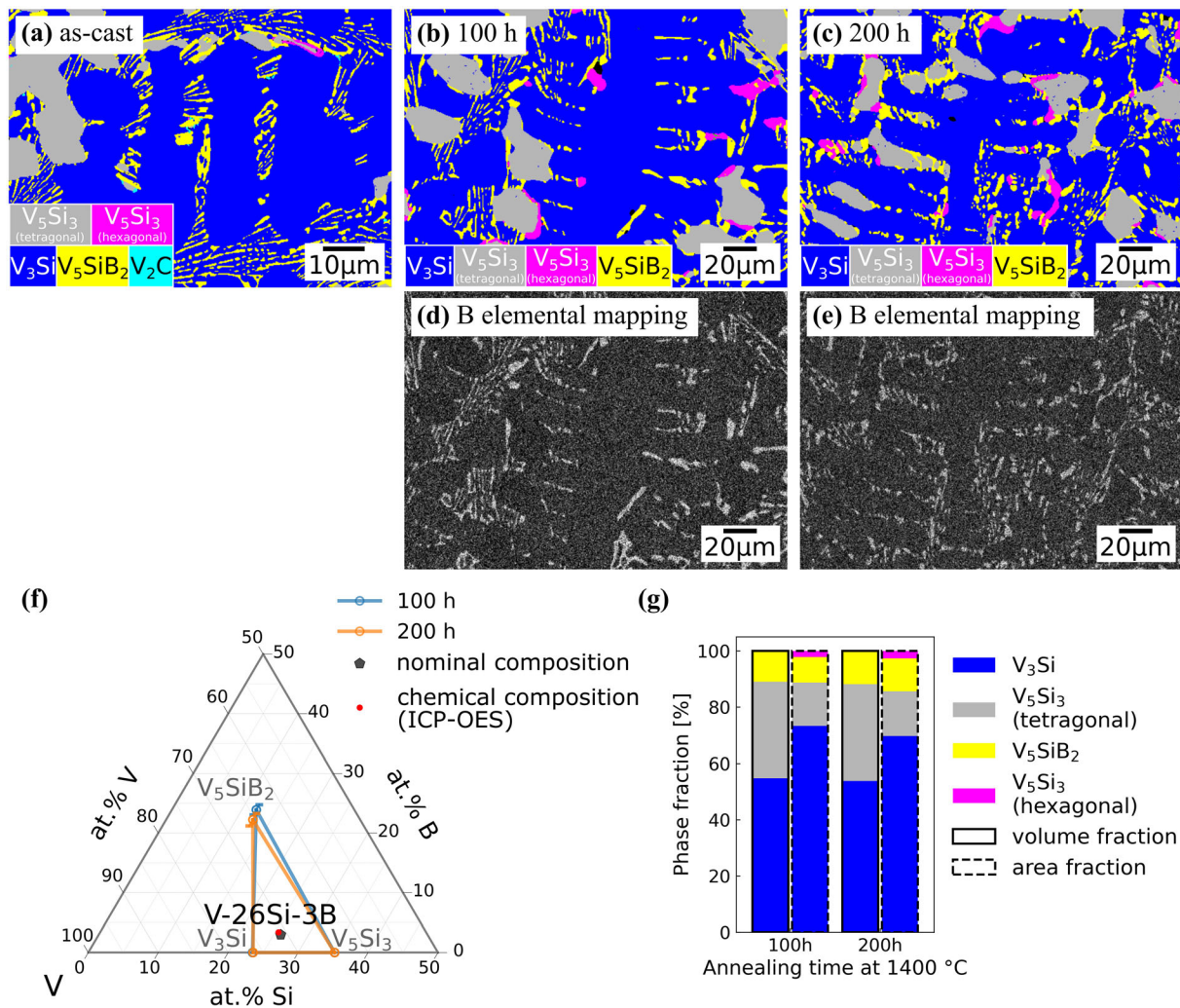


Fig. 8 Experimental microstructures (EBSD phase mappings) of alloy V-26Si-3B in the (a) as-cast condition and after annealing for (b) 100 h and (c) 200 h. (d)-(e) the B elemental mappings of the annealed alloys. (f) The phase compositions measured by EDS

(marked with open circles), where the error bars are plotted along the fixed B and Si contents for the standard deviations exceeding 0.3 at.% Si and B. (g) The evolution of phase volume and area fractions showing that the equilibrium state at 1400 °C was reached after 100 h

this work, while the composition of the V_5SiB_2 phase of this phase field can be determined using the annealed alloys V-3Si-38B as discussed below.

In the as-cast alloy V-3Si-38B, the VB primary phase, the V_3B_2 phase, the V_8SiB_4 phase and the V_{ss} - V_5SiB_2 eutectic were observed (Fig. 12a) in agreement with the XRD analysis (Table 2). The precipitation of the V_8SiB_4 phase in the as-cast state is not expected based on the reported liquidus projection,^[28,29] but can be caused by the slow cooling rate in the levitation melter. After 100 h of annealing at 1400 °C, the V_3B_2 phase had increased in size and separated the VB phase and the V_8SiB_4 phase (Fig. 12b). As the annealing time was increased from 100 to 200 h, the V_3Si and V_{ss} phases dissolved (Fig. 12c), and the particles of the V_5SiB_2 phase were surrounded by the V_8SiB_4 phase. Despite the fact that the alloy V-3Si-38B did

not reach a phase equilibrium state at 1400 °C after annealing for 200 h, the measured phase composition of V_5SiB_2 in the alloy V-3Si-38B annealed at 1400 °C for 200 h corresponds to the composition of the V_5SiB_2 phase in the phase field of VB- V_8SiB_4 - V_5SiB_2 assuming the VB- V_8SiB_4 coexistence line (Fig. 12d).

3.2 Constructing the Isothermal Section at 1400 °C

Based on the findings discussed above and the measured phase compositions of the alloys marked in Fig. 13, the isothermal section at 1400 °C was assessed as shown in Fig. 13. It should be noted that the phase field of VB- V_8SiB_4 is assumed as a coexisting line. Compared to the isothermal section of V-VB- V_5Si_3 proposed by Nunes et al.^[9] at 1600 °C (Fig. 1), the presence of the recently found

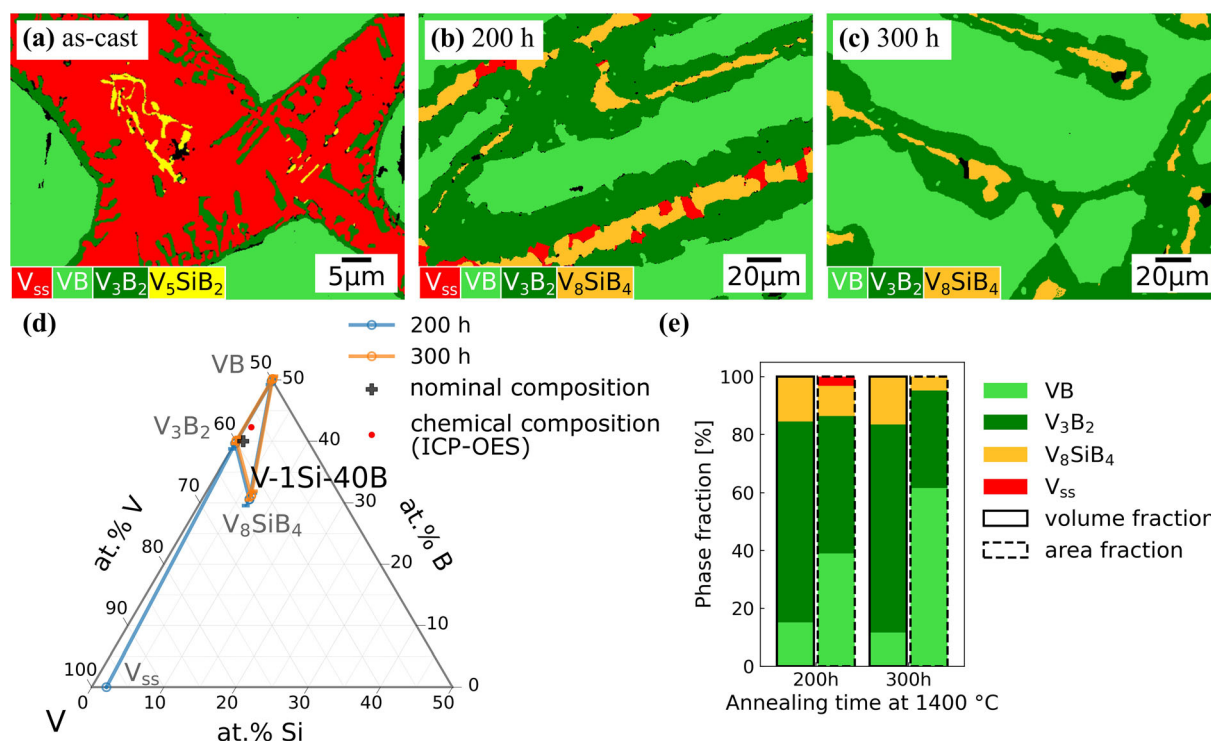


Fig. 9 Experimental microstructures (EBSD phase mappings) of alloy V-1Si-40B in the (a) as-cast condition and after annealing for (b) 200 h and (c) 300 h. (d) The phase compositions measured by EDS (marked with open circles), where the error bars are plotted

V_8SiB_4 phase^[17] is responsible for the microstructural difference at 1400 °C. The V_5SiB_2 phase field at 1600 °C (Fig. 1) is partially replaced by the phase field of V_8SiB_4 - V_5SiB_2 at 1400 °C (Fig. 13). Accordingly, it divides the V_5SiB_2 - V_3Si phase field at 1600 °C into three phase fields at 1400 °C, i.e., the V_3Si - V_8SiB_4 , V_3Si - V_8SiB_4 - V_5SiB_2 and V_3Si - V_5SiB_2 phase fields. Similarly, the VB - V_5SiB_2 phase field at 1600 °C is divided into VB - V_8SiB_4 - V_5SiB_2 and VB - V_5SiB_2 phase fields. Furthermore, the V_5SiB_2 phase of the V_{ss} - V_3B_2 - V_5SiB_2 , V_{ss} - V_3Si - V_5SiB_2 and VB - V_3B_2 - V_5SiB_2 phase fields at 1600 °C (Fig. 1) is replaced by the V_8SiB_4 phase (Fig. 13). Like the binary coexisting line of V_{ss} - V_5SiB_2 at 1600 °C, the phase field of V_{ss} - V_8SiB_4 is still represented by a coexisting line at 1400 °C.

along the fixed B and Si contents for the standard deviations exceeding 0.3 at.% Si and B. (e) The evolution of phase volume fractions showing that the equilibrium state at 1400 °C was almost reached after 300 h, even if the negligible V_{ss} was detected by XRD

3.3 Comparison to the Binary Phase Diagrams

The measured B content of the V_3B_2 phase in Fig. 13 is comparable to the reported binary V-B phase diagram,^[15] which indicates an acceptable accuracy of the EDS measurement for a V-boride phase. By contrast, the EDS results of V-silicide phases (V_3Si and V_5Si_3) deviate from the reported V-Si system.^[13] As shown in Fig. 14, the measured Si content of the V-rich V_3Si phase in the V_{ss} - V_3Si - V_8SiB_4 phase field in this work is around 4 at.% lower than that reported in the binary V-Si phase diagram,^[13] while the measured Si content of the Si-rich V_3Si phase in the V_3Si - V_5SiB_2 - V_5Si_3 phase field is around 1 at.% lower. Furthermore, the measured Si content of the V_5Si_3 phase is around 2.5 at.% lower than that reported in the binary V-Si phase diagram.^[13] Compared to the EDS results in this work, the phase compositions of V_3Si and V_5Si_3 measured by Nunes et al.^[9] agree well with the

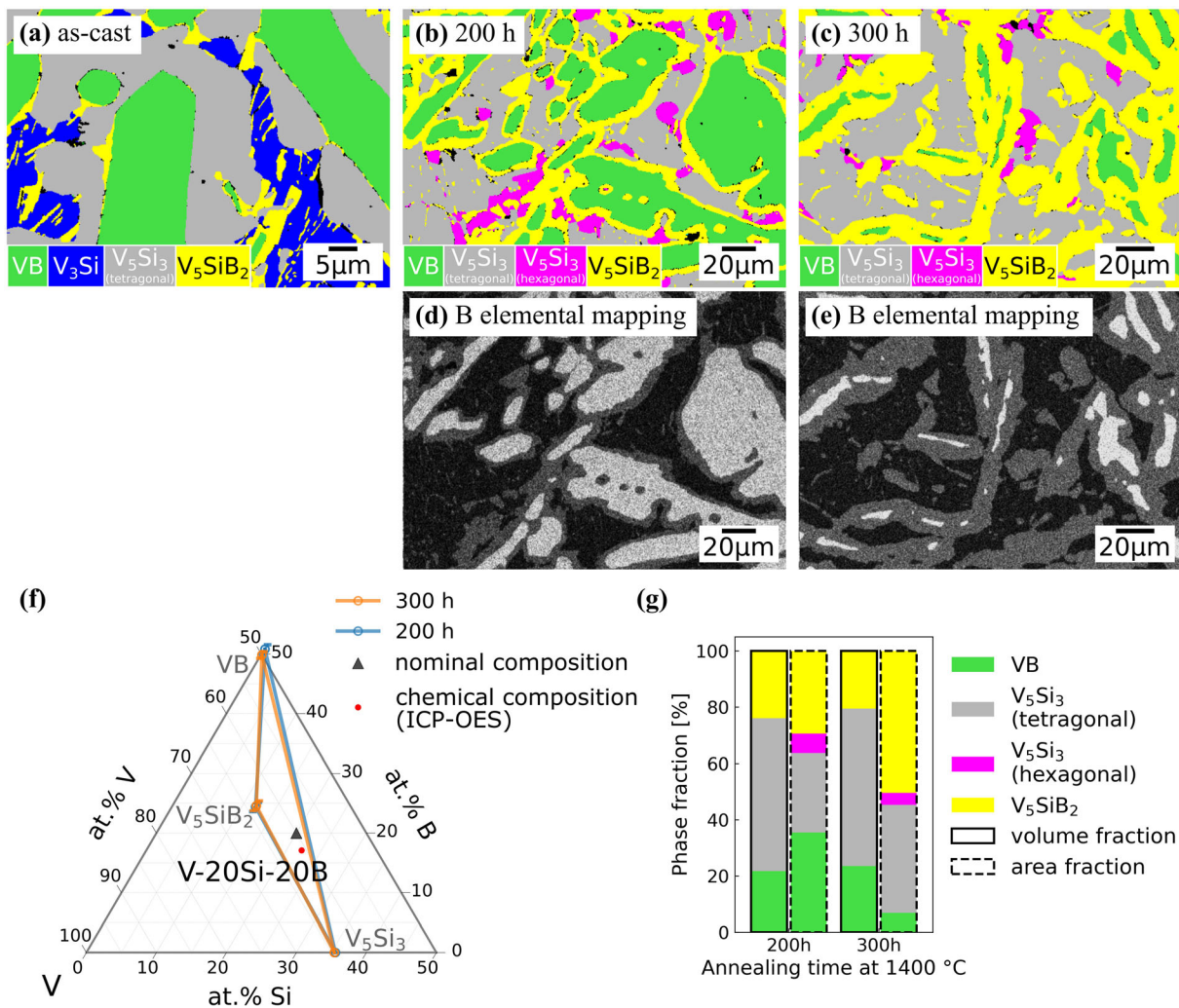


Fig. 10 Experimental microstructures (EBSD phase mappings) of alloy V-20Si-20B in the (a) as-cast condition and after annealing for (b) 200 h and (c) 300 h. (d)–(e) The B elemental mappings of the annealed alloys. (f) The phase compositions measured by EDS

binary V-Si phase diagram (Fig. 14). However, the measured composition of V_{ss} at 1400 °C in this work agrees well with the binary V-Si phase diagram,^[13] while the composition measured by Nunes et al.^[9] at 1600 °C is around 2 at.% higher than the one in the V-Si binary phase diagram (Fig. 14).

To confirm the validity of the EDS results for the V₃Si phase investigated in this work, the relationship between the lattice parameter and the phase composition of V₃Si

(marked with open circles), where the error bars are plotted along the fixed B and Si contents for the standard deviations exceeding 0.3 at.% Si and B. (g) The evolution of phase volume and area fractions showing that the equilibrium state at 1400 °C was reached after 200 h

determined by Jorda and Muller^[31] was used. This relationship is shown as a dashed line in Fig. 15, where the experimental results obtained in the present work are scattered around that line (black symbols). According to this relationship,^[31] the compositions of the V₃Si phase in both the V_{ss} -V₃Si-V₈SiB₄ and the V₃Si-V₅SiB₂-V₅Si₃ phase fields were calculated using the lattice parameters obtained by XRD (Fig. 15) and are indeed comparable to the EDS results as shown in Fig. 14.

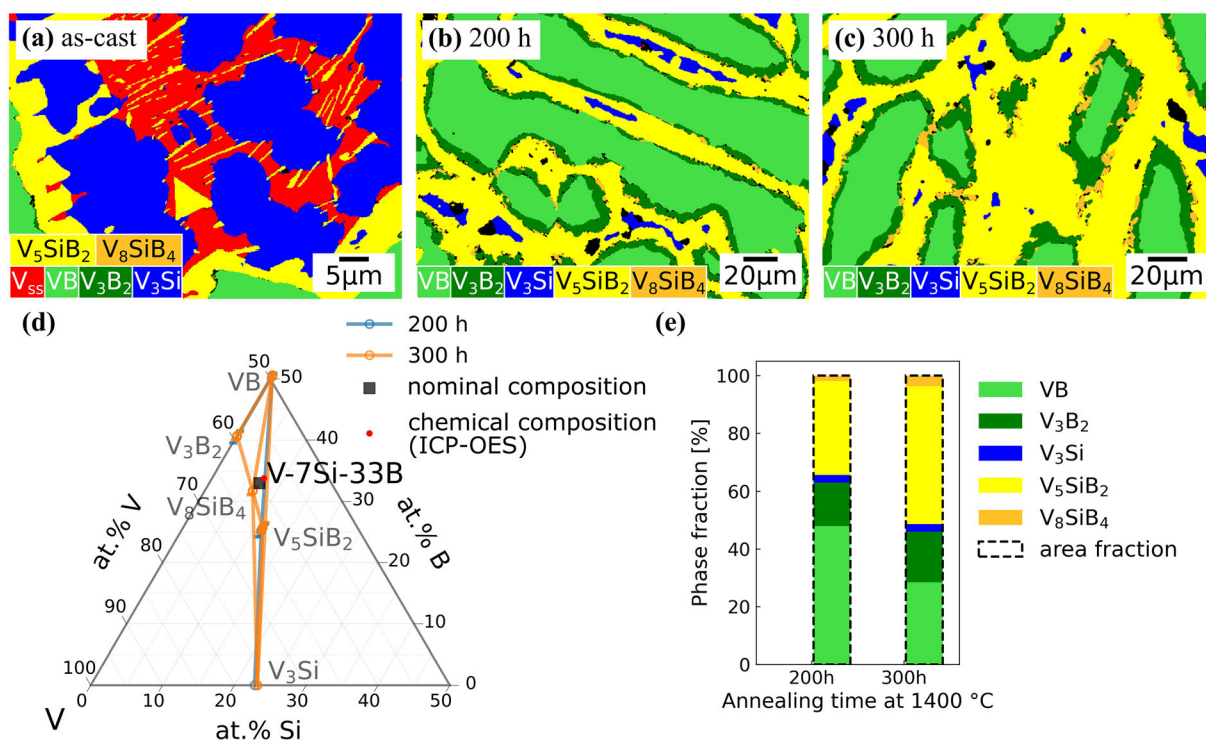


Fig. 11 Experimental microstructures (EBSD phase mappings) of alloy V-7Si-33B in the (a) as-cast condition and after annealing for (b) 200 h and (c) 300 h. (d) The phase compositions measured by EDS (marked with open circles), where the error bars are plotted

along the fixed B and Si contents for the standard deviations exceeding 0.3 at.% Si and B. (e) The evolution of phase volume and area fractions showing that the equilibrium state at 1400 °C was not reached even after 300 h

For additional confirmation, an alloy with the nominal composition of V-37.5Si corresponding to the stoichiometric composition of the V_5Si_3 phase was produced via arc-melting. As expected, the as-cast alloy V-37.5Si is almost a single-phase alloy, except for the V_3Si phase and the hexagonal V_5Si_3 phase with negligible area fractions (Fig. 16a and b). The chemical composition of the alloy determined by ICP-OES, i.e., V-36.4 ± 0.3 Si, is almost identical to the phase composition of V_5Si_3 based on EDS, i.e., V-35.9 ± 0.2 Si.

4 Summary

The phase equilibria in the V-rich of the V-Si-B system at 1400 °C were experimentally investigated and then the isothermal section was constructed. The stabilities of both the V_5SiB_2 and V_8SiB_4 ternary phases were confirmed. Compared to the isothermal section at 1600 °C,^[9] the appearance of the V_8SiB_4 phase at 1400 °C has the following consequences:

1. The solubility range of the V_5SiB_2 phase decreases as the temperature decreases from 1600 to 1400 °C;

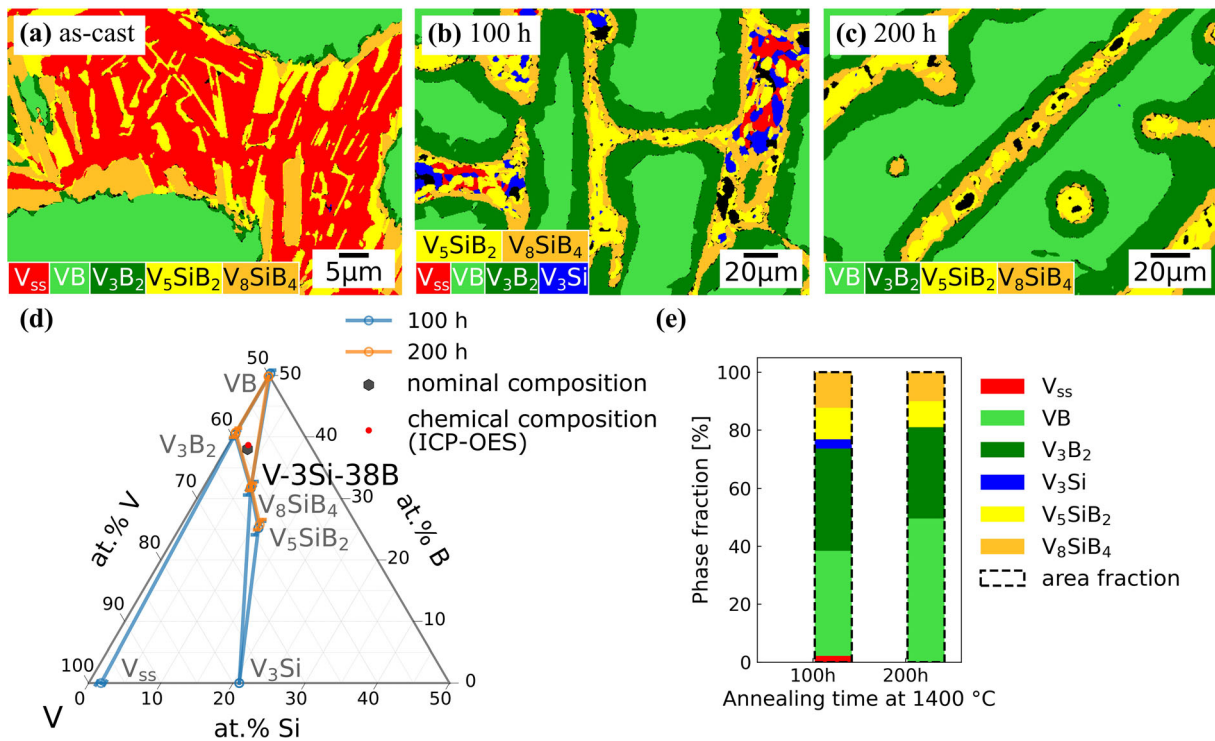


Fig. 12 Experimental microstructures (EBSD phase mappings) of alloy V-3Si-38B in the (a) as-cast condition and after annealing for (b) 100 h and (c) 200 h. (d) The phase compositions measured by EDS (marked with open circles), where the error bars are plotted

along the fixed B and Si contents for the standard deviations exceeding 0.3 at.% Si and B. (e) The evolution of phase volume and area fractions showing that the equilibrium state at 1400 °C was not be reached after 200 h

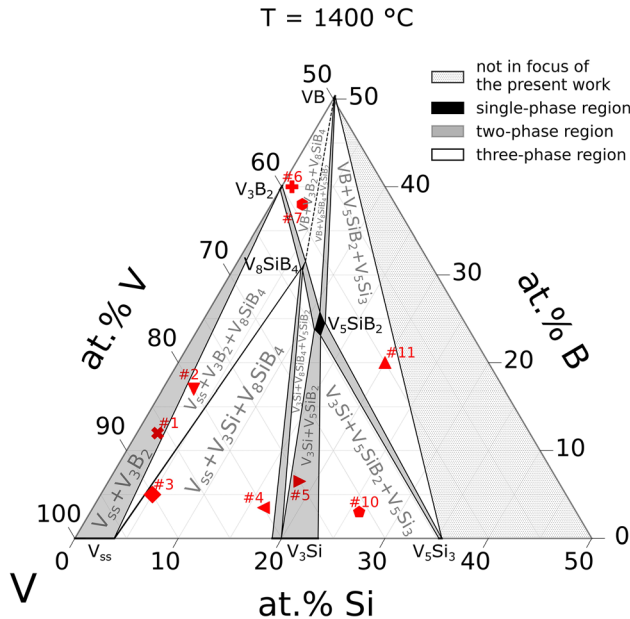


Fig. 13 The isothermal section of the V-rich corner of the V-Si-B system at 1400 °C based on the marked alloys, where the phase field of VB- V_8SiB_4 is assumed as a coexisting line

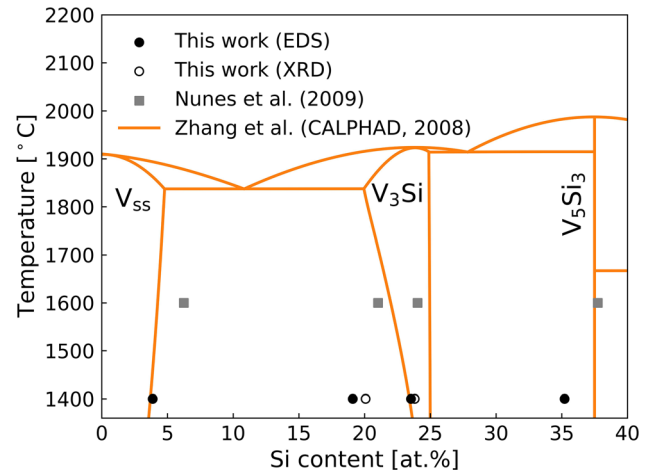


Fig. 14 The phase compositions of V_{ss} , V_3Si and V_5Si_3 measured at 1400 °C (this work) and measured by Nunes et al. [9] at 1600 °C are compared to those of the binary V-Si phase diagram calculated by Zhang et al. [14], where the open symbols represent the compositions calculated according to the relationship between the lattice parameter and the phase composition of V_3Si reported by Jorda and Muller [31] shown in Fig. 15

- The V_3Si - V_5SiB_2 phase field at 1600 °C is divided into the V_3Si - V_8SiB_4 , V_3Si - V_8SiB_4 - V_5SiB_2 and V_3Si - V_5SiB_2 phase fields at 1400 °C, while the VB - V_5SiB_2 phase field at 1600 °C is divided into VB - V_8SiB_4 - V_5SiB_2 and VB - V_5SiB_2 phase fields;
- The V_{ss} - V_3B_2 - V_5SiB_2 , V_{ss} - V_3Si - V_5SiB_2 and VB - V_3B_2 - V_5SiB_2 three-phase fields at 1600 °C are replaced by the V_{ss} - V_3B_2 - V_8SiB_4 , V_{ss} - V_3Si - V_8SiB_4

and VB - V_3B_2 - V_8SiB_4 three-phase fields at 1400 °C, respectively.

Acknowledgments This work was supported by the Deutsche Forschungsgemeinschaft (DFG), Germany, under project number 410338871. The authors would like to thank C. Thomas (ER-C-1, FZ Jülich) for providing access to the arc-melter, Dr. W. Behr (ZEA-1, FZ Jülich) and T. Koppitz (ZEA-1, FZ Jülich) for their assistance in heat treatment, Dr. E. Wessel (IEK-2, FZ Jülich) and Dr. D. Grüner (IEK-2, FZ Jülich) for their assistance in SEM investigation as well as EBSD and EDS measurements, M. Ziegner (IEK-2, FZ Jülich) for supporting the XRD analysis. W. G. Yang thanks Dr. D. Sergeev (NETZSCH Analyzing & Testing) for fruitful discussion about phase diagrams.

Funding Open Access funding enabled and organized by Projekt DEAL.

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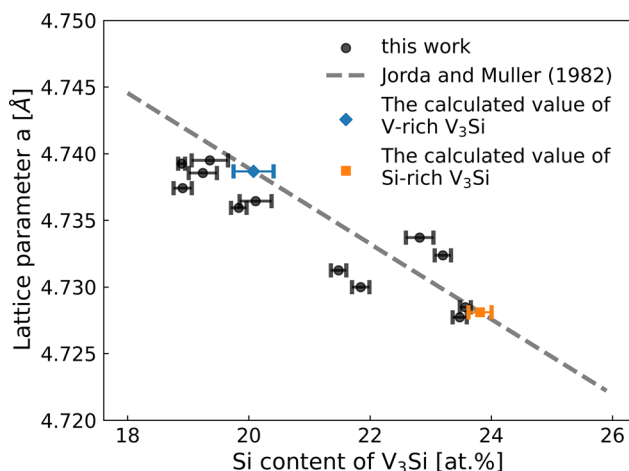
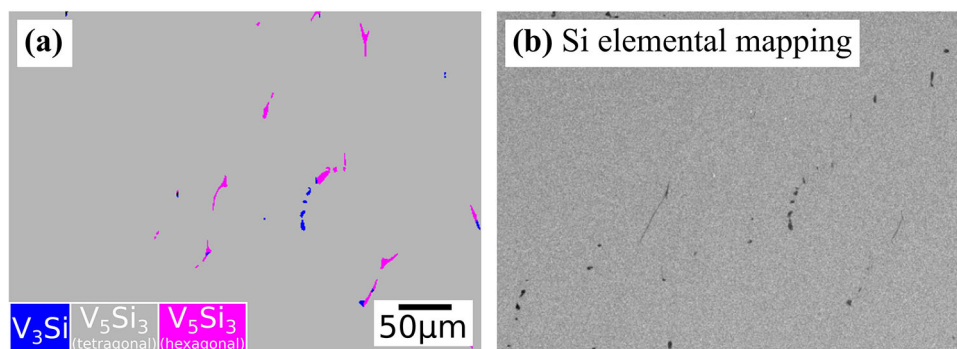


Fig. 15 The relationship between the lattice parameter and the phase composition of V_3Si compared to the dashed line reported by Jorda and Muller [31]. Using this relationship (dashed line), the phase compositions of the V-rich and Si-rich V_3Si were calculated

Fig. 16 (a) The microstructure (EBSD phase mapping with a scanning step size of 0.88 μm) of the as-cast alloy V-37.5Si. (b) The corresponding Si elemental mapping. The alloy consists of almost only the tetragonal V_5Si_3 phase



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