SCP 11.1:

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

Georg Hasemann[1], Weiguang Yang[2], Mustafa Carrion Saldaña[3], Bronislava Gorr[4], Ruth Schwaiger[2,5], Manja Krüger[1]

[1] Otto–von–Guericke University Magdeburg, Institute of Materials, Technologies and Mechanics, Universitätsplatz 2, 39106, Magdeburg, Germany georg1.hasemann@ovgu.de, manja.krueger@ovgu.de

[2] Forschungszentrum Jülich GmbH, Institute of Energy Materials and Devices, Structure and Function of Materials (IMD-1), Leo–Brandt–Str.1, 52425, Jülich, Germany w.yang@fz-juelich.de, r.schwaiger@fz-juelich.de

[3] University Siegen, Institute of Materials Technology, Paul–Bonatz–Strasse 9-11, 57076, Siegen, Germany Mustafa.CarrionSaldana@uni-siegen.de

[4] Karlsruhe Institute of Technology, Institute for Applied Materials–Applied Materials Physics (IAM–AWP), Hermann–von–Helmholtz–Platz 1, 76344, Eggenstein-Leopoldshafen, Germany bronislava.gorr@kit.edu

[5] Chair of Energy Engineering Materials, Faculty 5, RWTH Aachen University, Templergraben 55, 52056, Aachen, Germany

Introduction

Most high-temperature properties, e.g. high-temperature strength and creep resistance, are correlating with the high melting temperature. Thus, similar to molybdenum-based alloys, vanadium-based alloys are promising candidates for high-temperature structural applications due to the high melting temperature of vanadium and a comparably 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.

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. [1] using XRD measurement in 1957. According to the XRD results of the three alloys, Kudielka et al. found two three-phase phase fields, namely ~$V_{0.7}B_{0.3}$–VB–V_5SiB_2 and V_5SiB_2–V_3Si–$D8_8$.

The latest systematic experimental investigation of the isothermal section of the V–Si–B system was carried out by Nunes et al. [2] at 1600 °C in 2009. They produced the samples via arc-melting under argon followed by a heat treatment at 1600 °C for 24/ 72 h under a high vacuum). The samples were furnace cooled to room temperature after heat treatment. Based on wavelength-dispersive spectroscopy measurements, they proposed the isothermal section of the V–Si–B system at 1600 °C in the V_{ss}–VB–VSi_2 region of the V–Si–B system. Nunes et al. [2] found that the B solubility in V_{ss}, V_3Si and V_5Si_3 was negligible, as was the Si solubility in V_3B_2 and VB and confirmed the stabilities of the two ternary phases at 1600 °C, V_5Si_3B and V_5SiB_2, and observed a solubility range of the V_5SiB_2 phase.

Most recently, we have observed a new ternary phase, V_8SiB_4 [3], 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 [3]. The presence of the new ternary phase at 1400 °C indicates the major difference between the isothermal sections of the V-rich V–Si–B system at 1400 °C and 1600 °C. Thus, this work aims to experimentally investigate the isothermal section of the V-rich V–Si–B system, especially at 1400 °C.

Materials and Methods

For producing samples, the raw materials 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.%). For each of the investigated V–Si–B alloy compositions having B concentration lower 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 B concentration higher than 30 at.%, a 10 g button was produced by remelting three times in a conventional arc-melter, followed by re-melting 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, the inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 7600, Thermo Fisher Scientific, USA) was performed. As-cast buttons were cut in half using the 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 at least 100 h under a high vacuum (1.5×10^{-5} mbar) and furnace cooled within 3 h below 200 °C.

For metallographic preparation, the samples were embedded in a cold mounting resin (Epoxy 2000, Cloeren Technology, Wegberg, Germany), and subsequently ground down to 2000 grit using SiC paper, followed by polishing down to 1 µm diamond suspension and finished using colloidal silica. A Zeiss Merlin (Zeiss Microscopy, Oberkochen, Germany) scanning electron microscope (SEM) was used to observe the microstructures using the backscattered electron (BSE) mode. EDS spot measurements were performed to quantitatively measure the chemical compositions of phases with the electron high tension (EHT) of 10 kV.

X-ray diffraction (XRD) measurements were performed on the polished bulk samples at room temperature by using a diffractometer EMPYREAN (Malvern Panalytical, UK) or a diffractometer D8 ADVANCE (Bruker, USA) to identify the crystal structures of phases. The lattice parameters of the phases were determined using the software GSAS-II and the Pawley refinement.

Results

The isothermal section at 1400 °C was experimentally assessed, based on experimental alloys and is shown in Fig.1 [4]. 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_{ss}–VB–V_5Si_3 proposed by Nunes et al. [2] at 1600 °C, the presence of the recently found V_8SiB_4 phase [3] is responsible for main changes at 1400 °C. The V_5SiB_2 phase field at 1600 °C is partially replaced by the phase field of V_8SiB_4–V_5SiB_2 at 1400 °C. 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 is replaced by the V_8SiB_4 phase. 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.

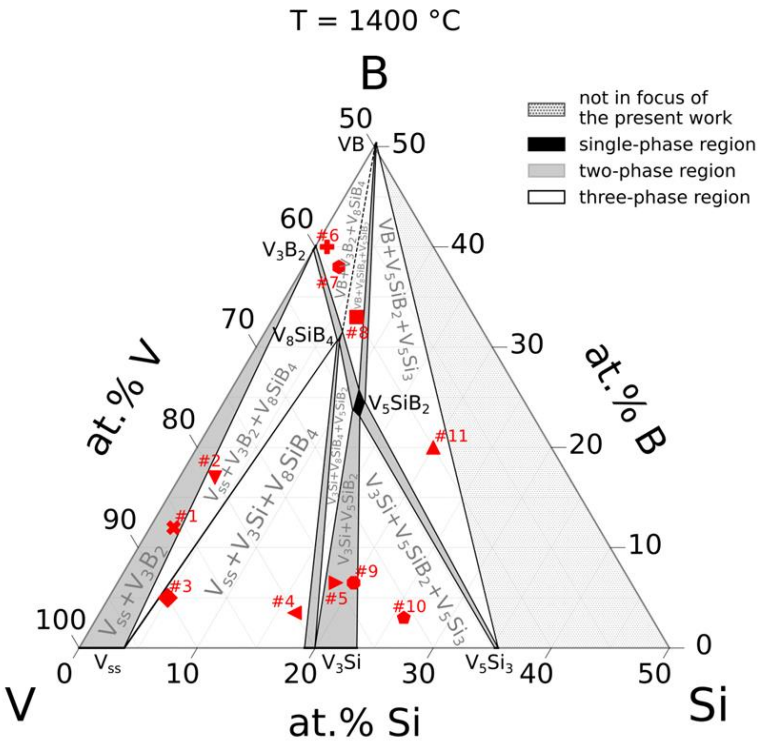

Fig.1 The isothermal section of the V-rich corner of the V-Si-B system at 1400 °C based on the marked alloys, where the phase field of VB-V_8SiB_4 is assumed as a coexisting line [4].

References

[1] H. Kudielka, H. Nowotny, G. Findeisen, Untersuchungen in den Systemen: V-B, Nb-B, V-Si-B und Ta-B-Si, Mh. Chem. 88 (**1957**) 1048–1055.

[2] C.A. Nunes, B.B. De Lima, G.C. Coelho, P.A. Suzuki, Isothermal Section of the V-Si-B System at 1600°C in the V-VSi2-VB Region, J. Phase Equilibria Diffus. 30 (**2009**) 345–350. https://doi.org/10.1007/s11669-009-9533-y.

[3] W.G. Yang, R.S. Touzani, G. Hasemann, M. Yazlak, M. Ziegner, B. Gorr, R. Schwaiger, M. Krüger, V8SiB4 — A new ternary phase in the V–Si–B system, Intermetallics. 151 (**2022**) 107691. https://doi.org/10.1016/j.intermet.2022.107691.

[4] W. Yang, G. Hasemann, M. Carrion Saldaña, B. Gorr, R. Schwaiger, M. Krüger, Phase Equilibria in the V-Rich Region of the V-Si-B System at 1400 °C, J. Phase Equilibria Diffus. (**2025**). https://doi.org/10.1007/s11669-025-01177-4.