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The phase diagram of the La–Rh system

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Abstract

The phase diagram of the La–Rh system (0–70 at.% Rh) was investigated using differential thermal analysis, micrographic analysis, X-ray diffraction and electron microscopy. Eight compounds are formed in this system, one of which was not previously known (La_3Rh_2). The existence of most of the compounds reported earlier has been confirmed, except two compounds which have to be deleted (La_3Rh and La_5Rh_3). The shape of the diagram is markedly different from that reported in the current literature and shows in the 30–70 at.% Rh range melting points lower by about 100–150 °C. The rhodium-rich side of the diagram has not been investigated owing to the high melting points of the corresponding alloys.

1. Introduction

During an assessment of the La–Rh system [1] it became evident that a large part of the diagram had been drawn tentatively while other parts were incomplete and, following the indications of Okamoto and Massalski [2], could be considered thermodynamically improbable. Concerning the crystallographic data, the structures of some of the phases claimed to exist were not resolved and therefore the exact compositions could not be determined. Moreover, on examining the thermodynamics and the crystallochemistry of the rare earths (R) with rhodium, the available data appeared to be only partially known and often conflicting, with most of them being schematized and assumed to be similar to those for adjacent rare earths. Therefore it was decided to undertake a re-examination of some representative R–Rh systems to determine the phase diagram and the existence, stability and crystal structure of the corresponding R–Rh phases.

In this paper we report the results obtained for the La–Rh system.

2. Experimental details

Elemental lanthanum was a commercial product obtained from Koch–Light Laboratories, UK (purity 99.8 wt.%), while 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 mass about 1.0 g each were prepared by melting weighed amounts of the two elements in the form of fine turnings for lanthanum and powder for rhodium, pressed into small pellets, in a semilevitation high frequency induction furnace. The samples were then transferred to the differential thermal analysis equipment and one or two thermal cycles were performed at heating and cooling rates of 10 or 20 °C min^{-1}. For compositions richer than 50 at.% Rh only one heating run was carried out. The temperature measurements were accurate to ± 5 °C. Some difficulties were encountered with alloys in the range 30–50 at.% Rh owing to undercooling effects. After several thermal cycles it was decided to take into account mainly thermal effects obtained on heating.

X-ray investigations were carried out on powders and single crystals using a Guinier–Stoe camera with silicon as an internal standard ($a = 5.4306$ Å) 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 programme [3].

Metallographic examination was carried out using standard techniques; a diluted $FeCl_3$ solution was used as the etching agent.

Further identification of unknown 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 La–Rh system derived from the analyses carried out as described

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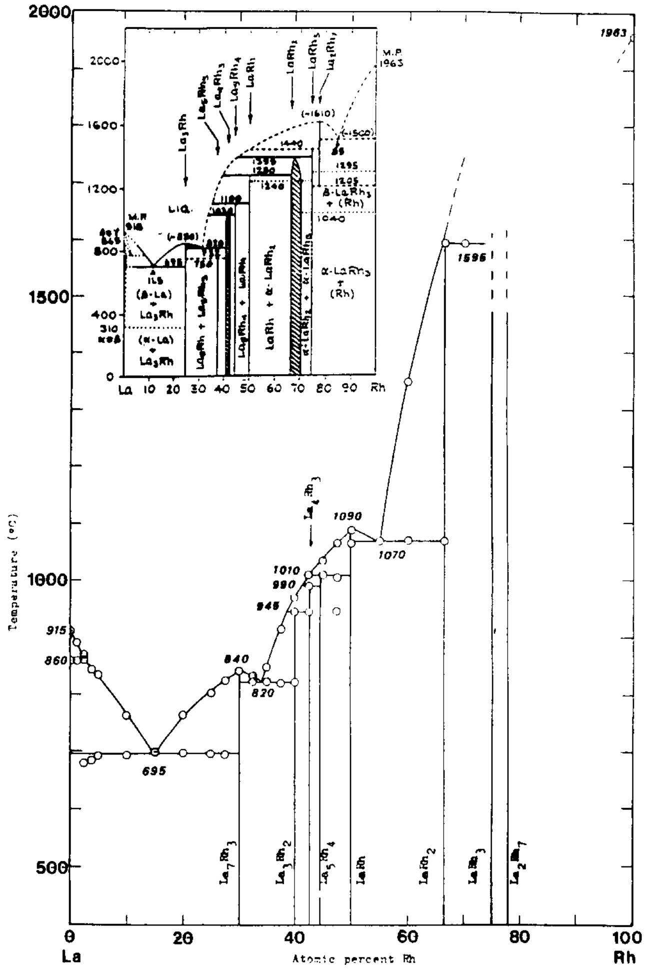

Fig. 1. La–Rh phase diagram.

in Section 2. The figure also shows, as an inset, the phase diagram proposed in the current literature [4, 5] and based on the work of Singh and Raman [6]. Table 1 contains the crystallographic data for the intermediate phases.

The melting point and transformation temperature of the lanthanum used in the present investigation are close to the values given by Gschneidner for pure R elements (918 and 865 °C respectively) [7] and exhibit deviations which are in the range of the experimental temperature determination.

The solubility of rhodium in lanthanum seems to be negligible, since no severe effect on the transformation temperature was observed. The solubility of lanthanum in rhodium has not been investigated owing to the high melting points of the corresponding alloys.

Eight intermediate phases appear to be formed in this system, two of which showing high temperature polymorphism. All these phases, except perhaps $LaRh_2$, appear to be "line compounds".

At least three eutectic points occur: at 15 at.% Rh and 695 °C, 34 at.% Rh and 820 °C, and 55 at.% Rh and 1070 °C.

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

Compound	Structure type	Lattice constants (Å)			References
		a	*b*	*c*	
La_7Rh_3	Th_7Fe_3	10.202		6.506	This work
	(hP20–$P6_3mc$)	10.145		6.434	8.9
		10.200		6.500	9
		10.192		6.498	10
La_3Rh_2	Er_3Ni_2	8.970		17.024	This work
	(hR15–$R\bar{3}$)				
La_4Rh_3	Th_3P_4	8.961			This work
	(cI28–$I\bar{4}3d$)	8.922			6, 12
La_5Rh_4	Sm_5Ge_4	7.601	15.111	7.802	This work
	(oP36–$Pnma$)	7.597	15.09	7.735	13
LaRh	CrB	3.985	11.143	4.247	This work
	(oC8–$Cmcm$)	3.986	11.144	4.245	14
		3.986	11.14	4.253	6
$LaRh_2$	$MgCu_2$	7.648			This work
	(cF24–$Fd\bar{3}m$)	7.646			6
		7.647			16
		7.648			15
β-$LaRh_3$	$NbBe_3$	5.326		26.46	6
	(hR12–$R\bar{3}m$)				
α-$LaRh_3$	$CeNi_3$	5.305		17.59	6
	(hP24–$P6_3/mmc$)				
β-La_2Rh_7	Er_2Co_7	5.333		39.46	6
	(hP36–$P6_3/mmc$)				
α-La_2Rh_7	Ce_2Ni_7	5.296		26.13	6
	(hR18–$R\bar{3}m$)				

3.1. La_3Rh

Singh and Raman [6] reported the existence of La_3Rh and proposed for the powder pattern of this phase a tentative orthorhombic indexing based on the Fe_3C-type structure by doubling the corresponding *a* and *c* parameters. In the course of this investigation we have found that the lanthanum-richest compound corresponds to La_7Rh_3; the powder pattern reported by Singh and Raman can indeed be indexed with a Th_7Fe_3-type structure.

3.2. La_7Rh_3 (congruent melting, 840 °C)

This phase replaces the old La_3Rh. The hexagonal Th_7Fe_3-type structure has been determined by Geballe *et al.* [8] and later confirmed by Raman [9] and Olcese [10]. Several lattice parameter determinations around the stoichiometric composition showed the absence of a solid solution range for La_7Rh_3.

3.3. La_5Rh_3

This compound reported by Singh and Raman [6] could not be found in the present investigation. The powder photographs of several alloys in the range 30–40 at.% Rh, in the as-cast state as well as after annealing at the temperatures proposed by Singh and Raman, always showed only the presence of La_7Rh_3 and La_3Rh_2. Therefore we can reasonably exclude the existence of La_5Rh_3.

3.4. La_3Rh_2 (peritectic formation, 945 °C)

This phase replaces La_5Rh_3. It crystallizes with the rhombohedral Er_3Ni_2-type structure and is isomorphous with the other R_3Rh_2 compounds [11].

3.5. La_4Rh_3 (peritectic formation, 990 °C)

Singh and Raman first reported La_4Rh_3 [6]. Later, Virkar *et al.* [12] proposed for La_4Rh_3 the anti-Th_3P_4-type structure with a lattice parameter value of 8.922 Å. To obtain agreement with their density data and with the appearance of the microstructures of the alloys in the 40–45 at.% Rh range, these authors postulated atomic vacancies in the rhodium sites, shifting the composition slightly towards a lanthanum-richer stoichiometry. However, the lattice parameter reported by Virkar *et al.* and presumably by Singh and Raman, was obtained by the powder method using as internal standard "semiconductor grade" silicon with $a = 5.4199$ Å, which is far from the currently accepted value of $a = 5.4306$ Å. Powder determinations have shown the lattice parameter of La_4Rh_3 to be $a = 8.961$ Å and the measured and calculated densities to be 7.96 and 7.98 g cm^{-3} respectively. Therefore no atomic vacancies are needed. Moreover, complete single-crystal determinations confirmed this assumption, with a final R value of 0.02. The rhodium positional parameter was 0.0566, in very good agreement with Virkar *et al.*'s value of 0.057.

3.6. La_5Rh_4 (peritectic formation, 1010 °C)

The crystal structure of this phase was resolved by Raman [13]. It is isotypic with the orthorhombic Sm_5Ge_4- (or Gd_5Si_4-) type structure and was confirmed in the present investigation.

3.7. LaRh (congruent melting, 1090 °C)

Dwight *et al.* [14] first prepared this compound. It crystallizes with the orthorhombic CrB-type structure and has been confirmed later by Singh and Raman and in the present investigation. Differently from the reported phase diagram, it is a congruent melting compound at 1090 °C.

3.8. $LaRh_2$ (peritectic formation, 1595 °C)

The last compound examined in the present investigation was the well-known Laves phase $LaRh_2$ of $MgCu_2$ type. No indication of a high temperature modification has been found. Several lattice parameter determinations made around the stoichiometric composition ranged from 7.647 to 7.649 Å, showing no appreciable solid solution for this phase.

3.9. $LaRh_3$ and La_2Rh_7

The remaining α and β-$LaRh_3$ and α- and β-La_2Rh_7 have not been examined owing to the high melting points of the corresponding alloys. They were taken from the work of Singh and Raman [6], but some uncertainties in the thermodynamics of their formation require further investigation.

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