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HEAT OF FORMATION OF YTTRIUM–BISMUTH ALLOYS

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ABSTRACT

In the Y–Bi system the formation heats were measured using a direct isoperibol calorimeter. The following values were found for the two known compounds:

YBi (solid state, 300 K) $\Delta H_{form} = -22.0 \pm 0.5$ kcal/g-at.

Y_5Bi_3 (solid state, 300 K) $\Delta H_{form} = -19.5 \pm 0.5$ kcal/g-at.

INTRODUCTION

As it is known the elements of the VA group react with the metals of the group IIIB forming a series of very stable compounds. This is shown by the high values both of the melting points (e.g. YSb 2000°C[1], YBi 2020°C[2], NdBi 1900°C[3]) and of the heats of formation (as observed for the MeAs compound[4] whose heats of formation are between −30 and −40 kcal/g-at., and for some MeSb phases).

Generally in these systems the phases have simple crystal structures related to few structural types, each corresponding to a series of isotypic compounds characterized by high binding energy (bonds are probably partially ionic or covalent besides being metallic[6]). This makes the systematic study of such substances and of their thermodynamics very interesting.

Of particular interest is the evaluation of the heats of formation and it seemed specially convenient to use the method of direct calorimetry because the reactions between the elements described take place easily and violently and lead to the formation of phases of well-defined composition often with congruent melting.

While starting a plan of work of this type it was considered useful, in order to reduce measurement errors, to study systematically whole systems rather than single compounds.

The heats of formation of the Y–Bi alloys are given in this first paper. The most recent study on the Y–Bi system is that of Schmidt, McMasters and Lichtemberg[2] who studied the equilibrium diagram. This is shown in Fig. 1 from which the existence of Y_5Bi_3 and YBi is evident.

With regard to phases of the type R_4Bi_3 (known for several rare earths[7,8] and whose formation often corresponds to peritectic reactions, generally occurring at very

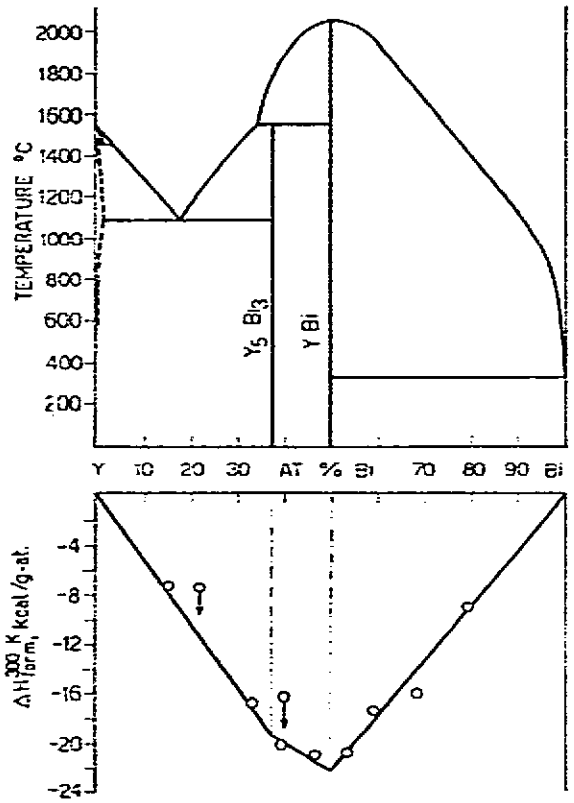

Fig. 1. Phase diagram[2] and heats of formation of yttrium–bismuth alloys.

high temperature), yttrium apparently does not form a compound of this type or, at least, there is a remarkable reluctance to its formation. On the other hand the sequence of phases proposed by Schmidt et al. was observed again during the preparation of a number of alloys (to be used as reference standards for the samples obtained in the calorimeter), although on the powder photograms of two samples were noticed some weak, not identified, lines.

CALORIMETRIC MEASUREMENTS

The metals used (obtained by the Koch Light Lab. Ltd.) are Bi purity 99.999% and Y 99.9%. The two elements (for a total weight of about 5–6 g) were first finely reduced to powder (using for Y a milling machine operating under A), carefully mixed, compacted, and introduced into a iron-crucible having very thin walls (eventually lined with a 0.05 mm tantalum sheet).

The sample was then placed inside the calorimeter; this (which has been described elsewhere[9]) consists of a bomb containing a small tantalum furnace for heating the sample till the reaction started. The bomb is submerged in an oil bath whose temperature is followed by 18 thermocouples in series. From the elevation of the bath temperature the total evolved energy is evaluated after the reaction, during a

certain number of calibration runs purely using electrical heating. The electric energy is measured by a standard watt-hour meter.

After each ΔH measurement, the sample, taken from the calorimeter, was submitted to a number of examinations in order to elucidate the real occurred course of the reaction, the reaching of the equilibrium state, and eventual alterations (side reactions, etc.).

TABLE 1

DATA OBTAINED IN THE MEASUREMENT OF THE HEATS OF FORMATION OF YTTRIUM–BISMUTH ALLOYS

Alloy number	*Analytical composition at. % Bi*	ΔH_f *(300 K) (kcal/g-at. ±0.5)*	*Comments*
1	15.2±0.3	-7.3_5	see Fig. 2a
2	21.7±0.1	(−7.5)	the appearance of the sample shows that the alloy has reacted only partially
3	33.2±0.1	−16.7	
4	39.7±0.2	−19.9	see Fig. 2b
5	40.2±0.2	(-16.2_5)	the appearance of the sample shows that the alloy has reacted only partially
6	46.5±0.3	-20.9_5	
7	53.8±0.1	−20.8	see Fig. 2c
8	59.1±0.1	-17.4_5	
9	68.4±0.2	-16.0_5	
10	79.2±0.1	−9.0	

Not all the samples prepared (either due to a large grain size of the powders or for initial inadequate heating) reacted completely inside the calorimeter. The alloys which were taken into consideration and have been reported in Table 1 had the appearance either of melted ingots or of compact, well sintered, samples.

EXPERIMENTAL

The examinations carried out on all the samples were the following ones:

Chemical analysis

After dissolution in aqua regia the separation of the two elements was effected by precipitation of Bi as sulphide; Bi was then determined with 8-hydroxyquinoline and Y with oxalic acid.

Metallographic examination

It was performed, on the largest section of the specimen, by using known techniques, taking care that, specially for the yttrium-rich alloys, the samples, highly oxidable, were conveniently protected.

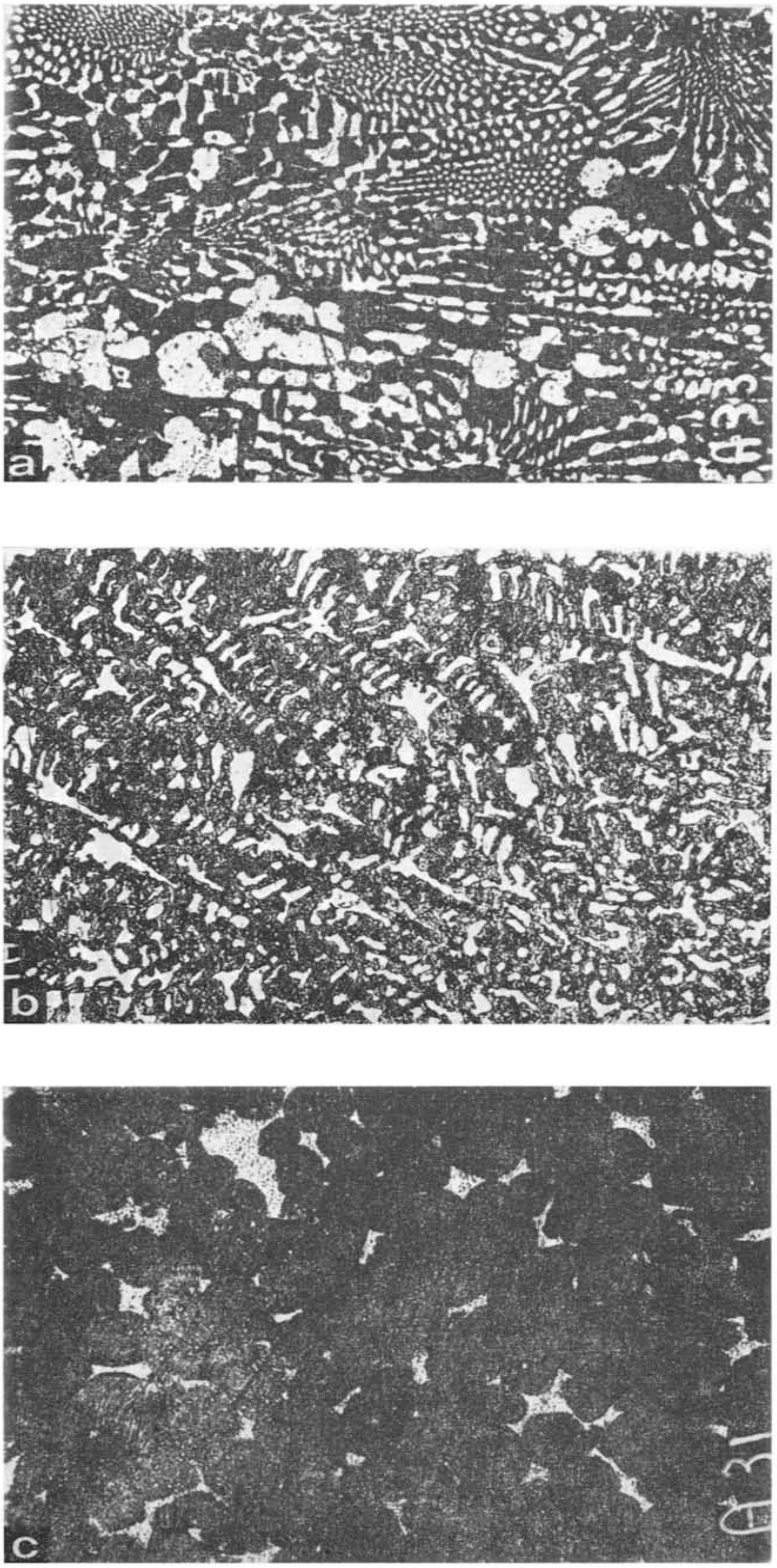

Fig. 2. Metallographic examinations of samples of yttrium–bismuth alloys after reaction: (a) alloy number 1, 15.2 at. %Bi, small quantities of Y (dark) and Y/Y_5Bi_3 eutectic, air-etched, ×100; (b) alloy number 4, 39.7 at. %Bi, Y_5Bi_3 (dark) + YBi, air etched, ×200; (c) alloy number 7, 53.8 at. %Bi, YBi (dark) + Bi, air etched, ×200.

X-ray examination

This was carried out by using the Debye method (powders prepared under A) with the Kα radiations of Cu and Fe.

RESULTS

The results obtained are summarized in Table 1 and in Fig. 1. Owing to the working conditions of the calorimeter (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 formation heats can be considered as measured at 300 K, excluding the effects due to the eventual quenching of disorder, etc., from a certain higher temperature. Analogously to other similar measurements it was considered that an error of ± 0.5 kcal/g-at. of all measurements includes this effect too, besides those tied to the uncertainty of composition, measure errors, etc.

In Table 1 the values concerning two samples (No. 2 and No. 5) were reported which, although referring to alloys not in equilibrium, can all the same be useful to determine an upper limit of ΔH.

By extrapolation from the reported data we obtain, for the two compounds, the following values:

Y_5Bi_3 (solid state, 300 K) $\quad \Delta H_f = -19.5 \pm 0.5$ kcal/g-at.

YBi (solid state, 300 K) $\quad \Delta H_f = -22.0 \pm 0.5$ kcal/g-at.

Finally it may be useful to notice the rather regular decrease in the formation heat for the following three NaCl-type compounds: YAs (38.7 ± 1.7), YSb (26.5 ± 1) and YBi (22.0 ± 0.5).

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