Phase Equilibria: Materials for the Future
APDIC 4th World Round Robin Seminar

IoM3 London, UK

Sponsors

The Spencer Group

Ceravision®

SGTE

MSI

APDIC

Argentina Committee for Phase Diagrams, ARGENTINA
ASM International®, USA
Associated Phase Diagram and Thermodynamics Committee, POLAND
BOSNIA & HERZEGOVINA, BULGARIA, CROATIA, CZECH REPUBLIC
HUNGARY, MONTENEGRO, ROMANIA, SERBIA, SLOVAKIA, SLOVENIA
Baikov Institute of Metallurgy and Materials Science, RUSSIA
Brazilian Committee for Phase Diagrams of Materials, BRAZIL
Chemica e Chimica Industriale, University of Genova, ITALY
Chinese Phase Diagram Committee, PR CHINA

Deutsche Gesellschaft für Materialkunde, GERMANY
Groupe de Thermodynamique et Diagrammes de Phases, FRANCE
The Indian Institute of Metals, INDIA
The Institute of Materials, Minerals & Mining, UK
Japanese Committee for Alloy Phase Diagrams, JAPAN
Korean Committee of Computational Materials Science and Engineering, KOREA
Materials Science International Services, GERMANY
Royal Institute of Technology, SWEDEN
Ukrainian Phase Diagram and Thermodynamic Commission, UKRAINE
Phase Equilibria: Materials for the Future

APDIC 4th World Round Robin Seminar

This APDIC WRRS is primarily concerned with the practical use of phase diagrams for industry and commerce, and also teaching the subject for that purpose. The seminar comprises a full day of talks covering fundamental aspects through to industrial applications.

Institute of Materials, Minerals and Mining
1 Carlton House Terrace,
London, UK

25 June 2012

Organised by the Materials Chemistry Committee of the IoM3
Programme

Morning Session: Fundamentals 10:00-13:00

10:00 Introduction
   Prof. Tetsuo Mohri (Hokkaido University, Japan – chair APDIC WRRS committee)
10:15 How to Read and Apply Phase Diagrams
   Prof. Rainer Schmid-Fetzer (Clausthal University of Technology, Germany – IoM3 Hume-Rothery prize winner, 2010)
10:45 Experimental methods
   Dr. Andy Watson (University of Leeds, U.K. – chair of IoM3 Materials Chemistry Committee)
11:15 From ab initio to CALPHAD modelling
   Prof. Catherine Colinet (INPG, Grenoble, France)
11:45 Calculation of phase equilibria from critically assessed thermodynamic data
   Dr. Alan Dinsdale – (NPL, U.K. - IoM3 Hume-Rothery prize winner, 2000)
12:15 Cluster Variation Method
   Prof. Tetsuo Mohri (Hokkaido University, Japan – chair APDIC WRRS committee)
12:45 Discussion

Afternoon Session: Applications 14:00-17:00

14:00 Thermodynamics and Phase Diagrams for Lithium-ion Batteries
   Prof. Hans Seifert (K.I.T., Karlsruhe, Germany)
14:30 The Success of CALPHAD in the Development of Gas Turbine Materials – A Historical Perspective.
   Mr. Colin Small, (Rolls Royce plc, UK)
15:00 Applications of Phase Equilibria in Aluminium Alloy Products and Processes
   Dr. Paul Evans, (Technology Strategy Consultants, Warwick, UK)
15:30 Phase Equilibria: Materials for Nuclear Fission Energy Systems
   Prof. Rudy Konings (Institute for Transuranium Elements, Karlsruhe, Germany, Germany)
16:00 Thermodynamics of Portland Cement Hydration
   Prof. Fred Glasser FRSE FIMM (University of Aberdeen, UK. – IoM3 Hume-Rothery prize winner, 2011)
16:30 Discussion
How to Read and Apply Phase Diagrams
Rainer Schmid-Fetzer
Clausthal University of Technology, Germany

Abstract

It is a commonplace that phase diagrams form the basis to understand the behaviour of materials. However, the wealth of information stored in phase diagrams is often not exploited, mainly because of two reasons:

• A lack of education in reading and understanding phase diagrams forms a hurdle.
• The link between an actual materials process and phase diagrams may not be obvious.

This dilemma is depicted in Fig. 1, and it is a pity that this frequently results in discarding the benefits of applying phase diagrams as a very useful tool in so many fields of materials engineering, such as alloy design, solidification, heat treatment, soldering, materials compatibility and so on.

Let me show you a phase diagram
Adapted from dilbert.com/strips/comic/2012-04-06/

Figure 1. This common reaction to phase diagrams results in discarding the benefits of applying them as a most useful tool in materials engineering.

This presentation aims at an audience with no (or forgotten) prior exposure to phase diagrams, such as mechanical engineers or physicists, but also to all those in the materials field who want to make the best out of phase diagrams.

Starting from the very basics of phase diagrams and phase equilibria we will go through reading unary, binary and ternary phase diagrams, including liquidus projections. The key information provided at a fixed point of state variables (pressure, temperature, composition of system) is the equilibrium constitution:

• Type of phase(s) occurring: Liquid, solid solutions, gas, intermetallics, other compounds.
• Fraction (amount) of each phase occurring.
• Composition of each phase occurring.

Applications demonstrated include interface reactions, alloy solidification and heat treatment. The path from initial off-equilibrium state towards equilibrium is emphasized. Phase diagrams calculated from Calphad-type thermodynamic databases are especially useful for multicomponent systems. The complete constitution information is obtained in easy-to-read property diagrams for alloys or series of alloys. This also allows comparing the constitution developed during solidification of an alloy for the two extreme cases of Equilibrium versus Scheil solidification. All phase diagrams shown in this work are for real materials (no A-B-C systems).
Experimental Methods

Andy Watson,
IMR, The University of Leeds, UK

Introduction

There can be little doubt that the most important and fundamental aspect of Materials Science is the chemistry of the materials themselves. The constituent chemical elements in a material and in what form they coexist has a direct influence on the chemical, physical and mechanical properties of that material. The phase diagram is a convenient way of showing how the phase assemblage changes with the conditions of composition, temperature and pressure and has become an invaluable tool in materials development and processing. Despite the advances in computational techniques for the prediction of phase equilibrium, the phase diagram is still an important building block in the materials modelling process, and as there is still no reliable and accurate method of deriving a phase diagram from first principles; experimentation is still the best way to construct a phase diagram. This has the added advantage that it links materials modelling to real life as it is based on experimental observation. As the phase diagram depicts the state of thermodynamic equilibrium, it follows that an experimental study of thermodynamic properties will also yield invaluable information, and it is through Computational Thermodynamics where these two complementary fields are brought together.

Experimental Determination of Phase Diagrams

Thermal Analysis

As the phase diagram can be considered as the graphical representation of the thermodynamic equilibrium of a system, then it follows that on crossing a phase boundary there will be a corresponding change in the thermodynamic properties. This is the principle of Thermal Analysis, where for example, the point of solidification of an alloy can be determined by detecting the evolution of the heat of fusion. This can be visualised considering Fig. 1, which shows schematically, the cooling curve resulting from cooling alloy C in a simple eutectic system. By monitoring the alloy temperature as a function of time as it cools, the locations of the phase boundaries can be realised as kinks in the cooling curve as the heat of fusion is released on solidification.

Figure 1: Simple cooling curve analysis

Figure 2: Schematic diagrams showing arrangement of thermocouples in DTA and DSC
This is a relatively inaccurate method for phase diagram determination and is highly cooling rate dependent as kinetic factors often suppress the initiation of the solidification process. A development of this technique uses two thermocouples; one measuring the temperature of the sample and the second the temperature of an inert reference substance (Fig. 2). The differential between the two signals and is plotted against time. In this technique (differential thermal analysis – DTA), heat effects are more easily seen and appear as peaks rather than inflections. A more refined and accurate development is DSC (differential scanning calorimetry) where the heat flow between the sample and reference is measured.

Despite the increased accuracy over thermal analysis, both DTA and DSC are still prone to kinetic effects, most of which can be alleviated by carrying out the experiment during sample heating as well as cooling. Figure 3 shows a schematic of a theoretical DTA trace as a phase boundary is crossed during heating and cooling – note the opposite 'sense' of the peak in each case. Using the standard convention of endothermic events resulting in the trace falling, a 'peak' results from cooling the sample as the heat of transformation is released. On heating the sample, this appears as a 'trough' as the heat of transformation is absorbed.

![Figure 3: Idealised DTA traces for heating and cooling (bottom). The peaks represent the heat change associated with a change in system enthalpy (top).](image)

As mentioned above, thermal analysis measurements are by their nature dynamic measurements and thus prone to errors owing to kinetic considerations. This becomes more of a problem as the temperature of the measurement is reduced. For the determination of phase boundaries at lower temperatures, it is useful to use non-dynamic methods where time can be allowed for equilibrium to be achieved before this is quenched in the sample by fast cooling. Typical analysis techniques employed in the study of the quenched material are X-ray analysis and Scanning Electron Microscopy employing EDX.
**X-ray Analysis**

Monochromatic X-rays, when incident on a crystal, will be diffracted by the atomic planes in the crystal lattice. Constructive interference of the diffracted beams will occur at certain angles of incidence, and through Bragg’s relationship, the interplanar distances (d) of the material can be calculated (Fig. 4). The constructive interference is recorded either by film or an X-ray detector resulting in a characteristic X-ray *diffraction pattern* of the diffracting phase (Fig. 5).

![Figure 4: Diffraction of X-rays](image)

![Figure 5: XRD pattern for quartz](image)

The *disappearing phase technique* is used for the determination of phase boundaries where kinetic constraints make dynamic techniques of little use. It involves preparing a number of samples with differing compositions within the binary/ternary/multicomponent system. The samples are heated to a specific temperature for a time long enough to allow equilibrium to be reached after which they are rapidly quenched to retain the phase structure. By comparing the sequence of diffraction patterns it can be seen at which compositions the phase boundaries occur (Fig. 6). There are uncertainties with this technique however, in that it relies on the composition intervals chosen. Calculating the lattice parameters of the phases and plotting these as a function of composition will improve the accuracy of the technique.

![Figure 6: XRD patterns resulting from the analysis of a number of alloys across a hypothetical binary system](image)

**SEM/EDX**

XRD is an excellent technique for phase analysis based on characteristic X-ray diffraction patterns, however phase composition is more easily determined by a combination of Scanning Electron Microscopy coupled with Energy Dispersive X-ray analysis. SEM is used to study small objects at magnifications and resolutions much higher than possible by optical (light) microscopy.
Figure 7 shows a schematic representation of the scanning electron microscope. High-energy electrons are accelerated towards the sample. The electrons are absorbed resulting in the emission of other species (Fig. 8). Secondary electrons are detected to give a high-resolution image. A back-scattered electron image will give a view of the surface of the sample, the contrast being indicative of the atomic number of the element from which the electrons are reflected – higher atomic number atoms reflect more strongly. This, in itself, is a useful analysis tool to give an rough idea of relative composition of the sample, but for high precision qualitative and quantitative work, analysis of the emitted X-rays that result from the interaction between the incident electrons and the atoms in the sample can give an accurate measurement of phase composition. The energy spectrum of the emitted X-ray is characteristic of the atom from which it originates. Thus, by examining the total energy spectrum from the sample, or from beneath the electron beam (Fig. 9), it is possible to know the composition.

This enables the phase composition and hence location of the phase boundaries to be pinpointed with some accuracy. However, there are limitations. The X-rays do not only originate from the surface of the sample, but also from the interior. The activation volume can be anything up to 2 μm beneath the surface, depending on the accelerating voltage of the electron beam. The danger therefore, is that the activation volume includes material from another phase of a different
composition from that expected leading to errors in the analysis. A relatively new and particularly powerful technique for the determination of phase boundaries and phase relationships using SEM/EDX is the use of Diffusion Couples. Here, two blocks of materials of different compositions (often pure components, but not necessarily) are clamped together in intimate contact. After an appropriate heat treatment allowing equilibration, the sample is quenched and sectioned revealing a microstructure containing all of the equilibrium phase relationships along the diffusion path between the two extreme compositions denoted by the couple. Appropriate analysis by SEM/EDX can then elucidate much of the phase diagram. One carefully chosen diffusion couple (or triple) experiment can take the place of a number of experiments involving the heat treatment of single-composition samples.

Experimental Determination of Thermodynamic Properties

The Phase Diagram can be considered as a visual representation of the thermodynamic equilibrium state of a system. It follows therefore, if the thermodynamic properties of a system is known, it should be possible to determine the phase equilibrium within a system for a set of fixed conditions of temperature, pressure, etc. Therefore, the experimental determination of thermodynamic properties is a very useful if often neglected subject. Measurements can be split into two distinct types; the measurement of heat change (enthalpy changes) and the determination of Gibbs energies (component activities in solutions, vapour pressures...).

Calorimetry

It is not possible to measure enthalpy itself, but changes in enthalpy are easily realised using an appropriate calorimeter. Useful thermodynamic quantities that can be determined by calorimetry are enthalpies of formation ($\Delta H_f$), enthalpies of mixing ($\Delta H_{mix}$), enthalpies of transformation ($\Delta H_{tr}$) and heat capacity ($C_p$). As the name implies, calorimetry means the measurement of heat and there are a number of methods at the disposal of the thermochemist. The actual measurement could involve temperature change, EMF or even a quantity of liquid, but one thing that is common to all of the methods is that the measured quantity has to be related to a known heat change through an appropriate calibration.

One of the simplest forms of calorimetry, which is often used in combustion work to determine the heats of formation of compounds is isoperibol calorimetry. The calorimeter itself (where the heat change is measured) is placed in a vessel, which is held at a constant temperature (Fig. 10). Appropriate shielding is placed between the calorimeter and the surrounding vessel in order to
minimise heat transfer. The calorimeter temperature is measured as a function of time. The reaction for which the heat effect is required is initiated in the calorimeter at time B (see Fig. 10), which results in a temperature rise. As the reaction goes to completion (which may be very fast for a combustion reaction) the temperature begins to fall as heat is gradually lost to the surroundings. By extrapolation of the temperature to the initiation time (AC and D) a corrected temperature rise (ΔT) can be calculated. The heat effect is given as $Q = WΔT$ where $W$ is the ‘water equivalent’ of the calorimeter. This is derived by measuring a known heat effect inside the calorimeter. This can be the combustion of a substance, the heat effect of which is well known. Heat losses are controlled and corrections are made, but a better method is to remove these altogether. Adiabatic calorimetry aims to do this by surrounding the calorimeter cell with a furnace that maintains the same temperature in the surroundings as inside the calorimeter cell (Fig. 11). The Adiabatic calorimeter designed by Dench is used for the determination of enthalpies of formation of metallic alloys by direct reaction. A pressed compact of intimately mixed element powders is heated from a predetermined safe temperature (the highest temperature at which no alloying takes place) to a final temperature (the lowest temperature where alloying is complete during the duration of the measurement – say half an hour). The energy required to do this, as delivered by the sample heater, is measured. Adiabatic conditions are achieved by the surrounding furnace controlled by the differential thermocouple which maintains equal temperature inside and outside the calorimeter cell. By comparing the heat supplied to the sample heater for the alloying run with separate runs involving the pure components only, the enthalpy of formation of the alloy can be easily determined.

![Figure 11](image-url)  
**Figure 11:** The 'Dench' Adiabatic Direct Reaction Calorimeter

An alternative approach is to measure the heat flow to and from the calorimeter cell in response to a heat effect taking place within it. In the *Tian-Calvet* calorimeter, most of the heat produced in the calorimeter cell is conducted to the surroundings along thermocouple wires that together comprise a thermopile (Fig. 12). By virtue of the Seebeck effect, the EMF generated in the thermopile is proportional to the heat flux along the thermocouple wires of the thermopile. This type of calorimeter is extremely sensitive and is the basis for most calorimeters in use in materials science today. A major development of this apparatus is the twin microcalorimeter (Fig. 13) as constructed by Kleppa and further developed by Laffitte and co-workers. In the case of the twin calorimeter, as the name suggests, the apparatus consists of two calorimetric cells and it is the difference between the EMF produced by the pair of cells that is measured. One of the cells acts as a reaction cell whilst the second cell acts as a reference. This makes the instrument remarkably
sensitive with the added advantage that in principle, measurements can be made over a
temperature scan. The maximum temperature of operation for such instruments (depending on
the specific type and materials used in construction) can be in the region of 1500°C. An alternative
arrangement of the thermopile is to place the cells in tandem rather than side by side, with the
reaction cell lying above the reference cell in a detector assembly within a tube furnace. This
particular arrangement, although convenient for removing and replacing the detector, suffers
from a loss in sensitivity in comparison with the side-by-side configuration.

Figure 12: The Tian-Calvet Calorimeter. The
cell (A) is connected to the surroundings (C)
by a thermopile

Figure 13: Kleppa’s twin microcalorimeter.
Legend A: Main heater, B: Top heater, C: Heat
Shield, D: Aluminium / nickel jacket, E:
Calorimeter, F: Protection Tube, G: Radiation
Shields, H: Dropping Tube

The high sensitivity and configuration of these types of instruments make them particularly useful
for drop calorimetry. As the name suggests, a sample is dropped into the calorimeter, usually from
room temperature to elevated temperature inside the reaction cell of the instrument, measuring
the heat effect associated with heating the sample and that owing to any reaction that may take
place within the cell. The technique is very versatile. In its simplest form, it can be used to
measure heat contents, the measurement corresponding to $H_{T2} - H_{T1}$, where $T2$ is the temperature
of the calorimeter and $T1$ the dropping temperature. Because of the ease by which samples can be
introduced into the apparatus, enthalpies of reaction at higher temperatures can be easily
determined. For example, enthalpies of formation by direct reaction are relatively straightforward
to measure. Compacted mixtures of component powders can be dropped into the calorimeter,
with the compound for study forming within the calorimeter itself. By comparing the heat effect
(Fig. 14) with those for dropping the single components themselves, the enthalpy of formation can
be easily obtained. If direct reaction is difficult (maybe because of kinetic constraints) and
alternative is to dissolve the preformed compound material in an appropriate solvent within the
calorimeter. Again, comparing the heat effect with those for dissolving the pure components of
the compound in the same solvent will reveal the enthalpy of formation. A particular
thermodynamic quantity that is readily accessible by this technique is the determination of
enthalpies of mixing of liquids. In a binary system, for example, a liquid bath of one component is held at temperature within the calorimeter, and the second component is added sequentially. The heat effects are recorded which, when allowing for the enthalpy increment of the added samples (heat required to raise them from the dropping temperature to the calorimeter temperature) an enthalpy of mixing curve can be derived. In a higher-order system, such as a ternary system, it’s often convenient for the starting composition of the liquid bath to be a fixed ratio of two components.

Figure 14: Typical thermogram resulting from a direct reaction drop. Note the curve has positive (endothermic) and negative (exothermic) parts. The former resulting from heating the mixed compact and the latter from the formation of the compound. The two effects are superimposed rather than sequential (endothermic is up).

Figure 15 shows measured enthalpies of mixing in the Au-In-Sn system as a function of Au content along three fixed ratios of In:Sn. The curve in Fig. 14 is a plot of thermopile EMF against time. The integral of this curve, with a suitable calibration, gives the total heat effect.

Figure 15: Integral enthalpies of mixing of Au-In-Sn liquid alloys at 609°C as a function of Au content. The reference states are pure liquid Au and liquid In/Sn alloy

The major source of uncertainly with drop measurements stem from the fact that the larger proportion of the total heat effect is due to the enthalpy increment of the dropped sample. This may be many orders of magnitude larger than the heat effect of interest. Therefore instrument sensitivity and stability are critical to the production of reliable enthalpies.
Vapour Pressure Measurements

Calorimetry can only reveal enthalpy, which is only a component of the Gibbs energy representing the state of equilibrium within a system. It is necessary to combine enthalpies with other thermodynamic quantities in order to be able to fix the Gibbs energy. Vapour pressure measurements lead to component activities and/or equilibrium constants, which in turn give partial Gibbs energies. A number of techniques to measure vapour pressures are available, but probably the most common is that employing Knudsen Effusion (Fig. 16). The Knudsen cell containing the material under study, has a lid with a precisely machined effusion orifice of known diameter. If the mass of material effused over a period of time \( t \) is known, then the vapour pressure can be determined. However, knowing the mass of the effused material precisely can be a challenge. Thus, Knudsen cells are usually combined with analysis equipment such as a mass spectrometer, which can also identify the nature of the effusing species (Fig. 17).

The effusing molecular beam is ionised by monoenergetic electrons and is accelerated through a magnetic field to the detector. The magnetic field separates ions into groups of charge/mass ratio allowing identification. The ionic intensity of the individual species is a function of the vapour pressure. As the activity of the effusing species is a ratio of its vapour pressure above the alloy and above the pure component, this is also given as a ratio of the ionic peak intensities as recorded by the mass spectrometer above the alloy and above the pure component; no actual measurement of pressure is required. Because it is necessary to measure the ionic intensities above both the alloy and the pure components, it is convenient to use multiple Knudsen cells containing the alloy under study and the reference materials (pure components – Fig. 18).
If a chemical reaction can be harnessed in a galvanic cell so that the energy changes associated with it can be realised electrochemically, then the EMF produced by the cell will lead directly to the Gibbs energy change for the reaction. In its simplest form, for example, the Gibbs energy change associated with the oxidation of a metal (M) can be described as in Fig. 19.

A pelleted mixture of a metal and its oxide in close contact with a platinum wire acts as one electrode in the cell, whilst the second electrode is oxygen at a pressure of 1 atm (101,325 Pa). With an appropriate electrolyte to allow ionic conduction, the Gibbs energy change for the oxidation of metal M is a function of the open-circuit EMF of the cell as measured between the two platinum leads and the number of electrons transferred in the oxidation reaction (in this case, 2). F is the Faraday constant (23,066). Critical to EMF studies is the choice of electrolyte. As the measurements are often made over an elevated range of temperature, it’s important that the electrolytes are stable and do not react with the electrodes themselves. Also, the electrolyte should not allow electronic conduction, otherwise the cell reaction can proceed without making the external circuit between the electrodes. Thus, the EMF measured between the electrodes will not be truly representative of the reaction in the cell. Electrolytes can be liquid, such as a eutectic mixture of lithium and potassium chlorides as has been used in the study of lead-free solders, or solid, such as ZrO₂ doped with Y₂O₃. Doping with the aliovalent ions leads to oxygen vacancies in the lattice which allow ionic conduction.
With appropriate experimental design, the technique can be quite powerful. Figure 20 shows experimental apparatus that has been used for the determination of activities in metallic solutions. In this example, the In activity in Ag-Cu-In liquid alloys has been measured. This apparatus has been built by Leszek Zabdyr and co-workers at the Polish Academy of Sciences in Krakow.

Figure 20: EMF cell for measuring the In activity in Ag-Cu-In liquid alloys

The graphic above is of the cell itself. It comprises a ZrO$_2$-Y$_2$O$_3$ tube containing the liquid alloy together with a piece of In$_2$O$_3$. This tube also acts as the electrolyte. Electrical connection to this electrode is by a rhenium-tipped kanthal wire. The ZrO$_2$-Y$_2$O$_3$ tube sits within a mixture of Ni metal and NiO, forming the positive electrode of the cell. Electrical contact is made using a Pt wire. The whole cell sits within a furnace and is continually swept with argon. Measurements of EMF are taken at different temperatures and for different melt compositions.

Figure 21 shows how the activity of In in the ternary liquid can be determined with this cell. The electrochemical cell is described at the top of the figure with the negative electrode comprising the liquid alloy and the In$_2$O$_3$ sample, and the positive electrode the mixture of Ni metal and NiO. Half cell reactions can be written for each electrode which can then be combined to give the total cell reaction. If the Gibbs energy of formation of the two oxides are known, the In activity in the ternary liquid alloy can be easily determined as a function of alloy composition and temperature.

\[
\Delta G = -6FE = 3\mu^{\circ}_{Ni} + \frac{3}{2}\mu^{\circ}_{O_2} + \mu^{\circ}_{In_2O_3} - 3\mu^{\circ}_{NiO} - (2\mu^{\circ}_{In} + 2RTlna_{In}) - \frac{3}{2}\mu^{\circ}_{O_2}
\]

\[
lna_{In} = \frac{-3\Delta G^{\circ}_{f,NiO} + \Delta G^{\circ}_{f,In_2O_3}}{2RT} + \frac{3EF}{RT}
\]

Figure 21: The determination of In activity from EMF measurements
Conclusions

The above brief discussion is an attempt to show the wide variety of techniques that are available for the determination of phase diagrams and thermodynamic properties. It is far from comprehensive, but hopefully gives a flavour of what is possible. With the advent of computational thermodynamics, of which experimental observation is an integral part, it is critical that such techniques are not lost but continually developed.

Acknowledgements

The following resources were used in the preparation of this extended abstract:


Acknowledgements are also extended to Laszlo Benzce of the Eotvos Lorand University, Budapest, Hungary, and to Leszek Zabdyr of the Polish Academy of Sciences, Aleksander Krupkowsi Institute of Metallurgy and Materials Science, Krakow, Poland.
From ab initio to CALPHAD modelling

Catherine Colinet\textsuperscript{a}, Jean-Claude Tedenac\textsuperscript{b}
\textsuperscript{a} Science et Ingénierie des Matériaux et Procédés, Grenoble INP, UJF, CNRS, 38402 Saint Martin d’Hères Cedex
\textsuperscript{b} Institut de Chimie Moléculaire et des Matériaux I.C.G., UMR-CNRS 5253, Université Montpellier II, Place E. Bataillon , 34095 Montpellier Cedex 5, France

Introduction

Nowadays first-principles calculations based on density functional theory have achieved considerable reliability for the prediction of the properties of materials. These calculations are based on the density functional theory (DFT) \cite{1}. The exchange-correlation part of the energy functional which is not known may be treated in the local density approximation (LDA) proposed by Kohn and Sham \cite{2}. The most common way for improving the LDA is to use the generalized gradient approximation (GGA) proposed by Perdew and co-workers \cite{3-5}. Several parameterizations have been developed such as the Perdew-Wang (PW91) \cite{3, 4} and the Perdew-Burke-Ernzerhof (PBE) \cite{5}. At present, several codes are available: Wien2k \cite{6}, VASP \cite{7}, ABINIT, SIESTA, CASTEP etc. In all the computer routines, one needs only to specify the atomic numbers of the constituent elements and information about their arrangement in space: translation vectors and atomic positions of the species in the unit cell of the structure. Table 1 presents some of the thermodynamic and mechanical properties of the bulk accessible to \textit{ab-initio} calculations.

**Table 1:**

<table>
<thead>
<tr>
<th>Structural properties</th>
<th>Lattice parameters, atomic positions. Defects</th>
<th>Electronic properties</th>
<th>Electronic density of states (DOS), gaps. Thermoelectricity.</th>
</tr>
</thead>
</table>

Optimization of lattice parameters and lattice stabilities

\textit{Pure Si}

Tremendous amount of work has been devoted to pure Si as well experimentally as theoretically. Here we have performed \textit{ab initio} calculations of the total energies of silicon in the two structures A4 (cF4, Fd\{-3\}m, N°227, prototype C-diamond) and A5 (tI4, I41/amd, N°141, prototype β-Sn). The results are presented in Fig.1. The pressure at which the two forms are in equilibrium at T=0K is obtained by the common tangent to the E=f(V) curves.
C11b-MoSi₂ compound

At low temperature, MoSi₂ crystallizes in the C11b structure (I16, I4/mmm, No139, prototype MoSi₂). The Mo atoms occupy the 2a Wyckoff positions (0, 0, 0) and the Si atoms occupy the 4e Wyckoff positions (0, 0, z). We have performed *ab-initio* calculations and obtained the following lattice parameters \(a = 3.2216 \, \text{Å}, \, c = 7.8751 \, \text{Å}\) and \(z = 0.33536\). These values are in excellent agreement with the experimental values \(a = 3.2056 \, \text{Å}, \, c = 7.845 \, \text{Å}\) and \(z = 0.33528\) [8].

**Enthalpies of formation of binary alloys**

Nowadays, a large number of enthalpies of formation of binary alloys have been obtained using *ab-initio* methods. We present here the results obtained in the Ga-Ti system [9]. The enthalpy of formation, \(\Delta H(\text{Ga}_x\text{Ti}_{1-x})\) at zero pressure is obtained from the minimum total energy of the compound (expressed per atom) by subtracting the composition-weighted minimum total energies of pure orthorhombic (A11) Ga and pure hexagonal close-packed (A3) Ti:

\[
\Delta_x H(\text{Ga}_x\text{Ti}_{1-x}) = E_{\text{Ga}_x\text{Ti}_{1-x}}^\text{min} - x E_{\text{A11-Ga}}^\text{min} - (1-x) E_{\text{A3-Ti}}^\text{min}
\]

The \(E^\text{min}\) values are obtained after relaxation, this implies a zero pressure. At \(T=0 \, \text{K}\) and \(p=0 \, \text{Pa}\), the formation enthalpy equals the calculated formation energy, when the zero-vibration contribution is ignored, since it is much smaller than the formation energy. The results are presented in Fig. 2. The enthalpies of formation of the compounds which are stable form a convex hull: the ground state line.
Prediction of the stability of ternary phases

Experimental investigations performed in the Ti-Zr-Si ternary system evidenced two solid solutions, the first one (S1 of Mn$_5$Si$_3$ type) along the quasi-binary section $x_{Si}=0.375$ and the second one (S2, structure not clearly established) along the quasi-binary section $x_{Si}=0.333$. We performed first principles calculations of enthalpies of formation of ternary compounds along two quasi-binary sections $x_{Si}=0.375$ and $x_{Si}=0.3333$ [12]. At low temperature, two ternary compounds C$_{22}$-Ti$_3$Zr$_3$Si$_3$ and D$_8$$_8$-Ti$_4$Zr$_5$Si$_3$ are stable (see Fig. 3). After that, we demonstrated the existence at high temperature of two solid solutions, (TiZr)$_5$Si$_3$ with the Mn$_5$Si$_3$-type structure and (TiZr)$_2$Si with the Fe$_2$P-type structure and calculated an isothermal section at 1323 K (Fig. 4); for the pure elements we adopted the lattice stabilities of Dinsdale [13]. There is a good agreement with the experimental results in the Ti rich region where a three phase domain between S1, S2, and the bcc-TiZr solid solution was observed [14, 15].

Fig. 2: Calculated enthalpies of formation of GaTi compounds.

Fig. 3: Enthalpies of formation of C$_{22}$ compounds along the section $x_{Si}=0.333$ and D$_8$$_8$ compounds along the section $x_{Si}=0.375$.

Fig. 4: Calculated isothermal section at 1323K.
Defect enthalpies of formation

Ab initio calculations are well suited to obtain the defect enthalpies of formation in intermetallic phases. As an example, we show the results obtained in the Si$_3$Ti$_5$ compound [16] which crystallizes in the D$_8$$_8$$_8$ structure (hP16, P6$_3$/mcm, No193, prototype Mn$_5$Si$_3$). The unit cell contains four Ti at 4d sites at (1/3, 2/3,0), six Ti at 6g sites at (x$_{Ti}$, 0, ¼), and six Si at 6g sites at (x$_{Si}$, 0, ¼). Therefore three sublattices must be defined: α (6g sites of Si), β1 (6g sites of Ti), β2 (4d sites of Ti). More, we have considered the possibility that Si or Ti atoms occupy the 2b Wyckoff positions of the structure because these sites have relatively large size (sublattice γ). The enthalpies of formation of supercells containing each one of the eight possible point defect were calculated (Fig. 5). The constitutional defects are Ti antisites for Ti-rich alloys and Si in interstitial position on 2b sites of the structure for Si-rich alloys.

![Fig. 5. Energies of formation of Si$_3$Ti$_5$ supercells containing one defect.](image)

Thermodynamic properties at non-zero temperature

At non-zero temperature and constant pressure, the equilibrium state of a system is defined by the minimum of the Gibbs free energy. The non-zero thermodynamic data are obtained by combining ab-initio calculations and statistical thermodynamic. The Gibbs free energy is the sum of the ground state energy of the static lattice, the PV term, the vibrational free energy of the phonons, and the electron excitation free energy:

$$G(P,T) = E(V) + PV + F_{vib}(V,T) + F_{el}(T)$$

In the Debye model [17], the vibration Helmholtz free energy is expressed as function of the Debye temperature by:

$$F_{vib} = \frac{9}{8} N_k \theta_D^2 - N_k T D(\theta_D/T) + 3 N_k T \ln(1 - \exp(-\theta_D T))$$

The knowledge of the equation of state and of mechanical properties of the considered material allows to obtain the Debye temperature [18, 19]. Using this method, Tao et al. [20] found a temperature of 2304 K for the transition of D8$_1$-Ta$_5$Si$_3$ to D8$_m$-Ta$_5$Si$_3$ which is close to the experimental temperature of 2434 K.
More generally, the $F_{\text{vib}}(V,T)$ term is determined as a sum of the free energies of all phonons assuming that vibrations are independent. There exist several methods to get the phonon spectrum from ab initio [21, 24].

In the simple Sommerfeld model [22, 23], the electronic contribution to the Helmholtz free energy has the expression:

$$F_{el}(T) = -\frac{\pi^2}{6} n(\varepsilon_F) k_B T^2$$

where $n(\varepsilon_F)$ is the electronic density of states at the Fermi-level. This expression can be used if the electron states are probed in a sufficiently narrow range around the Fermi level. The general treatment for non-zero temperature needs the introduction of the Fermi-Dirac distribution.

**Treatment of the solid solutions.**

When stoichiometric compounds are involved, the ab-initio calculations furnish the total energy at $T = 0$ K. When solid solutions are involved, the situation is rather more complicated. Besides the cluster expansion which will be the subject of the talk of T. Mohri, it is possible to perform ab-initio calculations of energies of formation of special quasi random structures (SQS). The SQS concept [25, 26] was proposed in order to mimic a random solution phase by reproducing the pair and multiple-body correlations using a small size supercell. SQS’s for fcc, bcc and hcp solutions have been generated [27, 29]. The calculations must be performed on both volume relaxed structures and internal relaxed SQS’s. It is also possible to perform calculations in supercells [30]. A supercell of the considered lattice is created and the atoms distributed randomly on the sites. We have considered the case of the Mg$_2$Si-Mg$_2$Sn solid solution. Fig. 6 presents the values of the enthalpies of mixing. A drastic effect due to the relaxation of the positions of the atoms is observed.

![Fig. 6: Enthalpies of mixing in the Mg$_2$Si-Mg$_2$Sn solid solution.](image-url)
Conclusions

We have shown some simple examples of *ab initio* calculations. Nowadays these *ab initio* calculations are performed in complex phases such as σ and μ. They can be used to solve practical problems in multi-component systems when thermodynamic data are not accessible experimentally: lattice stabilities, enthalpies of formation of ternary phases. The *ab initio* calculations of the defect enthalpies of formation allow to define the number of sublattices and their occupancy necessary for the CALPHAD modelling of the phase etc.

*Note*: The DFT calculations presented in this paper have been performed with VASP [7], making use of the PAW technique [31]. For GGA exchange correlation functional, the PBE parameterization [5] was used.

References

Introduction

Anyone who uses materials needs to have some understanding of phase diagrams. Even at the basic level phase diagrams can provide vital information such as the melting temperature, whether a material is likely to corrode, will it react with a container or is it likely to be harmful to the environment. A detailed understanding of phase diagrams can provide so much more [1]. Traditionally phase diagrams have been determined by experiment, from studies of thermal arrests and the analysis of compositions of phases in equilibrium. It has always been recognised however that phase equilibria and thermodynamic data are intimately connected but this link has not been really useful until the advent of computers which has allowed the possibility that phase diagrams can be calculated directly from critically assessed thermodynamic data [2,3,4]. Experimental measurements are still essential and will be for the foreseeable future but the process of critical assessment does provide a framework through which best use can be made of whatever experimental data are available. Indeed various types of apparently unconnected experimental data are directly related to the thermodynamic properties and the phase diagram eg. phase equilibria, melting temperatures, partial pressures, enthalpies of mixing, heat capacities. Thermodynamic modelling provides a way in which all these different forms of data can be reduced to one single set of data which represent the totality of the experimental data underpinned by rigour imposed by thermodynamics. This paper is concerned with describing what is actually meant by the process of critical assessment, how thermodynamic properties can be modelled as functions of temperature and composition and the various databases and software packages available for the calculation of phase equilibria. Finally various case studies will be presented to show how calculations have been used in areas of practical importance to industry and the environment.

Phase diagrams and thermodynamics

A large number of apparently different sorts of measurements are directly related to the phase diagram. Even for a single property, experimental measurements from different sources may show considerable scatter making it difficult to judge which set of data is most reliable and also consistent with the measurements of other properties. An example of this is shown in figure 1 for alloys in the Fe-Cu system. There seems to be rather poor agreement between different measurements of the enthalpies of mixing in the liquid phase (figure 1a) and it is unclear which set of data are most reliable. There is much better agreement between the various measured activities in the system (figure 1b) and the determinations of the phase diagram (figure 1c). The aim behind a critical assessment of data for a system is take all data for the system, for example those shown in Figures 1a to 1c, and reduce them to a set of coefficients for each phase which represents the way in which the Gibbs energy varies with temperature and composition. Figure 1d shows the variation of the Gibbs energy for the liquid, bcc and fcc phases as the composition changes from Fe to Cu calculated using the set of assessed coefficients.

For each composition the stable configuration is the one with the lowest value of the Gibbs energy. At 1200°C the Gibbs energies of the fcc and liquid phases cross over. For compositions rich in Fe the fcc phase is most stable while for those rich in Cu the liquid phase is most stable. For compositions with appreciable amounts of both Fe and Cu the lowest Gibbs energy is actually for a
mixture of two phases, an Fe rich fcc phase and a Cu rich liquid phase as shown on the phase diagram, Figure 1c. The shape of each of the three Gibbs energy curves in Figure 1d show a tendency towards two distinct minima, one for Fe rich compositions and one for Cu rich compositions. If the temperature is lowered to 1000°C where the fcc Gibbs energy curve is lowest for all compositions, this tendency gives rise to a miscibility gap between two fcc phases.

Figure 1. Fe-Cu system: (a) Enthalpies of mixing in liquid (b) activity of Cu in liquid at 1600°C (c) phase diagram (d) Variation of Gibbs energy of phases with composition at 1200°C.

Figure 1d provides the basis behind the calculation of phase diagrams from critically assessed thermodynamic data. The accuracy and reliability of phase diagram calculations depend completely on the quality of the underlying critically assessed data and models used to represent and extrapolate such Gibbs energy data in composition and temperature. Figure 2a shows the fitted heat capacity for the different phases of pure Sn. The familiar white tin, with the bct structure, transforms on cooling at 13°C to the so-called grey form based on the diamond structure. White Sn melts at 232°C. These heat capacity data can be converted to describe how the Gibbs energy varies with temperature i.e. the solid line in Figure 2b. However for this to be useful
it is necessary to know how the Gibbs energy changes even for ranges of temperature where the phase of the element is not stable i.e., the dotted lines in Figure 2b. Figure 2a shows that the heat capacity of the three stable phases of Sn is quite different and in order to model the extrapolation of the Gibbs energy of phases with temperature it is important to take into account differences in heat capacity. It is also important to have data for phases which are unstable at all temperature for the pure element, e.g., data for bcc Cu are necessary in order to derive the data shown in Figure 1 even though fcc Cu is the stable crystalline phase. Much work has gone into defining data for the elements in a number of different phases. Most critical assessments are based in those defined by SGTE [5,6].

Figure 2 (a) Heat capacity of phases of Sn (b) Gibbs energy of stable phases of Sn relative to those of bct-a5 (white tin)

The variation of the Gibbs energy of a phase with composition depends on the nature of the phase and the thermodynamic models generally used attempt to reflect this either in terms of the species formed (e.g., gas phase), the number of sublattices and the respective number of sites (crystalline phases) or some other understanding of the nature of mixing within the phase. For alloy systems, e.g., the Fe-Cu system shown in the Figure 1, the Gibbs energy of a phase can be thought of in terms of three major contributions, a) its difference for each component from that of the chosen reference state b) from ideal mixing of the components and c) an excess term associated with non-ideal mixing. These different contributions are shown in detail in Figure 3. Once data for component binary systems have been defined well tested, reliable mathematical models, such as those shown in figure 4, are then used to extrapolate the binary excess Gibbs energy contributions into ternary and multicomponent systems. Ternary parameters are introduced where appropriate to correct for any deviation between calculated and experimental values.
A number of software packages embody the principles of phase diagram calculations outlined above. These include MTDATA [7], ThermoCalc [8], Pandat [9] and FactSage [10]. Each of these packages have particular strengths and weaknesses. General databases or databases for specific types of materials are also available with each of these packages.

There are several examples where phase equilibrium calculations have demonstrated their value to industry and many of these have been described in the SGTE Casebook [11]. One example is shown in figure 5. Figure 5a is an isopleth or cut through the phase diagram for the Ag-Cu-Sn-Pb system between compositions corresponding to a ‘conventional’ Pb-Sn electrician’s solder and a newer ‘SAC’ lead free solder and represents the phases that could be formed by contamination of a lead free solder by small amounts of lead from an existing solder or component terminations. Figure 5b shows the amounts of phases calculated to form on solidifying a SAC solder with 25% Pb contamination. An analysis of such plots can lead to an understanding of the microstructure of the solidified material, its strength and brittleness.
References

Cluster Variation Method

Tetsuo Mohri
Research Center for Integrative Mathematics
and
Division of Materials Science & Engineering,
Faculty of Engineering, Hokkaido University
Sapporo 060-8628, Japan Tel/Fax: +81 11 706 6348

Introduction

Bragg-Williams approximation (Bragg and Williams, 1934) has been most widely employed in various calculations of alloy phase equilibria. This is due to the mathematical simplicity to extend it to complicated crystal structures and multicomponent systems. In fact, most of commercial software of phase equilibria calculations are coded based on Bragg-Williams approximation.

It has been, however, demonstrated that the Bragg-Williams approximation does not provide an accurate result in many thermodynamic calculations including a phase diagram. One of the serious deficiencies in the Bragg-Williams approximation is that the atomic correlation is not properly incorporated in the entropy formula. Even if atomic interaction is limited to nearest neighbor pairs, the atomic correlation generally extends over distant pairs, and it is essential to include wide range of atomic correlations in the entropy formula.

Cluster Variation Method (Kikuchi, 1951; hereafter abbreviated as CVM) has been regarded as one of the most reliable theoretical tools in dealing with atomic correlations. A microscopic approach of alloy phase equilibria based on CVM starts with the description of configurational variable.

Among configurational variables, the most primitive one is the point probability \( x_i(p) \) which specifies the probability of finding a species \( i \) (either \( A \) or \( B \)) on a given lattice point \( p \). It is realized that this is nothing but a concentration of species \( i \) for a disordered phase. The probability, \( y_{ij}(p,q) \) of finding species \( i \) and \( j \) in a pair of lattice points \( p \) and \( q \) is termed pair probability. Like point probability, a pair probability is nothing but the concentration of pair configurations in a given lattice. The probability for a multibody configuration such as triangle, tetrahedron, square etc. can be defined in a similar way and these are termed cluster probabilities or cluster concentrations.

CVM describes the entropy as well as free energy in terms of these cluster probabilities and the biggest cluster included in the entropy formula is termed basic cluster. CVM forms a hierarchy structure in terms of the basic cluster and the Bragg-Williams approximation is nothing but a point approximation in the CVM hierarchy.

It is readily realized that cluster probabilities are not independent but mutually interrelated. In fact, when we confine ourselves to point cluster probability, \( x_i \), and pair probability, \( y_{ij} \), two kinds of conditions among them are identified. One is the normalization condition which is written for point and pair probabilities, respectively, as:

\[
\sum_i x_i = 1
\]

and

\[
\sum_i \sum_j y_{ij} = 1
\]

The second condition is termed geometrical condition given as
\[ x_i = \sum_j y_{ij}. \]

In fact, geometrical condition describes the relation between clusters of different type, and when the size of a basic cluster increases it is quite cumbersome to formulate the geometrical conditions among sub-clusters involved in the basic cluster. This is one of the difficult aspects of CVM.

The most conventional approximation employed in the fcc-based system is the *tetrahedron approximation* (Kikuchi, 1974) in which the nearest neighbor tetrahedron cluster is taken as the basic cluster. The entropy within the tetrahedron approximation is written as

\[
S_{\text{tetra}} = k_B \cdot \ln \frac{\left( \prod_{i,j} (N \cdot y_{ij})! \right)^6 \cdot N!}{\left( \prod_i (N \cdot x_i)! \right)^5 \cdot \left( \prod_{i,j,k,l} (N \cdot w_{ijkl})! \right)^2}
\]

One can see that not only the point and pair cluster probabilities but also tetrahedron cluster probability \( w_{ijkl} \) is explicitly considered, which improves the accuracy of the calculated result. In the present talk, several recent applications of CVM are reviewed. These include the first-principles phase diagram calculations, stability analysis and microstructure calculations.

**First-principles phase diagram calculation**

The starting point of the first-principles phase diagram calculation is to perform electronic structure total energy calculations on a set of ordered compounds. Then, with respect to a segregation limit, one can obtain heats of formation, \( \Delta E^{(n)} \), of each ordered compound, \( n \). According to the Cluster Expansion Method (Connolly and Williams, 1983) heats of formation can be expanded as

\[
\Delta E^{(n)}(r) = \sum_{m=0}^\infty v_m(r) \cdot \xi_m
\]

where \( v_m \) and \( \xi_m \) are \( m \)-body effective cluster interaction energy and correlation function, (Sanchez and de Fontaine, 1978; Sanchez et al. 1984; Mohri et al. 1985a), respectively, and \( r \) is the inter-atomic distance. It should be noted that the correlation functions, which are obtained by a linear transformation of a set of cluster probabilities, depends on both the type of cluster, \( m \), and a phase, \( n \), while the effective cluster interaction energy is determined once the type of the cluster is specified.

Then, together with the entropy formula given above, the free energy of the system is written as

\[
\Delta F = \sum_{m=0}^\infty v_m(r) \cdot \xi_m - T \cdot k_B \cdot \ln \frac{\left( \prod_{i,j} (N y_{ij})! \right)^6 \cdot \left( N! \right)}{\left( \prod_i (N x_i)! \right)^5 \cdot \left( \prod_{i,j,k,l} (N w_{ijkl})! \right)^2}.
\]
By minimizing the free energy with respect to correlation functions and volume, equivalently atomic distance \( r \),

\[
\frac{\partial \Delta F}{\partial \{\xi_m\}} = 0, \quad \frac{\partial \Delta F}{\partial \{c_m\}} = 0,
\]

one can obtain equilibrium state. Several recent results on Fe-based system are demonstrated in the presentation.

**Stability analysis**

In the discussion of the stability of a system, one needs to distinguish the relative stability and the intrinsic stability of the system. The relative stability can be discussed based on the magnitude of the heats of formation among competing phases, while the intrinsic stability suggests the stability of a system against fluctuations. Our main interest in this talk is the intrinsic stability.

It is known that the vanishing condition of the first order derivative of the free energy \( f(\varphi) \) with respect to \( \varphi \) provides the equilibrium condition. While the second order derivative \( \partial^2 f / \partial \varphi^2 \) is a measure of the stability of the system against the fluctuations of the variables, \( \varphi \). The positive second order derivative assures the restoring force towards the equilibrium state.

As was discussed above, the free energy of the CVM is a multi-value function of correlation functions or cluster probabilities symbolically written as:

\[
f[\{\xi\}] = f(T, v_2; \xi_1, \xi_2, \xi_3, \ldots)
\]

It is, therefore, common practice to discuss in the k-space rather than in the real space (de Fontaine 1975; Mohri et al. 1985b). The details are not provided in this abstract but the essential points are as follows. First, the second order derivative of the free energy is transformed in the k-space by Fourier transformation. By making use of the Hermitian property of the second order derivative matrix of the free energy, the matrix is diagonalized to extract the eigenvalues. If and only if all the eigen values are positive, stability prevails, which corresponds to a high temperature disordered phase, while if one of the eigen values goes through zero, the system becomes inherently unstable against the excitation, amplification and propagation of a particular wave vector associated with the negative eigen value. Hence the stability of the system is formally determined by the vanishing condition of the determinant of the free energy matrix and the highest temperature at which the determinant vanishes is defined as the instability temperature or Spinodal ordering temperature (de Fontaine, 1975).

Most of the phase diagram calculations have been focusing on phase boundaries. The author believes that one of the future extensions of the phase equilibria calculations is directed towards the stability analysis. Below and above the instability locus, the evolution of the microstructure is different and this can enlarge the possibility of the alloy design.

**Microstructure calculations**

Recently, the Phase Field Method (PFM) (Chen, 2002) has been attracting broad attentions. The local free energy density \( f_0 \) in Ginzburg Landau type free energy determines the final equilibrium
state as well as the path towards it, therefore the description of $f_0$ plays a determining role in the PFM. In the conventional PFM, the local free energy density is given by a phenomenological Landau type series expansion, while author’s group (Ohno, 2004, Mohri et al., 2006, Mohri, 2007) has been developing more atomistic PFM based on the local free energy density given by CVM, $f_{\text{CVM}}$. Accordingly, the free energy of the system is symbolically written as

$$F = \int \left\{ f_{\text{CVM}} \left( \xi_j \right) + \sum_i \kappa_i \cdot \left( \nabla \xi_i \right)^2 \right\} dV$$

where $\kappa_i$ is termed gradient energy coefficient for the $i$-th correlation function. Then, the time evolution of the correlation function is given by the TDGL equation,

$$\frac{\partial \xi_i}{\partial t} = -L_i \left( \frac{\partial f_{\text{CVM}}}{\partial \eta_i} \right) - \kappa_i \nabla^2 \xi_i$$

The advantages of such an approach are addressed in two points. One is that the atomistic nature of the CVM free energy leads to the first-principles PFM calculations. The other one is the possibility of performing multi-scale calculations from atomistic to microstructural scales. The major difficulty for the first-principles multi-scale calculation, however, is to perform proper coarse graining operation. Although rigorous recipe of the coarse graining operation based on statistical mechanics is available, the actual application to realistic problem is not easy. Our group developed a recipe by generalizing Kikuchi-Cahn’s procedure (Kikuchi and Cahn, 1962), and we calculated time evolution process of Anti Phase Boundary associated with disorder-L10 transition for Fe-based alloys. We discuss how to extend the theoretical framework of phase equilibria calculations to microstructure evolution calculations in the talk.

References


*A comprehensive review of CVM is published in Mohri, T. (2007) in the list above.*
Thermodynamics and phase diagrams for lithium ion batteries

Damian M. Cupid, Carlos Ziebert, Elke Schuster, Hans J. Seifert,
Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP)

The performance of lithium ion batteries, e.g. capacities and voltages, is fundamentally governed by the thermodynamics of the electrochemically active materials. The total energy stored in and released by an electrochemical cell during charge and discharge is controlled by the thermodynamics of the active electrode processes during operation. Thermodynamic data for anode and cathode materials and electrochemical reactions have to be known in detail to apply for instance the well-known Nernst equation. It relates the measurable cell voltage to the chemical difference across an electrochemical cell. At each state of discharge the thermodynamic parameters refer to the lithium stoichiometry and the open-circuit voltage of the cell is linked to the differences in the lithium chemical potential between anode and cathode. The free energy of the full cell reaction directly relates to heat and entropy of cell reaction. To derive the so-called "cell entropy term", the temperature dependence of the open circuit voltage has to be measured accurately in the temperature range of cell operation. By this so-called "entropymetry" very accurate information on the structure and crystal chemistry changes of electrode materials and the related phase diagrams can be derived [1, 2]. The thermal behaviour of electrochemical cells is directly related to the entropy term (reversible heat). This ΔS term can contribute more than 50% of the total heat generated at specific discharge rates. The state of charge (SOC) also influences this reversible heat generation. Additionally, internal ohmic cell resistances and possible side reactions have to be considered for analysis of thermal and enthalpic effects. In such cases Accelerating Rate Calorimeters (ARC) and Isothermal Battery Calorimeters (IBC) can provide detailed experimental data on heat generation and accompanied temperature changes. Fig. 1 shows our results from electrochemical cycling of a pouch cell of 40 Ah capacity under isothermal and adiabatic conditions, respectively. Temperatures on the surface of the cell were measured. During cycling the temperature under adiabatic conditions increases considerably more than under isothermal conditions. Additional investigations are required to separate the temperature contributions (heat generation) from entropy, cell resistance and side reactions, respectively.

Such information is of high relevance for analysis of battery operation and safety during regular use, misuse and mechanical impacts (accidents). Of practical electrochemical interest are also the maximum theoretical specific energies, temperature dependences of cell voltages as well as relationships between cell discharge curves and Gibbs phase rule.

In addition to the thermodynamic data, binary and ternary phase diagrams can serve as thinking tools to understand properties of electrodes and cell reactions. In this way the phase relationships at temperatures of cell operation are important, typically -30 to +50°C for lithium ion batteries. The stability of stoichiometric compounds and solid solution phases as well as the occurrence of metastable and amorphous phases have to be known to derive reliable information on cell reactions. Equilibrium and near-equilibrium conditions for electrode materials can be analyzed by experimentally determined and thermodynamically calculated isothermal sections. In this regard the (stepwise) voltage changes during cell reactions, plateau voltages and maximum theoretical specific energies can be derived. Similar data at temperatures of 400°C for reaction of lithium with MnO, Mn₃O₄, LiMnO₂, LiMn₂O₄ and Li₂MnO₃, respectively, were measured by Huggins and co-workers using coulometric titration [3]. The respective variations of lithium potential, component activities and partial oxygen pressures are shown in Fig. 2. Obviously the data are directly related to the tie triangles which are intersected by the connecting lines between the component lithium (Li) and the various oxide compounds. Thermodynamic calculations using the CALPHAD method
(Computer coupling of phase diagrams and thermochemistry) can support such analysis in a very efficient way.

A deep understanding of thermodynamics and phase diagrams at high temperatures is required for knowledge-based synthesis and processing of electrode materials with defined chemical compositions and microstructures. Phase diagrams of "Type 1, 2, and 3", respectively, have to be analyzed to fix optimal temperature, composition and (partial) pressure conditions for preparation and manufacturing of the materials in a reproducible way.

Fig. 1: Isothermal (left) and adiabatic cycling (right) of a 40 Ah pouch cell.

Fig 2: Ternary phase diagram in the Li-Mn-O system at 400°C with Li potentials, component activities and partial pressures of oxygen indicated [3].
Fig. 3 shows a second type phase diagram in the Li-Mn-O system indicating phase stabilities of stoichiometric compounds and solid solutions at an oxygen partial pressure of 0.2 bar. This phase diagram includes the most important battery active material Li$_{1+x}$Mn$_{2-x}$O$_4$ (Cubic Spinel). The processing of the material requires exact knowledge of the homogeneity range extension and the decomposition temperatures. The Li-rich phase boundaries of the Li$_{1+x}$Mn$_{2-x}$O$_4$ phase was therefore investigated by Luo and Martin [4] and Gao and Dahn [5] and in our present work (Fig. 3, right). The results of our work show good agreement with those of Luo and Martin [4], in which the position of the Li-rich boundary was determined using thermal analysis. In our work X-ray diffraction analysis of quenched samples was used and Vegard’s rule was applied.

Fig. 3: Second type phase diagram in the Li-Mn-O system covering the whole composition range (left) and Li-rich boundary of the cubic spinel phase (right).

Key data for the thermodynamic optimization of Li-based oxide systems using the CALPHAD method, are the enthalpies of formation of the compounds from the oxides and elements, respectively. To derive such data, high temperature drop solution calorimetry was applied first for the stoichiometric LiMn$_2$O$_4$ cubic spinel phase. The solution peaks from drop-in experiments in sodium molybdate at 700°C are shown in Fig. 4.

Fig. 4: Heat flow signals measured from LiMn$_2$O$_4$ cubic spinel phase dropped into HT solution calorimeter.
Data for enthalpies, entropies, specific heats and chemical potentials as well as phase diagram data can be used for developing analytical descriptions of the Gibbs Free Energies for all phases in particular binary and ternary systems (thermodynamic optimization). These data can be stored in Computer databases and used for calculations in composition and temperature ranges not subject to experimental investigations before. Such work is presently carried out in our lab.

References:


Acknowledgements

The authors thank the German Research Foundation (DFG) for the financial support of the "Priority Programme 1473" WenDeLib – Materials with New Design for Improved Lithium Ion Batteries.
Introduction

On the 15th May 1941 the Gloster E28/39 first took to the air powered by a Whittle W1 engine. This engine had a thrust to weight ratio of 1.2 to 1 and was mechanically much simpler and more compact than the piston engines then in service. This made it a very attractive propulsion system that was capable of taking aircraft to much higher speeds and altitudes in a very fuel efficient manner. However, to achieve this the engine ran at far higher temperatures and stresses than the piston engines of the time, which necessitated the use of the most advanced, strongest, most heat resistant alloys then available. These were mainly austenitic and ferritic stainless steel with a maximum operating temperature around 600°C. In comparison, a modern Rolls-Royce Trent gas turbine has a thrust to weight ratio of around 5.4 to 1. It operates at a maximum temperature of around 1700°C and is around 50% more efficient that than the W1. The high temperatures components are made of nickel based superalloys containing 14 or 15 controlled elemental additions and are capable of running for 10,000 hours at temperatures 200°C above their melting points. This step change in performance and capability has only been achieved through the development of new classes of alloys and a thorough understanding of their chemistry, microstructure and processing. In the early days this was achieved using traditional, empirically based, methods, limited phase diagram information and rudimentary prediction of phase stability.

The First Gas Turbine Materials

The alloys used in the first generation of gas turbines had been developed over many years using a ‘try it and see’ approach. Little was known about what alloying additions would do and there was only limited phase diagram information, usually in the form of published binary, ternary or pseudo-higher order diagrams. The application of phase diagrams to alloy development was thus limited and the traditional approach dominated. Typical alloys in the combustor and turbines were Fe –based materials alloyed with other transition metals, mainly chromium, to provide solid solution strengthening and the required degree of corrosion resistance. This approach resulted in alloys that could be used at moderate stresses and up to temperatures in the region of 600 to 650°C. However these alloys suffered from significant creep degradation on long term exposure at temperature and were found to become metallurgically unstable, precipitating deleterious carbides and topologically close packed sigma phase, both of which significantly limited the component life. In addition, as new, more efficient engines were designed, the temperatures and stresses increased, thus requiring ever more capable alloys. New types of alloy were required.

Ni-Based Superalloys

In the early 1940's a new class of high performance, high temperature alloys was under development based on titanium and aluminium additions to Ni-20%Cr. This resulted in high strength, high temperature capable alloys with good oxidation resistance and excellent creep performance. The improvement in properties was brought about by the precipitation of a coherent, ordered phase, based on Ni₃Al, in a disordered Ni-solid solution. This combination of
phases proved to be phenomenally successful as a high temperature material and has provided the base for Ni-based superalloy development over the last 70 years. As the alloy complexity has increased to meet the ever increasing temperature and strength requirement, instability was encountered, primarily with regard to $\sigma$ phase. This phase is extremely brittle and its formation results in a dramatic loss of properties as Cr and other alloying additions are removed from the bulk of the alloy. This led to the development of the PHACOMP approach and the concept of ‘sigma safe’. The method relies on the concept of an average electron-hole number, made up of the weighted average electron hole number of the elements in the alloy. It is simple and quick to use and produces a number that can be used as a measure of the degree to which an alloy is susceptible to $\sigma$ phase formation, the larger the number, the greater the susceptibility. However the number has no physical meaning, has to be found for each alloy and does not consider other equally deleterious phases such a mu, R or Laves. It is also incapable of providing information on phase stability ranges or phase boundaries. Despite these limitations, PHACOMP was tremendously successful and made a major contribution to superalloy design up to the mid 1980’s.

**Applications of Calphad to Gas Turbine Alloys.**

By the mid 1980’s Ni-based superalloy chemistry was becoming increasingly complex. Not only were the major elements being controlled but it was becoming critical to control the minor additions and, in some cases, the impurity levels. The PHACOMP approach was embedded in the development programmes but it could not provide quantitative predictions and a better understanding of the effects of changing alloying chemistries was needed to speed up the development programme and minimise cost. Published, paper based, phase diagrams could not help as it is a multi-dimension problem with up to 15 variables.

It was around this time that the CALPHAD approach became sufficiently mature to be applied to these types of problems. The initial step was to construct an integrated thermodynamic database for the Ni-Al-Co-Cr-Hf-Mo-TA-Ti-W-Zr-B-C system and to validate it against the known behaviour of existing alloys. This was successfully done and gave the alloy development teams a tool that could accurately predict alloy behaviour without having to melt, process and analyse real alloy samples. This reduced the cost of the development programme by reducing the number or iterations needed to define the chemistry and thus also shortened the time taken to complete these stages. It also gave them a tool that enabled them to understand what alloying elements were doing, how elements partitioned into different phases and why changes in one element resulted in unexpectedly large shifts in phase equilibria. As a result of this success and with increasing confidence in the predictions, Rolls-Royce started to apply CALPHAD to its Ni-based superalloy disc development programmes in the mid 1980’s and the chemistry of RR1000, which has just entered service in the Trent 900 and Trent 1000, was defined using this approach.

However, CALPHAD at this time was not user friendly, it had grown out of an academic background and the programme used to generate the outputs required specialist knowledge and skill to use. In order to be useful this situation had to change, a non-specialist user programme or interface was required that would provide the wider population of superalloy metallurgists with the opportunity to generate results in a more applications oriented format. These became available in the late 1990’s and were the launch platform for the widespread use of calculated phase equilibria in the superalloy field, finding application in alloy and process development, phase analysis and in understating degradation mechanisms. All of which it is still used for today.
The Future

CAPLHAD today is a well-established technology finding widespread application in many fields and in many material systems. Provided there is a well-defined, validated, database it is capable of quickly providing robust predictions with a high degree of accuracy and which find application in the traditional field of alloy and process development. However, when this capability is linked to kinetic and process models it can provide an essential input into process models that, one day, may provide location specific microstructural and mechanical properties in real components without having to manufacture them. This ultimate goal is some way off but the initial steps in this area are now being taken and CALPHAD is seen as essential in the development of materials and process modelling.

Also, as the current classes of alloys come to the end of their development new types of alloy based on chemistries complexly outside of the traditional field are being explored, stimulating not only phase diagram modelling in new systems but also work in the physical metallurgy of the phase equilibria that underpins it. The future of CAPLAHD looks bright!
Applications of Phase Equilibria in Aluminium Alloy Products and Processes

P.V. Evans and R.A. Ricks,
Technology Strategy Consultants

Introduction

Aluminium alloys are generally not used in a state of thermodynamic equilibrium. They frequently contain metastable precipitates or intermetallic phases, with process routes deliberately designed to avoid attainment of equilibrium. In age hardening systems for example, the equilibrium precipitates are usually incoherent with the aluminium lattice, and are consequently unable to form on a fine enough scale to provide a significant contribution to mechanical properties. Alloy systems without the benefit of a suitable alternative metastable precipitate sequence generally won't show an ageing response (e.g. Al-Mg).

Even alloys relying on solid solution strengthening are usually in a metastable state at their operating temperatures. This can sometimes cause problems when alloys are exposed to high enough temperatures in service to promote precipitation: not only can there be a loss of strength, but the precipitation may be focussed at grain boundaries, potentially leading to issues with localised corrosion.

Although thermodynamic equilibrium is not generally of relevance regarding the properties of the final product, it is frequently far more relevant during the processing of the materials. Figure 1 shows the general process streams operating in the aluminium industry.

In this talk we will consider examples drawn from various locations along the process stream.

Aluminium-hydrogen

Whatever the end use of aluminium, it will very likely have undergone some form of molten metal treatment prior to casting. These treatments are designed to improve the quality of the melt, which in the aluminium world usually means one of three things: controlling the level of dissolved hydrogen, reducing the amount of non-metallic inclusions in the melt, or controlling the level of dissolved alkali metals. Of these, hydrogen is the only contaminant whose presence is controlled by equilibrium considerations.

Hydrogen is reasonably soluble in liquid aluminium, but relatively insoluble in solid aluminium. Figure 2 shows the almost order of magnitude reduction in solubility at the melting point [1].
The solubility of hydrogen in molten aluminium follows Sieverts’ Law [2], with a square root dependence on the partial pressure of hydrogen in the atmosphere in contact with the melt. As is well known, this arises from the diatomic molecules in the gas state dissociating on passing into solution in the melt.

\[ \begin{align*} H_2(gas) & \rightleftharpoons 2H(melt), & K_{eq} = \frac{S^2}{P_{H_2}} \end{align*} \]

where $K_{eq}$ is the temperature dependent equilibrium constant, $S$ is the activity of hydrogen in the melt ($\sim$ concentration) and $P_{H_2}$ the partial pressure of hydrogen in the atmosphere in contact with the melt.

Although the partial pressure of hydrogen in the atmosphere is vanishingly small, atmospheric humidity provides a ready source of hydrogen, since aluminium will react readily with water vapour to form alumina and hydrogen. Hence it is found that the level of dissolved hydrogen in aluminium equilibrates with the absolute humidity, which can manifest itself as a substantial difference in equilibrium levels found in winter or summer, as shown in Figure 3.

Figure 2: Solubility of hydrogen in aluminium

Figure 3: Effect of humidity on equilibrium dissolved hydrogen in aluminium

Figure 4: Plant data for hydrogen level in melt exiting a holding furnace
The “summer” curve in Figure 3 relates to an ambient temperature of 40°C, and 80% relative humidity. But even that doesn’t compete with the humidity levels in a gas fired furnace, as commonly used in the industry, also shown in Figure 3. Given that melting and holding furnaces typically run in the range 700-800°C, and are well mixed, it is understandable that hydrogen levels exiting furnaces are usually found in the range 0.3-0.7 ml/100g. Typical plant data for gas levels exiting a holding furnace running at ~725-750°C are shown in Figure 5, clearly demonstrating the attainment of equilibrium in the furnace.

Unfortunately, this level of hydrogen is excessive for the majority of products, and would result in unacceptable levels of porosity, which can cause problem as cast, and in downstream processing. The acceptable level of hydrogen depends on the end use: for some aerospace plate products, targets are <0.1 ml/100g. Even for undemanding commodity wrought products, target levels may be < 0.25 ml/100g.

Degassing reduces hydrogen levels to acceptable values, by purging the melt with a flow of dry inert gas, typically argon. The melt is simultaneously stirred, to generate a fine distribution of bubbles. Figure 5 shows a batch degasser, used to treat up to ~1 tonne of melt in shape casting. In the wrought industry, furnace sizes are so large (e.g. ~100 tonnes), that degassing is done “in-line”: the melt flows continuously through a degasser, en route to a casting station.

![Figure 5: Batch degasser](image)

![Figure 6: Schematic diagram of bubble in a melt (red dissolved hydrogen atoms, red diatomic hydrogen molecules and blue argon atoms).](image)

The understanding of equilibrium between the melt and gas phases is crucial in order to develop process models and hence degassing practices. As the inert gas bubbles rise through the melt, local equilibrium is established between the partial pressure of hydrogen building up in the bubble ($P_{H_2}$), and the concentration of dissolved hydrogen remaining in the adjacent denuded boundary layer in the melt, $H_b$. This is shown schematically in Figure 6. The hydrogen flux exiting the melt will depend on both the total area of melt-bubble interface (hence a small bubbles size is desirable), and the difference in hydrogen concentration between the bulk, $H_b$, and the equilibrium level in the boundary layer. At the same time, a boundary layer is established at the top surface of the melt, where local equilibrium is again established with atmospheric humidity.

Between them, these two processes determine the overall degassing response of the system. Figure 7 shows a measured degassing curve for a 350kg melt, and a prediction using a kinetic model based on these principles [3].
The act of measuring the dissolved hydrogen itself is another area where an understanding of hydrogen equilibrium is critical. All on line measurement tools operate by allowing a small gas cavity, or recirculating gas loop to reach equilibrium with the melt. The partial pressure of hydrogen in the gas is then measured, e.g. by measuring the thermal conductivity (as in ABB’s AlScan [4]), or electrochemically (as in Foseco’s AlspekH [5]). In all such technologies, it is the gas partial pressure being measured: the level of dissolved hydrogen is then calculated from knowledge of equilibrium. There are still issues with the fact that such measurement devices use equilibrium data for aluminium binary alloys, and it assumed higher order commercial alloys can be treated additively. The extremely few measurements of equilibrium in more complex alloys suggests this is not always the case.

Aluminium extrusion: dynamic in situ equilibration

Most common extrusion alloys are based on the Al-Mg-Si system (AA6xxx) often with additions of Cu, Mn. This is a precipitation hardening system, based on the Al-Mg2Si pseudo-binary eutectic. Figure 8 shows schematically the process stream for extrusion.

Extrusion logs are homogenised after casting, typically ~550°C, the objective being dissolution of soluble Mg2Si eutectic, along with formation of Mn dispersoids, and phase transformation of cast intermetallics (the latter processes are often rate limiting).

It should be noted that after extrusion, there is no formal solution heat treatment prior to ageing, hence the thermal treatments of homogenisation, preheating and extrusion are required to deliver solutionised metal into the quench.

It might be thought quenching rapidly after homogenisation would be desirable, preserving Mg and Si in solid solution, and retaining it during extrusion and quenching, in order to maximise the subsequent ageing response. Perhaps surprisingly, a slower cooling rate may be deliberately applied, resulting in extensive re-precipitation of incoherent β’-Mg2Si needles. TEM microstructures from homogenised billet which have been quenched or slowly cooled are shown.
in Figures 9a and 9b. Note the precipitates seen in Figure 9b would be considered as very over-aged, and would contribute little in the way of strengthening in the final product.

The extrusion process has been carefully designed to optimise both productivity and mechanical properties, relying on a dynamic attainment of equilibrium \textit{in situ}. Encouraging the loss of solute from solution before extrusion lowers the flow stress, allowing the extrusion press to run faster. But a correct selection of billet preheat temperature, combined with the heat of deformation during extrusion, will carry the extrudate above the solvus, re-dissolving the precipitates, just before the extrudate is quenched. For this process to work, the precipitates formed after homogenisation must not be too coarse, otherwise they will not re-dissolve in short time available above the solvus. Hence the carefully specified cooling rate.

Figure 10 shows schematically the thermal history of the metal as it is preheated to a temperature \~450°C. The heat of deformation increases the temperature above the solvus line, revolutionising precipitates, before the extrudate is quenched.
The amount of deformation heating depends on the details of the extrusion, mainly the extrusion ratio (strain) and the strain rate (speed). Practices need to be fine-tuned for each product to ensure the extrudate achieves a temperature above the solvus, but below the solidus: otherwise incipient melting is observed. As seen in the pseudo binary phase diagram, Figure 11, the window for process control diminishes for richer alloys.

**Aluminium rolling : retrospective alloy development**

Brazing sheet is a clad aluminium rolled product widely used heat exchangers. The core is typically AA3xxx, with a cladding of Al-10%Si. This is a very elegant product, with one small problem: what to do with the inevitable process scrap (ingot crops, edge trims, etc.)? The core and clad are metallurgically bonded so can’t be separated. On re-melting, the scrap has an average composition typically:

Al -1.4%Si -0.8%Mn-0.1%Mg

This comprises around an order of magnitude more Si than can be tolerated in most rolled products. The more successful the sales of brazing sheet, the more scrap is created. The industry solution was to register a new alloy designed to absorb the scrap: AA4015. Its typical application is in the low cost (painted) building sheet market. But its perennial problem is it has rather poor
mechanical properties compared to conventional building sheet, shown in Figure 12. The low work hardening rate doesn't allow the shortfall in strength to be made up by simply increasing the cold rolling reduction.

A common solution to increase the work hardening in the wrought aluminium industry is to increase the Mg level. When that was tried by a client in this case, the surprising result was that the delivered mechanical properties showed no improvement (Figure 13).

![Figure 13: Effect of Mg additions on as rolled yield strength of AA4015](image)

With hindsight, this should not have been surprising. There is a very good reason that the industry has historically specified low silicon levels in many commercial rolling alloys: it dramatically reduces the solubility of elements such as magnesium.

An isothermal section of the Al-Mg-Si diagram is shown in Figure 14. Increasing the Mg level simply advances the alloy into a tie triangle, with the solid solution level pegged by one corner of the triangle. In this particular example, the client’s process route incorporates a coil to coil hot rolling process: this entails successive ~50% reductions, interspersed with holding times in the coil at ~350°C for many minutes. It would be harder to design a better process to drive a system to equilibrium in the solid state!

A very similar response was found with Mn additions for very similar reasons. Armed with this understanding, a thermodynamic study was undertaken to find a solute addition which could deliver a significant work hardening response, and be retained in solution during hot rolling. It was found that Cu could be added up to perhaps 0.6 or 0.8 wt.%, and provided the Mg level was kept low enough, should be retained in solution [7].

![Figure 14: Isothermal Al-Mg-Si section [6]](image)
Figure 15: Effect of Cu on strength of AA4015

Figure 15 shows the as rolled yield strength for a series of alloys based on AA4015 with a range of copper additions. The measured strength compare very favourably to strengths predicted on the assumption of retained copper in solution, and a knowledge its contribution to the work hardening response in aluminium. Of course solving the issue of mechanical properties by copper additions undoubtedly raises other problems with e.g. the corrosion response.

Conclusions

These examples have been chosen to try and demonstrate the importance of setting phase equilibria predictions in a larger context. There are times when thermodynamic equilibrium is achieved, either unavoidably or by design, and other times when the process route has evolved to avoid equilibrium at all costs. Perhaps the most important applications of phase equilibria relate to the provision of realistic local equilibrium boundary conditions which are required by microstructural kinetic models during processing.

Whilst there are clearly understandable gaps in the availability of reliable experimental data concerning metastable phase equilibria, there is also a very concerning absence of equilibrium data for hydrogen in ternary or quaternary alloys.

Nuclear fuels are truly materials under extreme conditions. They operate at relatively high temperatures (1500 K for conventional Light Water Reactors, 2400 K for Fast Reactors, 1000 K for Molten Salt Reactors), are subjected to intense radiation, and undergo a significant change in chemistry during fission. As a result phase changes, chemical reactions and material transport can take place during operation, resulting in extreme cases in restructuring of the original material. It is therefore very important to accurately know and predict the high temperature behaviour of nuclear fuels and their evolution with burn up of the fuel. In case of accidents in a nuclear reactor, the fuel may experience ever more extreme conditions that may result in melting of the fuel, reactions with the structural components of the reactor core and, eventually, with the concrete of the containment building.

Due to the high temperatures, equilibrium thermodynamics have been applied for many years for the description of the chemistry and phase relations of nuclear fuels. Extensive high temperature studies of UO$_2$ and PuO$_2$, the main components of current nuclear fuels, and the corresponding metal-oxygen phase diagrams were made already in the 1950s and 1960s and have laid the basis for our current understanding. However, questions remained and new measurements performed at the Institute for Transuranium Elements (ITU) using Knudsen cell mass spectrometry and self-crucible laser melting have revealed interesting new results, shedding new light on the UO$_2$-PuO$_2$ phase diagram, a key system for nuclear fuels. For the interpretation of the results a close link with CALPHAD modelling (collaboration with CEA-Saclay) has proven to be extremely useful, as will be demonstrated in the presentation.

During operation the fission products formed in the fuel can undergo complex chemical interactions that can be well understood using thermochemical calculations. The results of such calculations can be related to observations from post-irradiation examinations. Particularly for the fission products with low solubility in the oxide matrix this is important, as most of the volatiles (I, Cs, Te) belong to this group. During accidental conditions the risks and consequences of eventual radioactive releases are especially due to these elements, and especially during beyond-design accidents their interaction with the environment is crucial. A number of examples will be presented that show the usefulness of thermodynamic modelling and simulations.

Some of the next generation reactors have innovative fuels, and the example of the Molten Salt Reactor will be discussed. The MSR fuel is a mixture of fluoride salts (LiF-BeF$_2$) containing a fertile material (ThF$_4$) and a fissile material (UF$_4$ or PuF$_3$). Since it is a molten phase, solubility issues play a crucial role in the design of the fuel and the prediction of its behaviour. A thermodynamic approach is crucial for this, as will be shown. Again, the relevance of a combined experimental and computational approach, including atomistic simulations, will be highlighted.
Thermodynamics of Portland Cement Hydration

F.P.Glasser
University of Aberdeen, Old Aberdeen, AB24 3UE Scotland
f.p.glasser@abdn.ac.uk

Introduction

Portland cement (PC) is a manufactured product, first developed nearly 200 years ago. It is made and used in two stages: first, raw materials are proportioned and pyroprocessed. The indurated product is interground with calcium sulphate and perhaps other mineral powders and supplied as a fine powder, typically with a surface area 3000-5000 cm²/g. To use, stage 2, this powder is mixed with water and sized mineral aggregate - sand or crushed rock or mixtures thereof - to develop products such as mortar (fine mm size aggregate) and concrete (fine and coarse aggregate): other fillers and supplementary cementing materials may also be added.

Once water is added, set and strength gain occur spontaneously and irreversibly resulting in a durable, strong product requiring ~275-450kg cement/m³ of hardened product. Such is the success of Portland cement that, worldwide, cement production approaches two thousand million tonnes per annum. However, its production is also responsible for 5-8% of world CO₂ emissions.

The engineering properties of hardened cement and concrete are governed by formulation, mixing, transport, emplacement and cure. Much of the quality of the hardened product is thus achieved on site. This differs from, say, steel, where the material characteristics are predetermined and controlled under factory conditions. Of course Portland cement products can be made under controlled conditions, in precast plants, but the flexibility of a fluid material, and the ability to make complex shapes in situ, is thereby reduced.

Given the market success of PC, it might be supposed that the material science of Portland cement is well developed but this is not so: we have a great deal of empirical experience, but fundamental knowledge especially of the hydration process and of the impact of reactive supplementary cementing materials such as fly ash and slag, is often incomplete. Thus a sharp distinction exists between the clinker production process, which is guided and informed by thermodynamics at every step, and the hydration process which rests to an important extent on empirical considerations.

Thermodynamics and the production process

The chemistry of the production process is strongly linked to the development of inorganic thermodynamics of oxide minerals. Several texts review the historic evolution of knowledge [1-3]. Since four oxides - CaO, Al₂O₃, Fe₂O₃ and SiO₂ - comprise about 95% of a cement clinker (the calcined product emerging from the kiln), relationships between phase composition and processing conditions are established on the assumption that these oxides reach a phase equilibrium at peak firing temperatures, ~1450°C, and that this equilibrium is subsequently (with the exception of certain rapid polymorphic transitions) preserved during cooling. Given a bulk analysis in wt% oxide, the phase proportions corresponding to minimum heat content at the eutectic was calculated by the relationships shown in Table 1.
Table 1. The Bogue calculation

<table>
<thead>
<tr>
<th>Mass % of phase</th>
<th>Formula for calculation of mass% [3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄AF*</td>
<td>3.04 Fe₂O₃</td>
</tr>
<tr>
<td>C₃A</td>
<td>2.65 Al₂O₃ - 1.69 Fe₂O₃</td>
</tr>
<tr>
<td>C₂S</td>
<td>8.60 SiO₂ + 1.08 Fe₂O₃ + 5.07 Al₂O₃ - 3.07 CaO</td>
</tr>
<tr>
<td>C₃S</td>
<td>4.07 CaO - 7.60 SiO₂ - 1.43 Fe₂O₃ - 6.72 Al₂O₃</td>
</tr>
</tbody>
</table>

- Shorthand: C=CaO, A=Al₂O₃, F=Fe₂O₃, S=SiO₂

Bogue, who first developed the formula, was well aware that equilibrium might not be attained in the course of reaction and that the content of residual free CaO in a well-proportioned mix was a measure of non-equilibrium. Since free lime can be reliably determined by a chemical extraction method, a correction was recommended requiring free lime to be subtracted from the total chemical “CaO” prior to commencing the calculation. Bogue was also well aware that the “ferrite” phase of clinker had a variable Al/Fe ratio: the “C₄AF” formula was approximate and he suggested the necessary corrections could be made if, by some independent means, the ferrite composition could be determined experimentally.

The calculation is still used routinely as a guide to optimising clinker mineralogy. More advanced equations, based on an improved understanding of the interaction of phase equilibrium with cooling kinetics, are available [4]. The differences arise because of the failure to resorb C₃S in the course of freezing, thereby leading to an underestimation of its actual content.

Control of clinker phase composition

As with other types of multiphase materials, the clinker properties depend on mineral composition, so both clinker chemistry and mineralogy must be controlled. For example, and restricting the calculation to an equal weight basis, the heat of hydration of C₃S is much higher than that of C₂S so low heat-of-hydration cements are formulated to have high clinker ratios of C₂S/C₃S. Thus thermodynamics are routinely used by manufacturers to optimise properties.

Hydration

In view of these successes it may therefore surprise newcomers to the field that thermodynamics have not generally been applied to the hydration process. Several reasons— not all valid— have been advanced to “explain” why thermodynamics are not more widely applied. For example:

- The system is made chemically more complex by addition of water as well as by other reactive components added at the grinding stage, notably calcium sulphate: at least two more components, sulphate and water, have to be considered.
- The most important hydrate phase is a semi-amorphous calcium silicate hydrate gel-like phase, shorthand C-S-H; it is metastable under all conditions and is therefore supposed not to be amenable to equilibrium thermodynamic calculations.
- Other and ill-defined metastable phenomena seem to influence the observed phase composition.
- Accumulating a database of the thermodynamic properties of relevant substances and calculations for a six component system would be very complex. Moreover, “kinetics” may permit complex and unpredictable reaction paths.
The application in recent decades of techniques such as electron microscopy coupled with imaging, X-ray diffraction, aqueous solution analysis, etc., have greatly improved our knowledge of cement hydration. However these observations are often not well-linked. Cement scientists, by deciding that thermodynamic methods are not useful, have thus deprived themselves of a useful tool with which to integrate results. As a result, the full potential of cement based materials fails to be achieved.

Control of properties will be achieved by

- Calculation of the mineralogy of the hydrate system, including its temperature dependence
- Developing property-composition correlations between the nature and amount of hydrates and the engineering properties of the hardened composite, for example, strength
- Appreciate and integrate the mediating effect of kinetics on the evolution of property-composition correlations.

Applied thermodynamics

An example suffices. In the 1990’s it became commonplace to replace part of the cement clinker with ground limestone, itself mainly calcium carbonate. Claims were made that by intergrinding clinker and limestone, properties of hardened concrete could be improved: better strengths and reduced permeability were achieved. Physical benefits were also claimed, including better flow properties of the fresh mix resulting in less need for compaction. But it was also supposed that calcium carbonate was chemically an inert filler. It was unlikely that all these claims could be simultaneously be true.

From a study of the literature, Matschei and colleagues [5] concluded that calcium carbonate was not an inert filler but reacted with the aluminate phase of cements forming calcium hemi- and monocarbonate aluminate hydrates. The phases were synthesised and their thermodynamic properties determined: calcium carbonate is reactive although the maximum % was low: only a few wt.% . However the mineralogical action is complex as sulphate, hydroxide and carbonate compete for anion sites in the constituent phases with concomitant alteration of their relative stabilities.

Normal commercial cements are undersaturated with respect to gypsum: the added sulphate (i) is absorbed on C-S-H and (ii) forms mixtures of crystalline AFm and AFt. These solids, especially AFm and AFt, buffer the aqueous sulphate concentration to a few millimolar. When calcite is added, it reacts within days or weeks displacing sulphate from early-formed sulphate AFm forming instead the more stable monocarboaluminate. The sulphate thus displaced cannot form gypsum, which remains undersaturated, but instead reacts with AFm, portlandite and water forming more AFt. This reaction direction is supported by direct observation as well as by calculation. The resulting diminution in amount of free water as well as the low physical density of ettringite, AFt, increases the specific volume occupied by the solids. Since the increase occurs mainly after the cement has set, i.e., after becoming rigid, the free porosity and permeability decrease as reaction progresses and, as a consequence of better space filling, the compressive strength increases. The effect is not large, only a few % , but justifies the addition of limestone to “extend” the cement while at the same time, enabling less cement to be used and thereby reducing specific CO₂ emissions per unit mass of cement.

The extent to which the calcite-sulphate reaction affects the specific volume of cement solids, and hence the optimum limestone addition, has to be the subject of calculation. The calculation is sensitive not only to chemistry, notably to cement alumina concentration and ratio of alumina/sulphate, but also to temperature. Thus the optimum addition may be different in concrete intended for service in cold climates than in hot.
A number of general lessons emerge from these and other calculations:

- The hydrate matrix of Portland cement consists of metastable phases but these are reproducibly obtained and are readily and reproducibly characterised by modern experimental techniques.
- The solids do not necessarily have fixed compositions owing to solid solution formation but the variation can be quantified.
- The amount and composition of hydrate phases can be calculated and the internal chemistry of anions and cations (typically OH, SO$_4$, and CO$_3$) controlled by a series of buffering reactions. Thus we have a relatively limited number of internal states controlled by solid-aqueous phase distributions not, as is often concluded, an infinite range of internal states.
- True, the composition limits of the buffered regions are slightly “fuzzy” owing partly to the presence of soluble alkali derived from cements but the general principle of having a limited range of internal states, termed regimes, remains.
- Phase compositions within these regimes are sensitive to temperature. Cement is often hydrated at temperatures up to 60°C (or more) owing to self-heating in the course of hardening. Large differences in thermal regimes may affect the internal mineralogy with the additional possibility of seasonal changes occurring in outdoor service.
- We are only at the beginning of exploring the connections between mineralogical stability, and composition to determine the impacts of phase development on engineering properties. We are about to enter a new era with respect to improving our control of cement properties.
- The eventual objective, to make more efficient use of materials, is facilitated and quantified by application of thermodynamic methods.

I thus strongly recommend systematic application of the applied thermodynamics of cement hydration, including data base enhancement. Space limitations preclude me from developing applications involving reaction of cement with its service environment but this is an obvious topic for application, especially as existing test methods cannot hope to embrace the many and varied service environments in which concrete is used. Improving the performance and durability of existing materials is an important but often overlooked way of reducing the environment impact of cement production and use.

References