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The dysprosium–tin phase diagram

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Abstract

The dysprosium–tin phase diagram was established by means of differential thermal, X-ray and microscopic analyses of 22 alloys. Seven intermetallic compounds were found to exist in the system. Dy_5Sn_3 melts congruently at 1870 °C, and undergoes a polymorphous transformation at 1823 ± 6 °C. The intermetallics Dy_5Sn_4, $Dy_{11}Sn_{10}$, DySn, Dy_4Sn_5, $DySn_2$, $DySn_3$ are formed peritectically at 1712 ± 11, 1605 ± 12, 1208 ± 3, 1166 ± 7, 1138 ± 3 and 747 ± 6 °C respectively. $DySn_3$ exists in a narrow temperature range, in two polymorphous modifications. The transformation $\beta\text{-}DySn_3 \rightarrow \alpha\text{-}DySn_3$ occurs at 608 ± 12 °C, and at 499 ± 2 °C α-$DySn_3$ decomposes to $DySn_2$ and the tin-rich melt. The dysprosium-rich eutectic crystallizes at 1204 ± 10 °C and contains 13 at.% tin. The solid-state solubility of tin in dysprosium is about 3 at.%, and that of dysprosium in tin is negligible.

1. Introduction

A reliable Dy–Sn phase diagram has not yet been reported. The following Dy–Sn compounds are now established: Dy_5Sn_3 (Mn_5Si_3-type structure) [1, 2], Dy_5Sn_4 (Sm_5Ge_4-type) [3], $Dy_{11}Sn_{10}$ ($Ho_{11}Ge_{10}$-type) [3], $DySn_2$ ($ZrSi_2$-type) [4], and $DySn_3$ [5, 6]. The last compound is not thought to form [4] under standard conditions of temperature and pressure. Heavy rare earth metals have been known to form stannides of this stoichiometry with the $AuCu_3$-type structure only at high pressures [5]. It was found that $DySn_3$ with the structure $GdSn_{3-x}$ can be synthesized during prolonged annealing at 400 °C [6]. Information on temperatures and modes of phase formation is scarce. It has been suggested [3] that Dy_5Sn_4 and $Dy_{11}Sn_{10}$ melt incongruently; however, neither temperatures nor decomposition products were reported.

We have recently determined [7] the congruent melting point for Dy_5Sn_3 (1870 °C) and predicted that the intermetallics Dy_5Sn_4 and $Dy_{11}Sn_{10}$ are formed according to the following reactions: $L + Dy_5Sn_3 \rightarrow Dy_5Sn_4$ (1730 ± 156 °C) and $L + Dy_5Sn_4 \rightarrow Dy_{11}Sn_{10}$ (1555 ± 88 °C) respectively. The temperature of the eutectic reaction $L \rightarrow \langle Dy \rangle + Dy_5Sn_3$ has been estimated to be 1176 ± 64 °C.

Chen and Zheng [8] reported the following melting temperatures for these compounds: 1140 °C for Dy_5Sn_3, decomposing peritectically according to the reaction $Dy_5Sn_3 \rightarrow L + Dy_5Sn_4$; 1160 °C for Dy_5Sn_4, according to the reaction $Dy_5Sn_4 \rightarrow L + Dy_{11}Sn_{10}$; 1175 °C for $Dy_{11}Sn_{10}$, according to $Dy_{11}Sn_{10} \rightarrow L +$ DySn. In addition to these well known stannides, the existence of the intermetallics Dy_8Sn_9 and $DySn_4$ (melting incongruently at 1134 and 442 °C respectively), and Dy_2Sn, DySn and Dy_4Sn_7 (melting congruently at 1237, 1222, 1154 °C respectively), was established.

All the above mentioned studies suggest that the dysprosium–tin diagram [8] may be incorrect. For this reason it was felt that a complete careful investigation of dysprosium–tin alloys should be made.

On the basis of the various data available, some general tendencies relevant to the phase diagrams of R–X systems (where R is a rare earth, X ≡ Ge, Sn, Pb) were established [9] and the unknown phase diagrams for R–Sn were predicted, in particular that of the Dy–Sn system, which was considered as a reference system for experimental study of the Dy–Sn alloys.

2. Experimental procedure

The metals used were specified to be 99.9995% tin and 99.76% dysprosium. Alloys of 22 compositions were prepared by arc-melting on a water-cooled copper hearth under a purified argon atmosphere. To improve the homogeneity, the buttons were turned over and remelted three times. Although the weight loss on alloying was insignificant, the compositions of the alloys were corrected compared with those of the starting mixtures,

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TABLE 1. Structural components, phase contents of dysprosium–tin alloys and phase transformation temperatures

Tin content (at.% Sn)	Structural components and phase content[a]	Thermal analysis results (°C)											
		Liquidus	L ⇄ ⟨Dy⟩ + Dy_5Sn_3	α-Dy_5Sn_3 ⇄ β-Dy_5Sn_3	L + Dy_5Sn_3 ⇄ Dy_5Sn_4	L + Dy_5Sn_4 ⇄ $Dy_{11}Sn_{10}$	L + $Dy_{11}Sn_{10}$ ⇄ DySn	L + DySn ⇄ Dy_4Sn_5	L + Dy_4Sn_5 ⇄ $DySn_2$	L + $DySn_2$ ⇄ β-$DySn_3$	α-$DySn_3$ ⇄ β-$DySn_3$	α-$DySn_3$ ⇄ L + $DySn_2$	Equilibrium with L, ⟨Sn⟩ and $DySn_2$ participation
0	Dy	1425	–	–	–	–	–	–	–	–	–	–	–
2.1	⟨Dy⟩	1400	–	–	–	–	–	–	–	–	–	–	–
5.9	⟨Dy⟩ + eutectic (⟨Dy⟩ + Dy_5Sn_3)	1340	1200	–	–	–	–	–	–	–	–	–	–
10.2[b]	⟨Dy⟩ + eutectic (⟨Dy⟩ + Dy_5Sn_3)	1275	1195	–	–	–	–	–	–	–	–	–	–
12.3	(⟨Dy⟩) + eutectic (⟨Dy⟩ + Dy_5Sn_3)	1225	1200	–	–	–	–	–	–	–	–	–	–
27.9	Dy_5Sn_3 + eutectic (⟨Dy⟩ + Dy_5Sn_3)	1670↓	1205	–	–	–	–	–	–	–	–	–	–
36.6	Dy_5Sn_3 + (eutectic (⟨Dy⟩ + Dy_5Sn_3))	1860	1220	1820	–	–	–	–	–	–	–	–	–
37.6	Dy_5Sn_3 + (?)	1870	–	1820	–	–	–	–	–	–	–	–	–
40.8[b]	Dy_5Sn_3 + Dy_5Sn_4	1870	–	1830	–	–	–	–	–	–	–	–	–
42.2	Dy_5Sn_3 + Dy_5Sn_4	1850	–	–	1720	–	–	–	–	–	–	–	–
45.5	Dy_5Sn_4 + ($Dy_{11}Sn_{10}$)	1735	–	–	1705	1590	–	–	–	–	–	–	–
48.5	$Dy_{11}Sn_{10}$ + DySn	1690	–	–	–	1625	1205	1160	1140	–	–	–	–
48.5[c]	$Dy_{11}Sn_{10}$ + DySn	1675	–	–	–	1610	1205	–	–	–	–	–	–
50.4	DySn + (?)	1625	–	–	–	–	1210	1160	1140	–	–	–	–
50.4[c]	DySn + (?)	1615	–	–	–	1595↓	–	1160	1140	–	–	–	–
51.3[c]	DySn + Dy_4Sn_5	1635	–	–	–	1610↓	1210	1165	1140	–	–	–	–
56.6	Dy_4Sn_5 + $DySn_2$	1495	–	–	–	–	1210	1170	1135	–	–	–	–
56.6[c]	Dy_4Sn_5 + $DySn_2$	1500	–	–	–	–	–	1180	1140	–	–	–	–
57.3	Dy_4Sn_5 + $DySn_2$	1400	–	–	–	–	–	1170	1130	–	–	–	–
62.9	(Dy_4Sn_5) + $DySn_2$	1165	–	–	–	–	–	–	1135	–	–	–	–
62.9[c]	(Dy_4Sn_5) + DySn	1170	–	–	–	–	–	–	1140	–	–	–	–
67.2	$DySn_2$ + (⟨Sn⟩)	1150	–	–	–	–	–	–	1140	–	–	–	–
70.7	$DySn_2$ + ⟨Sn⟩	1125	–	–	–	–	–	–	–	740	595	–	–
75.4	$DySn_2$ + ⟨Sn⟩	1085	–	–	–	–	–	–	–	750	615	–	–
85.4	$DySn_2$ + ⟨Sn⟩	995	–	–	–	–	–	–	–	750	615	–	–
95.4	$DySn_2$ + ⟨Sn⟩	740	–	–	–	–	–	–	–	–	–	500	235
99.1	$DySn_2$ + (⟨Sn⟩)	–	–	–	–	–	–	–	–	–	–	–	230

The temperatures were determined from the thermal curves on heating, marked ↓, which were determined from the cooling curve.

[a] ⟨ ⟩ means solid solution, and ( ) a small quantity of the phase.

[b] Data are from ref. 7.

[c] Heat treated alloys; the rest of the data given refer to as-cast alloys.

taking into account that the volatility of dysprosium is greater than that of tin.

The samples studied were both as-cast and heat treated at 1000 °C for 100 h in argon. The samples were subjected to differential thermal analysis (DTA), X-ray and metallography examinations, as is described fully elsewhere [10].

The crystal lattice parameters were refined by a computer program using the least squares fit.

3. Results and discussion

The results obtained are shown in Tables 1 and 2 together with the data reported previously. The phase diagram that resulted from this investigation is shown in Fig. 1.

The compound richest in dysprosium, Dy_5Sn_3, melts congruently at 1870 °C. The structural data are in agreement with those available (see Table 2). Some

TABLE 2. Crystal structure data of dysprosium stannides

Phase	Structure	Unit cell dimensions (Å)	Reference	Remarks
Dy	Hexagonal Mg	$a = 3.5915 \pm 0.0002$ $c = 5.6501 \pm 0.0004$	11	
Dy	Hexagonal Mg	$a = 3.589 \pm 0.001$ $c = 5.646 \pm 0.002$	This work	Starting dysprosium
⟨Dy⟩	Hexagonal Mg	$a = 3.586 \pm 0.001$ $c = 5.643 \pm 0.001$	This work	In the alloy containing 2.1 at. % Sn
⟨Dy⟩	Hexagonal Mg	$a = 3.580 \pm 0.001$ $c = 5.636 \pm 0.003$	This work	In the alloy containing 5.9 at.% Sn
α-Dy_5Sn_3	Hexagonal Mn_5Si_3	$a = 8.889$ $c = 6.491$	1	
α-Dy_5Sn_3	Hexagonal Mn_5Si_3	$a = 8.884$ $c = 6.484$	2	
α-Dy_5Sn_3	Hexagonal Mn_5Si_3	$a = 8.880 \pm 0.002$ $c = 6.492 \pm 0.003$	This work	In the alloy containing 37.6 at.% Sn
β-Dy_5Sn_3	Structure not resolved			
Dy_5Sn_4	Orthorhombic Sm_5Ge_4	$a = 7.966$ $b = 15.38$ $c = 8.105$	3	
Dy_5Sn_4	Orthorhombic Sm_5Ge_4	$a = 7.96 \pm 0.01$ $b = 15.36 \pm 0.02$ $c = 8.11 \pm 0.01$	This work	In the alloy containing 45.5 at.% Sn, specimen in the capillar
$Dy_{11}Sn_{10}$	Tetragonal $Ho_{11}Ge_{10}$	$a = 11.54$ $c = 16.90$	3	
$Dy_{11}Sn_{10}$	Tetragonal $Ho_{11}Ge_{10}$	$a = 11.503 \pm 0.009$ $c = 16.88 \pm 0.03$	This work	In the alloy containing 48.5 at.% Sn, specimen in the capillar
DySn	Structure not resolved			
Dy_4Sn_5	Structure not resolved			
$DySn_2$	Orthorhombic $ZrSi_2$	$a = 4.391 \pm 0.002$ $b = 16.233 \pm 0.005$ $c = 4.300 \pm 0.002$	4	
$DySn_2$	Orthorhombic $ZrSi_2$	$a = 4.381 \pm 0.003$ $b = 15.210 \pm 0.009$ $c = 4.290 \pm 0.003$	This work	In the alloy containing 67.2 at.% Sn
α-$DySn_3$	Orthorhombic $GdSn_{3-x}$	$a = 4.387 \pm 0.003$ $b = 4.336 \pm 0.004$ $c = 21.804 \pm 0.009$	6	
β-$DySn_3$, HP*	Cubic $AuCu_3$	$a = 4.659 \pm 0.001$	5	

HP, high pressure phase.

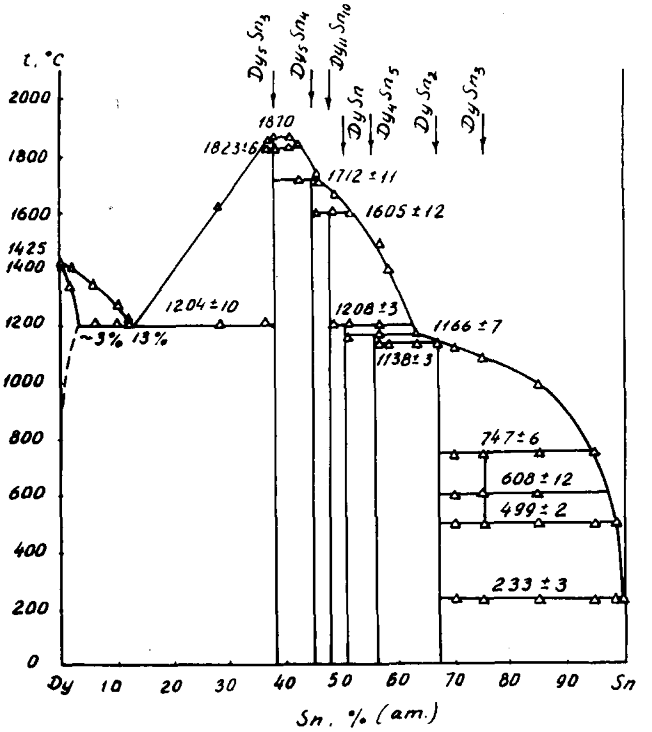

Fig. 1. The dysprosium–tin phase diagram.

thermal effects near the melting point at 1823 ±6 °C (mean square deviations are given) extending from the alloy with 36.6 at.% tin toward the alloy containing 40.8 at.% tin were found, thus suggesting a polymorphous transformation in this compound, similar to transformations of some R_5Sn_3 intermetallics [12].

It was found that Dy_5Sn_4 and $Dy_{11}Sn_{10}$ are formed peritectically: $L+Dy_5Sn_3 \rightarrow Dy_5Sn_4$ (1712 ±11 °C) and $L+Dy_5Sn_4 \rightarrow Dy_{11}Sn_{10}$ (1605 ±12 °C). The agreement of our crystal structure data and those obtained from the literature for these compounds is satisfactory (see Table 2).

Specimens of alloys containing 48.5–56.6 at.% tin demonstrate thermal effects occurring at 1200–1210 °C, and their values indicate the formation of the equiatomic phase: $L+Dy_{11}Sn_{10} \rightarrow DySn$, 1208 ±3 °C. The microstructure of the alloy close to the equiatomic alloy (51.3 at.% tin) contains polyhedrons of DySn compound with a small quantity of second phase on the boundaries.

The peritectic reaction $L+DySn \rightarrow Dy_4Sn_5$ occurs at the temperature of 1166 ±7 °C. The composition of Dy_4Sn_5 was established by comparing values of the thermal effects. This compound was observed first. The structures of DySn and Dy_4Sn_5 were not solved.

The stannide $DySn_2$ is formed at 1198 ±3 °C in the reaction $L+Dy_4Sn_5 \rightarrow DySn_2$. The structure and lattice parameters coincide with available data (Table 2).

The as-cast alloy containing 48.5 at.% tin (two-phase region $Dy_{11}Sn_{10}+DySn$) also showed thermal effects at 1125 and 1150 °C due to the formation of Dy_4Sn_5 and $DySn_2$; however, heat treatment at 1000 °C removed them. This indicates incomplete formation of DySn and Dy_4Sn_5 in peritectic processes while crystallizing.

Thermal curves of specimens having more than 67 at.% tin, besides liquidus and solidus, showed three effects at 747 ±6, 608 ±12 and 499 ±2 °C. The largest belongs to the alloy having 75 at.% tin. Powder patterns of the alloys in this concentration range reveal only the existence of $DySn_2$ and ⟨Sn⟩ phases. That is why, taking into account the available information referred to above [5, 6], we may safely interpret the first effect as the peritectic formation temperature of the high-temperature modification, β-$DySn_3$. The stannide richest in tin, $DySn_3$, exists in a narrow temperature range, and at 499 ±2 °C decomposes according to the reaction $\alpha\text{-}DySn_3 \rightarrow L+DySn_2$. At 608 ±12 °C a polymorphous transformation evidently occurs. Apparently, β-$DySn_3$ has the $AuCu_3$-type structure [6], and α-$DySn_3$ has the $GdSn_{3-x}$-type structure [5]. Therefore, the high temperature is one of the factors, as is the pressure, which stabilizes this compound. This interpretation of the thermal effects could be confirmed by X-ray investigation above 500 °C.

The eutectic crystallization $L \rightarrow \langle Dy \rangle + Dy_5Sn_3$ takes place at 1204 ±10 °C and at 13 at.% tin.

The degenerative equilibrium with the melt, with participation of ⟨Sn⟩ and $DySn_2$, is observed at 233 ±3 °C; however, its character (eutectic or peritectic) was not determined.

The solid solubility of dysprosium in tin is negligible. The maximum solid solubility of tin in α-dysprosium at eutectic temperature is about 3%.

None of the compounds investigated showed noticeable homogeneity ranges.

The existence of the compounds Dy_2Sn, Dy_8Sn_9, Dy_4Sn_7, $DySn_4$ [8] was not confirmed.

The melting point of dysprosium used was 1425 °C, the polymorphous transformation temperature being 1410 °C, as compared with accepted [13] values of 1412 and 1381 °C respectively.

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