JPEDAV (2004) 25:134-139
DOI: 10.1361/15477030418541
1547-7037/$19.00 ©ASM International

Evaluation of the Invariant Reactions of the V-B System

Belmira Benedita de Lima, Carlos Angelo Nunes, Gilberto Carvalho Coelho, Paulo Atsushi Suzuki, and Peter Rogl

(Submitted 7 October 2003; in revised form 17 December 2003)

To determine the phase relations of various Me-Si-B (Me-metal) ternary systems we have been studying, it is necessary to experimentally re-evaluate the related Me-B binaries. The objective of this work is to report our data concerning the invariant reactions of the V-B system. The V-B alloys were prepared via arc melting and characterized through x-ray diffraction (XRD) and scanning electron microscopy (SEM). The liquid compositions proposed for the reactions L ↔ V_{ss} + V_3B_2, L + VB ↔ V_3B_2, L ↔ VB_2 + B_{ss} are, respectively: 12%, 19%, and 95% (at.% B). A congruent formation for VB and a peritectic formation for V_5B_6 through the reaction L + V_3B_4 ↔ V_5B_6 are proposed.

1. Introduction

In recent years, several studies have been carried out to evaluate the potential of Me-Si-B alloys (Me = metal) for structural applications at high temperatures [2003Ito, 2003Pin, 2002Sch, 2002Par]. Considering the complex demands on materials for such applications, different types of data have to be considered to provide useful information concerning processing and application of these materials. Among these data, those associated with phase equilibria are of primary interest due to the fundamental information they provide in terms of microstructural stability, a significant issue for application at high temperatures. We have been involved in the task of assessing and obtaining phase equilibrium data for relevant Me-Si-B ternary systems (where Me = Ti, Zr, V, Nb, Ta, Cr, Mo). In the course of these studies the need to re-evaluate several Me-B binaries due to either inconsistencies or disagreements in the literature has been made clear. In a recent paper on the Nb-B system [2003Bor], we have provided new information on phase equilibria that significantly alters the currently assessed Nb-B phase diagram and confirms the phase relations proposed by Rudy and Windisch [1966Rud].

The objective of this work is to report our data on the evaluation of the invariant reactions of the V-B system. Figure 1 shows the currently assessed V-B phase diagram [Massalski2]. It is based on the phase equilibria data of Spear and Gilles [1969Spe], Rudy and Windisch [1966Rud], and Nowotny et al. [1959Now]. The liquidus was calculated by Spear et al. [1981Spe] from Gibbs energy functions optimized with respect to thermochemical and phase diagram data. In fact, Fig. 1 is essentially the phase diagram as proposed by Rudy and Windisch [1966Rud] with incorporation of the V_5B_6 and V_2B_3 phases. It is worth mentioning that in a previous evaluation of this system, Spear et al. [1987Spe] explicitly stated that the composition data for the liquid phase involved in the peritectic reactions of this system are not well established.

Belmira Benedita de Lima, Gilberto Carvalho Coelho, and **Paulo Atsushi Suzuki,** FAENQUIL, Departamento de Engenharia de Materiais (DEMAR), Polo Urbo-Industrial, Gleba AI-6, Caixa Postal 116, 12600-970, Lorena São Paulo, Brazil; **Carlos Angelo Nunes** FAENQUIL, Departamento de Engenharia de Materiais (DEMAR), Polo Urbo-Industrial, Gleba AI-6, Caixa Postal 116, 12600-970, Lorena São Paulo, Brazil and Institut für Physikalische Chemie, Univ. Wien, Währingerstrasse 42, A-1090 Wien, Austria; and **Peter Rogl,** Institut für Physikalische Chemie, Univ. Wien, Währingerstrasse 42, A-1090 Wien, Austria. Contact e-mail: cnunes@demar.faenquil.br.

2. Experimental Procedure

For this study, the V-B alloys were prepared by arc melting V (min. 99.75 wt.%, Wah Chang, Albany, OR) and B (min. 99.5 wt.%, Alfa AESAR, Word Hill, MA) under pure argon (min. 99.995%) on a water-cooled copper hearth using a non-consumable tungsten electrode and a Ti getter. Five melting steps were carried out for each alloy in an effort to produce homogeneous samples. Table 1 shows the nominal composition of each alloy as well as their possible composition range based on the mass losses occurred during the arc melting process. The alloys are referenced in this work by their nominal compositions. All compositions are in atomic percent unless otherwise mentioned.

The as-cast ingots were characterized by scanning electron microscopy (SEM) using back-scattered electron (BSE) images and x-ray diffraction (XRD). For the SEM analyses, the as-cast samples were hot mounted in resin, ground with SiC sand paper (#120-1000) and then polished with a colloidal silica suspension (OP-S). The BSE images were obtained with a LEO 1450VP SEM microscope. For the XRD experiments, the as-cast alloys were mechanically ground and then sieved to below 176 μm. The measurements were carried out at room temperature using Ni-filtered Cu K_α radiation in a Seifert Isodebyeflex-1001 diffractometer. The measurement conditions were 25° ≤ 2θ ≤ 60°, 0.05° step and 2*s* counting time per point. The phases present in each sample were identified based on the JCPDS files [1988JCP] and simulated diffractograms from the PCW program [1996Kra]. Data for the simulated diffractograms were taken from Villars and Calvert [1991Vil] and from Bolmgren and Lundström [1990Bol].

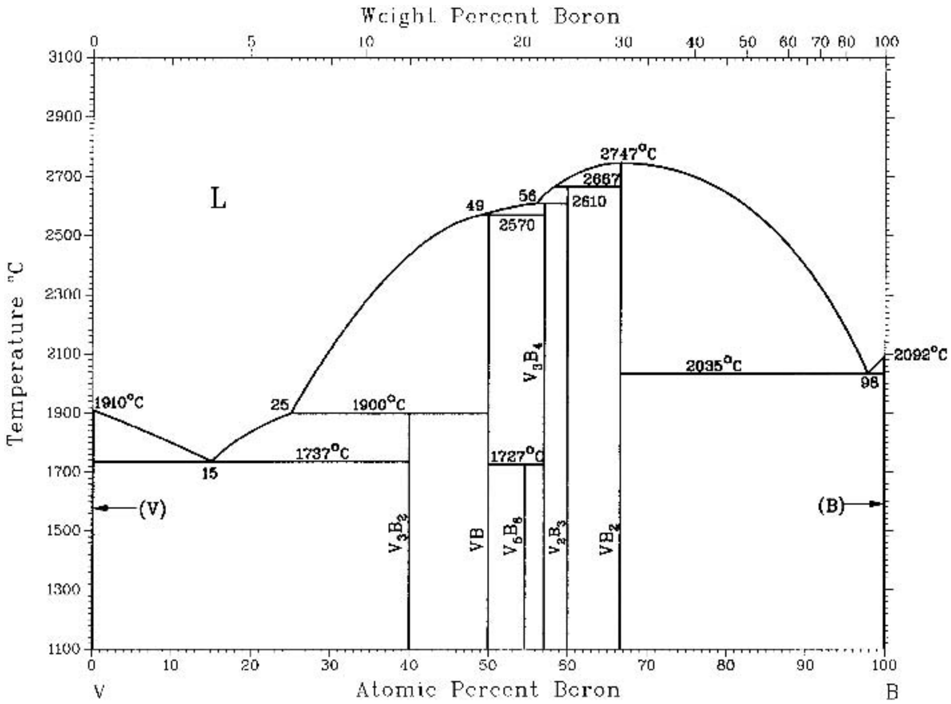

Fig. 1 V-B Phase Diagram [Massalski2]

3. Results and Discussion

The x-ray diffractograms of V89B11, V88B12 (Fig. 2a), V87B13, and V85B15 alloys indicated the presence of V_{ss} (vanadium solid solution) and V_3B_2 phases in their microstructures. The SEM/BSE micrograph of the V89B11 alloy (Fig. 3a) shows primary V_{ss} dendrites and a eutectic microstructure formed by V_{ss} and V_3B_2 phases in the interdendritic region. Figure 3b shows a SEM/BSE micrograph of the V88B12 alloy, where a typical eutectic microstructure formed by V_{ss} and V_3B_2 phases is present with no indication of primary phases. In agreement with the previous results, the SEM/BSE micrographs of alloys V87B13 (Fig. 3c) and V85B15 showed primary precipitation of the V_3B_2-phase and the V_{ss}+V_3B_2 eutectic in the last solidification region. These results confirm the eutectic reaction $L \leftrightarrow V_{ss}+V_3B_2$ in the V-rich part of the V-B phase diagram; however, with the liquid eutectic composition near 12 at.% B instead of 15 at.% B as proposed in Fig. 1.

The x-ray diffractogram of the V81B19 alloy (Fig. 2b) indicated the presence of V_{ss} and V_3B_2 phases in its microstructure as in the case of the previous alloys. The SEM/BSE micrograph of this alloy (Fig. 3d) shows primary grains of V_3B_2 embedded in a eutectic matrix formed by V_{ss} and V_3B_2. V_{ss} halos are observed around the primary V_3B_2 grains. In addition to V_{ss} and V_3B_2, the VB phase was also present in the microstructure of V80B20 alloy (Fig. 2c). Figure 3(e) shows a SEM/BSE micrograph of this alloy with primary VB grains enveloped by V_3B_2 and the V_{ss} + V_3B_2 eutectic in the last solidification region. These results confirm the peritectic formation of V_3B_2 through the reaction $L+VB \leftrightarrow V_3B_2$; however, with the peritectic liquid composition near 19 at.% B instead of 25 at.% B (Fig. 1).

Table 1 Nominal V-B Alloy Compositions and Composition Range for Each Alloy Prepared in This Work Based on the Mass Losses That Occurred During the Arc-Melting Process

Sample	Nominal V-B Alloy Compositions		Mass Losses, %	Composition Range, at.% B
	at.% V	at.% B		
V89B11	89.01	10.99	0.025	10.89-10.99
V88B12	88.06	11.94	0.035	11.80-11.95
V87B13	86.97	13.03	0.258	12.07-13.05
V85B15	85.00	15.00	0.005	14.98-15.00
V81B19	81.00	19.00	0.663	16.79-19.11
V80B20	80.02	19.98	0.420	18.62-20.05
V78B22	78.05	21.95	0.015	21.90-21.95
V75B25	75.00	25.00	0.000	25.00-25.00
V72B28	72.00	28.00	0.136	27.64-28.03
V60B40	60.00	40.00	0.472	39.07-40.13
V52B48	52.07	47.93	0.878	46.56-48.20
V50B50	50.00	50.00	0.711	48.96-50.21
V48B52	47.92	52.08	0.778	51.02–52.32
V45.45B54.55	45.41	54.59	0.968	53.37-54.89
V44B56	44.00	56.00	1.076	54.72-56.34
V43B57	43.00	57.00	0.768	56.13-57.24
V40B60	33.00	67.00	0.718	66.46-67.22
V33B67	33.00	67.00	0.802	66.40-67.25
V6B94	6.05	93.95	0.149	93.94-93.99
V4B96	4.00	96.00	0.982	95.95-96.23

The V78B22, V75B25, V72B28, V60B40, and V52B48 alloys all followed the same solidification path of the V80B20 alloy, thus presenting VB (primary), V_3B_2, and V_{ss}

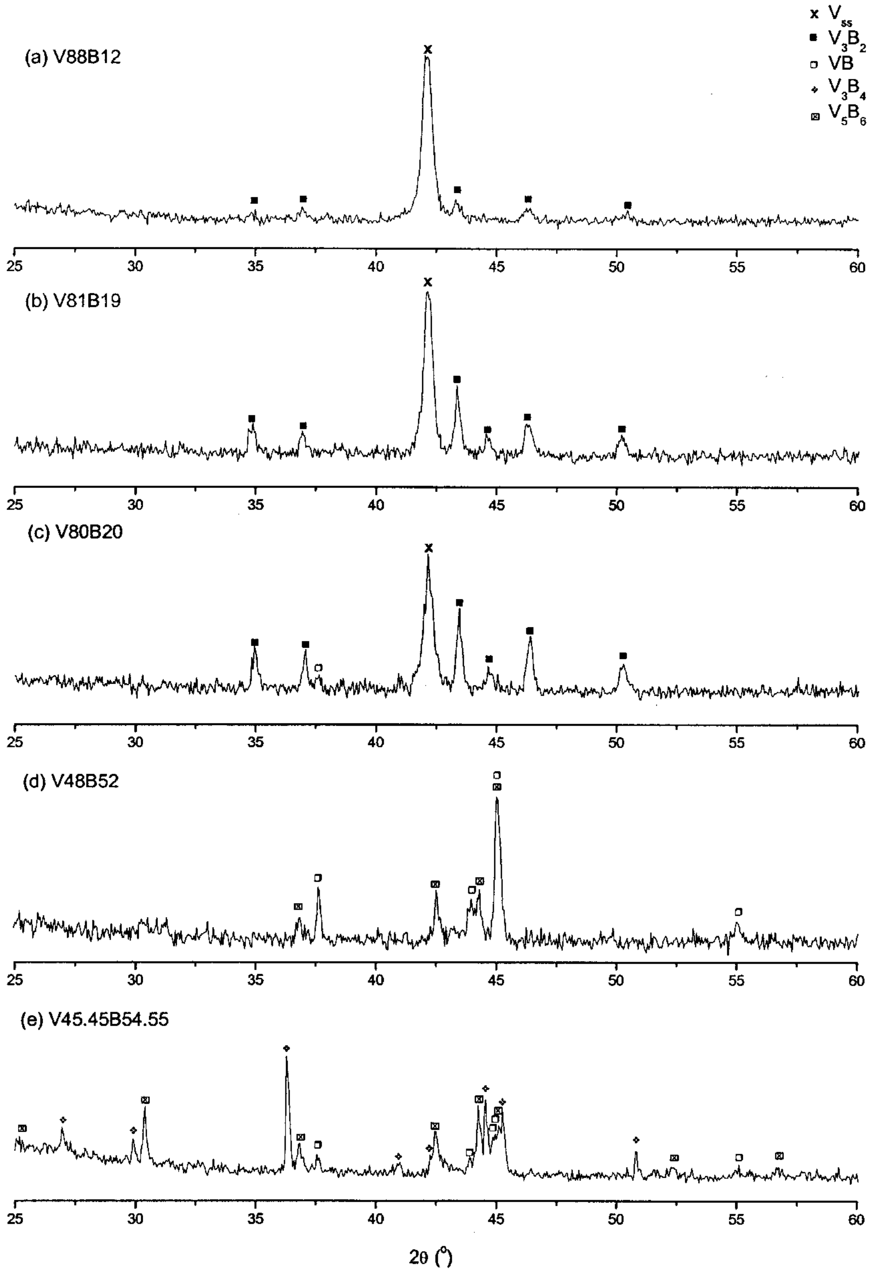

Fig. 2 X-ray diffractograms of as-cast V-B alloys: **(a)** V88B12, **(b)** V81B19, **(c)** V80B20, **(d)** V48B52, and **(e)** V45.45B54.55

in their microstructures. The amount of VB increases for higher B contents due to a more extensive solidification interval in the L+VB two-phase field. In the case of alloy V50B50 the XRD data indicated only the presence of the VB-phase, in agreement with the SEM/BSE characterization where a single-phase microstructure was observed. These results suggest a congruent formation for VB, in disagreement with Fig. 1, which proposes, for the V50B50 composition primary precipitation of V_3B_4 with a peritectic subsequent formation of VB (L + $V_3B_4 \leftrightarrow$ VB).

Before discussing the B-richer invariant reactions, it is necessary to review the more important results of a recent study we have carried out to assess the thermal stability of the V_5B_6-phase [2003Nun]. That study was motivated by the observation of V_5B_6 in several as-cast samples in the 52-56 at.% B region, and we have shown that the V_5B_6-phase is formed from the liquid through the peritectic reaction L + $V_3B_4 \leftrightarrow V_5B_6$. In the phase diagram shown in Fig. 1, a solid-state formation (peritectoid) is proposed for this phase. Discussion of the following results takes this fact into account.

The VB and V_5B_6 were the only phases identified in the x-ray diffractogram and SEM images of the V48B52 alloy as shown in Fig. 2(d) and 3(f), respectively. Thus, considering respectively the congruent and peritectic formation of VB and V_5B_6, the eutectic reaction L $\leftrightarrow$ VB+V_5B_6 is proposed. The x-ray diffractograms of V45.45B54.55 (Fig. 2e) and V44B56 alloys showed the presence of V_3B_4,

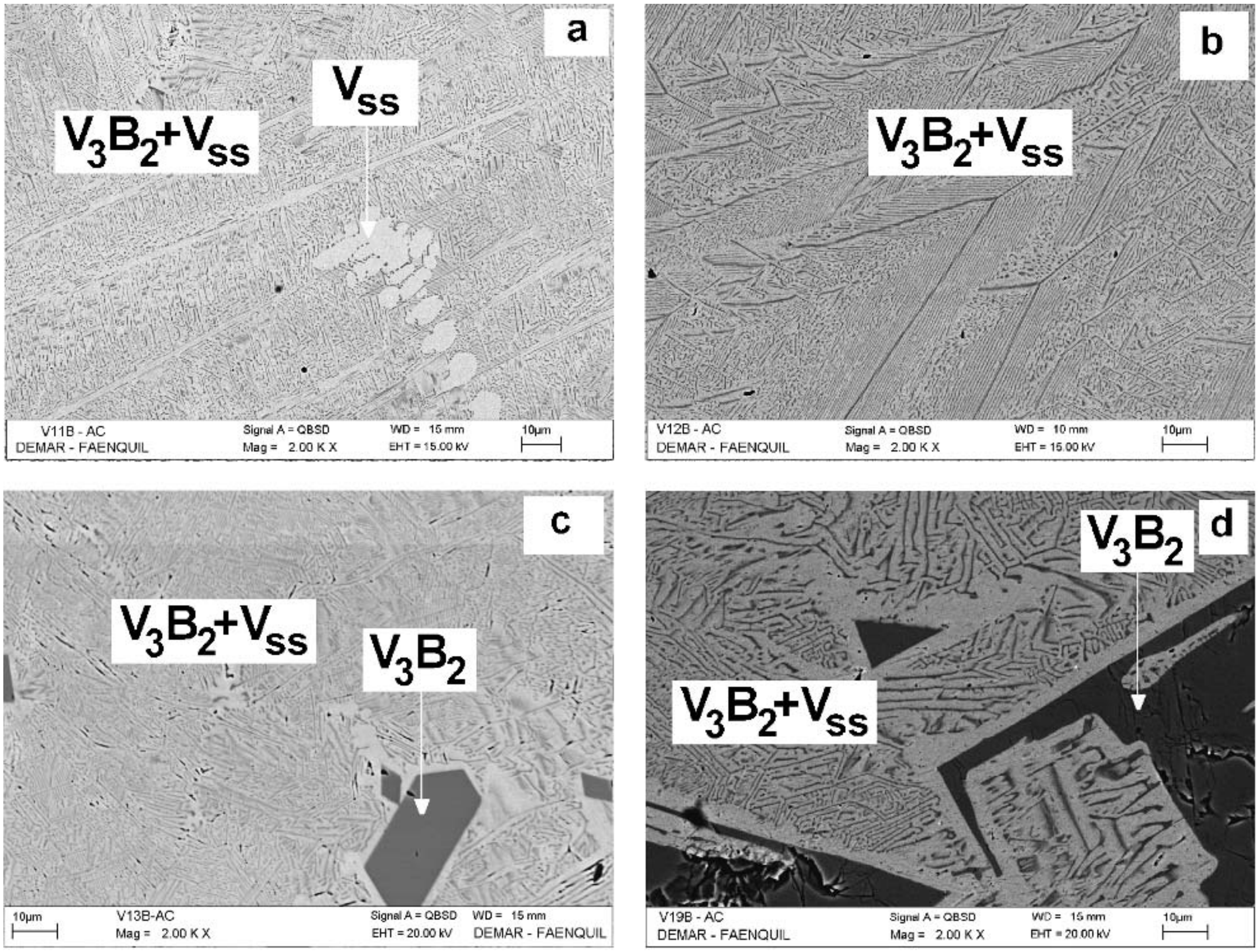

Fig. 3 SEM/BSE images of as-cast V-B alloys: **(a)** V89B11, **(b)** V88B12, **(c)** V87B13, **(d)** V81B19

V_5B_6, and VB phases in their microstructures. Note that V45.45B54.55 corresponds to the V_5B_6-phase composition. V_3B_4 primary grains were observed in the microstructures of both alloys as depicted in Fig. 3(g), which shows a SEM/BSE micrograph of the V45.45B54.55 alloy.

The x-ray diffractogram of V43B57 indicated the presence of V_2B_3 and V_3B_4 phases in a microstructure where the V_2B_3 primary grains were surrounded by V_3B_4. In addition to V_2B_3 and V_3B_4, VB_2 was also identified in the V40B60 alloy, the SEM/BSE images showing the VB_2-phase enveloped by V_2B_3. Thus, these results confirm the peritectic formation of V_3B_4 and V_2B_3 as well as the compositions of the liquid phase involved in the invariant reactions, as shown in Fig. 1.

The x-ray diffractogram of alloy V33B67 indicated only the presence of the VB_2 phase and the SEM/BSE images showed a typical single phase microstructure, in agreement with the proposal of a congruent formation for this phase as shown in Fig. 1.

SEM/BSE micrographs showed primary precipitation of VB_2 in the V6B94 alloy (Fig. 3h) and of B_{ss} in the V4B96 alloy, both with a eutectic VB_2+B in the last solidification region. These results suggest that the liquid composition of the $L \leftrightarrow VB_2+B_{ss}$ eutectic is at 95 at.% B instead of 98 at.% B_{ss} as shown in Fig. 1. The eutectic composition proposed here is more likely considering the solubility of vanadium in β-rhombohedral boron at a minimum of 1.6 at.%, as determined by Garbauskas et al. [1986Gar].

Table 2 summarizes the results of this investigation by showing the composition of the liquid phase involved in each of the invariant reactions of the V-B system.

4. Summary

In this study we evaluated the invariant reactions of the V-B system with respect to their nature and the composition of the liquid involved in each reaction. The following results are not in agreement with literature data for this system: the liquid compositions associated with the reactions $L \leftrightarrow V_{SS} + V_3B_2$ and $L + VB \leftrightarrow V_3B_2$ are 12 at.% B and 19 at.%B, respectively; the VB-phase forms congruently; the V_5B_6-phase forms from the liquid through the peritectic reaction $L + V_3B_4 \leftrightarrow V_5B_6$; a new eutectic reaction $L \leftrightarrow VB + V_5B_6$ is proposed; the liquid composition associated with the reaction $L \leftrightarrow VB_2 + B_{SS}$ is approximately 95 at.% B.

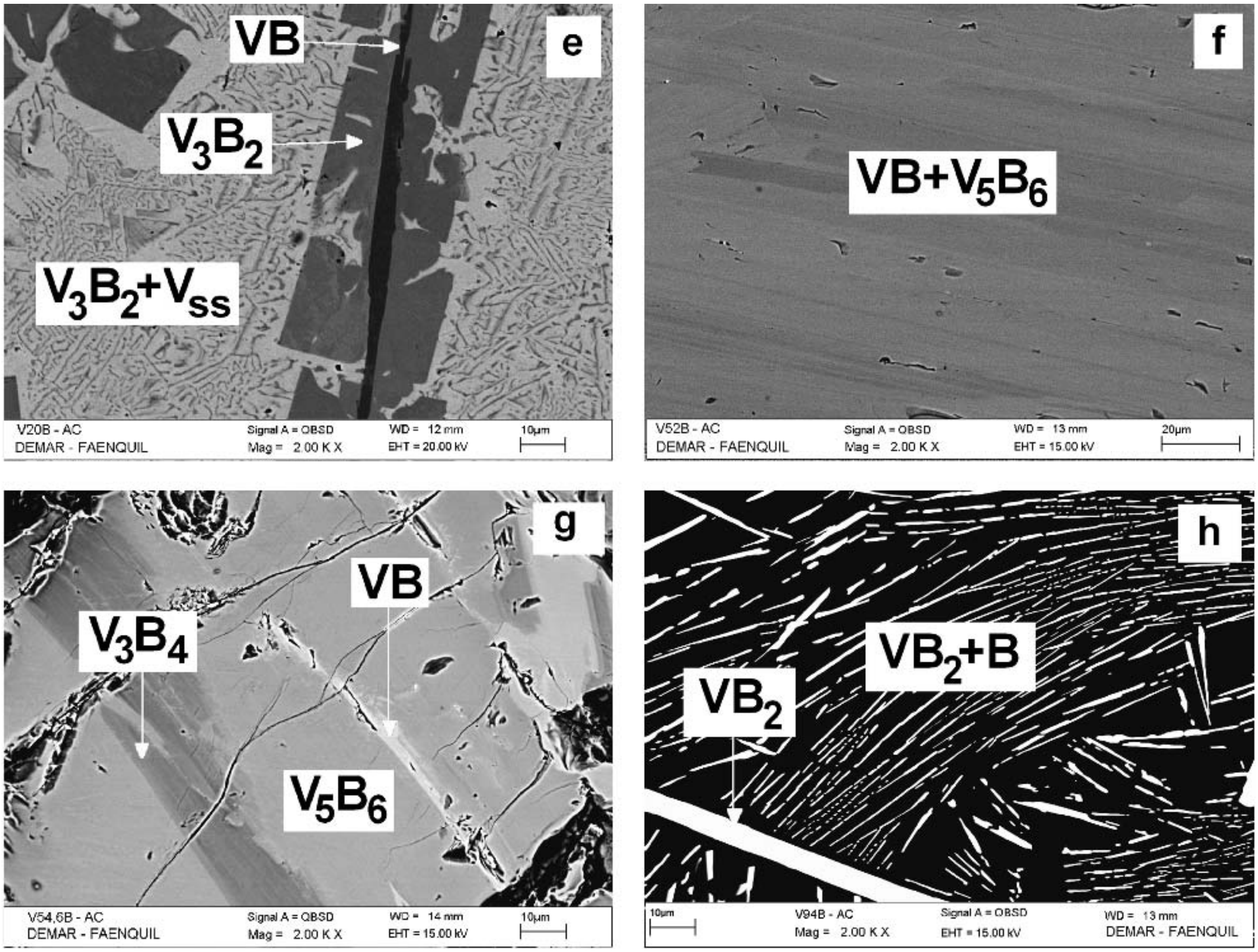

Fig. 3 (cont.) SEM/BSE images of as-cast V-B alloys: **(e)** V80B20, **(f)** V48B52, **(g)** V45.45B54.55, **(h)** V6B94

Table 2 Compositions of the Liquid Phase in the Invariant Reactions of the V-B System Based on the Present Study

Reaction	Compositions of the Liquid Phase, at.% B	Reaction Type
$L \leftrightarrow V_{SS} + V_3B_2$	12	Eutectic
$L + VB \leftrightarrow V_3B_2$	19	Peritectic
$L \leftrightarrow VB$	50	Congruent
$L \leftrightarrow VB + V_5B_6$	~52	Eutectic
$L + V_3B_4 \leftrightarrow V_5B_6$	~53	Peritectic
$L + V_2B_3 \leftrightarrow V_3B_4$	56	Peritectic
$L + VB_2 \leftrightarrow V_2B_3$	57	Peritectic
$L \leftrightarrow VB_2$	67	Congruent
$L \leftrightarrow VB_2 + B_{SS}$	95	Eutectic

Acknowledgments

This work is part of the activities related to the CNPq-DRL 910077/00-2, “MSIT-Brazil network” project. Carlos Angelo Nunes thanks CAPES (Fundação de Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brasília, Brazil) for the financial support during his studies at Universität Wien under grant BEX2362/02-3. Belmira Benedita de Lima acknowledges CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brasília, Brazil) for a scholarship under grant 141043/99-7. The authors also acknowledge Wah Chang (Albany, OR) for providing the pure vanadium material used in this work.

References

2003Ito: K. Ito, M. Kumagai, T. Hayashi, and M. Yamaguchi: “Room Temperature Fracture Toughness and High Temperature Strength of T_2-Mo_{ss} and $(Mo,Nb)_{ss}$-T_1-T_2 Eutectic Alloys in the Mo-Si-B System,” *Scripta Mater,* 2003, *49*(4), pp. 285-90.

2003Pin: D.M. Pinto Júnior, C.A. Nunes, G.C. Coelho, and F. Ferreira: “Liquidus Projection of the Nb-Si-B System in the Nb-rich Region,” *Intermetallics*, 2003, *11*(3), pp. 251-55.

2003Bor: L.A. Borges Júnior, G.C. Coelho, C.A. Nunes, and P.A. Suzuki: “New Data on Phase Equilibria in the Nb-rich Region of the Nb-B System,” *J. Phase Equilibria,* 2003, *24*(2), pp. 140-46.

2003Nun: C.A. Nunes, B.B. Lima, G.C. Coelho, P.Rogl, and P.A. Suzuki: “On the Stability of the V_5B_6-phase,” *J. Alloys Compds.,* in press, 2003.

2002Sch: J.H. Schneibel, M.J. Kramer, and D.S. Easton: "A Mo-Si-B Intermetallic Alloy with a Continuous Alpha-Mo Matrix," *Scripta Mater.,* 2002, *46*(3), pp. 217-21.

2002Par: J.S. Park, R. Sakidja, and J.H. Perepezko: "Coating Design for Oxidation Control of Mo-Si-B Alloys," *Scripta Mater.,* 2002, *46*(11), pp. 765-70.

1996Kra: W. Krans and G. Nolze: "POWDERCELL – a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powders patterns," *J. Appl. Crystallogr.,* 1996, *29,* pp. 301-03.

1991Vil: P. Villars and L.D. Calvert: "Pearson's Handbook of Crystallographic Data for Intermetallic Phases," 2nd ed, ASM International, Materials Park, OH, 1991, four volumes.

1990Bol: H. Bolmgren, T.J. Lundström: "A New Binary Boride, Nb_5B_6," *J. Less-Common Metals,* 1990, *159*(1-2), L25-L27.

1988JCP: Anon.: Selected Powder Diffraction Data for Metals and Alloys, 1st ed, JCPDS, Swarthmore, PA, 1988.

1987Spe: K.E. Spear, P.K. Liao, and J.F. Smith: "The B-V (Boron-Vanadium) System," *Bull. Alloy Phase Diagrams,* 1987, *5*(8), pp. 447-54.

1986Gar: M.F. Garbauskas, J.S Kaper, and G.A. Slack: "The Incorporation of Vanadium in β-Rhombohedral Boron as Determined by Single-Crystal Diffractometry," *J. Solid State Chem.,* 1986, *63,* pp. 424-30.

1981Spe: K.E. Spear, J.H. Blanks, and M.S. Wang: "Thermodynamic Modeling of the V-B System," *J. Less-Common Metals,* 1981, *82,* pp. 237-43.

1969Spe: K.E. Spear and P.W. Gilles: "Phase and Structure Relationships in the Vanadium-Boron System," *High Temp. Sci.,* 1969, *1*(1), pp. 86-97.

1966Rud: E. Rudy and St. Windisch, Tech Rept. N°AFML-TR-65-2, Part I, Vol. X, Wright-Patterson Air Force Base, OH, 1966.

1959Now: H. Nowotny, F. Benesovsky, and R. Kieffer: "Beitrag zum Aufbau des Systems Vanadin-Bor," *Z. Metallkde.,* 1959, *50,* pp. 258-61 (in German).