Microstructural Characterization of As-Cast V-Si Alloys and Reevaluation of the Invariant Reactions Involving the Liquid Phase of the V-Si System

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Alloys containing Me-Si-B (Me - Refractory Metal) are of great interest for high temperature structural applications and accurate knowledge of its low order systems (binaries and ternaries) is important to predict the phase relations in the multicomponent alloys. Recent reevaluations of binaries containing Me-Si found out that the accuracy of the description of this type of systems could be improved. Knowing this, a reevaluation of the invariant reactions in the V-Si system via microstructural characterization of as-cast alloys is presented. Alloys of key compositions were prepared by arc melting pure V (min. 99.75%) and Si (min. 99.998%) and characterized via scanning electron microscopy (SEM) using back-scattered electron (BSE) mode, energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The results of this study confirmed the solid phases, the nature of the invariant reactions and determined new compositions for the liquid participating in certain invariant reactions.

Keywords: *V-Si system, phase diagrams, silicides, solidification.*

1. Introduction

Accurate description of binaries and ternaries phase diagrams is of fundamental importance for the development of thermodynamic databases to predict phase relations and to define processing conditions for multicomponent alloys.

Reviews of the V-Si system were published by Smith[1,2] and Schlesinger[3], consolidating the information available in the literature up to 1981, 1985 and 1990, respectively. All reviews are in good agreement, the following solid phases are considered stable: (V), V_3Si, V_5Si_3, V_6Si_5, VSi_2 and (Si). The (V) phase dissolves important amount of Si while the solubility of V in (Si) is negligible. The phase V_3Si has an important range of solubility whereas the V_5Si_3, V_6Si_5 and VSi_2 phases are stoichiometric. Smith[1] initially considered the V_3Si phase with peritectic formation but the investigation of Jorda and Muller[4] indicated it as congruent and also established its range of solubility. This new information was taken into account in the latter reviews[2,3]. The compounds V_5Si_3, VSi_2 are also formed via congruent transformations while V_6Si_5 is a product of a peritectic reaction ($L + V_5Si_3 \leftrightarrow V_6Si_5$), decomposing eutectoidically at lower temperature ($V_6Si_5 \leftrightarrow V_5Si_3 + VSi_2$). Four eutectics reactions are found in this system: (1) $L \leftrightarrow (V) + V_3Si$; (2) $L \leftrightarrow V_3Si + V_5Si_3$;

(3) $L \leftrightarrow V_6Si_5 + VSi_2$; (4) $L \leftrightarrow VSi_2 + (Si)$. Table 1 shows the crystallographic data for the stable solid phases of this system. Zhang et al.[5] assessed the V-Si system taking into account the available data for phase equilibria and thermodynamic properties and also performed differential thermal analysis (DTA) experiments. Their optimization is in good agreement with the phase diagram proposed by Smith[2]. Figure 1 shows the superposition of the V-Si phase diagram proposed by Smith[2] and that calculated by Zhang et al.[5] where the vertical lines indicate the nominal compositions of the alloys prepared in this work.

Recent investigations carried out in our group[6-10] have contributed to better description of phase diagrams of several Me-Si (Me-metal) binaries, revealing the need to reevaluate the phase relations in these systems. Thus, in this work the invariant reactions involving the liquid phase of the V-Si system have been reevaluated via microstructural characterization of as-cast alloys.

2. Experimental Procedure

V-Si alloys with masses between 2 and 8 g were prepared by arc melting V (min. 99.8 wt.%) and Si (min. 99.998 wt.%) under argon (min. 99.995%) in a water-cooled copper hearth using non-consumable tungsten electrode and Ti

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Table 1: Crystallographyc data[11] of the stable solid phases in the V-Si system.

Phase	Pearson symbol	Space Group	Strukturbericht designation	Prototype
(V)	cI2	Im-3m	A2	W
V_3Si	cP8	Pm-3m	A15	Cr_3Si
V_5Si_3	tI32	I4/mcm	$D8_m$	W_5Si_3
V_6Si_5	oI44	Immm	…	V_6Si_5
VSi_2	hP9	$P6_222$	C40	$CrSi_2$
(Si)	cF8	Fm-3m	A4	C (Diamond)
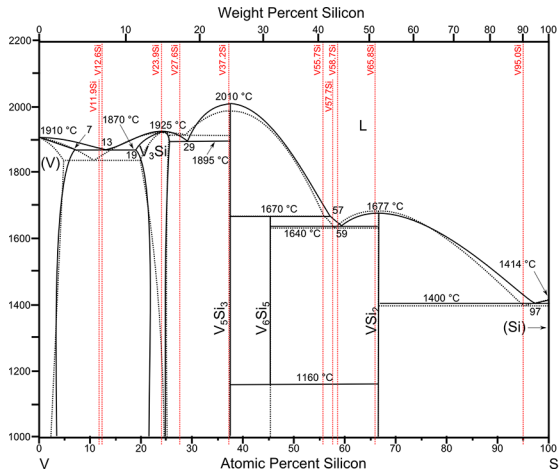
Figure 1: V-Si Phase Diagram proposed by Smith[2] (solid lines) and Zhang et al.[5] (dashed lines). Vertical lines indicate the assumed compositions of the alloys prepared in this work.

getter. Five melting steps were carried out for each alloy to produce chemically homogeneous samples. After melting the alloys were weighted to evaluate possible mass losses during arc melting.

The alloys were characterized through scanning electron microscopy (SEM) in the back-scattered electron mode (BSE), Energy-Dispersive X-ray Spectroscopy (EDS) and X-ray diffraction (XRD).

For the SEM/EDS analyses the alloys were hot mounted in resin, ground with SiC abrasive paper (#120 → #4000) and polished with colloidal silica suspension (OP-S). The images were obtained in a 1450VP (LEO) and TM3000 (Hitachi) SEM instruments. The EDS analyses were carried out using a Swift ED3000, Oxford Instruments.

For the XRD experiments, the as-cast alloys were mechanically ground and sieved to below 80 Mesh (177 μm). The measurements were carried out at room temperature using Ni-filtered Cu-Kα radiation in an Empyrean (Panalytical) diffractometer. The measurement conditions were 20°<2θ<90°, 0.02° step. The phases were identified based on Villars and Calvert crystallographic data[11] and the Powder Cell software[12].

The liquid compositions of the invariant reactions were estimated based on the microstructure of the alloys: either according to the transitions of primary precipitation between two consecutive samples or when the microstructure of the sample was 100% eutectic. In the first case the estimated composition for the liquid is the average between the calculated compositions attributing the mass loss to Si in the two consecutive samples. In the second case it is the average between the nominal composition and the calculated one attributing mass loss to Si.

3. Results and Discussion

The results will be presented according to the Si contents of the alloys, from the lowest to the highest. Table 2 shows the chemical compositions of the alloys prepared in this work, i.e. their nominal composition and their composition range based on the mass losses occurred during the arc melting (attributing all the mass losses to either V or Si). In the following text as well as in Figure 1, the alloys are referred to their calculated compositions attributing all the mass losses to Si vaporization (column 4 of Table 2). Table 3 indicates the phases present in each alloys, as determined via XRD.

The XRD results of V11.9Si and V12.6Si alloys have indicated the presence of (V) and V_3Si in their microstructure. Figure 2 (a, b) shows SEM/BSE micrograph of these alloys where an eutectic formed by (V) and V_3Si is observed in both of them. However, the V11.9Si alloy presents primary precipitation of (V) while V12.6Si alloy shows primary precipitation of V_3Si. The presence of (V) primary precipitates in V11.9Si alloy and of V_3Si in V12.6Si alloy indicates that the liquid eutectic composition is in the 11.9 - 12.6 at.% Si (i.e. 12.3 ± 0.3 at.% Si) interval, which is between 10.8 assessed by Zhang et al.[5] and 13 at.% proposed by Smith[2].

The XRD results of V23.9Si alloy have shown only V_3Si phase in the microstructure of this alloy, confirmed by single-phase observation in the SEM/BSE analysis. This result confirms the congruent formation of V_3Si phase, in agreement with the proposal of Smith[2] and Zhang et al.[5].

The XRD results of the V27.6Si alloy have indicated the presence of V_3Si and V_5Si_3 phases in its microstructure. Figure 3 shows a SEM/BSE micrograph of this alloy indicating a full eutectic microstructure formed by V_3Si and V_5Si_3. The presence of a 100% eutectic microstructure in this alloy indicates that the composition of the eutectic liquid is between 27.6 and 28.0 at.% Si (i.e. 27.8 ± 0.2 at.% Si), a value slightly lower than that found by Smith[2] but equal to that proposed by Zhang et al.[5].

Table 2: Compositions of the alloys produced in this work.

Alloy Composition (a)	Nominal composition (at. % Si) (b)	Mass loss during arc-melting(%)	Composition Range (at. % Si)	
			(c)	(d)
V11.9Si	11.96	0.02	11.93	11.97
V12.6Si	13.00	0.28	12.57	13.03
V23.9Si	24.00	0.09	23.89	24.02
V27.6Si	28.02	0.36	27.61	28.11
V37.2Si	37.50	0.33	37.19	37.60
V55.7Si	56.01	0.54	55.68	56.24
V57.7Si	58.01	0.60	57.67	58.27
V58.7Si	58.97	0.42	58.74	59.15
V65.8Si	66.70	1.96	65.85	67.63
V95.0Si	94.98	2.55	94.84	96.39

(a) Adopted composition; (b) composition based on the weighted masses of V and Si, before arc melting; (c) calculated composition attributing mass losses to Si; (d) calculated composition attributing mass losses to V.

Table 3: XRD identification of the phases present in the alloys produced in this work.

Alloy	Phase 1	Phase 2	Phase 3
V11.9Si	(V)	V_3Si	
V12.6Si	(V)	V_3Si	
V23.9Si	V_3Si		
V27.6Si	V_3Si	V_5Si_3	
V37.2Si	V_5Si_3		
V55.7Si	V_5Si_3	V_6Si_5	VSi_2
V57.7Si	V_6Si_5	VSi_2	
V58.7Si	V_6Si_5	VSi_2	
V65.8Si	VSi_2		
V95.0Si	VSi_2	(Si)	
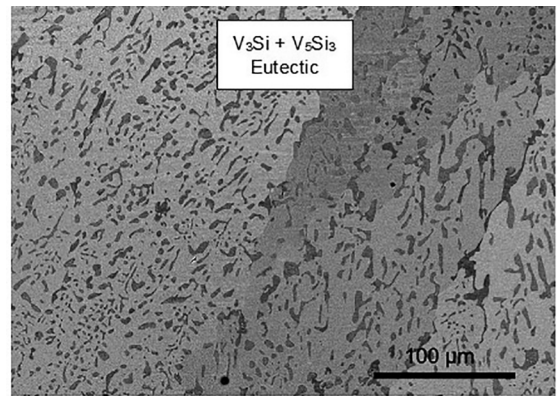
Figure 3: SEM/BSE micrograph of the V27.6Si as-cast alloy.
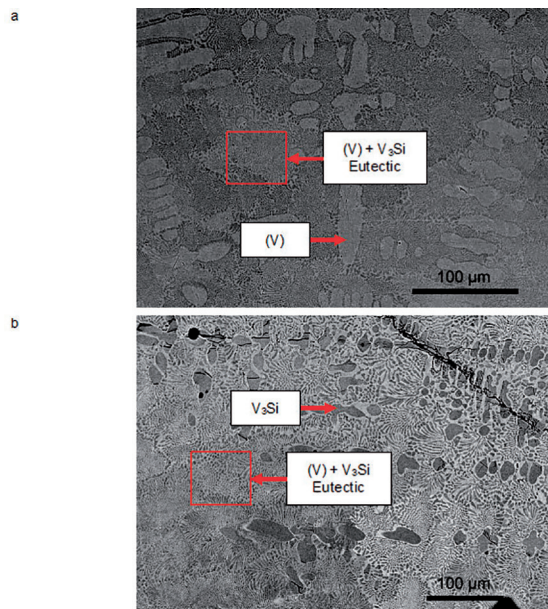
Figure 2: SEM/BSE micrograph of: (a) V11.9Si; (b) V12.6Si as-cast alloys.

The XRD results of V37.2Si alloy have indicated only V_5Si_3 phase in its microstructure, supported by the SEM/BSE analysis. This result confirms the congruent formation of the V_5Si_3 phases, in agreement with Smith[2] and Zhang et al.[5].

Figure 4 shows SEM/BSE micrographs of the V55.7Si (a, b), V57.7Si (c) and V58.7Si (d) alloys. XRD results have indicated the presence of V_6Si_5 and VSi_2 in all these alloys as well as V_5Si_3 in the V55.7Si alloy. SEM/BSE micrographs from all these alloys presented a eutectic formed by V_6Si_5 and VSi_2 in the last regions to solidify. Alloy V55.7Si micrograph shows small fractions of V_5Si_3 primary precipitation and pro-eutectic V_6Si_5. The microstructure of V57.7Si alloy presents near fully V_6Si_5 + VSi_2 eutectic microstructure and few V_6Si_5 primary precipitates. The micrograph of V58.7Si alloy shows primary precipitation of VSi_2. The presence of V_5Si_3 primary precipitates in the V55.7Si alloy and V_6Si_5 primary precipitates in the V57.7Si alloy suggests that the composition of the liquid in the peritectic reaction involving V_6Si_5 is between 55.7 and 57.7 at.% Si (i.e. 56.7 ± 1.0 at.% Si) in accordance (considering the estimated error) with the 57 at.% proposed by Smith[2] and 56.2 at.% proposed by Zhang et al.[5]. The presence of V_6Si_5 primary precipitates in V57.7Si

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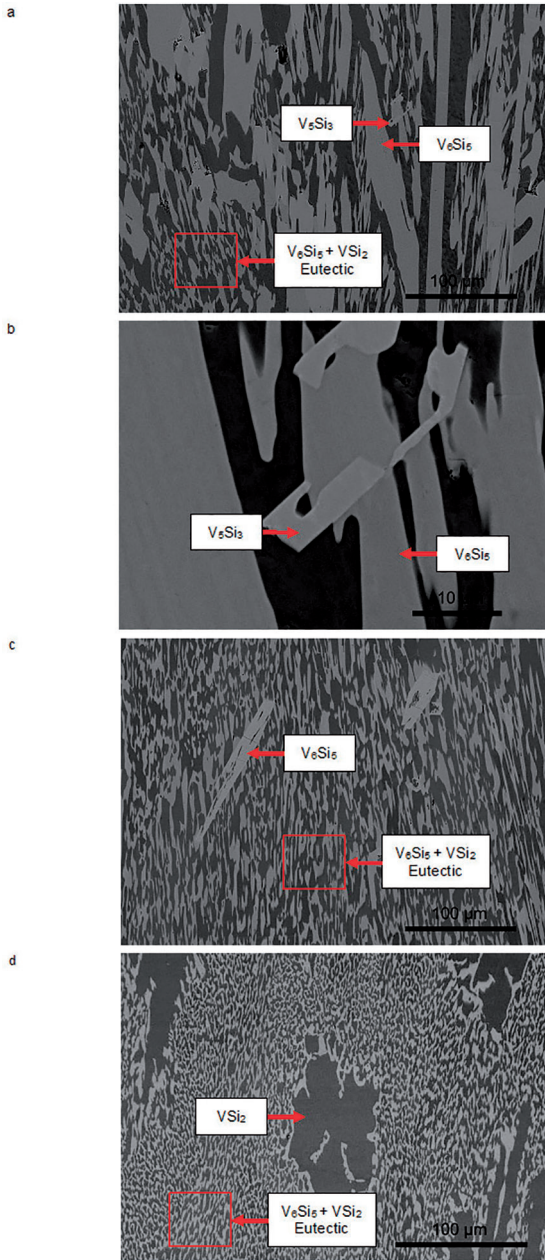
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Figure 4: SEM/BSE micrographs of the: (a,b) V55.7Si, (c) V57.7Si and (d) V58.7Si as-cast alloys.

alloy and VSi_2 primary precipitates in V58.7Si alloy indicates that the composition of the liquid in the $V_6Si_5 + VSi_2$ eutectic is between 57.7 and 58.7 at.% Si (i.e. 58.2 ± 0.5 at.% Si). Our proposed composition for the eutectic liquid is between 57.6 (assessed by Zhang et al.[5]) and 59 at.% (proposed by Smith[2]).

The XRD results of V65.8Si alloy have indicated only the VSi_2 phase. The SEM/BSE micrographs of this alloy have shown a major VSi_2 microstructure, confirming the congruent formation of VSi_2 as proposed by Smith[2] and Zhang et al.[5].

The XRD results of the V95.0Si alloy have indicated the presence of VSi_2 and (Si) in its microstructure. Figure 5 shows a SEM/BSE micrograph of this alloy with a fully eutectic microstructure formed by VSi_2 and (Si). The presence of a 100% eutectic microstructure indicates that the composition of the liquid in the VSi_2 + (Si) eutectic is between 94.8 and 95.0 at.% Si (i.e. 94.9 ± 0.1 at.% Si). Our proposal for the liquid composition is richer in V than the 97 at.% proposed by Smith[2] but in agreement with the assessment of Zhang et al.[5].
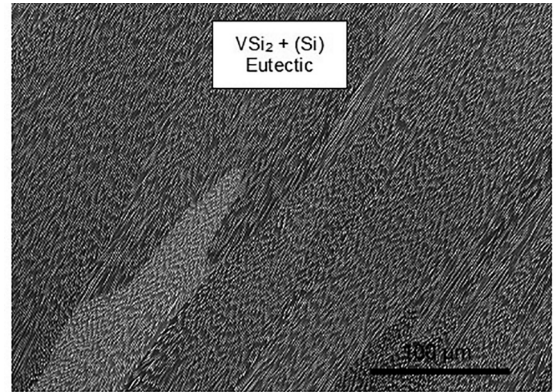

Figure 5: SEM/BSE micrograph of the V95.0Si as-cast alloy.

The microstructural analysis of these alloys, therefore, confirms all the solid phases and invariant reactions in the V-Si phase diagram. The proposal for the liquid phase compositions in the invariant reactions is summarized in Table 4.

4. Conclusions

The results of microstructural characterization (SEM/BSE + EDS + XDR) of the as-cast V-Si alloys investigated in this

Table 4: Liquid compositions at invariant reactions in the V-Si system.

Invariant reaction	Liquid Composition, at.% Si Zhang et al.[5]	Liquid Composition, at.% Si Smith[2]	Liquid Composition, at.% Si This work
$L \leftrightarrow (V) + V_3Si$	10.8	13	12.3 ± 0.3
$L \leftrightarrow V_3Si$	25	~24 (a)	Not evaluated
$L \leftrightarrow V_3Si + V_5Si_3$	27.8	~29	27.8 ± 0.2
$L \leftrightarrow V_5Si_3$	37.5	37.5	Not evaluated
$L + V_5Si_3 \leftrightarrow V_6Si_5$	56.2	57	56.7 ± 1.0
$L \leftrightarrow V_6Si_5 + VSi_2$	57.6	~59	58.2 ± 0.5
$L \leftrightarrow VSi_2$	66.7	66.7	Not evaluated
$L \leftrightarrow VSi_2 + (Si)$	94.7	97	94.9 ± 0.1

(a) Approximate value obtained by reading the phase diagram

study confirmed the solid phases, the nature of the invariant reactions and determined new compositions for the liquid participating in certain invariant reactions of this system. The compositions of the liquid phase that participates in the invariant reactions are suggested as: (1) In the (V) + V_3Si eutectic the liquid composition is 12.3 at.% Si; (2) In the V_3Si + V_5Si_3 eutectic the liquid composition is 27.8 at.% Si; (3) In the V_5Si_3 + L peritectic the liquid composition is 56.7 at.% Si; (4) In the V_3Si + V_5Si_3 eutectic the liquid composition is 58.2 at.% Si; and finally in (5) In the VSi_2 + (Si) eutectic the liquid composition is 94.9 at.% Si.

5. Acknowledgements

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