Computational thermodynamics and CALPHAD modeling prove useful for selecting and developing new magnesium alloys.

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Lightweighting is a well-known strategy for increasing energy efficiency and reducing greenhouse gas emissions. Magnesium, the lightest structural metal, will thus see increased use in a wide range of structural and functional applications for energy generation and storage, propulsion, and transportation[1]. Current industrial applications for magnesium alloys are confined to nonstructural or semi-structural components, due to the limited mechanical properties of conventional Mg-Al-based alloys such as AZ91 (Mg-9Al-1Zn) and AM60 (Mg-6Al-0.3Mn). New magnesium alloys are being developed with higher strength, ductility, and creep resistance at room and elevated temperatures[2-3].

This article summarizes an ongoing effort to establish a scientific foundation of computational thermodynamics and kinetics of magnesium alloys to achieve accelerated design and optimization of these alloys for weight reduction in the transportation industries. All compositions are listed as wt% unless otherwise stated.

**Computational thermodynamics and alloy design**

Originated from the early work of Kaufman and Bernstein[4], the CALPHAD (CALculation of PHAse Diagrams) technique—based on computational thermodynamics of alloy systems—has matured over the past few decades. Many commercial software packages, such as Thermo-Calc, FactSage, and Pandat, have become important integrated computational materials engineering (ICME) tools used in the development of new materials and products[5]. This section demonstrates examples of applying computational thermodynamics and CALPHAD modeling in the development of new creep-resistant magnesium alloys using the Pandat code and its PanMagnesium database[6].

**Mg-Al system**

Aluminum is the most widely used alloying addition in magnesium for strengthening and castability. Figure 1(a) shows the calculated Mg-Al phase diagram. Two eutectic reactions are important to the phase constitution of Mg-Al binary alloys:

1) 450°C L → Al + Mg2Al3
2) 436°C L → Mg + Mg17Al12

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Commercial cast and wrought magnesium alloys (AZ91, AM60, and AZ31) contain less than 10% Al, and the microstructure of these Mg-Al based alloys is generally characterized by formation of the Mg$_{17}$Al$_{12}$ phase. The low eutectic temperature (436°C) of the Mg$_{17}$Al$_{12}$ phase limits the application of Mg-Al alloys to temperatures below 125°C, above which the discontinuous precipitation of the Mg$_{17}$Al$_{12}$ phase leads to substantial creep deformation\cite{2}. Therefore, possible approaches for improving creep resistance in Mg-Al based alloys include: suppressing the formation of the Mg$_{17}$Al$_{12}$ phase; pinning grain boundary sliding; and slowing solute diffusion in the magnesium matrix.

**Mg-Al-Ce system**

Earlier experimental work\cite{6, 7} shows that adding rare earth elements (RE) in the form of mischmetal can improve the creep resistance of Mg-Al based alloys, especially when aluminum content is low (less than 4%). This led to the development of AE series alloys, AE42 (Mg-4Al-2RE) and AE44 (Mg-4Al-2RE), where the mischmetal RE generally contains more than 60% Ce (balance La, Nd, and Pr). Figure 1(b) shows the calculated liquidus projection of the Mg-Al-Ce system in the Mg-rich corner. Generally, the liquidus temperature decreases with Al addition (up to at least roughly 10%) and Ce (also up to at least roughly 10%), with the following two type II invariant reactions marked at 871K (598°C) and 835K (562°C), respectively:

1) 598°C L + (Al,Mg)$_2$Ce → Mg + Mg$_{12}$Ce
2) 562°C L + (Al,Mg)$_2$Ce → Mg + Al$_{11}$Ce$_3$

The calculated solidification paths of AE42 and AE44 alloys using the Scheil model, based on the assumption of complete mixing in the liquid but no diffusion in the solid, are superimposed in the phase diagram shown in Fig. 1(b). Based on simulation results, the solidification sequence for both alloys is as follows:

1) Nucleation of primary magnesium: L → L + Mg
2) Binary eutectic reaction: L → L + Mg + (Al,Mg)$_2$Ce
3) Type II invariant reaction:
   L + (Al,Mg)$_2$Ce → L + Mg + Al$_{11}$Ce$_3$
4) Ternary eutectic reaction:
   L → Mg + Al$_{11}$Ce$_3$ + Mg$_{17}$Al$_{12}$

Adding 2.4% Ce to Mg-Al alloys results in the formation of Al$_{11}$Ce$_3$, in addition to the Mg$_{17}$Al$_{12}$ phase in the Mg-Al binary system. More detailed calculation shows that 15% Ce is required to completely suppress the formation of the Mg$_{17}$Al$_{12}$ phase in the Mg-4Al alloy based on the Scheil model\cite{8}, which can be used as guidance to design the ternary alloy, avoiding Mg$_{17}$Al$_{12}$ phase formation in elevated temperature applications. Figure 1(b) also shows the solidification sequence of the AE416 (Mg-4Al-16Ce) alloy as follows:

1) Nucleation of (Al,Mg)$_2$Ce phase:
   L → L + (Al,Mg)$_2$Ce
2) Binary eutectic reaction:
   L → L + Mg + (Al,Mg)$_2$Ce
3) Type II invariant reaction:
   L + (Al,Mg)$_2$Ce → L + Mg + Mg$_{12}$Ce
4) Binary eutectic reaction: L → Mg + Mg$_{12}$Ce

The eutectic temperatures for Al$_{11}$Ce$_3$, (Al,Mg)$_2$Ce, and Mg$_{12}$Ce phases are calculated as 560°C, 622°C, and 867°C, respectively, which are all significantly higher than that of the Mg$_{17}$Al$_{12}$ phase (436°C). The Scheil model was also used to calculate the fraction of phases formed in the three AE alloys according to the above solidification paths. Calculation results are summarized in Table 1 and compared with commercial AM50 (Mg-5Al-0.3Mn) alloy. In AE alloys, 4-5% Al is generally needed for die castability, while it is very expensive to use 16% Ce (e.g., AE416 alloy) to suppress formation of Mg$_{17}$Al$_{12}$. On the
other hand, AE44 alloy has a significantly lower fraction of Mg17Al12, and thus, much better high-temperature strength compared with AE42 or AM50 alloy. Therefore, the AE44 alloy was selected for the Corvette engine cradle application where the operating temperature approaches 150°C[9].

Mg-Al-Ca system

The Mg-Al-Ca system was investigated to replace the more expensive AE alloys. Figure 1(c) shows the calculated liquidus projection of the Mg-Al-Ca system, superimposed by the solidification paths of three Mg-Al-Ca alloys, AX51 (Mg-5Al-1Ca), AX52 (Mg-5Al-2Ca), and AX53 (Mg-5Al-3Ca), calculated using the Scheil model. Based on simulation results, the solidification sequence for AX51 and AX52 alloys are as follows:

1) Nucleation of primary magnesium: \( L \rightarrow L + Mg \)
2) Binary eutectic reaction: \( L \rightarrow L + Mg + (Mg,Al)_2Ca \)
3) Type II invariant reaction:
   \( L + (Mg,Al)_2Ca \rightarrow L + Mg + Mg_17Al_{12} \)
4) Binary eutectic reaction: \( L \rightarrow Mg + Mg_17Al_{12} \)

AX53 alloy has a different ternary eutectic reaction where Mg2Ca is formed instead of Mg17Al12, resulting in a slightly different solidification path:

1) Nucleation of primary magnesium: \( L \rightarrow L + Mg \)
2) Binary eutectic reaction: \( L \rightarrow L + Mg + (Mg,Al)_2Ca \)
3) Ternary eutectic reaction:
   \( L \rightarrow Mg + (Mg,Al)_2Ca + Mg_{2}Ca \)

Both (Mg,Al)2Ca (C36) and Mg2Ca (C14) phases have high eutectic temperatures and are beneficial to the creep resistance of Mg-Al-Ca alloys, likely due to the grain boundary strengthening mechanism[10]. The Scheil model was also used to calculate the fractions of (Mg,Al)2Ca, Mg2Ca, and Mg17Al12 phases formed in all the AX alloys according to the above solidification paths, and results are summarized in Table 2. It only requires 2.8% Ca to completely suppress the formation of Mg17Al12 in the Mg-5Al alloy[9], which compares to 15% Ce needed in the Mg-4Al alloy. Therefore, Ca is more effective (and less expensive) than rare earth elements (such as Ce) in suppressing the Mg17Al12 phase formation in Mg-Al based alloys. AX53 alloy is presently being evaluated by General Motors for automotive powertrain applications.

High-throughput diffusion multiples for atomic mobility database development

While the thermodynamic characteristics and equilibrium phase diagrams for magnesium and its alloys are reasonably well understood, the phase transformation and diffusion behavior of these alloys is not yet clear[11]. Diffusion multiples can be used to generate plenty of diffusion data to fill this gap. A diffusion multiple is an assembly of several metal blocks arranged in a predesigned geometry to allow many diffusion couples and triples to be assembled in a single sample[12,13].

To study major magnesium alloy systems, diffusion multiples provide large amounts of binary diffusion profiles for nine binary systems (Mg-Al, Mg-Zn, Mg-Sn, Mg-Ca, Mg-Sr, Mg-Mn, Al-Zn, Al-Mn, and Mn-Zn) as input to diffusivity extraction. Figure 2(a) shows an example of an Mg-Mn diffusion multiple heat treated at 600°C for 48 hours. No intermetallics layer

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**TABLE 2 — SCHEIL SIMULATION AND EXPERIMENTAL RESULTS OF SECOND PHASES OF MG-AL-Ca ALLOYS (BASELINE: AM50 ALLOY)**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Scheil calculation, vol%</th>
<th>Measurement, vol%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Mg,Al)2Ca</td>
<td>Mg2Ca</td>
</tr>
<tr>
<td>AX51</td>
<td>2.0</td>
<td>0</td>
</tr>
<tr>
<td>AX52</td>
<td>4.1</td>
<td>0</td>
</tr>
<tr>
<td>AX53</td>
<td>5.8</td>
<td>0.1</td>
</tr>
<tr>
<td>AM50</td>
<td>—</td>
<td>—</td>
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</table>
is observed and the concentration profile is measured across the Mg-Mn interface using EPMA (electron probe micro-analysis). By using the forward simulation method\cite{13}, the interdiffusion coefficients are extracted, as shown in Fig. 2(b). This is thought to be the first time that the interdiffusion coefficients of the hcp (Mg) phase of an Mg-Mn system are reported. Results clearly show that the forward simulation method can be used to extract impurity diffusion coefficients, whereas the Sauer-Freise method\cite{14} shows wide scatter of data near pure Mg.

A preliminary atomic mobility database of Mg alloys of the Mg-Al-Zn-Mn-Sn-Ca-Sr system is established based on assessment of diffusion data in the literature using the CALPHAD approach. The self-diffusion, impurity diffusion, and interdiffusion coefficients are input to generate the atomic mobility. Empirical methods for estimating the self-diffusion and impurity diffusion coefficients are used to obtain the unavailable data. Most of the literature data are on the diffusion of the Mg-Al binary system below 420°C. Impurity diffusion coefficients of Zn and Sn in hcp (Mg) are reported. For Mn, Ca, and Sr, no experimental data exist yet. Because Al, Mn, Ca, Sn, and Sr do not have a stable hcp structure, the related atomic mobility parameters are estimated using empirical methods. Due to the scarcity of literature data, this preliminary database is still at its early stage and will be improved with ongoing diffusion experiments. Figure 3 shows the calculated interdiffusion coefficients in the Mg rich region of the Mg-Al system along with experimental data\cite{15,17}.

**Precipitation simulation using KWN model**

The classic KWN (Kampmann-Wagner-numerical) precipitation model\cite{18} implemented in the PanPrecipitation module of the Pandat software is used to simulate the precipitation of magnesium alloys during the aging process. This model features the capability of simulating nucleation, growth, and coarsening simultaneously. The PanMagnesium thermodynamic database and the preliminary atomic mobility database are used to generate driving force, phase equilibria, and diffusivity for quantitative simulation.

Coupling to the PanMagnesium thermodynamic database and the preliminary atomic mobility database described above, the precipitation of Mg$_2$Sn at 200°C in two supersaturated Mg-Sn alloys is simulated. The shape of the Mg$_2$Sn precipitate is not
spherical according to experimental observations\textsuperscript{[19]}. By assuming a shape-preserved growth, the precipitate’s shape could be treated as a sphere. The conversion method described by Zhang, et al.\textsuperscript{[20]}, is used to calculate the equivalent particle size. Figure 4(a) shows that the calculated number density for the two Mg-Sn alloys is in agreement with the experimental data. Figure 4(b) shows the predicted radius for Mg-1.9 at% Sn alloy at 240 hours is 128 nm, which is consistent with the experimental value of 112 nm. However, for the Mg-1.3 at% Sn alloy, the simulated radius at 1000 hours is 160 nm, which is lower than the experimental value of 197 nm, but still within the experimental error range.

**Summary**

Computational thermodynamics and CALPHAD modeling, when combined with critical experimental validation, can be used to guide the selection and development of new magnesium alloys. It is demonstrated that Ca is more effective than RE elements (such as Ce) in suppressing the formation of the Mg$_{17}$Al$_{12}$ phase in binary Mg-Al alloys and introducing more thermally stable phases in the ternary alloys, thus improving their creep resistance and strength at elevated temperatures. AE44 alloy is used in engine cradle applications and AX53 alloy is being developed by GM for automotive powertrain applications.

The diffusion-multiple method, assembling several metal/alloy blocks in a predesigned geometry, allows many diffusion couples and triples in a single sample and is a high-throughput technique for extracting diffusivities for multicomponent alloy systems. A preliminary atomic mobility database of Mg alloys is established based on literature data and estimation from empirical methods. A precipitation simulation based on the classical KWN model has been demonstrated in Mg-Sn alloys, showing good agreement with experimental results.\textsuperscript{~AM&P}

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