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The phase diagram of the Yb-Si system

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Abstract

The phase diagram of the Yb–Si system has been studied up to about 80 at.% Si by means of multitechnique investigations: differential thermal analysis (DTA), X-ray diffraction (XRD), optical microscopy (LOM), electron probe microanalysis (EMPA) and complemented with tensimetric measurements using the Knudsen effusion–mass spectrometry (KE–MS) and Knudsen effusion–weight loss (KE–WL) techniques. Besides the four already known intermediate phases: Yb_5Si_3 (Mn_5Si_3 -type), YbSi (CrB-type), Yb_3Si_5 (Th_3Pd_5 -type) and $YbSi_{2-x}$ (AlB₂-type), two new compounds have been found and completely characterized: Yb_5Si_4 (Sm_5Ge_4 -type) and Yb_3Si_4 (Ho_3Si_4 -type). Two eutectics occur in this system: at less than 1 at.% Si (815 °C) and at about 82 at.% Si (1145 °C).

Keywords: Rare earth compounds; Crystal structure; Phase diagram; Thermal analysis; X-ray diffraction

1. Introduction

Rare earths (R) and transition metal silicides form a class of fascinating materials for fundamental interface physics and for technological interest. This interest is even higher if Yb–Si intermediate phases are considered, where mixed valence instabilities can be compared between bulk silicides and interface reaction products.

Concerning the Yb–Si system, the phase diagram reported in Massalski [1] has been drawn simply considering the known existing phases and a presumed similarity with the Er–Si system. It seemed therefore worthwhile to study the whole system in order to provide information concerning phase equilibria and crystal chemistry, especially for the preparation of new compounds which could show interesting physical properties.

Recently, a paper of Grytsin et al. [2] reported the study of the Si-rich end of the Yb–Si system (above 60 at.% Si) with a careful examination of the complex crystal chemistry of the ytterbium disilicides and some physical properties of Yb₃Si₅. We substantially agree with their findings, even if with minor differences probably depending on the experimental techniques adopted.

In this paper we report, firstly, the results obtained in the determination of the phase diagram.

Elemental silicon used in this investigation was 'electronic grade' type (purity 99.999 wt.%). Several samples of commercially available ytterbium were tested for their purity; it is well known that pure ytterbium metal, free of heavy pollutant elements, due to its high vapor pressure, can be easily obtained by sublimation techniques. However, other light elements, like hydrogen, may be present and affect greatly the melting point and the transformation temperature, raising the first and depressing the second by several degrees [3]. The metal utilised here showed a melting point of 820 °C and a transformation temperature of 780 °C, not much different from the accepted values: 819 °C and 795 °C, respectively [4], for the hydrogen-free metal.

Owing to the high vapor pressure of ytterbium and to the high melting temperatures reached in this system, the alloys were prepared in two steps. Firstly, the two elements, in the form of small pieces, were pressed together in Ta crucibles, closed by arc welding under pure argon and high-frequency induction melted, shaken to ensure homogeneisation and cooled to room temperature; these first reaction products were examined in the as-cast state. Then, proper portions were used for differential thermal analysis and annealing procedures.

Specimens for thermal analysis, closed by arc welding into Mo crucibles, were transferred to the DTA equipment

^{2.} Experimental

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and subjected to heating and cooling cycles at rates of 10 or 20 °C/min; the temperature measurements were accurate to within ± 5 °C. Specimens to be annealed were closed in Ta crucibles by arc welding under argon, then sealed under vacuum in quartz ampoules.

For silicon contents not higher than about 75 at.%, no contamination of the alloys due to reactivity towards the container materials was observed, even at high temperatures, but not higher than 1650-1700 °C.

X-ray examination was performed on powders, using a Guinier-Stoe camera with Cu K α radiation; pure silicon was used as internal standard (a=5.4308 Å). The X-ray intensities were compared with those calculated by means of the LAZY-PULVERIX program [5].

Metallographic examination was performed with standard techniques; due to the good stability of these alloys in moist air no particular care was necessary in their handling. Further identification of the phases was carried out with the aid of electron microscopy and microprobe analyses; the standards utilized for semiquantitative determinations were pure silicon, ytterbium and the known Yb–Si line compounds.

The equilibrium vapor pressure over the various two solid phase regions were measured by the Knudsen effusion-mass spectrometry (KE–MS) and Knudsen effusion-weight loss (KE–WL) techniques in order to confirm the equilibrium between the adjacent phases [6]. All ytterbium silicides studied by tensimetric method decompose in the *T* range investigated (508–1122 °C) by loss of Yb(g) only. By linear extrapolation of the temperature dependence of the measured Yb(g) vapor pressures in equilibrium over the condensed phases, we obtain a further independent check of the temperatures for some invariant equilibria between the different silicides.

3. Results and discussion

Fig. 1 shows the phase diagram of the Yb–Si system as obtained using the experimental techniques described in Section 2. Table 1 contains the crystallographic data for the intermediate phases formed in this system.

If we compare our findings with those reported by Grytsiv et al. [2] for the Si-rich side of the diagram, two main differences appear. A nearly systematic difference of about 10–15 degrees in the temperatures obtained from the thermal analysis (lower for Ref. [2]) depending probably on methodology adopted, i.e. we used closed Mo crucibles with heating and cooling rates of 10 or 20 °C/min and Pt/Pt-Rh18 thermocouple while the above authors operated with Sc₂O₃ open crucibles under He, with a rate of 50 °C/min and W/W-Re20 thermocouple. Concerning the crystal chemistry of the couple of compounds Yb₃Si₅ and YbSi_{2-x}, in several Guinier powder patterns we also observed some extra weak reflections not ascribable to the

known phases, indicating indeed a much more complex situation than that reported in old studies [7]. The hypothesis of derivative structures suggested by Ref. [2] is correct but only single crystal investigations would be necessary to determine these crystal structures and therefore their composition. For these reasons we prefer to present in Fig. 1 a simplified sketch for this region of the diagram.

Additions of silicon to ytterbium probably give rise to a reaction of the eutectic type at 815 °C (about 5 degrees below the melting point of the Yb used in this investigation); the composition of the eutectic, not easily definable by microscopy, should be less than 1 at.% Si. The effect of ytterbium addition on silicon has not been investigated owing to experimental difficulties, but also in this case we observe a eutectic reaction, as determined by DTA and micrographic analyses, at 1145 °C and 82 at.% Si.

3.1. Yb₅Si₃

The first compound, starting from Yb, corresponds to Yb_5Si_3 [8]; it is formed by a peritectic reaction at 1630 °C and crystallizes with the hexagonal Mn_5Si_3 -type of structure. The variations in the lattice constant values (Table 1) show the possibility for this compound of a little solid solubility range on the Si-rich side. The lowest values, however, are probably due to the use of a Yb metal containing hydrogen which has been shown to decrease the unit cell dimensions of the Mn_5Si_3 - and Cr_5B_3 -type compounds formed by divalent rare earths and alkaline earths with XIV and XV group elements (Ref. [9] and references cited therein). The lattice values of our samples, prepared at high temperatures at which the hydrogen can escape through the wall of the Ta containers, should be more reliable.

3.2. Yb_5Si_4

It is one of the two new phases found in this system. It is formed by a peritectic reaction at about 1680 °C, but the temperature is only indicative as thermal analysis above 1650 °C shows some problems due to the reactivity of these alloys with the container material. The Guinier powder pattern could be indexed with an orthorhombic cell whose dimensions suggested isotypism with Sm_5Ge_4 . An intensity calculation carried out with the same positional parameters as for Sm_5Ge_4 [10] confirmed this hypothesis.

3.3. YbSi

On the equiatomic composition we confirm the formation of YbSi [11]. It is a congruent melting compound at a temperature a little higher than 1700 °C, with the same uncertainty in the temperature as for Yb₅Si₄. The crystal structure corresponds to the orthorhombic CrB-type; the lattice constant values are nearly the same in all de-



Fig. 1. The phase diagram of the Yb-Si system.

terminations [12,13] and therefore can be considered a line compound.

3.5. Yb₃Si₅

3.4. Yb_3Si_4

This is the second new compound we found in this system. It is formed by a peritectoid reaction at 980 °C and crystallizes with the orthorhombic Ho_3Si_4 -type; this new structure type, recently determined by single crystal X-ray diffraction measurements [14], is characterised by a stacking of slabs of YbSi (CrB-type) and Yb_3Si_5 (Th_3Pd_5-type). The exact stoichiometry should be Yb_8Si_{10.67}, depending on the fractional occupation (1/3) of the 8*f* site in the *Cmcm* space group. A crystal structure refinement, however, would be necessary to confirm for Yb the same situation as for Ho, but up to now attempts to find a single crystal apt to data collection failed.

Yb₃Si₅ was firstly reported by Iandelli et al. [7] who determined the crystal structure by X-ray powder methods and studied its valence instability. Its structure, Th₃Pd₅type, can be obtained from the AlB₂-type by choosing a larger unit cell, related to the preceding values by $a' \approx$ $a\sqrt{3}$ and $c' \approx c$, removing from each Si hexagonal atomic plane one sixth of the Si atoms and allowing small rearrangements of the positional parameters of both Yb and Si. The crystal structure was then confirmed by single crystal determination [2,15], while the magnetic and other physical properties were the object of several investigations, especially by photoemission spectroscopy [2,16–18]. The results obtained gave evidence of mixed valence behaviour for Yb in the bulk (valence 2.52), whilst the Yb atoms at the surface, or just below, are in a divalent state.

Table 1 Crystallographic data for the intermediate phases of the Yb–Si system

Compound	At.% Si	Structure type	Lattice constants (Å)			Notes	Ref.
			a	b	С		
Yb ₅ Si ₃	37.5	Mn ₅ Si ₃	8.264(1)	_	6.254(1)		This work
		$hP16-P6_3/mcm$	8.255(1)	_	6.239(1)	Si-rich	This work
		-	8.23	_	6.19		[8]
			8.258(1)	_	6.239(1)		[20]
			8.25(1)	_	6.28(1)		[21]
			8.215	_	6.186		[22]
Yb ₅ Si ₄	44.44	Sm_5Ge_4 oP36-Pnma	7.262(2)	14.784(4)	7.700(2)		This work
YbSi	50	CrB	4.180(1)	10.314(2)	3.762(1)		This work
		oC8-Cmcm	4.19(1)	10.35(2)	3.77(1)		[11]
			4.178(5)	10.31(1)	3.768(2)		[12]
			4.18	10.31	3.77		[13]
Yb ₃ Si ₄ ^a	57.1	Ho ₃ Si ₄ oC18.67-Cmcm	4.158(1)	23.489(4)	3.772(1)		This work
Yb ₃ Si ₅	62.5	Th ₃ Pd ₅	6.515(1)	-	4.094(1)		This work
		$hP8-P\overline{6}2m$	6.5152(2)	_	4.0911(2)		[2]
			6.512	_	4.090		[7]
			6.508(2)	_	4.092(1)	s.c.	[15]
YbSi _{2-x}	62.5-63.5	AlB ₂	3.781(1)	_	4.101(1)		This work
		hP3-P6/mmm	3.770(1)	_	4.098(1)	Si-rich	This work
			3.784	_	4.098		[6]
			3.771	_	4.098		[23]
Yb ₂ Si ^b	33.33	Anti-PbCl ₂ oP12-Pnma	7.501(8)	4.781(6)	8.951(5)		This work

s.c., single crystal.

^a See Section 3.4.

^b See Section 3.7.

Fractional, intermediate valence value has been observed also in Si–Yb interfaces with a valence value of 2.37 [19]. Yb₃Si₅ is formed by a peritectoid reaction at 965 °C, a temperature value in substantial agreement with that

evaluated from vapour pressure measurements: T =

 $Yb_3Si_5 \rightarrow Yb_3Si_4 + YbSi_{2-x}$

 977 ± 34 °C, for the equilibrium

3.6. $YbSi_{2-x}$

Rare earth disilicides crystallize with three main structural types, ThSi_2 , GdSi_2 , AlB_2 , closely related to one another. GdSi_2 can be considered an orthorhombic deformation of the tetragonal ThSi_2 -type; generally it is indicated as the modification stable at low temperature and transforms to the ThSi_2 -type at temperatures that increase from Pr to Dy. The AlB_2 -type is a representative of a transposition structure of ThSi_2 and appears from Gd to Lu.

In no case however, except perhaps in the ThSi₂ type, disilicides realize a stoichiometric 1:2 ratio, so these compounds can be better represented by RSi_{2-x} with *x* values which change sensibly along the series, from one author to another and with improvements in the determination techniques.

 $YbSi_{2-x}$ firstly reported by Iandelli et al. [7] has been

recently studied by Grytsiv et al. [2]; it is formed by a peritectic reaction at 1425 °C at about 63 at.% Si and decomposes at 770 °C with a eutectoid reaction:

$$YbSi_{2-x} \rightarrow Yb_3Si_5 + Si_5$$

The decomposition temperature estimated from the results of vapor pressure measurements is $T=783\pm30$ °C, in good agreement with the DTA value.

It crystallizes with the Si-defective AlB_2 structure and the lattice constant values indicate a narrow solid solubility range from 62.5 to 63.5 at.% Si [2].

3.7. Further compounds

Due to the high similarity of Yb with Ca and to the existence of the very stable Ca₂Si compound [24], anti-PbCl₂ type, we tried to prepare the isotypic compound Yb₂Si. DTA on alloys around 33.33 at.% Si performed on as-cast as well as on annealed samples at high and low temperatures did not reveal any thermal effect other than eutectic or melting. X-ray powder patterns of these alloys, and even of those from powders obtained by low-temperature slow reaction of the two elements, always showed the reflections due to Yb and Yb₅Si₃. Only in one case a Guinier powder pattern of a sample on the 5/3 composition, prepared at high temperature and quenched,

showed, among the strong lines of Yb_5Si_3 , seven reflections which could be indexed with an orthorhombic cell pertaining to the anti-PbCl₂ structure type whose lattice constant values (Table 1) could support the existence of Yb_2Si . No other indications of its existence, however, could be thereafter obtained; this question therefore is still open and further work is needed to solve it.

4. Concluding remarks

The phase diagram of the Yb–Si system has been investigated almost in the whole composition range finding two new intermediate phases: Yb_5Si_4 and Yb_3Si_4 . Compared to the Ca–Si system, which is expected to be very similar, no great similarities appear: CaSi and YbSi are isotypic, CrB-type, then only two other phases have the same stoichiometry but not the crystal structure adopted, indicating that in this case valence electron concentration more than atomic dimensions drive compound formation and the valence instabilities of ytterbium when alloyed with silicon increase this possibility. The shape of the diagram and the high temperature reached, moreover, show Yb more similar to heavy rare earths than to alkaline earth elements.

At present the work concerning the Yb–Si system is progressing in two directions.

- Determination of the thermochemical properties of the intermediate phases by means of vapor pressure measurements over the various biphasic regions. The enthalpy changes for the high temperature decomposition reactions have been determined and the heat of formation of the intermediate Yb–Si phases derived therein. The results so far obtained will be reported separately [25]. Some results have been anticipated here.
- An investigation concerning the determination of the physical properties of the Yb–Si compounds in a wide temperature range (specific heat, magnetic susceptibility, electrical resistivity) [26].

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