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THE HEAT OF FORMATION OF NEODYMIUM–BISMUTH ALLOYS

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ABSTRACT

The heats of formation of Nd/Bi alloys were measured using an isoperibol direct calorimeter. For the various existing compounds the heats of formation (for the reaction among solid phases at 300 K) correspond to the following values (kcal/g-at.): Nd_3Bi, -15.0 ± 0.7; Nd_5Bi_3, -22.2 ± 0.7; Nd_4Bi_3, -25.0 ± 0.5; NdBi, -26.6 ± 0.5; $NdBi_2$, -21.0 ± 0.5. The results obtained are briefly discussed.

INTRODUCTION

The different rare-earth metals generally form with the same element a sequence of compounds having the same coordination (and often isostructural). For each one in this series of compounds, following the variations in the rare earth atomic size and of its valence a more or less gradual variation of properties is noted. For series of this type a correlation between structural and thermodynamic data may be useful. The study of the group of compounds formed by the rare earths with arsenic, antimony and bismuth (for which the binding energy is remarkably high, which is probably due to ionic and covalent contributions besides the metallic one) seems to be of particular interest[1].

A regular investigation of the thermochemical properties of the rare earth bismuthides was started. In a previous paper[2] the results of the measurement of the heat of formation for the Y–Bi system were reported. In this work the results obtained in the study of the entire Nd–Bi system are recorded.

EXPERIMENTAL

The intermediate phases existing in the Nd–Bi system are listed in Table 1 and the equilibrium diagram, already known[6], is given in Fig. 1. In this last one is noted the absence of the Nd_5Bi_3 phase, which was identified by x-rays only. As it can be observed four of the five existing phases are probably formed by peritectic reactions occurring, however, at rather high temperature.

The measurement of the heat of formation was executed with a direct method, employing Bi at 99.999% and Nd at 99.9% obtained by the Koch Light Lab. Ltd. The calorimeter used was the same one utilized for the Bi–Y alloys[7]; the reaction

TABLE 1

STRUCTURAL DATA OF THE NEODYMIUM-BISMUTH COMPOUNDS

Compound	*Structure*	*Unit cell dimensions (Å)*	*Reference*
Nd_3Bi	unknown	—	6
Nd_5Bi_3	hexagonal Mn_5Si_3	$a = 9.374$, $c = 6.535$	5
Nd_4Bi_3	cubic anti Th_3P_4	$a = 9.553$	4
NdBi	cubic CsCl	$a = 6.42$	3
$NdBi_2$	unknown	—	6

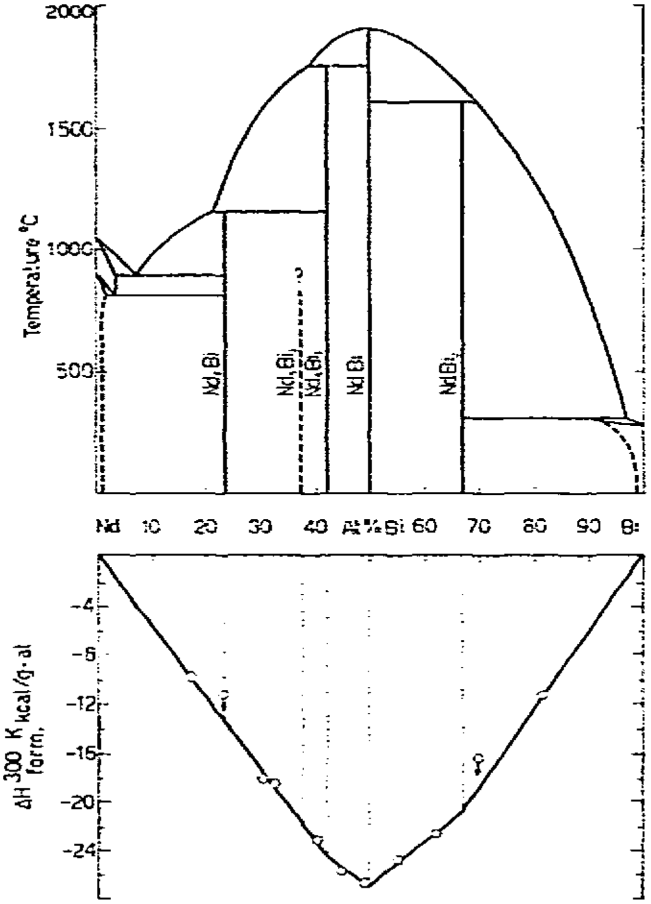

Fig. 1. Neodymium–bismuth diagram and heat of formation for the reaction in the solid state.

among the metals (finely mixed together for a total weight of about 6 grams) took place inside the calorimeter itself.

The samples taken from the calorimeter, after the reaction and the calibration runs, resemble melted, fragile and compact masses. On all samples, in order to control the real achievement of the equilibrium state and the absence of eventual side reactions, the hereinafter mentioned examinations were made. The various operations, as well as the initial preparation of the powder mixtures to be introduced into the calorimeter, were performed in an argon atmosphere, due to the oxidizability of neodymium and, particularly, of its bismuthides.

Chemical analysis

Dissolved in aqua regia, separation of Bi as sulphide and its subsequent determination with 8-hydroxyquinoline; Nd is determined with $(COOH)_2$. As in the calorimeter the reaction between the metals takes place inside an iron container (eventually lined with a thin tantalum sheet) the absence of these metals in the sample was also controlled.

Metallographic examination

The samples, after the usual polishing, were etched with the following solution: $HNO_3(1\%)+CH_3COOH(19\%)+H_2O(20\%)+(CH_2OH)_2(60\%)$. For the neodymium-rich alloys the attack by the air was often sufficient.

X-ray examination

The powder method was used with both Cu and Fe $K\alpha$ radiations.

RESULTS

The results (Figs. 2a–d) obtained in all the above-mentioned examinations were valued, in every case, for themselves as well as in comparison with those obtained on some standard samples prepared in the conventional way for different typical compositions. In spite the presence of different peritectic reactions most of the samples, also owing to the high local increase of the temperature during the synthesis, had reached the equilibrium state. (It has to be noted, however, that a certain number of samples, among those prepared, was put aside either because the reaction was not complete or because at the time of the synthesis the container exploded inside the calorimeter.)

The data obtained are compared with the equilibrium diagram in Fig. 1 and are reported in Table 2. The following values have been extrapolated from them, for the different compounds, including Nd_5Bi_3 whose existence seems to be confirmed: Nd_3Bi, -15.0 ± 0.7; Nd_5Bi_3, -22.2 ± 0.7; Nd_4Bi_3, -25.0 ± 0.5; NdBi, -26.6 ± 0.5; $NdBi_2$, -21.0 ± 0.5 (ΔH in kcal/g.at. for the reaction in the solid state).

All the above values can be considered as referring to 300 K because the outside thermostat of the calorimeter was maintained at this temperature. After the reaction, the sample cools down to the same temperature whilst measurements are performed.

We think that the uncertainty reported includes (besides the errors of measurement, composition variation, etc.) a final quenching at 300 K of some situation stable at a somewhat higher temperature.

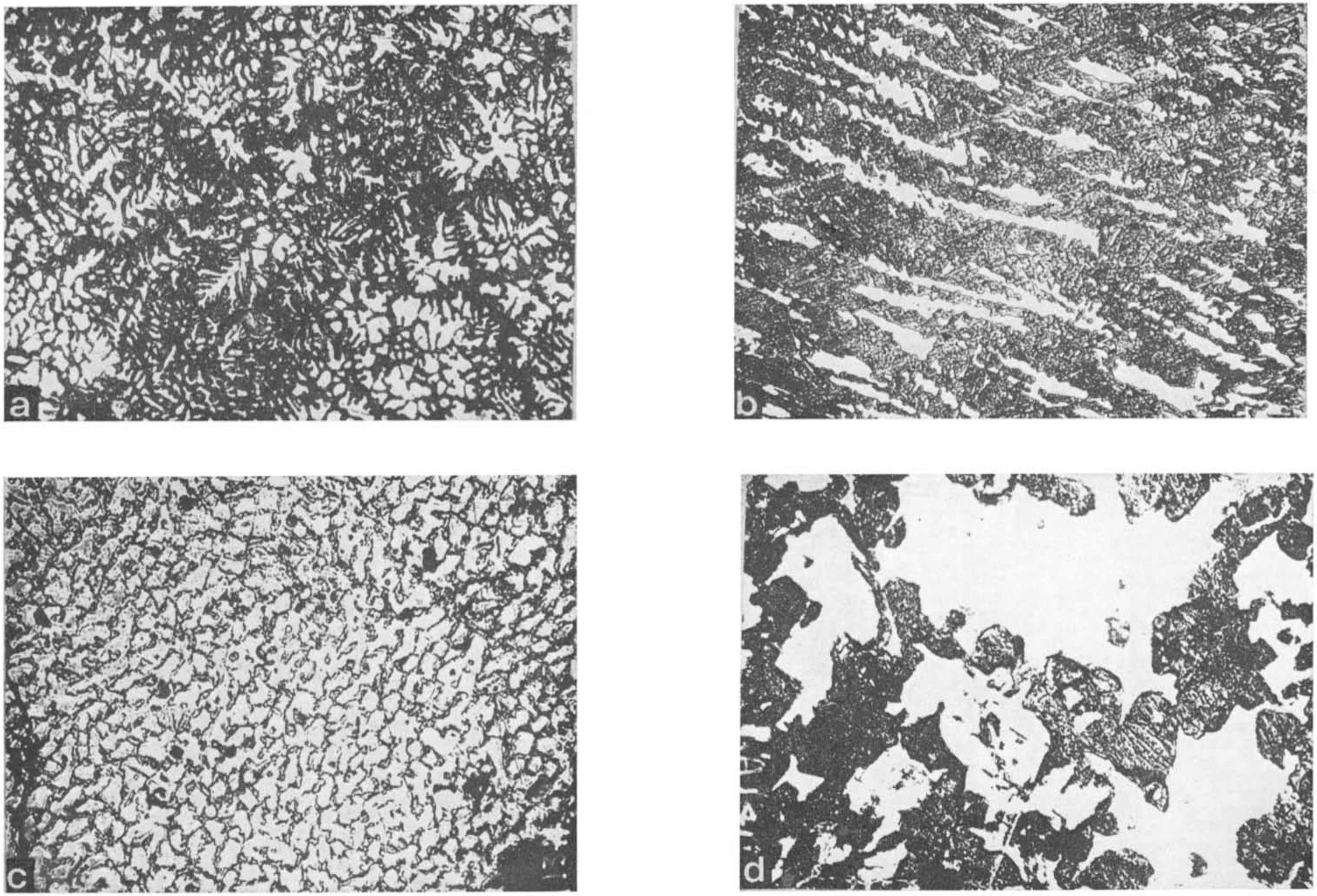

Fig. 2.Metallographic examination of samples of neodymium-bismuth alloys after reaction: (a) alloy number 3, 30.5 at. %Bi, air-etched, × 200; (b) alloy number 5, 40.1 at. %Bi, × 200; (c) alloy number 7, 48.9 at. %Bi, × 200; (d) alloy number 9, 61.9 at. %Bi, air-etched, × 500.

TABLE 2

ΔH OF FORMATION OF NEODYMIUM–BISMUTH ALLOYS (SOLID STATE REACTION AT 300 K)

Alloy number	*Analytical composition (at. %Bi)*	*ΔH (kcal/g-at.)*
1	17.3 ±0.4	−9.6 ±0.5
2[a]	23.0 ±0.1	(−11.1)
3[b]	30.5 ±0.4	−18.0 ±0.5
4	32.2_5 ±0.3	-18.3_5 ±0.5
5[b]	40.1 ±0.4	-22.9_5 ±0.5
6	44.6 ±0.3	−25.6 ±0.5
7[b]	48.9_5 ±0.4	−24.6 ±0.5
8	55.4 ±0.2	−24.8 ±0.5
9[b]	61.9 ±0.3	−22.5 ±0.5
10[a]	69.5 ±0.2	(−16.2)
11	81.2_5 ±0.4	−11.2 ±0.5

[a] For these alloys the reaction was not complete. The data reported, however, could have a certain interest as limit values. [b] For these alloys the micrographic appearance has been reported, respectively, in Fig. 2.

CONCLUSION

Concluding we observe that the stabilities of the phases, obtained respectively from the trend of the melting points and of the ΔH, are in agreement. Particularly for the composition 1:1 we obtain maximum values for the melting point and for the heat of formation. Another point of interest is that the absolute values of ΔH are substantially higher than those obtained in typical metallic systems, and can therefore be considered as a further indication of the predominance of other types of binding over the metallic one.

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