Journal of Thermal Analysis, Vol. 41 (1994) 1305-1318

THE DECISIVE ROLE OF CALORIMETRIC MEASUREMENTS IN EQUILIBRIUM PHASE DIAGRAM CALCULATIONS

P. J. Spencer

Lehrstuhl für Theoretische Hüttenkunde, RWTH Aachen, Kopernikusstr. 16, D-52074
Aachen, Germany

Abstract

In this paper, examples are given of how calorimetric values can give greater certainty to phase equilibria calculated from thermodynamic data. Errors that may arise when phase diagram evaluations are carried out largely from the basis of Gibbs energy information only are illustrated by reference to recent evaluations of the Ti–Si system and the resulting calculated oxidation behaviour of titanium silicides. The importance of calorimetric values for calculation of metastable phase equilibria is demonstrated by results of work on the AlN–TiN hard-metal coating system. Finally, suggestions are made with regard to areas of work where calorimetric data are urgently needed.

Keywords: activity, equilibrium, Gibbs energy, metastable, phase diagram

Introduction

The calculation of phase diagrams using thermodynamic principles and experimental thermodynamic data has become a well-established technique for determining both stable and metastable phase constitution in materials of many different types. In particular, such calculations are invaluable in providing information for multicomponent systems for which the time and costs required for experimental phase equilibrium studies are forbidding. An optimum procedure in such cases seems to be the combination of calculation methods based on critically evaluated thermodynamic data for constituent binary and, if possible, ternary systems, with fewer, carefully defined experimental measurements to provide missing information.

Critical for reliable phase diagram calculations are calorimetric measurements of various types. Whilst the phase boundaries of a system are defined by the relative positions of the Gibbs energy curves or surfaces for the different phases as a function of composition, temperature, etc., it is enthalpies of formation and mixing which establish the order of magnitude of the Gibbs energies,

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

enthalpies of fusion which determine, for example, the shape of the liquidus around maximum-melting compounds, enthalpies of transformation and dissociation which give rise to changes in slope of phase boundaries, heat capacity changes which influence the temperature dependence of other thermodynamic functions, etc.

In this paper, examples will be given of how calorimetric values can give greater certainty to phase equilibria calculated from thermodynamic data. In particular, the importance of calorimetric values for guaranteeing a reliable theoretical background to important practical problems will be demonstrated.

Examples of the practical importance of calorimetric values

Oxidation of titanium–silicon alloys

Protection of metallic materials against high-temperature oxidation can only be achieved by the formation of stable oxide scales, in nearly all cases Cr_2O_3, Al_2O_3 or SiO_2, because only these oxides have a sufficiently slow growth rate [1]. A necessary prerequisite for the formation of a dense and continuous scale on the surface of an alloy is that the oxide concerned is the most stable of all the oxides which can be formed from the components of the alloy. Hence, thermodynamic calculations of the oxide stabilities have to take into account the activities of the alloy components and perhaps those of the oxides also. Al_2O_3 and SiO_2 are among the most stable oxides and even for temperatures approaching 1000°C and higher, they still retain a sufficiently slow growth rate to provide protective scales.

There is generally no difficulty in forming Al_2O_3 or SiO_2 scales on existing Fe-, Ni-, and Co-based alloys because none of the other components of these alloys forms an oxide of comparable stability. Expressed in another way, the oxides of Al and Si form at very much lower oxygen partial pressures than do the oxides of the other alloy components.

A much more complex situation arises if intermetallic phases with titanium as one of the major components are involved. The partial pressures of oxygen at which Al_2O_3 and TiO form are very similar, and TiO will form at oxygen partial pressures which are several orders of magnitude lower than those required for formation of SiO_2.

It is therefore vital to know how the activities of oxide-forming components of an alloy vary with the concentration of the component and with temperature, so that correct information on the stability of oxides on intermetallics can be obtained. The activity data required to assess oxide stability are an integral part of the set of coefficients resulting from the thermodynamic evaluation of an alloy system using the CALPHAD approach [2].

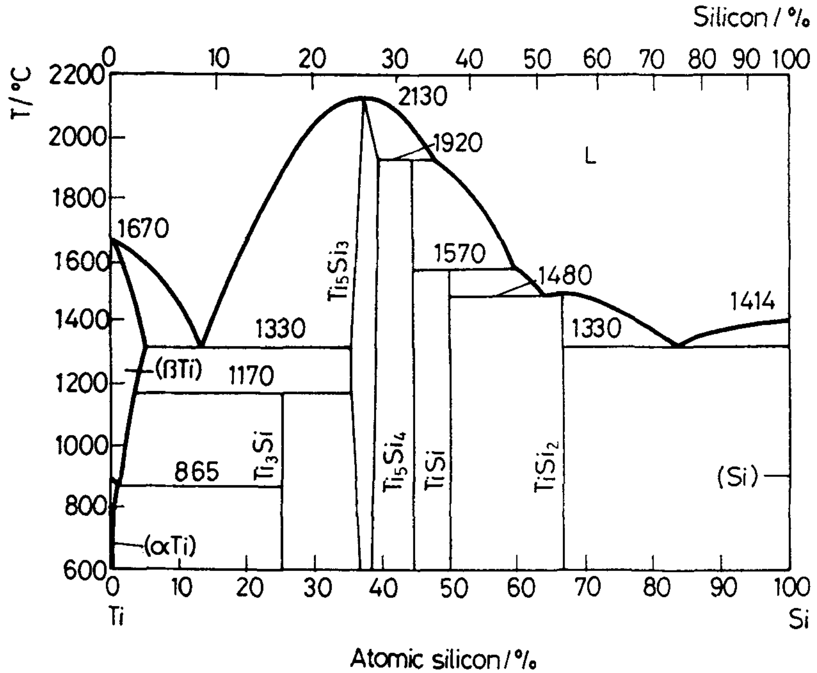

Fig. 1 The Ti–Si system as reported by Massalski [3]

In the titanium–silicon system (Fig. 1 [3]), 5 intermetallic phases are present. Thermodynamic evaluations of the system using available experimental thermodynamic and phase diagram data have been reported by Vahlas *et al.* [4] and by Paajunen [5]. The calculated phase diagrams resulting from the two evaluations are shown superimposed on one another in Fig. 2. There is excellent agreement both between the two calculated diagrams and with the phase diagram reported by Massalski [3].

Nevertheless, if the comparison of the results of the two evaluations is extended to the enthalpies of formation of the intermetallic compounds and to the variation of activity values across the system, some significant differences are revealed. Table 1 lists values for the enthalpies of formation at 300 K of the titanium silicides as calculated from the coefficient sets reported in [4 and 5].

The table clearly shows that the data from [5] result in enthalpies of formation which are considerably more exothermic for the higher silicon compounds. This corresponds to less satisfactory accord with the available experimental results, as illustrated in Fig. 3, which presents a plot of experimental and calculated enthalpies of formation as reported by Vahlas *et al.* [4].

The effect of the differences in the enthalpies of formation as obtained from the data of [4] and [5] on the calculated variation of activity values across the

Ti–Si system is illustrated for a temperature of 1000°C in Fig. 4 a and b. These diagrams were calculated and plotted using the program ChemSage [9].

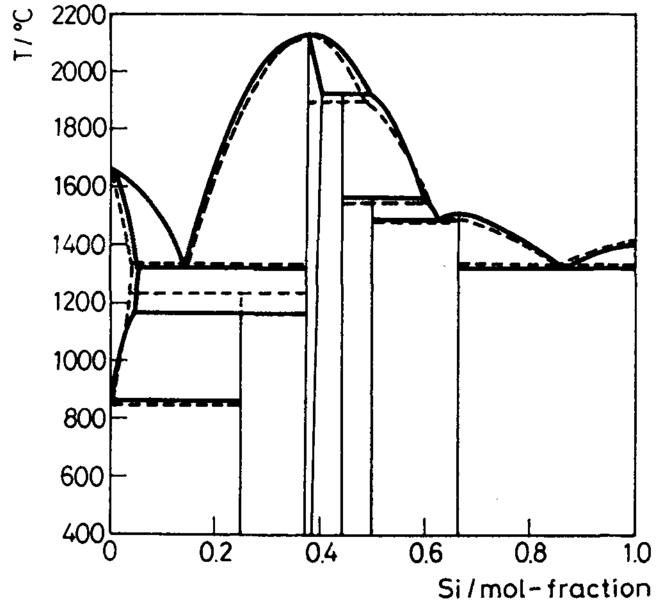

Fig. 2 The Ti–Si system as calculated from the data reported in Ref. 4 (– – –) and 5 (—)

In particular, the log of the Ti activity change across the compound $Ti_{.333}Si_{.667}$ as calculate from the two data sets is 4.56 and 2.14 respectively. The magnitude of this difference in Ti activity has important implications for the predicted oxidation behaviour of the higher silicides. This is illustrated in Fig. 5a and b, which shows the stable oxide phases formed by oxidation of $Ti_{.5}Si_{.5}$ at different oxygen partial pressures, calculated using data from [4 and 5].

Table 1 Calculated enthalpies of formation at 300 K of the titanium silicides as obtained from data of [4] and [5]

Compounds	$\Delta_f H$ (300 K)* / J·mol^{-1}	
	Ref. 4	Ref. 5
$Ti_{0.333}Si_{0.667}$	–56 967	–92 873
$Ti_{0.5}Si_{0.5}$	–68 000	–83 180
$Ti_{0.556}Si_{0.444}$	–71 000	–78 291
$Ti_{0.625}Si_{0.375}$	–72 409	–73 474
$Ti_{0.75}Si_{0.25}$	–66 565	–67 522

*Si (diam) and Ti(hcp) standard states

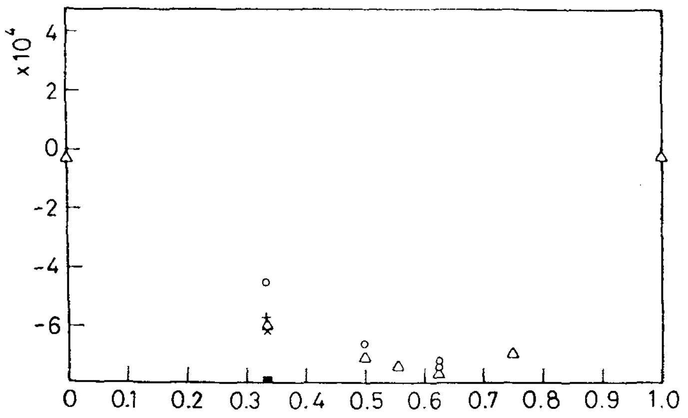

Fig. 3 Calculated [4] (Δ) and experimental [6–8] (o, x, +) enthalpies of formation for the solid phases of the Ti–Si system

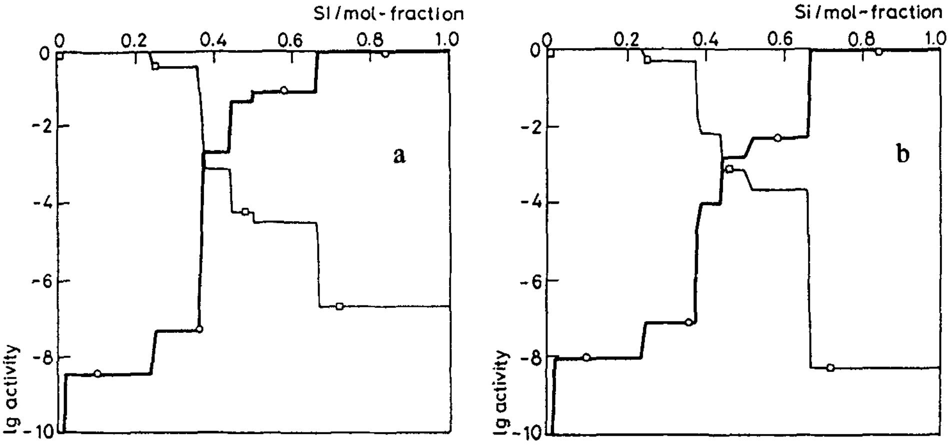

Fig. 4 Activity of Si and Ti in the Ti–Si system at 1000°C Si(diam) and Ti(bcc) standard states (a. Ref. [4], b. Ref.[5])

There are clearly pronounced differences in the two sets of results. Most important is the prediction that SiO_2 remains stable at the lowest O_2 partial pressure according to [4] (Fig. 5a), whereas the data from [5] predict that TiO will be the stable oxide phase formed on $Ti_{.5}Si_{.5}$ at the corresponding oxygen partial pressure (Fig. 5b).

The results demonstrate that the calculated oxidation behaviour is very dependent on the evaluated activity data for the alloy components.

In the example discussed here, it is evident that the experimental enthalpies of formation are decisive in allowing correct 'optimized' thermodynamic coef-

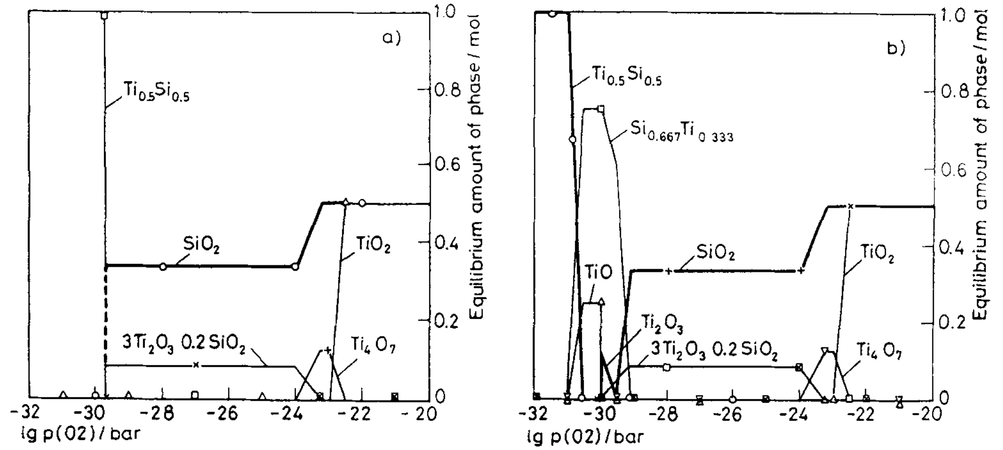

Fig. 5 Oxidation of a $Ti_{.5}Si_{.5}$ alloy as a function of oxygen partial pressure (Data From a. Ref. [4], b. Ref. [5])

ficients for the Ti–Si system to be obtained and hence correct oxidation behaviour of the titanium silicides to be predicted. While a very good description of the Ti–Si phase diagram is obtained with two different sets of Gibbs energy coefficients [4, 5], it is necessary to reproduce satisfactorily the experimental enthalpy of formation data in order to provide a correct prediction, or interpretation, of oxide scale formation.

Stability ranges of metastable coatings in the AlN–TiN system

A major application of hard metal carbides and nitrides is as coatings for tool materials. CVD (Chemical Vapour Deposition) techniques have frequently been used to produce such coatings, but there is ever-increasing use of PVD (Physical Vapour Deposition) methods, whereby a material of known composition is transferred from a target (e.g. by sputtering) to a substrate maintained at a lower temperature. PVD processes are of particular importance because they enable homogeneous, multicomponent phases with improved properties to be deposited easily. The stoichiometry of these phases can be controlled by adjusting the process parameters, and variation of the substrate temperature can in some cases be used to deposit materials in different crystalline structures or as an amorphous phase.

Metastable coatings in the AlN–TiN system have been found to possess very good wear-resistant properties and although hexagonal AlN and fcc(NaCl) TiN show virtually no miscibility in the solid state under equilibrium conditions (Fig. 6), codeposited mixtures of the two nitrides using PVD techniques result in a metastable cubic (Ti,Al)N solution phase being formed over a wide composition range [10]. This material displays significantly improved properties over those of the component nitrides.

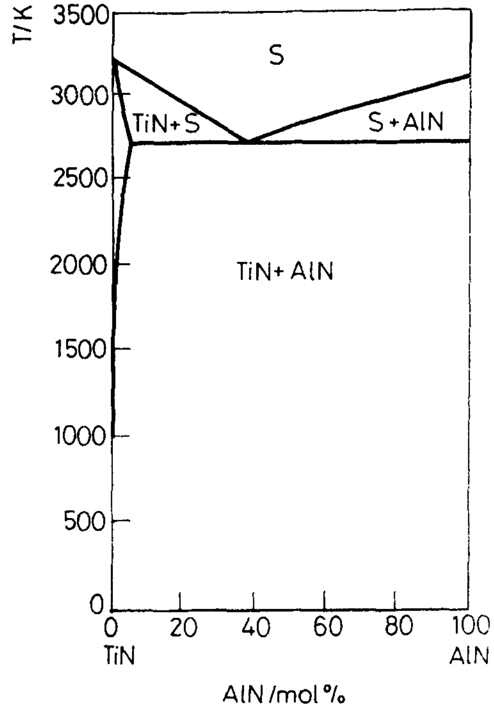

Fig. 6 Calculated TiN–AlN phase diagram [11]

Attempts are now being made to use thermodynamic calculation techniques to predict the stability ranges of metastable phases in PVD-deposited mixed nitride, carbide, boride, etc. coatings [11]. These calculations, if successful, will provide an important basis for the design and development of new coating materials. The basis for the calculations is the hypothesis made by Saunders and Miodownik [12] with regard to the deposition of metallic alloys on low-temperature substrates. They suggest that, due to the low substrate temperatures used, diffusion cannot take place to produce separation into a multiphase structure in the deposited materials. As a result a single phase coating is formed from the phase with the lowest Gibbs energy at the overall coating composition and substrate temperature concerned. Using this hypothesis Saunders and Miodownik were able to predict accurately the ranges of stability (both stable and metastable) of different phases found in codeposited alloys at low substrate temperatures.

In the case of hard-metal coatings, the difficulty facing such thermodynamic calculations is the need to obtain

– thermodynamic values (lattice stabilities) for the pure nitrides, carbides, etc. in different metastable as well as stable structures

– thermodynamic properties of mixing for the metastable and stable phases in the coating systems concerned.

Enthalpy values are decisive in establishing reliable data for both types of missing information. Although various estimation methods have been used to

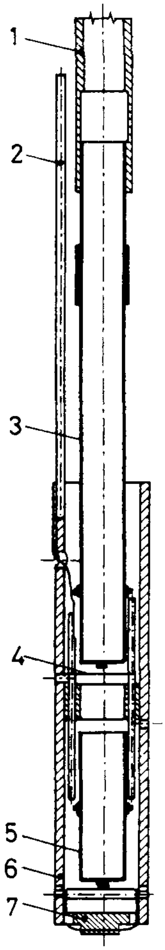

Fig. 7 High-temperature drop calorimeter used to determine enthalpies of metastable-stable phase transformations in the AlN–TiN system [15]. 1 – charging tube, 2 – capillary tube, 3 – measuring cell, 4 – thermopile, 5 – reference cell, 6 – holder tube, 7 – bottom plate

derive enthalpies of transformation from stable to metastable structures and to predict enthalpies of mixing e.g. [11, 13, 14] it is imperative that these estimated numbers be substantiated by comparison with reliable experimental calorimetric values.

To carry out this comparison and to check the reliability of various methods of estimation, Stolten [15] has performed drop calorimetry measurements on specimes in the AlN–TiN system. The experimental apparatus is shown in Fig. 7.

Specimens for five compositions across the AlN–TiN system were prepared by sputtering a target consisting of appropriate proportions of pure aluminium and titanium in a controlled nitrogen atmosphere onto an Al-foil substrate. The structure of the resulting specimens was investigated by X-ray analysis. Whilst 3 of the specimens displayed a single phase fcc(NaCl) structure corresponding to that of TiN, specimens at high AlN concentrations were unsuitable for calorimetric studies because of the presence in them of phases with structures other than the hexagonal AlN structure.

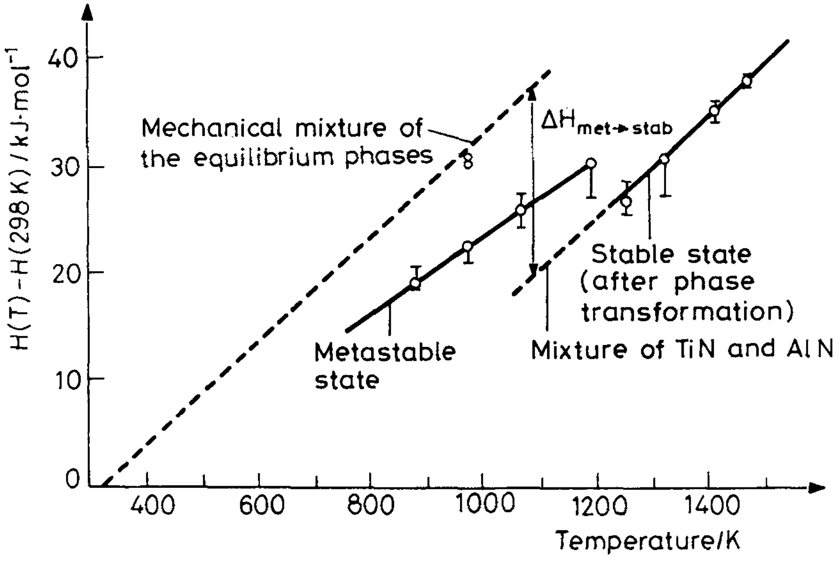

Fig. 8 Determination of the metastable to stable transformation enthalpy of a (Ti,Al)N specimen

The 3 (Ti,Al)N specimens displaying a metastable single phase fcc structure were used for calorimetric measurements to determine the enthalpy of the metastable single phase to stable 2-phase (AlN+TiN) transformation. Calibration was carried out using Al_2O_3 samples. For each (Ti,Al)N specimen, approximately eight to ten individual measurements were carried out (of which five were calibration measurements) at eight different temperatures. The resulting H(T)-H(298 K) curve for a $Ti_{.82}Al_{.18}N$ specimen is illustrated in Fig. 8.

Based on the 3 results for the transformation enthalpy at different overall compositions and assuming regular solution behaviour for the metastable fcc(Ti,Al)N mixtures, a plot of Gibbs energy against composition can be made. The intercept of this curve at the pure AlN axis provides a value for the lattice stability, G(AlN,fcc)–G(AlN,hex), of AlN in the metastable fcc structure (Fig. 9).

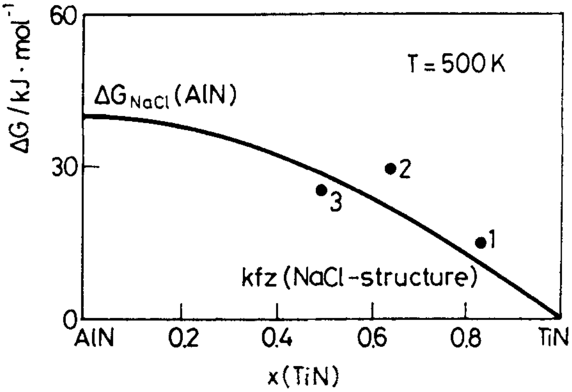

Fig. 9 Gibbs energy of the metastable fcc(TiN) to stable AlN+TiN transformation as a function of composition

In order to calculate the ranges of stability of the metastable fcc(Ti,Al)N and hex(Al,Ti)N solution phases as a function of composition, a Gibbs energy of transformation curve for metastable hex(Al,Ti)N to stable AlN+TiN, analogous to that just described for the fcc(Ti,Al)N phase must also be derived. This was achieved by Stolten using estimation and calculation methods described in his doctor's thesis [15]. His plots of Gibbs energy *vs.* composition for the fcc(Ti,Al)N and hex(Al,Ti)N phases are compared with estimated values from [11] in Fig. 10.

Using the hypothesis that in coatings deposited on a low-temperature substrate it is the single phase with the lowest Gibbs energy that is stable at a given overall composition, it can be seen from Fig. 10 that thermodynamic data for the AlN–TiN system predict that a metastable hex(Al,Ti)N phase will be formed at compositions up to about 30 mol% TiN and a metastable fcc(Ti,Al)N phase at higher TiN concentrations.

In the case of the Ti–Al–N system, it is possible to check this prediction against the experimental evidence obtained by Knotek and Leyendecker [10] from an analysis of the structure of coatings produced by sputtering.

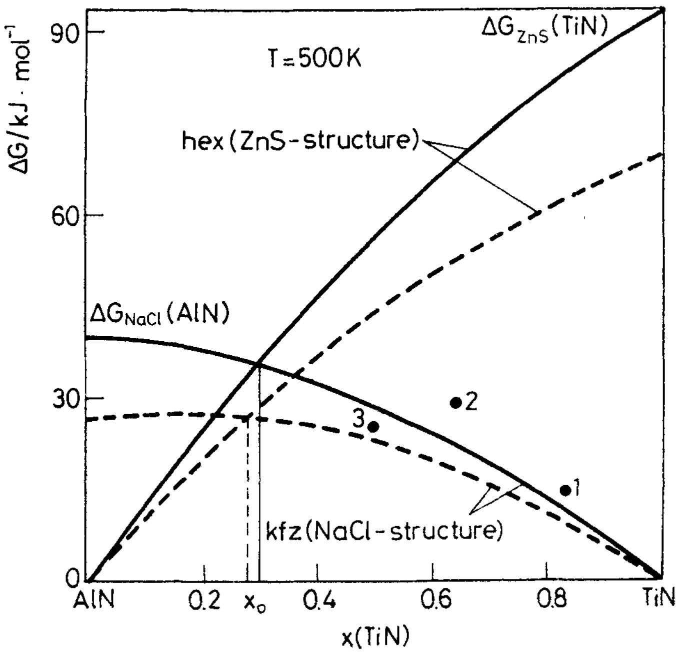

Fig. 10 Gibbs energy *vs.* composition curves for the hex(Al,Ti)N and fcc(Ti,Al)N phases in the AlN–TiN system. (Estimated data from Ref. 11) – – –

Figure 11 illustrates the experimental range of the fcc(Ti,Al)N phase. This extends from TiN to just over 60 mol% AlN, thus giving good support to the calculated range.

On the basis of these results, it can be anticipated that calorimetric measurements of transformation enthalpies in hard-metal coating systems such as that discussed here would give a firmer basis to subsequent thermodynamic calculations of the ranges of composition and temperature in which metastable coating structures will be formed as a result of physical vapour deposition processes.

Phase diagram 'problem areas' requiring experimental calorimetric data

The above examples illustrate the central role of calorimetric values in thermodynamic calculations of phase equilibria.

There remain particular difficulties in the thermodynamic representation of a system which are still the subject of considerable discussion and for which calorimetric measurements are urgently needed. Among these are:

The behaviour of the heat capacity of pure liquid elements at temperatures below the normal melting point.

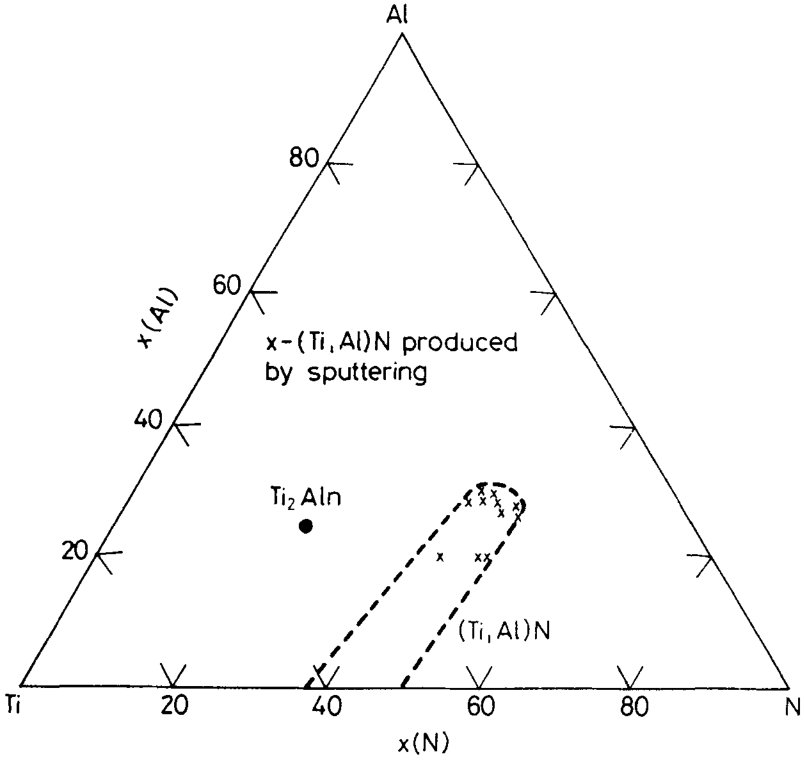

Fig. 11 Experimental range of the fcc(Ti,Al)N phase in the Ti–Al–N system (Ref. 10)

The temperature dependence of C_p(liq) is needed for an accurate description of the mixing properties of the liquid phase e.g. in systems formed by elements of widely different melting points. The frequently made assumption that the heat capacity of a liquid metal remains constant with temperature below the melting point can lead to poor description of phase equilibria involving the liquid phase at lower temperatures, e.g. low-melting eutectics. Experimental C_p values for undercooled liquid metals would be extremely helpful in establishing a reliable, temperature dependent C_p equation.

Lack of experimental thermodynamic data for the liquid phase of alloy systems.

Because of the difficulties of carrying out thermodynamic measurements at high temperatures, thermodynamic evaluation of high-melting alloy systems may be forced to resort to over-simplified descriptions of mixing properties in the liquid phase. This situation could be greatly improved upon if just one or two measurements of the enthalpy of fusion of selected alloy compositions were available. In combination with experimental values for solid alloys, determined at more accessible experimental temperatures, these enthalpies of fusion would provide reasonable, order-of-magnitude mixing properties for the liquid phase.

Lack of thermodynamic data for ternary compounds.

In progressing from binary to higher-order systems in phase diagram calculation work, a stumbling block is often the lack of thermodynamic values for ternary compounds. As a result, solubility boundaries involving such phases can be significantly in error and a poor representation of the phase equilibria in the ternary system may result. Measurements of the enthalpies of formation of ternary compound phases would enable a much more reliable thermodynamic evaluation of ternary phase equilibria to be carried out and thus give greater confidence in proceeding further to calculations in still higher-order systems.

Conclusions

Calorimetric measurements are frequently the 'key-element' in producing a correct thermodynamic description of stable or metastable phase equilibria in an alloy system. There is still an urgent need for calorimetric numbers to enable a variety of practical problems to be reliably interpreted and resolved. It is a matter of some concern that the current trend away from experimental calorimetric work be reversed as soon as possible.

References

1 A. Rahmel and P. J. Spencer, Oxidation of Metals, 35 (1991) 53.
2 CALPHAD, Computer Coupling of Phase Diagrams and Thermochemistry, L. Kaufman (Ed.), Pergamon, 1977 onward.
3 T. B. Massalski (Ed.), Binary Alloy Phase Diagrams, ASM, Metals Park, Ohio 1986.
4 C. Vahlas, P.-Y. Chevalier and E. Blanquet, CALPHAD, 13 (1989) 273.
5 M. Paajunen, unpublished work, Helsinki Univ. of Technology, 1989.
6 D. A. Robins and I. Jenkins, Acta Metallurgica, 3 (1955) 598.
7 Yu. M. Golutvin, Zh. Fiz. Khim., 30 (1956) 2251.
8 L. Topor and O. J. Kleppa, Met. Trans. A, 17 (1986) 1217.
9 G. Eriksson and K. Hack, Met. Trans. B, 21B (1990) 1013.
10 O. Knotek and T. Leyendecker, J. Solid State Chem., 70 (1987) 318.
11 P. J. Spencer and H. Holleck, High Temp. Sci., 27 (1990) 295.
12 N. Saunders and A. P. Miodownik, CALPHAD, 9 (1985) 283.
13 H. Stolten, P. Spencer and D. Neuschütz, J. Chim. Phys., 90 (1993) 209.
14 A. F. Guillermet and G. Grimvall, J. Phys. Chem. Solids, 53 (1992) 105.
15 H. Stolten, Doktorarbeit, RWTH Aachen, 1991.

Zusammenfassung — Vorliegend wird beschrieben, wie kalorimetrische Werte eine größere Gewißheit über die anhand thermodynamischer Angaben berechneten Phasengleichgewichte liefern können. Fehler, die sich aus der Auswertung von Phasendigrammen ergeben können, die zum größten Teil nur auf der Basis von Informationen der Gibbs' schen Energie erfolgten, werden in Bezug auf die vorliegende Auswertung des Ti/Si/Systemes und in Bezug auf das resultierende berechnete Oxidationsverhalten von Titansiliziden illustriert. Die Bedeutung kalorimetrischer Werte für die Berechnung metastabiler Phasengleichgewichte wird durch die Resultate einer Arbeit über das Hartmetallbeschichtungssystem AlN-TiN demonstriert. Abschließend werden Vorschläge in Bezug auf Arbeitsbereiche gemacht, wo kalorimetrische Werte dringend benötigt werden.