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Isothermal cross-section of the Ce-Ru-Si phase diagram at 600°C

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Abstract

The interaction of the components in the Ce-Ru-Si system at 600°C was investigated over the whole concentration range by X-ray powder and monocrystal diffraction, metallography, and X-ray microprobe analysis. The formation of the previously reported phases, $CeRu_2Si_2$ and $CeRu_3Si_2$, was confirmed and six new ternary compounds were observed. The crystal structures of the compounds $CeRuSi_3$, $CeRuSi_2$, and CeRuSi were determined.

Keywords: Rare earths compounds; Phase equilibria; Ternary system

1. Introduction

The ternary compounds RE-TM-X (RE=rare earth, TM=transition metal, X=Si or Ge) are known to exhibit a number of interesting properties such as heavy-fermion superconductivity, Kondo behavior, anomalous magnetism, and/or intermediate valency. The present investigation has obtained data about the interaction of the components in the Ce-Ru-Si ternary system and about the crystal structure of three new ternary intermetallic compounds.

The binary systems bounding the ternary system have been described in detail in the literature. In Ref. [1] the Ce-Si binary system is reported as a review of the all previous works, in which this binary system was investigated in the whole concentration range by X-ray powder diffraction, DTA and metallographic analyses. Six intermediate phases were found in this work: Ce_5Si_3, Ce_3Si_2, Ce_5Si_4, CeSi, $Ce_3Si_{5,}$ and $CeSi_{2-x}$. Except $CeSi_{2-x}$ all intermediate binary phases have a fixed composition. The homogeneity range of $CeSi_{2-x}$ stretches from 63.5 to 66.7 at.% Si.

According to Munitz et al. [1], at 600°C, cerium and silicon do not dissolve any noticeable ammount of the second component. Crystal structure and lattice parameter

Table 1
Crystal structure and lattice parameter data for the intermediate phases in the Ce-Si system [1]

Phase	Composition, at.% Si	Space group	Prototype	Lattice parameters, nm		
				a	*b*	*c*
Ce_5Si_3	37.5	I4/mcm	W_5Si_3	0.7868		1.373
Ce_3Si_2	40	P4/mbm	U_3Si_2	0.780		0.434
Ce_5Si_4	44.4	$P4_12_12$	Zr_5Si_4	0.793		1.504
CeSi	50	Pnma	FeB	0.8302	0.3962	0.5964
Ce_3Si_5	62.5	Imma	α-$GdSi_2$	0.4192	0.413	1.392
$CeSi_2$	63.5 to 66.7	$I4_1/amd$	α-$ThSi_2$	0.4192		1.390

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Table 2
Crystal structure and lattice parameter data for the intermediate phases in the Ce-Ru system [2]

Phase	Composition, at.% Ru	Space group	Prototype	Lattice parameters, nm		
				a	*b*	*c*
Ce_3Ru	25	Pnma	Fe_3C	0.7242	0.9863	0.6419
Ce_7Ru_3	30	$P6_3$ mc	Th_7Fe_3	0.9802		0.6261
$Ce_{16}Ru_9$	36	R3m	$Ce_{16}Ru_9$	1.3645		2.2742
Ce_4Ru_3	42.9	C2/m	Ce_4Ru_3	0.8400	1.3837	0.5985
$CeRu_2$	66.7	Fd3m	$MgCu_2$	0.7545		

Table 3
Crystal structure and lattice parameter data for the intermediate phases in the Ru-Si system [4]

Phase	Composition, at.% Si	Space group	Prototype	Lattice parameters, nm		
				a	*b*	*c*
Ru_2Si[a]	33.3	Pnma	Co_2Si	0.5279	0.4005	0.7418
Ru_5Si_3[a]	37.5	Pbam	Rh_5Ge_3	0.52457	0.9819	0.40236
Ru_4Si_3	42.9	Pnma	Rh_4Si_3	0.51936	0.40216	0.1.7343
RuSi	50	Pm3m	CsCl	0.2909		
Ru_2Si_3	60	Pbcn	Ru_2Si_3	1.1057	0.8934	0.5533

[a] Not existing at 600°C.

data for the binary phases of the Ce-Si system are summarized in Table 1 [1].

The interaction of the components in the Ce-Ru binary system was studied in detail by Palenzona [2]. There are five intermediate phases in the Ce-Ru system: $CeRu_2$, Ce_4Ru_3, $Ce_{16}Ru_9$, Ce_7Ru_3, Ce_3Ru. All intermediate phases form peritectically and exist at fixed compositions. Both Ce and Ru do not dissolve any noticeable ammount of the second component. Crystal structure and lattice parameter data for the binary phases of the Ce-Ru system are summarized in Table 2 [2].

The binary phase diagram Ru-Si was investigated in ref. [3]. There are five intermediate phases in the Ru-Si system: Ru_2Si_3, RuSi, Ru_4Si_3, Ru_5Si_3, and Ru_2Si. Two of them, Ru_5Si_3 and Ru_2Si, exist at the temperatures above 1330 and 1225°C respectively and are not considered in our work performed at the 600°C. Ruthenium does not dissolve silicon at 600°C, the maximum solubility of ruthenium in silicon was found to be 3 at.% at 1370°C but has an insignificant value at 600°C. All intermediate phases have fixed compositions.

Crystal structure and lattice parameter data for the intermediate Ru-Si phases are summarized in Table 3 [4].

Table 4
Crystal structure and lattice parameter data published for two of the ternary intermediate phases of the Ce-Ru-Si system

Phase	Space group	Prototype	Lattice parameters, nm			Ref.
			a	*b*	*c*	
$CeRu_2Si_2$	I4/mmm	$CeAl_2Ga_2$	0.4195		0.97972	[5]
$CeRu_3Si_2$	$P6_3/m$	$LaRu_3Si_2$	0.568		0.712	[6]

Systematic studies of the ternary Ce-Ru-Si system through the whole concentration range have not previously been performed. Nevertheless, some information has been reported concerning crystallographic and physical properties of two ternary compounds, $CeRu_2Si_2$ and $CeRu_3Si_2$. The crystallographic data that has been published for these two phases are given in Table 4 with references.

2. Experimental details

The present investigation was done with 114 samples having masses of about 1 g. They were prepared in an electric arc furnace under an argon atmosphere with a nonconsumable tungsten electrode and a water cooled copper hearth. The purity of cerium was 99 at.%, the purity of ruthenium and silicon was better than 99.9 at.%. Titanium was used as a getter during melting. The alloys were remelted two times in order to achieve complete fusion and homogeneity. Alloys with melting losses not exceeding 1 wt.% were chosen for the experiments. All alloys after melting were subjected to a homogenizing anneal in evacuated double-walled quartz ampoules containing titanium chips as getters. Annealing was performed in a resistance furnace at 600°C for 720 h with subsequent quench into ice water.

Metallography, X-ray powder diffraction, and electron probe X-ray analyses were used in the present investigation. In the metallographic studies, Ru-rich samples (>60 at.% Ru) were etched in an HNO_3+HCl (3:1) solution. A mixture HNO_3+H_2O (2:1) was used for etching alloys with <50 at.% Ce. Ce-rich samples (>50 at.% Ce) were etched by highly dilute HNO_3. Micro-

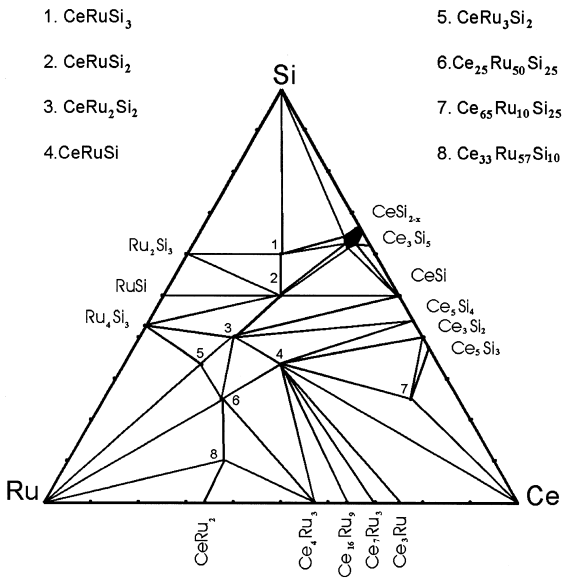

Fig. 1. Isothermal cross-section of the Ce-Ru-Si system at 600°C.

structures were examined with a 'Neophot 32' microscope at magnifications of 250x and 400x.

X-ray phase analyses were performed with an URS-60 generating unit with Cr K_α radiation (λ=0.229092 nm) for RKD-57 cameras having asymmetric film loading. For precision lattice parameters, one or the other of the following was used:

- ''DRON-2.0'' with Fe K_α radiation, λ=0.193728 nm;
- ''DRON-3.0'' with Cu K_α radiation, λ=0.154178 nm;
- FR-552 focusing monochromator camera with Cu $K_{\alpha 1}$ radiation, λ=0.154051 nm and Ge as an internal standard.

Electron probe X-ray analyses were performed with a 'Comebax Microbeam' analyzer. This device was used for

Table 6
Results of microprobe X-ray analyses of some alloys from the Ce-Pd-Ge ternary system

Alloy composition, (at.%)			Number of phases	Composition of phases, (at. %)		
Ce	Ru	Si		Ce	Ru	Si
30	20	50	2	25	25	50
				50	0	50
25	25	50	1	25	25	50
25	30	45	3	20	20	40
				25	25	50
				50	0	50
20	40	40	1	20	20	40
25	40	35	3	20	20	40
				33	33	34
				25	50	25
33.3	33.3	33.4	1	33	33	34
20	50	30	2	17	50	33
				25	50	25
50	20	30	3	33	33	34
				60	0	40
				65	10	25
25	50	25	1	25	50	25
15	65	20	3	17	50	33
				25	50	25
				0	100	0
30	50	20	3	25	50	25
				33	57	10
				57	43	0
40	40	20	3	33	33	34
				25	50	25
				57	43	0
50	30	20	2	33	33	34
				75	25	0
70	10	20	3	33	33	34
				100	0	0
				65	10	25
40	50	10	3	25	50	25
				33	57	10
				57	43	0
50	40	10	2	33	33	34
				57	43	0

Table 5
Crystal structure and lattice parameter data for the ternary intermediate phases in the Ce-Ru-Si system

N Phase	Space group	Prototype	Lattice parameters, nm		
			a	*b*	*c*
1. $CeRuSi_3$	I4mm	$BaNiSn_3$	0.4207(3)	–	0.9926(7)
$CeRuSi_2$[a]	$P2_1/m$	$NdRuSi_2$	0.4482(2)	0.4088(1) β=102.46(6)°C	8.305(2)
3. $CeRu_2Si_2$	I4/mmm	$CeAl_2Ga_2$	0.4190(2)		0.9790(5)
4. CeRuSi	Pnma	TiNiSi	0.7105(4)	0.4256(2)	0.7301(3)
5. $CeRu_3Si_2$	$P6_3/m$	$LaRu_3Si_2$	0.5718(4)		0.7112(4)
6. $Ce_{25}Ru_{50}Si_{25}$					
7. $Ce_{65}Ru_{10}Si_{25}$					
8. $Ce_{33}Ru_{57}Si_{10}$					

[a] Has been studied on a monocrystal.

phase identification of the individual grains in the microstructure by energy dispersive analyses of secondary electrons in combination with determination of the position and intensity of characteristic X-ray wavelengths.

DTA experiments were executed on high temperature VDTA-8M_2 equipment. (W-W/Re thermocouples) in BeO crucibles. Pure Fe, Cu and Pt metals were used as calibration standards.

3. Results and discussion

Results from the present measurements were used in the construction of the isothermal cross-section of the Ce-Ru-Si phase diagram at 600°C (Fig. 1). The binary phase α-$CeSi_{2-x}$ has a noticeable extension into the ternary space of the diagram. Other binary compounds from the Ce-Si, Ce-Ru, and Ru-Si systems exist at fixed compositions. It is found that the interaction of Ce, Ru and Si leads to the formation of at least eight ternary compounds, including the two phases already reported.

The crystallographic data obtained for the ternary compounds are given in the Table 5. The powder diffraction method was applied for determining the structure of $CeRuSi_3$, $CeRu_2Si_2$, CeRuSi, and $CeRu_3Si_2$. The structure of $CeRuSi_2$ was examined on a monocrystal.

Investigation of the powder diffraction data of alloys with the compositions $Ce_{25}Ru_{50}Si_{25}$, $Ce_{65}Ru_{10}Si_{25}$, and $Ce_{33}Ru_{57}Si_{10}$ leads to the speculation that even more ternary phases may exist at or near these compositions. However, no crystal structure determinations were performed because suitable monocrystals were not obtained. Support for our belief in the existence of these additional phases is based on results of X-ray microprobe analyses of alloys with nearly single phase compositions, and of alloys corresponding to two-phase and three-phase regions. These results are presented in Table 6.

The DTA technique was used for obtaining the melting temperatures of the following compounds (accuracy ±5°C):

$CeRu_3Si_2$ – 1352°C;
$CeRu_2Si_2$ – 1605°C;
$CeRuSi_3$ – 1592°C;
$Ce_{25}Ru_{50}Si_{25}$ – 1420°C;
$CeRuSi_2$ – 1500°C;
CeRuSi – 1365°C;
$Ce_{65}Ru_{10}Si_{25}$ – 1765°C.

According to the data of the microstructure analyses and DTA, the phases $CeRu_3Si_2$, $CeRu_2Si_2$, $CeRuSi_3$, and CeRuSi form from the liquid phase.

The interaction of the components in the ternary Ce-Ru-Si system proceeds by a complicated path and leads to the formation of eight compounds. Unlike to the ternary systems, in which the second component is Pt or Pd, in the Ce-Ru-Si system such compounds as $(RE)_2$ (TM)Ge_6 with Ce_2CuGe_6 type of the structure and Ce(Ru,Si)$_2$ with the AlB_2 type of the structure do not exist. The intermetallic $CeRuSi_2$ phase is the second compound with the new $NdRuSi_2$ type of structure.

Acknowledgements

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