Calorimetric Study Coupled With A Numerical Optimization Technique For The Ca-Sb System

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ABSTRACT

The enthalpies of formation of liquid alloys and intermetallic compounds of the (Ca-Sb) system have been measured by direct reaction calorimetry (drop method). The phase relations are discussed from the results of differential thermal analysis (DTA) coupled with a numerical optimisation technique.

1. INTRODUCTION

The Ca-Sb system presents several compounds without solubility domains. Only primary solution shows the extended composition. Intermediate compounds are formed by very exothermic reactions. Fundamental information of phases detected in the Ca-Sb system are summarised in Table 1.

- The primary β -calcium phase contains up to 3.8 % Sb at eutectic temperature (650°C) following Niyazova, Vakhobov and Dzhuraev /1/.
- The calcium-rich phase is probably Ca_2Sb , following Eisenmann and Schäfer /2/.
- The Ca_5Sb_3 phase was characterised by Martinez-Rippoll and Brauer /3/ and seems to be the compound identified as Ca_7Sb_4 by Brauer and Muller /4/ or as Ca_3Sb_2 by Niyazova *et al.* /1/.
- The median compound is $\text{Ca}_{11}\text{Sb}_{10}$; its structure and the formula were established by Deller and Eisenmann /5/. This corresponds to a compound presented by Niyazova *et al.* /1/ as CaSb .
- The antimony-rich compound is CaSb_2 as proposed by Deller *et al.* /5/, instead of CaSb_3 as suggested by Niyazova *et al.* /1/.
- The primary antimony solution reaches a maximum of 5.8 at % Ca at 585 °C.

Table 1:
(Ca-Sb) Crystal Structure Data

Phase	Space Group	Pearson Symbol	Parameters/nm			Reference
			a	b	c	
βCa	$\text{Im } \bar{3} \text{ m}$	cI2	0.4480			7
Ca_2Sb	I4mmm	tI12	0.467	0.467	1.628	2
Ca_5Sb_3	Pnma	oP32	1.2505	0.9512	0.8287	3
$\text{Ca}_{11}\text{Sb}_{10}$	I4/mmm	tI84	1.194	1.194	1.740	5
CaSb_2	P21/m	mP6	0.4676	0.4177	0.9084	5
Sb	R3m	hR2	0.37598		1.05475	7

Fig 1: The Ca-Sb phase diagram according to Massalski *et al.* [6].

As shown in Figure 1, the diagram compiled by Massalski *et al.* [6] gives the same melting temperatures as given in the literature.

The present work reports the results of the Ca-Sb system using differential thermal analysis (DTA) in the antimony rich part and calorimetric determinations of enthalpies of formation of liquid and of two phase alloys. A numerical optimisation technique is also presented.

2. EXPERIMENTAL AND RESULTS

Antimony and calcium were prepared from Ventron-Alfa products and their purities were 99.99 and 99.95 % respectively. For (DTA) experiments, samples were prepared by two methods:

- For ($X_{Ca} \leq 0.33$) alloys, pure metals were put into a silica tube under vacuum and heated at

860 °C during two days, then kept at 620 °C during another two days and slowly cooled.

- For ($0.33 < X_{Ca} \leq 0.67$) alloys, pure metals were layed on an alumina crucible before they were put into the silica tube. The heating temperature was successively 1050 °C and 800 °C during two days. DTA used a SETARAM furnace with tungsten resistor; the sample and the alumina reference were set in an alumina crucible inside a pyrex tube under argon flow (Argon U; liquid air). The differential signal and temperature signal were obtained by means of Pt-(PtRh 10%) thermocouples.

The calorimetric measurements were made using a Calvet calorimeter under argon flow near 800°C. The calibration was carried out by dropping antimony shots, taken at room temperature, in the calorimeter; the calorimetric signal was tied with the melting and heating enthalpy. Calcium samples were prepared and weighed in a glove box; they were added to the

antimony bath; the mean calcium partial enthalpy of mixing was obtained as well as the enthalpy of formation.

The results obtained in this work are summarised in Table 2 and the peak temperatures are given in Figure 2. For the equimolecular composition, the Ca-Sb system appears to be often in a metastable state which may be attributed to local segregation. The $\text{Ca}_{11}\text{Sb}_{10}$ compound shows a high melting temperature (1120 °C) which contrasts with the corresponding value of 985°C indicated by Niyazova *et al.* [1].

The X-ray analysis was carried out in a Lindemann tube. However, it was difficult to obtain good spectra, so that the results were missing for several samples. On the other hand microprobe analysis has been performed on Sb rich samples. The samples ($X_{\text{Sb}} = 0.90; 0.85;$

0.82; 0.78) were prepared under vacuum in silica tube at 800°C for 2 hours, then maintained at 585°C for 5 hours and air-quenched. They were polished without any liquid. The (Sb) phase was found not to contain any Ca component, so that we could not detect the CaSb_2 phase reported by Niyazova *et al.* [1]. The present results only suggest the existence of a Sb primary solid solution.

With respect to the eutectic composition of liquid, the Sb primary precipitate area and the eutectic precipitate area were tested by measuring the microphotograph of an alloy with $X_{\text{Ca}} = 0.85$. It is quite likely that these areas are proportional to the volume of the precipitates. As the specific gravity of Sb and CaSb_2 are 7.8 and 5.45 g cm⁻³ respectively, the eutectic composition is estimated to be $X_{\text{Ca}} = 0.78$.

Fig 2: Experimental points of the Ca-Sb diagram.

— Solidus points (DTA).

== Liquidus points (DTA).

* Liquidus points (Calorimetry).

Table 2

A: silica sealed ampoule (under vacuum) 2 days at 860°C, 2 days at 620°C

B: alumina crucible in silica sealed ampoule (under vacuum) 2 days at 1050°C, 2 days at 800°C

L: Liquid. ↑: increasing temperature; ↓: decreasing temperature.

X _{Sb} , %	RX Analysis		DTA Peak		Interpretation	Preparation
	Before DTA	After DTA	Out set	Maximum		
33 ↑	Ca + Ca ₂ Sb		309°C 660°C 840°C	420°C 1004°	?α and β Ca transformation Light peak β Ca+Ca ₂ Sb ⇌ L Ca ₂ Sb ₃ ⇌ Ca ₂ Sb+L Liquidus line	B
38 ↑			877°C		Ca ₂ Sb ₃ ⇌ Ca ₁₁ Sb ₁₀ +L Liquidus line	B
38 ↓		Ca ₂ Sb ₃ +Ca ₁₁ Sb ₁₀	825°C 606°C 554°C	1059°C		
50 ↑			555°C 618°C		metastable evolution CaSb ₂ + Ca ₁₁ Sb ₁₀ eutectic?	B
50 ↓			830°C 932°C		metastable evolution	
50 ↓		CaSb ₂ +Ca ₁₁ Sb ₁₀	610°C 560°C			B
50 ↑			567°C 606°C		metastable evolution	B
50 ↑			597°C		CaSb ₂ ⇌ Ca ₁₁ Sb ₁₀ + L	B
				1120°C	Liquidus line	
60 ↑			585°C		CaSb ₂ ⇌ Ca ₁₁ Sb ₁₀ +L	B
				1034°C	Liquidus line	
60 ↓				595°C 560°C		B
67 ↑	CaSb ₂		597°C		CaSb ₂ ⇌ Ca ₁₁ Sb ₁₀ + L	A
67 ↓		CaSb ₂	599°C	923°C	Liquidus line CaSb ₂ ⇌ Ca ₁₁ Sb ₁₀ +L	
70 ↑	(Sb) + CaSb ₂		440°C 585°C 613°C		(Sb) + CaSb ₂ ⇌ L CaSb ₂ ⇌ L? (metatable)	A
75 ↑	(Sb)+CaSb ₂		445°C 585°C 598°C		(Sb) + CaSb ₂ ⇌ L CaSb ₂ ⇌ Ca ₁₁ Sb ₁₀ + L Liquidus line	A
75 ↓		(Sb)+CaSb ₂	626°C 598°C	760°C	CaSb ₂ ⇌ Ca ₁₁ Sb ₁₀ + L	
80 ↑	(Sb)+CaSb ₂		587°C 597°C		(Sb) + CaSb ₂ ⇌ L CaSb ₂ ⇌ Ca ₁₁ Sb ₁₀ + L	A
		(Sb)+CaSb ₂		611°C	liquidus line	
90 ↑	(Sb)+CaSb ₂		587°C	628°C	(Sb) + CaSb ₂ ⇌ L	A
90 ↓		(Sb)+CaSb ₂		628°C	liquidus line	

3. ENTHALPY DETERMINATIONS

The Ca shots in the Sb-liquid bath reacted vigorously for forming of liquid alloy. When X_{Ca} increased, the reaction became slower. The calorimetric measurements were possible until $X_{Ca} = 0.60$. Three determinations were made at two temperatures (704°C and 750°C). For alloy with the composition $X_{Ca} = 0.39$, the X-ray analysis indicated both $CaSb_2$ and $Ca_{11}Sb_{10}$. For $X_{Ca} = 0.60$, phases of Ca_5Sb_3 and $Ca_{11}Sb_{10}$ were suggested. On the other hand, for $X_{Ca} = 0.64$, the results showed the Ca_5Sb_3 and Ca_2Sb structures. The results are summarised in Figure 3 and Table 3, providing information about the formation of liquid phase. These results suggest the linear domain of $Ca_{11}Sb_{10}$ inside the liquid phase and the linear domain of Ca_5Sb_3 arising from a reaction of Ca on $Ca_{11}Sb_{10}$. The present work also provides information about a point of liquidus line

($T = 805^\circ\text{C}$, $X_{Sb} = 0.725$). This result was confirmed by DTA.

In the liquid phase, the integral enthalpies of formation are given as follows:

$$\begin{aligned} T = 704^\circ\text{C} \quad \Delta H_f(X_{Ca} = 0.10) &= -17 \text{ kJ/mol of atoms.} \\ \Delta H_f(X_{Ca} = 0.20) &= -33.6 \text{ kJ/mol of atoms.} \end{aligned}$$

$$\begin{aligned} T = 750^\circ\text{C} \quad \Delta H_f(X_{Ca} = 0.10) &= -19 \text{ kJ/mol of atoms.} \\ \Delta H_f(X_{Ca} = 0.20) &= -36.5 \text{ kJ/mol of atoms.} \end{aligned}$$

$$\begin{aligned} T = 805^\circ\text{C} \quad \Delta H_f(X_{Ca} = 0.10) &= -20 \text{ kJ/mol of atoms.} \\ \Delta H_f(X_{Ca} = 0.20) &= -39 \text{ kJ/mol of atoms.} \end{aligned}$$

The minimum in the enthalpy curve, -107 kJ/mol of atoms, corresponds to the $Ca_{11}Sb_{10}$ ($X_{Sb} = 0.476$) composition and we obtain the following result.

Table 3
Enthalpy of formation of (Ca-Sb) alloys at 805°C

Calorimeter calibration:

Enthalpy changes during transformations:

$Sb(S, 32^\circ\text{C}) \rightarrow Sb(Liq, 805^\circ\text{C})$ and $Ca(S, 32^\circ\text{C}) \rightarrow Ca(S, 805^\circ\text{C})$

$H(Sb, Liq, 805^\circ\text{C}) - H(Sb, S, 32^\circ\text{C}) = 3427 \text{ J/mol of atoms.}$

$H(Ca, S, 805^\circ\text{C}) - H(Ca, S, 32^\circ\text{C}) = 6163 \text{ J/mol of atoms.}$

$100X_{Ca}$	ΔH_f (kJ/mol atom)	$100X_{Ca}$	ΔH_f (kJ/mol atom)
04.26	08.18	42.86	84.88
06.31	12.68	45.52	92.30
10.71	20.41	46.20	95.00
13.95	23.62	47.34	97.50
16.04	27.50	49.90	102.50
20.34	32.21	53.25	106.29
23.22	37.54	54.52	105.94
26.19	43.25	55.97	103.37
28.78	48.32	57.31	101.08
31.70	55.30	58.30	99.30
34.94	63.68	59.23	97.28
37.19	71.40	60.07	95.44
40.63	78.76		

$\Delta H_f (1/21 \text{ Ca}_{11}\text{Sb}_{10}; 805^\circ\text{C}) = -(107 \pm 3) \text{ kJ/mol of atoms}$
(referred to solid Ca and liquid Sb).

The enthalpy of formation of Ca_5Sb_3 was also obtained by extrapolation of the enthalpy curve for $X_{\text{Ca}} > 0.528$ until $X_{\text{Ca}} = 0.625$.

$\Delta H_f (1/8 \text{ Ca}_5\text{Sb}_3; 805^\circ\text{C}) = - (86 \pm 6) \text{ kJ/mol of atoms}$
(referred to solid Ca and liquid Sb).

Fig 3: Enthalpy of formation of the (Ca-Sb) alloys at 805°C.

4. REFINEMENT OF THE Ca-Sb SYSTEM USING LUCKAS PROGRAM

This program consisting of three principal subroutines has been written by Luckas and his group /7/; it allows to compute and to plot the phase diagram and the thermodynamic functions of binary systems.

This technique supplements the experimental data. The BINGSS program /7/ is a least square fitting program for binary system, using simultaneously phase diagram and thermodynamic data.

The program of BINFKAT /7/ uses polynomial descriptions for the excess terms of the Gibbs energy and it is used to calculate the phase diagram and draw thermodynamic functions for testing the results of BINGSS /7/. Finally with a plot program /7/, the experimental data which are inputs to BINGSS /7/ can be plotted together with the calculated curves.

4. 1. Input Of Experimental Values

Invariant: Sb-Sb ₂	Temperature: 587°C	X _{Sb} (liquid) = 0.82
Invariant: CaSb ₂ -Ca ₁₁ Sb ₁₀	Temperature: 597°C	X _{Sb} (liquid) = 0.79
Invariant: Ca-Ca ₂ Sb	Temperature: 620°C	X _{Sb} (liquid) = 0.125
Invariant: Ca ₂ Sb-Ca ₅ Sb ₃	Temperature: 840°C	X _{Sb} (liquid) = 0.22
Equilibrium: Liquid-Sb	Temperature: 628°C	X _{Sb} (liquid) = 0.90
Equilibrium: Liquid-Ca ₁₁ Sb ₁₀	Temperature (°C)	X _{Sb} (liquid)
	805	0.73
	923	0.67
	1034	0.50
	1050	0.38
	1004	0.325

Enthalpies of formation (J/mol of atoms) at temperature: 805°C

Ca ₁₁ Sb ₁₀	-107000	
Ca ₅ Sb ₃	-86000	
Liquid	-8200	X _{Sb} = 0.958
	-20400	X _{Sb} = 0.893
	-27500	X _{Sb} = 0.840
	-37500	X _{Sb} = 0.768
	-43200	X _{Sb} = 0.738

(referred to solid Ca and liquid Sb)

4. 2. Output Values From Computation

Invariant: Sb-CaSb ₂	Temperature: 587°C	X _{Sb} (liquid) = 0.82
Invariant: CaSb ₂ -Ca ₁₁ Sb ₁₀	Temperature: 597°C	X _{Sb} (liquid) = 0.79
Invariant: Ca-Ca ₂ Sb	Temperature: 619°C	X _{Sb} (liquid) = 0.182
Invariant: Ca ₂ Sb-Ca ₅ Sb ₃	Temperature: 840°C	X _{Sb} (liquid) = 0.22
Invariant: Ca ₁₁ Sb ₁₀ -Ca ₅ Sb ₃	Temperature: 1010°C	X _{Sb} (liquid) = 0.34
Equilibrium: Liquid-Sb	Temperature: 625°C	
X _{Sb} (liquid) = 0.90		
Equilibrium: Liquid-Ca ₁₁ Sb ₁₀ :	Temperature (°C)	X _{Sb} (liquid)
	805	0.71
	923	0.66
	800	0.60
	1120	0.51
	1050	0.36
	1004	0.335

Enthalpies of formation (J/mol of atoms) at 805°C referred to solid Ca and liquid Sb.

Ca₁₁Sb₁₀: - 109000

Ca₅Sb₃: - 86000

Liquid: - 7880 X_{Sb} - 0.95

- 16000 X_{Sb} - 0.90

- 25120 X_{Sb} - 0.85

- 33600 X_{Sb} - 0.80

- 40500 X_{Sb} - 0.75

5. CONCLUSION

The tracing (Figure 2) of a binary (Ca-Sb) system obtained from the present DTA and calorimetric measurements, suggests four stoichiometric compounds Ca₂Sb, Ca₁₁Sb₁₀, Ca₅Sb₃ and CaSb₂. This is consistent with the results recently compiled by Massalski *et al.* /6/. The differential thermal analysis enables us to give some points of diagram lines with sufficient reliability. The peritectic melting of CaSb₂ has been obtained in this work at 597°C.

Fig 4: Ca-Sb revised phase diagram.

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