Thermochimica Acta, 25 (1978) 252–256

Note

Thermodynamic and crystallographic properties of RPt intermetallic compounds

A. PALENZONA AND S. CIRAFICI
Istituto di Chimica fisica, Universita' di Genova, Genova (Italy)
(Received 4 October 1977)

After the RPd phases[1] another series of intermetallic, equiatomic compounds of the rare earths (R) with Pt has been examined in order to verify some of the correlations derived for RX_3 phases[2], where X = Sn, Pb, In, Tl and R = rare earths and Y, Th, U[3]. Moreover a systematic study of the crystallographic and thermodynamic properties of the common and often isomorphous phases of Pd and Pt could be useful for a better characterization of these two elements in respect of their alloying properties. Pd and Pt in many ways, e.g. atomic size, ionic dimensions, electronegativity, appear very similar to one another but give rise to different properties when combined with other elements.

The crystal structures of RPt compounds are known from work by Dwight et al.[4] but no evidence exists concerning the thermodynamics of their formation: the only available information is that "platinum reacts easily with rare earths".

EXPERIMENTAL

The R metals and Pt used in this research were commercial products from Koch-Light Laboratories, England (99.5%) and Johnson Matthey Ltd., England (99.9%) respectively.

The heats of formation were determined by means of the dynamic differential calorimetric method (DDC) previously described[5]. The alloys were prepared from equiatomic mixtures of the two elements, pressed into cylindrical pellets and closed under ultra pure argon by arc-welding in molybdenum crucibles as for DTA measurements. The sample and the reference were then heated at 20°C min^{-1} in a programmable heating furnace until the reaction between the two elements started at the reaction temperature (T_r), giving off the heat of formation which appeared on the thermograms as a sharp peak whose area was proportional to the above quantity. As soon as the thermal effect ceased, the heat source was cut off and the sample cooled to room temperature in order to quench the products of the reaction and to ascertain its completeness.

X-ray diffraction investigation was carried out using Cr $K\alpha$ radiation; to improve the quality of the diffraction patterns, acetylcellulose capillaries were employed.

Samples for microscopic examination were prepared on silicon carbide papers and by diamond polishing; as etching agent an alcoholic iodine solution was used.

RESULTS AND DISCUSSION

Table 1 contains the results obtained by X-ray investigation. La and Ce alloys crystallize with the CrB type of structure while from Nd to Er the structure type observed corresponds to the FeB type. Eu and Yb have not been examined. The reaction between Tm and Lu with Pt does not lead to the desired compound and the corresponding powder patterns show the presence of reflections due to other phases

TABLE 1

CRYSTALLOGRAPHIC DATA FOR RPt PHASES

*Comp.**	*Struct. type*	*Lattice constants (Å)*			*References*
		a	*b*	*c*	
LaPt	CrB	3.974	11.042	4.555	this work
		3.974	11.037	4.558	4
CePt	CrB	3.917	10.901	4.522	this work
		3.921	10.920	4.524	4
PrPt(h)	CrB	3.896	10.845	4.505	this work
		3.891	10.899	4.569	6
PrPt(l)	FeB	7.282	4.594	5.696	this work
		7.294	4.560	5.698	4
NdPt(h)	CrB	3.846	10.769	4.542	6
NdPt(l)	FeB	7.239	4.550	5.675	this work
		7.256	4.551	5.675	4
SmPt	FeB	7.148	4.510	5.638	this work
		7.152	4.525	5.626	4
GdPt	FeB	7.084	4.500	5.591	this work
		7.088	4.502	5.590	4
TbPt	FeB	7.021	4.491	5.558	this work
		7.018	4.494	5.561	4
DyPt	FeB	6.973	4.480	5.541	this work
		6.983	4.478	5.544	4
HoPt	FeB	6.947	4.462	5.526	this work
		6.951	4.470	5.532	4
ErPt	FeB	6.900	4.455	5.510	this work
		6.904	4.453	5.512	4
TmPt	FeB	6.855	4.446	5.496	4
YbPt	FeB	6.814	4.429	5.480	11
		6.805	4.416	5.492	12
LuPt	FeB	6.810	4.417	5.479	4

* (l) = low temperature modification, (h) = high temperature modification.

TABLE 2

THERMODYNAMIC PROPERTIES OF RPt PHASES

Comp.	*Struct. type*	*ΔH_f*[a] *kcal g atom^{-1}*	*T_r*[a] *(°C)*
LaPt	CrB	−20.8	630
CePt	CrB	−24.6	610
PrPt(h)	CrB	−24.3	650
NdPt	FeB	−23.7	700
SmPt	FeB	−22.3	720
GdPt	FeB	−21.4	380
TbPt	FeB	−20.8	880
DyPt	FeB	−20.4	920
HoPt	FeB	−20.0	910
ErPt	FeB	−19.4	1020
TmPt[b]	FeB	−18.8	
LuPt[b]	FeB	−17.8	

[a] T_r = temperature at which the reaction starts, ΔH_f = heat of formation at T_r.
[b] Values obtained by extrapolation.

as does micrographic examination. For PrPt the X-ray photographs were indexed with the CrB type of structure which could be ascribed to the high temperature modification for this compound. This result can be understood when it is remembered that the alloys are examined as soon as the formation reaction is terminated by cooling the sample to room temperature and this corresponds to a quenching of the alloy with the retention of the phase stable at high temperature. Moreover a DTA curve of PrPt showed a faint thermal effect at about 1360°C which could correspond to the transition temperature. After slow cooling to room temperature, X-ray examination

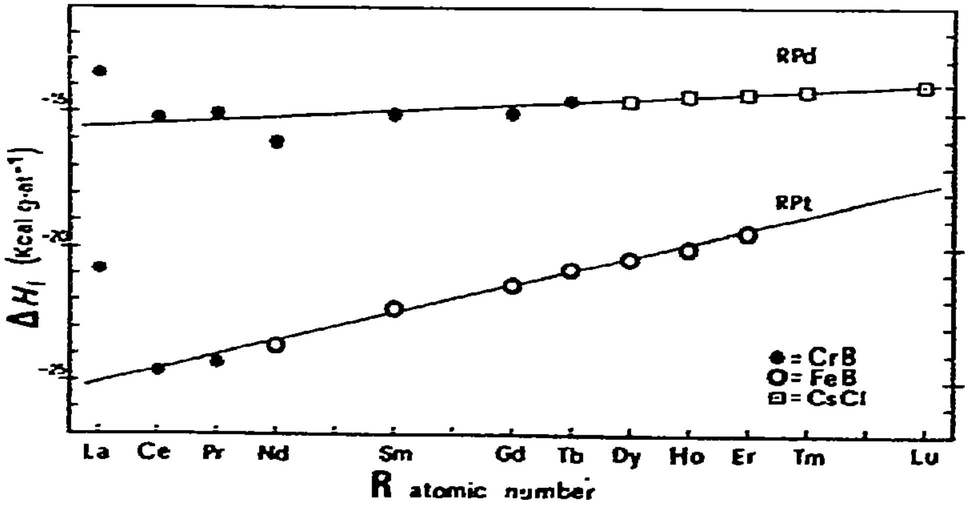

Fig. 1. Heats of formation for RPd and RPt compounds vs. rare earth atomic number.

showed the reflection of the well known FeB type structure. This behaviour has been observed recently by Parthe' and coworkers both for Pr and Nd[6].

Table 2 contains the results obtained by thermodynamic measurements on RPt phases. The reaction between elemental R's and Pt takes place at a temperature (T_r) which increases almost linearly from La (630°C) to Er (1020°C). The reaction is very fast, highly exothermic and the heat evolved is sufficient to melt the samples, which in most cases appeared homogeneous and single phase. For PrPt the value reported in Table 2 is ascribed to the CrB type modification for the reasons mentioned above but the heat of formation of the FeB type should be almost identical to that of the CrB type modification as shown by the faint thermal effect of the transformation. This conclusion is also justified by the similarity of the two structures involved. Tm and Lu never gave homogeneous products so the values reported in Table 2 were obtained by extrapolation from Fig. 1. Compounds of Eu and Yb have not been examined in this study.

Figure 1 shows the trend of the heats of formation for both series RPd and RPt compounds, with change of R's atomic number. The situation is almost identical, with a regular decrease from lighter to heavier rare earths (except for the values of La) in agreement with the prediction which can be derived from examination of the role of the lanthanide contraction in compound formation using the criterion of Gschneidner[7]. Even if three different structural types (CrB, FeB, CsCl) are considered, this criterion retains its qualitative validity.

It has been shown that the heats of formation of intermetallic compounds can be derived with a semiempirical equation due to Miedema and co-workers[8, 9] which, in its most recent version[10], gives a value of -23 kcal g atom^{-1} for LaPd and for LaPt a value of -22 kcal g atom^{-1}. While for the Pt compound the agreement between calculated and observed values is very good, this is not the case for Pd compounds which have experimental values much lower than the calculated ones. The above-mentioned equation consists essentially of two terms depending on two parameters: ϕ = electronegativity parameter and n_{WS} = electron density at the boundary of the Wigner-Seitz cell, which concur, with opposite sign, to the evaluation of the heats of formation. The values of the parameters ϕ and n_{WS} have been slightly changed during successive improvements of the Miedema relationship, especially for noble metals. At present it is difficult to decide which of the two parameters (or both) must be changed and in what direction, but it is probable that their reevaluation, taking into account new experimental data, could lead to more satisfactory results.

Thus work currently in progress concerns the determination of the heats of formation of equiatomic rare earth compounds both with transition and non transition elements.

REFERENCES

1 A. Palenzona and S. Cirafici, *Thermochim. Acta*, 12 (1975) 267.
2 A. Palenzona and S. Cirafici, *Thermochim. Acta*, 9 (1974) 419.
3 A. Palenzona and S. Cirafici, *Thermochim. Acta*, 13 (1975) 357.

4 A. E. Dwight, R. A. Conner and J. W. Downey, *Acta Crystallogr.*, 18 (1965) 837.
5 A. Palenzona and S. Cirafici, in R. S. Porter and J. F. Johnson (Eds.), *Analytical Calorimetry*, Vol. 3, Plenum Press, 1974, p. 743.
6 E. Parthe', private communication.
7 K. A. Gschneidner, *J. Less Common Met.*, 17 (1969) 1.
8 A. R. Miedema, *J. Less Common Met.*, 32 (1973) 117.
9 A. R. Miedema, R. Boom and F. R. De Boer, *J. Less Common Met.*, 41 (1975) 283.
10 A. R. Miedema, *J. Less Common Met.*, 46 (1976) 67.