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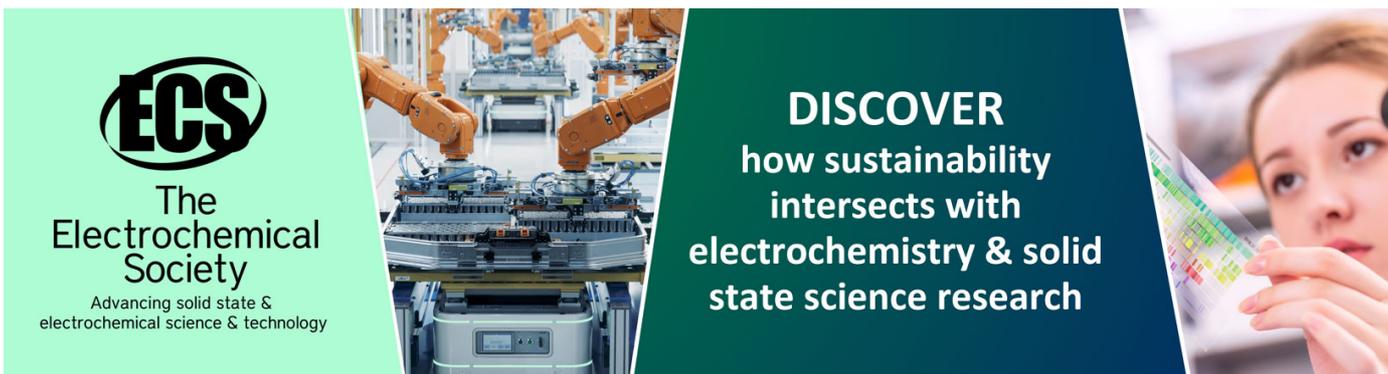
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Recent research progress on CALPHAD-based ICME modeling of magnesium alloys

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Abstract. Magnesium alloys combine several favorable attributes, including low density, high strength-to-weight ratio, good damping capability and so on. However, their application is limited by their relatively poor high-temperature performance and creep resistance. These deficiencies can be alleviated by the alloying-induced solid solution and precipitation strengthening. The integrated computational materials engineering (ICME) approach based on the calculation of phase diagram (CALPHAD) software is shown to accurately quantify the effect of alloying elements on the strengthening precipitates. Thus, it is quite instrumental for enhancing the alloy development process, alloy design, and manufacturing optimization. This paper summarizes the theoretical background of CALPHAD-based ICME, outlines the current research progress in this direction and provides some insights into future development.

1. Introduction

Magnesium (Mg) is a lightweight structural metal, which density (1.74 g/cm^3) is lower by 20% than that of aluminum (2.70 g/cm^3) and more than four times lower than that of carbon steel (7.89 g/cm^3). It is widely applied in industries where weight reduction is critical, including aerospace, automotive and portable electronic devices, given its favorable attributes such as high strength-to-weight ratio, good heat and electrical conductivity, excellent castability and good damping properties [1-5]. However, due to its lower high-temperature strength, as compared to aluminum and steel alloys, the application of Mg has been limited to room-temperature applications [6-8]. Alloying has become one of the most common methods for the strengthening of Mg alloys, introducing a solid solution strengthening and precipitation hardening effects. Modern Mg alloys usually are complex chemical systems including Al, Zn, Mn, Si, Sn, and rare earth elements like Gd, Nd, Y, and Sm [9-11]. To more efficiently develop multi-component Mg alloys, the equilibrium phase constructions, precipitation hardening mechanisms, and the process-structure-property relationship of the systems must be fully understood quantitatively.

Computational simulation such as CALPHAD (Calculation of phase diagrams) modeling holds promise to understand and predict structures and properties beyond known information [12]. Recently, the CALPHAD approach has been broadened to a holistic ICME (Integrated Computational Materials Engineering) framework in the design and development of new materials and products [13, 14]. The



application of this approach in the development of novel alloys, including Al, steel and high-entropy alloys, simplifies the composition design procedure and reduces the development cost [15-18].

This article presents a summary of recent research progress on the application of CALPHAD-based ICME modeling on Mg alloy development and discusses the future trend of this promising alloy development approach. It aims to provide a brief introduction of the fundamentals of the above-mentioned modeling method and to explore the application of this integrated simulation tool in the development of novel Mg alloys.

2. Optimization of Mg alloys

Current development of novel Mg alloys has been focused on the development of creep-resistant Mg alloys, high-strength high-ductility Mg alloys, and Mg-based composite.

Due to its hexagonal crystal structure, Mg alloys have been widely known to have poor mechanical properties at elevated temperatures. The addition of rare earth elements, including Y [19, 20], Ce [21], Nd [22, 23], Gd [19, 24], and Sm [25, 26], introduces dense and uniformly distributed nano-scale precipitate phases, which act as practical obstacles for dislocations and grain boundary motions. It is thus one of the essential methods to develop creep-resistant Mg alloys for elevated-temperature applications. Mg-RE-based alloys have been an increasing research and engineering focus in recent Mg alloys' community. For example, Mg-RE-based Elektron 21 from Magnesium Elektron [27] exhibited high creep resistance at 200°C and was used in engine parts of the military Apache helicopter.

The strength and ductility of Mg alloys need further improvement for increasing industrial needs. Mg-Li dual-phase alloy is an alloy that is lighter than pure Mg. Further addition of Y, Al, Si, Sn improves thermal-stability of the precipitate phase and thus further increase strength levels of Mg-Li alloys [28].

Mg-based composites reinforced by ceramic particles (SiC, Al₂O₃, etc.) combine high characteristics of strength, strength-to-weight ratio, and wear resistivity. Chen et al. [29] reported a new kind of SiC-reinforced Mg-Zn alloy that made a record-yield strength exceeding 700 MPa. On the other hand, in-situ Mg-based composite makes use of physical chemistry reactions of matrix and solute atoms to produce evenly distributed second phase, making it a great candidate for brake block applications [30].

It can be seen that nano-scale precipitate particle strengthening is the major approach for current Mg alloys strengthening. Combination of phase diagram calculation (CALPHAD) and ICME simulates the size, density, and distribution of nano-scale particles. Being supplemented by a quantitative understanding of the structure-property relationship of these materials, this information enables us to quantitatively calculate and predict the effects of different alloying elements on the final products' properties.

3. Fundamentals of CALPHAD-based ICME

CALPHAD-based ICME relies on the combination of CALPHAD and classical nucleation and growth theory. In classical nucleation theory,

$$J = \frac{dN}{dt} = Z\beta^* N_v \exp\left(-\frac{\Delta G^*}{k_B T}\right) \exp\left(-\frac{\tau}{t}\right) \quad (1)$$

where Z is the Zeldovich factor, which represents the probability that the nucleus, once having reached a critical size, grows into a stable phase; β^* is the rate at which atoms attach to nuclei; N_v is the number of available nucleation sites; ΔG^* is the free energy barrier for nucleation, which depends on thermodynamic driving force ΔG_v and interfacial energy γ ; τ is incubation time, describing the time for nuclei to grow to critical size; while k_B is the Boltzmann constant.

At the growth stage,

$$v = \frac{dR}{dt} = \frac{K}{R} \left(\frac{1}{R^*} - \frac{1}{R}\right) \quad (2)$$

$$\overline{R^3} - \overline{R_0^3} = \frac{4}{9} K t \quad (3)$$

$$K = \frac{2\gamma V_{at}^p}{(C^{\alpha\beta})[M]^{-1}[C^{\alpha\beta}]}$$

where $(C^{\alpha\beta})$ and $[C^{\alpha\beta}]$ where are the row and column vectors of the solute concentration differences between matrix α and precipitate β , while $[M]$ is the chemical mobility matrix.

From Equations (1-3), the nucleation and growth of nano-scale particles rely on the thermodynamic energy, interfacial energy, diffusion coefficient and so on. While CALPHAD provides thermodynamic energy and diffusion coefficient, the other parameters can be obtained through crucial experiments and other simulation methods. Simulation results include the precipitate kind, size and number density under different aging stages and conditions. Figure 1 is a flowchart for CALPHAD-based ICME.

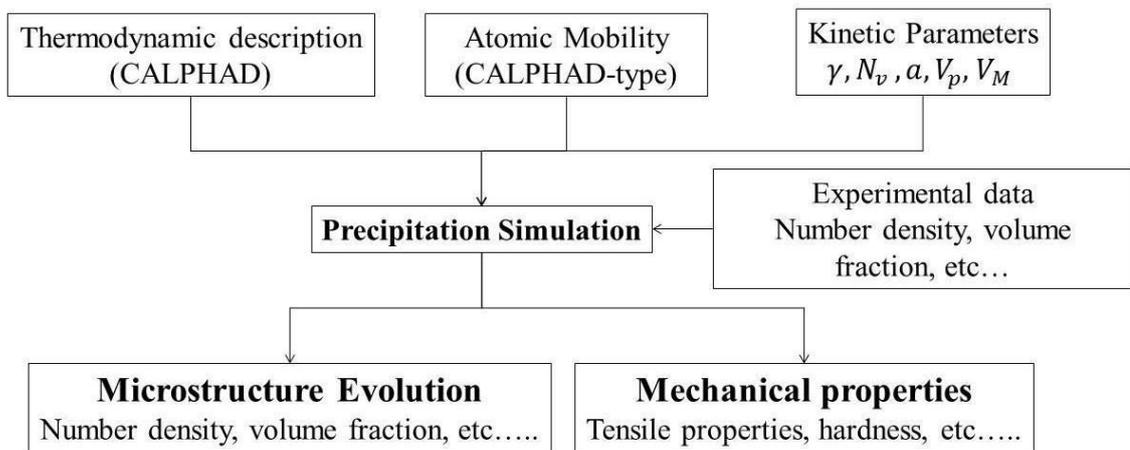


Figure 1. Schematic Procedure for CALPHAD-based ICME modeling [31]

The CALPHAD approach is a phenomenological thermodynamic methodology to obtain thermodynamic descriptions of multicomponent systems. The term thermodynamic description represents the parameters for Gibbs energies of all phases in the target system. The idea of classical CALPHAD approach is that: based on available information such as phase equilibria, heat capacities, formation enthalpies and structural information the Gibbs energy of each phase within the system is obtained and then used to predict phase constructions where data are lacking. The Gibbs energy model can be described as follows:

$$G_m^\varphi = G^{ref} + G^{id} + G^{ex} \quad (4)$$

Here G^{ref} defines a surface of reference. G^{id} is the molar configurational entropy. G^{ex} is the excess Gibbs energy, for which the models are determined according to the phase's crystal structure.

CALPHAD approach also gives atomic mobility of elemental species. It is obtained based on experimental information such as tracer diffusion, inter-diffusion and composition profiles of diffusion couples and used to extrapolate diffusion data beyond known conditions. In a system containing n elements, the diffusion coefficient of element B can be expressed as:

$$D_{Bj}^n = \sum_i (\delta_{iB} - x_B) x_i M_i \left(\frac{\delta \mu_i}{\delta x_j} - \frac{\delta \mu_i}{\delta x_n} \right) \quad (5)$$

where δ_{iB} is Kronecker delta, x_B is mole fraction of element B, M_i is mobility of element i , μ_i is chemical potential. $M_i = \exp\left(\frac{\Psi_i}{RT}\right) \frac{1}{RT}$. Here Ψ_i can be described using a similar way as Equation (4) and, thus, can be

calculated by the CALPHAD approach. Added with the chemical potential which is another form of thermodynamic energy, the diffusion coefficient can be modeled.

4. Current CALPHAD-based ICME database development for Mg alloys

4.1. CALPHAD Thermodynamic Database

The development of CALPHAD thermodynamic database is based on the key experimental data such as phase equilibria or phase transformation temperature. In phase equilibria identification experiments, Mg alloys are sealed in Ar/Hr protected quartz or glass tubes to avoid contact with air, then annealed at target temperatures for a sufficiently long time for equilibrium, followed by room-temperature quench. SEM, TEM or XRD then determine the phase constructions. Zhang et al. [32], Xia et al. [33] used such methods to evaluate phase equilibria of Mg-RE systems Mg-Nd-Zn and Mg-Sm-Zn. The determination of phase transformation temperatures relies on DSC or DTA. Schmid-Fetzer [34] was the first to seal Mg alloys in Ta tubes for DSC tests to avoid oxidation. Similar methods have been applied in the development of Mg-Al-Sn [34], Mg-Mn-Ni [35], Mg-Ca-Mn [35] systems' phase diagrams.

The development of Mg alloys' CALPHAD database has been an active research topic. At present, there have been several commercial Mg alloy CALPHAD databases, such as PanMg from CompuTherm (USA) [36]. It includes Al, Zn, Mn, Y, Gd and other in total 25 elements. In addition to phase diagram calculation, it is also capable of Scheil calculation to simulate solidification experiments and volume fractions [37, 38]. However, most of current Mg CALPHAD databases is focused on ternary or even binary systems. Quarternary systems are only reported for Mg-Mn-Fe-Ni [35], Mg-Ce-Gd-Y [39], Mg-Sn-In-Zn [40] and several other rare cases. Multi-component systems' descriptions are rarer, for which researchers usually extend from ternary systems, where critical data such as liquidus temperatures cannot be as accurate. Furthermore, the information of new Mg alloys is lacking. For example, Mg-RE-RE' alloys have drawn great interests in Mg community [41, 42]. However, to the best of the author knowledge, no CALPHAD databases for this group of alloys are available yet.

4.2. CALPHAD-Type Mobility Database

CALPHAD-type mobility database is developed according to diffusion coefficients that are experimentally measured. Das et al. [43] prepared Mg-Gd and Mg-Y diffusion couples, wrapped with Ta coil and annealed under Ar protection. They identified the compositional profiles near interfaces and simulated the mobility databases for the two systems. Zhong et al. [44] measured diffusion coefficients of Ca and Zn in Mg by a liquid-solid diffusion couple. Meanwhile, simulation is an increasingly effective way to obtain diffusion parameters. Zhou and Liu [45] applied high-throughput first principle calculations for the diffusion coefficients of 47 elements in the Mg matrix.

Mg alloys' mobility database is currently limited to binary systems such as Mg-Al [46], Mg-Zn [46], Mg-Ca [43] and several ternary systems Mg-Al-Sn [15]. MOBMG1 database from Thermocalc (Sweden) [47] simulates the diffusion of Al, Ca, Zn, Sn and other in total 23 elements in the Mg matrix. Other than diffusion coefficients, mobility databases can also be used to predict annealing time/temperature, diffusion couple compositional profile, solidification volume fraction, etc. However, compared to other mature alloys systems like Al or steel, there are shortages of Mg mobility database: not only there are limited systems reported, but also the interaction of solute atoms is not included. The accuracy and small inclusion have limited their wide applications.

4.3. Mg Alloys' ICME Database

Classical nucleation and growth theory have been used for simulation and calculation of precipitate hardening of Mg alloys for decades. Hutchinson [48] calculated the number density and volume fraction of

β - $Mg_{17}Al_{12}$ precipitates in AZ91 (Mg-9Al-Zn) during a 200°C isothermal annealing. The resulting simulation data correspond very well to 200°C experimental measurements. However, due to the lack of general thermodynamic and kinetic parameters, classical nucleation and growth model is limited to the system composition and temperature range that the key experimental information was obtained. It has limited prediction ability when alloy composition or aging temperature changes drastically. Such shortages are overcome when classical nucleation and growth model is combined with CALPHAD. As a comparison, Zhang C [49] integrated PanMg and Hutchinson's model within the ICME framework. The results are shown in figure 2. It is clear that Zhang's simulation yields a good agreement and prediction for the age-hardening response of A9, AZ31, AZ91 alloys at three different temperatures (150, 165, and 200°C).

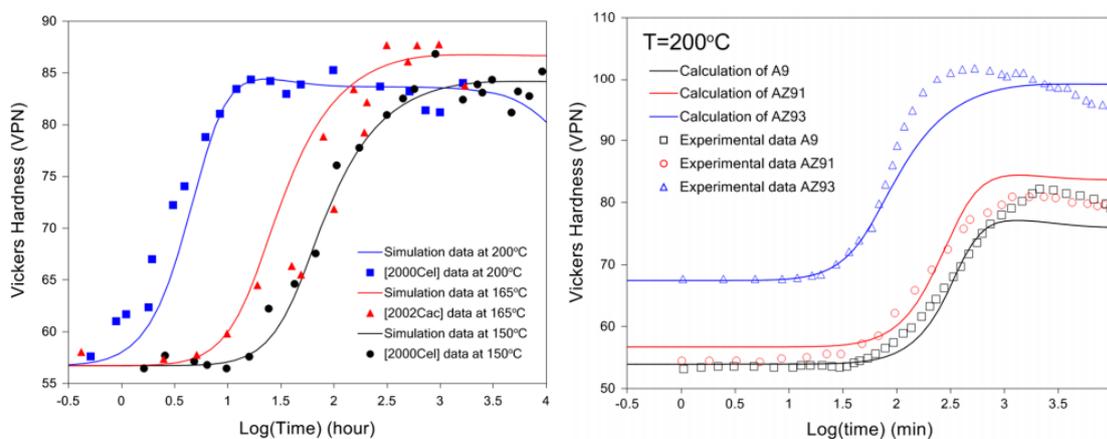


Figure 2. Simulated Age-Hardening Response of AZ91 Alloy at 150°C, 165°C, 200°C (a); Simulated Age-Hardening Response of A9, AZ31, AZ91 Alloy at 200°C (b)

Xia et al. [50] were the first to simulate precipitate particles in Mg-RE-based alloys (Mg-Nd-Zn and Mg-Sm-Zn). For Mg-Nd-Zn, they started with Mg-3Nd-0.2Zn as the target system. The critical experimental parameters (number density, volume fraction) of the significant strengthening particle β' were first obtained via TEM characterizations. The CALPHAD thermodynamic and mobility databases were built, accordingly. Eventually, the integration of CALPHAD databases and nucleation parameters were developed and optimized to experimental measurements. The obtained databases not only model and predict the evolution of β' particles, but also calculate the age-hardening response. The yield strength of various Mg-Nd-Zn alloys after different aging conditions was also calculated and compared to experimental data, from which good agreement was found.

Luo [51] applied ICME calculations for the Mg-Al-Sn system. Two kinds of precipitate phases were considered, $MgSn_2$ and $Mg_{17}Al_{12}$, either type of which dominates in different stages of aging. Luo developed Mg-Al-Sn ternary system first and included both strengthening phases for calculation. By comparing the Gibbs energies of $MgSn_2$ and $Mg_{17}Al_{12}$, the primary strengthening particles were determined under different aging conditions. The simulation results correspond well to experiments.

It is noteworthy that CALPHAD-based ICME can also be applied to the design and optimization of in-situ Mg-composites, where strengthening particles are produced by chemical reactions that are thermodynamically controlled. For example, Fan [52] calculated the effects of Mn, Nd, Ce, La, Ni on the thermodynamic reaction of AlN particles in Mg composite. The number density and volume fraction of strengthening particles can thus be predicted in these systems. Similar, yet more accurate, calculations can be performed for other Mg-based composites upon their integration with the CALPHAD database.

5. Conclusions

Mg alloys, because of their low density and high strength-to-weight ratio, are widely used in the industries where lightweight is crucial, including aerospace, automotive and consumer electronics. Strengthening of Mg alloys relies on careful control of nano-scale precipitate particles. CALPHAD-based ICME provides essential information for Mg alloys' composition and heat treatment condition design and optimization. Such databases can minimize experimental cost by quantitative modeling and predicting the evolution of materials' properties under different compositions and heat treatment conditions. From the above discussion, current Mg alloys' ICME databases can model and predict ternary Mg alloys' thermodynamic, mobility and precipitation quite well. However, more effort is in need for future development of Mg alloy ICME databases:

- ✓ Higher-order systems' databases are still lacking and require further research. For this purpose, more detailed experimental data are necessary, including unknown phases' crystal structure, chemical compositions, and thermodynamic stabilities;
- ✓ Sub-databases like thermodynamic and mobility need further optimization;
- ✓ A systematic understanding of structure-property relationship is required when combining CALPHAD databases and strengthening particle data. The final integration of CALPHAD, precipitate, and structure-property databases gives a reliable and highly efficient way to design novel Mg alloys to meet increasing industrial needs.

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