Thermodynamic and thermophysical databases of multi-component Al alloys and their applications to simulation of microstructure evolution

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Content

1. Background: Data bases are the core part of ICME

2. Thermodynamic and thermo-physical databases for Al alloy
   2.1 Thermodynamic database
   2.2 Diffusivity database
   2.3 Thermo-physical databases

3. Simulation of microstructure evolution
   3.1 Al-Cu-Mg-Si alloys during solidification
   3.2 Dissolution of Al-Mg-Si alloys
   3.3 Precipitation of $\beta''$ in Al-Mg-Si alloys

4. Summary
Al-based alloys are widely used as aeronautic and civil materials.

Two kinds of database

1. Normal database: collect the literature data and manage them
2. Scientific database: physically sound parameters are stored

No thermo-physical databases for Al alloys

Existing thermodynamic databases for Al alloys: limited literature data

Our work: (I). To establish thermodynamic and thermophysical databases (Since 2003) for Al alloys via a hybrid approach of Experi., FP and CALPHAD (II). To describe the microstructural evolution of Al alloys during processing routes (solidification, ageing etc.)
1. Background: Data bases are the core part of ICME

Our strategy to investigate the microstructure of Al alloys

- Thermodynamic database
- Thermophysical databases
- Phase field simulation
- TEM+3DAP

Quantitative description of microstructure evolution of Al alloys in solidification and heat treatment process
# Content

1. **Background:**

2. **Thermodynamic and thermo-physical databases for Al alloy**
   - 2.1 Thermodynamic database
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   - 2.3 Thermo-physical databases

3. **Simulation of microstructure evolution**
   - 3.1 Al-Cu-Mg-Si alloys during solidification
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4. **Summary**
2.1 Thermodynamic database of Al alloys (TCAL4)


2.3 Molar volume database for Al-Cu-Mg-Si

- **Molar volume of unary system**

\[ V(T, P) = V(T, P_0) + c(T) \ln \left( \frac{\kappa_T(T, P)}{\kappa_T(T, P_0)} \right) \]  

\( \kappa_T \) - Isothermal compressibility

\( c(T) \) - Parameter to fit the high pressure data

the molar volume at 1 bar

the pressure contribution for molar volume

- **Molar volume of binary solutions**

\[ Z = \sum_{i=1}^{2} x_i Z_i + Z^E \]  

where, \( x_i \)  indicates the mole fraction of component \( i \) a binary system,

\( Z^E \)  is the excess volume at 1 bar.

- **Molar volume of multicomponent solution phases**

The molar volume of multicomponent solution phases are extrapolated from the parameters of the binary systems.

- **Molar volume of compounds**

  - **Stoichiometric phases**

\[ Z_m = \sum_{i=1}^{2} x_i Z_i + a \]

\( a \) — variable to be evaluated

  - **Non-stoichiometric phases**

\[ Z_m = \sum y'_i y''_j y'''_k Z_{ijk} + Z^E_m \]
2.3 Molar volume database for Al-Cu-Mg-Si

Fig. 1 The calculated molar volumes. (a) The molar volume of liquid Al at 1 bar, (b) the molar volume of Al-Mg system at 1 bar.

2.3 Molar volume database for Al-Cu-Mg-Si

**Fig. 2** Calculated densities of (a) the Al-Cu-Si melts at 1300 K and (b) the Al-Mg-Si melts at 973 K.
2.3 Molar volume database for Al-Cu-Mg-Si

**Fig. 3 (a)** The variation of molar volume with temperature of 6061 commercial alloy.
The Arrhenius equation describing the temperature dependence of the viscosity holds for the pure liquids.

\[ \eta = \eta_0 \exp \left( \frac{E}{RT} \right) \]

- \( \eta_0 \) ----- the pre-exponential factor
- \( E \) ----- the activation energy
- \( R \) ----- is the universal gas constant.

2. Binary liquid – CALPHD-type equation

\[ \eta = c_A \eta_A + c_B \eta_B + c_A c_B \eta^E \]

3. Multicomponent liquid

The viscosities of multicomponent liquid phases are extrapolated from the parameters of the binary systems.
2.4 Viscosity database for Al-Cu-Mg-Si

Fig. 4 Calculated viscosity of (a) pure Al, (b) binary Al-Mg

F. Zhang, Y. Du, S. Liu et al., Calphad, 49 (2015) 79-86
Fig. 5 Calculated viscosities at the sections A, B, C of the Al-Cu-Si system compared with the Kobatake’s data
2.4 Viscosity database for Al-Cu-Mg-Si

Fig. 6 Calculated viscosities of A356, in comparison with the experimental data
2.5 Thermal conductivity database for Al-Cu-Mg-Si

- **Thermal conductivity of pure metals**

\[ \lambda_0 = A + B \cdot T + C \cdot T^{-1} \]

in which \( \lambda_0 \) is the thermal conductivity of pure elements or stoichiometric phases, and \( T \) is the absolute temperature.

- **Thermal conductivity of binary solutions**

\[ \lambda_{AB}^\alpha = x_A \cdot \lambda_A + x_B \cdot \lambda_B + x_A \cdot x_B \cdot \sum_{i=0}^{L_{AB}^\alpha} (x_A - x_B)^i \lambda_{AB} \]

where \( \lambda_{AB} \) is the thermal conductivity of \( \alpha \) solid solution. While \( x_A \) and \( \lambda_A \) are the mole fraction and thermal conductivity of pure element A, respectively. \( L_{AB} \) is the interaction parameter, which describes the effect of solute atoms on the thermal conductivity.

- **Impediment of heat transfer by interfaces**

\[ \lambda_{\alpha+\beta} = n_\alpha \cdot \lambda_\alpha + n_\beta \cdot \lambda_\beta - n_\alpha \cdot n_\beta \cdot \sum_{j=0}^{M_{\alpha+\beta}} j \lambda_{\alpha+\beta} \cdot (n_\alpha - n_\beta)^j \]

where \( \lambda_{\alpha+\beta} \) is the thermal conductivity of alloys in \( (\alpha) + (\beta) \) two-phase region. While \( n_\alpha \) and \( \lambda_\alpha \) are the mole fraction and thermal conductivity of \( \alpha \) solution phase. \( M_{\alpha+\beta} \) is the interface scattering parameter, which describes the impediment of interfaces on the heat transfer.
2.5 Thermal conductivity database for Al-Cu-Mg-Si

- Determination of thermal conductivity

\[ \lambda = \alpha \cdot \rho \cdot C_p \]

where:
- \( \lambda \) is thermal conductivity
- \( \alpha \) is thermal diffusivity
- \( C_p \) is the specific heat capacity
- \( \rho \) is density

\[ \Phi = 12.5 \text{ mm} \]
\[ d = 2.5 \text{ mm} \]

Fig. 7 NETZSCH LFA 457 laser conductometer
2.5 Thermal conductivity database for Al-Cu-Mg-Si

- Thermal conductivity of pure Al metal and Al-Cu solutions

**Fig. 8** Calculated thermal conductivity of pure Al metal.

**Fig. 9** Calculated thermal conductivity of Al-Cu solid solution.

Cong Zhang, Yong Du et al., Int. J. Thermophys., 36, 2869-80(2015).
2.5 Thermal conductivity database for Al-Cu-Mg-Si

- Thermal conductivity of Al-Si-Cu alloys

**Fig. 10** Calculated thermal conductivity of Al-Cu-Si alloys in the (Al)+Al₂Cu+(Si) three-phase region.
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3. Simulation of microstructure evolution
   3.1 Al-Cu-Mg-Si alloys during solidification (MICRESS)
   3.2 Dissolution of Al-Mg-Si alloys (DICTRA)
   3.3 Precipitation of β” in Al-Mg-Si alloys (Our own code)

4. Summary
### 3.1 Experimental data of Al-4.5Cu-0.5Mg-1.0Si wt. % alloy

**Experimental result (Al-4.5Cu-0.5Mg-1.0Si wt. %):**


**Fig. 11** Typical dendrite structure in transverse section of the directionally solidified Al-4.5Cu-0.5Mg-1.0Si (wt.%) alloy at a growth rate of 0.05 mm/s with a temperature gradient of 50 K/cm at the liquid–solid interface.

**Fig. 12** Crystal structure of Q phase.

### Tab.1 Phase information

<table>
<thead>
<tr>
<th>Phase</th>
<th>crystal system</th>
<th>Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Al)</td>
<td>Fcc</td>
<td>( a=4.056 ) Å</td>
</tr>
<tr>
<td>( Al_2Cu (\theta) )</td>
<td>Fct</td>
<td>( a=b=6.6 ) Å, ( c=4.87 ) Å</td>
</tr>
<tr>
<td>(Si)</td>
<td>Diamand</td>
<td>( a=5.430 ) Å</td>
</tr>
<tr>
<td>Q (( Al_3Cu_2Mg_9Si_7 ))</td>
<td>Hcp</td>
<td>( a=b=1.039 ) Å, ( c=0.402 ) Å, ( \gamma=120^\circ )</td>
</tr>
</tbody>
</table>

[Inorganic crystal structure database, 2008]
3.1 Multi-phase-field model and thermalphysical parameters

A general free energy function split into interfacial \( f^{\text{int}} \) and chemical energy \( f^{\text{chem}} \):

\[
F = \int_{\Omega} f^{\text{int}} + f^{\text{chem}}
\]

\[
f^{\text{int}} = \sum_{\alpha, \beta = 1, \ldots, N, \alpha \neq \beta} 4\sigma_{\alpha\beta} \left\{ -\frac{\eta^2}{\pi^2} \nabla \phi_\alpha \cdot \nabla \phi_\beta + \phi_\alpha \phi_\beta \right\}
\]

\[
f^{\text{chem}} = \sum_{\alpha = 1, \ldots, N} h(\phi_\alpha) f_\alpha (c_\alpha^i) + \tilde{\mu}^i \left( c^i - \sum_{\alpha = 1, \ldots, N} \phi_\alpha c_\alpha^i \right)
\]

The governing equations are as following:

\[
\dot{\phi}_\alpha = \sum_{\beta = 1, \ldots, N} \mu_{\alpha\beta} \left\{ \sigma_{\alpha\beta} \left[ \phi_\beta \nabla^2 \phi_\alpha - \phi_\alpha \nabla^2 \phi_\beta + \frac{\pi^2}{2\eta^2_{\alpha\beta}} (\phi_\alpha - \phi_\beta) \right] + \frac{\pi}{\eta_{\alpha\beta}} \sqrt{\phi_\alpha \phi_\beta} \Delta G_{\alpha\beta} \right\}
\]

\[
\dot{c}^i = \nabla \sum_{\alpha = 1, \ldots, N} \phi_\alpha M_\alpha \nabla \tilde{\mu}_\alpha^i
\]

\( \phi_\alpha \) phase-field, \( \sigma_{\alpha\beta} \) surface energy, \( \mu_{\alpha\beta} \) interface mobility, \( \eta_{\alpha\beta} \) interfacial width, \( M_\alpha \) mobility matrix, \( \Delta G_{\alpha\beta} \) chemical driving force.

I Steinbach et al. (1996) *Physica D* 135-147
Section I. Microstructure evolution during solidification

Fig. 13 Microstructure evolution in A2214 alloy during solidification due to the phase-field simulation. The simulation size is $540 \times 360 \ \mu \text{m}^2$, and the cooling rate is 0.25K/s.

Section I. Microstructure evolution during solidification

*Experiment* [Acta Materialia 50 2002 2199–2207]  
*Simulation (2D-cut)*

Fig. 14 Comparison of microstructure with experimental result

Section I. Microstructure evolution during solidification

Coarsening

Fig. 15 Reproduction of the forming process of dendrite coarsening corresponding to region B in Fig. 9 by using the phase-field simulation

Section I. Microstructure evolution during solidification

**Detachment**

Fig. 16 Reproduction of the forming process of detachment corresponding to and C in Fig. 9 by using the phase-field simulation

Section II. Effect of cooling rate on SDAS (secondary dendrite arm spacing)

**Theoretical model of SDAS:**

\[ \lambda_2 = K (Gv)^{-1/3} \propto (\dot{T})^{-1/3} \]

K: simplified coefficient, G: temperature gradient, v: growth rate, \( \dot{T} \): cooling rate

![Fig. 17 A typical longitudinal section of (Al) dendrite at cooling rate 0.75K/s with temperature gradient 50 K/cm due to the phase-field simulation.]

![Fig. 18 phase-field simulated SDAS and experimental data]

3.2 Dissolution of Al-Mg-Si alloys

**Mg$_2$Si dissolved in fcc**

Volume fraction of Mg$_2$Si = \( \frac{r_0^3}{(r_0 + R_{Al})^3} \)

**Fig.19** Simulated volume fraction for the dissolved Mg$_2$Si precipitate in fcc-(Al) matrix against temperature for AA6063 (Al-0.45 wt%Mg-0.40 wt%Si) along with experimental data

3.2 Dissolution of Al-Mg-Si alloys

The heat flow of DSC curve:

\[
\text{heat flow}(w/g) = \frac{d(f_{\text{liq}} \cdot H_{\text{liq}} + f_{\text{fcc}} \cdot H_{\text{fcc}} + f_{\text{Si}} \cdot H_{\text{Si}} - H_{\text{pure-Al}})}{\Delta t} \cdot \frac{\Delta T}{\Delta t}
\]

Volume fraction

Enthalpies

 Cooling rate

DICTRA simulation

Thermodynamic calculation

Liquid

3.2 Dissolution of Al-Mg-Si alloys

Fig. 20 DICTRA simulated DSC curves for (a) A356.0 (Al-0.3 wt% Mg-7 wt% Si), (b) A357.0 (Al-0.7 wt% Mg-7 wt% Si) at the cooling rate of 10 K/min, compared with the experimental data

Case 1: Database ; Case 2: Constant liquid diffusion (10^-9 cm^2/s)

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3.3 Precipitation of $\beta''$ in Al-Mg-Si alloys

- $\text{Mg}_5\text{Si}_6—\beta''$ strengthen the Al-Mg-Si alloy.

Fig 21. A typical low magnification micrograph of $\beta'$ needles in a (001) Al zone axis$^{[1]}$.

3.3 Precipitation of $\beta''$ in Al-Mg-Si alloys

Parameters: 0.36 at % Mg, 0.44 at % Si, T=473K, 125nm$^3$ (250$^3$ grids) ($\beta''$ phase have total 12 variants, we pick up 3 of them for simulations)

Fig 24. Simulation of the precipitation of Mg$_5$Si$_6$. 3 variants are considered.

4. Summary

(1) Thermodynamic and thermo-physical databases for Al alloys is developed by using an integrated approach of experiment, CALPHAD (CALculation of PHAse Diagrams) and first-principles calculations;

(2) The thermodynamic and thermophysical property databases are connected to phase field method to describe the microstructural evolution for several Al alloys during solidification, dissolution and age hardening.
Thank you for your attention!

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