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HEATS OF FORMATION OF GADOLINIUM—BISMUTH ALLOYS

G. BORZONE, A. BORSESE and R. FERRO

Istituto di Chimica Generale dell 'Università di Genova, Genoa (Italy)

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ABSTRACT

The heats of formation of Gd—Bi alloys were measured using a direct isoperibol calorimeter. The composition and equilibrium state of the samples were checked by metallographic and X-ray analyses.

The following values were found for the different compounds [ΔH form, reaction in the solid state, 300 K, kcal (g-atom)$^{-1}$ ± 0.5]: $Gd_{5+x}Bi_3$, −20.0 ± 0.7; Gd_5Bi_3, −20.9; Gd_4Bi_3, −22.0; GdBi, −23.1.

The results obtained were compared with those already achieved for other rare earth bismuthides.

INTRODUCTION

In the course of our systematic measurement of the heats of formation of binary alloys of the rare earths, the examination of a number of rare earth bismuthides was recently performed. The following systems have already been studied by our group: Y—Bi [1], La—Bi [2], Ce—Bi [3], Pr—Bi [4], Nd—Bi [5] and Dy—Bi [6].

In this work, the results obtained in the study of the Gd—Bi system are reported.

The Gd—Bi system

The complete phase diagram has not yet been determined. The sketch shown in Fig. 1 is based on suggestions by Gambino [7] adjusted to take into account the crystallographic work by Yoshihara et al. [8]. Gambino suggested the existence of the congruently melting 1 : 1 compound (m.p. ≈ 2000°C) and of an incongruently melting 4 : 3 compound (m.p. ~1500°C). Moreover, a Gd-rich phase having hexagonal symmetry and an incongruent melting point of about 1275°C was proposed for a stoichiometry near to Gd_2Bi.

In a systematic investigation of the crystal structures of rare earth-bismuthides, Yoshihara et al. confirmed the structures of GdBi, Gd_4Bi_3 and of Gd_5Bi_3, which were already known, and determined the structure of a phase having the composition $Gd_{5+x}Bi_3$. The crystal structures of the various phases are listed in Table 1.

According to an abstract [9], the thermodynamic properties of molten

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TABLE 1

Crystal structure data of bismuth—gadolinium phases

Phase	Structural type	Unit cell dimensions (Å)	Remarks	Ref.
$Gd_{5+x}Bi_3$	Orthorhombic	$a = 8.2267$, $b = 9.5313$, $c = 12.0814$		8
	~oP32-Y_5Bi_3	$a = 8.215$—8.230, $b = 9.541$—9.550, $c = 12.06_8 - 12.08_2$	Annealed samples, slowly cooled.	This work
		$a = 8.237$, $b = 9.532$, $c = 12.08_3$	Heterogeneous sample, as cast, also containing the hP16-Mn_5Si_3 type phase	This work
Gd_5Bi_3	Hexagonal	$a = 9.1580$, $c = 6.4186$, $c/a = 0.701$		8
	hP16-Mn_5Si_3	$a = 9.182$, $c = 6.426$, $c/a = 0.700$		13
		$a = 9.169$, $c = 6.428$, $c/a = 0.701$	Heterogeneous sample, as cast, containing also the previous phase	This work
Gd_4Bi_3	Cubic	$a = 0.385$		14
	cI28 anti-Th_3P_4	$a = 9.3858$		8
		$a = 9.386$—9.389		This work
GdBi	Cubic	$a = 6.3108$	Gd-rich 700°C	8
	cF8-NaCl	$a = 6.3085$	Bi-rich 700°C	
		$a = 6.316$		15
		$a = 6.309$—6.315		This work

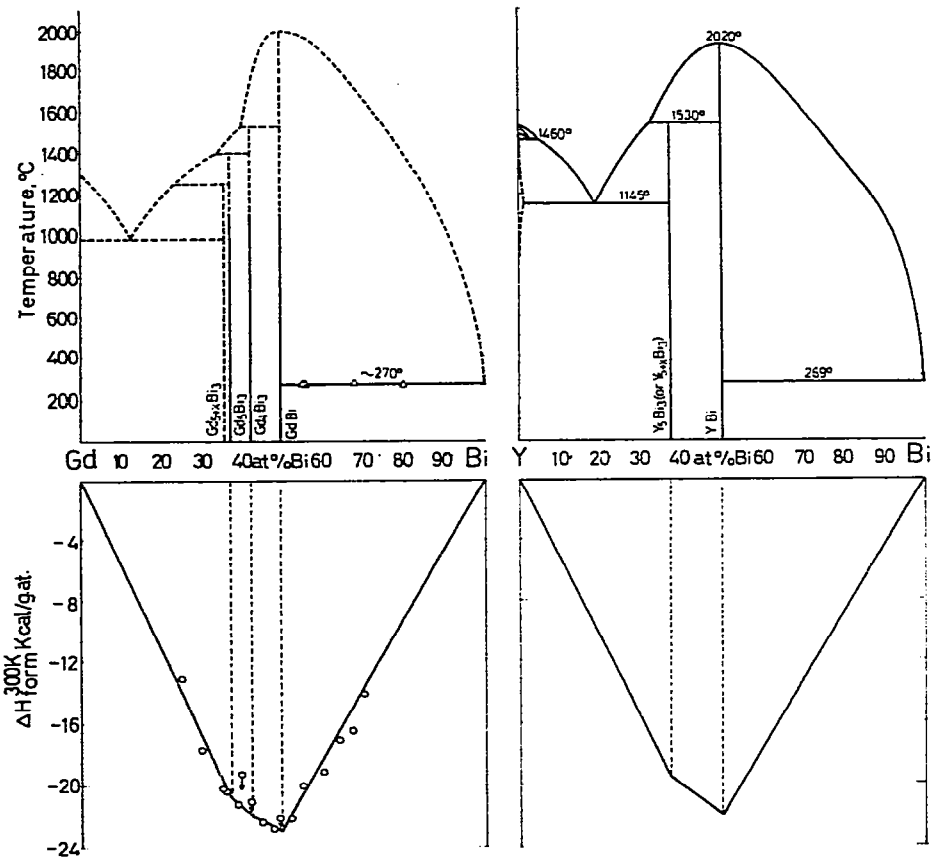

Fig. 1. Gd—Bi and Y—Bi alloys. On the left, are shown the heats of formation measured for the Gd—Bi alloys and a sketch of a possible shape of the phase diagram (a few data obtained by DTA have been inserted). These data are compared with those previously known for the Y—Bi system, reported on the right.

Gd—Bi alloys have been studied. It was observed that the system exhibits a large negative deviation from the ideal behaviour.

The energy band structures of Gd-pnictides have been studied by Hasegawa and Yanase [10], while a discussion of the chemical bonding in these compounds has been reported in an investigation of the superconductivity of La-pnictides [11].

EXPERIMENTAL

A number of Gd—Bi alloys were prepared directly into a calorimeter which was described in a previous paper [12]. The metals employed were Gd and Bi with nominal purities of 99.9% and 99.99%, respectively.

A number of alloys were also prepared as reference samples. These samples, after melting, were annealed on the basis of the indications given by the supposed phase diagram.

All the samples were subjected to metallographic and X-ray examinations.

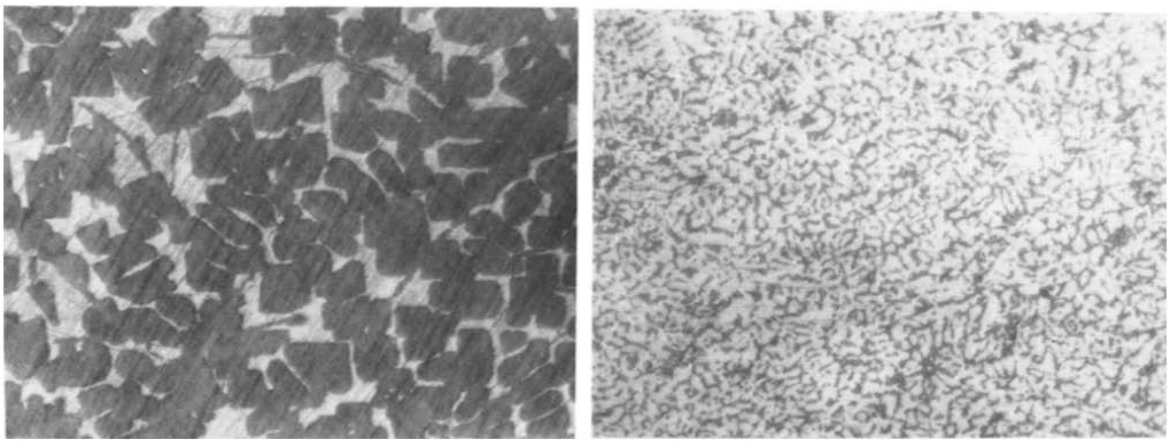

Fig. 2. Gd—Bi alloy 68.0 at. % Bi, annealed for 10 days at 950°C and etched in air. 200×. (GdBi, black + Bi.)

Fig. 3. Gd—Bi alloy 47.5 at. % Bi, prepared in the calorimeter (alloy 9 of Table 2). Etched in air. 200×. Nearly pure GdBi.

Metallographic examination

In the case of the calorimetric samples, this examination was performed on the largest section of the specimen by using known techniques, taking care that, especially for the gadolinium-rich alloys, the highly oxidisable samples were conveniently protected.

In order to evaluate the thermochemical data, samples which did not appear to be in the equilibrium state (altered samples, three-phase samples, partial peritectic transformations etc.) were rejected.

Figures 2 and 3 show the micrographic appearance of a reference sample and an alloy prepared in the calorimeter, respectively.

X-Ray examination

Powders of the various alloys were examined by the Debye method using CuK_α and FeK_α radiations.

Lattice parameters were obtained by a least-squares fit using the Nelson—Riley function.

The unit cell dimensions measured in this work are reported in Table 1 together with the data given in the literature. For each phase a certain range of parameter values was generally observed: this has been included in Table 1.

Both in the reference and in the calorimetric samples, only the intermediate phases already reported in the literature were observed.

DTA examination

For a few Bi-rich alloys, differential thermal analysis was also carried out. The invariant effects observed at low temperature were included in the phase

diagram sketched in Fig. 1. Their trend seems to be in agreement with the hypothesis that GdBi is the compound in the system richest in Bi (see also Fig. 2).

RESULTS

The data obtained in the thermochemical measurements are given in Table 2 and Fig. 1. In the figure, these data are compared with those relevant to the Y—Bi system. We note that the heats of formation have a similar trend.

The data concerning the different compounds are reported in Table 3 together with the data concerning the various rare earth bismuthides so far studied. We note that the data relevant to the Gd—Bi system are in good agreement with those of other rare earth bismuthides.

The high values of the heat of formation may also be related to the strong deviations from ideality observed for a number of R.E.—Bi molten alloys. These strong interactions are quite characteristic for the R.E.—pnictides, and the data concerning bismuth [typically —22 to—27 kcal (g-atom)$^{-1}$ for the 1 : 1 compound]seem to be in good agreement with those observed for Sb [—25 to —31 kcal (g-atom)$^{-1}$ for the same composition][16]and with a number of values reported for the monoarsenides [—35 to —38 kcal (g-atom)$^{-1}$] [17].

TABLE 2

Heats of formation of solid gadolinium—bismuth alloys at 300 K

$(1-x)Gd + x\ Bi = Gd_{1-x}Bi_x$

Alloy number	Nominal composition (x_{Bi})	$\Delta H_{form} \pm 0.5$ ** [kcal (g-atom)$^{-1}$]
1	0.250	—13.1
2	0.300	—17.7
3	0.350	—20.2
4	0.360	—20.4
5	0.385	-21.2_5
6 *	0.400	(-19.1_5)
7 *	0.420	(—21.1)
8	0.450	—22.4
9	0.475	—22.8
10 *	0.490	(—22.1)
11	0.520	-22.1_5
12	0.550	—20.0
13	0.600	-19.0_5
14	0.640	—17.0
15	0.670	—16.4
16	0.700	—14.0

* For these alloys the reaction in the calorimeter was not complete.

** Interpolated values of ΔH_{form} for the various intermediate compounds: Gd_5Bi_3: —20.9 ± 0.5; Gd_4Bi_3: —22.0 ± 0.5; GdBi: —23.1 ± 0.5. To the phase $Gd_{5+x}Bi_3$ (having a slightly uncertain composition) the value —20.0 ± 0.7 may be attributed.

TABLE 3

Heats of formation of selected R.E.—Bi compounds.

R.E.	$\Delta H_{form} \pm 0.5$ [kcal (g-atom)$^{-1}$]					
	$R.E._2Bi$	$R.E._{5+x}Bi_3$	$R.E._5Bi_3$	$R.E._4Bi_3$	R.E.Bi	$R.E.Bi_2$
La				−24.7	−26.5	
Ce	−19.5		−21.9	−24.2	−27.4	≤−18.5
Pr				−22.4	−23.9	
Nd			−22.2 *	−25.0	−26.6	−21.0
Gd		−20.0 *	−20.9	−22.0	−23.1	
Dy		−19.5			−23.0	
Y			−19.5		−22.0	

* For these compounds, the probable error is ±0.7.

As far as R.E.—Bi alloys are concerned, the data of the compounds of the Gd—Bi system seem to confirm a small decrease in the heat of formation on passing from the alloys of the light to those of the heavy rare earths. A similar trend was observed for the antimonides.

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