Thermochimica Acta 513 (2011) 100–105

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Heat contents of the intermetallics V_3Ge and V_5Ge_3 and thermodynamic modeling of the Ge–V system

Xiaoming Yuan[a], Weihua Sun[a], Yoonsung Chung[b], Honghui Xu[a], Shuhong Liu[a], Yong Du[a,*], Philip Nash[b], Dewen Zeng[c]

[a] State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, China
[b] Thermal Processing Technology Center, Illinois Institute of Technology, 10 West 32nd St., Chicago, IL 60616, USA
[c] College of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, China

ARTICLE INFO

Article history:
Received 19 September 2010
Received in revised form 5 November 2010
Accepted 9 November 2010
Available online 25 November 2010

Keywords:
Ge–V
Microstructure
Phase diagram
Calorimetry
DSC

ABSTRACT

Fourteen alloys were prepared by arc-melting the pure elements and annealing the alloys at 850 °C for 30 days. The annealed alloys were examined by X-ray diffraction (XRD), scanning electron microscope with energy dispersive X-ray analysis (SEM/EDX), differential scanning calorimetry (DSC) and drop calorimeter. The major experimental results are as follows. (I) The heat contents of V_3Ge and V_5Ge_3 were measured by drop calorimeter from 400 to 900 °C. (II) The microstructure analysis of as-cast alloy $V_{87.1}Ge_{12.9}$ indicates that the eutectic composition of liquid $\leftrightarrow$ (V) + V_3Ge is above 12.9 at.% Ge, and that of $V_{2.9}Ge_{97.1}$ shows that the eutectic composition of liquid $\leftrightarrow$ $V_{17}Ge_{31}$ + Ge is close to 97.1 at.% Ge. (III) The invariant reaction temperatures of liquid + $V_{11}Ge_8$ $\leftrightarrow$ $V_{17}Ge_{31}$ and liquid $\leftrightarrow$ $V_{17}Ge_{31}$ + Ge are at 960.0 ± 2 °C and 930.7 ± 2 °C, respectively. Based on the experimental results in this study and in the literature, the Ge–V system was modeled by CALPHAD approach.

1. Introduction

The Ge–V system was first reviewed by Smith [1], and later optimized by Wang et al. [2]. However, a thermodynamic investigation of the Ge–V system is still needed due to the following reasons. Firstly, the Ge–V phase diagram and thermodynamic data available in the literature are limited. It is of interest to perform new experiments to check the literature data and supply new data for a revised thermodynamic modeling. Secondly, Wang et al. [2] ignored the measured enthalpy of mixing [3] and partial enthalpy of V in liquid [4–6] in their optimization, and their predicted values do not agree with the experimental data [3–6]. Thirdly, the calculated phase diagram shows a fictitious miscibility gap for liquid phase at high temperature [2], as shown in Fig. 1.

The present work is devoted to perform a full thermodynamic investigation of the Ge–V system by a combination of experiments and CALPHAD approach.

2. Evaluation of the experimental data

As shown in Table 1 [7–10], the Ge–V system consists of four compounds (V_3Ge, V_5Ge_3, $V_{11}Ge_8$, and $V_{17}Ge_{31}$) and three solution phases (liquid, (V) with bcc_A2 structure, and Ge with diamond_A4 structure). Since this system was previously evaluated by Smith [1], all the phase diagram and thermodynamic data available for the Ge–V system are briefly reviewed and presented in Table 2.

2.1. Phase diagram data

Savitskii et al. [11] and Svechnikov et al. [12] made the major contribution to the general feature of the Ge–V phase diagram. They agree that there are four compounds: V_3Ge, V_5Ge_3, $V_{11}Ge_8$ and $V_{17}Ge_{31}$. The congruent melting temperatures of V_3Ge reported by different authors are 1900–2000 °C [8], 1690 °C [11], 1925 °C [12] and 1920 °C [13] respectively. Thus, the congruent melting temperature of V_3Ge was taken as 1920–1925 °C in the optimization. The reported congruent melting temperatures of V_5Ge_3 are 1900–2000 °C [8], 1930 °C [11] and 2013 °C [12], respectively. Since the reported melting temperature for V_5Ge_3 is scattered [8,11,12], the assessed value of 1965 ± 35 °C from Smith [1] was used in the optimization. Savitskii et al. [11] reported that the homogeneity of V_3Ge between 1400 and 1650 °C has a composition range of ∼3–4 at.%, while three other groups [8,12,14] reported a narrow homogeneity range with a slight Ge-deficiency. No observable homogeneity range was reported for the other compounds. As a result, all four compounds were treated as line compounds in the optimization. The reported maximum solubility of Ge in (V) is ∼4.5 at.% at 1760 °C [12] and ∼3 at.% at 1590 °C [11]. The solubility data [11,12] were considered to be reliable in the present modeling.

---

[*] Corresponding author. Tel.: +86 731 88836213; fax: +86 731 88710855.
E-mail address: yongducalphad@gmail.com (Y. Du).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.11.018

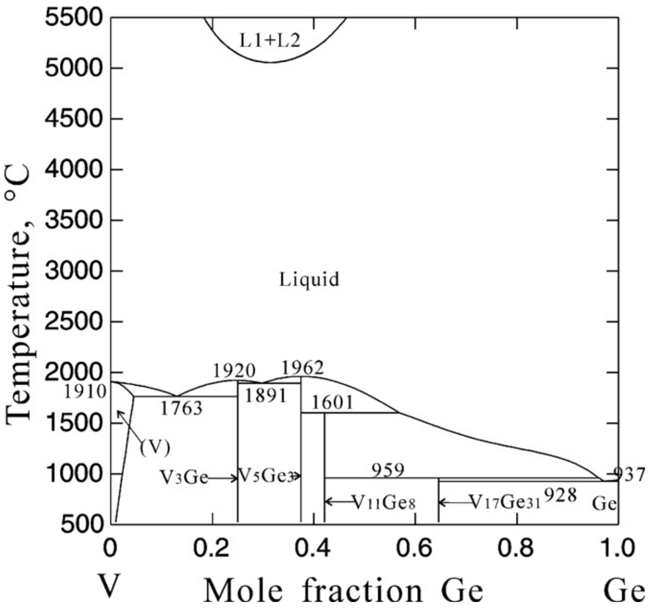

Fig. 1. Ge–V phase diagram calculated by Wang et al. [2], which shows a fictitious miscibility gap for liquid phase at high temperature.

2.2. Thermodynamic data

The enthalpy of mixing in liquid (ΔH_{mix}) at 1500 °C within 60–100 at.% Ge was measured by Shlapak et al. [3] using calorimetry. Using calorimeter, three groups of authors [4–6] measured the partial enthalpy of V in liquid Ge ($\Delta\overline{H}_V$) at different temperatures, 1001 °C [4], 1600 °C [5] and 1024 °C [6]. However, the measured partial enthalpy of V in infinitely dilute liquid is scattered, −52.8 kJ/mol [4], −51.4 kJ/mol [5] and −37.8 kJ/mol [6]. Consequently, the measured enthalpy of mixing [3] was used in the optimization, while the partial enthalpy data [4–6] were used to check the reliability of the modeling.

Table 3
Calculated enthalpy of formation along with the experimental data[a].

V_3Ge	V_5Ge_3	$V_{11}Ge_8$	$V_{17}Ge_{31}$	Method	Temperature, (°C)	Reference
−36.2	−45.9	−45.5	−35.0	KEMS	25	[18]
		−51.6		Calorimetry	1028	[6]
	−44.3			Calorimetry	25	[17]
−44.8	−47.7	−46.6	−26.8	emf	800	[15,16]
−35.3	−41.5	−39.9	−26.2	Calculated	25	[1]
−35.1	−45.1	−46.5	−32.4	Calculated	25	[2]
−36.0	−43.8	−46.1	−35.0	Calculated	25	This work

[a] In kJ/(mol·atoms).

As shown in Table 3, two groups of authors contributed to the measurement of enthalpies of formation (ΔH_f) for the four compounds. Eremenko et al. [15,16] measured ΔH_f at 800 °C using electromotive force (emf) method, while Zarembo et al. [18] obtained the value for ΔH_f at 25 °C using Knudsen effusion mass spectrometry method (KEMS). Except for the data for V_3Ge and $V_{17}Ge_{31}$, their results agree well with each other. Besides, both Yassin et al. [6] and Kleppa and Jung [17] measured ΔH_f for $V_{11}Ge_8$ and V_5Ge_3 at 25 °C by means of calorimeter. The measured ΔH_f for V_5Ge_3 is −44.3 kJ/mol [17], which agrees well with −45.9 kJ/mol [18], and ΔH_f for $V_{11}Ge_8$ is −51.6 kJ/mol [6], which is slightly lower than −45.5 kJ/mol [18]. During the present optimization, the measured ΔH_f for the four compounds from Zarembo et al. [18] were used.

3. Experimental procedure

In view of the lack of the thermodynamic data for the intermetallics in the Ge–V system, drop calorimetry was used to measure the heat contents (H_T–H_{298K}) of V_3Ge and V_5Ge_3. Firstly,

Table 1
Crystal structure data of the phases in the Ge–V system.

Phase	Pearson lattice designation	Prototype	Reference
Liquid	–	–	–
(V)	*cI*2	W	[7]
V_3Ge	*cP*8	Cr_3Si	[8]
V_5Ge_3	*tI*32	W_5Si_3	[7]
$V_{11}Ge_8$	*oP*76	$Cr_{11}Ge_8$	[9]
$V_{17}Ge_{31}$	*tP*184	–	[9]
Ge	*cF*8	Diamond	[10]

Table 2
Summary of the phase diagram and thermodynamical data in the Ge–V system.

Type of data	Experimental technique	Reference	Quoted mode[a]
Phase diagram within 0–100 at.% Ge	DTA[b], MA[b], XRD,	[11]	+
Phase diagram within 0–100 at.% Ge		[12]	+
Congruent melting point of V_3Ge and V_5Ge_3	XRD, MA[b]	[8]	+
Congruent melting point of V_3Ge		[13]	+
Homogeneity of V_3Ge	MA[b], XRD	[14]	
Enthalpy of formation of V_3Ge, V_5Ge_3, $V_{11}Ge_8$ and $V_{17}Ge_{31}$	emf[b]	[15,16]	+
Enthalpy of formation of V_5Ge_3	emf[b]	[17]	+
Enthalpy of formation of $V_{11}Ge_8$	Drop calorimetry	[6]	Δ
Enthalpy of formation of V_3Ge, V_5Ge_3, $V_{11}Ge_8$ and $V_{17}Ge_{31}$	KEMS[b]	[18]	+
Enthalpy of mixing within 60–100 at.% Ge	Calorimetry	[3]	+
Partial enthalpy of V in liquid	Calorimetry	[5]	Δ
Partial enthalpy of V in liquid	Drop calorimetry	[6]	Δ
Partial enthalpy of V in liquid	Calvet Calorimeter	[4]	+
Heat contents of V_3Ge and V_5Ge_3	Drop calorimetry	This work	+
Liquidus within 73–100 at.% Ge	DSC, XRD, MA[b]	This work	+

[a] Whether the data are used or not used in the optimization is indicated by the following symbols: + used; Δ not used but for checking the modeling.

[b] DTA = differential thermal analysis; DSC = differential scanning calorimetry; MA = microstructure analysis; emf = electromotive force; KEMS = Knudsen Effusion Mass Spectrometry.

Table 4
Summary of the phases and phase transition temperatures for the alloys in the Ge–V system annealed at 850 °C for 30 days.

No.	at.% Ge	Phases[a]	Phase transition temperature (°C)[b]
#1	12.9	V_3Ge, (V)	–
#2	31.0	V_3Ge, V_5Ge_3	–
#3	54.0	$V_{11}Ge_8$, $V_{17}Ge_{31}$	959.6[b]
#4	73.1	$V_{17}Ge_{31}$, Ge	929.9[b], 969.0[b], 1303.6[b]
#5	75.9	$V_{17}Ge_{31}$, Ge[d]	931.3[b], 960.4[b], 1323.6[b]
#6	77.6	$V_{17}Ge_{31}$, Ge	930.2[b], 967.7[b], 1268.6[b]
#7	80.9	$V_{17}Ge_{31}$, Ge	1191.2[b]
#8	83.1	$V_{17}Ge_{31}$, Ge	932.1[b], 971.0[b], 1202.7[b]
#9	88.1	$V_{17}Ge_{31}$, Ge	931.4[b], 971.3[b], 1115.0[c]
#10	93.0	$V_{17}Ge_{31}$, Ge	930.6[b], 971.4[b], 1031.7[c]
#11	95.0	$V_{17}Ge_{31}$, Ge	930.5[b], 970.9[b]
#12	97.1	$V_{17}Ge_{31}$, Ge	930.2[b]

[a] Phases were identified by XRD method.
[b] Obtained from DSC measurement with a heating and cooling rate of 3 °C/min.
[c] Obtained from DSC measurement with a cooling rate of 2 °C/min.
[d] Contains trace amount of $V_{11}Ge_8$.

two alloys were prepared by arc melting the pure elements (99.98 wt.% V and 99.999 wt.% Ge) under high-purity argon atmosphere. Then the alloys were examined by XRD to make sure that single V_3Ge or V_5Ge_3 phase was obtained. Next, the measurement of heat content from 400 to 900 °C at intervals of 100 °C was conducted using a Multi-detector High Temperature Calorimeter Ligne 96(MHTC 96) from Setaram (Lyon, France). At each temperature, six individual measurements were performed for each alloy, and the average value was taken to be the experimental value. The detailed experimental procedure has been reported elsewhere [19].

In addition to the measurement of heat contents, another twelve alloys were also prepared using the same method to measure the Ge–V phase diagram. The compositions of the alloys are listed in Table 4. Since the weight losses during arc melting were less than 1.5 wt.%, no chemical analysis for the alloys was conducted. The present experiment focuses on two parts: microstructure analysis of the as-cast alloys and phase transition temperature measurement.

The microstructure of as-cast alloys was examined by optical microscopy (Leica DMLP,Wetzlar, Germany) and scanning electron microscopy (JSM-5600LV, Japan Electron Optics Laboratory, Japan) with energy dispersive X-ray analysis (SEM/EDX). Phase identification was preformed by means of XRD. These experiments are performed to check the general features of the Ge–V phase diagram.

The phase transition temperatures in the range 73–100 at.% Ge were measured using annealed alloys at 850 °C. The as-cast alloys were sealed in evacuated quartz tubes and annealed at 850 °C for 30 days, and then water-quenched. The differential scanning calorimetry (DSC) apparatus (DSC404C, NETZSCH, Germany) was used to measure the phase transition temperatures. Both the sample holder and reference material are Al_2O_3. Solid pieces with a weight of about 15 mg were taken from the quenched alloys. The measurements were carried out between room temperature and 1450 °C with a heating and cooling rate of 2 or 3 °C/min in argon atmosphere. The temperature was measured with a Pt–Pt/Rh thermocouple and calibrated to the melting temperatures of Al (660.32 °C), Au (1064.18 °C), Bi (271.37 °C), and In (156.61 °C). The accuracy of the temperature measurement was estimated to be ±2 °C. The invariant reaction temperatures were determined from the onset of the signal on the heating curve. Since the last thermal effect on heating for liquids is too weak to be detected, the first thermal effect signal on cooling curve was taken for the liquidus temperature. Taking the first thermal effect as the liquidus from the cooling curve is reasonable since the employed cooling rate is very slow (2 or 3 °C/min). It was assumed that the supercooling phenomenon would be negligible under such a low cooling rate.

4. Thermodynamic models

4.1. Unary phases

The Gibbs energy function ${}^0G_i^{\Phi}(T) = G_i^{\Phi}(T) - H_i^{SER}$ for the pure elements i (i = Ge, V) in the Φ (Φ = Ge, (V), or liquid) phase is described by the following equation:

$$ {}^0G_i^{\Phi}(T) = a + b\cdot T + c\cdot T\cdot \ln(T) + d\cdot T^2 + e\cdot T^3 + f\cdot T^{-1} + g\cdot T^7 + h\cdot T^{-9} \qquad (1) $$

where H_i^{SER} is the molar enthalpy of the stable element reference (SER) at 298.15 K and 1 bar. The Gibbs energy functions for pure Ge and V are taken from the SGTE compilation by Dinsdale [20].

4.2. Solution phases

The (V) and liquid phases are modeled as disordered solution phases. The Gibbs energy is given as follows:

$$ \begin{aligned} G^{\Phi} - H^{SER} &= x_{Ge}\cdot {}^0G_{Ge}^{\Phi} + x_V\cdot {}^0G_V^{\Phi} + R\cdot T\cdot (x_{Ge}\cdot \ln x_{Ge} + x_V\cdot \ln x_V) \\ &\quad + x_{Ge}\cdot x_V\cdot [a_0 + b_0\cdot T + (x_{Ge} - x_V)(a_1 + b_1\cdot T) \\ &\qquad + (a_2 + b_2\cdot T)(x_{Ge} - x_V)^2 + \cdots] \end{aligned} \qquad (2) $$

where H^{SER} is the abbreviation of $x_{Ge}\cdot H_{Ge}^{SER} + x_V\cdot H_V^{SER}$, Φ denotes the phase (Φ = liquid or (V)) and R is the gas constant.

4.3. Intermetallic compounds

The Gibbs energy per mole of $Ge_xV_{(1-x)}$ compound is described by:

$$ \begin{aligned} &{}^0G_m^{Ge_xV_{(1-x)}} - x\cdot H_{Ge}^{SER} - (1-x)H_V^{SER} = \\ &A + B\cdot T + C\cdot T\cdot \ln(T) + x\cdot {}^0G_{Ge}^{SER} + (1-x)\cdot {}^0G_V^{SER} \end{aligned} \qquad (3) $$

in which A, B and C are the parameters to be evaluated in the procedure of optimization.

5. Results and discussion

The measured heat contents of V_3Ge and V_5Ge_3 along with the predicted results using Neumann–Kopp rule are shown in Fig. 2. The maximum discrepancy is about 20% between the measured data and the values predicted using Neumann–Kopp rule. Thus, parameter C in Eq. (3) was adjusted in the thermodynamic optimization of V_3Ge and V_5Ge_3 phases.

The microstructures of the as-cast alloys 1($V_{87.1}Ge_{12.9}$) and 12($V_{2.9}Ge_{97.1}$) are presented in Fig. 3. As shown in Fig. 3a, alloy 1 shows an existence of eutectic structure and primary (V) phase, which indicates that the eutectic composition of liquid ↔ (V) + V_3Ge is above 12.9 at.% Ge. According to Fig. 3b, alloy 12 shows an almost complete eutectic structure of $V_{17}Ge_{31}$ and Ge. Such a microstructure indicates that the eutectic composition of liquid ↔ $V_{17}Ge_{31}$ + Ge is very close to 97.1 at.% Ge.

Table 4 lists the measured phase transition temperatures of the alloys. The measured eutectic temperature of liquid ↔ $V_{17}Ge_{31}$ + Ge is 930.7 ± 2 °C. The measurement of alloy 3, which consists of $V_{11}Ge_8$ and $V_{17}Ge_{31}$, shows that the peritectic temperature of liquid + $V_{11}Ge_8$ ↔ $V_{17}Ge_{31}$ is 959.6 ± 2 °C. However the DSC measurements of alloy 4, 6, 8–11, which consist of $V_{17}Ge_{31}$ and Ge, show that the peritectic temperature is about 970 °C. The reason for this discrepancy can be explained by the nucleation barrier of $V_{11}Ge_8$ during heating. Due to the lack of nucleation sites for the formation of $V_{11}Ge_8$, the DSC signal for alloys 4, 6, 8–11 rises to about 970 °C. In contrast to alloys 4, 6, 8–11, the measured peritectic temperature for alloy 5 is 960.4 °C, as trace amounts of $V_{11}Ge_8$ phase exist

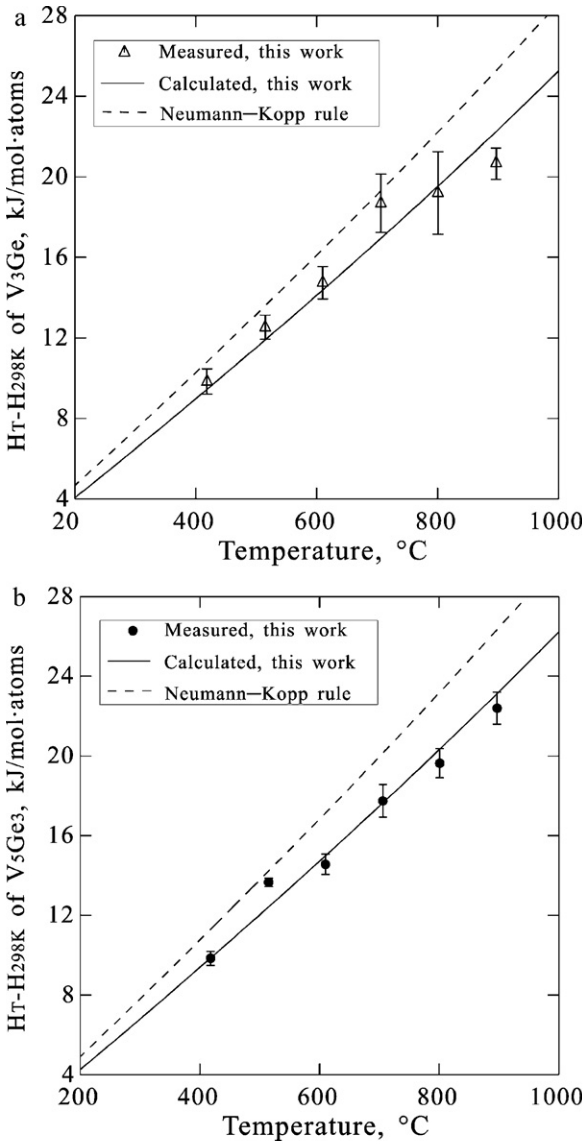

Fig. 2. Calculated heat contents of the compounds according to the present modeling and Neumann–Kopp rule, compared with the experimental data. (a) V_3Ge, (b) V_5Ge_3.

in alloy 5 and could supply the nucleation sites for $V_{11}Ge_8$. This further confirms the nucleation barrier of $V_{11}Ge_8$. The present work indicates although DSC is an effective method to measure phase transition temperatures, it could yield erroneous results due to slow kinetics (such as nucleation barrier) of reactions during measurement. Thus the peritectic temperature for liquid+$V_{11}Ge_8 \leftrightarrow V_{17}Ge_{31}$ is taken as $960.0 \pm 2\,^{\circ}C$. The presently obtained invariant reaction temperatures and liquidus temperatures are consistent with those obtained by Savitskii et al. [11].

Based on the literature data and experimental data in this work, the Ge–V system was optimized with the PARROT module of the Thermo-Calc software [21]. During the first stage of the optimization, only the thermodynamic data, including ΔH_{mix}, ΔH_{f} for the four compounds and H_{T}–H_{298K} of V_3Ge and V_5Ge_3, were considered. ΔH_{mix} is related to the coefficients a_0, a_1 and a_2 in Eq. (2), while ΔH_{f} and H_{T}–$H_{\text{298\,K}}$ are related to the coefficients A and C in Eq. (3), respectively. Consequently, these coefficients (a_0, a_1, a_2, A and C) can be adjusted using these thermodynamic data. Secondly parameters b_0, b_1 and b_2 in Eq. (2) and B in Eq. (3) were assessed using all the invariant reaction data to describe the general features of the phase diagram. Next, the experimental data on solubility of (V) and liquidus were utilized to refine the preliminary optimization. Finally, all of the selected experimental data were used in order to get a self-consistent set of thermodynamic parameters. The finally obtained parameters are listed in Table 5.

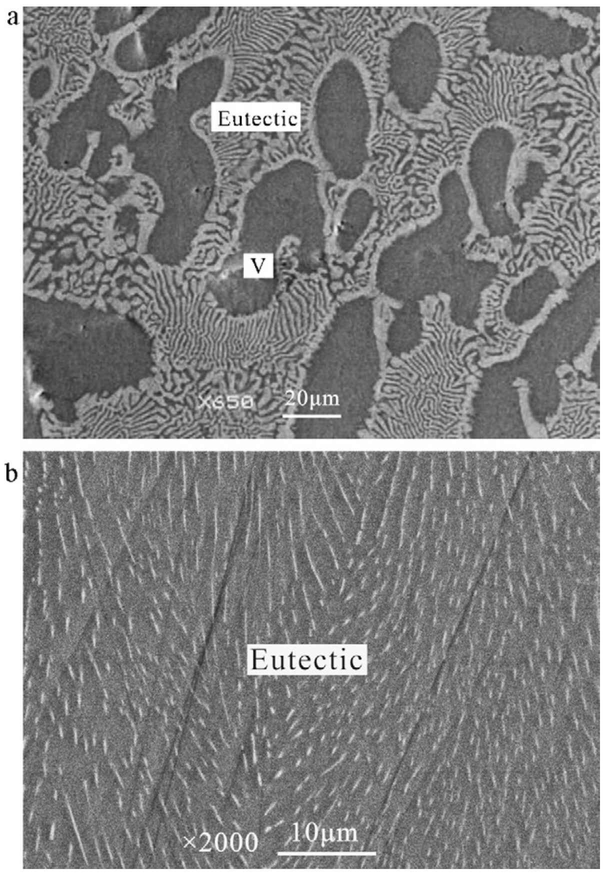

Fig. 3. Back scattering image of the as-cast alloy. (a) Alloy 1 ($V_{87.1}Ge_{12.9}$), (b) Alloy 12 ($V_{2.9}Ge_{97.1}$).

According to present modeling, the fictitious miscibility gap, which existed in the work of Wang et al. [2], is removed. The optimized Ge–V phase diagram along with the reliable experimental data from the present work and literature [11,12] is presented in Fig. 4. A good agreement between the calculation and experiment is obtained. The comparisons between the measured and calculated invariant equilibria are listed in Table 6. The calculated maximum

Table 5
Summary of the thermodynamic parameters in the Ge–V system.[a]

Phase	Model	Parameters
Liquid	$(Ge,V)_1$	${}^{0}L^{\text{liquid}}_{\text{Ge,V}} = -56,039 - 31.15T$ ${}^{1}L^{\text{liquid}}_{\text{Ge,V}} = 21,783$ ${}^{2}L^{\text{liquid}}_{\text{Ge,V}} = -18,941 + 27.412T$
(V)	$(Ge,V)_1$	${}^{0}L^{(\text{V})}_{\text{Ge,V}} = -102,964$
V_3Ge	$V_{0.75}Ge_{0.25}$	${}^{0}G^{V_3Ge}_{V:Ge} - 0.25 \cdot {}^{0}G^{\text{diamond}}_{\text{Ge}} - 0.75 \cdot {}^{0}G^{\text{bcc}}_{\text{V}}$ $= -35,430 - 17.772T + 1.9674T \cdot \ln(T)$
V_5Ge_3	$V_{0.625}Ge_{0.375}$	${}^{0}G^{V_5Ge_3}_{V:Ge} - 0.375 \cdot {}^{0}G^{\text{diamond}}_{\text{Ge}} - 0.625 \cdot {}^{0}G^{\text{bcc}}_{\text{V}}$ $= -43,584 - 9.763T + 0.6861T \cdot \ln(T)$
$V_{11}Ge_8$	$V_{0.579}Ge_{0.421}$	${}^{0}G^{V_{11}Ge_8}_{V:Ge} - 0.421 \cdot {}^{0}G^{\text{diamond}}_{\text{Ge}} - 0.579 \cdot {}^{0}G^{\text{bcc}}_{\text{V}}$ $= -46,141 - 2.798T$
$V_{17}Ge_{31}$	$V_{0.354}Ge_{0.646}$	${}^{0}G^{V_{17}Ge_{31}}_{V:Ge} - 0.646 \cdot {}^{0}G^{\text{diamond}}_{\text{Ge}} - 0.354 \cdot {}^{0}G^{\text{bcc}}_{\text{V}}$ $= -35,009 + 3.467 \cdot T$

[a] In J/(mol atoms) and temperature (T) in Kelvin.

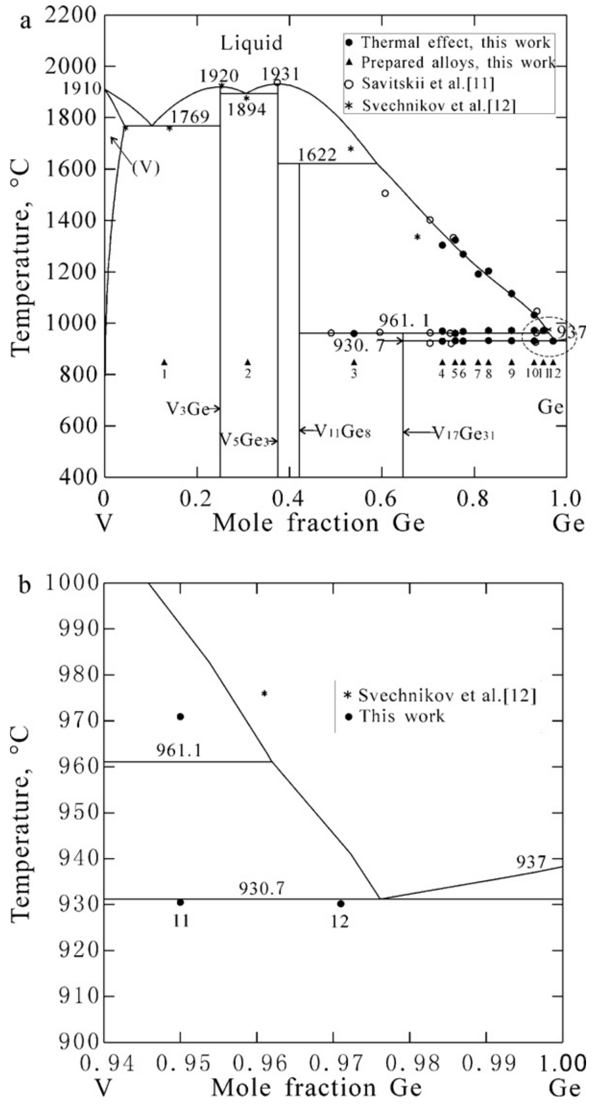

Fig. 4. Calculated Ge–V phase diagram along with the reliable experimental data from present work and the literature [11,12]. (a) from V to Ge, (b) magnified region in (a).

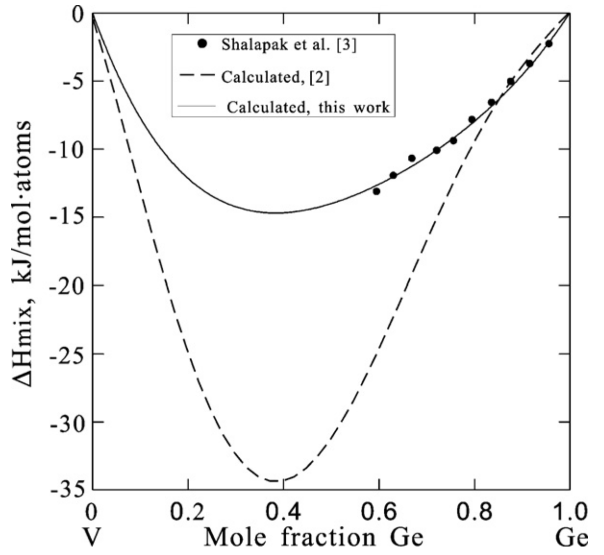

Fig. 5. Calculated enthalpy of mixing in liquid at 1500 °C along with the experimental data [3]. The references are liquid for both V and Ge.

solubility of Ge in (V) is 4.3 at.%, which is in agreement with the experimental value of 4.5 at.% [12]. The calculated peritectic temperature of liquid + $V_5Ge_3 \leftrightarrow V_{11}Ge_8$ is at 1622 °C, which is higher than 1575 °C [11] but lower than 1679 °C [12]. Due to the limited experimental data at high temperatures and relatively large error associated with high temperature measurements, the calculated results are considered to be acceptable.

The calculated enthalpy of mixing at 1500 °C in liquid, in comparison with the experimental data from Shalapak et al. [3], is shown in Fig. 5. The fit to the experimental data is fairly good. Fig. 6 compares the calculated partial enthalpy of V in liquid with the experimental data [4–6]. The presently computed partial enthalpy of V shows a reasonable agreement with the experiment [4,5]. The calculated partial enthalpy of V in infinitely dilute liquid is −53.0 kJ/mol, which is consistent with the value of Castanet [4] and Esin et al. [5]. As shown in Figs. 5 and 6, the previous calculation of thermodynamic properties for liquid [2] disagrees with the experiments [3–6]. In addition, the previously calculated partial enthalpy of V in liquid [2] decreases with increasing V content, which contradicts to the experiments [4,5]. In the present modeling, only 5 parameters were used to describe the liquid phase, compared to the 8 parameters in the previous calculation [2]. Nevertheless, the fit to the thermodynamic data (ΔH_{mix} and $\Delta\overline{H}_V$) is noticeably improved using fewer parameters.

The calculated standard enthalpies of formation for the compounds together with the experimental data are listed in Table 3. The calculated and experimental data show good agreement within estimated experimental errors. The calculated heat contents for V_3Ge and V_5Ge_3 using the present parameters are presented in Fig. 2. The comparison shows an excellent agreement between the calculation and experiment.

Table 6
Calculated invariant reactions compared with experimental results.

Reaction	Composition (at.% Ge)			Temperature (°C)	Reference
$L \leftrightarrow (V) + V_3Ge$	10.2	4.3	25	1769	Calculated, this work
	~14	~4.5	25	1759	Measured, [12]
$L \leftrightarrow V_3Ge$	25	25		1920	Calculated, this work
	25	25		1920	Measured, [13]
$L \leftrightarrow V_3Ge + V_5Ge_3$	30.6	25	37.5	1894	Calculated, this work
	30.7	25	37.5	~1876	Measured, [12]
$L \leftrightarrow V_5Ge_3$	37.5	37.5		1931	Calculated, this work
	37.5	37.5		~1930	Measured, [11]
$L + V_5Ge_3 \leftrightarrow V_{11}Ge_8$	58.9	37.5	42.1	1622	Calculated, this work
	~54	37.5	42.1	~1575	Measured, [11]
$L + V_{11}Ge_8 \leftrightarrow V_{17}Ge_{31}$	96.2	42.1	64.6	961.1	Calculated, this work
	~95.8	42.1	64.6	960.0	Measured, this work
$L \leftrightarrow V_{17}Ge_{31} + Ge$	97.5	64.6	100	930.7	Calculated, this work
	~97.1	64.6	100	930.7	Measured, this work

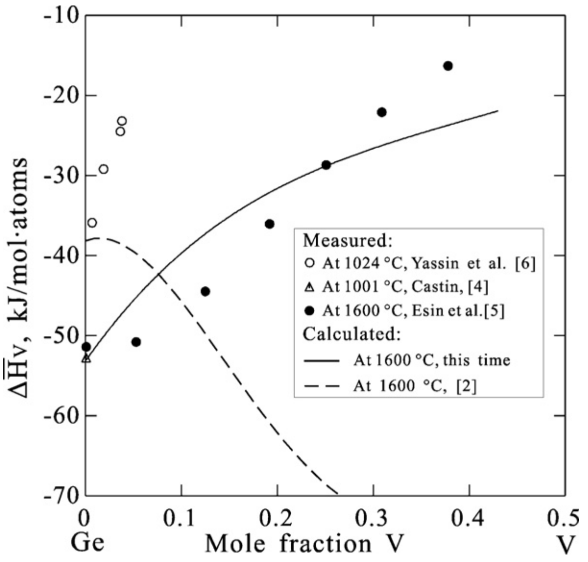

Fig. 6. Calculated partial enthalpy of V in liquid at 1600 °C along with experimental data [4–6]. The reference of V is liquid.

6. Conclusions

The Ge–V system has been investigated by experiments. Fourteen alloys were prepared and examined by XRD, SEM/EDS, DSC and drop calorimeter. These experimental results provide new phase diagram data and thermodynamic data for V_3Ge and V_5Ge_3, which make a thorough thermodynamic modeling possible.

A set of self-consistent thermodynamic parameters for the Ge–V system was obtained by optimizing the present experimental results and critically assessed literature data. The calculated results show good agreement with the experimental data. Noticeable improvements have been made, in comparison with the previous modeling.

Acknowledgments

The financial support from the Creative Research Group of the National Natural Science Foundation of China (Grant No. 50721003), key project of the National Science Foundation of China (Grant No. 50831007) and the National Science Foundation, USA under grant No. 0600690 are gratefully acknowledged. The Thermo-Calc Software AB in Sweden is gratefully acknowledged for the provision of the Thermo-Calc software. Thanks are also due to Alexander von Humboldt Foundation of Germany for the donation of Leica DMLP.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.11.018.

References

[1] J.F. Smith, The Ge–V (germanium–vanadium) system, Bull. Alloy Phase Diagrams 2 (1981) 205–209.
[2] C.P. Wang, A.Q. Zheng, X.J. Liu, Thermodynamic assessments of the V–Ge and V–Pt systems, Intermetallics 16 (2008) 544–549.
[3] A.N. Shlapak, E.A. Beloborodova, G.I. Batalin, Enthalpies of mixing of binary molten alloys of germanium with vanadium and titanium, Zh. Fiz. Khim. 52 (1978) 2097–2099.
[4] R. Castanet, Limiting partial enthalpies of solution of 3d transition metals in liquid germanium, J. Less-Common Met. 103 (1984) L1–L3.
[5] R.O. Esin, S.E. Demin, V.V. Litovskii, Heats of formation of molten alloys of vanadium and chromium with germanium, Zh. Fiz. Khim. 58 (1984) 2363–2364.
[6] A. Yassin, M. Gilbert, R. Castanet, Enthalpies of formation of binary systems of Ti, V, Mo and Hf with Ge, J. Alloys Compd. 322 (1–2) (2001) L9–L22.
[7] H. Holleck, H. Nowotny, F. Benesovsky, The system vanadium–germanium, Monatsh. Chem. 94 (1963) 497–501.
[8] V.L. Zagryazhskii, N.V. Kuzmenko, Magnetic susceptibility of vanadium germanides, Tr. Ural. Politekh. Inst. 167 (1968) 155.
[9] H. Voellenkle, A. Wittmann, H. Nowotny, Germanides of the transition metals V, Cr, Mo, and Mn, Monatsh. Chem. 95 (1964) 1544–1549.
[10] M.E. Straumanis, E.Z. Aka, Lattice parameters, coefficients of thermal expansion, and atomic weights of purest Silicon and Germanium, J. Appl. Phys. 23 (1952) 330–334.
[11] E.M. Savitskii, Y.V. Efimov, K. Eichler, O.I. Zvolinskii, Structure and properties of vanadium–germanium alloys, Izv. Akad. Nauk SSSR Metal. (1974) 214–220.
[12] V.N. Svechnikov, Y.A. Kocherzhinskii, G.F. Kobzenko, V.M. Pan, A.K. Shrin, Phase equilibriums in alloys of high-melting metals, Metallofizika 52 (1974) 3–22.
[13] R.M. Waterstrat, American Dental Association Health Foundation at the National Bureau of Standards, unpublished results, 1980.
[14] M.K. Borzhitskaya, V.L. Zagryazhskii, V.I. Surikov, A.K. Shtolts, Stoichiometry of lower ganadium germanide, Tr. Ural. Politekh. Inst. 186 (1970) 207–209.
[15] V.N. Eremenko, G.M. Lukashenko, V.R. Sidorko, Thermodynamic properties of vanadium germanides, Dokl. Akad. Nauk SSSR 230 (1976) 1133–1134.
[16] V.N. Eremenko, L.V. Goncharuk, G.M. Lukashenko, R.I. Polotskaya, V.R. Sidorko, Thermodynamic properties of manganese, chromium, and vanadium germanides at elevated temperatures, High Temp-High Pressures 11 (1979) 477–483.
[17] O.J. Kleppa, W.G. Jung, Standard enthalpies of formation of metal germanides (M_5Ge_3; M = titanium, vanadium, manganese, iron, cobalt, nickel) by high-temperature calorimetry, High Temp. Sci. 29 (1990) 109–123.
[18] S. Zarembo, R.J. Kematick, C.E. Myers, Thermodynamics of phase formation in the V–Ge system, J. Alloys Compd. 299 (1–2) (2000) 126–136.
[19] R.X. Hu, P. Nash, Q. Cheng, L.J. Zhang, Y. Du, Heat capacities of several Al–Ni–Ti compounds, Thermochim. Acta 486 (1–2) (2009) 57–65.
[20] A.T. Dinsdale, SGTE data for pure elements, CALPHAD 15 (1991) 317–425.
[21] B. Sundman, B. Jansson, J.O. Andersson, The thermo-calc databank system, CALPHAD 9 (1985) 153–190.