THERMODYNAMIC ANALYSIS OF Li-CONTAINING Al-Mg-Si ALLOYS

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ABSTRACT

In the present work, Al-Li-Mg-Si phase diagram was extrapolated from the ternary subsystems by using Thermo-Calc software. Based on the assessed phase diagrams and the thermodynamic data, the thermodynamic description of the ternary systems were developed. The calculated Al-Li-Mg-Si phase diagram was used to investigate the equilibrium phase distribution as a function of temperature for the Li-contained 6000 series alloys. Some selected sections through the diagram were presented with a brief explanation.

Keywords: *thermodynamic calculation, phase diagram, Al-Li based alloy, thermodynamic model*

1. INTRODUCTION

Al-Li based alloys have low density, high elastic modules and high strength properties which make these alloys attractive for aerospace application, the high strength is produced by the precipitation hardening process. The addition of elements can form incoherent dispersoid or semicoherent precipitates and change microstructure and mechanical properties of alloys[1].

In the previous investigation[2] on Li-containing 6000 series, it was found that addition of Li in Al-Mg-Si alloys lead to a complex interaction between Li atoms and vacancies and between lithium and other solute elements. In order to obtain proper mechanical properties, it is important to control the precipitation process and phase transformation of alloys. So, the phase diagram of the alloy system is of great value to alloy designing and processing. CALPHAD (Calculation of Phase Diagram) method using thermodynamic models coupled with key experimental data is an economic way to obtain the description of phase relations[3].

The aim of the present research is to develop a thermodynamic description of the Al-Li-Mg-Si system, and construct phase diagram by means of Thermo-Calc software[4], Some selected sections through the diagrams are presented so that specific alloy composition can be decided as a guide for the future experimental work.

2. THERMODYNAMIC DESCRIPTION

2.1 Reference states

The Al-Li-Mg-Si quaternary system is extrapolated from the ternary subsystems (Al-Li-Mg, Al-Li-Si, Al-Mg-Si, Li-Mg-Si). The Gibbs energy of individual phase of the systems is described by sublattice models[5] relative to the so-called "standard element reference" (SER), i.e., the enthalpies of the pure elements in their defined reference phase at 298.15K. Expressions recommended by SGTE (Scientific Group Thermodata Europe) are used for the Gibbs energy of pure elements. The SGTE-description is:

$$^{0}G_i(T) - H_i^{SER}(298.15K) = A + B \cdot T + C \cdot T \cdot \ln(T) + D \cdot T^2 + E / T + \cdots \quad (1)$$

2.2 Thermodynamic model

The liquid and solid solution phases are treated as completely random solution, and are described with a one-sublattice model for which the Gibbs energy expression is:

$$G_m = \sum_i X_i {}^0G_i + R \cdot T \times \sum_i X_i \cdot \ln(X_i) + {}^E G_m \qquad (2)$$

where X_i is the mole fraction of element i(i=Al, Li, Mg, Si) in the quaternary system, and ${}^0G_i$ is the molar Gibbs energy of each pure element after eq.1. ${}^E G_m$ is the excess Gibbs energy, for a binary system, ${}^E G_m$ is expressed in Redlich-Kister polynomials a:

$${}^E G_m = X_1 \cdot X_2 \cdot \sum_i L_{i(12)} \cdot (X_1 - X_2)^i \qquad (3)$$

where $L_{i(12)}$ is the binary interaction parameter taken from previous assessments[ ]. $L_{i(12)}$ can be temperature dependent and two terms are usually used, i.e. $L_{i(12)}=a+bT$.

In a multi-component system, the excess Gibbs energy of the liquid and solid solution phase can be extrapolated from those of the binary systems. Muggianus method is used to extrapolate in Thermo-Calc software. For a ternary system, the mole fraction of three components are X_1, X_2, X_3 respectively, ${}^E G_m$ is expressed in Muggianus polynomials a:

$$\begin{aligned} {}^E G_m = {} & X_{1(12)} \cdot X_{2(12)} \cdot \sum_i L_{i(12)} \cdot (X_{1(12)} - X_{2(12)})^i + X_{2(23)} \cdot X_{3(23)} \cdot \sum_i L_{i(23)} \cdot (X_{2(23)} - X_{3(23)}) \\ & + X_{3(31)} \cdot X_{1(31)} \cdot \sum_i L^i_{i(31),1} \cdot (X_{3(31)} - X_{1(31)}) + X_1 \cdot X_2 \cdot X_3 \cdot \Omega \end{aligned} \qquad (4)$$

where $X_{1(12)}=X_1+0.5X_3$, $X_{2(12)}=X_2+0.5X_3$, $X_{2(23)}=X_2+0.5X_1$, $X_{3(23)}=X_3+0.5X_1$, $X_{3(31)}=X_3+0.5X_2$, $X_{1(31)}=X_1+0.5X_2$, and Ω is the ternary interaction parameter.

The same method can be used to extrapolate to a higher order system.

There are three stable intermetallic compounds in the Al-rich corner of Al-Li-Mg-Si system. The AlLiSi phase and Mg_2Si phase are treated as line compounds, AlLi phase is nonstoichiometric phase. Different sublattice models are chosen for three compound phases, (Al,Li)1 (Li,Va)1 for AlLi phase, where Va means vacancy.

Data of Gibbs energy of pure element (${}^0G_i$) are taken from the work of Dinsdale[6]. The thermodynamic parameters L and Ω are taken from the thermodynamic database set up by the present authors. These data do not be provided because of the space requirements of the present paper.

3. APPLICATION OF Al-Li-Mg-Si SYSTEM

Once the thermodynamic of the various phase are defined, phase equilibrium can be calculated using Thermo-Calc software packages. Because the quaternary system is extrapolated from the binary and ternary systems, and the calculated binary and ternary diagrams are very accurate compared to the ternary measurements, so the calculation extended to the quaternary system can be regarded exact.

It need to be noted here that in Li-containing alloys the main hardening phase, in fact, is not the equilibrium AlLi phase, but a metastable phase called δ'-Al_3Li. which has an ordered L12 structure. The solves with respect to the metastable δ' move towards higher Li contents in the matrix compared to the equilibrium solves between Al and AlLi, but for most Al-Li based alloys Li content is high enough and has great distance to solves. Therefore, hardening potential does not reduce. If a proper Gibbs energy model for the δ' phase is available, the calculation will be more accurate.

6000 series alloys are very useful commercial aluminum alloys with medium strength, which depends on precipitation hardening of Mg_2Si phase. The addition of lithium leads to change of the precipitation behavior. Fig.1 is the calculated isothermal diagram at 170 ℃ for Li-contained 6000 series alloy.

Different content of Li and Mg elements will leads to co-precipitation of different phases after artificial aging at 170 ℃. As Li content increases, increasing Mg content promotes the precipitation of Mg_2Si.

Wei et al has investigated the precipitation behavior of Al-Li-0.6Mg-0.8Si alloys. The result showed that there were precipitation of AlLiSi phase and δ′ phase, no Mg_2Si precipitates for 1.7%Li alloy and 2.6%Li alloy. In Fig.1, the points labeled A and B are the location of this two alloys, it can be seen that both A and B lie in field containing AlLiSi and AlLi phase without Mg_2Si phase. The results agree with experimental one obtained by Wei[7].

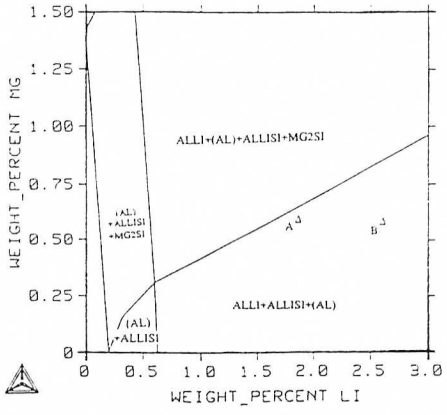

Figure 1. The isothermal section for the Al-Li-Mg-Si alloy of 0.8wt % Si at 170 ℃

When Mg content is increased, the equilibrium phases are changed. Fig.2 and 3 show equilibrium phase distribution as a function of temperature for two Al-Li-Mg-Si alloys. At typical aging temperature, it is the AlLi and AlLiSi phase that are the equilibrium precipitates for 0.6wt% Mg alloy, but for 1.5wt% Mg alloy, AlLi and Mg_2Si are the predominant precipitates, and the amount of AlLiSi phases obviously decreases.

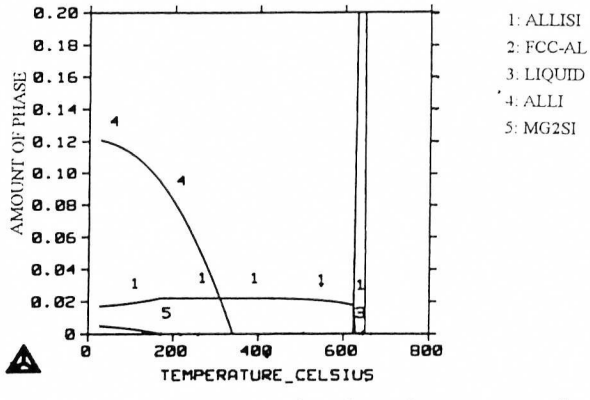

Figure 2. The amount of each phase present as a function of temperature for the alloy containing 1.7wt%Li, 0.6wt% Mg, and 0.8wt%Si.

Fig.3 also shows that at high temperature the AlLiSi phase is an equilibrium precipitate, as the matrix becomes over-saturated with Li, AlLi phase begin to precipitate which dissolves more Li. A further decrease in temperature leads to a over-saturation of the matrix with Mg, and Mg_2Si phase begin to form. Finally , as the amount of Mg_2Si precipitates increases, AlLiSi phase dissolves and liberates more Si.

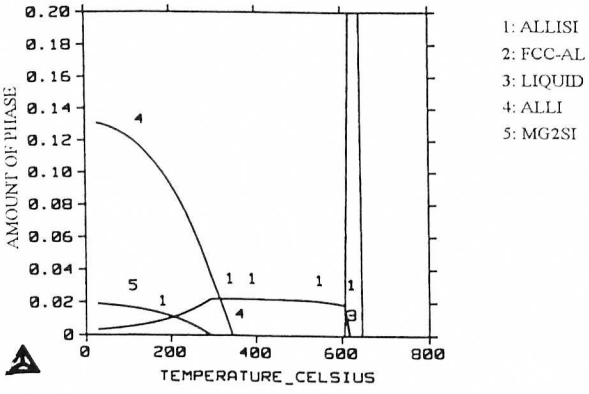

Figure 3 The amount of each phase presents as a function of temperature for the alloy containing 1.7wt%Li, 1.5wt%Mg, and 0.8wt%Si.

the AlLiSi precipitates do not have significant hardening effect, and it bounds Si and inhibits the formation of Mg_2Si , and therefore reduces the extent of age hardening. In order to improve the strength , composition of an alloy and heat treatment should be selected to get more Mg_2Si phase instead of AlLiSi phase. Based on Fig. 4 it can be concluded that at high temperature the AlLiSi phase is stable precipitate and appear in very large range. So it is difficult to inhibited precipitation of AlLiSi phase during solution treatment, but for specific alloy with proper content of Li,Mg,Si, AlLiSi phase can be controlled and more amount of Mg_2Si phase appears by aging treatment.

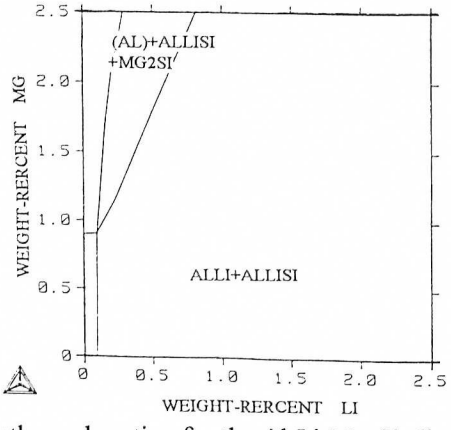

Figure 4 The isothermal section for the Al-Li-Mg-Si alloy of 0.8wt % Si at 550 ℃

Previous research indicated that the content ≤ 2%Li is necessary to obtain good mechanical properties for Al-Li based alloys. For Al-Li-Mg-Si alloy containing 1.7% Li and 1.2%Li, proper contents of Mg, Si can be determined from the isothermal section at 170 ℃ (see Fig. 5, 6). Based on Fig. 5, 6, both of points labeled A, B lie in the (AlLi+Al+Mg_2Si) field, the alloys with composition A and B will obtain precipitation of AlLi and Mg_2Si phase without AlLiSi phase by aging treatment at

170 ℃. Fig. 7 and 8 show the equilibrium phase distribution as a function of temperature for the Al-1.7Li-2.4Mg-0.8Si alloy (A) and the Al-1.2Li-1.8Mg-0.5Si alloy (B). At typical aging temperatures Mg_2Si and AlLi phases are predominant equilibrium precipitates, and little AlLiSi phase appears. The co-precipitation of these phase can lead to high strength of Al-Li based alloys.

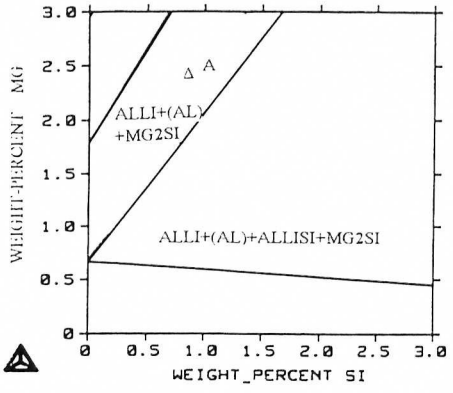

Figure 5 The isothermal section for the Al-Li-Mg-Si alloy of 1.7wt % Li at 170 ℃

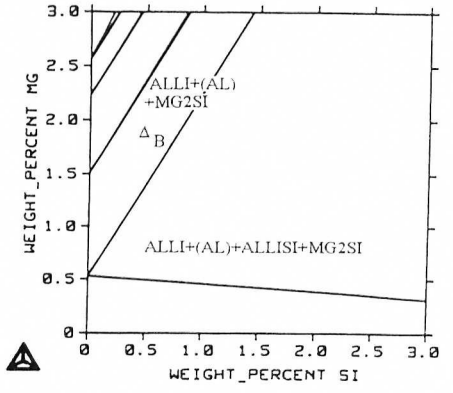

Figure 6 The isothermal section for the Al-Li-Mg-Si alloy of 1.7wt % Li at 170 ℃

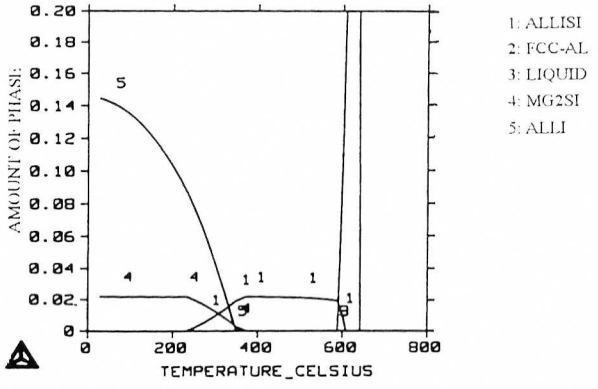

Fig. 7 The amount of each phase presents as a function of temperature for the alloy containing 1.7wt%Li, 2.4wt% Mg, and 0.8wt%Si.

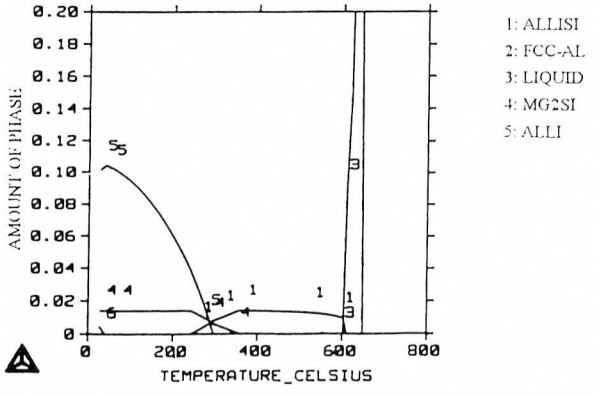

Fig. 8 The amount of each phase presents as a function of temperature for the alloy containing 1.2wt%Li, 1.8wt% Mg, and 0.5wt%Si.

4. CONCLUSION

Thermodynamic description of Al-Li-Mg-Si system was constructed using Thermo-Calc software based on ternary system. The calculated Al-Li-Mg-Si phase diagram was used to predict phase equilibrium in Li-contained quaternary alloys, the results agreed with the experimental one. The calculated phase diagrams provided a reasonable framework and can be used as a guide for the future experimental work.

ACKNOWLEDGMENTS:

The authors would like to express their gratitude to Royal Institute of Technology, Sweden for supplying the Thermo-Calc software, and Aeronautical Science Foundation of China for their support.

REFERENCES:

[1] T. H. Sanders, Jr. and E. A. Starke, Jr. : Aluminum-Lithium Alloys, 1989, 1.
[2] Z. W. Huang, R. E. Smallman, et al: Mater. Sci. and Tech., 7(1991), 205.
[3] P. Kolby: Proc. Fourth ICAA VIII, (1994), 2
[4] B. Sundman, in "User Aspects of Phase Diagrams", ed. F. H. Hayes, (1991), 130.
[5] M. Hillert and M. Staffansson: Acta Chem. Scand. ,(1970), 24.
[6] A. T. Dinsdale: CALPHAD, 15(1991), 317
[7] B. C. Wei. et al: Effect of Li Content on Aging Responses and Mechanical Properties of an Al-Li-Mg-Si Alloys, this proceedings.