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Constitution of Magnesium Alloys

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Abstract

Multi-component magnesium alloys exhibit a complex constitution, requiring computational thermodynamics for a quantitative treatment that goes beyond "just" phase diagrams. The basis for this approach is a thermodynamic Mg alloy database, which is developed in an ongoing long-term project in our group since many years. Three distinctive features of this database are highlighted in this report: (i) Combination of own key experimental work with theoretical modeling to generate consistent data, (ii) Systematic quality control of the database using a variety of elaborated cross-checks, and (iii) Complete and entire composition range descriptions for all pertinent binary or ternary subsystems whenever possible. The latter point is decisive for the capability to use this tool for new alloys, far beyond the composition limits of conventional Mg alloys. It is demonstrated by correctly predicting the phase formation in aluminum-rich six component alloys. Also, new Mg-solder alloys can be tackled that are essentially Zn-rich.

Introduction

Quantitative access to all available thermodynamic and phase diagram data in a consistent, numerical and easily readable form is – at least for multicomponent alloys – virtually impossible without the use of computational thermochemistry. The fundamental idea goes back to the introduction of the Calphad method by Larry Kaufman in 1970 [1]. In a nutshell it is to calculate all these data, ranging from stable and metastable phase equilibria down to the chemical potentials, from a unique set of thermodynamic model parameters of the alloy system. A review of the Calphad method [2] and a recent summary on assessment techniques and database design [3] are given elsewhere.

Major thermodynamic databases are mainly available from developers of commercial thermodynamic software packages such as Pandat (www.computherm.com), Thermocalc (www.thermocalc.com), Factsage (www.factsage.com), MTDATA (www.npl.co.uk/mtdata), more sources are given in [3]. A specific aspect in developing a magnesium alloy database, in comparison to steel and Al alloys, is the substantially smaller pool of experimental data in the published literature. In addition to thermodynamic assessment work it is thus mandatory to perform original experimental work in a combined approach in order to generate a trustworthy Mg alloy database. This is the typical approach in our ongoing work in this field, some results of which will be shown below. Sample compositions for key experiments are selected by preliminary thermodynamic calculations. Such samples are prepared in high purity and the workhorse methods to analyze phase equilibria or transitions are X-ray diffraction (XRD), metallographic analysis, scanning electron microscopy with energy dispersive X-ray microanalysis (SEM/EDX), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). It is the purpose of this study to highlight some real world applications of this approach and also to outline the current scope and structure of the database and the important aspect of its validation.

Selected applications of the Mg alloy database

Phase equilibria in Mg-Al-Zn-Mn system provide crucial information for the advancement of AZ and AM alloy series. Specifically, the liquidus and solidus data reported for commercial AZ and AM alloys are generally based on thermal analysis. The following two points have been clarified by performing own experiments combined with computational thermodynamics [4]: (i) The measured "liquidus" temperature generally does not represent the actual equilibrium one, in other words, the primary precipitate for these Mg-alloys cannot be detected in the thermal analysis. (ii) The measured "solidus" does not correspond to the equilibrium solidus and not even to the end of non-equilibrium solidification process. The measured "solidus" is often associated with the *starting* precipitation of $Mg_{17}Al_{12}$ phase and, importantly, the solidification process of these Mg-alloys ends at much lower temperature. This example shows that it is possible to predict even non-equilibrium effects [4].

In specific studies on AZ31 based alloys it could be shown that the current thermodynamic description can be successfully combined with a phase field simulation approach aiming at a microstructure control [5]. It was also shown helpful in better understanding the influence on manganese on the microstructure of AZ31 and a possible relation with grain refining [6].

Al-rich alloys in the system Al-Zn-Mg-Cu-Sc-Zr were also studied by thermodynamic calculations [7]. Phase formation was compared with experimental data obtained by DTA and microstructural analysis. Calculated phase diagrams, such as shown in Fig. 1, phase amount charts and enthalpy charts together with non-equilibrium calculations under Scheil conditions reveal significant details of the complex phase formation. All calculated data are predictions from the current thermodynamic database developed for Mg-alloys and not from a specialized Al-alloy database. Our basic concept is to assess the entire phase equilibria in the complete composition range of each subsystem as far as possible.

As a result, this database is also quite useful for Al-alloys with adequate alloying elements. That, in turn,

provides support for a reasonable application of this database for advanced Mg-alloys beyond the conventional composition ranges.

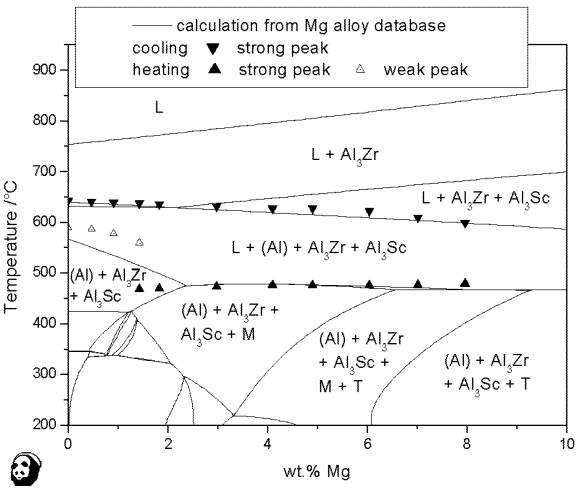

Figure1: Calculated vertical section of the Al-Zn-Mg-Cu-Sc-Zr phase diagram for constant 8 wt.% Zn, 2 wt.% Cu, 0.3 wt.% Sc, and 0.3 wt.% Zr in the Al-rich region [7].

Current scope of the Mg alloy database

The thermodynamic Mg alloy database is developed in an ongoing long-term project in our group since many years. This database currently includes most of the elements used in Mg-alloys including some micro-alloying elements and impurities, and covers most of the phases appearing in commercial magnesium alloys. 17 components (Ag, Al, Ca, Ce, Cu, Fe, Gd, Li, Mg, Mn, Nd, Sc, Si, Sr, Y, Zn and Zr) and a total of 285 phases are included in the current database. 80 of them are modeled as solution phases; the additional 205 phases are stoichiometric. Complete or partial thermodynamic descriptions are developed for many binary and ternary systems as listed in Tables I and II. This means the current database works in a much wider composition range in many sub-systems, as demonstrated above in Fig. 1. The ongoing effort is to complete the description of important interactions among these elements, as well as the extension to new elements.

Table I lists all the binaries in the 17-component system. Thermodynamic descriptions are fully developed for the binaries in green color, which means that there is no composition limits if calculations are carried out for these binary systems. Binaries in yellow color are also developed in the entire composition range, but need further improvements. For these binaries, phase relationships are calculated with larger deviation. No model parameters are developed for those binaries shown white.

Table I. Current Status of Binary Systems

	Al	Ca	Ce	Cu	Fe	Gd	Li	Mg	Mn	Nd	Sc	Si	Sr	Y	Zn	Zr
Ag	Ag-Al	Ag-Ca	Ag-Ce	Ag-Cu	Ag-Fe	Ag-Gd	Ag-Li	Ag-Mg	Ag-Mn	Ag-Nd	Ag-Sc	Ag-Si	Ag-Sr	Ag-Y	Ag-Zn	Ag-Zr
Al		Al-Ca	Al-Ce	Al-Cu	Al-Fe	Al-Gd	Al-Li	Al-Mg	Al-Mn	Al-Nd	Al-Sc	Al-Si	Al-Sr	Al-Y	Al-Zn	Al-Zr
Ca			Ca-Ce	Ca-Cu	Ca-Fe	Ca-Gd	Ca-Li	Ca-Mg	Ca-Mn	Ca-Nd	Ca-Sc	Ca-Si	Ca-Sr	Ca-Y	Ca-Zn	Ca-Zr
Ce				Ce-Cu	Ce-Fe	Ce-Gd	Ce-Li	Ce-Mg	Ce-Mn	Ce-Nd	Ce-Sc	Ce-Si	Ce-Sr	Ce-Y	Ce-Zn	Ce-Zr
Cu					Cu-Fe	Cu-Gd	Cu-Li	Cu-Mg	Cu-Mn	Cu-Nd	Cu-Sc	Cu-Si	Cu-Sr	Cu-Y	Cu-Zn	Cu-Zr
Fe						Fe-Gd	Fe-Li	Fe-Mg	Fe-Mn	Fe-Nd	Fe-Sc	Fe-Si	Fe-Sr	Fe-Y	Fe-Zn	Fe-Zr
Gd							Gd-Li	Gd-Mg	Gd-Mn	Gd-Nd	Gd-Sc	Gd-Si	Gd-Sr	Gd-Y	Gd-Zn	Gd-Zr
Li								Li-Mg	Li-Mn	Li-Nd	Li-Sc	Li-Si	Li-Sr	Li-Y	Li-Zn	Li-Zr
Mg									Mg-Mn	Mg-Nd	Mg-Sc	Mg-Si	Mg-Sr	Mg-Y	Mg-Zn	Mg-Zr
Mn										Mn-Nd	Mn-Sc	Mn-Si	Mn-Sr	Mn-Y	Mn-Zn	Mn-Zr
Nd											Nd-Sc	Nd-Si	Nd-Sr	Nd-Y	Nd-Zn	Nd-Zr
Sc												Sc-Si	Sc-Sr	Sc-Y	Sc-Zn	Sc-Zr
Si													Si-Sr	Si-Y	Si-Zn	Si-Zr
Sr														Sr-Y	Sr-Zn	Sr-Zr
Y															Y-Zn	Y-Zr
Zn																Zn-Zr

: Full description : Full description for major phases : Extrapolation

In addition to the binaries, thermodynamic descriptions for several key ternaries are also developed. Ternary Mg-systems containing the most important alloying elements Al, Ca, Ce, Li, Mn, Si and Zn are listed in Table II. Thermodynamic descriptions for the ternaries in green color are fully developed; the current database therefore works in the whole composition and temperature ranges in these ternary systems. Thermodynamic descriptions for those in the yellow color are also developed, but need further validation by experimental data. Thermodynamic descriptions for the remaining two ternaries (shown white) are obtained by extrapolations of the constituent binaries. Table II is comprehensive and shows all possible ternary systems for this 8 component subset of the Mg-database.

Table II: Key Ternary Systems for the Mg-Al-Ca-Ce-Li-Mn-Si-Zn subset of the Mg-database

Mg-Al-Ca	Mg-Al-Ce	Mg-Al-Li	Mg-Al-Mn	Mg-Al-Si	Mg-Al-Zn
	Mg-Ca-Ce	Mg-Ca-Li	Mg-Ca-Mn	Mg-Ca-Si	Mg-Ca-Zn
		Mg-Ce-Li	Mg-Ce-Mn	Mg-Ce-Si	Mg-Ce-Zn
			Mg-Li-Mn	Mg-Li-Si	Mg-Li-Zn
				Mg-Mn-Si	Mg-Mn-Zn
					Mg-Si-Zn

Additionally, other thermodynamic descriptions for ternary system are included in the Mg-database The Mg-containing systems are listed in Table III. The non-Mg-containing systems are listed in Table IV. The color code is the same as in Table II.

Table III: Additional selected ternary Mg-Systems included in the Mg-database

Mg-Ag-Al	Mg-Ag-Cu	Mg-Al-Cu	Mg-Al-Gd	Mg-Al-Sc	Mg-Al-Sr	Mg-Al-Y
Mg-Cu-Li	Mg-Cu-Si	Mg-Cu-Y	Mg-Cu-Zn	Mg-Li-Gd	Mg-Mn-Gd	Mg-Mn-Sc
Mg-Mn-Y	Mg-Mn-Zr	Mg-Y-Zr				

Table IV: Additional selected ternary non-Mg-Systems included in the Mg-database

Ag-Al-Cu	Al-Ca-Ce	Al-Ca-Fe	Al-Ca-Li	Al-Ca-Si	Al-Ce-Gd	Al-Ce-Nd
Al-Ce-Si	Al-Ce-Y	Al-Cu-Li	Al-Cu-Mn	Al-Cu-Nd	Al-Cu-Si	Al-Cu-Zn
Al-Fe-Mn	Al-Fe-Si	Al-Gd-Nd	Al-Gd-Y	Al-Li-Mn	Al-Li-Si	Al-Mn-Sc
Al-Mn-Si	Al-Nd-Y	Al-Si-Y	Al-Si-Zn	Al-Sn-Zn	Ca-Fe-Si	Ca-Li-Si
Ca-Sr-Zn	Cu-Fe-Si	Cu-Sn-Zn	Fe-Mn-Si	Mn-Y-Zr		

Database validation

Some general aspects concerning the development of the Mg-database with a larger number of additional references validating its content were given earlier [8]. The most important aspects of quality assurance were given specifically in [9] and are further developed in more general terms [3]. These important aspects, concerning artifact-free and thermodynamically reasonable construction, have been used to scrutinize the Mg alloy database and will not be discussed further at this point.

The current thermodynamic database for magnesium alloys has furthermore been extensively tested and validated using the published experimental data [10, 11, 12, 13, 14, 15, 16, 17 18, 19]. Some sub-quaternary systems of this database have been critically assessed: Mg-Al-Ca-Ce, Mg-Al-Ca-Li, Mg-Al-Ce-Li, Mg-Al-Cu-Zn, Mg-Mn-Y-Zr, but not published yet. The quaternary systems Mg-Al-Li-Si [20] and Mg-Ce-Mn-Sc, Mg-Gd-Mn-Sc, Mg-Mn-Sc-Y [21, 22] were thermodynamically modeled and used for technical applications. These comparisons are condensed into a small number of diagrams, highlighting important data, as shown below.

For the reliability of the calculated phase diagrams the fitting of the invariant temperatures are of paramount importance. Since the measured temperatures of the invariant reactions are not affected by super-cooling related problems, these nonvariant data are perfect criteria for comparison of experimental with calculated data as shown in Figure 2.

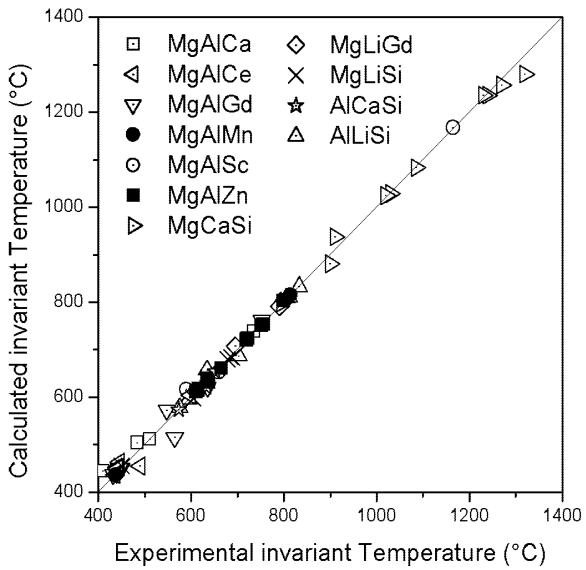

Figure 2: Invariant temperatures for various ternary alloys included in PanMagnesium 5.0: Comparison between calculated and experimental data.

For the Mg-Al-Mn system the reliability is checked in detail [23]. The experimental data are plotted in Figure 3a and 3b as comparison between calculated results and experimental data. The same was done for the system Mg-Mn-Zn [24]. The same experimental data are shown on the liquidus surface of the Mg-rich corner in Figure 4, also indicating the primary crystallizing phase.

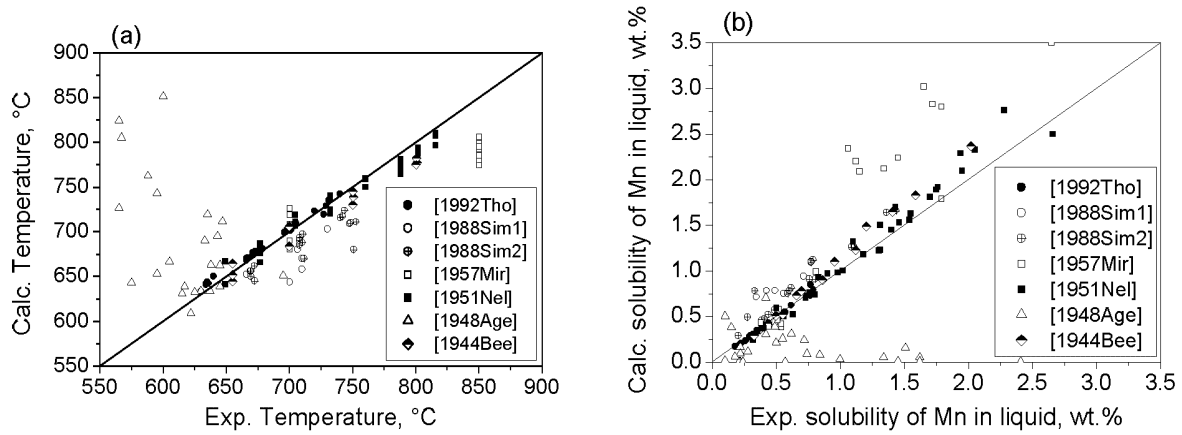

Figure 3: Comparison between calculated results and experimental data for all alloy samples in the Mg-Al-Mn system. (a) Liquidus temperature at a given composition, (b) Solubility of Mn in liquid at a given temperature and Al composition. The straight line in Figs. (a) and (b) is a visual aid corresponding to perfect agreement between experimental values and the calculated results from the present thermodynamic model [23].

This comparison in Figure 3 enables easy identification of those groups of experimental data that are not consistent with the bulk of experimental work. There is a reasonable agreement with this bulk of experimental data and the calculated values. Moreover, there is a reasonable agreement with the primary solidifying phases as shown in Figure 4.

The experimental data for the commercially very important Mg-Al-Zn alloys are shown in Figures 5a and 5b. The liquidus surface of the Mg-rich corner is given in Figure 5a. The same experimental data is plotted in Figure 5b as comparison between calculated results and experimental data [25].

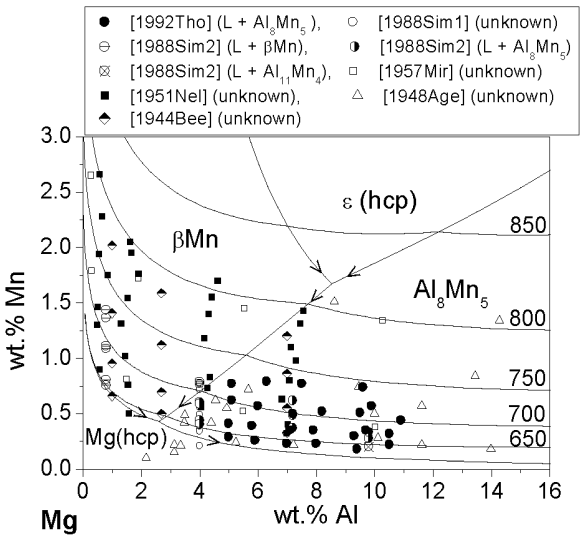

Figure 4: Calculated partial liquidus surface, the thick lines indicate monovariant reaction lines and the thin lines represents the isotherms. Superimposed are the compositions of experimental alloys further compared to calculated data of the liquidus surface in Figure F3. The primary solid phase is specified in some experimental data.

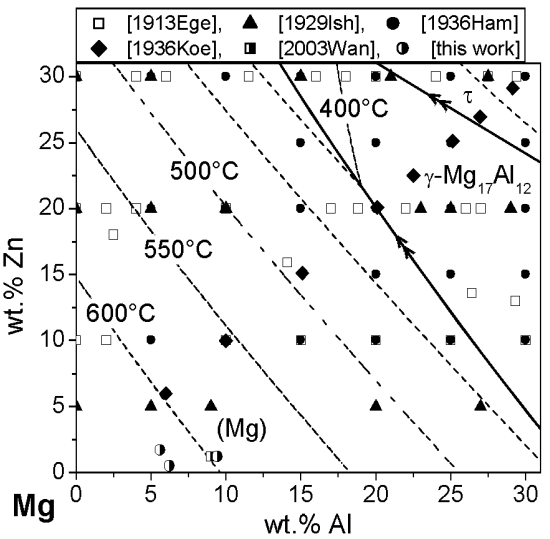

Figure 5a: Calculated partial Mg–Al–Zn liquidus surface and experimental alloy compositions. The thick lines indicate monovariant reaction lines and the dashed lines represent isotherms at an interval of 50 °C [25].

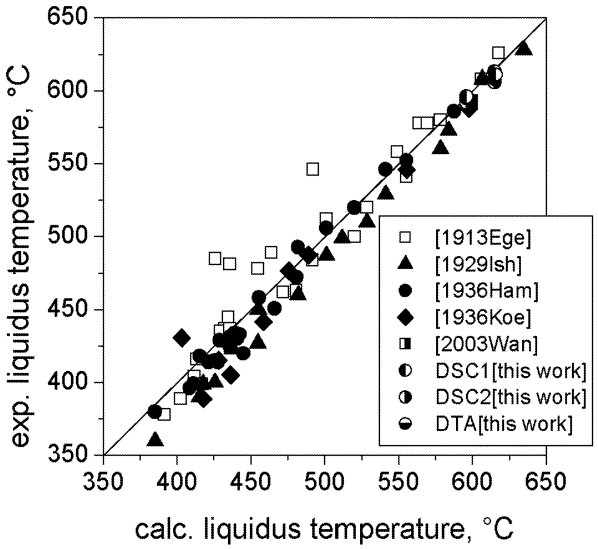

Figure 5b: Comparison between calculated and experimental liquidus temperature for all alloy samples in the Mg-Al-Zn system. The straight line is a visual aid corresponding to perfect agreement between experimental and calculated results[25].

Measured liquidus temperatures for other ternary Mg-alloy systems are compared in Figure 6 with calculations from the magnesium database. These miscellaneous Mg-X-Y systems include the alloying elements Al, Ca, Ce, Gd, Li, Sc, and Si.

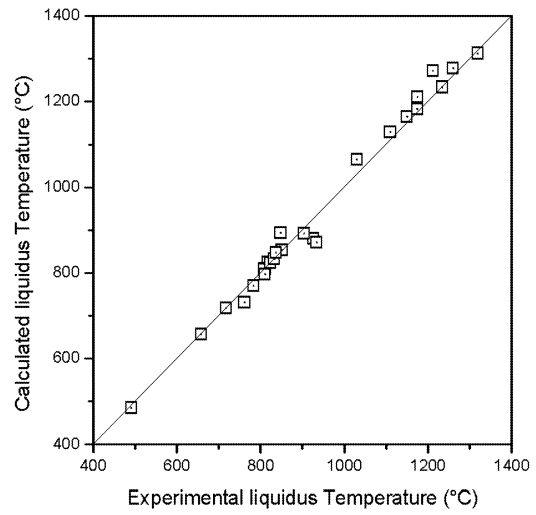

Figure 6: Liquidus temperatures for various ternary magnesium alloys outside the Mg-Al-Mn-Zn system, with alloying elements Al, Ca, Ce, Gd, Li, Sc, Si: Comparison between calculated and experimental data.

Additionally a selected comparison of experimental data and calculated phase equilibria is given below. This demonstrates the feasibility to perform reasonable calculations with the Mg database even in some very high alloyed regions with vanishing Mg-content. For the Al-Li-Si system a comparison between calculated and experimentally measured DTA data is given in Figure 7 [26]. Figure 8 shows a calculated vertical section in the Al-Ce-Si system at constant 90 at.% Al including the DSC/DTA signals measured [16].

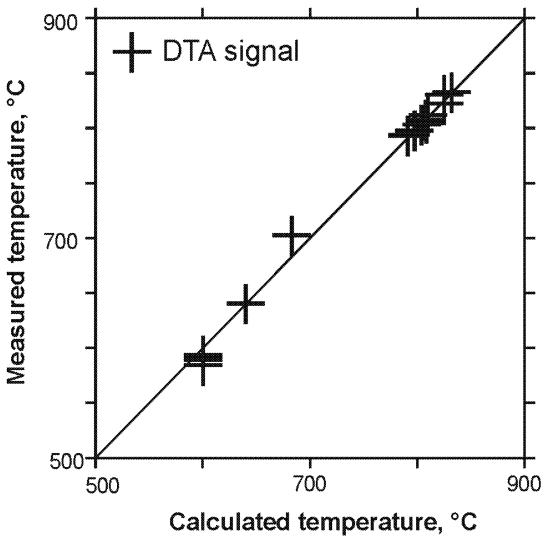

Figure 7: Comparison between calculated and experimentally measured DTA data for the Al-Li-Si system [6].

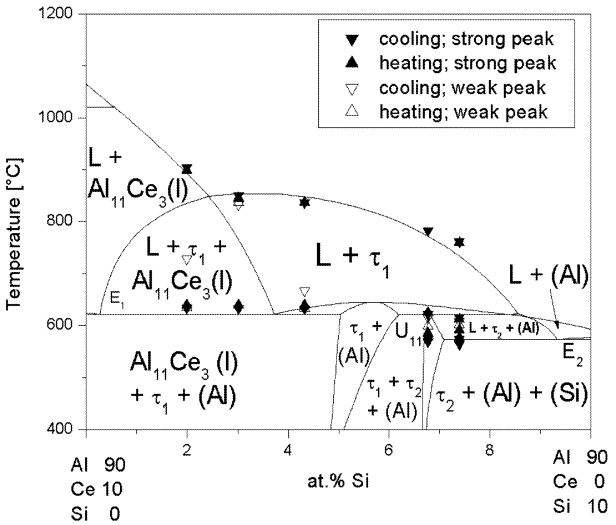

Figure 8: Calculated vertical section $Al_{90}Ce_{10}$ - $Al_{90}Si_{10}$ at constant 90 at.% Al including the DSC/DTA signals measured in [16].

Outlook

The effort is ongoing in our group to complete the description of important interactions among the included elements, as well as the extension of the Mg database to new elements. This has to be done by performing original key experiments combined with Calphad assessments subject to quality assurance and also incorporating first-principle calculations where appropriate, as depicted in Ref. [19]. Another goal is to demonstrate additional useful applications of this database within the tool of computational thermodynamics to Mg alloy development and the advancement of processing of Mg alloys.

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