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HEAT OF FORMATION OF La_4Bi_3 AND LaBi COMPOUNDS

A. BORSESE, R. CAPELLI, S. DELFINO AND R. FERRO
Università di Genova, Istituto di Chimica Generale, Viale Benedetto XV, 3-C.A.P. 16132, Genova (Italy)

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ABSTRACT

In the La–Bi system the formation heats were measured using a direct isoperibol calorimeter. The following values were found:

LaBi (solid state, 300 K) $\Delta H_{form} = -26.5 \pm 0.5$ kcal/g-at.

La_4Bi_3 (solid state, 300 K) $\Delta H_{form} = -24.7 \pm 0.5$ kcal/g-at.

INTRODUCTION

The results of the formation heat measurements in the Y–Bi and Nd–Bi alloy systems were given in previous papers[1,2]. The data obtained for the formation heats of La–Bi alloys and particularly those concerning the La_4Bi_3, LaBi (and $LaBi_2$?) compounds are given here.

La_4Bi_3[3] and LaBi[4] belong to the series of compounds, anti-Th_3P_4-type, known for the bismuthides of the rare earths from La to Tb, and NaCl-type, known for the bismuthides of all the rare earths, respectively. For these series of compounds the lattice parameter regular trend is well known and the high melting points have evidenced their high stability. According to Gambino[5], in the lighter rare earths systems the R_4Bi_3 compounds melt congruently, whilst the RBi compounds decompose peritectically. The contrary happens for the rare earths having a smaller atomic diameter. It is particularly interesting to study the thermodynamics of these phases, because besides having few data of this kind also the equilibrium diagrams are very little known.

Among the rare earths–bismuth systems, the only phase diagram recently[6] studied entirely is Nd–Bi. For this system, the existence of the compounds: Nd_3Bi, Nd_5Bi_3, Nd_4Bi_3, NdBi and $NdBi_2$ was evidenced by both thermal and X-ray examinations. The melting points are very high with just one maximum around 1900 °C for NdBi.

Ce–Bi is another system of bismuthides for which an investigation of the whole diagram is known[7]. Probably such a diagram is not correct in every detail and this because presumably the cerium used had a rather low purity (about 93 wt. %).

However, considering a partial re-examination in the Bi-rich part of the system[8] and the measurements carried out by Olcese[9], the probable sequence of phases is: Ce_3Bi, Ce_4Bi_3, CeBi, $CeBi_2$ and $CeBi_3$.

For the following systems some partial data are known:

Pr–Bi[10]: Only the Pr-rich part was studied: the rare earth richest phase existing in the system seems to be Pr_4Bi_3 which, according to Gambino, should melt incongruently.

Gd–Bi[5]: For this system, in an examination of the Gd-rich side, the Gd_2Bi and Gd_4Bi_3 incongruently melting phases as well as the congruent GdBi compound were described.

Dy–Bi[5]: In this system, in the Dy-rich part, the following phases were observed: Dy_3Bi_2 and DyBi melting incongruently and congruently, respectively.

All the above systems are similar in that they have rather high melting temperatures.

THE LANTHANUM–BISMUTH SYSTEM

For the La–Bi system, object of the present study, the existence of La_4Bi_3, congruently melting, and of LaBi, incongruently melting, is known. Considering probable analogies with the other rare earths systems the existence of other intermediate phases is possible although it may be extremely difficult to evidence them. This is a result of the remarkable difficulties arising from the sluggishness of the various peritectic reactions in these systems while trying to obtain samples in equilibrium. With regard to the above we also have to remember that some La–Bi alloys having a composition near to La_5Bi_3 were prepared by Hohnke and Parthe[11]. These, however, could not evidence the presumable existence of a phase isostructural with Nd_5Bi_3 owing to the very high reactivity of the alloys. At last, while effecting this work, the probable existence of a phase having a composition near to $LaBi_2$ was observed.

CALORIMETRIC MEASUREMENTS

The samples were prepared by using La with a purity of 99.9% and Bi of 99.999% purity obtained by Koch Light Lab. Ltd. In order to have reference samples, first of all some specimens were prepared, duly melted and annealed so as to be able to check the phases existing after a sufficiently slow cooling. The phases observed on these samples were La_4Bi_3 and LaBi. With long annealing (~200–250 h at 900 °C), near the 67–70 at.% Bi composition, samples of homogeneous appearance were obtained; some show several diffraction lines different from those of the other previously mentioned phases.

The sample preparation, the chemical analysis, the metallographic and X-ray (powder method) examinations were carried out following the techniques[1,2] already described.

The measurement of the formation heats in this case was also carried out using a direct isoperibol calorimeter[12]. This consists of a kind of calorimetric bomb immerged in an oil-bath. Inside the bomb there is a tantalum resistence furnace which is used for heating until the reaction in the mixture of the two metals starts. The two metals finely ground, well mixed and compacted, are contained in an iron crucible lined by a thin tantalum sheet. The change of the oil-bath temperature, measured by means of a thermopile, makes it possible to determine the evolved heat, utilizing the results obtained during heating runs performed by a measured quantity of electric energy. The same, previously mentioned, control and analysis techniques were also employed for the examination of the alloys prepared in the calorimeter. The microphotographs of two samples prepared in the calorimeter and having a composition near to La_4Bi_3 and to LaBi, respectively, are shown in Fig. 1.

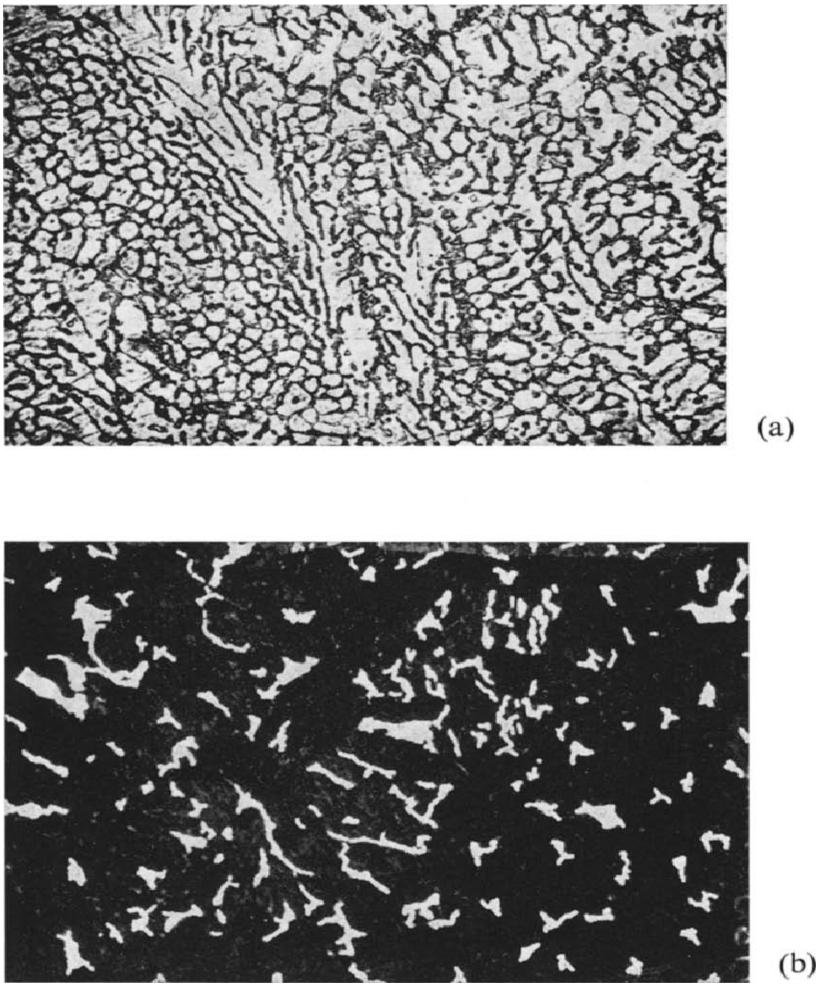

Fig. 1. Microphotographic examination of samples of La–Bi alloys after reaction. (a) Alloy number 5, 39.0_5 at.% Bi, small quantity of La (dark) and La_4Bi_3, air-etched, ×200. (b) Alloy number 10, 58.2_5 at.% Bi, LaBi (dark) and Bi, air-etched, ×500.

RESULTS

The results obtained are reported in Table 1 and in Fig. 2. The formation heats can be considered as measured at 300 K. The sample, inside the calorimeter, is surrounded by a thermostat at 27±0.01 °C and, while measuring it cools down to this temperature. The error of ±0.5 kcal/g-at. ascribed to all measurements is considered to include both the real measure errors and the uncertainty of composition as well as the effects due to eventual quenching of disorder, etc. from a certain temperature higher than 300 K.

TABLE 1

DATA OBTAINED IN THE MEASUREMENT OF THE HEATS OF FORMATION OF LANTHANUM-BISMUTH ALLOYS IN THE SOLID STATE

Alloy No.	*Analytical composition (at. % Bi ± 0.2)*	ΔH_{form} *(300 K) (kcal/g-at. ± 0.5)*
1	25.2	-15.0_5
2	29.1	-18.3
3	35.2	-21.2
4	38.6	-22.3_5
5	39.0_5	-22.8_5
6	44.5_5	-25.4_5
7	47.3	-25.8
8	51.5_5	-25.9
9	52.6_5	-23.6
10	58.2_5	-22.3
11	61.9	-20.2_5
12	76.9	-12.2
13	84.9	-8.0_5

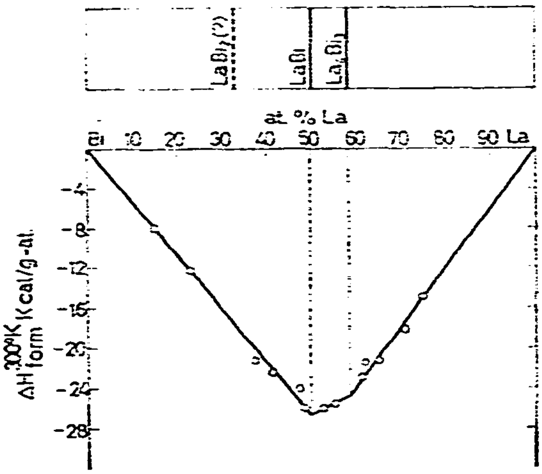

Fig. 2. Heats measured in the La–Bi system during the formation of the La_4Bi_3 and LaBi compounds.

It should be noticed, however, that only the La_4Bi_3 and LaBi phases were observed in the alloys prepared inside the calorimeter. The data obtained for compositions different from these ones can therefore be considered correct provided the state of complete equilibrium does not include other phases. Anyhow these data are useful because their trend makes it possible to extrapolate more accurate values of ΔH for the two compounds. Presumably the existence of other eventual intermediate phases would not substantially change the trend given in Fig. 2. This also because, in analogy for instance with the Nd–Bi system, other eventual phases might be formed due to peritectic reactions.

Concluding it may be useful to compare the ΔH values (kcal/g-at; 300 K) obtained for La_4Bi_3 (−24.7) and LaBi (−26.5) with the corresponding values of Nd_4Bi_3 (−25.0) and NdBi (−26.6) which, as it may be seen, are very near between them. A close analogy of values had already been found for the similar compounds[13] LaAs (−36.5±2.2) and NdAs (−36.3±1.8).

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