

STABILITY AND INTERMEDIATE PHASE FORMATION

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A close relation between thermal data and the thermodynamic stability of intermetallic compounds is pointed out. Several series of intermediate phases formed by metals of the *A* and transition groups with elements of groups *IB* to *IVB* have been considered. The dependence of the thermal and thermodynamic stabilities on the atomic size, the electronic configuration, the electronegativity and the melting temperature of the component is discussed.

A full interpretation of intermetallic compound formation is not yet possible, notwithstanding the most recent theoretical developments in the physics of the metallic state. On the other hand, it is well known that the metallic and semimetallic phases do not follow the classical valence rules, which a fortiori are not able to predict the composition, crystal structure or stability of the intermediate phases.

Many experimental data relating to intermetallic compounds are now available in the literature, in the form of solved crystal structures and thermal and thermodynamic data. Correlations between them have been proposed in recent years by several authors [1, 2]. Thermodynamic predictions have been made by Miedema [3], using essentially two variables: Φ^* , which can be considered closely related to the chemical potential, the work function and the electronegativity, and n_{ws} , which should represent the electron density at the surface of the Wigner–Seitz cell for each element.

Among the intermetallic phases, the lanthanide compounds are of great interest, for both fundamental and applied research. Such interest appears quite justified considering the characteristics of these metals.

The rare earths are generally thought of as a family of elements characterized by a close similarity to one another, as well as by a regular variation in the chemical and physical properties. This results from the successive addition of *4f* electrons, which are only relatively weakly involved in bond formation. The main effects are the “lanthanide contraction”, the general stability of the +3 oxidation state (with the principal exceptions of Ce and Sm, Eu, Yb, that can assume, respectively, the +4 and the +2 oxidation states) and the smooth variation of the electronegativity and consequently Miedema’s variables.

Other physical properties of the rare earths, such as the melting and transition temperatures or the transition heats, can also be regarded as consequences of this regular filling-up of the 4*f* shell. In Fig. 1, the "reduced" temperatures are drawn vs. the atomic number of the rare earth, and the trend of the "reduced" atomic volumes too is shown, where the term "reduced" simply means that each value is

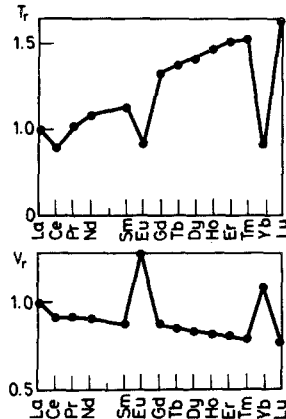


Fig. 1 Trends of "reduced" temperatures and "reduced" volumes for rare earth metals vs. the atomic number of *R*

referred to the corresponding lanthanum value. It is observed that opposite behaviours are displayed.

In this paper we shall show three possible ways in which the data on the thermal and thermodynamic stabilities of intermetallic compounds can be arranged. For this purpose we shall consider phases formed by elements of the IIA, IIIA and transition metal groups (*M*), with elements from groups IB to IVB (*X*). In particular, we shall examine compounds formed by the rare earths (*R*).

Correlation between thermal and thermodynamic data for series of isostoichiometric compounds

For some series of compounds formed by rare earth metals, for example RCd and RMg, Gschneidner [1] observed that closely similar trends can be obtained if ΔG_f^0 , the relative volume contraction consequent to formation of the compound and assuming the analogous process concerning La as reference and the "reduced" temperature are considered as functions of the atomic number of the rare earth metal. The "reduced" temperature is defined, in the case of phase formation, as the

ration between the melting or peritectic temperature of the phase and the melting temperature of the corresponding rare earth, both in K.

In fact, only for a few series of intermetallic compounds is the free enthalpy of formation available. However, it is assumed that the trend followed by ΔG_f^0 is the same as that of ΔH_f^0 , as the entropy of formation can be considered practically constant or to vary only slightly from one compound to another in the same series.

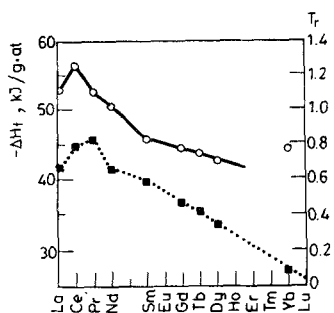


Fig. 2 ΔH_f^0 and "reduced" temperature behaviour for RTl_3 compounds versus R atomic number

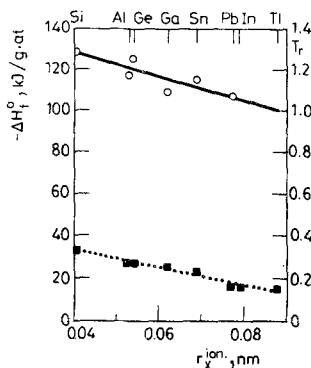


Fig. 3 ΔH_f^0 and "reduced" temperature behaviour for UX_3 compounds ($X = Al, Ga, In, Tl; Si, Ge, Sn, Pb$) vs. X ionic radius

Hence, the trend of the heats of formation for a given series of compounds may be regarded as representing quite satisfactorily how the thermodynamic stability of such phases vary with respect to the various parameters. As an example, Fig. 2 compares the trend of ΔH_f^0 for the compounds RTl_3 with the trend of the "reduced" temperature, as a function of the atomic number of the rare earth. It can be observed that these two trends are closely related except for $YbTl_3$, where Yb behaves as a divalent metal.

We can extend this procedure to series of isostoichiometric compounds formed by other elements M , different from the rare earths. For instance, we can consider the series of compounds UX_3 , where $X = Al, Ga, In, Tl; Si, Ge, Sn, Pb$, for which the heats of formation [4] and the melting temperatures [5] are reported in the literature. As the metal M does not vary in this case, we can choose the ionic radii as the crystal chemical variables, related to the size of the atoms X . Figure 3 shows that, in this case too, similar trends are obtained both for ΔH_f^0 and the "reduced" temperature. Moreover, for the unknown values of T_m for UTl_3 and UIn_3 we can predict melting temperatures between 1070° and 1100° and between 1150° and 1200° , respectively.

Another interesting extension of this procedure is given by the study of the thermal and thermodynamic stabilities of isostoichiometric phases formed by the transition elements of a long period with different elements of the same group *B*. As an example, we can compare the ΔH_f^0 and the "reduced" temperature for a series of 5:3 phases [6, 7] to demonstrate the dependence of the stability on the electronic configuration or

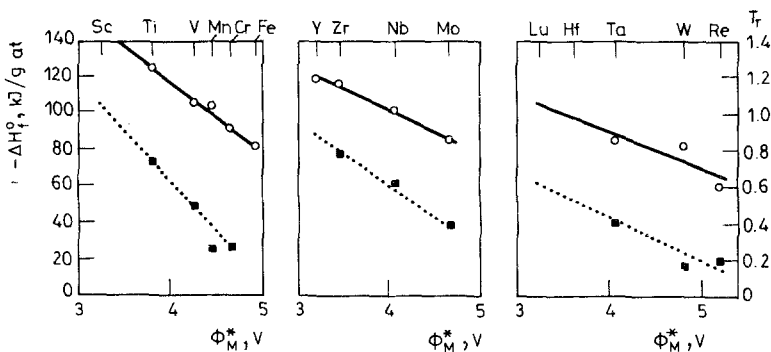


Fig. 4 ΔH^0 and "reduced" temperature behaviour for M_5Si_3 compounds vs. the "electronegativity parameter" of *M*

on the electronegativity. For the compounds M_5Si_3 , for which a number of these data are available, the quite similar trends obtained for ΔH_f^0 and for the "reduced" temperature vs. the "electronegativity parameters" of *M* obtained from Miedema *et al.* [8] are shown in Fig. 4. Both the thermal and the thermodynamic stabilities of these phases decrease with increasing Φ_M^* ($\Delta\Phi^*$ for the whole phase decreases). If we consider the corresponding compounds formed by Ge, Sn and Pb, we can see that the stability falls roughly to zero and the phase is not formed in correspondence with $\Phi_M^* \sim \Phi_x^*$.

Stabilities of phases formed by elements of an *A* group with the same *B* element

Examples of this kind are frequent in the literature, where the temperature factor is studied using both the "reduced" temperature [9] and Raynor's stability index [10, 11, 12]. This index is obtained by taking into account the characteristic temperature of the phase, its composition and the melting temperatures of the two components. In particular, Raynor's index can be advantageously used to study the thermal stabilities of different phases occurring in the equilibrium diagrams (with the same element *X*). As an example, we can consider the phases formed by the rare earths with Cd [12]. In

general, a better fit is obtained if we plot the “reduced” temperatures or Raynor’s indices with respect to the melting temperatures of the elements, instead of their atomic numbers. This allows the comparison of phases formed by elements M that

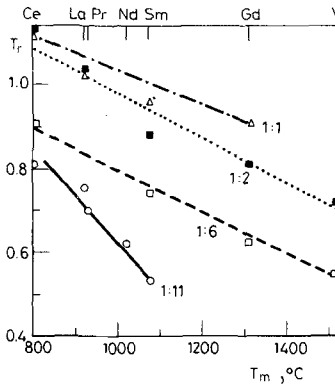


Fig. 5 Raynor's index behaviour versus R melting temperature for R -Cd phases

are not rare earths. As can be seen from Fig. 5, straight lines are generally obtained. For the composition RCd_{11} , the thermal stability falls after $SmCd_{11}$ ($EuCd_{11}$ does exist, but with a different structure type from that for the trivalent rare earths).

Stabilities of phases formed by a given metal of an A group with different elements of a B group

As an example of this application, we can consider the 1 : 1 phases formed by La with the elements of groups IB , IIB and $IIIB$. The “reduced” temperatures for these phases are plotted in Fig. 6 vs. a fixed sequence of the elements of each group. Three

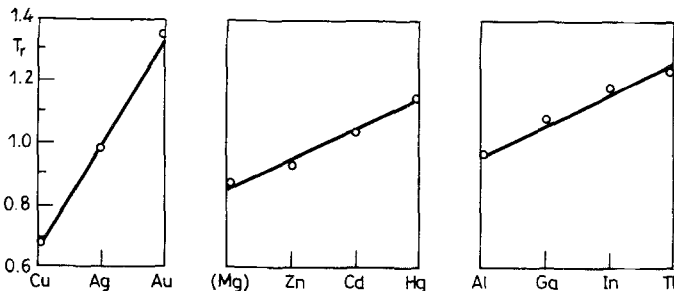


Fig. 6 Trends of “reduced” temperatures for 1 : 1 phases formed by La with the IB , IIB , $IIIB$ group elements

straight lines are obtained, with different slopes, but showing a general increase in stability going down each group. If analogous trends for the different *A* elements are considered, we can observe that the maximum stability generally corresponds to the phases formed by the elements of group IIIA.

Conclusion

For the series of compounds described, the thermal data can be used to establish a sequence of stability among the intermetallic phases, even when thermodynamic data are not available. Obviously, it is necessary to have as starting data a number at least two for each series considered of well-defined, accurate thermal values to describe the linear trends relative to the examined compounds.

We can also demonstrate the dependence of the thermal and atomic stabilities on several atomic parameters, such as the size, the atomic number, the electronegativity or the melting temperature of the constituent atoms.

Evaluations of thermal stability can be useful in the study of intermetallic phases, e.g. when phases in the same series or of near stoichiometry in an equilibrium phase diagram are compared.

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Zusammenfassung — Es wird auf eine enge Beziehung zwischen thermischen Daten und der thermischen Stabilität von intermetallischen Verbindungen hingewiesen. Verschiedene Serien von intermediären Phasen der Metalle der A- oder Überganggruppen mit den Elementen der Gruppen IB bis IVB werden

in Betracht genommen. Die Abhängigkeit der thermischen und thermodynamischen Stabilität von der Atomgröße, der Elektronenkonfiguration, der Elektronegativität und dem Schmelzpunkt der Metallkomponenten wird diskutiert.

Резюме — Отмечается тесная связь между термическими данными и термодинамической устойчивостью интерметаллических соединений. С этой целью рассмотрен ряд промежуточных фаз, образующих металлами группы А или переходных групп с элементами групп IB–IVB. Обсуждена зависимость термической и термодинамической устойчивости от размера атомов, электронной конфигурации, электроотрицательности и температур плавления металлических компонент.