Journal of Alloys and Compounds, 194 (1993) 63–66
JALCOM 529

Phase diagram of the Ce–Rh system

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(Received September 21, 1992)

Abstract

The phase diagram of the Ce–Rh system (0–70 at.% Rh) was investigated using differential thermal analysis, micrographic analysis, X-ray diffraction and electron microscopy. Seven compounds are formed in this system. Their existence was already known and has been confirmed in the present investigation. Ce_4Rh_3 and β-Ce_5Rh_3 previously reported have been deleted. The shape of the diagram is very different from that reported in the current literature, with melting points in the 20–60 at.% Rh range being lower by several hundreds of degrees Celsius. The rhodium-rich side of the system could not be investigated due to the reaction of the alloys with the container material at temperatures higher than 1350 °C.

1. Introduction

After the determination of the lanthanum–rhodium system [1] it became obvious that most of the rare earth–rhodium diagrams reported in the literature had been drawn only hypothetically; this situation was particularly evident for the cerium–rhodium system [2, 3]. Although the intermediate compounds seem to be well known, at least from a crystallographic point of view, great uncertainties exist in the shape of the diagram and in the melting properties of these phases.

As cerium intermetallic compounds often show interesting electronic, magnetic and transport properties, it was decided to re-examine the Ce–Rh phase diagram in order to obtain reliable information on the preparation of the phases.

2. Experimental details

Elemental cerium was a commercial product obtained from Koch-Light Laboratories, UK (purity, 99.8 wt.%). Rhodium was obtained from Johnson-Matthey, UK (purity, 99.9 wt.%) and was outgassed under a dynamic vacuum for 5 h at 800 °C.

Samples of about 1.0 g were prepared by melting weighed amounts of the two elements (in the form of fine turnings for cerium and powder for rhodium, pressed into small pellets) in a water-cooled, copper heart arc furnace under an argon atmosphere. The samples were transferred into molybdenum crucibles, closed by arc welding and placed in the differential thermal analysis equipment, where one or two thermal cycles were performed at heating and cooling rates of 10 or 20 °C $\min^{-1}$. For compositions richer than 65 at.% Rh only one heating run was carried out. The temperature measurements were accurate to within ± 5 °C. Some difficulties arose for alloys in the 30–50 at.% Rh range due to the slowness in reaching equilibrium conditions. After several thermal cycles it was decided to take into account the thermal effects obtained on heating.

X-ray investigations were carried out on powders and single crystals using a Guinier-Stoe camera and an Enraf Nonius CAD 4 automatic four-circle diffractometer with graphite-monochromated Mo Kα radiation. The powder intensities were calculated using the LAZY-PULVERIX program [4].

Metallographic examination was carried out using standard techniques; diluted "aqua regia" was used as the etching agent for high Rh-containing alloys.

Further identification of the phases was performed with the aid of electron microscopy and microprobe analysis. The standards used for semiquantitative determinations were pure metals and the other known phases of the system.

3. Results and discussion

Figure 1 shows the phase diagram of the Ce–Rh system derived from the analyses carried out as described in Section 2. Figure 2 shows the phase diagrams reported in the literature [2, 3]. Table 1 contains the crystallographic data for the intermediate phases.

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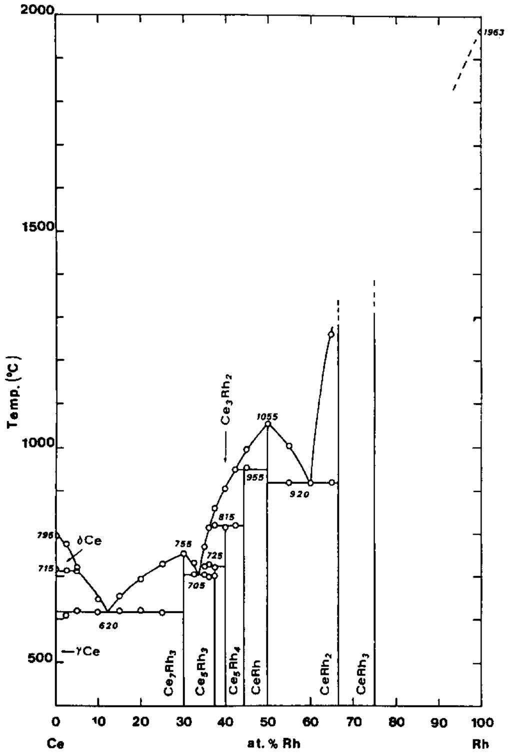

Fig. 1. Phase diagram of the Ce–Rh system obtained in the present investigation.

The melting point and transformation temperature of cerium used in the present investigation are close to the values given by Gschneidner [16] for the pure elements (798 and 726 °C respectively), the deviation for the former falling in the error range of the experimental temperature determination.

The solubility of rhodium in cerium seems to be very limited as no severe effect on the transformation temperature was observed. The solubility of cerium in rhodium has not been investigated owing to the high melting points of the corresponding alloys.

Seven intermediate phases are formed in this system all of which, except perhaps CeRh$_2$, appear to be line compounds.

At least three eutectic points occur: at 12.5 at.% Rh and 620 °C, 34 at.% Rh and 705 °C and 60 at.% Rh and 920 °C.

3.1. Ce$_7$Rh$_3$ (congruent melting, 755 °C)

This phase was identified by Raman [5] as the Ce$_3$Rh composition and later studied by Olcese [6]. We confirm its existence and structure. Several lattice parameter determinations around the stoichiometric composition showed the absence of a solid solution range for this phase.

3.2. Ce$_5$Rh$_3$ (peritectic formation, 725 °C)

Ghassem and Raman [11], in a review on the intermediate phases formed in some R–Rh systems, reported the existence of Ce$_5$Rh$_3$ with two crystallographic modifications depending on temperature, but in both cases no structural details were given. In the present investigation we have observed from single-crystal examination that Ce$_5$Rh$_3$ crystallizes with the tetragonal Pu$_5$Rh$_3$ structure type, but we obtained no indications of a polymorphic modification. Moreover, the powder pattern of Ce$_5$Rh$_3$ (Pu$_5$Rh$_3$ type) can be indexed with good agreement on the basis of a cubic structure (the b.c.c. Er$_5$Ir$_3$ type proposed by Blazina *et al.* [17]), following the relationships: $a_{\text{cub}} = (2)^{1/2} a_{\text{tetr}}$ and $a_{\text{cub}} \approx 2.45 c_{\text{tetr}}$. Therefore we believe that Ce$_5$Rh$_3$ exists only with one structure, corresponding to the Pu$_5$Rh$_3$ type.

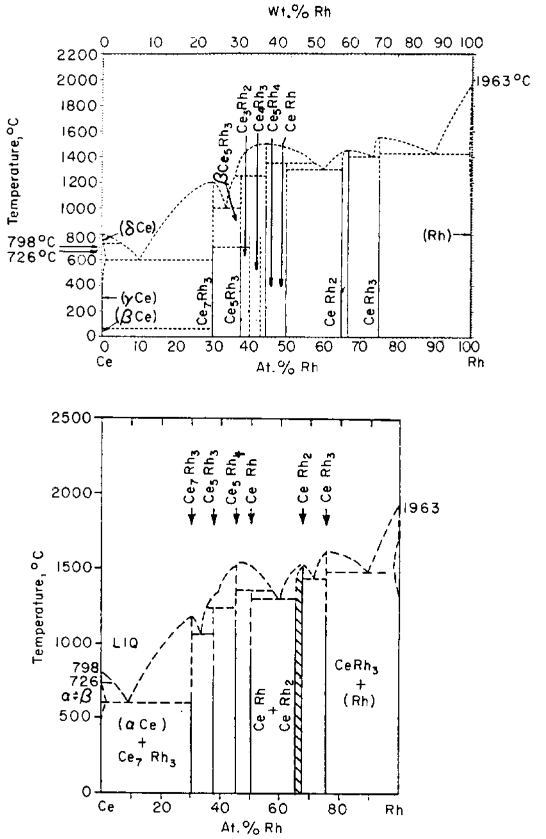

Fig. 2. Phase diagram of the Ce–Rh system: upper part, ref. 2; lower part, ref. 3.

3.3. Ce$_3$Rh$_2$ (peritectic formation, 815 °C)

The structure of this compound was investigated by Le Roy *et al.* [7] who found it to be isomorphous with the rhombohedral Er$_3$Ni$_2$ type. Single crystal and powder diffraction data have confirmed these results. Also in this case no indication of an extended solid solution range was found.

3.4. Ce$_4$Rh$_3$

This compound reported by Ghassem and Raman [11] could not be found in the present investigation.

TABLE 1. Crystallographic data for the intermediate phases of the Ce–Rh system

Compound	Structure type	Lattice constants (Å)			Notes	Reference
		a	*b*	*c*		
Ce_7Rh_3	Th_7Fe_3	10.051	–	6.378	P	This work
	(hP20-$P6_3mc$)	10.005	–	6.356	[a]	5
		10.023	–	6.376		6
Ce_5Rh_3	Pu_5Rh_3 (tP32-$P4/ncc$)	11.260	–	6.450	P, SC	This work
Ce_3Rh_2	Er_3Ni_2	8.858	–	16.794	P, SC	This work
	(hR45-$R\bar{3}$)	8.835	–	16.76		7
Ce_5Rh_4	Sm_5Ge_4	7.467	14.841	7.624	P	This work
	(oP36-$Pnma$)	7.434	14.86	7.604		8
CeRh	CrB	3.845	10.964	4.174	P	This work
	(oC8-$Cmcm$)	3.852	10.986	4.152		9
		3.855	10.966	4.153		10
$CeRh_2$	$MgCu_2$	7.545	–	–	P[b]	This work
	(cF24-$Fd\bar{3}m$)	7.543	–	–	P[c]	This work
		7.538	–	–		11
		7.547	–	–	Ce-rich	11
		7.534	–	–	Rh-rich	11
		7.550	–	–		12
		7.539	–	–		13
$CeRh_3$	$AuCu_3$	4.022	–	–	P[c]	This work
	(cP4-$Pm\bar{3}m$)	4.023	–	–		14
		4.012	–	–		5
		4.020	–	–		11
		4.024	–	–		15

P, powder diffraction; SC, single-crystal diffraction.

[a] Prepared as Ce_3Rh composition.

[b] At 65 at.% Rh.

[c] At 70 at.% Rh.

We prepared several alloys around this composition but always obtained two-phase samples. All the powder patterns obtained from these alloys in the as-cast state as well as after annealing at several temperatures showed the presence of lines corresponding to the adjacent phases Ce_3Rh_2 and Ce_5Rh_4. Therefore we can reasonably exclude the existence of Ce_4Rh_3.

3.5. *Ce_5Rh_4 (peritectic formation, 955 °C)*

Single-crystal studies were used by Raman [8] to establish the crystal structure of Ce_5Rh_4. It is orthorhombic and isotypic with the Sm_5Ge_4 (or Gd_5Si_4) type. The present work confirms these findings.

3.6. *CeRh (congruent melting, 1055 °C)*

It was probably the first compound found in this system. It was investigated by Dwight *et al.* [9] who found that it crystallizes with the orthorhombic CrB-type structure. This was confirmed in subsequent studies by Canepa *et al.* [10] and in the present investigation. Different from the reported phase diagrams it is a congruently melting compound (1055 °C).

3.7. *$CeRh_2$ and $CeRh_3$*

These compounds have not been investigated in detail during this research. Therefore no information is available concerning their melting behaviour. Their crystal structures are well known and correspond to the $MgCu_2$ and $AuCu_3$ types respectively. Examination of the lattice constants reported in the literature reveals no strong indications for the existence of wide solid solution ranges.

Acknowledgments

This research was supported by the Italian CNR under "Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate".

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