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COMMENTS ON INTERMETALLIC THERMOCHEMISTRY

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Abstract

The need of a concerted multi-disciplinary approach in the investigation of intermetallic systems and the role of thermochemistry are underlined. The activity carried out in the Author's laboratory in the alloy thermodynamics is summarized. The different instruments (calorimeters) built in laboratory are briefly presented and their performance discussed.

The results obtained in the measurement of the enthalpy of formation mainly of several rare earth alloys are described. The characteristics of the Eu and Yb thermochemistry and crystallochemistry are finally underlined.

Keywords: intermetallic thermochemistry, alloy thermodynamics, crystallochemistry

1. Introduction

The experimental investigation and the description of intermetallic systems are generally based on the concerted use of several complementary techniques. The identification, in a certain alloy system, of the intermediate phases and their full characterization require different examinations such as structural (diffractometric) analyses accompanied, for instance, by those carried out by (optical, electronic) microscopy, microprobe analyses, etc.

In order to define the stability ranges (of temperature and composition) of the phases, thermal analysis and, more generally, thermodynamic measurements are necessary.

Moreover, both from a fundamental point of view and taking into consideration possible technological applications, the determination of phase equilibria and of the state diagram should be considered as a valuable complete, in-depth study. Thermochemical data play a relevant role in the evaluation and assessment of the alloy properties and are of particular interest as input data in computational procedure and in the optimisation and prediction of phase equilibria in simple and complex systems.

The determination of the formation functions is one of the bases of experimental thermodynamics. Results obtained by means of vapour pressure methods, electromotive force measurements and calorimetric investigations have been widely discussed and used.

Following Predel [1] we may underline that an investigation of the dependence of thermodynamic functions on composition and temperature is a relevant step in the investigation of an intermetallic system. To understand the differences in bonding of closely related intermetallic compounds, correlations between thermodynamic and structural properties are very interesting. These correlations may be very useful for the prediction of the values relevant to intermetallic phases for which experimental data are scarce or very difficult to measure. However, we have to underline, that thermodynamic data obtained through theoretical or semi-empirical models, very often differ from those obtained by experimental method. For the design of new metallic materials and their synthesis, development of experimental investigation and methods on binary alloys, possibly extended to more complex systems (ternary, quaternary) should be *urgently* considered, in order to improve quantity and reliability of the data.

2. Comparison between experimental and calculated enthalpy of formation data

A well-known and largely used relation for the computation of the ΔH of formation is represented by the semi-empirical Miedema formula [2]:

$$\Delta_f H = \frac{f(x_A, x_B, V_A^{2/3}, V_B^{2/3}, a_A, a_B, (\Phi_B^* - \Phi_A^*))}{\frac{1}{n_{WS_A}^{1/3}} + \frac{1}{n_{WS_B}^{1/3}}} \cdot P \cdot \left[-(\Phi_B^* - \Phi_A^*)^2 + \frac{Q}{P}\left(\frac{1}{n_{WS_A}^{1/3}} + \frac{1}{n_{WS_B}^{1/3}}\right)^2 - \frac{R}{P} \right] + \left(x_A H_A^T + x_B H_B^T\right)$$

where:

- A and B are the two alloying elements,
- $V^{2/3}$, $n^{1/3}$, a, $\Phi^{\bullet}$,R, H^T are the semi-empirical parameters evaluated and reported in [2]

- $n_{WS}^{1/3}$ is the electron density at the boundary of the Wigner-Seitz atomic cell
- x alloy composition molar fraction; V elemental atomic volume;
- $(\Phi_B^* - \Phi_A^*)$ difference of the chemical potential for electronic charge
- a_A and a_B empirical parameters
- P empirical parameter which assumes different values according to whether A and B are both transition, both non-transition, or transition and non-transition elements.
- Q/P is assumed to be constant. The R/P value, which is zero when A and B are both transition metals, is given by the product of two elemental constant R_A^* and R_B^* when A and B are transition and non-transition elements respectively.
- the H^T parameters are non-zero only for H, B, C, Si, Ge, N and P.

An example of application is shown in Fig.1 and Table 1, where experimental and calculated values have been collected for a number of exothermic compounds (aluminides and silicides). We may see the rough agreement between the two sets of data, even if generally, more exothermal values are obtained experimentally than by computation. Notice that in many cases there is a substantial scattering between the different experimental values, probably due to the various experimental techniques used (see [38, 39] for a discussion on this point).

As a comment to this point, we may notice that the Miedema formula is certainly useful when only an estimation of the magnitude of the exothermicity is required. If, however, precise information is needed, also in order to perform data optimization, sound experimental values, even if in a restricted number, will be essential. More generally we may say that a judicious combination of experimental and computational methods may be the best choice to achieve a full description of the intermetallic system and to reduce the difficult and lengthy experimental investigations to a few crucial compositions.

In this context, besides the Miedema formula, it could be noteworthy to mention the suggestion for a systematics of the stability of intermetallic phases given for instance by Pettifor [40], on the basis of maps built for all the binary combinations by using the “Mendeleev number” of the elements involved.

An interesting contribution was also given by Brewer, who especially considered a bond model for strong generalized Lewis acid-base interactions in intermetallics [41] and a procedure for calculation of the heat of formation of the intermetallics [42].

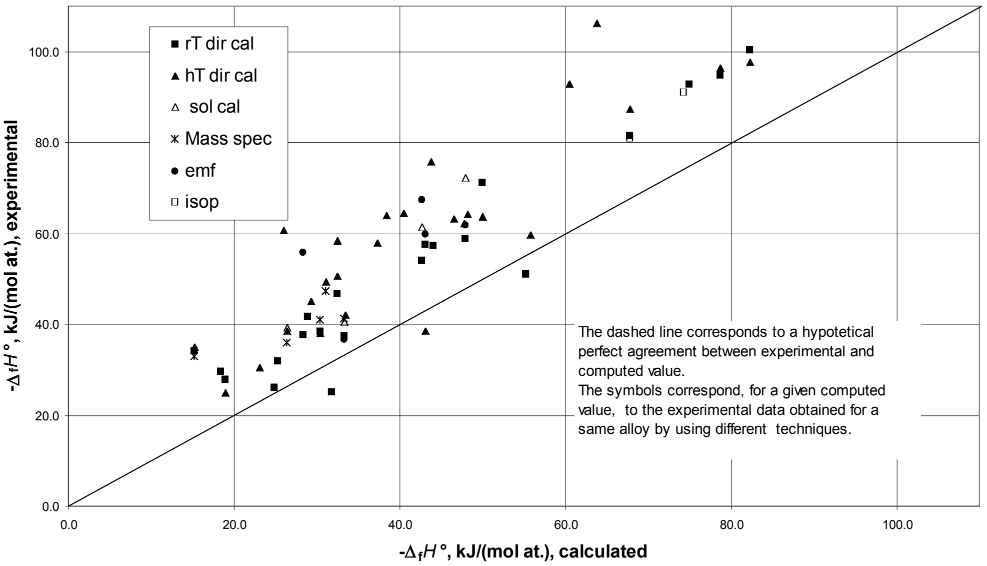

Fig.1. Enthalpy of formation of selected aluminides and silicides of transition metals. Comparison between experimental and calculated [2] values (see Table1).

rT, hT = room, high temperature; dir. cal. =direct calorimetry; sol. Cal. = solution calorimetry; Mass spec.= mass spectrometric vapour pressure measurements; isop = isopiestic.

3. Remarks on experimental thermodynamics of alloys

Among the different thermodynamic properties we will give special attention to the evaluation of the formation thermodynamic functions that is ΔH and ΔG of formation of the alloys. This means that we may mainly refer to calorimetric, vapour pressure and emf measurements. A few notes will follow on these topics.

3.1. Formation calorimetry techniques in Alloy chemistry

Several reviews on experimental alloy thermodynamics by means of calorimetric techniques have been published. We may especially mention Kubaschewski [43], Calvet and Prat [44], Predel [45,46], Hemminger and Höhne [47], Ipser and Komarek [48], Rouquerol and Zielenkiewicz [49], Sommer [50], Bros [51,52], Castanet [53], Kleppa [54], Colinet [55], and Randzio [56,57].

Table 1. Comparison between computed and measured formation enthalpies of selected aluminides and silicides

-$\Delta_f H$ experimental (kJ/mol at.)

reference state Al (cF4-Cu) or Si (cF8-C) and Me solid in the form stable at T= 298 K (if not otherwise stated)

Phase	-$\Delta_f H$ (kJ/mol at.) calculated [2]	room T dir. cal.	H.T. dir. cal.	Solution calorimetry	Vapour pressure	emf	Unknown method	Ref.
FeAl	31.7	25.1						[3]
		23.8						[4]
		26.5						[5]
							25.1	[6]
$FeAl_2$	24.8	26.5						[5]
		26.2						[3]
$FeAl_3$	18.9	29.5						[5]
				25.0 in acid				[7]
		27.9						[3]
CoAl	42.7	54.1						[5]
				64.0 in acid				[7]
				60.0 in liq. Al ref.Al fcc, 1100K				[8]
				61.3 in liq. Al, 1030K				[9]
						61.0 ref. Al fcc, 1000K		[10]
							60.3	[11]
							67.4	[12]
							62.9	[6]
Co_2Al_5	28.8	41.8						[5]
$CoAl_3$	25.3	32.0						[5]
Co_2Al_9	18.3	29.7						[5]
Ni_3Al	33.2	40.2						[5]
		37.6						[13]
				40.6 in liq. Al				[14]
				41.3 in liq. Al				[15]
					41.4 ref. Al liq. 1600K			[16]
						47.0 ref. Al fcc, 980K		[17]
						36.8 ref. Al fcc, 1273K		[18]
NiAl	47.9	58.8						[13]
				71.3 in liq. Al. ref. Al liq.,1023K				[19]
				67.0 in liq. Al. ref.Al fcc, 1023K				[20]
						67.0 ref.Al fcc., 980K		[17]
						62.0 ref.Al fcc., 1273K		[18]
							62.9	[6]
							63.0	[11]
Ni_2Al_3	43.1	57.7						[13]
						70.0 ref. Al fcc., 980K		[17]
						59.8 ref.Al fcc., 1273K		[18]

Table 1. Continuing

$NiAl_3$	28.3	37.7						[13]
						56.0 ref.Al fcc., 980K		[17]
RuAl	47.7	62.1						[20]
RhAl	63.7	106.3						[20]
Pd_2Al	67.8	81.6						[21]
			87.3					[22]
					81.0 ref. 373 K			[23]
Pd_5Al_3	74.3				91.0 ref. 373 K			[23]
PdAl	84.3	100.4						[21]
				92.5 precipitation cal.				[24]
			91.3					[25]
					95.0 ref. 373 K			[23]
Pd_2Al_3	79.9	80.3						[21]
					80.0 ref. 373 K			[23]
$PdAl_3$	55.2	51.0						[21]
					51.0 ref. 373K			[23]
OsAl	43.1		38.6					[20]
IrAl	60.4		92.8					[20]
Pt_3Al	50.0	71.1						[26]
			63.6					[27]
Pt_3Al_2	74.9	92.9						[26]
PtAl	82.2	100.4						[26]
			97.6					[25]
Pt_2Al_3	78.7	95.0						[26]
			96.5					[27]
$PtAl_4$	44.0	57.3						[26]
FeSi	26.3	37.7 comb.cal.						[28]
				39.3 in liq. Al.				[29]
			38.6					[30]
					35.9			[31]
Co_2Si	30.4	38.5						[5]
			37.9					[30]
					41.0			[32]
CoSi	31.1		49.3					[30]
					47.3			[32]
$CoSi_2$	15.2	34.3						[5]
			34.9					[30]
					32.9			[32]
Ni_5Si_2	29.2		45.1					[30]
Ni_2Si	32.5	46.9						[33]
			50.6					[30]
NiSi	33.4		42.0					[34]
RuSi	32.4			58.1solute + solvent drop cal.				[35]
			58.3					[36]
Ru_2Si_3	26.0		60.7					[36]
Rh_2Si	38.3		63.9					[36]
RhSi	43.8			75.0 solute + solvent drop cal.				[35]
			75.8					[36]
Pd_3Si	37.3		57.9					[36]
Pd_2Si	48.2			64.5 solute + solvent drop cal.				[33]
			64.2					[36]
Os_2Si_3	23.1		30.5					[37]
IrSi	40.4			63.8 solute + solvent drop cal.				[35]]
			64.4					[37]
Pt_2Si	46.5		63.3					[37]
				61.7 solute + solvent drop cal.				[33]
PtSi	55.8		59.6					[37]
				59.4 solute + solvent drop cal.				[33]

H.T.= high temperature; dir.cal.= direct calorimetry; comb. cal. =combustion calorimetry

For the calorimetric determination of the ΔH of formation some general comments about instrumental problems have been discussed by us in [39]. However, besides the instrumental characteristics of the calorimeters, formation calorimetry may be classified according to the different steps followed during the measurements used to obtain the ΔH of formation.

In the following, we will rely on the schematic subdivision of alloy calorimetry into indirect and direct reaction calorimetry.

Indirect Reaction Calorimetry

This is based on the measurement of the enthalpy changes involved in a certain reaction carried out separately on the components and the compound respectively: the enthalpy of formation is then obtained by the difference between these two values.

According to the type of reaction involved, we may have:

Solution calorimetry for alloy systems we may refer to aqueous or to metallic solvents:

- Aqueous solvents are not very convenient for metallic substances, owing to the high values of the heats of solution as compared with the heats of formation.

- Metallic solvents such as liquid Sn, liquid Al, which are particularly suitable especially for Sn and Al alloys respectively, are mainly employed. At higher temperature Cu or Ge and their alloys have been used.

Combustion calorimetry: This mainly corresponds to the reaction with O_2, or with F_2. This type of calorimetry involves strongly exothermic reactions. Besides the enthalpy of formation of oxides or halogenides (for which combustion calorimetry is a direct calorimetric method), good results have also been obtained in the investigation of sulfides, silicides, borides, etc.

Direct Reaction Calorimetry

The formation reaction itself (the synthesis of the alloys from the solid metals) takes place into the calorimeter. There is the need to start the reaction inside the component mixture and have it running in a controlled manner. Different ignition methods have been proposed. In particular we may refer to room and high temperature direct calorimetry.

Room temperature synthesis direct calorimetry: (Small furnace calorimeters). A number of intermetallic compounds may be synthetized inside the calorimeter from an appropriate mixture of the component metals by heating the mixture using a small electric coil. (“Self–propagating reactions” “gas-free combustion synthesis”). This method is especially convenient for highly exothermic alloys obtainable from low melting and/or highly reactive metals.

High temperature synthesis calorimetry: The direct synthesis of the alloys (exothermic and also endothermic) from a component mixture can be conveniently carried out in high-temperature calorimeters.

According to the *heating regime* we may have:

- continuous heating mode when the sample is continuously heated up to the reaction temperature, as in the DTA technique (scanning calorimetry, DTA, etc)
- high temperature thermostatted calorimeters. A typical calorimeter pertaining to this category is the *drop calorimeter* technique. The sample (for instance a pellet of the component mixture) is dropped from a lower temperature (often room temperature) thermostat into the high temperature calorimetric cell. The calorimetric cell is maintained at a temperature high enough to ensure that the reaction occurs.

Notice that, whatever the calorimetric techniques used may be (room, high temperature, etc.), an accurate check of the state, composition, etc. of the synthesized alloy is necessary (for instance by X-ray diffraction, optical and electronic microscopy, electron-probe microanalysis, etc.).

3.2. Comments on Electromotive force measurements (emf)

Electrochemical techniques are used in studying the thermodynamics of metallurgical systems. Several reviews should be mentioned [58-63].

Measurements of the electromotive force of a suitable galvanic cell may be a good method to obtain thermodynamic properties of alloys, but the following criteria have to be fulfilled. The cell reaction should be *well defined and reversible and the electrolyte a truly ionic conductor.* This means that we should have a time-independence of the emf at constant temperature, reproducibility of a value regardless of whether the equilibrium temperature is approached from higher or lower temperature, no drift or polarization effects. The emf should be measured after the passage of a small amount of current in both directions. Moreover, the electrolyte must have rather low vapour pressure, must be stable at the temperature involved and exhibit only ionic conductivity. The charge of the more electropositive ion has to be known exactly and only one reaction should occur at the electrode interface $A \rightarrow A^{z+} + ze$. Consequently any oxidizing or reducing agents must be avoided in the electrolyte, as must reactions of the electrodes and electrolyte with materials used in the construction of the galvanic cell.

Attention must also be paid to minimizing the thermoelectric emf developed by the cell. The furnace in which the cell is inserted should have very small temperature gradients to guarantee a uniform cell temperature which should be high enough to enable a diffusion process and to avoid concentration gradients between the interior and the surface of the electrode.

Both liquid and solid electrolytes may be used. Advantages and limitations of high temperature concentration cells with liquid electrodes and electrolyte have been discussed by Moser [60]. General comments on the solid electrolyte electromotive force cells and their application to reactive metals (such as rare earth) and alloys have been reported by Colinet and Pasturel [64].

For details on the choice of the construction material, and on the preparation of the electrolyte as for instance the eutectic mixtures (70 RbCl+ 30 LiCl mass% T_{fus} ~ 312°C, 46 LiCl+ 54 KCl mass% T_{fus} ~ 350°C, 38 NaCl+ 62 $CaCl_2$ mass% T_{fus} ~ 500°C, etc) see for instance Vassiliev and Vu Dihn Khue [65] and Mikula [62]. Problems concerning avoiding moisture, oxidizing agents etc., have been discussed [66,67].

For a detailed list of several types of solid elctrolytes and their employment see the reference-rich review by Pratt [68]. According to this review and Katayama [69], a general description for the solid electrolyte types could be the following:

Oxide (anionic conductor O^{2-}): ZrO_2-base, ThO_2-base, HfO_2-base, etc.

Oxide (cationic conductor): β-Alumina, Pyrex, Fused silica (Na^+), etc.

Complex oxides (protonic conductor): perovskite type $BaCe_{1-x}M_xO_{3-y}$, $CaCe_{1-x}M_xO_{3-y}$, $CaZr_{1-x}M_xO_{3-y}$ (M= Sm, Yb, Y, Nd, Gd, In)

Halide (anionic conductor): CaF_2, MgF_2, PbF_2, $BaCl_2$

Other cationic conductors:

halide (CuCl, α-AgI, $RbAg_4I_5$), sulfide (CaS-base, MgS, etc.), sulfate (Li_2SO_4, Na_2SO_4, K_2SO_4).

Other, so-called superionic conductors (SICON), such as NaSICON ($Na_3Zr_2Si_2PO_{12}$) and LiSICON $Li_{14}Zn(GeO_4)_4$.

Experimental aspects of solid galvanic cell methods have been reviewed by [61, 67, 70]. Applications and extensions of these methods have been discussed by Bretschneider and Schaller [71] and Hertz and co-workers [72], Jacob and Waseda [66] and Kleykamp [67]. Investigations based on the use of emf method with solid electrolytes have been discussed by Katayama et al. [73, 74].

The partial Gibbs energies are directly obtained from the measured electromotive cell potential E. The integral thermodynamic formation functions of the alloys may then be derived. The molar enthalpy ΔH and molar entropy ΔS can be calculated from E=f(T) with the application of the Gibbs-Helmoltz relation.

An important contribution to the evaluation of the reliability of the data obtained by these techniques has been given by Colinet and Pasturel [64]. They observed that the results obtained for a group of alloys of a certain system, from the emf of the different prepared cells, lead to a series of Gibbs energies of reactions. The Gibbs energy of formation of a given compound is then deduced by a linear combination of these reaction values. If in a certain system, therefore, the Gibbs energy of formation of a given compound is deduced from, for example, n Gibbs energy of reaction measurements, the quoted uncertainty is then n-times that of the first measurement. As for the enthalpy of formation, this is deduced from the temperature variation of the Gibbs energies.

Thus, the uncertainty also *depends on the temperature range* covered by the emf measurements. In the alloys of the rare earth metals (R metals), for instance, it has been observed that it may be quite large in the R-rich regions.

Nevertheless, these emf measurements are important as, in principle, they make it possible to obtain Gibbs energy, enthalpy and entropy of formation values all at the same time.

Similar considerations may be applied also to other indirect methods such as those based on vapour pressure measurements.

3.3. Vapour pressure methods

Several reviews have been given in the past (Kubaschewski [75], Predel [45], Hertz and Gachon [76], Komarek and Ipser [48], Neckel [77], Tomiska [78], Ipser [79]) and according to Ipser [79], we may divide the vapour pressure methods into four groups: static methods; dynamic methods; effusion methods and equilibration methods.

Static methods

According to this method a substance is heated in an evacuated container until equilibrium is established with the corresponding gas phase. Different kinds of instruments are used for the measurement of the pressure.

Dynamic methods

In the *boiling point method* there are two possibilities: either the pressure is held constant while the temperature is slowly changed until boiling is observed, or viceversa.

The *transpiration method* in principle is quite versatile and fairly reliable, provided certain precautions are observed, because the equilibration is not easy to achieve. A steady measured stream of inert gas is passed over the alloy at constant temperature and carries away the volatile components of the alloy at a rate which is a function of the relative pressures and of the rate of gas flow. The vapour is condensed on a cool finger and the vapour pressure can be calculated from the weight change of the sample or from the amount of collected vapour and the volume of the inert gas, based on the ideal gas law.

Effusion methods

For vapour pressure measurements in the low pressure molecular flow region, the two principal methods by Knudsen and by Langmuir are based on the rate of evaporation in a vacuum. Evaporation can occur either from an open surface (Langmuir method) or through a small open orifice from a cell in which the gas phase is saturated with the vapour (Knudsen method). The best known and widely used Knudsen effusion techniques are mass loss and collection methods, recoil momentum techniques and Knudsen cell mass spectrometry (Knudsen combined with the analysis of the effused vapour by mass spectrometry) [48, 77-79].

Equilibration methods

These are the methods in which a condensed sample is brought into equilibrium with a gas phase.

The following may be included:

Isopiestic (or pseudo-isopiestic) methods:This method is based on the tendency toward equilibrium of a series of samples at various temperatures under an imposed vapour pressure of the more volatile component B (the vapour pressure of the two components should differ by, at least, three orders of magnitude). The apparatus contains a series of crucibles stacked in a vertical tube enclosed in a furnace with a temperature gradient. The crucible on the bottom (corresponding to the lowest temperature in the furnace, T_1) contains the pure volatile component B. The other crucibles (placed at progressively increasing temperatures, T_x) will contain, for instance, weighed samples of the other component which, after a sufficient length of time, will equilibrate with the volatile component vapour, giving the compositions for which at the temperature T_x the vapour pressure of B is equal to that over pure B at T_1.

Dew-point method: This method is based on the vapour condensation of the volatile component of an alloy in a closed system, for instance a sealed, transparent ampoule in a gradient furnace. The temperature of the cold end of the ampoule is lowered slowly until the vapour of the volatile component starts to condense. From the observed temperature of condensation it is possible to calculate the partial pressure of this element in the sample, which is kept at a constant higher temperature.

4. Activities carried out in the Author's laboratory

For a long time now, in the Authors' Laboratory, besides crystallochemical and phase diagram investigations, attention has been given to thermodynamic studies by using mainly *calorimetric techniques.* Methods based on the so-called direct calorimetry have been employed. Different types of "direct" calorimeters (working respectively at *room* and *high temperature*) have been built and used systematically in the study of the different groups of alloys. These instruments have been described in several papers. A short presentation of their up-dated versions is reported here.

Adiabatic small furnace direct calorimeter [80, 81]: The small furnace calorimeter is inserted in an Al-block suspended in a container placed in a thermostat controlled at 25±0.01°C. This type of calorimeter is based on the Öfchen-Kalorimeter suggested by Kubaschewski [3]. The aneroid-isoperibol calorimetric apparatus designed in our laboratory contains four calorimeters. The temperature trend of each calorimeter is followed by 80 thermocouples in series, differentially connected to the thermopile belonging to another reference calorimeter. Each calorimeter consists of a thick Al cylinder containing two small furnaces (these are used for starting the reaction in the sample and for electric calibration respectively). When the apparatus, inside a thermostat, is in thermal equilibrium, the pellet, weighing about 10-12 g, placed in the central part of the calorimeter and enclosed in a special container (stainless steel, tantalum) is heated by a small electric heater until the reaction starts. The electric energy dissipated in the calorimeter in the reaction run is then compared with that needed to obtain the same temperature/time response in a number of calibration runs. The building features of the calorimeter, the adjustments of its thermal characteristics and its behaviour as an "integrating" instrument have already been described and discussed. This apparatus has been applied to systems with one low-melting metal such as Au-Al, Pd-Al, Mg-Ge, Mg-Bi [80] and several alloys of the rare earth metals (with Al, In, Pb, Sb, Bi, etc.) [82]. This kind of calorimeter can only be used for exothermic alloys obtainable from easily reacting components, that is, when the synthesis is a "self-sustaining reaction". While studying the performance of the calorimeter, it was estimated that, for fairly or highly exothermic alloys, an error of ±2 kJ/mol atom could be ascribed to all measurements. This includes both instrumental errors and any uncertainties due to a small composition change, and/or to possible disorder quenching from a higher temperature.

In order to control this, all the samples synthesized in the calorimeter, were usually subjected to a number of analyses (optical microscopy, EPMA, X-ray diffractometry) to check composition and the equilibrium state, also by comparison with the characteristics of reference samples prepared by conventional techniques.

*High temperature drop direct calorimeter:*This calorimeter and its working characteristics have been described in [83]. The core of the calorimeter is inserted inside a furnace in a vacuum tight work tube. The calorimetric detector consists of twenty Pt/Pt-Rh10% thermocouples connected in series to form a thermopile which detects the temperature difference between the upper measuring cell and a lower reference cell. The lather contains a nichrome block in which a thermocouple is inserted to measure the operating temperature of the calorimeter. The measuring cell contains a nichrome sample-receiving vessel. The working procedure consists in dropping the sample, made up of a mixture of the powdered metals (0.5 ÷1.0 g) enclosed in a small, sealed tantalum container, from an overhead room temperature thermostat into the calorimeter, which is maintained at high temperature (typically 600 ÷ 900°C). The thermal effect resulting from the change in the heat content and the reaction heat is then compared with that measured in a subsequent dropping of the alloy synthesized in the first run. The calibration of the thermal effects is made by using a series of standard specimens, such as pure Ag, which are dropped into the calorimeter in similar conditions.

In comparison with the previously described small-furnace calorimeter, the high temperature calorimeter extends the range of alloys which can be investigated by direct calorimetry. At high temperature, the synthesis may also be obtained for weakly exothermic alloys. In an evaluation of the overall accuracy based on the instrument performance, the measurement procedure and the characterization of the synthesized samples, an uncertainty of ±4% was generally obtained.

The method of solution calorimetry was also employed in the construction of two instruments, based on dissolution in a liquid tin bath [4] and in an aqueous solution HCl bath respectively [81]. On the other hand, a quasi-isodiabatic drop calorimeter was built for the measurement of the incremental enthalpy of samples dropped from an above-standing furnace maintained at a certain high temperature into a room temperature calorimeter characterized by an imposed constant heat flow towards a surrounding thermostatted metallic block. Details on this instrument may be found in [84]. Some measurements, moreover, have been carried out by using a commercial DSC calorimeter [85, 86]. Beside calorimetric measurements, in some instances, other types of techniques such as emf have been used on R-Pb alloys [87, 88] and several Y-Al and R-Ni alloys [89, 90], and vapour pressure on Yb-Ni alloys[91].

Special attention has been dedicated to the study of rare earth (R) alloys. A summary of the R-Me alloy systems investigated in the Authors' laboratory is presented in Table 2. Generally, in order to study $\Delta_f H$ versus composition, for each system the complete range of compositions was analysed.

The investigation of a few selected ternary alloys has also been started, both for systems in which all three binary interactions are very strong (Al-Ni-R or Al-Pd-R) [105, 106] and systems in which two of the components and therefore two of the

Table 2. Genova Laboratory thermochemical investigation in alloy chemistry.

The alloy systems which have been especially studied are collected here with a few remarks. References relevant to the last R-M investigated system are reported.

Binary Rare Earth Alloys

Mg-Yb, direct high temperature and DSC calorimetry [92]

Ni-R (R= Ce, Sm, Dy, Yb) direct high temperature calorimetry, emf and vapour pressure measurements [90, 91, 93]

Ag-R (R =La, Ce) direct high temperature calorimetry, the investigation is in progress;

Au-R (R= La, Gd, Tb, Dy, Ho, Yb) direct high temperature calorimetry [94].

Zn-R (R= Nd) direct and HCl solution calorimetry [95].

Al-R (R= Y, La, Ce, Pr, Nd, Yb) direct small furnace calorimetry; the high stability of the RAl_2 compounds has been noticed [89, 96]. A very good agreement with the experimental data by Colinet [97], Sommer [98] and Kleppa and coworkers [99] has been observed.

In-R (R= La, Gd) only partial information was obtained by means of direct calorimetry. The reaction between La and In starts in the calorimeter at a very low temperature, but often does not reach the final equilibrium state [100]; **In-Gd** direct small furnace calorimetry, the investigation is in progress;

Sn-R (R = Y, La, Ce) direct small furnace calorimetry: the trends of the enthalpy of formation have been discussed [101]; **Sn-Nd, Sn-Gd** direct small furnace calorimetry the investigation is in progress;

Pb-R (R = Y, La, Yb, Lu) for these systems also measurements of C^p have been carried out. E.m.f. measurements moreover have been considered in addition to the direct calorimetry [88, 102]; **Pb-Gd**, direct small furnace calorimetry, DSC and emf, the investigation is in progress;

As-R (R= La) direct small furnace calorimetry [94];

Sb-R (R= Y, La, Ce, Pr, Nd, Sm, Gd, Er, Dy) the very high stability of the phases near to the 1:1 composition has been pointed out [103]. Values between -120 ÷ -130 (kJ/mol at.) have generally been observed. The trends of the formation enthalpies have been discussed and compared with the shape of the phase diagrams.

Bi-R (R= Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er, Yb) the systematic trends of the heats of formation along the trivalent rare earth series have especially been discussed. The peculiar behaviour of Yb (divalent) has been pointed out [94, 104];

Te-R (R= Ce) direct small furnace calorimetry [94];

Ternary Rare Earth Alloys

Measurements of the heat of formation of ternary alloys systems have been started. A first group of ternary alloys which has been investigated is:

Al-Ni-R

For **AlNiR (R= La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb)** the enthalpies of formation at 300K for these phases have been determined [105].

A similar investigation on the **RNi_2Al_3 (R= La, Ce, Pr, Tb)** phases is in progress. For R= Ce several alloys in the range 0÷40 at%Ce have been studied by high temperature direct calorimetry [106].

Al-Pd-R

AlPdR phases (R= Nd, Sm, Gd) Preliminary investigation by high temperature drop calorimetry is in progress

Analysis of selected **R'-R"-Me** systems has also been performed

Ce-Nd-Al system: experimental and thermodynamic optimization study is in progress

R-Sb-Bi (R= La)

Some measurements of the heat of formation in the LaSb-LaBi solid solutions have been carried out [81].

Other Binary Systems

Magnesium Alloys

Mg-Ge, Mg-Sn, Mg-Pb direct small furnace calorimetry [107], quasi-iso-diabatic calorimetry [108].

Aluminium Alloys

Following transition metal systems have been studied:

Al-Fe, Al-Ni, Al-Pd, Al-Pt, Al-Au, direct small furnace calorimetry [109]

Tin Alloys

Pt-Sn, Au-Sn, Sn solution calorimetry [110]

Thorium Alloys

Bi-Th direct small furnace calorimetry [111]

boundary binary systems, are very similar to each other (Nd-Pr-Sb, R-Sb-Bi) [81], so that the ternary interactions may be averaged between the binary ones. This work is now in progress and, in some cases is carried out in combination also with a revision of the phase diagrams. Some partial isothermal section of R-Ni-Al systems have been determined [112, 113].

The systematic collection of thermodynamic data made it possible to contribute to an evaluation of the rare earth alloying behaviour according to the characteristics of the different metals involved.

A discussion of the R alloying behaviour requires an evaluation of the R-Me reactivity as a function of the Me involved and as dependent on the specific R considered.

As for the first point, Fig.2 gives an indication of the trend in the alloying behaviour as dependent on the position of the partner Me in the Periodic Table. Fig.2 shows indeed the different phase diagrams reported in literature for one of the first R with the elements of the 5th row of the Periodic Table. We see the change of the interaction strength between R and Me on going from the left to the right. In the first

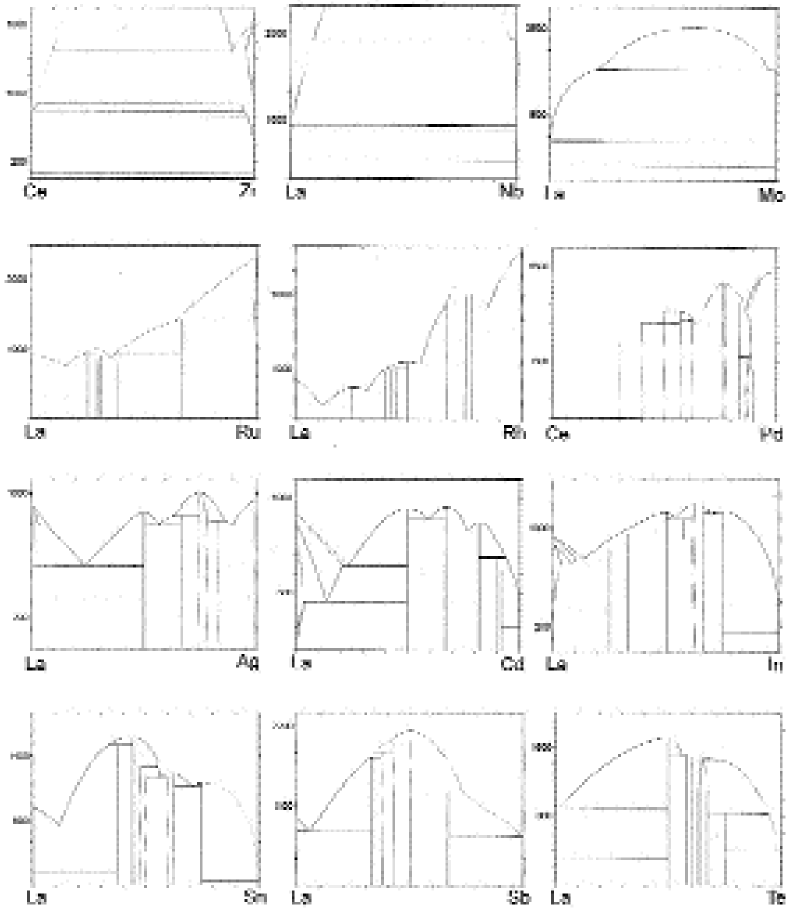

Fig.2. R-Me phase diagrams (atomic %) of trivalent lanthanides with the elements of the 5th row of the Periodic Table (for Tc no information is available). On the basis of the literature data, La or Ce have been selected. Notice that several diagrams are still provisional and approximate

groups we have no compounds and then several (generally “point”) compounds with high melting temperature on the extreme right-hand side of the Table. A similar trend is observed in the other rows of the Periodic Table. These trends may be related to the different bonding mechanism present in the different alloys. Fig.3 depicts the average bond character attributable, according to Gschneidner [114], to the R-Me alloys formed with the Me of the different groups of the Periodic Table.

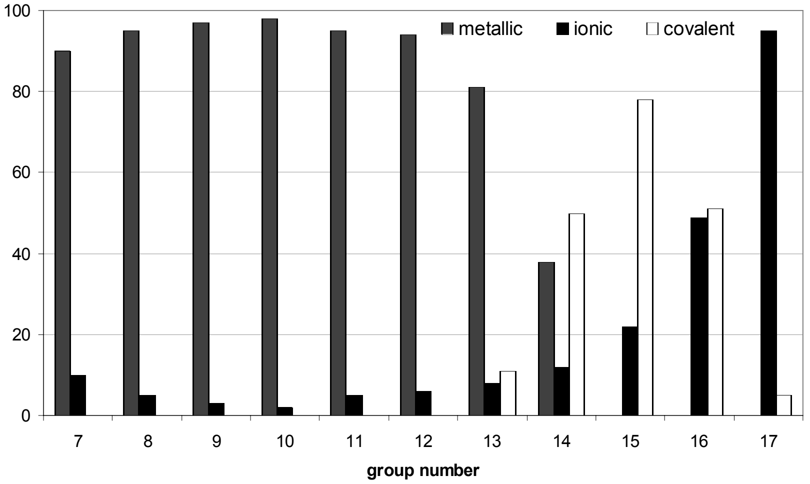

Fig.3. Bonding character, as suggested in [114], shown by the binary rare earth alloys with the elements belonging to different groups of the Periodic Table (from the 7th , Mn group, to the 17th, halogens group)

As for the second aspect of the rare earth alloying behaviour as depending on the peculiarities of the different R, it is well known that, for the trivalent R elements, we have a smooth regular trend in the constitutional properties of the alloys. These progressive variations are indeed observed in phase structures, lattice parameter values, phase equilibria, thermodynamic properties which may be related to atomic properties such as the atomic dimensions. A more complex behaviour is on the contrary observed in optical and magnetic properties which depend on the specific electronic configuration of the different rare earths.

However, considering this trend, the alloys of the divalent Eu and Yb elements often present characteristic deviations. In fact, these metals often show an alloying behaviour more similar to that of the Ca group elements. Eu and Yb are the only lanthanide metals which, in their normal solid state have electron configuration corresponding to two conduction electrons, and which can therefore be considered divalent in their standard states. These metals are divalent not only in the elemental state, but also in several of their compounds, also depending on the characteristics of the other component element. However, they can also form compounds containing the metal in the (III) state valence. In this case, during the formation reaction of the compound, Yb is promoted to the trivalent state and a “promotion” energy must be considered. In comparison with a similar compound of a trivalent R, this results in a less exothermic $\Delta_f H$. In fact, for the compounds containing Yb(III), within the overall energy balance, we have a partial compensation in the $\Delta_f H$ due to to the promotion energy term [82, 102, 115, 116].

The role that thermochemical investigation may play in the study of this behaviour can be exemplified considering, for instance the data reported in Fig.4. We see the agreement between the crystallochemical and thermodynamic data, indicating a quasi-two valence state for Yb in the Pb alloys and an intermediate value for Al alloys (these data are in agreement with other measurements [117-119]).

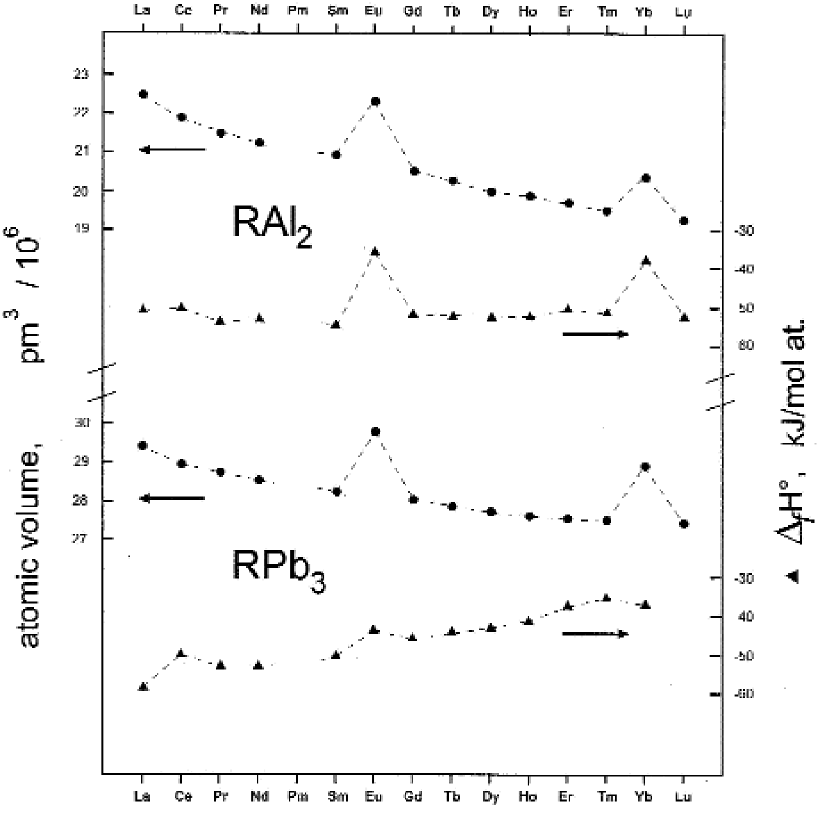

Fig.4. RAl$_2$ and RPb$_3$ alloys. Comparison between the trend of the atomic average volume and the formation enthalpy. Notice the deviations from the average trends of the Eu and Yb values

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