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Abstract

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INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF CERIUM-LEAD, PRASEODYMIUM-LEAD, AND NEODYMIUM-LEAD ALLOYS

The thermodynamic properties of alloys of the rare-earth elements have so far been little studied. The phase diagrams of the Ce—Pb and Pr—Pb systems have been determined with insufficient accuracy, and for the Nd—Pb system no phase diagram is available ([1]). It is assumed that all the above-mentioned diagrams are of the same type as the phase diagram for the La—Pb system. For this system the existence of the compounds $LaPb_3$, LaPb, La_2Pb has been established. Within the concentration ranges from 0.97 to 0.75, from 0.75 to 0.50, from 0.50 to 0.33, and from 0.33 to 0.005 in atomic fractions of Pb, heterogeneous regions exist.

By the method of measuring the saturated vapor pressure we determined the activities of lead in its alloys with cerium, praseodymium, and neodymium. Alloys with lead concentrations corresponding to the indicated heterogeneous regions were investigated. In each region 3-4 alloys were studied. The apparatus and experimental procedure are described in work ([2]). Rare-earth elements of 99.9% purity and spectrally pure lead were used for preparing the alloys.

The method of measuring vapor pressure makes it possible to determine the activity a_i of one of the components of an alloy and the change in chemical potential upon formation of the alloy by the formula:

$$\Delta\mu_i = RT \ln a_i.$$

Measurements of the rate of evaporation of lead from the alloys (the evaporation rate is proportional to the vapor pressure) were carried out in the temperature range 700-900°; the activity of lead in the alloys was calculated for temperatures of 720-800°. The data are given in Table 1.

Table 1

Activities of lead

Atomic fraction Pb	Alloy	a_i, T = 993°K	a_i, T = 1073°K	Atomic fraction Pb	Alloy	a_i, T = 993°K	a_i, T = 1073°K
1.0		1.0	1.0	0.50–0.33	Ce–Pb	0.0063	0.0123
0.97–0.75	Ce–Pb	0.776	0.794	0.50–0.33	Nd–Pb	0.0199	0.0316
0.97–0.75	Nd–Pb	0.776	0.794	0.50–0.33	Pr–Pb	0.0133	0.0219
0.97–0.75	Pr–Pb	0.776	0.794	0.33–0.005	Ce–Pb	0.0003	0.0014
0.75–0.50	Ce–Pb	0.524	0.661	0.33–0.005	Nd–Pb	0.0008	0.0036
0.75–0.50	Nd–Pb	0.417	0.525	0.33–0.005	Pr–Pb	0.00005	0.0002
0.75–0.50	Pr–Pb	0.205	0.302				

Next, using known formulas, the partial enthalpies and entropies of formation of the alloys were found, and, by graphical integration of the Duhem–Margules equation, the integral enthalpies and entropies of formation of the alloys. Table 2 gives the values of the partial thermodynamic functions for lead.

Table 2

Partial thermodynamic functions in the interval 993-1073°K

Atomic fraction Pb	Alloy	$\Delta\bar{H}_{Pb}$, kcal/g-at	$\Delta\bar{S}_{Pb}$, cal/deg·g-at	Atomic fraction Pb	Alloy	$\Delta\bar{H}_{Pb}$, kcal/g-at	$\Delta\bar{S}_{Pb}$, cal/deg·g-at
1.0		0	0				
0.97-0.50	Ce–Pb	−0.6	−0.1	0.50-0.33	Ce–Pb	−17.8	−7.8
0.97-0.50	Nd–Pb	−0.6	−0.1	0.50-0.33	Nd–Pb	−12.3	−4.5
0.97-0.50	Pr–Pb	−0.6	−0.1	0.50-0.33	Pr–Pb	−12.8	−4.3
0.75-0.50	Ce–Pb	−6.1	−4.8	0.33-0.005	Ce–Pb	−40.8	−24.9
0.75-0.50	Nd–Pb	−6.1	−4.4	0.33-0.005	Nd–Pb	−39.9	−25.9
0.75-0.50	Pr–Pb	−4.9	−2.1	0.33-0.005	Pr–Pb	−36.7	−17.4

It may be noted that the integral enthalpies of formation of the alloys for all three systems differ only slightly from one another (Fig. 1). This indicates a similar type of interaction of the rare-earth metals studied with lead.

Table 3

Integral thermodynamic functions in the interval 993-1073°K

Atomic fraction Pb	Alloy	ΔH, kcal/g-at	ΔS, cal/deg · g-at
0.75	Ce–Pb	−10.4	−6.7
0.75	Nd–Pb	−9.8	−6.0
0.75	Pr–Pb	−8.7	−3.8
0.50	Ce–Pb	−14.6	−8.2
0.50	Nd–Pb	−13.0	−7.6
0.50	Pr–Pb	−12.4	−5.4
0.33	Ce–Pb	−13.6	−8.3
0.33	Nd–Pb	−13.3	−8.6
0.33	Pr–Pb	−12.1	−5.7

Fig. 1. Integral enthalpies of formation of the alloys Ce–Pb (1), Nd–Pb (2), Pr–Pb (3).

metals with lead. The negative sign of the entropies of formation of the alloys is associated with the sign of the enthalpies of formation, i.e., with the strengthening of the bonds between atoms in the alloy.

The error in determining the activity of lead is 1%; the error in calculating the enthalpy of formation of an alloy is 20%, and that of the entropy is 25%.

Our data confirmed the existence of three intermetallic compounds in the Nd–Pb system, of the compound CePb, and of heterogeneous regions coinciding with the phase diagram for the La–Pb system.

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Note: Figure translations are in progress. See original paper for figures.