

THERMOCHEMISTRY OF BINARY ALLOYS OF LANTHANUM WITH 3d-TRANSITION METALS

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The enthalpy of mixing for liquid binary alloys of lanthanum with 3d-transition metals (Sc, Ti, V, Cr, and Fe) is determined by a calorimetric method within the field of compositions rich in lanthanum. Data for the partial enthalpy of mixing in the La – 3d-metal system with infinite dilution demonstrates a complex relationship of a change in it in the series of 3d-metals connected with gradual filling of the 3d-zone due to alloy formation with lanthanum.

Keywords: lanthanum, 3d-metal, calorimetry, enthalpy, d-zone, electron structure, density of states.

INTRODUCTION

The bases of a contemporary approach to studying the thermodynamic properties of alloys for transition metals have been developed by G. M. Lukashenko and his pupils [1]. The systematic study of the thermochemical properties of alloys of transition metals with rare-earth metals (REM) is of interest for studying the general features of the reaction of components in molten metals. The thermodynamic properties of melts of transition metals and REM have not been determined completely due to the complexity of their theoretical and experimental study. The possibility of theoretical calculation of the energy of forming these alloys has so far been limited, and therefore reliable experimental data are of considerable interest, including reference values for theoretical and model calculations. In the last ten years the number of studies of binary alloys of REM with 3d-metals has increased. The first systematic study of the enthalpy of mixing of 3d-metals (Mn, Fe, Co, Ni, Cu) with REM was carried out in [2], and later the enthalpy of mixing was studied for alloys of copper with Eu, Dy, Yb [3], and liquid alloys Co – Dy [4], Co – Ce, and Co – Sm [5]. For all of the test alloys the considerable exothermic effects were established for alloy formation increasing in the REM series from La to Lu. This thermochemical behavior agrees with data for the enthalpy of formation of solid alloys [6] and the nature of phase equilibria in binary systems [7].

Nonetheless there are no values of the enthalpy of mixing for the majority of melts of REM with transition metals, and this makes it impossible to follow the change in the value of the enthalpy of formation over the whole series of transition metals (for example from Sc to Cu). For alloys of lanthanum with 3d-metals there is practical interest (thermoelectric materials, amorphous alloys, hydrogen accumulators [6]) and values of the enthalpy of mixing over a wide range of concentration have only been obtained for alloys with Mn, Co, Ni, and Cu [1]; the data are limited for other systems (La – Fe [8]), or they are entirely absent (alloys of lanthanum with Sc, Ti, V, and Cr).

The aim of the present work is to determine the enthalpy of mixing of lanthanum with 3d-metals and to analyze its change in the series of 3d-metals.

For a comparative characteristic it is convenient to use the ultimate value of the partial enthalpy of mixing for a 3d-metal with infinite dilution ($\Delta\bar{H}_{\text{TM}}^{\circ}$). This characteristic does not depend on concentration and it may be considered as a reference property quantitatively specifying the energy of reaction of components in a melt. In the present work a study was made of values of $\Delta\bar{H}_{\text{TM}}^{\circ}$ for liquid alloys La – 3d-transition metals (Sc, Ti, V, Cr, Fe) rich in lanthanum at 1700-1773 K.

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EXPERIMENTAL PROCEDURE

The enthalpy of mixing (dissolution) was determined by an experimental method of high-temperature calorimetry in a device described in [3]. In a calorimeter of this type there is exchange between the cell and the isothermal shell. During tests the change in temperature ΔT was determined for a melt with introduction into it of solid additions of metal. The thermal effect of the dissolution process for the addition was calculated by numerical integration of the curve for the dependence of ΔT on time for occurrence of the process t and it was presented in the form of a sum of contributions:

$$k \int_0^t \Delta T(t) dt = \Delta H_i^T + \Delta \bar{H}_i,$$

where k is the molar coefficient of calorimeter heat exchange that is determined in calibration tests; ΔH_i^T is the enthalpy of heating for one mole of metal-addition from 298 K to temperature T according to data in [9]; $\Delta \bar{H}_i$ is the partial enthalpy of mixing for the i -th component. On introducing refractory metals into a melt having a melting temperature higher than that of the melt, $\Delta \bar{H}_i$ corresponds to the enthalpy of dissolution, and the enthalpy of mixing may be calculated taking account of the enthalpy of melting for this metal in the system La – M (M is Ti, V, Cr). Tests were performed in an atmosphere of purified helium (pressure about 10^5 Pa) at 1770-1773 K. The purity of the test metals was, mass%: 99.86 La, 99.86 Sc, 99.97 Ti, 99.90 V, 99.95 Cr, 99.95 Fe, 99.96 W, 99.96 Mo. Molybdenum and tungsten were used as calibration materials. Crucibles made from molybdenum were used that do not react with melts rich in lanthanum at these temperatures, and crucibles of hafnium dioxide were used with high concentrations of $3d$ -metal. The values of $\Delta \bar{H}_i$ obtained were processed statistically in the form of an α -function ($\alpha(x) = \Delta \bar{H}_i (1 - x_i)^{-2}$) by the least squares method using Forsyth orthogonal polynomials according to the procedure in [2]. As a result of calculations based on the Gibbs-Durham equation smoothed values of the α -function were obtained, and also the partial enthalpy of mixing for components and integral enthalpy of mixing with a confidence range equal two mean square deviations of the smoothing function.

EXPERIMENTAL RESULTS

The system La – Sc. The partial enthalpy of mixing of the system La – Sc was determined at 1700 K in the region of compositions from 0 to 50 at.% scandium. Tests were carried out in crucibles made from molybdenum and hafnium dioxide (with a significant scandium content in the melt). Lanthanum and molybdenum were used as calibration

TABLE 1. Partial and Integral Enthalpy of Mixing (kJ/mole) in Systems La – Sc at 1700 K and La – Fe at 1723 K

x_{La}	La – Sc		La – Fe	
	$\Delta \bar{H}_{\text{Sc}}$	ΔH	$\Delta \bar{H}_{\text{Fe}}$	ΔH
1.00	-5.3 ± 1.3	0	7.5 ± 1.4	0
0.95	-2.6 ± 0.9	-0.19 ± 0.03	5.8 ± 1.3	0.32 ± 0.10
0.90	-0.7 ± 0.4	-0.27 ± 0.04	4.9 ± 1.3	0.59 ± 0.09
0.85	-0.8 ± 0.4	-0.24 ± 0.06	2.9 ± 1.2	0.78 ± 0.10
0.80	1.7 ± 0.4	-0.16 ± 0.06	-1.1 ± 1.2	0.80 ± 0.12
0.75	2.3 ± 0.3	-0.02 ± 0.08	-6.7 ± 1.1	0.50 ± 0.11
0.70	2.6 ± 0.3	0.15 ± 0.09	-12.6 ± 1.2	-0.18 ± 0.12
0.65	2.6 ± 0.3	0.50 ± 0.12	-17.0 ± 1.6	-1.25 ± 0.15
0.60	2.5 ± 0.4	0.50 ± 0.15	-	-
0.55	2.2 ± 0.4	0.66 ± 0.2	-	-
0.50	1.9 ± 0.4	0.79 ± 0.3	-	-

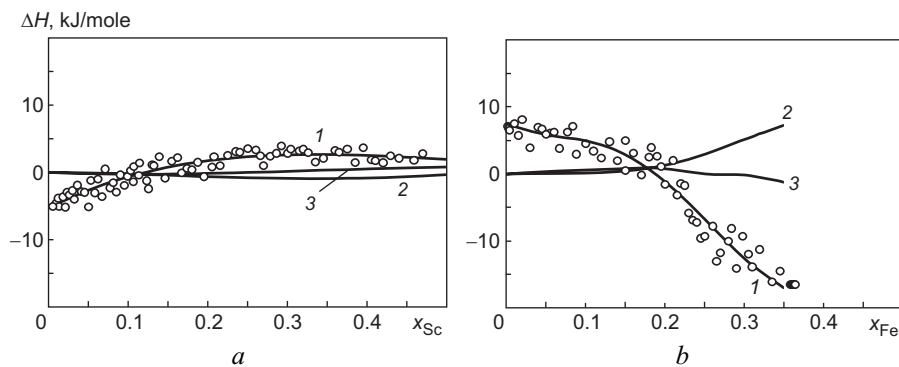


Fig. 1. Enthalpy of mixing in the systems La – Sc (a) and La – Fe (b): 1) $\Delta\bar{H}_{\text{TM}}^{\circ}$; 2) $\Delta\bar{H}_{\text{La}}^{\circ}$; 3) ΔH

materials. Experimental values of the partial enthalpy of mixing for scandium were treated statistically in the form of α -functions that for this system may be represented by the equation:

$$\alpha_{\text{Sc}}(x) = -5.29 + 49.31x_{\text{Sc}} - 46.61x_{\text{Sc}}^2.$$

Smoothed values for the enthalpy of mixing of La – Sc melts calculated according to the values of the α -function are provided in Table 1 and Fig. 1a. The partial enthalpy of mixing for scandium with infinite dilution is $\Delta\bar{H}_{\text{Sc}}^{\circ} = -5.3 \pm 1.3$ kJ/mole.

Systems La – Ti, La – V, and La – Cr. The partial enthalpy of dissolution of titanium, vanadium and chromium in molten lanthanum was measured in the range of compositions containing not more than 8 at.% of the transition metals, in crucibles made from molybdenum. The system La – Ti was studied at 1773 K, and the systems La – V and La – Cr were studied at 1700 K. From experimental data there was calculation of the partial enthalpy of mixing of transition metals with lanthanum converted to the liquid supercooled 3d-metal. The ultimate partial enthalpy of mixing for 3d-metals is: $\Delta\bar{H}_{\text{Ti}}^{\circ} = -16.1 \pm 2.9$ kJ/mole at 1773 K; $\Delta\bar{H}_{\text{V}}^{\circ} = 21.0 \pm 3.5$ kJ/mole at 1700 K; $\Delta\bar{H}_{\text{Cr}}^{\circ} = -4.1 \pm 1.5$ kJ/mole at 1700 K.

The system La – Fe. The partial enthalpy of mixing for iron in the La – Fe system was determined at 1723 K in the region of compositions 0-35 at.% iron. Tests were performed in crucibles made from molybdenum and hafnium oxide, and lanthanum and tungsten were used at the calibration materials. Experimental data for the partial enthalpy of mixing for scandium may be presented in the form of an α -function:

$$\alpha_{\text{Fe}}(x) = 7.51 - 42.35x_{\text{Fe}} + 596.66x_{\text{Fe}}^2 - 2910.75x_{\text{Fe}}^3 - 3730.34x_{\text{Fe}}^4 + 14227.95x_{\text{Fe}}^5.$$

The partial and integral enthalpies of mixing in molten La – Fe calculated from the values of the α -function are presented in Table 1 and in Fig. 1b. The partial enthalpy of mixing of iron has a small absolute values and it changes sign in the region of compositions of about 20 at.% iron. The maximum value of it is $\Delta\bar{H}_{\text{Fe}}^{\circ} = 7.5 \pm 1.4$ kJ/mole.

DISCUSSION OF RESULTS

Results of calorimetric studies for molten lanthanum with 3d-metals (Sc, Ti, V, Cr, Fe) combined with published data for the enthalpy of mixing of lanthanum with the rest of the 3d-metals [2] present a complete picture reflecting the specific nature of the reaction of components of the melts in question. The values of $\Delta\bar{H}_{\text{TM}}^{\circ}$ demonstrate a complex dependence on the sequence number of 3d-metal (Fig. 2a). In melts of La with Sc, Ti, V, Cr, Mn, and Fe there is weak interaction of components, that appears as small absolute values of $\Delta\bar{H}_{\text{TM}}^{\circ}$ and it is confirmed by the form of the phase diagrams showing absence of intermetallic compounds [7]. In contrast in binary alloys La – Co, La – Ni, and La – Cu there is a large negative value of the enthalpy of mixing and many intermetallic compounds exist, including those that melt congruently. The strongest reaction of components occurs in the system La – Ni within which a stable compound LaNi_5 forms having the most exothermal enthalpy of formation $\Delta_f H = -159$ kJ/mole [6].

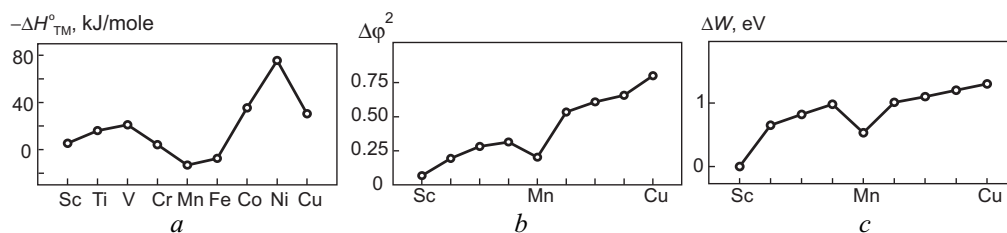


Fig. 2. Variation of ultimate partial enthalpy (a), difference in electronegativity (according to Polling) of components (b) and difference in values of electron work function for components (c) in melts of La with 3*d*-metals

Previously it has been established [5] that the energy of alloy formation in systems of REM with transition metals is governed by transfer of electrons from REM atoms to atoms of the transition metal. A regular change in the value of the enthalpy of mixing may be explained on the basis of considering traditional metal chemistry factors (Fig. 2b, c), and in fact the difference in electronegativity of components and the difference in the work function of an electron (that in turn is connected with the difference in the position of the Fermi levels). A change in the first values of partial enthalpy of mixing in the 3*d*-metal series correlates with the change in the corresponding metal chemistry characteristics. The correlation is disturbed in the case of the systems La – Cr and La – Cu. For more complete explanation of the features of the change in the enthalpy of mixing in the series of the alloys studied it is possible to use data for the electron structure of components considering it from the position of the theory of metal zonal structure.

According to this theory with alloy formation its valent zone forms as a result of complex superposition of valent zones of the components [10]. Here electrons are transferred from the higher energy levels, supplied by the component with the greater value of Fermi energy (E_F), to the lower positioned levels formed by metal with the less value of E_F . In an approximation of the model of strict zones the release of energy will be greater, the greater the difference in the Fermi levels of components, the higher the density of the occupied states close to the Fermi level for a component with the greater value of E_F , and also the greater the density of unoccupied states close to the Fermi level for the component with the lower value of E_F .

For estimate modelling of curves for the densities of electron states an approach suggested in [11] has been used. Within the framework of this approach the zone for conductivity of metals is described by a model of almost free electrons. In order to describe the *d*-zone the Haydock and Kelly calculation [12] was used where it was obtained in a general form the curve of the density of the states in *d*-zones for transition metals for different crystal structures. In this case we used results of their calculations for the BCC-structure as the premelting structure for Sc, Ti, Cr, V, Mn, Fe, and La and the FCC-structure as that for premelting of Co, Ni, and Cu. Parameters of the *d*-zone for components (width of the *d*-zone and the position of its center with respect to the bottom of conductivity zone) were taken from [13], additionally taking account of the radii of the first coordinate sphere in the corresponding melts [14]. The population density of the *d*-zones was estimated from data in [13] for the number of *d*-electrons per atom of transition metal, and the relative position of the zones was evaluated from the mutual position of the E_F [15] assuming that work function $W \approx -E_F$, and the energy of an electron in a vacuum was taken for the zero reading.

The results of the estimate modelling described for some 3*d*-metals and lanthanum are presented in Fig. 3. By means of this scheme it is possible to explain more clearly the features of the energetics of alloy formation of lanthanum with 3*d*-metals. The regular increase in exothermic effects in the series Sc → Ti → V may be stated with confidence as connected with the increase in the difference of E_F for components (respectively 0 → 0.65 → 0.82 eV/at.). Weakening of the exothermic effect for alloy formation in the system La – Cr (with retention of a considerable difference in the Fermi levels for the components, $\Delta E_F = 0.98$ eV/at.) is apparently connected with the stability of the half-filled *d*-zone for chromium, and as a consequence with the low density of the unoccupied states close to the Fermi level for Cr (Fig. 3). For alloys of the system La – Mn further weakening of the reaction may be explained by a sharp reduction in the difference ΔE_F that for this system is 0.53 eV/at. A subsequent increase in the effects of alloy formation in the series

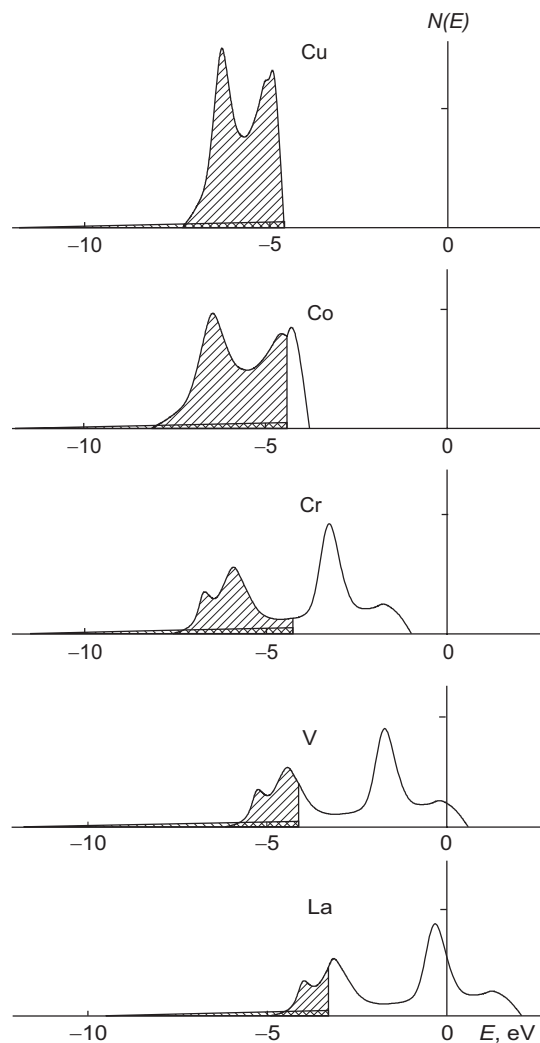


Fig. 3. Scheme of energy zones for the valent electrons of components; $N(E)$ is the density of the state (in nominal units)

$\text{Fe} \rightarrow \text{Co} \rightarrow \text{Ni}$ is explained first by the successive increase in the value of ΔE_F ($1.01 \rightarrow 1.11 \rightarrow 1.2$ eV/at.), and second by a successive increase in the density of unoccupied states close to the Fermi level of the transition metal. Thermal effects of alloy formation in the system $\text{La} - \text{Cu}$ ($\Delta E_F = 1.2$ eV/at.) are reduced due to the fact that the d -zone for copper is almost completely filled, and electrons from higher placed levels in lanthanum may only enter at levels introduced by the zone of conductivity of copper whose density of states is insignificant.

Thus, the study carried out makes it possible to conclude that the energetics of alloy formation in melts of lanthanum with $3d$ -metals may be explained on the basis of considering the electron structure of components from the position of zonal theory for the structure of metals.

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