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HEAT OF FORMATION OF PRASEODYMIUM–BISMUTH ALLOYS

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ABSTRACT

In the Pr–Bi system the heats of formation were measured using a direct isoperibol calorimeter. The composition and equilibrium state of the samples have been checked by chemical, metallographic and X-ray analyses. The following values were found for the two known compounds (reaction in the solid state, 300 K):

PrBi, $\Delta H = -23.9 \pm 0.5$ kcal/g-at.

Pr_4Bi_3, $\Delta H = -22.4 \pm 0.5$ kcal/g-at.

The results obtained, compared with those already achieved in other RE–Bi systems, are briefly discussed.

INTRODUCTION

Further to the measurements already performed on the heats of formation of the rare earths bismuthides (Y–Bi[1], Nd–Bi[2], La–Bi[3]) we now refer to the results obtained for the Pr–Bi system.

For this system only the Pr-rich part of the phase diagram has been studied[4]. This part of the diagram is shown in Fig. 1. In the same figure is also represented (dotted lines) the central part of the system as it may be deduced according to Gambino[5]. The known phases existing in the system are Pr_4Bi_3 (cubic, anti Th_3P_4-type $a = 9.600$) and PrBi (cubic, NaCl type $a = 6.461$)[6].

In this work, no indication of the presumable existence of other phases was obtained, neither while preparing reference samples nor while performing calorimetric measurements. Particularly, for the $PrBi_2$ composition, both the micrographic appearance and the powder photographs exclude the existence of the compound 1:2, which is not the case for the La–Bi system.

EXPERIMENTAL

The measurement of the heats of formation was performed by the method of direct calorimetry as reported for the previously examined bismuthides. The pre-

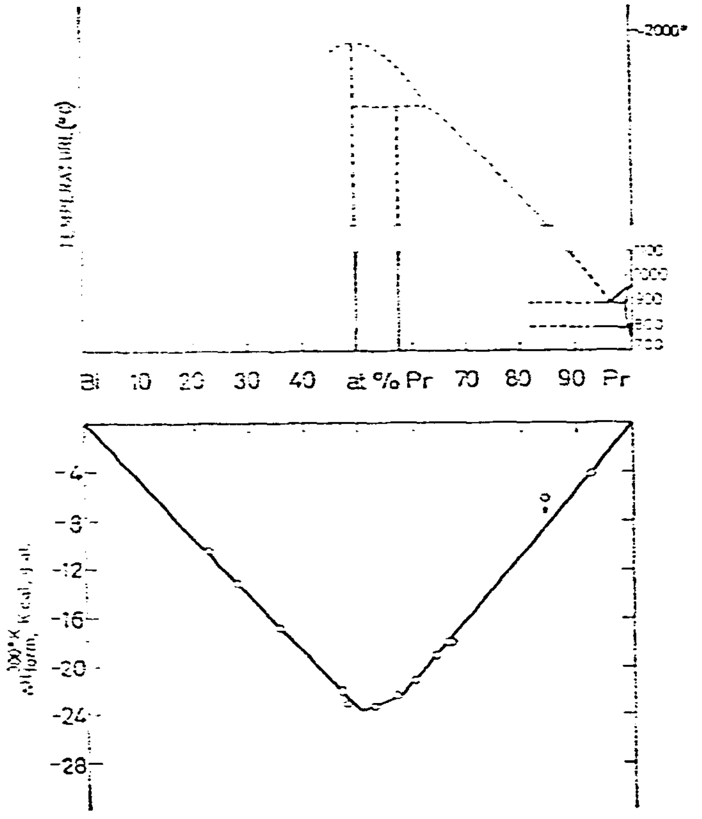

Fig. 1. Suggested form of the Bi–Pr phase diagram and ΔH of formation in the solid state.

paration techniques, chemical analysis, metallographic and X-ray examinations were the same as those previously described.

The samples were prepared using 99.9% Pr and 99.999% Bi obtained from Koch-Light Lab. Ltd. The reference samples were prepared, melted and annealed in order to be able to check the phases existing after a slow cooling.

For the compounds Pr_4Bi_3 and PrBi the unit cell edges $a = 9.61_0$ and $a = 6.46_0$, respectively, were observed to be in good agreement with the literature data previously reported.

Metallographic appearance typical for alloys prepared in the calorimeter are shown in Fig. 2.

RESULTS

The results obtained in the calorimetric measurements are reported in Table 1 and summarized in Fig. 1. Comparison with the presumed form of the equilibrium diagram, as a first approximation, seems to confirm the ΔH trend.

All the values given can be considered to be measured at 300 K, because the sample inside the calorimeter is surrounded by a thermostat at 27 ± 0.01 °C and, while

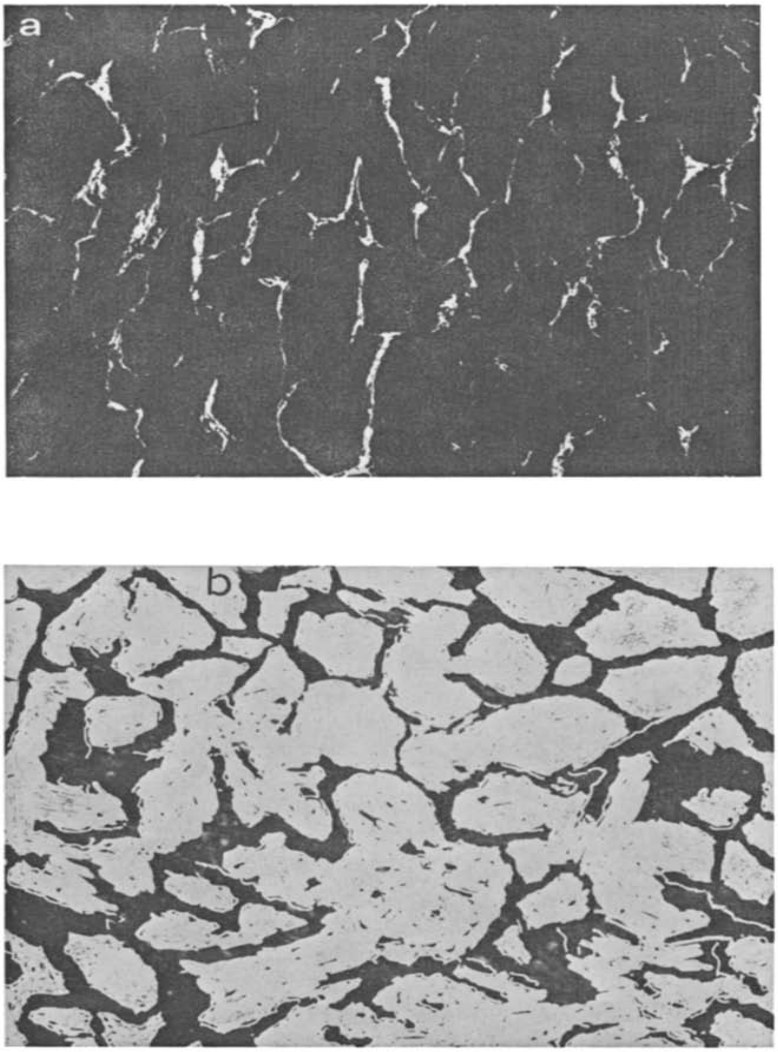

Fig. 2. Metallographic examination of Bi–Pr alloys etched in $HNO_3 + CH_3COOH$ diluted in glycerol. (a) Alloy number 5, 47.6 at. % Pr (×200). (b) Alloy number 8, 60.0 at. % Pr (×500).

measuring, it cools down to this temperature. The uncertainty of ±0.5 kcal/g-at. reported for all the data, is believed to include, apart from the measurement errors (composition variation, etc.), the effects of the eventual quenching to 300 K of some situation stable at a somewhat higher temperature.

From the data reported the following values of the ΔH of formation for the two compounds (solid state reaction, 300 K) can be extrapolated:

Pr_4Bi_3: -22.4 ± 0.5 kcal/g-at.

PrBi: -23.9 ± 0.5 kcal/g-at.

TABLE 1

ΔH OF FORMATION OF Pr–Bi ALLOYS

Alloy No.	*Analytical composition at. % Pr*	*ΔH_{Form} (300 K) (k cal/g-at. ±0.5)*
1	22.6 ± 0.3	-10.2_5
2	27.2 ± 0.1	-13.2
3	35.5 ± 0.1	-16.8
4	46.8 ± 0.2	-22.0_5
5	47.6 ± 0.1	-23.2
6	52.5 ± 0.2	-23.4
7	57.0 ± 0.2	-22.3_5
8	60.0 ± 0.1	-21.2
9	64.1 ± 0.3	-19.6
10	65.0 ± 0.1	-18.1
11	66.5 ± 0.2	-18.1
12[a]	84.2 ± 0.1	(-5.8)
13	91.2 ± 0.1	-4.1

[a] For this alloy the reaction was non-complete. The data reported, however, could have a certain interest as limit value.

CONCLUSIONS

In a recent work Miedema[7] described a simple model from which it is possible to evaluate the heats of formation of several binary alloys. When transition metals are involved the energy effects are described in two terms: the first one is tied to the electronegativity difference between the two metals; the second is connected with the discontinuity of electron density at the boundary of dissimilar Wigner-Seitz atomic cells.

For alloys of a transition element with a *p* metal a negative constant term is added. In this last case (corresponding to the alloys here considered) the heat of formation is obtained from the following relationship:

$$\Delta H = \mathrm{f}(c)[-Pe(\Delta\varphi^*)^2 + Q(\Delta n)^2 - R]\cdot 23$$

The values of the constants are:
$P = 0.85\ \mathrm{V}^{-1}$, $Q/P = 0.175\ \mathrm{eV}^2/(\mathrm{dens.\ units})^2$, $R/P = 1.36\ \mathrm{eV}^2$, (23, of course, is the conversion constant from eV/g-at. to kcal/g-at.); φ^* is a parameter, which is not too far from the work function of the element, and n is the electron density of the element at the boundary of the Wigner-Seitz cell; $\mathrm{f}(c)$ represents the trend of the heat of formation against the concentration, suggested for ordered alloys. The values of the $\mathrm{f}(c)$ function for system whose ΔH/concentration curves have a minimum at the equiatomic composition have been reported by Miedema himself.

It seemed useful to have a comparison between the data so far measured for the different rare earths bismuthides and those calculated with the relationship mentioned above. In Fig. 3 the experimental curves of the Y–Bi, La–Bi (≅ Nd–Bi) and Pr–Bi

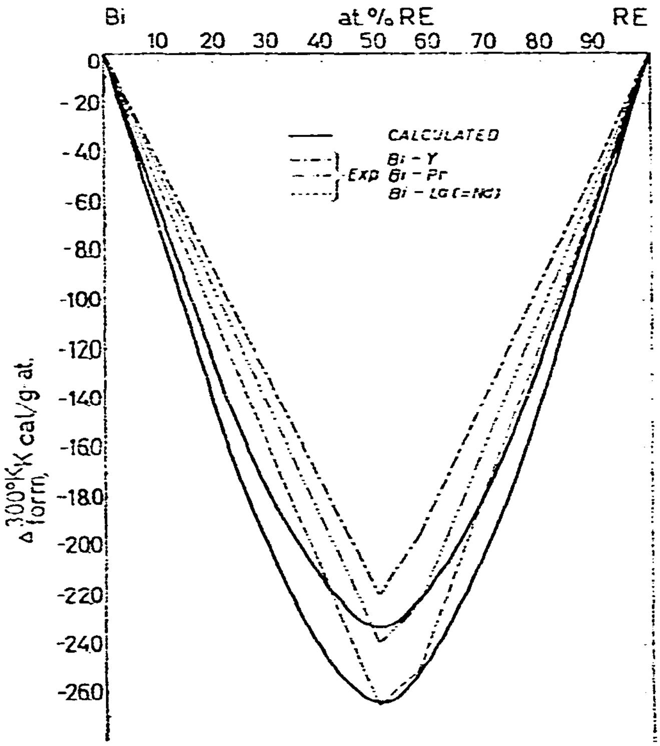

Fig. 3. Experimental and calculated values of the ΔH of formation of Bi–RE alloys. Of the two calculated curves, the upper one refers to Bi–Y system, the other to the Bi–RE alloys.

alloys have been reported. In the same figure are reported the curves obtained from the Miedema equation. Two curves only have been calculated: one is for yttrium ($\varphi_Y^* = 2.95$, $n_Y = 1.4$) and one for a generic rare earth ($\varphi_{RE}^* = 2.8$, $n_{RE} = 1.0$) as it was not possible to give significantly different values to the specific parameters of the several rare earths. For bismuth $n_{Bi} = 1.2$ (as reported by Miedema) has been used, while it was necessary to use $\varphi_{Bi}^* = 4.3$ (accepted value of the work function) instead of $\varphi^* = 3.9$ (as suggested by Miedema). Even within the uncertainties mentioned above a fairly good agreement is noted between measured and calculated values (as already observed in the La–Pb system[8]). This shows further the utility of Miedema's model and, considering the magnitude of the term $-Pe[\Delta\varphi^*]^2$, shows that a partial ionic contribution can be considered typical of these compounds.

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