Journal of Alloys and Compounds, 191 (1993) 155–158
JALCOM 504

Standard enthalpies of formation of lanthanum alloys, La + Me (Me ≡ Ru, Rh, Pd, Os, Ir, Pt), by high-temperature calorimetry

N. Selhaoui and O. J. Kleppa
James Franck Institute, University of Chicago, 5640 S. Ellis Avenue, Chicago, IL 60637 (USA)

(Received September 7, 1992)

Abstract

The standard enthalpies of formation of lanthanum alloys, La + Me (Me ≡ Ru, Rh, Pd, Os, Ir, Pt) were determined by direct synthesis calorimetry at 1473 ± 2 K. The following values of $\Delta_f H^o_m$ (in kJ g^{-1} $atom^{-1}$) are reported: $LaRu_2$ −(10.3 ± 2.8); $LaRh_2$ (57.5 ± 1.7); LaRh −(56.3 ± 2.3); LaPd −(76.2 ± 1.8); $LaPd_3$ (−77.1 ± 2.2); $LaOs_2$ −(9.0 ± 1.1); $LaIr_2$ −(62.9 ± 2.2); $LaIr_3$ (−49.7 ± 2.2); $LaPt_2$ −(90.0 ± 2.9); LaPt −(92.1 ± 4.6). The results are compared with predicted values from the models of Miedema *et al.*, of Watson and Bennett, and of Colinet and Pasturel, and with earlier data for some of the corresponding yttrium and scandium alloys.

1. Introduction

The thermodynamic properties of the alloys formed between early transition metals and late transition metals are very interesting from both a technological and a theoretical point of view. During recent years, we have pursued a systematic study of the thermochemistry of these alloys. Originally this study was centered on the equi-atomic compounds formed between Ti, Zr and Hf and the platinum group metals [1].

More recently we have measured the standard enthalpies of formation of Y + Me alloys [2] and Sc + Me alloys [3], where Me is an element from either the platinum group or the iron group of metals. In the present communication, our study is extended to the alloys of the Group III metal La with Ru, Rh, Pd, Os, Ir and Pt.

In the course of the present investigation we have measured the standard enthalpies of formation of ten intermetallic phases in the six considered systems by direct synthesis calorimetry. Our results are compared with thermochemical data in the published literature, with corresponding values for the yttrium and scandium alloys, and with predicted values from Miedema's semi-empirical model [4], from Watson and Bennett's model [5] and from Colinet and Pasturel's model [6].

2. Experimental details

2.1. General

A survey of the available phase diagrams of the binary systems [7, 8] shows that most of the considered intermetallic compounds have fairly high melting points. However, since strong chemical interaction between the metals was expected, we decided to attempt to measure their enthalpies of formation by direct synthesis from the elements. All measurements were carried out at 1473 ± 2 K in our modified Setaram-type calorimeter. Details of the construction of this unit as well as of the "liner" assembly have been given in an earlier report [9].

The output signal from the thermopile of this calorimeter is recorded graphically and simultaneously integrated on an Apple IIe computer. The reaction chamber of the calorimeter consists of a thin-walled BN crucible which protects the Pt20Rh "liner" from the contents of a 15 mm diameter BeO crucible in which the actual reaction takes place. All experiments were performed in an atmosphere of argon gas that was purified by passing the gas over titanium powder at about 1173 K. Calibration of the calorimeter was achieved by dropping small pieces of 2 mm diameter high-purity copper wire from room temperature into the calorimeter. The enthalpy of pure copper at 1473 K was taken from Hultgren *et al.* [10], 46 465 J mol^{-1}. The calibrations were reproducible within ± 1.5%.

2.2. Materials

The metallic purities and the sizes of the materials that were used are summarized in Table 1. The lump lanthanum metal was stored in a vacuum desiccator and fine shavings were prepared just before we made the pellets. All the metals were purchased from Johnson-Matthey, AESAR Group with the exception of rhodium

0925-8388/93/$6.00

TABLE 1. Metallic purity and description of the materials used in the calorimetric measurements

Metal	Metallic purity (%)	Comments
La	99.9	Lump, vacuum remelted
Ru	99.9	−100 mesh powder
Rh	99.9	−100 mesh powder
Pd	99.95	−200 mesh powder
Os	99.8	−80 mesh powder
Ir	99.95	−150 mesh powder
Pt	99.99	−200 mesh powder

which was purchased from Engelhard. The impurity levels in the metals are insignificant compared with our experimental errors.

3. Results and discussion

The standard molar enthalpy of formation of the compound La_m Me_n is obtained from the enthalpy effects associated with the following two reactions:

$$mLa\ (s, 298.15) + nMe\ (s, 298.15) = La_mMe_n\ (s \text{ or } l, 1473) \quad (1)$$

and

$$La_mMe_n\ (s, 298.15) = La_mMe_n\ (s \text{ or } l, 1473) \quad (2)$$

From reactions (1) and (2) we get:

$$mLa\ (s, 298.15) + nMe\ (s, 298.15) = La_mMe_n\ (s, 298.15) \quad (3)$$

Hence, the standard molar enthalpy of formation is obtained from:

$$\Delta_f H^0_m\ (La_mMe_n) = \Delta H_m(1) - \Delta H_m(2) \quad (4)$$

where $\Delta H_m(1)$ and $\Delta H_m(2)$ are the molar enthalpy changes associated with reactions (1) and (2).

Our experimental results are summarized in Table 2. The reported values $\Delta H_m(1)$ and $\Delta H_m(2)$ are averages of four to six experiments with standard deviations δ_a and δ_2. The uncertainty in $\Delta_f H^0_m$ was calculated from $\delta = (\delta_1^2 + \delta_2^2)^{1/2}$.

After the experiments, all alloy samples were examined by powder X-ray diffraction and by scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis. Our X-ray diffraction experiments showed traces of Ru and Os in the samples of Ru_2La and Os_2La. Examination of the products by SEM and energy dispersive X-ray microanalysis confirmed that PdLa, $PdLa_3$, PtLa, Ir_2La, and Rh_2La were all single phase, while Ir_3La and Pt_2La showed less than five mass percent of a second phase. This analysis also confirmed the presence of a small amount of Ru in Ru_2La and of Os in Os_2La. We believe that the errors in the measured enthalpies of formation arising from the presence of a small amount of a second reaction product are very small compared to our random errors. However, the presence of unreacted metal is more critical; in Table 2 we have marked our results for Ru_2La and Os_2La as indicative; *i.e.* subject to possible improvement by the use of another calorimetric method.

For LaPd and LaPt the reaction products from the direct synthesis experiments could not be removed from the BeO crucible. In order to obtain the heat contents of these compounds they were also synthesized by arc-melting. The arc-melted buttons were broken into appropriate-sized pieces that were used for the heat content measurements. The homogeneity and stoichiometry of these compounds were also checked by SEM

TABLE 2. Observed heats of reaction, average heat contents at 1473 K, and calculated standard enthalpies of formation in kJ g atom^{-1}[a]

Compound	$\Delta H_{obs} = \Delta H_m(1)$	$H^0_{1473} - H^0_{298.15} = \Delta H_m(2)$	$\Delta_f H^0_m$
Ru_2La	20.14 ± 1.71 (6)	30.47 ± 2.19 (5)	−10.3 ± 2.8[c]
Rh_2La	−23.77 ± 1.36 (5)	33.76 ± 1.06 (5)	−57.5 ± 1.7
RhLa	−14.95 ± 2.26 (5)	41.36[b]	−56.3 ± 2.3
PdLa	−26.83 ± 1.03 (6)	49.34 ± 1.51 (6)	−76.2 ± 1.8
Pd_3La	−42.96 ± 2.05 (6)	34.14 ± 0.81 (5)	−77.1 ± 2.2
Os_2La	+17.65 ± 0.8 (5)	26.51 ± 0.81 (4)	−9.0 ± 1.1[c]
Ir_2La	−29.36 ± 2.12 (6)	33.48 ± 0.38 (4)	−62.9 ± 2.2
Ir_3La	−16.32 ± 1.13 (5)	33.41 ± 1.86 (5)	−49.7 ± 2.2
Pt_2La	−57.92 ± 2.33 (6)	32.07 ± 1.75 (4)	−90.0 ± 2.9
PtLa	−65.74 ± 4.49 (5)	26.34 ± 1.06 (4)	−92.1 ± 4.6

[a]Numbers in parentheses indicate numbers of experiments averaged.
[b]Value taken from Hultgren *et al.* [10].
[c]Indicative values.

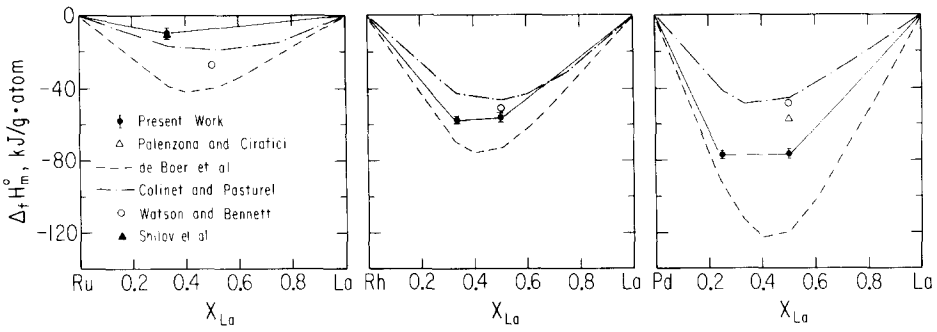

Fig. 1. Standard enthalpies of formation for alloys of La with Ru, Rh and Pd compared with earlier data of Shilov *et al.* [11], of Palenzona and Cirafici [12], and with predicted values of de Boer *et al.* [4], of Watson and Bennett [5], and of Colinet and Pasturel [6]. ‡ = present work; △ = Palenzona and Cirafici, – – – = de Boer *et al.*; – · – = Colinet and Pasturel; ○ = Watson and Bennett; ▲ = Shilov *et al.*

and energy-dispersive X-ray analysis. The RhLa compound similarly could not be removed from the BeO crucible. However, in this case the compound could not be prepared by arc-melting since it melts peritecticly [7, 8]. For this reason, the heat content of this compound at 1473 K was taken from Hultgren *et al.* [10], 41 360 J mol^{-1} at 1473 K.

Figure 1 shows a plot of our experimental results for La + Me (Me = Ru, Rh, Pd), while Fig. 2 gives our values for La + Me (Me = Os, Ir, Pt). All values in these figures are given in kilojoules per gram atom.

In Fig. 1 we see that for the $LaRu_2$ compound the calorimetric value of Shilov *et al.* [11], −11 kJ g $atom^{-1}$, is in good agreement with our value, −10 kJ g $atom^{-1}$. In the same figure we see that the experimental value for LaPd of Palenzona and Cirafici [12], −57 kJ g $atom^{-1}$, is much less exothermic than our own value, −76 kJ g $atom^{-1}$. However, in Fig. 2 we see that our experimental value for LaPt, −92 kJ g $atom^{-1}$, agrees well with the result of Palenzona and Cirafici [13], −87 kJ g $atom^{-1}$. The same figure shows that our experimental value for Ir_2La, −63 kJ g $atom^{-1}$, is in good agreement with the value of Rezukhina *et al.* [14], −61 kJ g $atom^{-1}$, obtained by the e.m.f. method. However the e.m.f. value of the enthalpy of formation of Pt_2La reported by Kemmler [15], −128 kJ g $atom^{-1}$, is much more exothermic than our own value −90 kJ g $atom^{-1}$. Note that there is a clear tendency for the enthalpies of formation to become increasingly negative in the sequences Ru, Rh, Pd and Os, Ir, Pt.

For all the considered alloys, predicted values of the enthalpies of formation are available from the semi-empirical theory of de Boer *et al.* [4] and from the model of Colinet and Pasturel [6]. For the equi-atomic alloys, predicted values are also provided by Watson and Bennett [5]. From Figs. 1 and 2 we see that the semi-empirical theory of de Boer *et al.* usually predicts *more* exothermic values than observed; however, for the Ir + La system there is good agreement with our experiments. Most of the predicted values from Watson and Bennett's model [5] are in good agreement with our experimental values except for the value for LaPd which is less exothermic than our value. The model of Colinet and Pasturel [6] usually predicts less exothermic values than observed; however, for the La + Pt system there is fairly good agreement with our experiments.

In Figs. 3 and 4 we compare our results for the La alloys with corresponding data for the Y and Sc alloys. We note first in Fig. 3 that the standard enthalpy of formation of PdLa, −76 kJ g $atom^{-1}$, is less exothermic

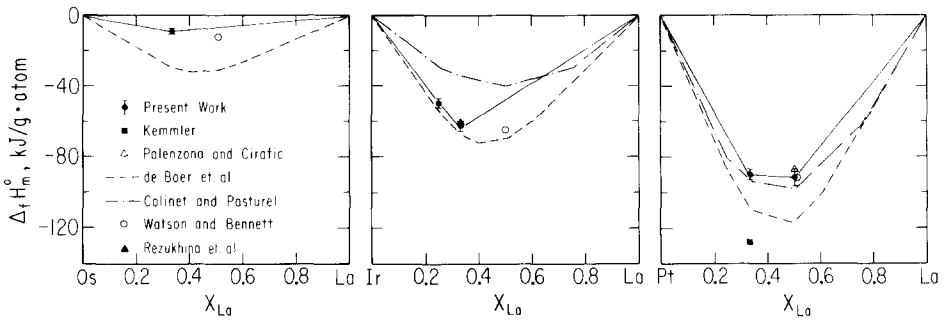

Fig. 2. Standard enthalpies of formation of La with Os, Ir and Pt compared with earlier experimental data of Rezukhina *et al.* [14], of Kemmler [15] and with predicted values of e Boer *et al.* [4], of Watson and Bennett [5], and of Colinet and Pasturel [6]. ‡ = present work; ■ = Kemmler; △ = Palenzona and Cirafici; – – – = de Boer *et al.*; – · – = Colinet and Pasturel; ○ = Watson and Bennett; ▲ = Rezukhina *et al.*

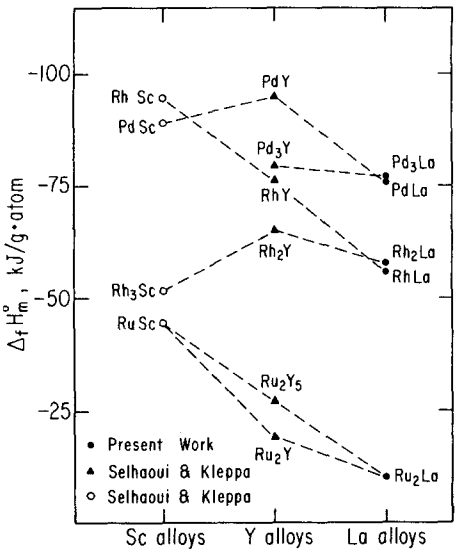

Fig. 3. Comparison of enthalpies of formation of La with Ru, Rh and Pd with corresponding data for alloys of Sc and Y. ●=present work; ▲=Selhaoui and Kleppa; ○=Selhaoui and Kleppa.

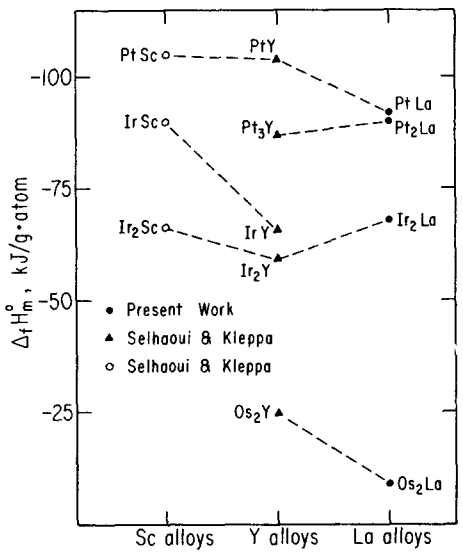

Fig. 4. Comparison of enthalpies of formation of La with Os, Ir and Pt with corresponding data for alloys of Sc and Y. ●=present work; ▲=Selhaoui and Kleppa; ○=Selhaoui and Kleppa.

than the values for PdSc, −89 kJ g atom^{-1} (3), and for PdY, −95 kJ g atom^{-1} (2); however, the values for Pd_3La and Pd_3Y are very similar, −77 kJ g atom^{-1} and −79 kJ g atom^{-1} (2) respectively. Similarly, the standard enthalpy of formation of RhLa, −56 kJ g atom^{-1}, is much less exothermic than those of the corresponding Y and Sc alloys, −76 kJ g atom^{-1} (2) for RhY and −94.5 kJ g atom^{-1} (3) for RhSc. Note also that the value for Ru_2La, −10 kJ g atom^{-1}, is much less exothermic than the corresponding values for Ru_2Y, −19.5 kJ g atom^{-1} (2) and RuSc, −44.5 kJ g atom^{-1} (3).

We note next in Fig. 4 that the value for PtLa, −92 kJ g atom^{-1}, is somewhat less exothermic than the corresponding values for PtY and PtSc, −104 kJ g atom^{-1} (2) and −105 kJ g atom^{-1} (3) respectively. However, while IrY, −66 kJ g atom^{-1} (3), is less exothermic than IrSc, −90 kJ g atom^{-1} (3), the values for Ir_2La, −63 kJ g atom^{-1}, Ir_2Y, −59 kJ g atom^{-1} (2), and Ir_2Sc, −66 kJ g atom^{-1} (3), are roughly comparable. Our experimental value for the enthalpy of formation of Os_2La, −9 kJ g atom^{-1}, is significantly less exothermic than that of Os_2Y, −25 kJ g atom^{-1} (2).

Acknowledgments

This investigation has been supported by NSF under Grant CHE-90-14789, and has also benefitted from the general facilities of the University of Chicago MRL. We are indebted to Dr. A. M. Davis who carried out the SEM and energy dispersive X-ray analyses.

References

1 L. Topor and O. J. Kleppa, *J. Less-Common Met., 155* (1989) 61, and references therein.
2 N. Selhaoui and O. J. Kleppa, *J. de Chimie Physique*, submitted for publication.
3 N. Selhaoui and O. J. Kleppa, *J. Alloys Comp.*, submitted for publication.
4 F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema and A. K. Niessen, *Cohesion in Metals. Transition Metal Alloys*, North-Holland, Amsterdam, 1988.
5 R. E. Watson and L. H. Bennett, *Calphad, 8* (1984) 307.
6 C. Colinet and A. Pasturel, *Calphad, 11* (1987) 335.
7 T. B. Massalski (ed.), *Binary Alloy Phase Diagrams, 2nd edn.*, ASM International, Materials Park, Ohio, 1990.
8 W. G. Moffat, *The Handbook of Binary Phase Diagrams*, Genium, Schenectady, N.Y., 1984.
9 O. J. Kleppa and L. Topor, *Thermochim. Acta, 139* (1989) 291.
10 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements*, ASM, Metals Park, Ohio, 1973.
11 A. L. Shilov, L. N. Padurets and M. E. Kost, *Russ. J. Phys. Chem., 57* (1983) 338.
12 A. Palenzona and S. Cirafici, *Thermochim. Acta, 12* (1975) 267.
13 A. Palenzona and S. Cirafici, *Thermochim. Acta, 25* (1978) 252.
14 T. N. Rezukhina, L. I. Kravchenko and B. S. Pokarev, *Metallofizika, No. 46* (1973) 21.
15 G. Kemmler, *Untersuchungen zur Stabilität von Lanthaniden - Platin Verbindungen, Kernforschungsentrum Karlsruhe, Report KFK 2452* (1977).