Journal of Alloys and Compounds 321 (2001) 183–200
www.elsevier.com/locate/jallcom

Thermochemistry of alloys of transition metals and lanthanide metals with some IIIB and IVB elements in the periodic table

S.V. Meschel*, O.J. Kleppa

The James Franck Institute, The University of Chicago, 5640 S. Ellis Avenue, Chicago, IL 60637, USA

Received 5 September 2000; accepted 5 December 2000

Abstract

We have conducted systematic studies in this laboratory of the thermochemistry of transition metal and rare earth alloys by high temperature calorimetric methods. An overview of the thermochemistry of the alloys of the transition metals and lanthanide metals with elements in the IIIB and IVB columns of the periodic table is presented. The enthalpies of formation of most of these compounds were determined by high temperature direct synthesis calorimetry. This review summarizes the trends between the enthalpies of formation of the TR–X and LA–X alloys (where X is a IIIB or IVB element) and the atomic numbers of the transition metal and lanthanide metal. We compare our measured enthalpies of formation of each alloy family for the 3d, 4d and 5d transition metal elements. We also compare our experimental measurements with predicted values on the basis of Miedema's semiempirical model. This review shows examples of a correlation between the enthalpies of formation of the alloys of the lanthanide elements with the non-metal elements in the IIIB and IVB columns in the periodic table. We also show some comparisons of our measured enthalpies of formation with the predictions of Gschneidner for the lanthanide alloys.

Keywords: Binary alloys; Calorimetry; Enthalpies of formation

1. Introduction

During the last few decades the investigation of binary intermetallic and metal–nonmetal compounds of transition metal and rare earth metals received considerable attention since it was found that a significant number of these alloys may be utilized in electronic and nuclear technology. Several of these alloys have rather exceptional qualities with respect to absorption of hydrogen gas and superconductivity. Many of these alloys have potential applications in high temperature industrial processes. We will briefly point out the particularly significant uses of the alloys in each family of compounds.

While this overview cannot possibly assess all the properties of these classes of compounds we do intend to review the work performed in this laboratory on compounds of transition metals and lanthanide metals and the elements in groups of IIIB and IVB in the periodic table. In this overview we are restricting ourselves to cite mostly work performed in this laboratory. We will also quote some other investigators whose measurements were based on calorimetry. This technique is usually the most reliable way to obtain enthalpies of formation.

Our experiments were carried out in a single unit differential microcalorimeter which has been described in an earlier communication from this laboratory [1,2]. The temperature was held at 1473±2 K for most of the measurements. When the experimental temperature is different from this, we indicate it in the table where the data appear.

Most of the results in this paper were obtained by direct synthesis calorimetry (DSC) and some by the so-called solute–solvent drop calorimetry (SSD) developed in this laboratory by Topor and Kleppa [3]. To date we have studied roughly 270 alloys in the considered families of compounds; 38 of these were measured by SSD, the rest by DSC or by solution calorimetry (seven alloys). In this review we will mainly discuss the concerns related to the DSC method. In our application of the direct synthesis method the standard enthalpies of formation were obtained as the difference between the results of two sets of measurements. In the first set the following reaction takes place in the calorimeter

---

*Corresponding author.
E-mail address: meschel@control.uchicago.edu (S.V. Meschel).

0925-8388/01/$ – see front matter
PII: S0925-8388(01)00966-5

$$\mathrm{ME}\ (\mathrm{s}, 298\ \mathrm{K}) + m\mathrm{X}\ (\mathrm{s}, 298\ \mathrm{K}) = \mathrm{MEX}_m\ (\mathrm{s\ or\ l}, 1473\ \mathrm{K}) \quad (1)$$

where m represents the molar ratio X/ME; ME is the considered metal; s denotes solid and l denotes liquid. The reacted pellets were reused in a second set of experiments in order to determine their heat contents

$$\mathrm{MEX}_m\ (\mathrm{s}, 298\ \mathrm{K}) = \mathrm{MEX}_m\ (\mathrm{s\ or\ l}, 1473\ \mathrm{K}) \quad (2)$$

The standard enthalpies of formation are given by

$$\Delta H_{\mathrm{f}}^{\mathrm{o}} = \Delta H_{\mathrm{m}}(1) - \Delta H_{\mathrm{m}}(2) \quad (3)$$

where $\Delta H_{\mathrm{m}}(1)$ and $\Delta H_{\mathrm{m}}(2)$ are the molar enthalpy changes associated with reactions (1) and (2).

Some of the early experiments on transition metals by DSC were carried out by Gachon, Charles and Hertz at the University of Nancy, France [4]. They pointed out some of the problems they encountered using this method. Some of the problems inherent in DSC relate to the fact that in order to achieve reliable results, the reaction between the two elements of the binary compound must proceed to completion in a finite interval of time (<3600 s). We noticed for example that in some of the 4d transition metal carbides which we attempted to study, the component elements do react, but the reaction takes such a long time that the measurements are unreliable. Some compounds which have very high melting points simply do not yield completely reacted phases at our working temperature of 1473 K, for example HfB_2, ZrB_2. It is also important to note that the reaction must take place without the loss a significant amount of material due to vaporization of either component. In some cases, when the reaction is slow, vaporization of one of the components may render the measurement unreliable. This was the case for SmB_2 at 1273 K, and for Yb alloys at 923 K. The reaction should also take place without any significant side reaction with the container material. Most often we use a boron nitride (BN) crucible to contain the samples. However, in some cases, when we noticed some interaction with the crucible material, we used a BeO crucible. This happened in very few cases, e.g. with ScAl, Sm_5Sn_3, Pr_5Si_3, Nd_5Si_3.

While in many cases some information is available about the considered phases, the phase diagrams unfortunately are far from complete [5]. Many of the phases which we studied have no published phase diagrams or the melting points are not available.

Other major concerns in DSC are the assessment of the completion of the reaction and the identification of the reaction product. Most often we have relied on X-ray diffraction to examine our products. As a rule, any sample which has a measurable amount of unreacted material (greater than about 3%) we consider as not reportable. If the compound is fully reacted, we assess whether or not we have the molar composition which we prepared, and also if there are significant amounts of secondary phases present. Again, as a rule, if we have more than about 10% of a secondary phase present, we report the standard enthalpy of formation as only indicative. If the secondary phase is present in more than 15%, we usually do not report the value at all. For many of the alloys which we studied the X-ray diffraction (XRD) patterns are listed in the ASTM powder diffraction file. We can then effectively make a comparison of the experimental patterns and the published patterns. However, in numerous cases the XRD patterns are not listed in the ASTM powder diffraction file. When the relevant information is available in Pearson's compilation of crystallographic data, we can generate the XRD patterns from published unit cell parameters and atomic coordinates [6]. We decided not to prepare any compounds for which structural information is not available. If the XRD technique is not conclusive, we can utilize SEM or X-ray microprobe analysis to further test our samples.

If the XRD pattern shows a small degree of incomplete reaction, some compounds may still be successfully prepared in the calorimeter by the DSC method, by maintaining a small excess of one of the components. We developed this technique for transition metal borides [7]. In the calorimetric measurements we correct both the molar enthalpy of reaction and the molar heat content for the excess of boron present. This technique was also found to be useful for determining the enthalpy of formation of some of the transition metal carbides, for example Mo_2C.

Some of the transition metal alloy samples which are crumbly in texture may fall apart in the calorimeter and contaminate the liner assembly. The evaluation of the measurements also becomes uncertain if the sample pellets do not remain intact in the crucible during the reactions. For such samples we sometimes introduced a modified technique by adding a small, weighed amount of pure silver powder (5–10 mol.%) as a neutral binder. Of course, this technique can only be used when neither component of the alloy interacts chemically with silver. Both the molar heat of reaction and the molar heat content are corrected for the heat content of silver at the reaction temperature. This technique was originally developed for handling transition metal borides; however, it also proved to be useful for transition metal silicides [7].

Reporting our enthalpy measurements we compare our experimental values with values reported in the published literature. Note, that our own measurements always refer to room temperature. In our communications, the tables may include the reference temperature or other conditions different from ours. In our graphs, we always plot the most exothermic value for the particular system. Generally, the enthalpies of formation measured by calorimetric techniques tend to agree quite well [8–14]. We observe less favorable comparison with values derived either from vapor pressure measurements or from EMF data.

On the basis of empirical and semiempirical models some methods have been proposed to estimate the enthalpies of formation of binary alloys and intermetallic compounds. de Boer et al. [15] predicted the enthalpies of formation from the work functions, molar volumes and electron densities at the boundary of the Wigner–Seitz cell of the component elements. The heat of formation of binary compounds (AB) which contain at least one transition metal, may be described in terms of a simple atomic model.The alloys are suggested to be constructed from Wigner–Seitz atomic cells characteristic of the pure metallic elements, A and B. The alloying energy then originates from the change in boundary conditions when dissimilar atoms are in contact. For a compound AB of two transition metals the enthalpy of formation according to de Boer et al. [15] is composed of two contributions (a) a negative contribution arising from the difference between the electronegativities of the two constituent metals A and B (measured by the difference in work functions) and (b) a positive contribution arising from the discontinuity in the electron density at the common interface of the dissimilar Wigner–Seitz cells when atoms A and B are brought together.

A concentration term is included to indicate the surface area of atomic cells and the degree to which atoms are surrounded by dissimilar neighbours. If one of the elements is not a transition metal an additional term R is introduced. This term is related to the hybridization of the d and p wave functions when the transition metal and the non-transition metal elements become nearest neighbours in the alloy.

As this semiempirical model was designed for transition metal alloys, the comparison with experimental values is usually quite good for intermetallic systems, but not as favorable for systems where the alloy is quite different in bonding from the intermetallic transition metal type systems. On the basis of this model a computer software was developed by Niessen et al. [16] to allow calculation of the predicted enthalpies of formation for alloys of lanthanide elements. In the tables we list the enthalpies of formation predicted by this model for each alloy.

In addition to the predictions by Miedema and coworkers there have been other theoretical studies by Gelatt et al., Pasturel et al. and Colinet et al., respectively, to predict the enthalpies of formation of compounds formed by transition metal and non-transition metal elements, for example B, Si, Al, on the basis of band theory [17–19]. Gelatt et al. were the first to provide a detailed theoretical analysis of the significant factors which contribute to the enthalpies of formation of transition metal–polyvalent metal systems [17]. Further work along these lines was carried out by Pasturel et al. [18]. Pasturel's theory of the 3d transition metal aluminides predicts a roughly parabolic dependence of the enthalpies of formation on the number of d electrons, with the weakest bonding in the middle of the series. In each family of systems we will point out the correlation of this theory with our experimental results.

Gelatt et al. conclude that there are two main contributions to the enthalpies of formation:

1. a negative (i.e. bonding) term which is due to the hybridization between the d band of the transition metal and the s and p bands of the polyvalent metal;
2. a positive (i.e. bond weakening) term which arises from the increase of separation between the transition metal atoms caused by the alloying process. Hence there is a narrowing of the d band of the transition metal and a lowering of the cohesive energy of the alloy.

The analysis of the contributions of these terms to the total energy of the transition metal–aluminium alloys in the 4d series led to the conclusions that the most negative enthalpies of formation should be found for alloys of Rh and Al [17]. We noted in previous communications that our measurements fully agree with this prediction [20]. Moreover, we noted also that our results show a similar effect in several other families of compounds, for example in gallides, silicides, germanides, and stannides [20,21].

To predict the trends of the enthalpies of formation for lanthanide alloys, Gschneider suggested that these should be related to the relative molar volumes and reduced temperatures. He suggested that these quantities should reflect the lanthanide contraction in the compounds compared to the contraction of the pure metals [22,23]. For example if the lanthanide contraction in the compounds from La to Lu become greater than in the corresponding pure metals then the enthalpies of formation are predicted to become more exothermic in the same sequence. In this scheme the reduced temperature (i.e. the ratio of the melting point of the compound to the melting point of the lanthanide element) and the ratio of the molar volume of the compound to the atomic volume of the pure element normalized with respect to the first member of the series (i.e. La) are used as indicators to predict the systematic behavior of the stability of the alloys. In our discussion of the enthalpies of formation of the lanthanide alloys we shall cite examples where these correlations agree and also where they disagree with the predictions by Gschneidner.

2. Borides

Many of the transition metal borides are utilized in high temperature technology. This is due to their highly refractory character, chemical inertness, hardness and thermal conductivity. A novel application of rare earth borides is in the area of high power electronic technology. LaB_6 and YB_6 are particularly good examples of such uses.

Transition and lanthanide metals combine with boron to form compounds with B:Me ratios ranging from 1:4 to 66:1. This wide range reflects the self-binding ability of boron. The boron atoms may occur as isolated atoms in metal-rich borides, as pairs, chains, two- or three-dimensional networks in the more boron-rich compounds.

Because of their inertness, most refractory borides cannot be studied by traditional solution calorimetry. Some of the early work on borides in this laboratory centered around the study of transition metal borides by the SSD developed by Topor and Kleppa [3]. For some of the compounds the enthalpies of formation have been measured by both SC and by DSC calorimetry, for example for FeB, CoB and NiB [7]. The agreement is quite good; however, the DSC method gives somewhat better precision. In order to ensure completion of the reactions and facilitate better handling of the transition metal boride samples we developed two techniques which are described in the introduction [7]. We used both adding a small excess of boron to ensure completion of the reactions and, when suitable, a neutral binder to improve the precision of measurements. In addition to the previously reported values for lanthanide borides we measured the enthalpies of formation of LaB_4 and Nd_2B_5 by the DSC method.

The phase diagram of the La–B system shows a congruently melting compound, LaB_6 (m.p. 2988 K) and a peritectically melting phase, LaB_4 (m.p. 2073 K) [5]. The enthalpy of formation of LaB_6 was measured by Topor and Kleppa by the SSD technique [3]. The XRD pattern of our LaB_4 product matched well the pattern in the ASTM powder diffraction file. However, we noticed approximately 5% LaB_6 as a secondary phase. The enthalpy of formation of LaB_4 is somewhat less exothermic than the value for LaB_6. This is quite reasonable when we consider that its melting point is more than 900°C lower. The melting point of LaB_4 is also significantly lower (by about 500°C) than those of the neighbouring lanthanide tetraborides. Therefore, it is reasonable to expect a somewhat less exothermic enthalpy of formation than for the neighbouring lanthanide tetraborides. Actually,the enthalpy of formation is comparable with the values for other compounds with the LAB_4 molecular composition.

The phase diagram of the Nd–B system shows one congruently melting phase, NdB_6 (m.p. 2883 K) and three peritectically melting phases, NdB_4 (m.p. 2623 K), Nd_2B_5 (m.p. 2273 K) and NdB_{66} (m.p. 2423 K) [5]. We reported the enthalpy of formation of NdB_4 by DSC in a previous communication [24]. Nd_2B_5 has a very interesting stoichiometric ratio. The only other lanthanide boride which we were able to prepare with this composition was Gd_2B_5 [24]. The XRD pattern of Nd_2B_5 is not included either in the ASTM powder diffraction file or in Pearson's compilation of crystallographic data [6]. The structure is listed as Sm_2B_5 type; however, since the atomic coordinates are not available for this compound, we could not generate the pattern by computer methods. However, Sm_2B_5 is isomorphous with both Nd_2B_5 and Gd_2B_5. We compared the XRD pattern of Nd_2B_5 with the pattern for Gd_2B_5 and found close agreement with the exception of an approximately 0.2° shift in the peaks.We also noticed the presence of a minor secondary phase of, approximately 5–7% of NdB_4. Our value for the enthalpy of formation of Nd_2B_5 (−38.9±1.9 kJ/mol of atoms) compares reasonably well with the corresponding value for Gd_2B_5, −43.1±1.4 kJ/mol of atoms. Note that the melting points are also quite similar. We have only a very approximate value for Sm_2B_5 (−39 kJ/mol of atoms), which is also comparable in magnitude. We did not tabulate a quantitative value for this compound because the formation reaction is so slow that we noticed some evaporation of Sm in the sample.

The only compound with higher B:ME ratio than 6:1 which we studied was AlB_{12} [25].

Table 1 shows the transition and lanthanide borides

Table 1
Standard enthalpies of formation of transition metal and lanthanide borides; data in kJ/mol of atoms

Compound	ΔH_f° (Expt.)	Method[a]	ΔH_f° (Pred.) [15,16]	Reference
ScB_2	−102.3±4.9	SSD	−69	[26]
TiB_2	−109.5±3.4	SSD	−74	[26]
VB_2	−70.7±4.2	SSD	−50	[26]
CrB_2	−39.8±1.1	SSD	−34	[27]
MnB	−35.8±2.4	SC	−47	[28]
MnB_2	−21.1±3.4	SC	−35	[28]
Mn_2B	−31.7±2.0	SC	−37	[28]
FeB	−32.3±2.2	SC	−38	[29]
	−29.3±0.7	DSC		[7]
Fe_2B	−22.6±2.7	SC	−30	[29]
CoB	−34.8±3.0	SC	−34	[29]
	−34.7±0.6	DSC		[7]
Co_2B	−19.4±2.3	SC	−28	[29]
NiB	−20.1±1.9	SC	−33	[29]
	−20.7±1.1	DSC		[7]
Ni_2B	−22.6±1.4	SC	−27	[29]
YB_4	−52.3±1.8	SSD	−38	[30]
YB_2	−35.7±2.6	DSC	−66	[7]
NbB_2	−60.3±1.5	DSC	−71	[31]
MoB	−28.7±1.0	DSC	−49	[31]
$RuB_{1.1}$	−22.2±1.0	DSC	−34	[32]
$RhB_{1.1}$	−35.5±1.0	DSC	−35	[32]
Pd_2B_5	−25.6±0.9	SSD	−22	[33]
LaB_6	−57.2±1.7	SSD	−20	[3]
LaB_4	−50.7±1.3	DSC	−38	[This work]
TaB_2	−53.3±2.0	DSC	−70	[7]
W_2B_5	−17.5±1.1	DSC	−31	[7]
ReB_2	−21.5±0.5	DSC	−28	[31]
$OsB_{2.5}$	−11.4±1.0	DSC	−22	[34]
$IrB_{1.35}$	−20.9±1.0	DSC	−36	[34]
Pt_2B	−20±2	SSD	−29	[33]
AlB_{12}	−11.4±0.6	DSC	+9	[25]
LaB_6	−57.2±1.7	SSD	−20	[3]
LaB_4	−50.7±1.3	DSC	−38	[This work]
CeB_4	−53.5±1.5	DSC	−38	[24]
PrB_4	−53.1±1.6	DSC	−38	[24]
PrB_6	−51.3±5.7	SSD	−20	[24]
NdB_4	−53.3±1.5	DSC	−38	[24]
Nd_2B_5	−38.9±1.9	DSC	−58	[This work]
Gd_2B_5	−43.1±1.4	DSC	−59	[24]
TbB_2	−34.2±1.8	DSC	−67	[35]
DyB_2	−30.2±1.3	DSC	−66	[36]
HoB_2	−27.9±1.5	DSC	−65	[37]
ErB_2	−27.3±2.2	DSC	−67	[38]
TmB_2	−30.6±3.0	DSC	−67	[39]
LuB_2	−29.8±0.9	DSC	−69	[40]

[a] DSC, direct synthesis calorimetry; SSD, solute–solvent drop calorimetry; SC, solution calorimetry.

studied in this laboratory, the calorimetric method used, the predicted values calculated on the basis of Miedema's semiempirical model and the references. The predicted values differ significantly from our experimental measurements. This may be because the model does not take the boron–boron bonding into consideration. This bonding effect is expected to contribute significantly to the stability of compounds with high boron content. The agreement is quite good only for CoB, $RhB_{1.1}$ and Pd_2B_5.

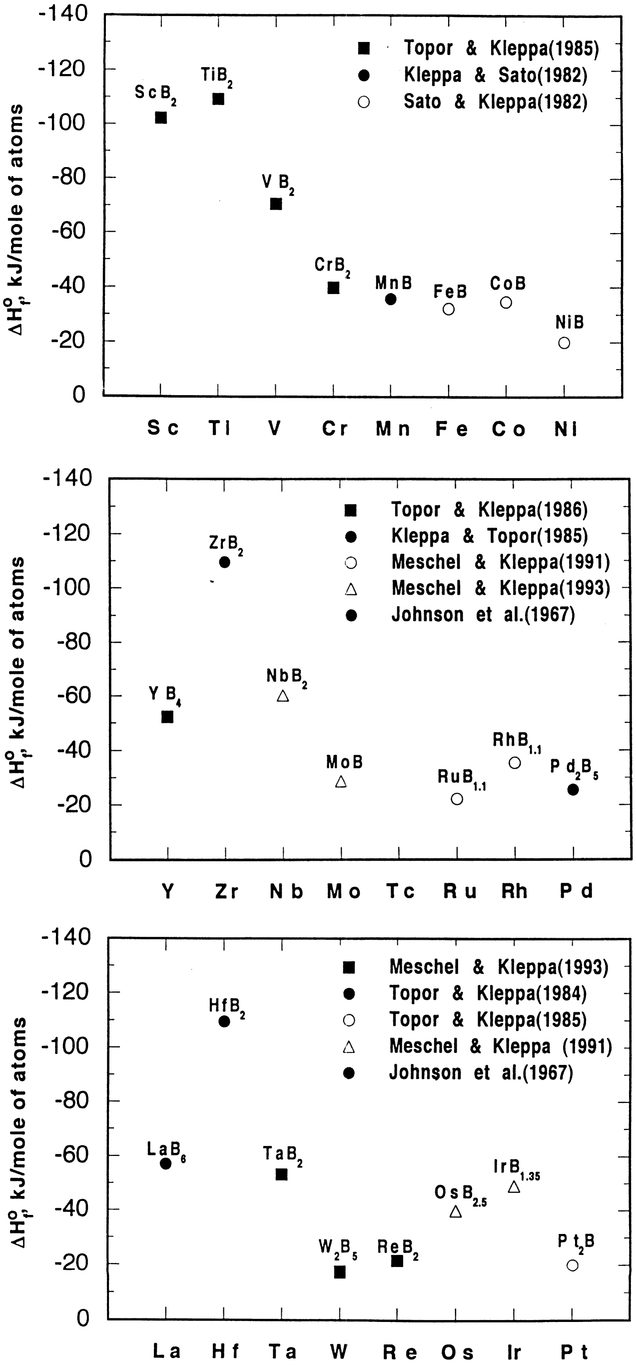

Fig. 1. Standard enthalpies of formation of some 3d, 4d and 5d transition metal borides. All data in kJ/mol of atoms apply to the most exothermic compounds..

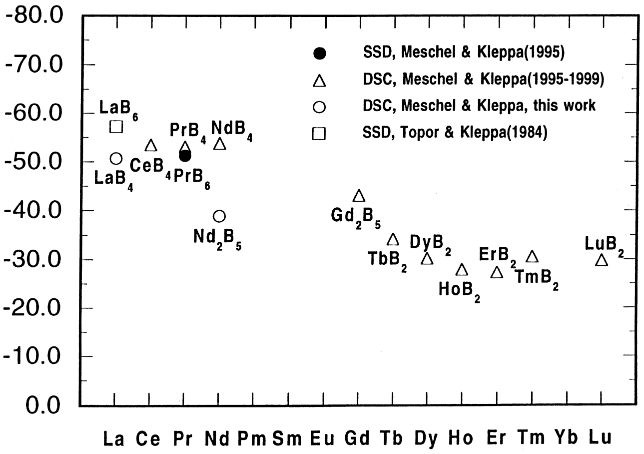

Fig. 2. Standard enthalpies of formation of some lanthanide borides. Data in kJ/mol of atoms.

In Fig. 1 we plot the enthalpies of formation of transition metal borides against the atomic number of the metallic element. The enthalpies of formation when plotted against the atomic number of the transition metal show very similar patterns for the 3d, 4d and 5d borides.In each family of systems there is a sharp rise from Sc, Y, La to Ti, Zr, Hf and then a subsequent decrease to a more or less flat range. We are citing the enthalpies of formation of ZrB_2 and HfB_2 from the study of Johnson et al. measured by fluorine bomb calorimetry [41]. The shape of the curves is somewhat similar to that of the 3d transition metal carbides. These are the only two families of compounds which we have studied where we do not find the roughly parabolic dependence of the enthalpies of formation on the atomic number of the transition metal which was predicted by Pasturel et al. [18].

In Fig. 2 we plot the enthalpies of formation of the lanthanide borides against the atomic number of the lanthanide element. It is difficult to assess any systematic variation of the enthalpies of formation within the lanthanide borides since the molecular compositions which we studied were quite different. However, it seems that within groups which have the same molecular composition the enthalpies do not vary very significantly, i.e. in sets for LAB_4 and LAB_2 the values are very similar.

3. Aluminides

The alloys of aluminum have been the subject of increasing interest for some time. Their resistance to high temperature oxidation makes them very suitable for a wide range of technological applications. We measured the enthalpies of formation of 39 aluminides nearly all by

Table 2
Standard enthalpies of formation of transition metal and lanthanide aluminides; data in kJ/mol of atoms

Compound	ΔH_f^o (Expt.)	Method[a]	ΔH_f^o (Pred.) [15,16]	Reference
ScAl	−41.1±1.5	DSC	−68	[43]
$ScAl_{1.78}$	−47.7±0.9	DSC	−62	[42]
$TiAl_3$	−36.6±1.2	DSC	−39	[43]
V_5Al_8	−34.0±0.5	DSC	−35	[43]
VAl_3	−27.8±0.9	DSC	−24	[43]
Cr_5Al_8	−16.9±1.8	DSC	−26	[43]
Mn_3Al_2	−23.4±0.8	DSC	−42	[43]
Mn_4Al	−15.1±1.0	DSC	−24	[43]
FeAl	−23.5±1.6	DSC	−32	[2]
CoAl	−53.4±1.4	DSC	−43	[43]
NiAl	−58.3±1.1	DSC	−48	[2]
YAl_2	−50.4±1.3	DSC	−64	[42]
Y_3Al_2	−40.0±1.6	DSC	−60	[44]
$ZrAl_2$	−52.1±1.6	DSC	−72	[44]
$ZrAl_3$	−48.4±1.3	DSC	−57	[44]
$NbAl_3$	−40.5±0.6	DSC	−29	[44]
Nb_3Al	−13.7±1.0	DSC	−28	[44]
Mo_3Al_8	−33.0±0.7	DSC	−17	[44]
Mo_3Al	−22.3±1.6	DSC	−15	[44]
RuAl	−62.1±1.7	DSC	−48	[20]
RhAl	−106.3±1.6	DSC	−64	[20]
PdAl	−91.9±4.1	SSD	−84	[42]
	−90.6±2.2	DSC		[42]
Pd_2Al	−87.3±1.8	DSC	−68	[44]
$LaAl_2$	−49.9±2.1	DSC	−65	[42]
La_3Al_{11}	−37.5±0.7	DSC	−47	[45]
HfAl	−39.9±2.0	DSC	−75	[45]
$HfAl_2$	−43.8±1.3	DSC	−65	[45]
$HfAl_3$	−40.6±0.8	DSC	−51	[45]
$TaAl_3$	−29.9±1.3	DSC	−30	[45]
Ta_2Al	−19.9±1.6	DSC	−37	[45]
WAl_4	−14.1±0.9	DSC	−10	[45]
Re_2Al	−29.6±0.9	DSC	−24	[45]
Re_4Al_{11}	−34.5±1.5	DSC	−20	[45]
$OsAl_2$	−44.9±2.2	DSC	−36	[46]
IrAl	−92.8±1.8	DSC	−60	[20]
PtAl	−100.2±4.4	SSD	−82	[42]
	−94.9±2.5	DSC		[42]
Pt_2Al_3	−96.5±1.2	DSC	−79	[45]
Pt_3Al	−63.6±2.1	DSC	−50	[45]
$LuAl_2$	−52.6±3.0	DSC	−63	[40]

[a] DSC, direct synthesis calorimetry; SSD, solute solvent drop calorimetry.

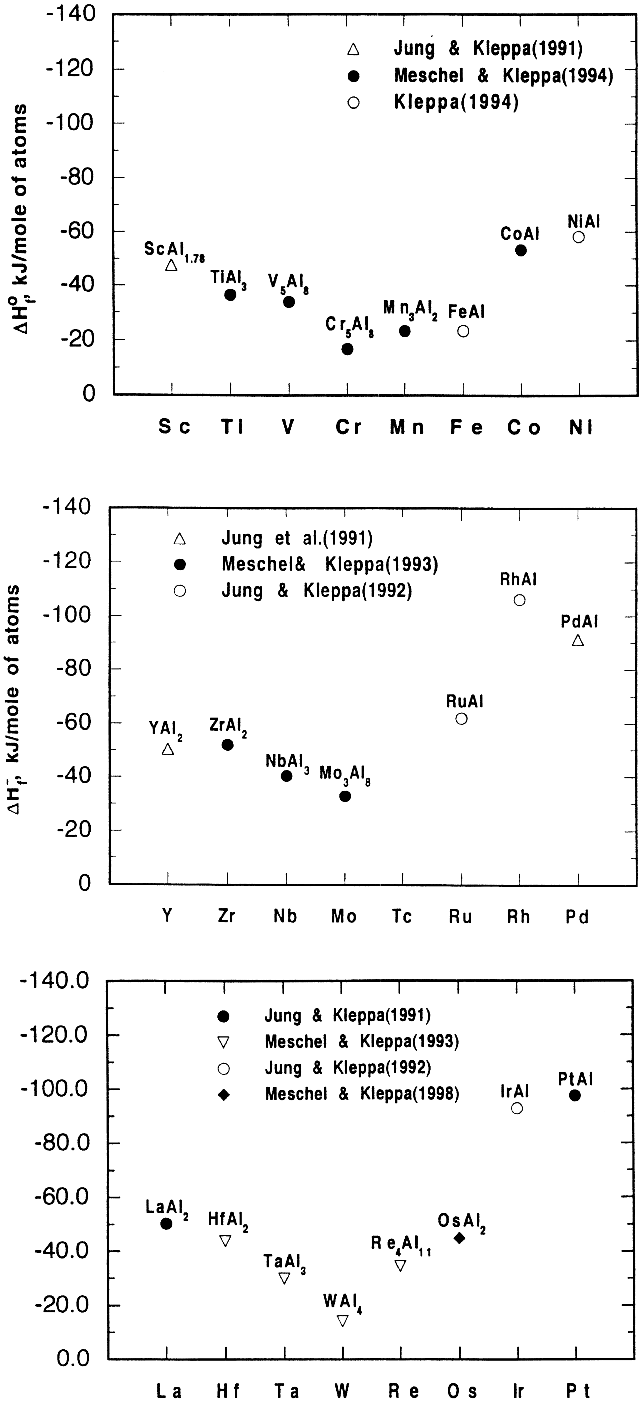

Fig. 3. Standard enthalpies of formation of some 3d, 4d and 5d transition metal aluminides. Data in kJ/mol of atoms.

DSC. However, the enthalpies of formation of PdAl and PtAl were determined by Jung et al. by SSD [42].

We summarize the measured enthalpies of formation along with the corresponding predicted values calculated from Miedema's semiempirical model in Table 2. For some of the transition metal aluminides the predicted enthalpies of formation agree reasonably well with the measured values (i.e. within about ±10 kJ/mol of atoms). However, there are many exceptions in all three sets of alloys.

In Fig. 3 we plot the enthalpies of formation of 3d, 4d and 5d transition metal aluminides against the atomic number of the metallic element. This figure shows that the enthalpies of formation when plotted against the atomic number of the transition element show a roughly parabolic dependence. This observation agrees well with the prediction of Pasturel et al. [18]. The absolute values of the enthalpies of formation decrease systematically from the Sc, Y, La group to Cr, Mo, W and then increase sharply to Ni, Pd, Pt. There is a noticeable minimum at Cr, Mo, W. The 4d aluminides show the most exothermic values of the three sets of alloys. The only exceptions to the stated trend are the reversals at PdAl and PtAl. The enthalpy of formation of RhAl is numerically the most exothermic value. This finding agrees well with the theoretical prediction by Gellatt et al. [17]. However, our data show that the 3d and 5d alloys are different in this respect. The most negative enthalpies of formation in these two groups are found for the end members, i.e. for Ni and for Pt [45].

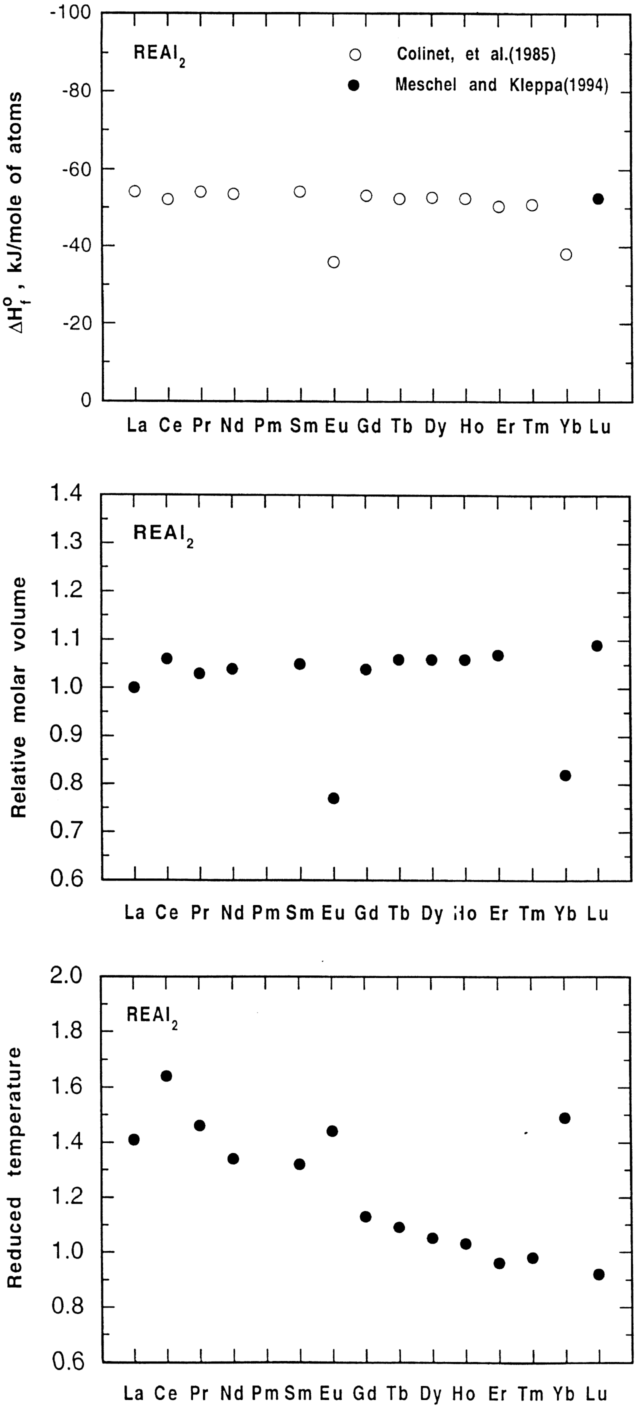

Fig. 4. Comparison of the standard enthalpies of formation of some lanthanide aluminides with relative molar volumes and reduced temperatures. Data in kJ/mol of atoms.

In Fig. 4 we plot the enthalpies of formation of the lanthanide aluminides against the atomic number of the lanthanide elements. Most of the enthalpies of formation of the lanthanide aluminides were by solution calorimetry measured by Colinet et al. [47]. We only determined the value for $LuAl_2$ [40] and $LaAl_2$ [42]. As the graph shows, with the exception of the values for the divalent lanthanides Eu and Yb, the enthalpies of formation do not show significant variation. This observation correlates reasonably well with Gschneidner's prediction. According to this prediction the relative molar volume ratio plotted against the atomic number of the lanthanide element yields a similar plot [22,23]. A plot of the reduced temperature shows significant decrease with increasing atomic number of the lanthanide element, which we do not observe in the experimental measurements.

4. Gallides

Our studies of transition metal and lanthanide gallides are still in progress. Therefore this overview represents only a partial assessment of the results reported so far.

Among the 3d transition metal gallides the alloys of Ti with Ga are of particular technical interest, since they may be used for soldering oxide materials.

The enthalpies of formation of the transition metal and lanthanide gallides which we have studied so far have all

Table 3
Standard enthalpies of formation of transition metal and lanthanide metal gallides; data in kJ/mol of atoms

Compound	ΔH^o_f (Expt.)	Method[a]	ΔH^o_f (Pred.) [15,16]	Reference
Sc_5Ga_3	−59.4±2.0	DSC	−59	[48]
Ti_2Ga	−39.0±1.4	DSC	−44	[48]
V_2Ga_5	−16.6±1.7	DSC	−18	[48]
Cr_3Ga	−11.8±1.8	DSC	−12	[48]
$FeGa_3$	−24.8±2.1	DSC	−10	[48]
$CoGa_3$	−29.4±2.2	DSC	−18	[48]
NiGa	−44.9±1.9	DSC	−37	[48]
YGa	−71.4±1.7	DSC	−73	[21]
YGa_2	−68.1±2.3	DSC	−65	[21]
Zr_2Ga	−53.4±2.1	DSC	−63	[21]
Nb_5Ga_3	−26.5±1.7	DSC	−27	[21]
Mo_3Ga	−16.6±2.5	DSC	−5	[21]
RuGa	−35.4±2.3	DSC	−34	[21]
$RuGa_2$	−41.0±1.6	DSC	−27	[21]
RhGa	−73.2±2.3	DSC	−53	[21]
$RhGa_3$	−44.9±1.2	DSC	−32	[21]
PdGa	−71.6±2.3	DSC	−79	[49]
Pd_2Ga	−64.4±2.0	DSC	−66	[49]
$TmGa_3$	−48.5±2.0	DSC	−49	[39]

[a] DSC, direct synthesis calorimetry; experiments were carried out at 1373 K. Reference states are TR(s) and Ga(s) at 298 K.

been measured by DSC at 1373 K. The reference states are TR (s), LA (s) and Ga (s) at 298 K.

In Table 3 we summarize the experimental results as well as the values predicted from Miedema's semiempirical model [15]. Apart from the values for the 3d and 4d transition metal gallides this table also includes a measurement for $TmGa_3$, which is the only lanthanide gallide value we have studied so far [39]. The experimental values agree quite well with the predicted values for alloys from Sc to Cr and for the Y, Nb and Ru gallides.

In Fig. 5 we plot the enthalpies of formation of the 3d and 4d gallides against the atomic number for the transition metal. The molar compositions of the alloys are indicated in the figure. The shapes of the two curves are very similar, they are roughly parabolic with the minima in the same location (Cr,Mo).

The enthalpies of formation for the 4d gallides are more exothermic than the corresponding values for the 3d gallides.The highest exothermic value is found for the alloy RhGa. This is consistent with the prediction of Gellatt et al. for 4d aluminides [17]. As for the corresponding aluminides this effect does not show up for the 3d gallides, where the end member, Ni, has the most exothermic enthalpy of formation.

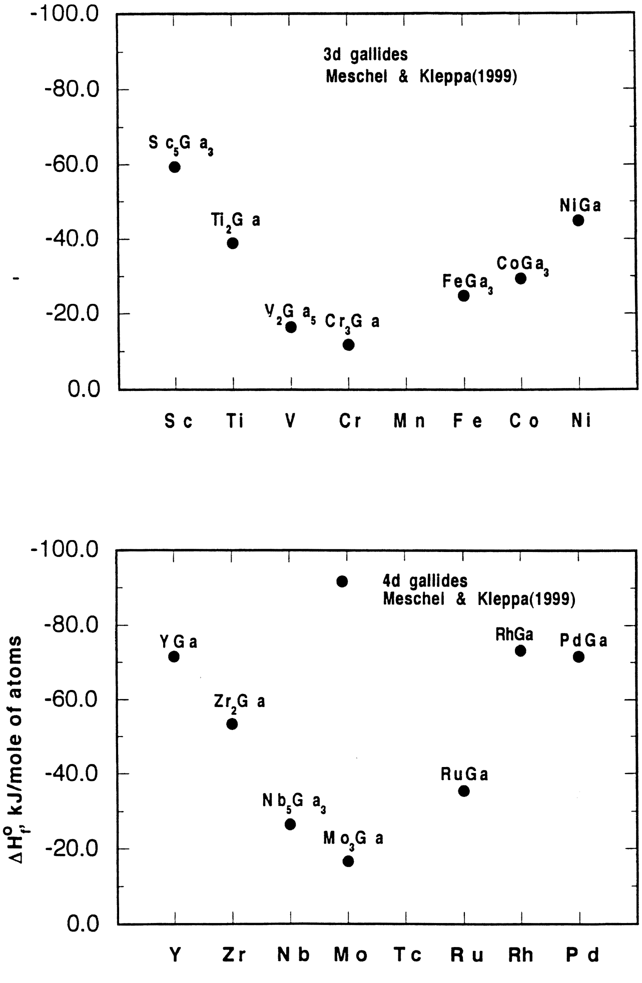

Fig. 5. Standard enthalpies of formation of some 3d and 4d transition metal gallides. Data in kJ/mol of atoms.

5. Carbides

In the first transition metal series all the elements form at least one carbide even though some of the reported phases are metastable at room temperature. Many of the binary carbides have a wide range of homogeneity. Hence, significant deviations from exact stoichiometry are common. The structures may usually be described as close packed arrangements of the metal atoms with the carbon atoms in interstitial sites. The chemical bonding typically is a mixture of covalent, ionic and metallic contributions. We measured the enthalpy of formation of TiC by SSD; the melting point of this compound is so high that the reaction time exceeded reliable measurement time at our working temperature of 1473 K [50].The heat of formation of Mn_5C_2 was measured by Kleppa and Hong by solution calorimetry [51].The enthalpies of formation of all the other carbides which we studied were measured by DSC [50].

Most of the carbides in the 4d and 5d transition metal series are very high melting. Several compounds which we attempted to prepare in the calorimeter at 1473 K, were found to yield incomplete reactions at this temperature. In some of the 4d and 5d systems no compound formation occurs at all. However, we were able to measure the enthalpies of formation of some 4d and 5d carbides, namely Y_2C, Mo_2C in the 4d series and LaC_2 in the 5d series. We already reported on our values for Y_2C and LaC_2 [52]. We are reporting a value for the enthalpy of formation of Mo_2C in this communication.

As the phase diagram shows, Mo_2C is one of the stable phases in this system (although the m.p. is not listed) [5]. In preliminary studies we prepared MoC and Mo_2C from −100 mesh Mo. Under our conditions Mo_2C seems to be the predominant phase. However, we observed about 5% unreacted metal in this sample.In order to facilitate completeness of reaction we used a finer Mo sample, with smaller particle size (3–7 μm), as well as a small excess of carbon in order to prepare the compositions $Mo_2C_{1.2}$ and $Mo_2C_{1.3}$. The technique of using a small excess of one of the components was described in a previous communication [7]. The XRD pattern of $Mo_2C_{1.2}$ matched the pattern of the α-Mo_2C listed in the ASTM powder diffraction file. The homogeneity range was reported as $X_C = 0.35–0.53$. The compound was also studied by neutron diffraction by Parthe and Sadagopan [53] and Christensen [54]. SEM and X-ray microprobe analysis also confirmed that our sample was largely a single phase. A second phase of another Mo carbide is present in an amount of less than 1%.

In order to improve the precision we also used the neutral binder technique for several compounds among the

Table 4
Standard enthalpies of formation of transition metal and lanthanide metal carbides; data in kJ/mol of atoms

Compound	ΔH_f^o (Expt.)	Method[a]	ΔH_f^o (Pred.) [15,16]		Reference
Sc_2C	−45.5±1.6	DSC	−56	−44	[52]
TiC	−92.9±8.9	SSD	−77	−76	[50]
V_4C_3	−40.3±1.2	DSC	−42	−48	[50]
Cr_7C_3	−14.1±0.8	DSC	−13	−22	[50]
Mn_5C_2	−8.9±1.5	DSC	−17	−21	[50]
	−10.0±0.5	SC			[51]
Mn_7C_3	−9.1±1.3	DSC	−18	−22	[50]
Fe_3C	+4.7±1.1	DSC	−1	−11	[50]
Co_2C	+2.8±1.3	DSC	+6	−9	[50]
Co_3C	+2.4±1.1	DSC	+4	−6	[50]
Ni_3C	+1.2±1.3	DSC	+7	−4	[50]
Y_2C	−31.8±1.3	DSC	−48	−37	[52]
Mo_2C	−11.6±1.3	DSC	−16	−27	[This work]
Al_4C_3	−18.3±1.0	DSC	–	−34	[55]
LaC_2	−27.2±1.4	DSC	−69	−60	[52]
CeC_2	−25.4±1.4	DSC		−62	[56]
PrC_2	−29.4±1.6	DSC		−63	[56]
NdC_2	−29.2±1.4	DSC		−63	[57]
SmC_2	−25.7±1.1	DSC		−65	[58]
GdC_2	−24.8±1.6	DSC		−65	[57]
TbC_2	−24.6±1.0	DSC		−66	[35]
DyC_2	−28.6±2.0	DSC		−66	[36]
HoC_2	−28.6±1.2	DSC		−64	[37]
ErC_2	−28.8±1.6	DSC		−67	[38]
TmC_2	−31.5±2.5	DSC		−67	[39]
LuC_2	−26.7±1.8	DSC		−69	[40]

[a] DSC, Direct synthesis calorimetry; SSD, solute–solvent drop calorimetry; SC, solution calorimetry.

3d transition metal carbides. We described this technique in a previous communication [7].

The only non-transition metal carbide which we studied was Al_4C_3 [55]. Its enthalpy of formation is included in Table 4.

In Table 4 we summarize the enthalpies of formation of the transition metal and lanthanide metal carbides studied in this laboratory, along with the predicted enthalpies derived from Miedema's semiempirical model.The enthalpy of formation of Mn_5C_2 was measured by direct synthesis [50] as well as by solution calorimetry [51] in this laboratory. The agreement is quite good. It is worth noting that there are two sets of predicted values by the Miedema model for this family of compounds. The fourth column lists the values derived on the basis of the calculations by deBoer et al. [15] while the fifth column gives the values of Niessen et al. [16]. Our experimental values compare somewhat better with the values of Niessen et al. [16]. For the Co and Ni carbides the experimental enthalpies of formation and the predicted values of Niessen et al. have different algebraic signs.

In Fig. 6 we present a systematic plot of the measured enthalpies of formation for the 3d carbides. This graph shows some interesting trends. The magnitude of the enthalpy of formation increases sharply from Sc to Ti, then decreases from Ti to Mn. For Fe, Co and Ni the values are small and endothermic, reflecting the metastability of these compounds. In this curve we do not observe the parabolic shape which we found for the aluminides and gallides. The shape is more similar to the curve for transition metal borides shown in Fig. 1. We noted that the shape of the curve is even more similar to the trend in 3d transition metal nitrides [50].

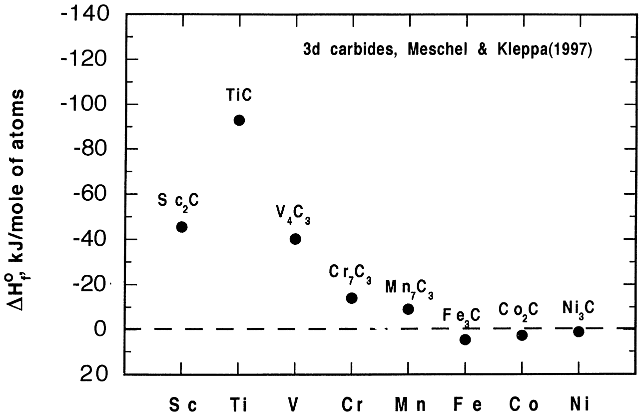

Fig. 6. Standard enthalpies of formation of some 3d transition metal carbides. Data in kJ/mol of atoms.

The lanthanide carbides are considered important by-products in the nuclear fission process. Hence, information concerning the thermochemical behavior of these compounds is important to our understanding of the properties of fission products in nuclear reactors moderated by graphite. In order to estimate the effects these products may have on the efficiency of the reactor, thermochemical data are of vital importance.

The early lanthanide carbides and LuC_2 all have a tetragonal CaC_2-type structure. We found no indication for the presence of the h.t.. cubic modification. The carbides of Ho, Er and Tm exhibit an orthorhombic modification [37–39]. These compounds are all very sensitive to oxygen and to moisture in the air.

Our measured enthalpies of formation are listed in Table 4. In general the predicted values do not agree with our experimental measurements. We plotted the enthalpies of formation of the lanthanide carbides in Fig. 7 against the atomic number of the lanthanide element. Note that we have no values for Pm, Eu and Yb. The experimental enthalpies of formation for all the LAC_2 compounds which we studied are all of comparable magnitude. We give an average value of −27.5±2.1 kJ/mol of atoms for the 12 compounds studied. As the graph indicates, the heat of formation shows little or no dependence on the number of f electrons. With the exception of the divalent Eu and Yb, the relative molar volume ratios when plotted against the atomic number are also very nearly constant for the LAC_2 compounds. Hence, in this case we find a reasonably good agreement with Gschneidner's prediction regarding the

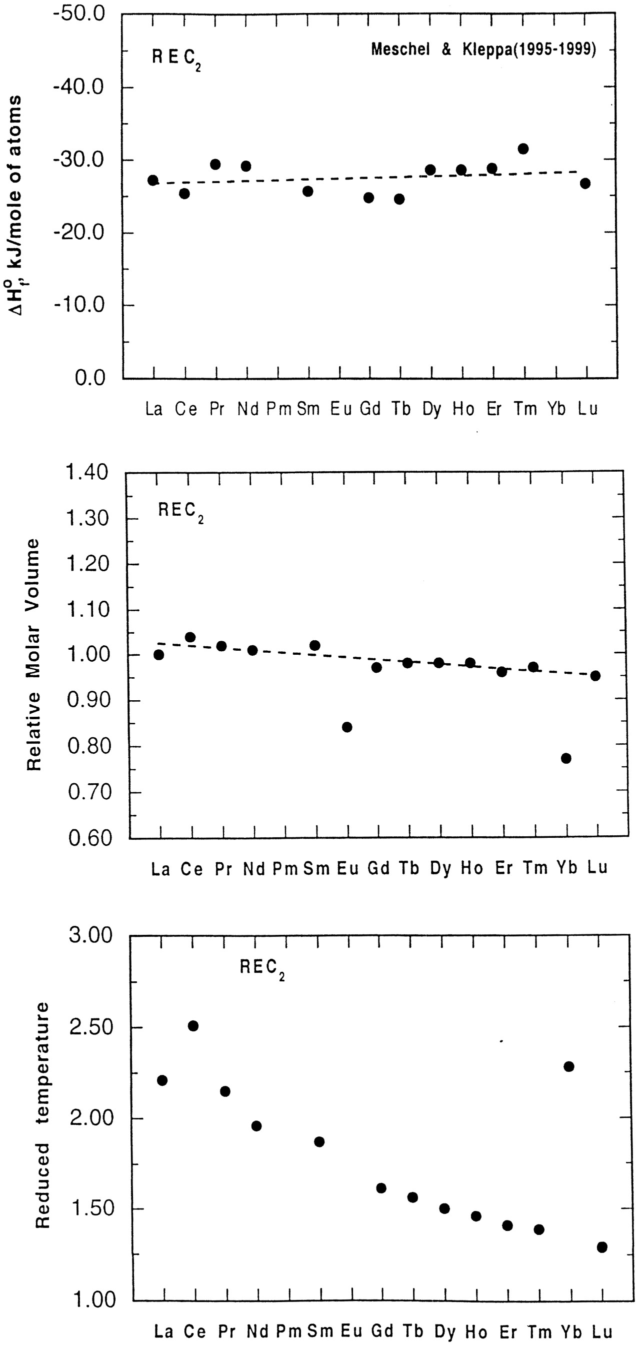

Fig. 7. Comparison of the enthalpies of formation of some lanthanide carbides with relative molar volumes and reduced temperatures. Data in kJ/mol of atoms.

correlation between the enthalpies of formation and the relative molar volumes [22,23].

6. Silicides

The silicides occupy an intermediate position between the interstitial and intermetallic compounds. Similarly to the borides, the special properties of these compounds are related to the electronic structure of the transition metal as well as to the tendency of silicon to combine into pairs, chains, and to form two- and three-dimensional networks. The bonding character may change with change in the ME:Si ratio. The silicides lower in Si content have more metallic character, while an increasing tendency toward covalent bonding generally occurs with increasing Si content.

The stability and resistance to oxidation make many of these alloys excellent candidates for high temperature structural applications, for aerospace applications and for high temperature coatings and furnace construction (Cr_3Si,Ti_5Si_3, Y, Zr, Nb and Mo silicides). Their relatively low electrical resistance allows their application for the design of microelectronic devices and integrated circuits (WSi_2, $TaSi_2$, PtSi). Some of the silicides exhibit superconducting properties for example, V_3Si, $CoSi_2$, Nb_3Si, PtSi.

Between 1986 and 1989, the enthalpies of formation of 16 transition metal silicides were measured by Topor and Kleppa by SSD. All the later work by the present authors were based on the use of DSC (70 alloys). We compared the results obtained by the two techniques for several compounds and found the agreement quite good for RuSi, RhSi, Pd_2Si, IrSi, PtSi and Pt_2Si. However, our value for Y_5Si_3 by DSC is somewhat more exothermic than the value measured by SSD [59]. Some of the transition metal silicides are very crumbly in texture. In these samples (15 alloys) we used a neutral binder (10 mol.% Ag) to insure better precision of the measurements. We discussed this technique in a previous communication [7].

In Table 5 we summarize the enthalpies of formation of the transition metal and lanthanide silicides studied in this laboratory along with the predicted values calculated from Miedema's semiempirical model [15,16]. The predicted values agree reasonably well with experiment for most of the 3d silicides except for the silicide of Ni. We find more disagreement in the 4d and 5d systems; for example, from Mo to Pd and from Ta to Ir the experimental values are quite different from the predicted values.

In Fig. 8 we present the enthalpies of formation for 3d, 4d and 5d transition metal silicides plotted against the atomic number of the metallic element. In each binary alloy we have plotted the most exothermic value for the particular system. The curves are very similar. The minima are in the same location (Cr, Mo) for the 3d and 4d silicides. For the 5d silicides the minimum is slightly displaced to Re. The curves show the familiar roughly parabolic shape. We have found the same shape for the curves of the transition metal aluminides and gallides. As for the aluminides and gallides, the enthalpies of formation are most exothermic for the 4d transition metal silicides. This is consistent with the prediction by Gelatt et al. [17]. However, the enthalpies of formation of the two end members in both the 4d and 5d families are exceptions to the pattern we found in the 3d silicides. We see that the

Table 5
Standard enthalpies of formation of some transition metal and lanthanide silicides; data in kJ/mol of atoms

Compound	ΔH_f^o (Expt.)	Method[a]	ΔH_f^o (Pred.) [15,16]	Reference
ScSi	−82.3±2.1	DSC	−80	[60]
Sc_5Si_3	−89.9±4.3	SSD	−69	[61]
TiSi	−72.6±1.9	DSC	−74	[60]
$TiSi_2$	−57.0±2.8	SSD	−55	[62]
Ti_5Si_3	−73.8±2.0	DSC	−68	[60]
Ti_5Si_4	−78.5±2.1	DSC	−74	[60]
VSi_2	−37.5±2.0	SSD	−29	[62]
V_5Si_3	−59.0±2.0	DSC	−46	[60]
V_3Si	−46.4±1.5	DSC	−34	[60]
CrSi	−34.2±1.6	DSC	−30	[60]
$CrSi_2$	−25.8±4.4	SSD	−15	[63]
Cr_5Si_3	−33.6±1.0	DSC	−31	[60]
Cr_3Si	−27.2±1.1	DSC	−24	[60]
MnSi	−39.4±1.7	DSC	−41	[60]
Mn_5Si_3	−34.0±1.2	DSC	−42	[60]
FeSi	−38.6±1.8	DSC	−26	[60]
CoSi	−49.3±1.3	DSC	−31	[60]
Co_2Si	−37.9±2.0	DSC	−30	[60]
$CoSi_2$	−34.9±1.1	DSC	−15	[60]
NiSi	−42.4±1.0	SSD	−33	[64]
Ni_2Si	−50.6±1.7	DSC	−32	[60]
Ni_5Si_2	−45.1±1.4	DSC	−29	[60]
YSi	−80.7±1.3	DSC	−78	[65]
Y_5Si_3	−71.7±3.6	SSD	−64	[59]
	−80.4±2.3	DSC		[65]
YSi_2	−61.8±1.4	DSC	−68	[65]
ZrSi	−94.5±2.3	DSC	−101	[65]
Zr_5Si_3	−71.7±4.8	SSD	−87	[59]
Zr_5Si_4	−91.9±1.9	DSC	−97	[65]
$ZrSi_2$	−60.3±1.7	DSC	−83	[65]
Nb_5Si_3	−64.6±2.4	DSC	−54	[65]
$NbSi_2$	−53.7±1.6	DSC	−43	[65]
Mo_5Si_3	−38.2±1.6	DSC	−28	[65]
$MoSi_2$	−47.9±2.1	DSC	−16	[65]
RuSi	−58.1±3.7	SSD	−32	[66]
	−58.3±2.1	DSC		[65]
Ru_2Si_3	−60.7±1.7	DSC	−26	[65]
RhSi	−75.0±2.5	SSD	−44	[66]
	−75.8±1.6	DSC		[65]
Rh_2Si	−63.9±2.4	DSC	−38	[65]
Pd_2Si	−64.5±2.5	SSD	−48	[64]
	−64.2±1.9	DSC		[65]
Pd_3Si	−57.9±1.9	DSC	−37	[65]
LaSi	−73.9±2.7	DSC	−76	[58]
$LaSi_2$	−56.8±2.5	DSC	−70	[56]
La_5Si_3	−60.1±2.6	DSC	−62	[58]
La_3Si_2	−61.6±1.6	DSC	−65	[58]
HfSi	−70.9±2.0	DSC	−91	[46]
Hf_3Si_2	−80.0±4.7	SSD	−83	[59]
Ta_5Si_3	−38.1±1.7	DSC	−55	[46]
$TaSi_2$	−46.0±2.5	DSC	−44	[46]
WSi_2	−27.3±2.0	DSC	−11	[46]
Re_2Si	−12.7±2.5	DSC	−20	[46]
OsSi	−40.0±10	SSD	−29	[66]
Os_2Si_3	−30.5±2.1	DSC	−23	[46]
IrSi	−63.8±3.7	SSD	−40	[66]
	−64.4±2.6	DSC		[46]
PtSi	−59.4±2.6	SSD	−56	[64]
	−59.6±2.1	DSC		[46]
Pt_2Si	−61.7±2.3	SSD	−47	[64]
	−63.3±2.3	DSC		[46]
Cu_3Si	−6.1±0.6	DSC	−4	[67]
La−silicides are listed with the 5d transition metal silicides				
CeSi	−71.1±3.3	DSC	−77	[56]
$CeSi_2$	−60.5±2.0	DSC	−69	[56]
Ce_5Si_3	−52.8±0.6	DSC	−63	[58]
PrSi	−78.1±1.9	DSC	−78	[56]
$PrSi_2$	−61.5±1.7	DSC	−69	[56]
Pr_5Si_3	−67.6±2.1	DSC	−64	[58]
NdSi	−78.7±2.5	DSC	−77	[57]
$NdSi_2$	−62.0±1.9	DSC	−69	[57]
Nd_5Si_3	−62.3±1.9	DSC	−64	[58]
SmSi	−79.7±2.9	DSC	−78	[58]
$SmSi_2$	−66.3±1.6	DSC	−69	[58]
Sm_5Si_3	−67.1±2.5	DSC	−64	[58]
GdSi	−75.6±2.3	DSC	−78	[40]
$GdSi_2$	−59.0±2.1	DSC	−68	[57]
Gd_5Si_3	−68.0±2.3	DSC	−64	[57]
TbSi	−80.9±1.8	DSC	−79	[35]
$TbSi_2$	−61.5±2.4	DSC	−68	[35]
Tb_5Si_3	−61.0±2.5	DSC	−65	[35]
DySi	−68.9±2.0	DSC	−79	[36]
$DySi_2$	−54.6±2.1	DSC	−68	[36]
Dy_5Si_3	−64.0±2.1	DSC	−65	[36]
HoSi	−80.9±2.2	DSC	−77	[37]
$HoSi_2$	−58.1±2.4	DSC	−66	[37]
Ho_5Si_3	−74.6±2.1	DSC	−64	[37]
ErSi	−84.9±2.5	DSC	−79	[38]
$ErSi_2$	−62.6±1.8	DSC	−68	[38]
Er_5Si_3	−70.7±3.1	DSC	−66	[38]
TmSi	−86.1±2.3	DSC	−79	[39]
$TmSi_2$	−64.9±2.8	DSC	−67	[39]
Tm_5Si_3	−76.1±2.3	DSC	−66	[39]
LuSi	−78.3±2.1	DSC	−80	[40]
Lu_5Si_3	−67.8±3.3	SSD	−68	[59]

[a] DSC, Direct synthesis calorimetry; SSD, solute–solvent drop calorimetry.

enthalpies of formation of YSi and LaSi have less exothermic values than ZrSi and Hf_3Si_2 while Pd_2Si and PtSi have lower values than RhSi and IrSi, respectively. On the other hand, the enthalpy of formation of RhSi is not the most exothermic value in this family of compounds. In this we note a difference from the behavior of the aluminides.

The only non-transition metal silicide which we studied was Cu_3Si [67]. The result is included in Table 5.

In the group of lanthanide silicides studied in this laboratory, only the value for Lu_5Si_3 was determined by SSD [59]; all the other compounds were measured by DSC. The enthalpy values are included in Table 5. Whenever possible we tried to study compounds with the stoichiometries LA_5Si_3, LASi or $LASi_2$ in order to observe the systematic changes.

In Fig. 9 we plot the enthalpies of formation of compounds with the stoichiometry 5:3 against the atomic number of the lanthanide element. This figure shows that the values display a small but very definite increase of the magnitude of the enthalpy of formation with atomic number. This trend shows a disagreement with Gschneid-

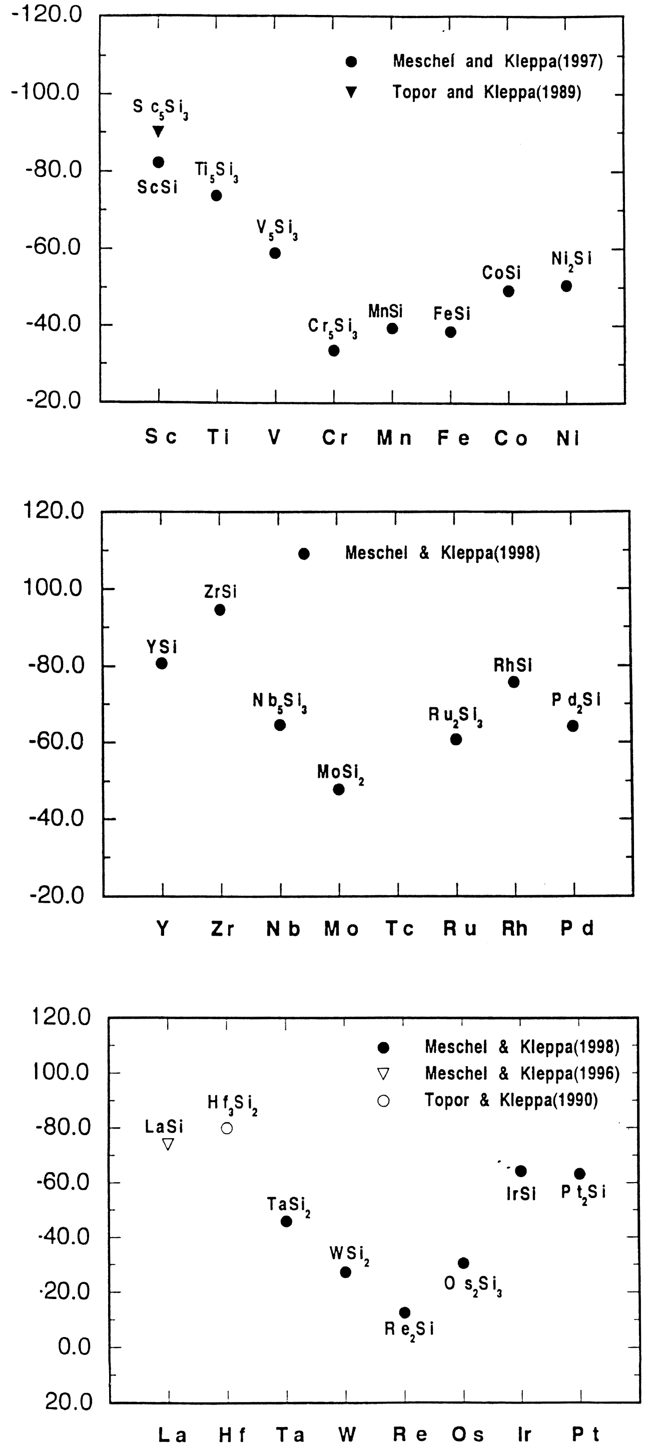

Fig. 8. Standard enthalpies of formation of some 3d, 4d and 5d transition metal silicides. Data in kJ/mol of atoms.

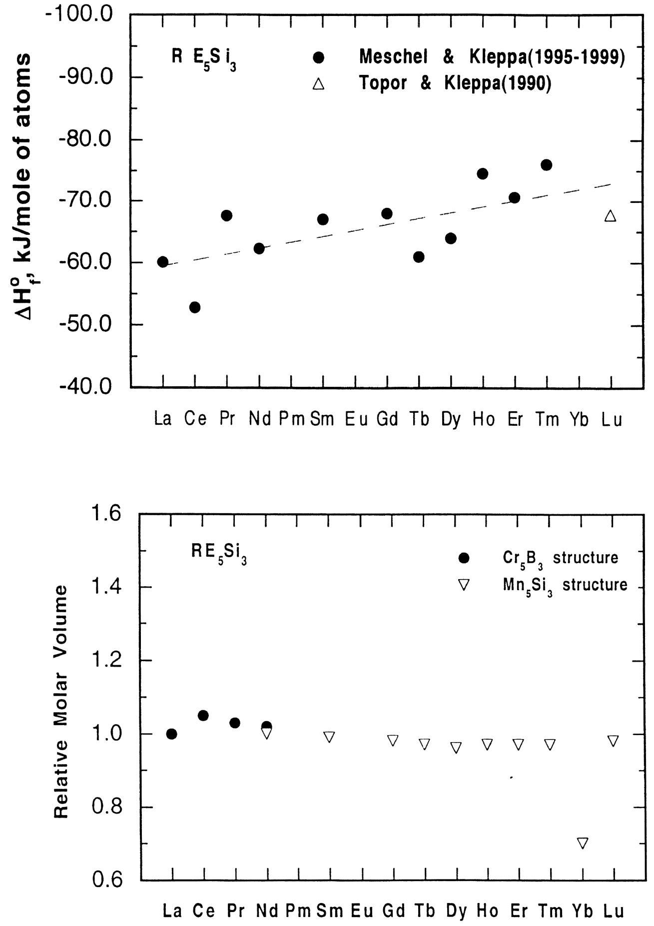

Fig. 9. Comparison of the standard enthalpies of formation for some lanthanide silicides of 5:3 stoichiometry with relative molar volumes. Data in kJ/mol of atoms.

ner's prediction for the correlation of enthalpies of formation with relative molar volumes. From the values of these quantities an approximately constant enthalpy of formation would be expected with the exception of the values for the divalent metals Eu and Yb [22,23]. Since the melting points are not available for many of the lanthanide silicides, we cannot compare our enthalpies of formation with the reduced temperature as suggested by Gschneidner [22,23].

7. Germanides

During the past 2 decades there has been an increased interest in the structure, physical properties and stability of transition metal germanides due to their potential application in the development of new materials for electronic technology and magnetic devices.

We have in this laboratory studied a considerable number of germanides both by SSD (seven alloys) and by the direct synthesis method (thirty-four alloys).

In Table 6 we list the standard enthalpies of formation of the transition metal and lanthanide germanides along with the predicted enthalpies calculated on the basis of Miedema's semiempirical model [15,16]. This table shows that there is reasonable agreement between the experimental and predicted enthalpies of formation to within ±5–10 kJ/mol of atoms. Some notable exceptions are the en-

Table 6
Standard enthalpies of formation of some transition metal and lanthanide germanides; Data in kJ/mol of atoms

Compound	ΔH_f^o (Expt.)	Method[a]	ΔH_f^o (Pred.) [15,16]	Reference
Sc_5Ge_3	−93.4±3.8	SSD	−75	[68]
Ti_5Ge_3	−70.8±2.4	SSD	−60	[69]
V_5Ge_3	−44.3±4.7	SSD	−33	[69]
Cr_5Ge_3	−15.7±1.1	DSC	−15	[69]
Mn_5Ge_3	−18.2±0.7	DSC	−33	[69]
Fe_5Ge_3	−10.4±0.8	DSC	−11	[69]
Co_5Ge_3	−19.6±0.6	DSC	−19	[69]
Ni_5Ge_3	−31.1±0.6	DSC	−22	[69]
Y_5Ge_3	−89.8±5.0	SSD	−74	[68]
Zr_5Ge_3	−81.1±5.6	SSD	−85	[70]
Nb_5Ge_3	−69.2±4.2	SSD	−39	[70]
Mo_5Ge_3	−16.7±0.5	DSC	−8	[70]
RuGe	−28.5±0.7	DSC	−14	[70]
RhGe	−56.9±1.1	DSC	−31	[70]
PdGe	−46.5±0.8	DSC	−51	[70]
Pd_2Ge	−52.3±0.9	DSC	−44	[70]
La_5Ge_3	−67.8±1.0	DSC	−73	[68]
Hf_3Ge_2	−74.6±7.9	SSD	−79	[71]
Ta_5Ge_3	−42.0±1.1	DSC	−41	[72]
Re_3Ge_7	+2.1±2.7	DSC	+9	[46]
$OsGe_2$	−3.7±2.5	DSC	0	[72]
IrGe	−33.1±0.9	DSC	−23	[71]
	−32.5±5.9	SSD		[71]
PtGe	−45.4±1.2	DSC	−43	[71]
Pt_2Ge	−37.1±1.6	DSC	−37	[71]
Cu_3Ge	−4.1±0.7	DSC	−4	[67]
$LaGe_{1.6}$	−75.4±2.2	DSC	−88	[46]
Ce_5Ge_3	−73.4±2.3	DSC	−74	[56]
$CeGe_{1.6}$	−76.6±1.9	DSC	−87	[56]
Pr_5Ge_3	−70.4±2.3	DSC	−74	[56]
$PrGe_{1.6}$	−81.7±1.7	DSC	−86	[56]
Nd_5Ge_3	−72.1±1.6	DSC	−74	[57]
$NdGe_{1.6}$	−80.2±1.9	DSC	−86	[57]
Gd_5Ge_3	−82.0±2.6	DSC	−74	[57]
Sm_5Ge_3	−90.8±2.0	DSC	−74	[58]
Tb_5Ge_3	−81.7±2.7	DSC	−74	[35]
Dy_5Ge_3	−92.4±2.3	DSC	−74	[36]
Ho_5Ge_3	−91.8±1.7	DSC	−74	[37]
Er_5Ge_3	−95.6±2.0	DSC	−75	[38]
Tm_5Ge_3	−91.3±1.9	DSC	−74	[39]
Lu_5Ge_3	−93.1±2.2	DSC	−75	[73]

[a] DSC, direct synthesis calorimetry; SSD, solute–solvent drop calorimetry.

thalpies of Sc_5Ge_3, Nb_5Ge_3 and RhGe where the predicted values are considerably less exothermic than our measured values. It is noteworthy that the algebraic sign for the experimental and predicted enthalpies of formation of Re_3Ge_7 agree.

In Fig. 10 we plot the enthalpies of formation against the atomic number of the 3d, 4d and 5d transition metal element. This figure shows that the curves follow the familiar roughly parabolic pattern as for the aluminides, gallides and silicides. Like the aluminides, gallides and silicides the 4d transition metal germanides have the most exothermic enthalpies of formation among the compounds formed by the 3d, 4d and 5d elements. In the 4d and 5d germanide groups we see a reversal in the pattern for two of the end members, which does not show up in the 3d germanide pattern. For example, the enthalpy of formation

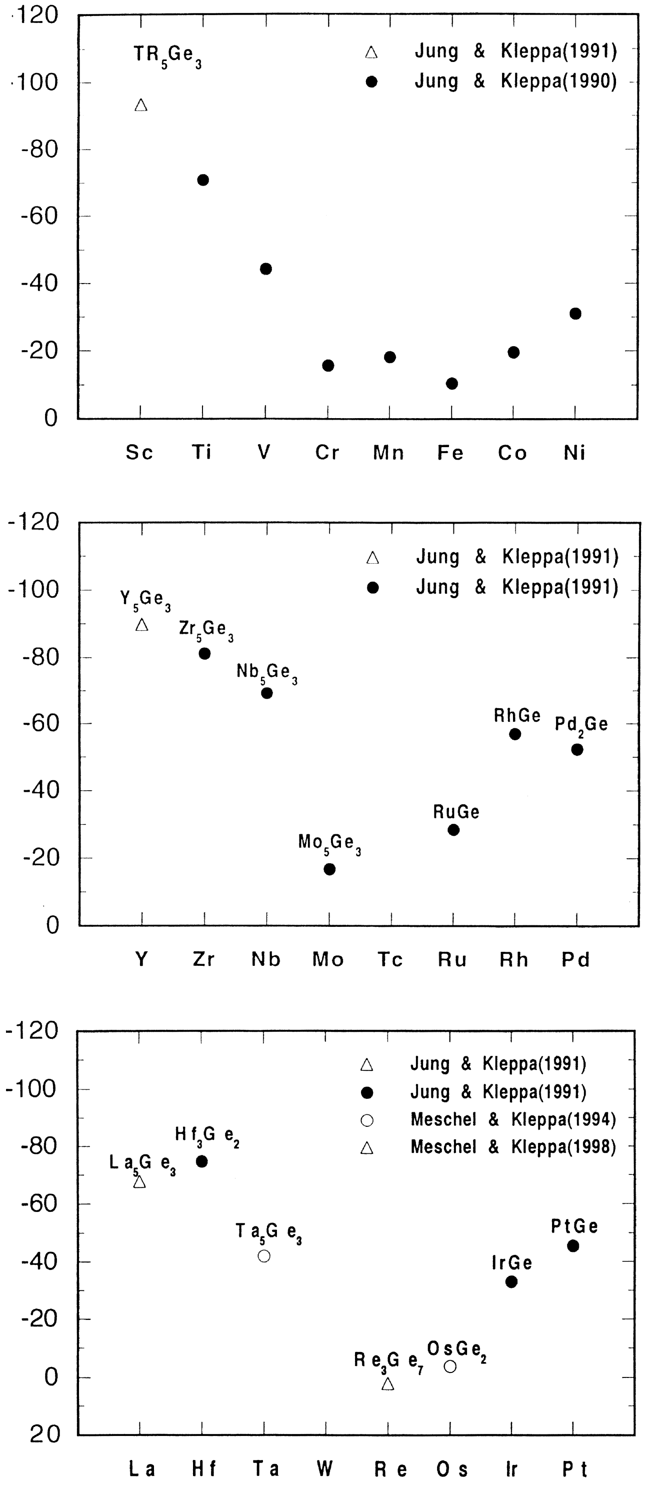

Fig. 10. Standard enthalpies of formation of some 3d, 4d and 5d transition metal germanides. Data in kJ/mol of atoms.

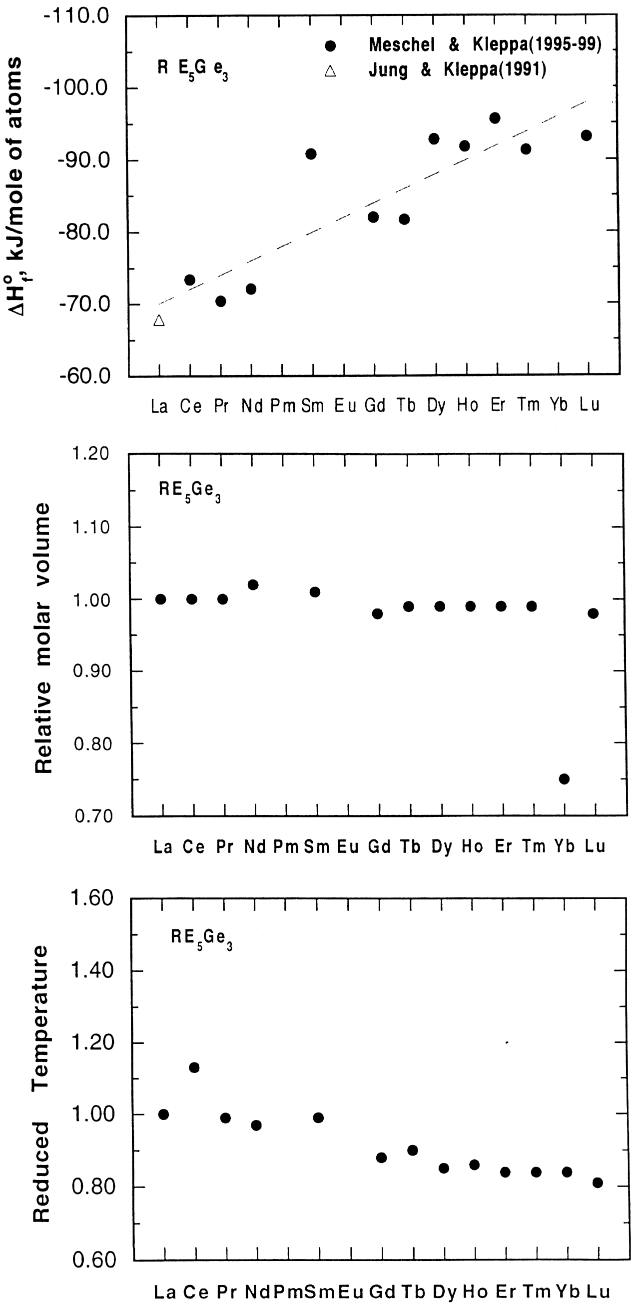

Fig. 11. Comparison of the standard enthalpies of formation of some lanthanide germanides of the 5:3 stoichiometry with relative molar volumes and reduced temperatures. Data in kJ/mol of atoms.

of RhGe is more exothermic than the value for Pd_2Ge and the heat of formation of Hf_3Ge_2 is more exothermic than the corresponding value for La_5Ge_3. We noticed similar reversals for silicides.

The enthalpies of formation of the lanthanide germanides are included in Table 6. Note that the predicted values are essentially constant. However, in our measured enthalpies of formation we see a definite increase to more exothermic values with increasing atomic number.

In Fig. 11 we plot the enthalpies of formation of the lanthanide germanides, where the structures all have LA_5Ge_3 stoichiometry, against the atomic number of the lanthanide element. The reduced temperatures decline with increasing atomic number. The relative molar volume ratios with the exception for the value for Yb_5Ge_3 are very nearly constant or may decline slightly when plotted against the atomic number. Hence, in this case Gschneidner's prediction regarding the correlation of the enthalpies of formation with the reduced temperatures and the relative molar volumes disagree strongly with our data [22,23].

8. Stannides

Early calorimetric studies by Predel and Vogelbein [74] and by Ferro et al. [8] show that transition metal stannides have relatively large negative enthalpies of formation; this indicates that the bonding between these metals and tin is quite strong.

The V–Sn and Nb–Sn systems are of considerable technological interest because of the superconducting properties of the V_3Sn and Nb_3Sn compounds. The Zr–Sn system is also of special interest because of the technological use of zirconium stannides in pressurized water reactors.

The enthalpies of formation of all the transition metal and lanthanide stannides which we have studied in this laboratory were measured by DSC. The results are recorded in Table 7. In this table we also include earlier enthalpy values as well as appropriate references for the 3d, 4d and 5d and lanthanide stannides along with the predicted values calculated on the basis of Miedema's semiempirical model [15,16].

The predicted enthalpies of formation are in reasonable agreement with the experimental results only for V_3Sn, Nb_3Sn, Pd_3Sn and PtSn. For the other alloys the differences are quite large.

In Fig. 12 we plot the enthalpies of formation of 3d, 4d and 5d transition metal stannides against the atomic number of the metallic element. In this figure we are citing the calorimetric enthalpies of formation for FeSn, CoSn and NiSn reported by Predel and Vogelbein [74]. The value for Mn_2Sn was derived from EMF measurements by Lukashenko et al. [75], while the value for $MoSn_2$ was assessed by Brewer and Lamoreaux [76]. The enthalpy of formation of La_5Sn_3 was measured by Borzone et al. [77] and by Borsese et al. [78]. Fig. 12 shows that the enthalpies of formation of the 3d, 4d and 5d stannides all exhibit the familiar, roughly parabolic curve. We observed similar systematic relationships for aluminides, gallides, silicides and germanides. In order to see the systematic changes among the 3d, 4d and 5d groups we selected the triads Ti–Zr–Hf, Co–Rh–Ir and Ni–Pd–Pt; these were the only triads for which the standard enthalpies of formation

Table 7
Standard enthalpies of formation of some transition metal and lanthanide stannides; data in kJ/mol of atoms

Compound	ΔH°_{f} (Expt.)	Method[a]	ΔH°_{f} (Pred.) [15,16]	Reference
Sc_5Sn_3	−70.2±1.8	DSC	−76	[79]
Ti_6Sn_5	−43.4±1.4	DSC	−52	[80]
V_3Sn	−21.7±1.4	DSC	−16	[80]
Y_5Sn_3	−72.8±2.9	DSC	−81	[79]
Zr_5Sn_3	−71.2±2.5	DSC	−81	[80]
Nb_3Sn	−15.2±2.3	DSC	−16	[80]
Ru_3Sn_7	−18.7±1.4	DSC	−9	[80]
$RhSn_2$	−42.1±2.4	DSC	−28	[80]
Pd_3Sn	−57.8±1.9	DSC	−52	[80]
Hf_5Sn_3	−49.2±2.1	DSC	−70	[80]
Ir_5Sn_7	−15.0±1.9	DSC	−24	[80]
$IrSn_2$	−12.9±1.6	DSC	−20	[80]
PtSn	−58.8±2.3	DSC	−57	[80]
Pr_5Sn_3	−75.3±1.4	DSC	−82	[79]
Nd_5Sn_3	−74.1±1.4	DSC	−82	[79]
Sm_5Sn_3	−77.9±2.0	DSC	−81	[58]
Gd_5Sn_3	−78.5±2.8	DSC	−81	[79]
Tb_5Sn_3	−73.1±3.1	DSC	−81	[35]
Dy_5Sn_3	−75.1±2.1	DSC	−81	[36]
Ho_5Sn_3	−73.5±2.3	DSC	−80	[79]
Er_5Sn_3	−72.3±2.1	DSC	−80	[38]
Tm_5Sn_3	−72.8±2.1	DSC	−80	[39]
Lu_5Sn_3	−75.1±2.7	DSC	−80	[73]
	−73.6±1.4	DSC		[40]

[a] DSC, direct synthesis calorimetry.

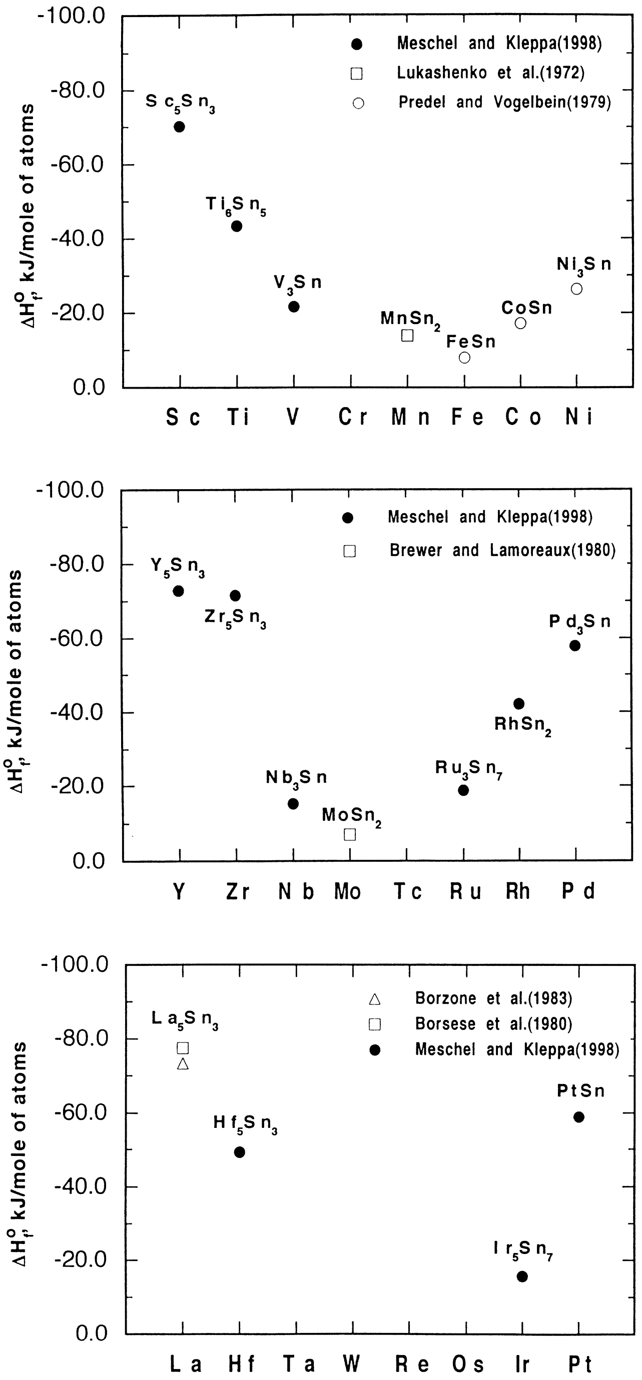

Fig. 12. Standard enthalpies of formation of some 3d, 4d and 5d transition metal stannides. Data in kJ/mol of atoms.

were available for all three groups. As we found for the aluminides, gallides, silicides and germanides, the stannides formed by the 4d elements have the most exothermic enthalpies of formation.

In Table 7 we summarized the enthalpies of formation of the lanthanide stannides studied in this laboratory. Within experimental error, the reported values are essentially constant, the average is −74.3±2.2 kJ/mol of atoms for 12 compounds. Note that we have no values for Pm, Eu and Yb. The enthalpies of formation predicted by Niessen et al. [16] are all somewhat more exothermic than the experimental values. However, these values are also nearly constant throughout the lanthanide series. The heats of formation predicted by Colinet et al. [81] by a modification of the Miedema model are somewhat less exothermic than the experimental values. However, these show a decreasing trend with increasing atomic number. We have not found such a trend in our experimental values.

In Fig. 13 we plot the enthalpies of formation of the lanthanide stannides against the atomic number of the lanthanide element. The heats of formation of La_5Sn_3 and Ce_5Sn_3 were determined calorimetrically by Borzone et al. and by Borsese et al. [77,78,82]. The systematic trend is quite clear in this set of systems for the stoichiometric ratios of the compounds are all the same. In this figure we also compare our own experimental enthalpies of formation with the relative molar volume ratios as suggested by Gschneidner [22,23]. The relative molar volume ratios (with the exception of Yb_5Sn_3) are nearly constant when plotted against the atomic number of the lanthanide element. Hence for these compounds the prediction based on the correlation of the enthalpy of formation with relative molar volumes agree reasonably well with our experimental data.

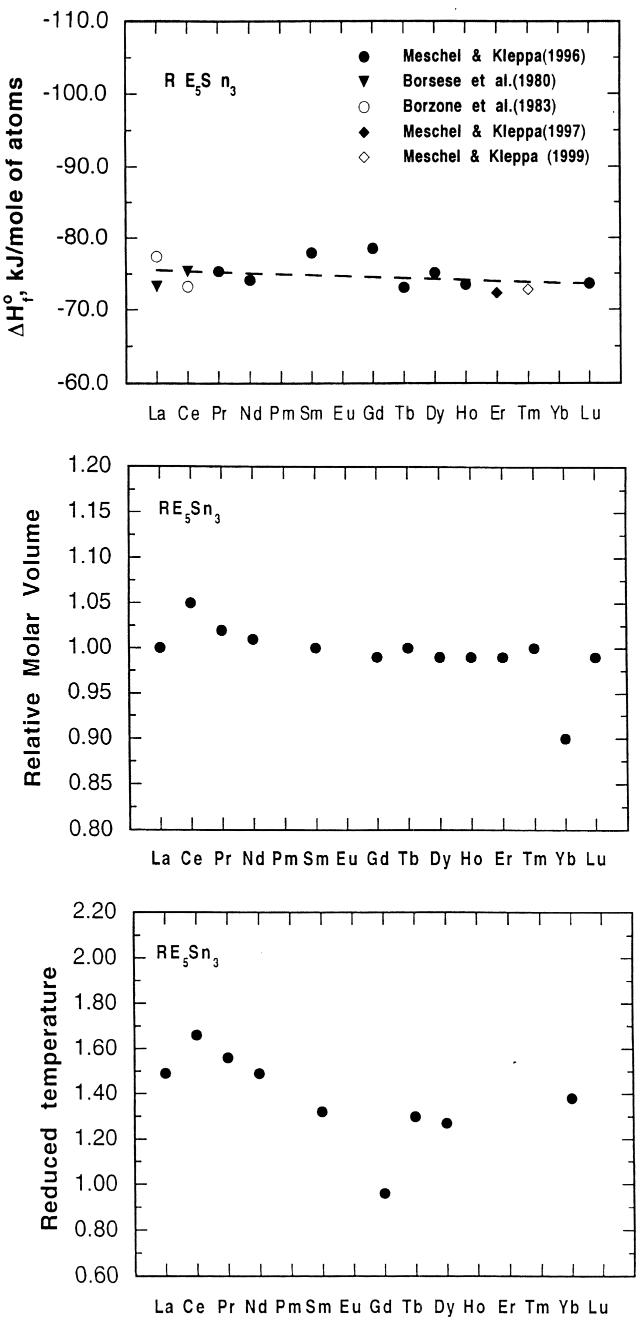

Fig. 13. Comparison of the standard enthalpies of formation of some lanthanide stannides with relative molar volumes and reduced temperatures. Data in kJ/mol of atoms.

9. Summary

In this laboratory we have carried out a systematic study of the thermochemical behavior of approximately 270 compounds of transition metal and lanthanide elements with the elements in the IIIB and IVb columns in the periodic table. We will summarize some general trends which we observed.

The direct synthesis method which was used to measure the enthalpies of formation of the majority of these compounds (235) has a number of advantages when the reaction is completed in a reasonable amount of time (1 h or less). The process is less cumbersome and the results are considerably more precise than those obtained by the solute–solvent drop technique. We found that our operating temperature of 1473 K is quite suitable for the enthalpy of formation measurements for compounds which do not melt above ~2773 K. This constraint explains our difficulties with measurements of the enthalpies of formation of 4d transition metal carbides, and with ZrB_2 and HfB_2, which both melt at considerably higher temperatures. Although it is usually preferable to select a congruently melting phase for the calorimetric measurements, we also studied many compounds which melt peritectically. In some cases we had no information about the melting points of the compounds or even the phase diagram of the system. Our average precision using the direct synthesis method is approximately ±1–2 kJ/mol of atoms.

For the TR–X alloys which we have studied so far (X=Al, Ga, Si, Ge, Sn) the plot of the enthalpy of formation against the atomic number of the transition metal yields a roughly parabolic curve. This is consistent with the prediction of Pasturel et al. [18] for transition metal aluminides. For each binary system we always plotted the most exothermic value that we found in the considered system. The minima of the curves are also roughly in the same position, near the middle of the series (Figs. 3, 5, 8, 10 and 12).

In these systems another general trend may be observed. The 4d transition metal compounds always have a higher exothermic enthalpy of formation than the corresponding 3d or 5d alloys. The Rh alloys have some of the highest exothermic values in these families, e.g. RhAl, RhGe, RhSi. This is consistent with the predictions of Gellatt et al. [17] for the 4d aluminides.

In the carbides and borides we see a somewhat different relationship between the enthalpy of formation and the atomic number of the transition metal (see Figs. 1 and 6). In both families we see an increase in magnitude from the first to the second member of the group and a subsequent decrease. After the decrease the curve levels off without showing significant changes. We cannot make any general statement regarding systematic changes in the enthalpies of formation of 3d, 4d and 5d carbides, since we have systematic values only for the 3d compounds. Apart from this, we measured the enthalpies of formation of some selected 4d and 5d carbides where the melting temperatures were suitable for our calorimeter notably the compounds Y_2C, Mo_2C and LaC_2. The transition metal nitrides show a similar trend when the heat of formation is plotted against the atomic number of the metallic element [50].

In our previous communications we attempted to make comparisons of the electronegativity differences of the components of the binary alloys and the enthalpies of formation. The available electronegativities have the same numerical values for the metallic components Fe–Co–Ni, for Ru–Rh–Pd and for Os–Ir–Pt. The nonmetallic elements Si, Ge, Sn also have the same electronegativity values. Therefore, if there is any correlation between the electronegativity differences and the enthalpies of formation, this might show up best by comparing Ru, Rh, Pd and Os, Ir, Pt silicides, germanides and stannides. However, the enthalpies of formation of Ru and Rh alloys with Si, Ge and Sn differ by nearly a factor of 2. In all cases the silicides have the most exothermic enthalpies of formation, and then the values decrease significantly to Ge and Sn. We also attempted to make a comparison of the melting points of the considered compounds. We found no correlation in any of the alloy families we studied (where the data were available). This suggests that the chemical bonding in these alloys is covalent rather than ionic as already noted by Colinet et al. [19] and by Pasturel et al. [18] for aluminides.

When we plotted the enthalpies of formation of the lanthanide compounds, LA–X, (where X=B, Al, Ga, C, Si, Ge, Sn) against the atomic number of the metallic element, we observed two distinctly different types of behavior. (Note again that we have no values for Pm, Eu and Yb.) For the aluminides, carbides and stannides the enthalpies of formation show no significant change when plotted against the atomic number of the lanthanide element. Hence, in these cases the enthalpies of formation of lanthanide aluminides, carbides and stannides show agreement with Gschneidner's prediction regarding the correlation between enthalpies of formation and relative molar volumes [22,23] (Figs. 4, 7 and 13). However, the agreement does not hold for the LA_5Si_3 and LA_5Ge_3 compounds, where we observe an increase in the magnitude of the heat of formation with increasing atomic number (Figs. 9 and 11). We do not as yet have enough data for the lanthanide gallides to state a trend. We found no correlation between the enthalpies of formation and the reduced temperatures for any of the lanthanide alloy families which we studied [22,23] (Figs. 4, 7, 11 and 13).

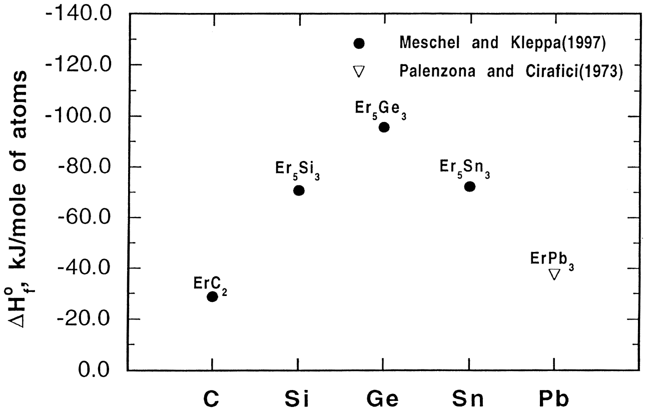

Fig. 14. Comparison of the standard enthalpies of formation of compounds of Er and elements in the IVB column in the periodic table.

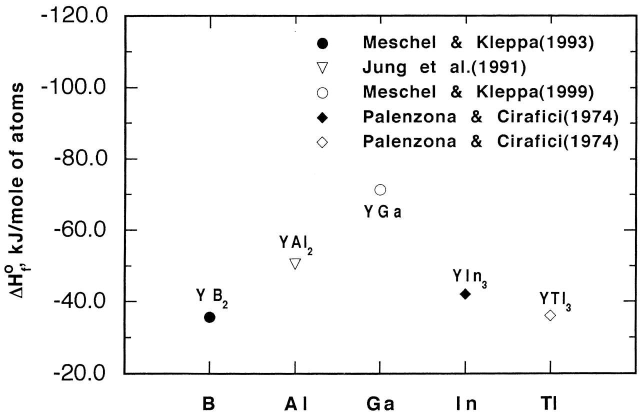

Fig. 15. Comparison of the standard enthalpies of formation of compounds of Y and elements in the IIIB column in the periodic table.

We noted in previous communications that the enthalpies of formation of the compounds of lanthanide elements with the IIIB and IVB elements in the periodic table show a roughly parabolic relationship when plotted against the IIIB or IVB elements [35–40,56,58,79]. We also observed this correlation for Sc and Y compounds [79]. For the IVB elements the germanides have the most exothermic value. In Fig. 14 we show an example of this systematic behavior. Where data are available, the enthalpies of formation of the gallides seem to have the most exothermic values in the IIIB set of compounds as exemplified in Fig. 15. A systematic study is in progress to measure the enthalpies of formation of the lanthanide gallides.

The enthalpies of formation of the transition metal alloys show a somewhat different picture. In the IVB set of compounds, where data are available, the maximum negative enthalpy of formation is usually found for the silicides [46]. We noted this difference in the thermochemical behavior of transition metal and lanthanide compounds with IVB elements in a previous communication which assessed the trends in the 5d silicides [46]. We find that the comparison is similar for 3d and 4d transition metal compounds. We also attempted to make a comparison for the compounds of the transition metals with the elements in group IIIB in the periodic table. For that group the correlation is not as clear. Some alloys between In or Tl and the transition metals do not form, or the heats of formation are not available for comparison. For the groups of Fe, Co, Ni, Mo, Ru, Rh, Pd, Os, Ir and Pt the aluminides have the highest exothermic enthalpies of formation. However, for Sc, Ti, Cr, Zr, Nb, Hf and Ta the borides have the most exothermic heats of formation.

Acknowledgements

This investigation has been supported by the Department of Energy under Grant DE-FGO2-88ER-45363 and has also benefited from the MRSEC facilities at the University of Chicago.

References

[1] O.J. Kleppa, L. Topor, Thermochim. Acta 139 (1989) 291–297.
[2] O.J. Kleppa, J. Phase Equil. 15 (1994) 240–263.
[3] L. Topor, O.J. Kleppa, J. Chem. Thermodyn. 16 (1984) 993–1002.
[4] J.C. Gachon, J. Charles, J. Hertz, Calphad 9 (1985) 29–34.
[5] T.B. Massalski, H. Okamoto, P.R. Subramanian, L. Kaczprzak, in: Binary Alloy Phase Diagrams, 2nd Edition, ASM, Metals Park, OH, 1990.
[6] P. Villars, C.D. Calvert (Eds.), Pearson's Handbook of Crystallographic Data for Intermetallic Phases, ASM, Metals Park, OH, 1985.
[7] S.V. Meschel, O.J. Kleppa, J. Chim. Phys. 90 (1993) 349–354.
[8] R. Ferro, R. Cappelli, A. Borsese, S. Delfino, G.B. Bonino, Rendiconti Sci. Fis. Mat. Nat. Accad. Naz. Lincei 54 (1973) 80–82.
[9] D. El Allam, M. Gaune-Escard, J.P. Bros, E. Hayer, Metall. Trans. 23B (1992) 39–44.
[10] Yu.M. Golutvin, E.G. Maslennikova, Russ. Metallurgy 1 (1971) 118–123.
[11] O. Kubaschewski, G. Heymer, Trans. Faraday Soc. 56 (1960) 473–478.
[12] A.W. Bryant, W.G. Bugden, J.N. Pratt, Acta Met. 18 (1970) 101–107.
[13] B. Predel, W. Vogelbein, U. Schallner, Thermochim. Acta 12 (1975) 367–375.
[14] Q. Han, R. Schmid-Fetzer, A. Belgacem-Bouzida, J. Charles, M. Notin, J. Hertz, J. Chim. Phys. 90 (1993) 445–450.
[15] F.R. deBoer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen, Cohesion in Metals. Transition Metal Alloys, Elsevier, Amsterdam, 1989.
[16] A.K. Niessen, F.R. deBoer, R. Boom, P.F. deChatel, W.C.M. Mattens, A.R. Miedema, Calphad 7 (1983) 51–70.
[17] C.D. Gelatt Jr., A.R. Williams, V.L. Moruzzi, Phys. Rev. B 27 (1983) 2005–2013.
[18] A. Pasturel, D. Nguyen-Manh, D. Mayou, J. Phys. Chem. Solids 47 (1986) 325–330.
[19] C. Colinet, A. Bessoud, A. Pasturel, Z. Metallkunde 77 (1986) 798–804.
[20] W.G. Jung, O.J. Kleppa, Metall. Trans. 23B (1992) 53–56.
[21] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 297 (2000) 162–167.
[22] K.A. Gschneidner Jr., J. Less-Common Metals 17 (1969) 1–12.
[23] K.A. Gschneidner Jr., Metals Mater. Proc. 1 (1990) 241–251.
[24] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 221 (1995) 37–41.
[25] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 227 (1995) 93–96.
[26] L. Topor, O.J. Kleppa, J. Chem. Thermodyn. 17 (1985) 1003–1016.
[27] L. Topor, O.J. Kleppa, J. Chem. Thermodyn. 17 (1985) 109–116.
[28] O.J. Kleppa, S. Sato, J. Chem. Thermodyn. 14 (1982) 133–143.
[29] S. Sato, O.J. Kleppa, Metall. Trans. 13B (1982) 251–257.
[30] L. Topor, O.J. Kleppa, High Temp. Sci. 22 (1986) 139–144.
[31]] S.V. Meschel, O.J. Kleppa, Metall. Trans. 24A (1993) 947–950.
[32] S.V. Meschel, O.J. Kleppa, Metall. Trans. 22A (1991) 1680–1683.
[33] O.J. Kleppa, L. Topor, J. Less-Common Metals 106 (1985) 269–276.
[34] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 177 (1991) 159–166.
[35] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 234 (1996) 137–142.
[36] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 233 (1996) 272–278.
[37] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 247 (1997) 52–56.
[38] S.V. Meschel, O.J. Kleppa, J. Chim. Phys. 94 (1997) 928–938.
[39] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 285 (1999) 179–184.
[40] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 224 (1995) 345–350.
[41] G.K. Johnson, E. Greenberg, J.L. Margrave, W.N. Hubbard, J. Chem. Eng. Data 12 (1967) 137–141.
[42] W.G. Jung, O.J. Kleppa, L. Topor, J. Alloys Comp. 176 (1991) 309–318.
[43] S.V. Meschel, O.J. Kleppa, in: J.S. Faulkner, R.G. Jordan (Eds.), Metallic Alloys: Experimental and Theoretical Perspectives, Kluwer, Dordrecht, 1994, pp. 103–112.
[44] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 191 (1993) 111–116.
[45] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 197 (1993) 75–81.
[46] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 280 (1998) 231–239.
[47] C. Colinet, A. Pasturel, K.H.J. Buschow, J. Chem. Thermodyn. 17 (1985) 1133–1139.
[48] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 290 (1999) 150–156.
[49] S.V. Meschel, O.J. Kleppa, Thermochim. Acta 292 (1997) 13–17.
[50] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 257 (1997) 227–233.
[51] O.J. Kleppa, K.C. Hong, J. Chem. Thermodyn. 10 (1978) 243–248.
[52] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 205 (1994) 165–168.
[53] E. Parthe, V. Sadagopan, Acta Cryst. 16 (1963) 202–205.
[54] A.N. Christensen, Acta Chem. Scand. A31 (1977) 509–511.
[55] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 227 (1995) 93–96.
[56] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 220 (1995) 88–93.
[57] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 217 (1995) 235–239.
[58] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 243 (1996) 186–193.
[59] L. Topor, O.J. Kleppa, J. Less-Common Metals 167 (1990) 91–99.
[60] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 267 (1998) 128–135.
[61] L. Topor, O.J. Kleppa, Metall. Trans. 20B (1989) 879–882.
[62] L. Topor, O.J. Kleppa, Metall. Trans. 17A (1986) 1217–1221.
[63] L. Topor, O.J. Kleppa, J. Chem. Thermodyn. 19 (1987) 69–75.
[64] L. Topor, O.J. Kleppa, Z. Metallkunde 77 (1986) 65–71.
[65] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 274 (1998) 193–200.
[66] L. Topor, O.J. Kleppa, Z. Metallkunde 79 (1988) 623–628.
[67] S.V. Meschel, O.J. Kleppa, Metall. Trans. 22A (1991) 2162–2165.
[68] W.G. Jung, O.J. Kleppa, J. Less-Common Metals 169 (1991) 85–92.
[69] O.J. Kleppa, W.G. Jung, High Temp. Sci. 29 (1990) 109–123.
[70]] W.G. Jung, O.J. Kleppa, J. Less-Common Metals 169 (1991) 93–103.
[71] W.G. Jung, O.J. Kleppa, J. Alloys Comp. 176 (1991) 301–308.
[72] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 216 (1994) L13–L15.
[73] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 245 (1996) L28–L29.
[74] B. Predel, W. Vogelbein, Thermochim. Acta 30 (1979) 201–215.
[75] G.M. Lukashenko, R.I. Polotskaya, K.A. Dyuldina, Russ. Metall. 4 (1972) 150–152.
[76] L. Brewer, R.H. Lamoreaux, Molybdenum: Physico-chemical properties of its compounds and alloys, in: L. Brewer (Ed.), Atomic Energy Review, Special Issue No. 7, Vienna: International Atomic Energy Agency, New York, 1980, pp. 106–107.
[77] G. Borzone, A. Borsese, R. Ferro, Z. Anorg. Allgem. Chem. 501 (1983) 199–208.
[78] A. Borsese, G. Borzone, R. Ferro, J. Less-Common Metals 70 (1980) 213–216.
[79] S.V. Meschel, O.J. Kleppa, J. Alloys Comp. 238 (1996) 180–186.
[80] S.V. Meschel, O.J. Kleppa, Thermochim. Acta 314 (1998) 205–212.
[81] C. Colinet, A. Pasturel, A. Percheron-Guegan, J.C. Achard, J. Less-Common Metals 102 (1984) 167–177.
[82] G. Borzone, A. Borsese, R. Ferro, J. Less-Common Metals 85 (1982) 195–203.