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THE DEVELOPMENT AND VALIDATION OF A NEW THERMODYNAMIC DATABASE FOR ALUMINUM ALLOYS

A. Markström[1], Y Du[2], S. H. Liu[2], L. J. Zhang[2], P. Mason[3], L. Kjellqvist[1], J. Bratberg[1], A. Engström[1], Q. Chen[1],

[1] Thermo-Calc Software AB, Norra Stationsgatan 93 (Plan 5), 113 64 Stockholm, Sweden
[2] State Key Lab of Powder Metallurgy, Central South University, Changsha, Hunan, 410083 P.R. China
[3] Thermo-Calc Software Inc, 4160 Washington Road, Suite 230, McMurray, PA 15317 USA

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Abstract

Computational thermodynamics is a powerful tool for alloy design as well as process optimization. The quality of the predictions is dependent on the quality of the thermodynamic database that is used. In this paper the development of a new thermodynamic database for Aluminum alloys is described. Examples of calculations for different kinds of Aluminum alloys and their applications are shown using the database and comparing where possible against experimental data, thereby validating its accuracy.

Introduction

Computational thermodynamics has been widely used in the Aluminum industry for decades in order to understand and model the behavior of existing alloys, accelerate the development of new alloys and also in the area of process optimization and the simulation of casting and heat treatment. Recent interest in Integrated Computational Materials Engineering (ICME) has put additional emphasis on the need for good quality data that extends to broad ranges of composition. With computational thermodynamics, composition and process parameters can be optimized and this reduces the lead time for alloy development and process improvement. With the Thermo-Calc software package [1] in conjunction with TCAL1 [2], a new thermodynamic database for Aluminum alloys, it is possible to calculate the influence that different elements have on the stability of, for example, different precipitates for Aluminum alloys and also the phases that precipitate out during solidification. Determination of phase fractions and the solubility of elements in different precipitates are also easily calculated. Through such calculations it is possible to optimize compositions for new alloys and also predict optimal solution heat treatment temperature ranges for new and existing alloys without performing many time-consuming and costly experiments.

Together with the mobility database, MOBAL2 [3], kinetic reactions can also be simulated with the use of DICTRA [1, 4] or TC-PRISMA [5]. DICTRA is a computer program for simulating diffusion controlled phase transformations in multicomponent alloy systems such as homogenization/aging of alloys, dissolution/coarsening of precipitates. TC-PRISMA is a computational tool for the simulation of precipitation reactions in multicomponent alloys.

Thermodynamic modeling

By adopting the CALPHAD [6, 7, 8,] technique, all available thermochemical information, both thermodynamic and phase equilibria data, are used to fit the model parameters used to describe the Gibbs energy of individual phases. The purpose is to obtain a consistent set of model parameters that can describe the thermodynamic properties of the system in a realistic way.

The Gibbs energy of each phase is described using the compound energy formalism [9]. The structure of a phase is represented by a sublattice model $(A, B)_k(D, E, F)_l(...)...$, where A and B mix on the first sublattice, and D, E and F mix on the second sublattice, and similarly if more sublattices are added. The sublattices (s) are indexed with the stoichiometric coefficients k, l,... (n^s) and one mole of formula units thus contains $k+l+...+n^s$ moles of atoms. The expression for the Gibbs energy of each phase is given by,

$$G_m = \sum {}^{\circ}G_{end} \prod y_J^s + RT \sum \sum n^s y_J^s \ln(y_J^s) + {}^{E}G_m + G_m^{magn} \quad (1)$$

The first term represents the surface of reference and is constructed by a summation over all end-members and the product $\prod \prod y_J^s$ contains one site fraction from each sublattice and they are identified by the constituents, J, in the end-member. The Gibbs energy of one formula unit of the compound represented by the end-member is ${}^{\circ}G_{end}$. The second term is the ideal entropy of mixing, ${}^{E}G_m$ represents the excess energy and G_m^{magn} the magnetic contribution. The excess energy is described by a generalized regular solution expression,

$${}^{E}G_m = \prod y_J^s \sum y_B^t L_{A,B:D:G...} + \prod y_J^s \sum \sum y_B^t y_D^u L_{A,B:D,E:G...} + ... \quad (2)$$

The commas in the subscript separates constituent on the same sublattice and the colons separates constituents in different sublattices. For the L parameters Redlich-Kister terms [10] in site fractions are used. $L_{A,B:D:G}$ is then described as

$$L_{A,B:D:G} = \sum_{v=0}^{k} (y_A^s - y_B^s)^v \cdot {}^{v}L_{A,B:D:G} \quad (3)$$

where ${}^{v}L_{A,B:D:G}$ can be temperature dependent.

Development of TCAL1

TCAL1 is a thermodynamic database which contains all the important phases for Aluminum based alloys within a 26-element framework [Al Cu Fe Mg Mn Ni Si Zn B C Cr Ge Sn Sr Ti V Zr Ag Ca H Hf K La Li Na Sc]. In total 349 solution and intermetallic phases are included.

Developed using the CALPHAD approach, TCAL1 is based on the critical evaluations of binary, ternary and in some cases higher order systems which enables predictions to be made for multicomponent systems and alloys of industrial importance. A hybrid approach of experiments, first-principles calculations and CALPHAD modeling have been used to obtain thermodynamic descriptions of the constituent binary and ternary systems and, in contrast to some other thermodynamic databases available for Aluminum alloys based on the CALPHAD approach, many of the binary and ternary systems in TCAL1 have been assessed over their entire composition range and temperature.

For example, in Figure 1, an isothermal section at 550 °C of the assessed Al-Fe-Si system [11] is shown. Two important ternary phases for current Aluminum alloys are $Al_{71}Fe_{19}Si_{10}$ (α-AlFeSi) and $Al_9Fe_2Si_2$ (β-AlFeSi), however, when developing new alloys and exploring new composition ranges it is important to have full descriptions of all the stable phases in the system and this is also important when considering processing paths and joining of dissimilar materials as well; this is one reason why so much emphasis has been put on evaluating the binary and ternary systems to their full range of composition in this database.

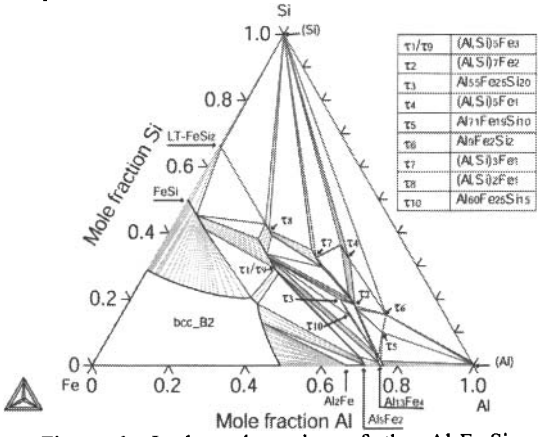

Figure 1. Isothermal section of the Al-Fe-Si system at 550 °C.

In total, 145 of the binary systems in this 26 element framework have been assessed to their full range of composition and TCAL1 also contains assessments of 56 ternaries in the Al-Cu-Fe-Mn-Mg-Ni-Si-Zn system. Additionally, 15 quaternaries and 1 quinary system have also been assessed.

The database has been validated where possible against higher order systems, such as data published for industrial alloys, some examples of which follow in this paper, and is the result of a long-term collaboration with academia that has involved extensive new experimental work as well as critical assessments of the published literature.

Thermodynamic calculations

Multi-component phase diagrams are very useful in alloy development since they show what phases could form at different temperatures during processing and operation. By the use of phase diagrams it is possible to see how an element is influencing the phase stabilities at varying temperatures. Such calculations can be made for multicomponent alloys using CALPHAD based tools such as Thermo-Calc, which is a software package used to perform thermodynamic and phase equilibria calculations for multi component systems.

In Figure 2 a multi-component phase diagram is shown for Al-0.5w%Fe-0.5w%Mg-Si. This shows what happens with the phase stability for Aluminum alloy A5005 if the Si content is increased. (A5005 contains less than 0.3w%Si). Comparison is made with experimental data from Philips [12] showing good agreement on the phase boundaries from liquidus to solidus. From this type of diagram it is possible to tailor the composition and heat-treatment to achieve the desired phase stability.

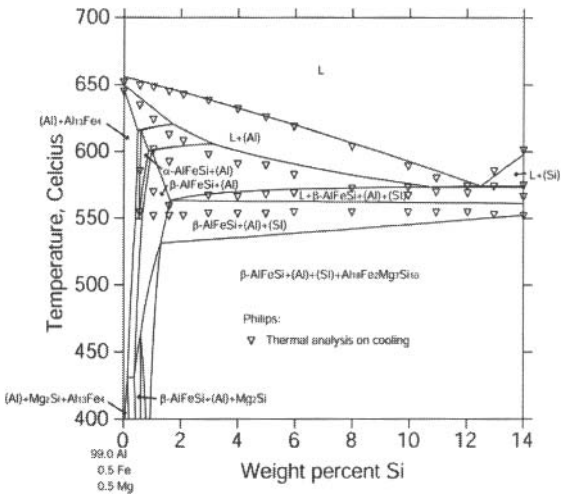

Figure 2. Calculated vertical section for the Al- 0.5 wt.% Mg- 0.5wt.% Fe-Si system along with experimental data [12].

While such isoplethal sections give information about the compositions and temperatures where phase transformations are expected to occur, they do not give quantitative information about the amounts of different phases which can instead be obtained from a property diagram via a Thermo-Calc step calculation. Figure 3 shows such a diagram where the amounts of the phases predicted to be thermodynamically stable at 400 °C are plotted against Si-content. With such calculations a metallurgist can tailor the alloy composition to achieve the desired amounts of different phases.

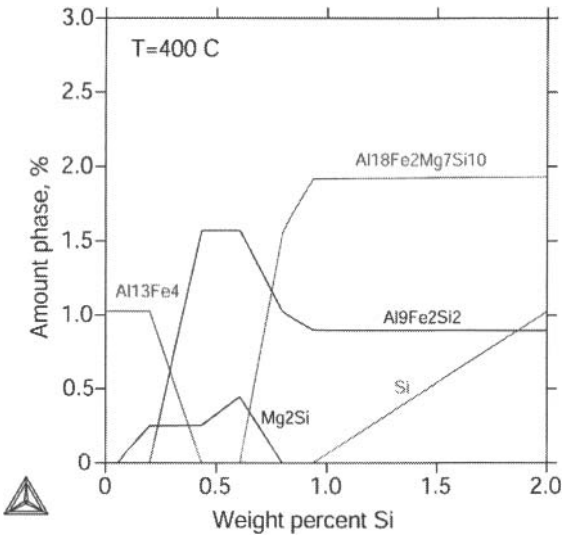

Figure 3. Variation of phase amount with Si for Al-0:5w%Fe-0.5w%Mg-Si alloys at 400 °C.

For Aluminum alloys, understanding solidification and the phases that are likely to precipitate during cooling are also very useful. In Figure 4 a solidification simulation, using the Scheil-Gulliver approximation [13], is shown for alloy AA3004 compared with experimental information from Bäckerud et al. [14].

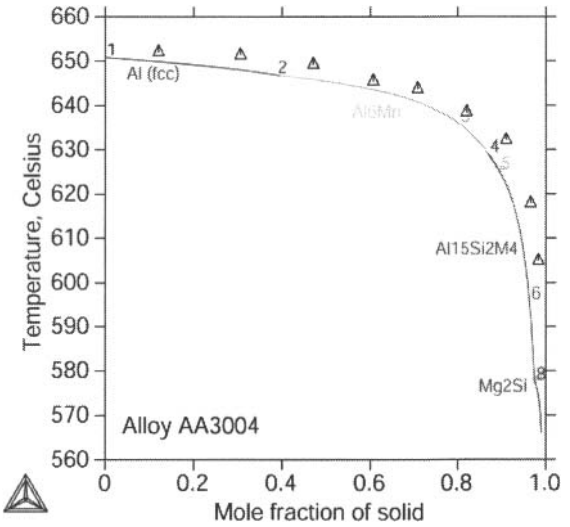

Figure 4. Solidification simulation compared with experimental result [14]. Al, Al_6Mn, $Al_{15}Si_2M_4$ and Mg_2Si were found in the microstructure as predicted from the calculation

The solidification simulation gives the solidification path, solidified phases and their composition under non-equilibrium conditions, for example micro-segregation. Figure 5 shows how the composition of the matrix (fcc) varies depending on the temperature at which it has formed. As illustrated by the figure, the Mg content in the matrix varies a lot depending on the solidification temperature.

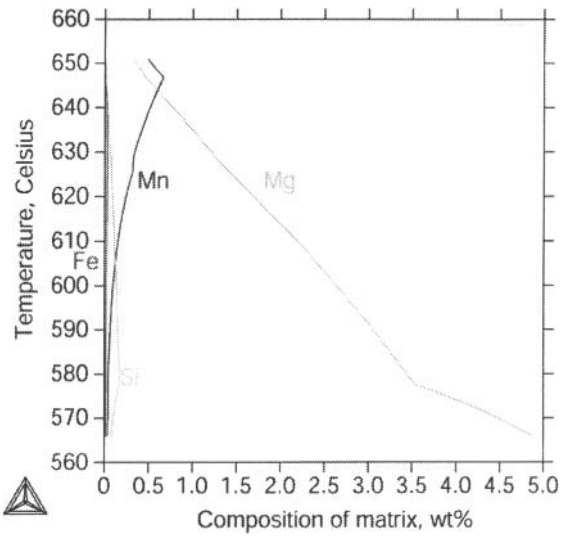

Figure 5. Composition of the matrix (fcc) depending on the temperature at which it has formed.

Kinetic simulation

Thermodynamic calculations while very useful, do not consider time. DICTRA is a software tool used for detailed simulations of diffusion controlled phase transformations for multi-component alloys where time is a parameter. Example applications include heat treatment, microsegregation during solidification, growth and dissolution of precipitates, coarsening and more, all important for the development of Aluminum alloys.

Figure 6 shows a simulation of a diffusion couple where Si is diffusing into an Al-0.53w%Fe-1.02%Mn alloy from an Al-0.99w%Si alloy. The calculation was performed with DICTRA using the TCAL1 database along with MOBAL2 which is a mobility database for Aluminum alloys that has also been developed in a CALPHAD like spirit. The result shows the phase fractions after heat-treatment at 600 °C for 4 days. The Al-0.99w%Si alloy is located below the interface and the Al-0.53w%Fe-1.02%Mn alloy above (where the interface is located at Distance equal to zero). As seen, Al_6Mn has been transformed into alpha-phase ($Al_{15}Si_2(Mn,Fe)_4$) above the interface due to the diffusion of Si into the alloy. This is in very good agreement with the experiment by Alexander and Greer [15]. They reported a micrograph of the interface where the alpha phase has been formed in the Al-0.53w%Fe-1.02%Mn alloy due to Si diffusion. The width of the alpha-phase zone is approximately 500μm which is close to that predicted by the simulation.

Through such calculations one can optimize temperature and heat-treatment times to achieve a desired microstructure or predict how an alloy will behave in real applications where diffusion plays a role.

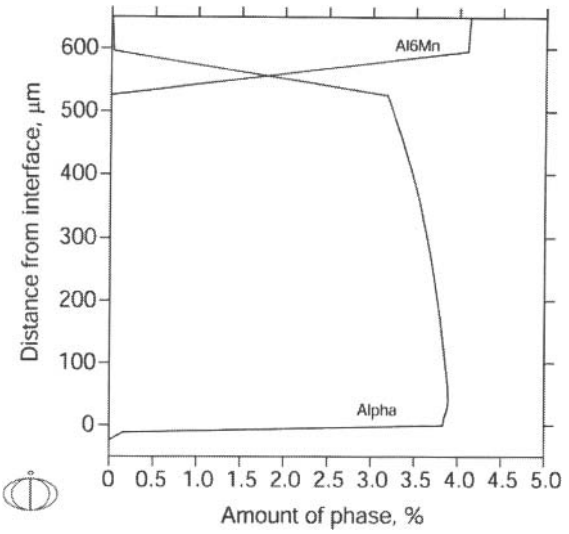

Figure 6. DICTRA simulation of the phase fraction at different distances from the interface for a diffusion couple with Al-0.99w%Si (below) and Al-0.53w%Fe-1.02w%Mn (above) after heat-treatment at 600 °C for 4 days.

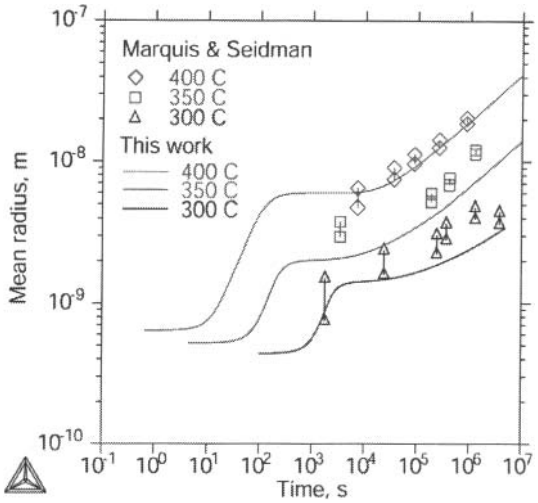

Figure 7. Calculated mean radius of Al_3Sc precipitates in an Al-2.2at%Mg-0.12at%Sc alloy at different temperatures compared with experimental information from Marquis and Seidman [19]

Precipitation simulation

With data for interfacial energy, volume, and elastic modulus in addition to available thermodynamic and kinetic data, TC-PRISMA [5] can be used to simulate the concurrent nucleation, growth, and coarsening of precipitate phases in multicomponent Aluminum alloys. This new computational tool is based on the Langer-Schwartz theory [16] and adopts the Kampmann-Wagner numerical approach [17] to solve the governing equation for the evolution of particle size distribution function. A general growth rate model [18] for precipitate particles in multicomponent systems has been developed and implemented. With this software, variations with time of mean radius, number density, volume fraction, and size distribution of precipitate particles can be simulated. Nucleation rate and precipitate composition can also be obtained during the simulation. Coupled with relevant microstructure-property models, the computer program could be used to estimate the change of mechanical properties of alloys upon aging or tempering.

Marquis and Seidman[19] have measured the size evolution for Al_3Sc precipitates in an Al-2.2at%Mg-0.12at%Sc alloy at 3 different temperatures. In Figure 7 a comparison has been made between calculated mean radius, using TC-PRISMA, and their measured values. As seen, the calculation reflects the measured values very well.

Summary

CALPHAD based software and databases have been employed within the aluminum industry for decades and are used to improve the understanding of existing alloys, accelerate the development of new alloys and also model process optimization. The quality of the predictions is dependent on the quality of the thermodynamic database that is used and the drive for new alloy development and better process models (in part driven by the interest in ICME) requires the further development of these databases. A new thermodynamic database, TCAL1, for Aluminum based alloys, containing 26 elements and 349 solution and intermetallic phases is described here. In total, 145 of the binary systems in this 26 element framework, and 56 ternaries in the Al-Cu-Fe-Mn-Mg-Ni-Si-Zn system, have been assessed to their full range of composition. Additionally, 15 quaternaries and 1 quinary system have also been assessed.

Different kinds of calculations have been made as part of the validation of this database for representative alloys for which there are experimental data to compare. Both thermodynamic phase equilibria calculations and kinetic simulations show good agreement between calculated and measured values.

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