

Thermal analysis and alloy phase diagrams

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Abstract

A summary of the activity performed in the investigation of metallic alloys over many years is presented.

General attention is given to research carried out by using thermoanalytical techniques and their application to the determination of phase diagrams. The results obtained in the systematic investigation of several binary and ternary systems involving rare earth metals are briefly outlined and discussed within a more general picture of the alloying behaviour of these metals.

A report with reference to the groups of alloys especially investigated and to a number of experimental difficulties encountered and solutions adopted is given.

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1. Introduction

An important step in investigating alloy systems is the definition of their phase diagrams. Knowledge of phase equilibria, phase stability, phase transformations are important reference points in the description and understanding both of the fundamental properties of the alloys and of their possible technological applications. Increasing interest in phase diagram science observed in alloys and, more generally, in materials science is clearly evident, for instance, by the growth in the number of publications, bibliographic books and journals, in which data relevant to phase diagrams are systematically reported and assessed, such as “Constitution of Binary Alloys” [1–3], “Binary Alloy Phase Diagrams” [4], “Multicomponent Alloy Constitution Bibliography” [5], “Ternary Alloys” [6], “Handbook of Ternary Alloy Phase Diagrams” [7], etc. Another clear indication of the relevance of these data and of their reliability is given by the different actions, often organised on an international basis, devoted to the assessment and critical evaluation of phase equilibria data. We may mention the activity of Alloy Phase Diagram International Commission (APDIC), Materials Science

International Team (MSIT) and data bases such as “Pauling File” [8].

The ever increasing spread of the calculation of phase diagrams (CALPHAD) methods [9–14] and of their applications is a further sign of the importance of phase diagram science and its development.

As for the connection between phase diagram science and technology, significant comments have been made for instance by Kao [15]. He underlined that phase diagrams, which are the most concise representation for a given system of the phase equilibria, are indispensable in understanding phase transformations, solidification, interfacial reactions and the related changes in microstructure. Their knowledge is, therefore, essential for the improvement and development of materials. Moreover, taking into account the continuous advances in thermodynamic modelling, the information that can be obtained is extended: these models may be used as input for kinetic models for quantitative predictions, for accurate evaluation of metastable equilibria, etc. In this field mention can be made to the brilliant and informative treatment presented by Cahn [16] in his recent book.

In connection with the above points, attention must naturally be focused on the several related experimental aspects and problems. It is well known that a sound experimental definition of a phase diagram has to be obtained from the results of a number of concerted investigations such as

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thermal analysis, thermodynamic analysis, micrographic examination and phase analysis and identification by means of techniques such as X-ray diffraction measurements, microprobe analysis, etc. Among these methods, thermal analysis plays a relevant role. This has been illustrated by different authors. Examples taken from the investigation of binary systems (rather than complex ones) are more frequently considered and will also be used here. This is because of the easier interpretation in such cases of the observed thermal effects and of the prominent role that thermal analysis methods may play in the definition of simple systems, while the ever increasing complexity of the systems being investigated requires the use of more and more auxiliary complementary techniques even if thermodynamic modelling may be very useful in simplifying the time-consuming experimental work.

Emphasis to the different experimental methodologies has already been given, for instance, by Hume-Rothery [17] who stressed the need to use different complementary techniques in the definition of ternary or more complex systems. The necessity of combining thermal analysis with microscopic techniques was especially highlighted, for example, in the determination of solid–liquid equilibria. In any case, going back to the years 1911–1912, we may mention the pioneering investigation carried out by Parravano and coworkers [18–20] in the determination by thermal analysis of the phase diagrams of quaternary alloy systems, such as Fe–Cu–Mn–Ni, Bi–Cd–Pb–Sn and Ag–Au–Cu–Ni.

For a long time now our laboratory has been involved in the study of alloy physical chemistry. The main topics of this work are: (a) identification and structural characterization of intermetallic phases (see for instance Refs. [21,22]), (b) alloy thermodynamics [23,24] and (c) phase diagram investigation (experimental determination, assessment and thermodynamic optimisation, see for references Table 1). The experimental investigation of phase diagrams (analysis of binary and ternary systems) represents a large part of the

activity in course. A summary of the systems experimentally studied is presented in Table 1. We may notice that rare earth (R metals) alloys have been mainly studied. A few comments about these alloys will be reported here; this is also because some problems encountered in the preparation and analysis of R-alloys may be relevant to the more general case of alloy investigations.

To this end a short description of the general alloying behaviour of these metals will be first presented and then some specific cases described and discussed.

2. Remarks on the general alloying behaviour of the rare earth metals

In discussing the general alloying behaviour of the R metals and properties of the R–Me alloys, we have to underline the effects of passing from one rare earth to another and consider the influence of the partner metal Me. To demonstrate the variety of reactions produced by the different elements with the rare earth metals, summaries such as those reported in Fig. 1 may be effective. In this figure the reactivity shown by the different elements (presented in the order in which they appear in the periodic table) with three typical R metals is symbolically indicated (La as representative of the alloying behaviour of the light trivalent rare earths, Gd of the heavy trivalent rare earths and Yb of the divalent rare earths). We see that the elements on the left of the table (apart from H, Be and Mg) do not form intermediate phases (compounds) with the R elements. The corresponding phase diagrams are of the simple types (simple eutectic, often with small solid solubility ranges and in a number of cases with miscibility gaps also in the liquid state). On the contrary the elements on the right of the periodic table generally form complex phase diagrams characterised by the existence of a certain number of compounds. See as an example the Au–Nd system [43] reported in Fig. 2, in which several

Table 1
Summary of the systems experimentally investigated in the authors' laboratory

Binary R–Me and ternary R–R'–Me (or R–Me–Me') systems ^a		Key references
Mg-systems	Mg–Ce, Mg–Pr, Mg–Nd, Mg–Sm, Mg–Gd, Mg–Tb, Mg–Dy, Mg–Ho, Mg–Er, Mg–Tm, Mg–Sc, Mg–Y, Mg–La–Y, Mg–Ce–Y, Mg–Pr–Y, Mg–Gd–Y, Mg–Yb–Y, Al–Mg–Sc, Mg–Al–Gd, Mg–Al–Dy, Mg–Al–Ho, Mg–Al–Er	Nd–Mg [25], Gd–Y–Mg [26], Al–Mg–Er [27,28]
Mn-systems	Mn–Pr, Mn–Nd, Mn–Y–Zr	Pr–Mn [29]
Ni-systems	Ni–Al–Sm, Ni–Al–Y	Ni–Al–Y [30]
Cu-systems	Cu–Ce–Sn, Cu–Pr–Sn, Cu–Nd–Sn, Cu–Yb–Sn	Pr–Cu–Sn [31]
Ag-systems	Ag–La, Ag–Ce, Ag–Pr, Ag–Nd, Ag–Tb, Ag–Dy, Ag–Ce–Ge, Ag–Ce–Si, Ag–Ce–Sn, Ag–Pr–Sn, Ag–Yb–Sn	Ag–La [32], Pr–Ag–Sn [33], Ce–Ag–Ge [34]
Au-systems	Au–Nd, Au–Gd, Au–Tb, Au–Ho, Au–Er, Au–Tm, Au–Ce–Sn	Au–Tb [35], Au–Ce–Sn [36]
Zn-systems	Zn–Gd, Zn–Dy, Zn–Er	Zn–Dy [37]
Al-systems	Al–Sc, Al–Sm	Al–Sm [38]
In-systems	In–Ce, In–Pr, In–Nd, In–Sm, In–Gd, In–Ce–Pd	Pr–In [39], In–Ce–Pd [40]
Tl-systems	Tl–La, Tl–Ce, Tl–Pr, Tl–Nd, Tl–Sm, Tl–Gd, Tl–Tb, Tl–Ho, Tl–Er, Tl–Y	Sm–Tl [41]
Si-systems	Si–Ce–Y	Si–Ce–Y [42]

^a Generally, in the case of binary systems the phase diagrams have been completely studied, in the case of ternary systems isothermal sections have been investigated.

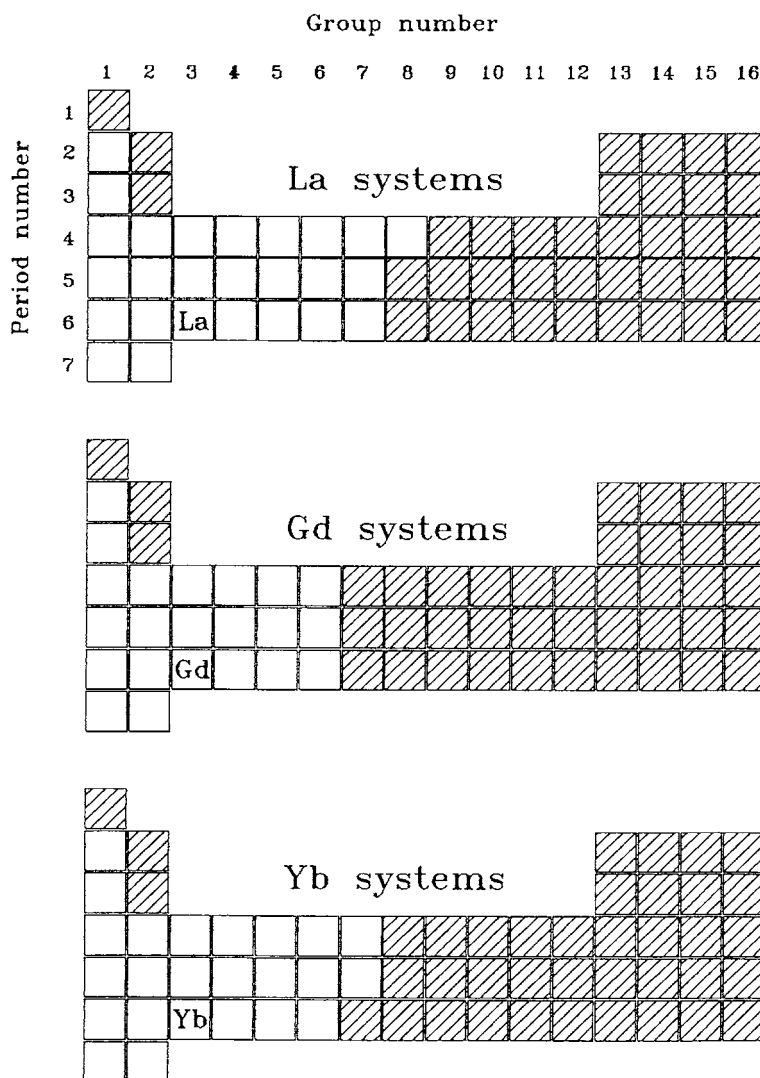


Fig. 1. Compound formation capability for three rare earth metals: La, Gd and Yb; hatched cells: formation of intermetallic compounds; blank cells: no compounds are formed.

intermediate phases are presented, some formed by congruent melting (NdAu , $\text{Nd}_{17}\text{Au}_{36}$ and $\text{Nd}_{14}\text{Au}_{51}$), others by peritectic reaction (Nd_2Au and NdAu_6). For a few of these phases a narrow (or very narrow) stoichiometry range has been proposed (point phases); $\text{Nd}_{14}\text{Au}_{51}$, on the other hand, is an example of phase corresponding to a certain field (solid solubility range) of stoichiometry. The equiatomic phase NdAu , finally, is an example of a phase existing in different structural forms.

Within the different R–Me phases, especially stable are the compounds formed with metals of the Pt family and with the semi-metals at the far right of the periodic table. These substances are characterised by the high or very high $\Delta_f H_{298\text{K}}^\circ$, melting temperatures, etc. As for the non-metals (chalcogens, halogens, etc.), they give very stable compounds with the R metals. The $\Delta_f G_{298\text{K}}^\circ$ of the oxides, for instance, are among the more negative in comparison with those of all the other metals.

A characteristic point which can be considered in the description of the R–Me alloy behaviour, is the property variation we observe when, maintaining the same partner Me, we change the R element passing from one rare earth metal to the other along the series. Considering only the so-called “trivalent” R (lanthanides with the exception of Eu and Yb, to which we may add Y on the basis of its atomic dimensions close to those of the heavy lanthanides) we generally have a progressive gradual variation of the constitutional data (phase diagrams, melting points, crystal structures, lattice parameters, $\Delta_f H$, etc.). An example, based also on our recent experimental work, is given in Fig. 3, where regularities in some R–Zn intermetallic compounds are highlighted. In particular the trends of the “reduced” melting temperatures T_R (ratio between the compound melting temperature and the melting temperature of the rare earth metal involved, both in Kelvin) and those of the average atomic volumes plotted against the atomic number of the rare earth

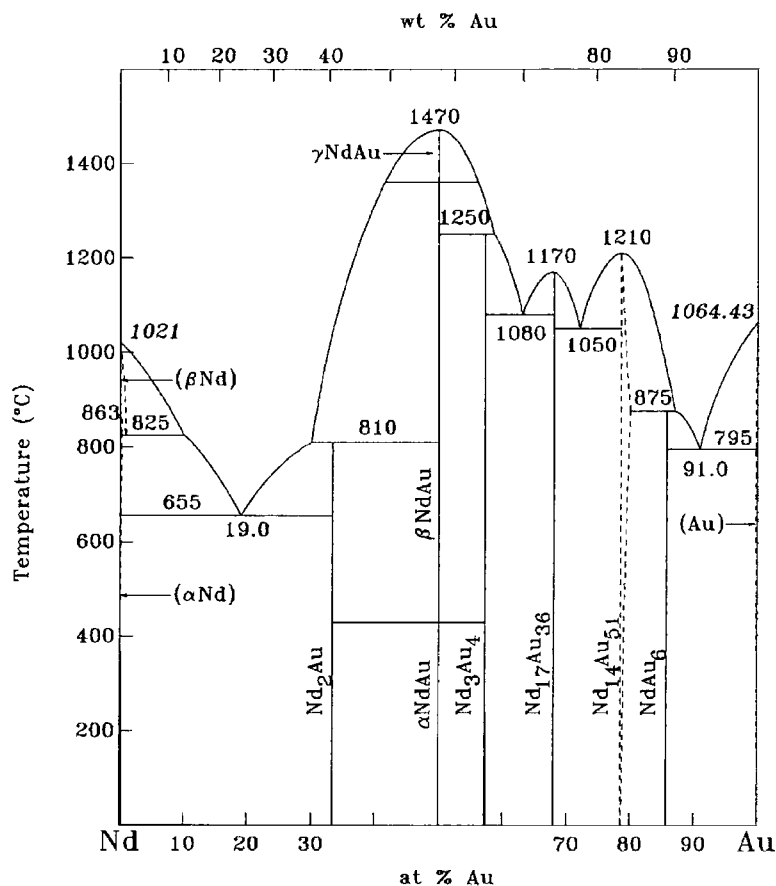


Fig. 2. The Nd–Au phase diagram [43].

metals are reported for the RZn , RZn_2 and RZn_3 phases. Generally, these parameters vary gradually across the trivalent lanthanide series (exceptions are the divalent rare earths, Eu and Yb) and they can be used for interpolation purposes.

As a final comment to this short description of the alloying behaviour of the rare earth metals we may add a few remarks on the applications of these alloys. A summary is given in Table 2 where a few selected R-based alloys are

presented. The beneficial effects on commercial alloys based on different metals (Mg, Al, Ti, Cr, Fe, Ni, Cu) of rare earth additions have been investigated. Many applications have been found: a summary of these is reported, for instance, in books such as Ref. [44]. In many of these applications the rare earths (R) are added as the naturally occurring mixture of elements as reduced from their ores (for instance, monazite). This material (called mischmetal) approximately contains 50% Ce, 30% La, 15% Nd and 5% Pr.

Table 2
Examples of application of commercial-grade rare earth elements and alloys [44]

Application	Rare earth alloys	Remarks
Magnetic materials	$SmCo_5$ and Sm_2Co_{17} , $Sm_2Fe_{17}C_x$, $Sm_2Fe_{17}N_x$, $Nd_2Fe_{14}B$, $\approx Tb_{0.3}Dy_{0.7}Fe_2$ phase "Terfenol", $PrNi_5$ compound (CaCu ₅ -type)	Permanent magnets (high energy product and high coercivity). Giant magnetostriction in an applied field. Magnetic refrigerator to obtain extremely low temperatures in conjunction with the nuclear magnetic cooling of copper
Hydrogen storage materials	RCO_3 , RFe_3 , several rare earth Laves phases, RNi_5 ($LaNi_5$), $La(Ni_{1-x}Al_x)_5$ ($x \approx 0.6$), $LaAlNi_2$	Rechargeable electrodes in electrochemical nickel–hydrogen batteries. Several applications including heat pumps, heat engines, isotope separation, hydrogen gas separation and purification, energy storage and catalysis
Magneto-optical materials	$Tb_{25}(Fe_{0.9}Co_{0.1})_{75}$ thin film	Information storage as magneto-optical discs
Oxide-dispersion strengthened (ODS)	Y_2O_3 (used as a dispersed oxide in superalloys)	High-strength, high temperature alloys for turbine blades, vanes and combustors
Lighter flints	Fe and mischmetal alloys	Ignition or sparking

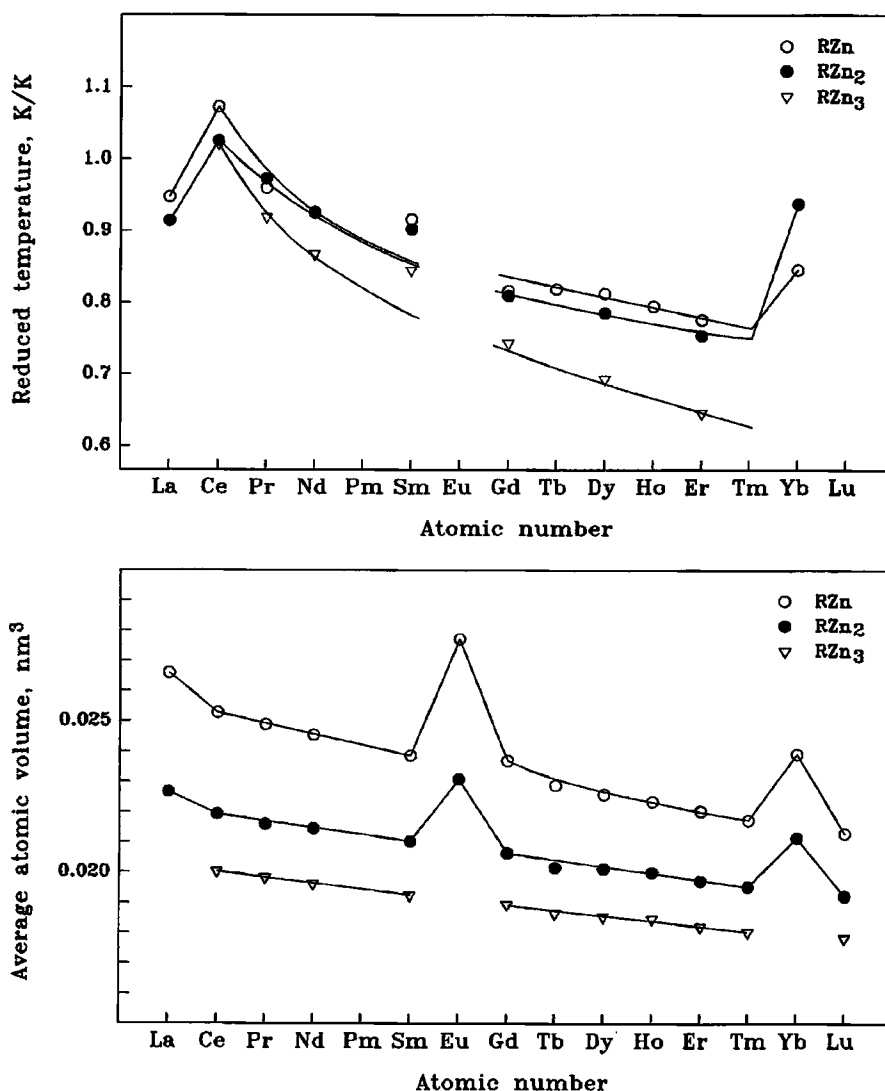


Fig. 3. RZn, RZn₂ and RZn₃ compounds with the different rare earth metals: upper part: trend of the reduced melting temperatures; lower part: trend of the average atomic volumes.

3. Remarks on the phase diagram investigation and the role of DTA

As mentioned before, the determination of a phase diagram is the result of concerted activities including a number of analyses carried out on samples more or less numerous depending on the complexity of the system (number of components, number and nature of the intermediate phases and of the invariant equilibria; for instance about 40 alloys in the case of a system such as that shown in Fig. 2). One of the first steps in the investigation corresponds to the preparation of the samples which should have the highest purity possible, being protected from contamination, and be in well-defined conditions. To this end, after the synthesis, proper thermal treatments have to be made generally in a recursive way taking into account the emerging characteristics of the diagram under definition.

The special role of the thermal methods (thermal analyses) is briefly discussed in the following.

A deep and detailed presentation and discussion of thermal analysis techniques and their application to alloy investigations has been reported by Hume-Rothery et al. [17] in their previously cited classic book on the determination of metallurgical equilibrium diagrams. Several types of apparatus have been described [45], going back to Le Chatelier following the publication in 1887 of a paper entitled “On the action of heat on clays” [46]. He also employed the now common practice of calibrating his apparatus by means of the melting (or boiling) points of substances obtainable in a high state of purity. His method, however, was not strictly differential, it was not until 12 years later that Roberts-Austen published a description of the apparatus which forms the basis of all modern differential thermal analysis instruments [47]. This technique, however, became

popular, mainly in the metallurgical field, only in more recent times. So, for instance, Etter [48] (quoted in [49]) stressed that the use of thermal analysis was emphasised in the past as a technique for studying metallic materials.

The corresponding vast literature is well known and it has been thoroughly discussed on several occasions such as meetings of national and international calorimetric associations. Only a few points therefore will be mentioned here; those we have especially found interesting and relevant to metal and alloy application.

3.1. Cooling curve types

A general classification of the various types of the cooling curves dates back to the work by Burgess [50] reported in [51], where T versus t , T and T' versus t , $(T-T')$ versus t , T versus $(T-T')$, T versus $(T-T')/\Delta T$, T versus dT/dt or T versus dt/dT curves were discussed (T is the temperature of the sample, T' that of the furnace or of a reference sample and ΔT is the temperature decrease in the sample).

For a number of reasons, however, included among which would be the reduced mass needed for the samples, the availability of several pieces of commercial equipments, the detailed and numerous discussions on the characteristics of the method, the influential effect of the application in a number of other, more or less closely, related fields, a progressive replacement of thermal analysis by differential thermoanalytical techniques has been apparent in both the metallurgical field and in phase diagram investigations.

3.2. Liquidus and solidus curves in phase diagrams

An excellent presentation of the application (and limits) of DTA methods to the determination of liquidus and solidus curves was presented by Evans and Prince in their investigation of the In–Pb system [52]. During solidification with a cooling rate of about 1–1.5 °C/min, a precise, reproducible determination of the liquidus was obtained. The problems encountered in determining the solidus were underlined. During cooling from the liquid, solidus temperatures were indeed obtained initially which do not correspond to the equilibrium curve. The solidified alloys were then annealed for several hours just below their measured solidus. On re-heating, melting was observed at a higher temperature than previously measured. The samples were then re-annealed just below the new observed temperature before re-heating. This cycle was repeated until the solidus temperature became reproducible (see Fig. 4).

3.3. Data evaluation

A broad discussion on the determination of solidus, solvus and liquidus temperatures has been given by Dharwadkar et al. in a paper concerning Ni-based alloys [53].

The extrapolated onset of a peak was used for the determination of the solidus and liquidus temperatures, the onset

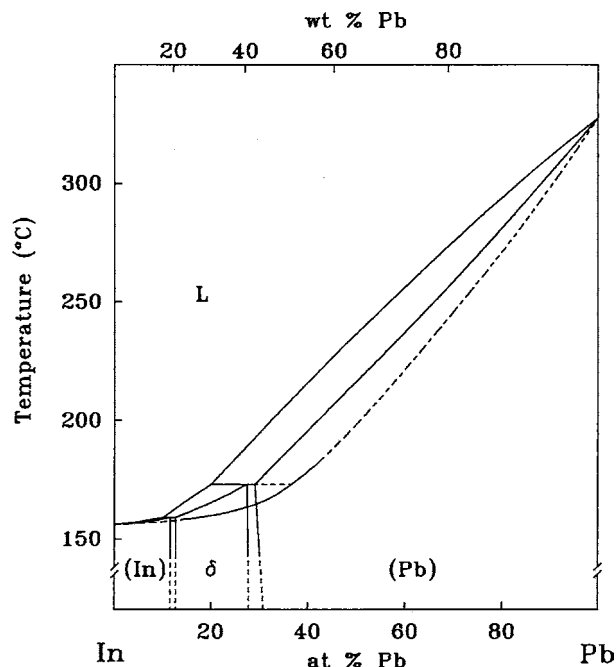


Fig. 4. In–Pb phase diagram as obtained from Evans and Prince [52]. The solid lines (—) refer to the liquidus and near-equilibrium solidus curves (after employing re-heating/cycling method) while the dashed line (---) refers to the non-equilibrium solidus curve.

being given by the intersection point of the extrapolated base-line and the tangent at the point of greatest slope of the leading edge of the peak [54].

As for the general method of evaluating the DTA curves, this may be an important point in quantitative thermoanalysis, in calorimetry, thermokinetics, etc. The problem of carrying out the “deconvolution” (the “dismearing”) of the experimental curve that is of the reconstruction of the true heat exchange function from the measured curve has been discussed by several authors. A good summary may be found in the book by Hemminger and Höhne [55]. Several contributions have been reported in the book edited by Zie-lenkiewicz [56].

3.4. Solid–solid transformation

Special attention to the application of DTA to solid–solid transitions in phase diagram determination was given by Zhu and coworkers [57–59]. They observed that the equilibrium solid/solid phase transition temperatures (which are needed in the construction of phase diagrams) cannot generally be obtained directly from the DTA data because of superheating or undercooling during the actual DTA operation. Methods to extrapolate the equilibrium onset temperature from the DTA data were therefore suggested and evaluated. It was shown that a linear extrapolation of the observed transition temperature as a function of the cubic root of the heating or cooling rate provides, at zero rate, values of a very good accuracy.

3.5. Smith thermal analysis

An improvement in the feedback control of the thermo-analytical instruments is obtained by the constant heat-flux method suggested by White [60] (who determined the heat flux from the temperature difference between the furnace space and the sample). Similar experiments were carried out by Cohn [61], but the most successful application of this method was that of Smith [62,63] who established a constant temperature difference across the wall of a cylindrical container (constructed of a material of low thermal conductivity) on the inside of which the sample is placed. The preselected constant temperature difference is maintained throughout the experiment by feedback furnace control so that heat is extracted from, or supplied to, the alloy at a constant rate, thereby maintaining the transformation process in conditions close to equilibrium. According to this technique (suggested by Smith and subsequently improved, see, for instance, Refs. [64,65]) it is the temperature difference between the sample and the internal wall of the furnace which is maintained constant. Heating (or cooling) rate is consequently defined. The measurement is performed in a furnace with low thermal mass, thereby giving the quick response demanded by the system program. The rate is governed by the value of $(T_f - T_s)$, a constant value of which is imposed by the controller (T_f is the temperature of the internal wall of the furnace and T_s the sample temperature). On the basis of the conditions assumed, when C_p is nearly constant and no transformation takes place in the sample, a nearly constant heating rate will be obtained. On the other hand, when for instance an invariant reaction takes place and the sample temperature tends to remain constant, a decrease in the heating rate will result from the controller action in order to maintain the pre-imposed $T_f - T_s$ value constant. An amplification of the characteristic “temperature halt” will be obtained and the completeness of the reaction will be favoured. As the temperature remains almost constant until the process is complete, the reaction dragging, very frequent for peritectic processes, is overcome, thus reducing spurious peaks due to “out of equilibrium” processes. When a monovariant equilibrium line is crossed, the specific heat variation produces a more or less sharp variation of the base-line slope.

This method has the advantage of a very high sensitivity and the ability to separate peaks at very close temperatures; on the other hand a drawback may be the great slowness of the measurements.

4. Thermal analysis of rare earth alloy systems: notes and remarks

In the definition of alloy phase diagrams a number of difficulties are generally met, a number of these may be especially remarkable in the case of rare earth alloys. Special problems generally found in the preparation and study of

these substances are related to the following points:

- high reactivity especially at high temperature (with oxygen, several crucible materials, etc.) of the rare earth metals and alloys and consequent difficulty in their handling and need for protective atmosphere (high purity argon) and special equipment (glove boxes), etc.;
- problems with the purity of the metals involved (difficulty in obtaining really pure rare earth metals and strong effects of several common impurities in changing their constitutional properties);
- high melting temperatures of a number of rare earth metals (especially heavy lanthanides) and alloys (particularly those with noble metals, semi-metals, etc.);
- High vapour pressure and volatility of some rare earth metals (such as Eu, Sm, Tm, Yb, etc.);
- problems due, for several rare earth metals, to the existence of different polymorphic transformations and their, often complex, interactions with other metals.

The above mentioned points (several of them, however, common to other families of metals) will be considered in the following, which presents as examples some binary R–X systems that have been investigated in our laboratories, paying particular attention to the thermal analysis techniques.

4.1. Comments on selected R–Me systems

Among the different R–Me systems, a few have been chosen and presented in the following in order not only to exemplify the peculiar alloying behaviour of the rare earth metals but mainly to illustrate a number of special problems which may be met when performing thermal analysis on such alloy systems.

4.1.1. R–Al systems

These systems are mentioned here as examples to underline the effects of the solubility of a partner element on the shape of the R-rich region of the phase diagram. The more or less large solubility in the different allotropic forms of the R element will generally result in a change of the melting and of the transformation temperatures. The arising lines defining the monovariant equilibria (such as $L \rightleftharpoons \beta$ and $\beta \rightleftharpoons \alpha$) in their crossing at lower temperatures may give different invariant equilibria (peritectic, eutectic, eutectoidal, catatctic). In the different R–Al alloys a progressive change in the equilibrium types has been observed and discussed [66]. Catatctic equilibria are observed for R = La, Ce, Gd and Dy, eutectoidal decomposition of the high temperature forms are shown by the Al-alloys with Pr, Nd and Sm.

4.1.2. R–In (and R–Tl) systems

The melting behaviour of the In (or Tl) rich alloys is characteristic; from the relatively high (congruent) melting point of the RIn_3 (RTI_3) compound, the melting temperature drops down to the melting point of In (Tl). The In (Tl) richest equilibrium can be considered therefore as a “degenerate

one” of an intermediate character between the limit cases of a eutectic equilibrium such as $L \rightleftharpoons RIn_3 + In$ (with the composition of the liquid very close to pure In) and a peritectic equilibrium such as $L \rightleftharpoons RIn_3 + In$. In the case of a eutectic, a decrease of the temperature should be observed from the melting point of In to the invariant point; in the case of the peritectic, on the contrary, an increase will be observed. The invariant temperature experimentally determined is indeed very close to the melting point of the pure metal. In order to solve the question and to make an accurate evaluation of such a change of temperature a special arrangement was adopted for the DTA sensor. In the two crucibles of the apparatus a specimen of the alloy and a piece of pure In were placed respectively in order to have a direct comparison of the melting temperatures. A decrease of about 3 °C was observed and it was therefore possible to define this equilibrium as a eutectic one.

4.1.3. R–Mn systems

The R–Mn systems are at the boundary between the R-systems forming compounds and those (with the elements at the left of the periodic table) in which no intermediate phases are formed (see Fig. 1). No compounds have been observed for the first rare earths (La and Ce), on going towards the heavier R compounds are formed with an increasing stability. With Pr and Nd a peculiar behaviour has been observed: formation of the compounds Pr_6Mn_{23} , Nd_6Mn_{23} and $NdMn_2$ which, however, are stable only at high temperature and on cooling finally decompose into the component metals. The invariant formation and decomposition temperatures correspond to very sluggish transformations: different thermal treatments (quenching, annealing) can substantially change the structure of the alloys. However it was only on the basis of this behaviour that it was possible to define the phase diagram. The sluggishness and metastability of the transformation prevented any reliable application of thermal analysis.

4.1.4. R–Mg systems

Nearly, all the binary phase diagrams of Mg with the different rare earth metals have been determined in our laboratory. Several isothermal sections of ternary systems $R'-R''-Mg$ of Mg with two different rare earth metals have also been defined. The dependence on the atomic radius of the aspects of the binary phase diagrams (number and formulae of the intermediate compounds) have been studied. A similar dependence was observed on the “average” atomic radius of a mixture $R'-R''$ and used for the calculation, in good agreement with the experimental data, of the ternary $R'-R''-Mg$ systems. In all the mentioned systems the Mg-rich regions are quite complex characterised by a high number of compounds and invariant equilibria, very close to each other. The employment of a combination of thermal analysis techniques (conventional DTA and Smith method) was necessary in order to obtain a detailed description of the systems.

4.1.5. R–Au systems

The examination of these systems (see Fig. 2) was characterized by strong undercooling effects. Such effects may be found in several alloy systems: however, they were fairly high in these systems (typically 40–50 °C in the gold-rich region for cooling rates of 10 °C/min for the invariant temperature corresponding to the gold-rich eutectic). The DTA curves obtained on cooling or on heating presented therefore large differences; generally the effects obtained on heating were used for building the phase diagram. This behaviour and the linear dependence of the cubic root of the cooling (or heating) rates have been discussed [35].

4.1.6. R–Zn systems

The sample containers made of Ta and sealed by electric welding were useful, in this case, during the DTA, not only for protecting the sample from contamination but also to avoid an appreciable Zn evaporation. Owing to the change of pressure (depending on the Zn content of the different alloys in the closed crucibles) the curves built from the thermal effects represent therefore “solubility limits” more than a real isobaric phase diagram [67].

5. Complex alloys, CALPHAD method

As a final comment to this summary of our work, reference can be made to two papers [27,28] by our research group in which the experimental investigation of the ternary system Al–Er–Mg has been combined with its thermodynamic modelling.

The combination of experiments and thermodynamic calculations is a powerful strategy when exploring multicomponent systems. Indeed, it was successfully applied to the study of the Al–Mg–Sc system [68–70]. Also in this case, experiments and thermodynamic calculations were carried on by an iterative procedure. Calculations were used to interpret experimental results and to select new key experiments: experimental results, in turn, were used to refine the thermodynamic description of the phases and to obtain more reliable calculation. The general good agreement between the optimized phase equilibria and the experimental information supports the reliability of the calculated phase equilibria in the whole temperature and composition range of the phase diagram.

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