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Cerium-silicon system

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Abstract

The Ce–Si phase diagram was constructed by means of differential thermal, X-ray and metallography examination of 15 as-cast key alloys. Ce_5Si_3 , Ce_3Si_2 , Ce_5Si_4 , CeSi were confirmed. Two cerium disilicides were found, $CeSi_{2-a1}$ (α -GdSi₂ structure type) and $CeSi_{2-a2}$ (α -ThSi₂ structure type). The two-phase region $CeSi_{2-a1}+CeSi_{2-a2}$ is very narrow. CeSi and $CeSi_{2-a1}$ melt congruently at 1630 and 1725 °C, respectively. The intermetallics Ce_5Si_3 , Ce_5Si_4 , $CeSi_{2-a2}$ form in peritectic reactions at 1260, 1335, 1500 and ~1575 °C, respectively. Three eutectics occur at 635, 1532±12 and 1198±2 °C and the compositions 10.5, 55 and 82 at% Si, respectively. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Ce–Si system shown in Ref. [1] is based mainly on the data of Benevovsky et al. [2]. The following cerium silicides were established to form in the system: Ce_5Si_3 (Cr_5B_3 structure type) [3], Ce_3Si_2 (U_3Si_2) [4], Ce_5Si_4 (Zr_5Si_4) [5], CeSi (FeB) [6], Ce_3Si_5 (α -GdSi₂) [6], CeSi₂ (α -ThSi₂) [7].

In Ref. [2] the exact composition of cerium disilicide with α -GdSi₂ structure type was not established. Benevovsky et al. [2] designated it CeSi_{2-x} thus specifying a deficiency of silicon. As a result of an evaluation of the available information, Munitz et al. [8] ascribed to this compound the composition Ce₃Si₅, as it is given in Ref. [1].

According to Ref. [1], Ce_5Si_3 , Ce_3Si_2 , Ce_5Si_4 , CeSi and $CeSi_2$ melt congruently at 1400, 1390, 1440, 1470 and 1620 °C, respectively. Ce_3Si_5 forms due to the peritectic reaction $L + CeSi_2 \leftrightarrow Ce_3Si_5$ at ~1560 °C. The mode and temperature of this compound formation was not established by Benevovsky et al. [2]. The Ce- and Si-rich eutectics are shown to crystallize at 650 °C (8 at% Si) and at 1200 °C (87 at% Si), respectively.

In accordance with Ref. [1], all the compounds, except $CeSi_2$ are line phases. The homogeneity region of $CeSi_2$ is

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from 64 to 66.7 at% Si. Yashima and Sato [9] showed the compound Ce_3Si_5 (or CeSi_{2-x}) to contain 63 at% Si instead of 62.5 according to Massalski [1].

Buyanov et al. [10] believe the interpretation of the character of phase equilibria in the region 62.5-66.7 at% Si [1] to be doubtful, and assume the formation of only the disilicide CeSi_{2-a} with a homogeneity range of 62.5-66.7 at% Si which undergoes a polymorphous transformation. The structures α -ThSi₂ and α -GdSi₂ were ascribed to the high- and low-temperature modifications of the compound.

Houssay et al. [11] report a continuous transition α -ThSi₂ $\rightarrow \alpha$ -GdSi₂ when the silicon content decreases, the homogeneity region being from 61.5 to 67 at% Si.

For the related system Pr–Si, Boutarek et al. [12] report three individual compounds O_1 , O_2 , and Q in the concentration interval 61.5–66.7 at% Si. The homogeneity regions were shown to be: $O_1 = 61.8-63.0$ at% Si; $O_2 =$ 64.3-65.2 at% Si; Q=65.4–66.3 at% Si. The compounds O_1 and O_2 were shown to crystallize in the orthorhombic α -GdSi₂-type structure. For the silicon-richest compound Q the tetragonal α -ThSi₂ structure has been reported. The O_2 compound was shown to melt congruently, the O_1 is supposed to form via a solid-state reaction. For the Q compound two ways of formation were discussed: $O_2 + \langle Si \rangle \leftrightarrow Q$ and $L + O_2 \leftrightarrow Q$.

For the other related system La–Si we have recently shown existence of two individual compounds in the concentration interval 62 to 67 at% Si [13] instead of one

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compound $LaSi_{2-a}$ discussed in Ref. [10]. The new compounds were named $LaSi_{2-a1}$ and $LaSi_{2-a2}$, thus specifying their location within the homogeneity range of the previously accepted compound $LaSi_{2-a}$. $LaSi_{2-a1}$ melts conguently and crystallizes in the α -GdSi₂ structure. The Si-richest compound $LaSi_{2-a2}$ with the α -ThSi₂ structure forms via the peritectic reaction $L + LaSi_{2-a1} \leftrightarrow LaSi_{2-a2}$. A similar character of phase equilibria in the concentration range under discussion can be expected for the Ce–Si system, as well.

Analysis of R-Si systems has shown that:

- 1. Congruent melting is not typical for the compounds R_5Si_3 , R_3Si_2 and R_5Si_4 of the light rare earths. Therefore the question of the way of formation of Ce_5Si_3 , Ce_3Si_2 and Ce_5Si_4 is open.
- 2. The congruent melting temperatures of the compounds CeSi and CeSi₂ [1] (1470 and 1620 °C, respectively) seem to be rather low, as the related compounds LaSi, PrSi, LaSi_{2-a1} and PrSi_{2-a} melt at 1620, 1657, 1730 and 1712 °C, respectively [13,14].

Thus, the Ce–Si system needs additional experimental research.

Based on the concept of a regular variation of the R-Si phase diagrams, as shown in Ref. [15], our prognosis of

the Ce–Si system is shown in Fig. 1. The temperatures of the invariant equilibria were estimated using a linear correlation of invariant temperatures versus the melting points of the rare earths as reported in Ref. [16].

Thus, the goal of the present work is to verify the above prognosis of the Ce–Si system by studying a minimum number of as-cast alloys.

2. Experimental procedure

The Ce–Si system was studied on as-cast alloys of 15 compositions. The alloys were prepared from Ce (99.4%) and Si (99.999%) by arc-melting and studied by X-ray diffraction, metallography, DTA analyses and, for a few samples by the Pirani–Altertum (P–A) method, as described in Ref. [13].

3. Results and discussion

The alloy compositions and phase compositions of the samples studied are given in Table 1 together with the phase transformation temperatures. The Ce–Si phase diagram resulting from our study is shown in Fig. 2. The existence and the crystal structures of the compounds



Fig. 1. Predicted Ce-Si phase diagram.

Table 1		
Composition and phase conter	t of as-cast Ce-Si alloys and	phase transformation temperatures

Alloy composition (at% Si)	Phase content	Thermal analysis results (°C)									
		Liquidus	$\begin{array}{c} L\leftrightarrow\!\langle\gamma\text{-}Ce\rangle\\ +Ce_5Si_3\end{array}$	$\begin{array}{c} L+Ce_{3}Si_{2}\\ \leftrightarrow Ce_{5}Si_{3} \end{array}$	$\begin{array}{c} L + Ce_5Si_4 \\ \leftrightarrow Ce_3Si_2 \end{array}$	$\begin{array}{l} L+CeSi\\ \leftrightarrow Ce_5Si_4 \end{array}$	L⇔CeSi +CeSi _{2-a1}	$\frac{L + \text{CeSi}_{2-a1}}{\text{CeSi}_{2-a1}}$	$\frac{L + \text{CeSi}_{2-a2}}{\text{CeSi}_{2-a2}}$	$\begin{array}{l} L + CeSi_{2-a1} \\ \leftrightarrow CeSi_{2-a2} \end{array}$	$\begin{array}{c} L \leftrightarrow \mathrm{CeSi}_{2-a2} \\ + \langle \mathrm{Si} \rangle \end{array}$
10.0	$\langle \gamma$ -Ce \rangle +eutectic ($\langle \gamma$ -Ce \rangle +Ce ₅ Si ₃)	655	635	-	-	-	-	-	-	-	-
12.0	Ce_5Si_3 + eutectic ($\langle \gamma$ -Ce \rangle + Ce_5Si_3)	775	635	-	-	-	-	-	-	-	-
37.5	$Ce_5Si_4 + Ce_5Si_3 + eutectic (\langle \gamma - Ce \rangle + Ce_5Si_3)$	1440	-	1260 ^a	1340	-	-	-	-	-	-
39.9	$Ce_3Si_2 + Ce_5Si_3$	1500	-	1260	1330	-	-	-	-	-	-
44.4	CeSi+Ce ₅ Si ₄	1575	-	-	-	1485	-	-	-	-	-
47.8	CeSi+Ce ₅ Si ₄	1605	-	-	-	1515	-	-	-	-	-
50.1	CeSi	1630	-	-	-	-	1520	-	-	-	-
53.0	$CeSi + eutectic (CeSi + CeSi_{2-a1})$	1605	-	-	-	-	1545	-	-	-	-
61.1	CeSi _{2-a1} +eutectic (CeSi+CeSi _{2-a1})	1680	-	-	-	-	1530	-	-	-	-
62.6	CeSi _{2-a1}	1720	-	-	-	-	-	1665	-	-	-
64.1	CeSi _{2-a2}	1715	-	-	-	-	-	-	1315	-	-
66.7	CeSi _{2-a2}	1695	-	-	-	-	-	-	-	1560	1200
68.0	$\text{CeSi}_{2-a2} + \text{eutectic} (\text{CeSi}_{2-a2} + \langle \text{Si} \rangle)$	1665	-	-	-	-	-	-	-	1590 ^b	1200
75.0	CeSi_{2-a2} +eutectic (CeSi_{2-a2} + $\langle \text{Si} \rangle$)	1455	-	-	-	-	-	-	-	-	1195
90.0	$\langle Si \rangle$ +eutectic (CeSi _{2-a2} + $\langle Si \rangle$)	1320	-	-	-	-	-	-	-	-	1195

^a Temperature taken on cooling.

^b Solidus temperature determined by the P-A method.

 Ce_5Si_3 , Ce_3Si_2 , Ce_5Si_4 and CeSi were confirmed. Two cerium disilicides were found to form named $CeSi_{2-a1}$ and $CeSi_{2-a2}$ in a similar way as in the La–Si system. The

crystal structure data and the lattice parameters of the compounds are shown in Table 2. Our results and literature data are presented.



Fig. 2. Ce–Si phase diagram resulted from this investigation: (\triangle) DTA data at heating, (∇) DTA data at cooling, (\Box) literature data, (\diamondsuit) solidus temperature according to Pirani–Altertum data.

Table 2 Crystal structure data of cerium silicides

Phase	Structure	Unit cell dimensi	ons (Å)	Remarks	Reference	
		a	b	с		
Ce ₅ Si ₃	Tetragonal Cr ₅ B ₃	7.89	_	13.77		[17]
5 5		7.878 ± 0.004	_	13.67±0.01	60.1Ce-39.9Si	This work
Ce ₃ Si ₂	Tetragonal U ₃ Si ₂	7.79	_	4.36		[17]
5 2	5 2	7.780 ± 0.006	_	4.367 ± 0.006	60.1Ce-39.9Si	
Ce ₅ Si ₄	Tetragonal Zr ₅ Si ₄	7.93	_	15.04		[17]
		7.935 ± 0.003	-	15.04 ± 0.01	62.5Ce-37.5Si	This work
		7.936 ± 0.001	_	15.029 ± 0.005	55.6Ce-44.4Si	This work
		7.936 ± 0.006	_	14.98 ± 0.02	52.2Ce-47.8Si	This work
CeSi	Orthorhombic FeB	8.302	3.962	5.964		[17]
		8.288 ± 0.004	3.964 ± 0.002	5.952 ± 0.003	52.2Ce-47.8Si	This work
		8.298 ± 0.004	3.961 ± 0.002	5.959 ± 0.002	49.9Ce-50.1Si	This work
		8.295 ± 0.003	3.961 ± 0.001	$5.958 {\pm} 0.002$	47Ce-53Si	This work
		8.284 ± 0.003	3.960 ± 0.002	5.954 ± 0.003	38.9Ce-61.1Si	This work
CeSi _{2-a1}	Orthorhombic α -GdSi ₂	4.19	4.13	13.92		[17]
2 41	_	4.190 ± 0.003	4.113±0.003	13.906 ± 0.007	47Ce-53Si	This work
		4.183 ± 0.002	4.105 ± 0.002	13.912 ± 0.005	38.9Ce-61.1Si	This work
		4.189 ± 0.001	4.109 ± 0.001	13.917 ± 0.003	37.4Ce-62.6Si	This work
CeSi _{2-a2}	Tetragonal α-ThSi ₂	4.27-4.16	-	13.88-13.84		[17]
2 42		4.154 ± 0.001	_	13.822 ± 0.005	35.9Ce-64.1Si	This work
		4.192 ± 0.001	_	13.913 ± 0.005	33.3Ce-66.7Si	This work
		4.188 ± 0.001	-	13.897 ± 0.005	32Ce-68Si	This work
		4.189 ± 0.001	_	13.920 ± 0.008	25Ce-75Si	This work
		$4.185 {\pm} 0.002$	_	13.907 ± 0.008	10Ce-90Si	This work

According to the results obtained, CeSi and CeSi_{2-a1} melt congruently at 1630 and 1725 °C, respectively. The compounds Ce₅Si₃, Ce₃Si₂ and Ce₅Si₄ form via peritectic reactions at 1260, 1335 and 1500 °C, respectively.

Three eutectic equilibria occur in the Ce-Si system:

 $L \leftrightarrow \langle \gamma - Ce \rangle + Ce_5 Si_3$ at 635 °C and 10.5 at% Si

 $L \leftrightarrow CeSi + CeSi_{2-a1}$ at 1532±12 °C and 55 at% Si

 $L \leftrightarrow CeSi_{2-a^2} + \langle Si \rangle$ at 1198±2 °C and 82 at% Si

The last temperature corresponds well to the data of Ref. [2].

The location of the invariant points was determined on the basis of microstructure examination (Fig. 3). Thus, in the alloys with 10 and 12 at% Si (Fig. 3a,b) small amounts of the primary phases and large amounts of the eutectic were observed. As the morphology of the primary grains is different, it is concluded that the eutectic composition is located between the compositions of the mentioned alloys. According to the X-ray diffraction results the above eutectic contains γ -Ce and Ce₅Si₃.

A comparison of the microstructures of the alloys with 53 and 61.1 at% Si (Fig. 3c,d) reveals a different character of the primary grains in the two alloys: light-gray in the alloy with 53 at% Si (Fig. 3c) and bright with the traces of solid-state transformations in the alloy with 61.1 at% Si (Fig. 3d,e). So, the alloys are located on both sides of the invariant eutectic point of the equilibrium $L\leftrightarrow CeSi +$

CeSi_{2-a1}. As derived from the X-ray examination, the mono- and disilicide with the structures of FeB and α -GdSi₂, respectively, take part in the eutectic reaction. The relative quantity of the eutectic in the alloy with 53 at% Si is higher than in the alloy with 61.1 at% Si, implying the eutectic composition to be more close to the alloy with 53 at% Si. The intersection of the primary crystallization curves of the phases CeSi and CeSi_{2-a1} with each other and with the invariant eutectic horizontal allows to conclude that eutectic contains ~55 at% Si.

The concentration intervals of CeSi_{2-a1} and CeSi_{2-a2} were determined by comparing the microstructures of the alloys with 61.1 to 66.7 at% Si (Fig. 3e-h). According to these microstructures, all the samples are single-phase. However, the alloys with 61.1 and 66.7 at% Si contain small quantities of the eutectics ($CeSi + CeSi_{2-a1}$) and $(\text{CeSi}_{2-a^2} + \langle \text{Si} \rangle)$, respectively. This is confirmed by the appearance of small thermal effects in the DTA curves at 1530 and 1200 °C, respectively. Thus, the Si-poor boundary of the homogeneity range of the CeSi_{2-a1} phase is located between 61.1 and 62.6 at% Si. The Si-rich boundary of the homogeneity range of the CeSi_{2-a^2} phase is located at the composition 66.7 at% Si. These confirm the results of Ref. [11] concerning location of the boundaries of the homogeneity region of CeSi_{2-a} at 61.5 and 66.7 at% Si.

Based on the results of our X-ray examination (Table 2) it can be seen that *a* and *c* lattice parameters of cerium disilicide with α -GdSi₂ structure measured for the alloy with 62.6 at% Si are essentially higher than those of



Fig. 3. Microstructures of as-cast Ce–Si alloys: (a) 10.0 at% Si, $\times 250$, $\langle \gamma$ -Ce \rangle + eutectic ($\langle \gamma$ -Ce \rangle +Ce₅Si₃); (b) 12.0 at% Si, $\times 500$, Ce₅Si₃+eutectic ($\langle \gamma$ -Ce \rangle +Ce₅Si₃); (c) 53.0 at% Si, $\times 250$, CeSi+eutectic (CeSi+CeSi_{2-a1}); (d) 61.1 at% Si, $\times 250$, CeSi_{2-a1}+eutectic (CeSi+CeSi_{2-a1}); (e) 61.1 at% Si, $\times 500$, CeSi_{2-a1}; (f) 62.6 at% Si, $\times 250$, CeSi_{2-a1}; (g) 64.1 at% Si, $\times 250$, CeSi_{2-a2}; (h) 66.7 at% Si, $\times 250$, CeSi_{2-a2}; (i) 68.0 at% Si, $\times 250$, CeSi_{2-a2}+eutectic (CeSi_{2-a2}+ $\langle Si \rangle$).

Table 3 Comparison of the predicted and experimental temperatures of invariant reactions in Ce–Si system

Phase transformation	Temperature (°C)				
	Predicted	Experimental			
$L \leftrightarrow \langle \gamma - Ce \rangle + Ce_5 Si_3$	625±25	635			
L+CeSi↔Ce ₅ Si ₄	1460 ± 10	1500			
L⇔CeSi	1590 ± 15	1630			

disilicide with α -ThSi₂ structure in the alloy with 64.1 at% Si. Therefore a continuous transition between the two structures as reported in Ref. [11] is hardly possible. Then thermal effects at ~1575 °C can be attributed to the invariant equilibrium L + CeSi_{2-a1} \leftrightarrow CeSi_{2-a2}. Hence, congruent melting is valid for the CeSi_{2-a1} phase with α -GdSi₂ structure, as it was observed in the La–Si system [13]. The distectic point occurs at a composition of about 63 at% Si.

The boundaries of the two-phase field CeSi_{2-a1} + CeSi_{2-a^2} are located between 62.6 and 64.1 at% Si. The results obtained did not allow us to establish their exact location. The stripped nature of the grains in the microstructures of the alloys with 61.1 to 64.1 at% Si (Fig. 3e-g) resulting from solid-state transformations allow us to conclude that the two-phase field boundaries shift towards Si-poorer compositions when the temperature decreases. So, the alloy containing 62.6 at% Si at high temperatures is located in the CeSi_{2-a1} single-phase field and at lower temperatures in the $CeSi_{2-a2}$ single-phase field. The absence of traces of the solid-state transformation in the microstructures of the alloys with 66.7 and 68 at% Si (Fig. 3h,i) is probably due to crystallization closer to the more equilibrium of these alloys. Thus, the homogeneity region of CeSi_{2-a1} becomes narrower when the temperature decreases. This agrees with data [2] corresponding to the absence of a homogeneity region of the phase with α -GdSi₂ structure.

Based on the absence of thermal effects in the range $CeSi+CeSi_{2-a1}$ at temperatures lower than the solidus, and also by analogy with the La–Si [13] and Pr–Si [12]

systems, we consider the phases with α -GdSi₂ and α -ThSi₂ structures to be individual compounds named CeSi_{2-a1} and CeSi_{2-a2}, rather than polymorphous modifications of the same compound CeSi_{2-a}.

Concluding, the present experimental results and the predicted phase diagram (Fig. 1) correspond well. Table 3 shows the comparison of the temperatures of invariant reactions as predicted and as determined experimentally.

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