The Pennsylvania State University

The Graduate School

Department of Materials Science and Engineering

# THERMODYNAMIC INVESTIGATION OF THE EFFECT OF ALKALI METAL IMPURIES ON THE PROCESSING OF AL AND MG ALLOYS

A Thesis in

Materials Science and Engineering

by

Shengjun Zhang

© 2006 Shengjun Zhang

Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

December 2006

The thesis of Shengjun Zhang was reviewed and approved\* by the following:

Zi-Kui Liu Professor of Materials Science and Engineering Thesis Advisor Chair of Committee

Long-Qing Chen Professor of Materials Science and Engineering

Earle R. Ryba Associate Professor of Materials Science and Engineering

Robert C. Voigt Professor of Industrial and Manufacturing Engineering

Gary L. Messing Distinguished Professor of Ceramic Science and Engineering Head of the Department of Materials Science and Engineering

\*Signatures are on file in the Graduate School

#### ABSTRACT

Aluminum and magnesium alloys are widely used in the automobile and aerospace industries as structural materials due to their light weight, high specific strength and good formability. However, they suffer from the poor hot rolling characteristics due to undesired impurities like calcium, potassium, lithium and sodium. They increase the hydrogen solubility in the melt and promote the formation of porosity in aluminum castings. During fabrication of aluminum alloys, they cause the hot-shortness and embrittlement due to cracking. They also led to "blue haze" corrosion which promotes the discoloration of aluminum under humid condition. The removal of these elements increases overall melt loss of aluminum alloys when aluminum products are remelted and recast.

Na is one of the common impurities in the Al and Mg alloys. In industry, primary Al is produced by the Hall-Héroult process, through the electrolysis of the mixture of molten alumina and cryolite ( $Al_2O_3+Na_3AlF_6$ ), the latter being added to lower the melting point. Therefore, Al inevitably contains some Na (>0.002%) without further treatment. The Na content in Al is influenced by the thermodynamics and kinetics of the electrolysis. Similarly, in the electrolytic production and subsequent processing of Mg, Mg is commonly in contact with molten salt mixtures of NaCl and MgCl<sub>2</sub>. Consequently, 2-20 wt. ppm Na is often found in Mg alloys. Besides originating from the industrial production process, Na can be introduced in laboratory experiments from alumina crucibles by the reaction between the molten Al-Mg alloys and the Na<sub>2</sub>O impurity in the alumina crucible.

The trace element K plays a similar role in Al alloys although it is seldom discussed.

No systematic theoretic research has been carried out to investigate the behavior of these impurities during the processing of aluminum alloys. The thermodynamic description of the Al-Ca-K-Li-Mg-Na system is needed to understand the effects of Ca, K, Li and Na on phase stability of aluminum and magnesium alloys.

As the first step of the thermodynamic description of the high-order system, the constitutive-binary systems were modeled in the present work using the CALPHAD technique combined with first-principles calculations. Then, ternaries and higher order systems can be modeled. For ternary systems without experimental data, the thermodynamic description is extrapolated by combining three constitutive-binary systems.

Alkali-metal induced high temperature embrittlement (HTE) and loss of ductility were investigated in Al-Li, Al-Mg and Mg-Li alloys. It was discovered that the alkali-metal-rich liquid-2 phase is the cause of HTE and the loss of ductility is proportional to the mole fraction of the liquid phase and the grain size. The calculated results are consistent with experimental observations in the literature and were used to determine HTE safe and sensitive zones, maximum and critical hot-rolling temperatures and the maximum allowable Na content in alloys, which can be used to industrial processing of Al and Mg alloys.

The degree of HTE is proportional to the mole fraction of the liquid-2 phase and the grain size.

# LIST OF FIGURES ......ix Chapter 1 1.1 12 Chapter 2 Chapter 4 DEVELOPMENT OF THE THERMODYNAMIC DATABASE OF THE

# **TABLE OF CONTENTS**

4.2.3 Ca-K system	
4.2.4 Ca-Na system	
4.2.5 K-Li system	
4.2.6 K-Na system	
4.2.7 K-Mg system	
4.2.8 Li-Na system	
4.2.9 Mg-Na system	
4.3 Model Parameter Evaluation	
4.3 Results and discussions	
4.3.1 Al-K system	
4.3.2 Al-Na system	
4.3.3 Ca-K system	40
4.3.4 Ca-Na system	
4.3.5 K-Li system	
4.3.6 K-Na system	
4.3.7 K-Mg system	
4.3.8 Li-Na system	
4.3.9 Mg-Na system	
4.4 The binary systems in the literature	
4.4.1 Al-Ca System	
4.4.2 Al-Li System	
4.4.3 Al-Mg System	
4.4.4 Ca-Li System	

4.4.5 Ca-Mg System	44
4.4.6 Li-Mg System	44
Chapter 5 THERMODYNAMIC INVESTIGATION OF THE EFFECT OF	
ALKALI-METAL IMPURITIES ON THE PROPERTIES OF ALUMINUM-LITHIUM	[
ALLOYS	75
5.1 Introduction	75
5.2 Phase evolution and comparison with experimental information	76
5.3 Suppression of alkali-metal-induced HTE in Al-Li alloys	79
5.4 Discussion	81
5.4.1 Embrittlement mechanism	81
5.4.2 Effect of grain size	82
5.4.3 Effect of Na-K ratio	86
5.5 Summary	86
Chapter 6 THERMODYNAMIC INVESTIGATION OF NA-INDUCED HIGH	
TEMPERATURE EMBRITTLEMENT IN AL-MG ALLOYS	100
6.1 Introduction	100
6.2 Phase diagrams and phase evolution	102
5.3 Mechanism of Na-induced HTE	104
6.4 Suppression of Na-induced HTE in Al-Mg alloys	106
6.6 Summary	114
Chapter 7 FUNDAMENTAL UNDERSTANDING OF NA-INDUCED HIGH	
TEMPERATURE EMBRITTLEMENT IN MG-LI ALLOYS	125
7.1 Introduction	125

7.2 Phase evolution and comparison with experimental information	126
Chapter 8 THERMODYNAMIC INVESTIGATION OF ALKALI-METAL-INDUCE	ED
HIGH TEMPERATURE EMBRITTLEMENT IN MULTI-COMPONENT AL AND M	G
ALLOYS	142
8.1 Introduction	142
8.2 Phase evolution	143
8.3 Alkali-metals-induced HTE in multi-component Al-based and Mg-based alloys	144
8.4 Summary	146
Chapter 9 CONCLUSIONS AND FUTURE WORKS	156
9.1 Conclusions	156
9.2 Future works	157
Appendix A THERMODYNAMIC DATABASE OF THE AL-CA-K-LI-MG-NA	
SENARY SYSTEM	158
Appendix B THE ORIGINAL INPUT FILES USED IN THERMO-CALC	181
Appendix C EXPERIMENTAL MECHANICAL PROPERTIES DATA OF AL AND	MG
ALLOYS IN THE LITERATURE	196
BIBLIOGRAPHY	201

viii

# LIST OF FIGURES

Fig. 2.1. The flowchart of computational materials science via CALPHAD and
first-principles methods
Fig. 3.1. The results from first-principles calculations on bcc solution phases
Fig. 4.1. Calculated Al-K phase diagram50
Fig. 4.2. Calculated Al-Na phase diagram51
Fig. 4.3. The enlarged view of Fig. 4.1. at the Al-rich side in comparison with previous work
by Murray [46] (dashed lines) and the experimental data $\circ$ by Scheuer [45]; $\blacktriangle$ by Fink et al.
[47]; $\Box$ by Ransley and Neufeid. [48]; $\blacklozenge$ by Hansen et al. [49] and by $\diamondsuit$ by Fellner et al.
[55]. (σ=8.67%)
Fig. 4.4. Calculated activity of Na in liquid in comparison with the experimental data $\diamondsuit$ at
1293 K and ▲ at 1353 K by Dewing [59] and • at 998 K by Brisley and Fray [60] in the
Al-Na system. ( $\sigma$ = 5.42%)
Fig. 4.5. Calculated Ca-K phase diagram54
Fig. 4.6. Calculated Ca-Na phase diagram in comparison with the experimental data by Rinck
<i>et al.</i> O [68]55
Fig. 4.7. Calculated Li-K phase diagram in comparison with the experimental data $\blacktriangle$ (liquid
miscibility data) • (solubility data) by Smith [72]
Fig. 4.8. The enlarged view of Fig. 4.7. at the Li-rich side in comparison with the
experimental data $\blacktriangle$ • by Smith [72]
Fig. 4.9. The enlarged view of Fig. 4.7. at the K-rich side in comparison with the
experimental data ▲ by Smith [72]

Fig. 4.10. Calculated K-Na phase diagram in comparison with the experimental data $\triangle$
$[74], \Box [76], \odot [78], \bullet [79], \diamondsuit [80]. (\sigma = 3.71\%)$
Fig. 4.11. Calculated activity of K and Na in liquid in comparison with the experimental data
○ • [87], $\triangle$ ▲[88], ■[89] in the K-Na system. ( $\sigma$ =9.28%)60
Fig. 4.12. Calculated enthalpy of mixing in the liquid phase at 384 K in comparison with the
experimental data $\bullet$ [86] in the K-Na system. ( $\sigma$ =4.43%)61
Fig. 4.13. Calculated enthalpy of mixing in the bcc phase at 298 K in comparison with the
results from first-principles calculations $\bullet$ in the Na-K system. ( $\sigma$ =7.75%)62
Fig. 4.14. Calculated K-Mg phase diagram in comparison with the experimental data $\blacktriangle$ • by
Klemm and Kunze [64]63
Fig. 4.15. Calculated activity of Mg in liquid in comparison with the experimental data $\bullet$ by
Lantratov [101] in the K-Mg system
Fig. 4.16. Calculated Li-Na phase diagram in comparison with previous work by Pelton [100]
(dashed lines) and the experimental data $\Box$ [92]; $\diamond$ [93]; $\blacktriangle$ [94, 95]; $\diamond$ [96]; $\bigtriangleup$ [97]; $\blacksquare$ [98];
•[105] and O [106]65
Fig. 4.17. Calculated Mg-Na phase diagram in comparison with the experimental data O by
Mathewson [44], $\triangle$ by Lantratov [101] and $\blacktriangle$ by Klemm and Kunze [64].
(σ=1.32%)66
Fig. 4.18. The magnified view of Fig. 4.17 at the Na-rich side in the Mg-Na system67
Fig. 4.19. Calculated activities of Na and Mg in liquid at 973K in comparison with the
experimental data $O(a_{Na}^{liq})$ and $\bullet(a_{Mg}^{liq})$ by Lantratov [101]. ( $\sigma$ =10.5%)68
Fig. 4.20. Calculated Al-Ca phase diagram by Ozturk <i>et al.</i> [10]69
Fig. 4.21. Calculated Al-Li phase diagram using COST2 database [41]70

Fig. 4.22. Calculated Al-Mg phase diagram by Yu <i>et al.</i> [8]71
Fig. 4.23. Calculated Ca-Li phase diagram Grobner et al. [40]72
Fig. 4.24. Calculated Ca-Mg phase diagram Yu et al. [9]73
Fig. 4.25. Calculated Li-Mg phase diagram using COST2 database [41]74
Fig. 5.1. Calculated isopleth section of Al-2.3Li-K(15 ppm)-Na alloys
Fig. 5.2. Calculated mole fraction of each phase vs. temperature curves
during the solidification of the Al-2.3Li-Na (476 ppm)-K (15 ppm) alloy90
Fig. 5.3. Calculated mole fraction of liquid-2 phase vs temperature with experimental detect
points ● (TEM, EDX and WDX), ▲ (mechanical properties tests) by Webster
[112]
Fig. 5.4. TEM picture showing discrete Na-K-rich liquid particles along the grain boundaries
in the Al-2.3Li-Na (476 ppm)-K (15 ppm) alloy at 394 K [112]92
Fig. 5.5. TEM picture showing discrete Na-K-rich liquid particles in a grain boundary triple
junction in the Al-2.3Li-Na (476 ppm)-K (15 ppm) alloy at 394 K [112]93
Fig. 5.6. Calculated content of each element in the liquid-2 phase vs. temperature curve for
the Al-2.3Li-Na (476 ppm)-K (15 ppm) alloy94
Fig. 5.7. Na and K content detected by WDX in the liquid-2 particles along the grain
boundaries in the Al-2.3Li-Na (476 ppm)-K (15 ppm) alloy at 394 K [112]95
Fig. 5.8. Distribution of elements in three grain boundary liquid particles detected by SIMS
in an Al-Li alloy containing 600 ppm Na and 9 ppm K [113]96
Fig. 5.9. Experimental ultimate tensile strength $\bigcirc$ [112] and the calculated amount of the
liquid-2 phase of the Al-2.3Li-Na (476 ppm)-K (15 ppm) alloy plotted as a function of the
process temperature

Fig. 5.10. HTE sensitive and safe zones as well as critical hot rolling temperatures and
maximum Na content of Al-2.3Li-K (15 ppm)-Na alloys
Fig. 5.11. The amount of liquid-2 phase vs the ratio of Na and K content in Al-2.3Li-Na-K
alloys at 600 K
Fig. 5.12. The amount of liquid-2 phase vs the ratio of Na and K content in Al-2.3Li-Na-K
alloys at 300 K
Fig. 6.1. Calculated isopleth section (Al-5Mg-Na)116
Fig. 6.2. Calculated mole fraction of each phase vs. temperature curvesduring the
solidification of the Al-5Mg-Na (1.8 ppm) alloy117
Fig. 6.3. Na content in the liquid-2 phase vs. temperature curve for the Al-5Mg-Na (1.8 ppm)
alloy118
Fig. 6.4. Calculated phase relations in comparison with the experimental data on the
reduction of area [2]. (a) The calculated mole fraction of each phase vs. temperature curves
during the solidification of Al-5Mg-Na alloys with different Na contents; (b) Effect of Na on
hot ductility of Al-5Mg alloys at different temperatures [2]119
Fig. 6.5. HTE sensitive and safe zones as well as critical hot rolling temperatures (the dashed
line) and maximum Na content of Al-5Mg-Na alloys120
Fig. 6.6. Calculated mole fraction of liquid-2 phase vs. the Mg content
Fig. 6.7. Experimental hot ductility • [2] and the calculated amount of the liquid-2 phase of
Al-5Mg-Na alloys plotted as a function of the Na content
Fig. 6.8. HTE sensitive and safe zones as well as critical hot rolling temperatures and
maximum Na content of the Al-Mg-Na alloys with different Mg contents

Fig. 6.9. Contour map of the critical hot-rolling temperature and the highest Na content (the
dashed line) of Al-Mg alloys with respect to Mg and Na content (a),and with the y axis
enlarged (b)124
Fig. 7.1. Calculated liquid projection of the Mg-Li-Na system
Fig. 7.2. Calculated isopleth section of Mg-3.6Li-Na alloys showing the HTE safe and
sensitive zone, the critical and maximum hot-rolling temperature as well as the maximum Na
content
Fig. 7.3. Calculated phase relations in comparison with the experimental data on the
reduction of area [126]. (a) Effect of Na on hot ductility of Mg-3.6Li-Na alloys at different
temperatures and strain rate. (b) The calculated mole fraction of each phase vs. temperature
curves during the solidification of Mg-3.6Li-Na alloys with different Na
contents
Fig. 7.4. Calculated phase relations in comparison with the experimental data on the 0.2 $\%$
offset yield strength [126]. (a) Effect of Na on hot ductility of Mg-3.6Li-Na alloys at
different temperatures and strain rate. (b) The calculated mole fraction of each phase vs.
temperature curves during the solidification of Mg-3.6Li-Na alloys with different Na
contents
Fig. 7.5. Calculated mole fraction of each element in the liquid-2 phase vs. temperature curve
for the Mg-3.6Li-Na (160 ppm) alloy
Fig. 7.6. Calculated isopleth section of Mg-5.8Li-Na alloys showing the HTE safe and
sensitive zone, the critical and maximum hot-rolling temperature as well as the maximum Na
content

Fig. 7.7. Calculated phase relations in comparison with the experimental data on the reduction of area [126]. (a) Effect of Na on hot ductility of Mg-5.8Li-Na alloys at different temperatures and strain rate. (b) The calculated mole fraction of each phase vs. temperature the solidification of Mg-5.8Li-Na alloys with curves during different Na Fig. 7.8. Calculated phase relations in comparison with the experimental data on the 0.2 %offset yield strength [126]. (a) Effect of Na on hot ductility of Mg-5.8Li-Na alloys at different temperatures and strain rate. (b) The calculated mole fraction of each phase vs. temperature curves during the solidification of Mg-5.8Li-Na alloys with different Na Fig. 7.9. Calculated mole fraction of each element in the liquid-2 phase vs. temperature curve for the Mg-5.8Li-Na (300 ppm) alloy.....137 Fig. 7.10. Calculated isopleth section of Mg-10.6Li-Na alloys showing the HTE safe and sensitive zone, the critical and maximum hot-rolling temperature as well as the maximum Na Fig. 7.11. Calculated phase relations in comparison with the experimental data on the reduction of area [126]. (a) Effect of Na on hot ductility of Mg-10.6Li-Na alloys at different temperatures and strain rate. (b) The calculated mole fraction of each phase vs. temperature curves during the solidification of Mg-10.6Li-Na alloys with different Na Fig. 7.12. Calculated phase relations in comparison with the experimental data on the 0.2 %offset yield strength [126]. (a) Effect of Na on hot ductility of Mg-10.6Li-Na alloys at different temperatures and strain rate. (b) The calculated mole fraction of each phase vs.

temperature curves during the solidification of Mg-10.6Li-Na alloys with different Na
contents140
Fig. 7.13. Calculated mole fraction of each element in the liquid-2 phase vs. temperature
curve for the Mg-11.6Li-Na (680 ppm) alloy141
Fig. 8.1. Calculated mole fraction of each phase vs. temperature curves
during the solidification of the Mg-11.4Li-0.09Mn-Na (564 ppm) alloy148
Fig. 8.2. Each element content in the liquid-2 phase vs. temperature curve for the
Mg-11.4Li-0.09Mn-Na (564 ppm) alloy
Fig. 8.3. Experimental elongation $\circ$ [128] and the calculated amount of the liquid-2 phase
(the dashed line) of Mg-11.4Li-0.09Mn-Na alloys plotted as a function of the Na content at
477 K
Fig. 8.4. Na content detected by the initial ISS spectra at the fracture surface in the
Al-11.4Li-0.09Mn-Na alloys151
Fig. 8.5. Calculated phase relations in comparison with the experimental data on the
reduction of area [127]. (a) Experimental elongation of the
Mg-11.2Li-1.52Al-0.03Ca-0.018Na-0.002K alloys at different temperatures and strain rates.
(b) The calculated mole fraction of each phase vs. temperature curves during the
solidification of Mg-11.2Li-1.52Al-0.03Ca-0.018Na-0.002K alloys with different Na
contents
Fig. 8.6. Calculated mole fraction of each element in the liquid-2 phase vs. temperature curve
for the Mg-11.2Li-1.52Al-0.03Ca-0.018Na-0.002K alloy
Fig. 8.7. Calculated phase relations in comparison with the experimental data on the
reduction of area [127]. (a) Experimental elongation of the

Mg-11.4Li-1.59Al-0.02Ca-0.14	Zr-0.015Si-0	0.018Na-0.002K allo	bys at differer	nt temperatu	res
and strain rates. (b) The calcula	ated mole frac	ction of each phase	vs. temperature	e curves dur	ing
the solidification of the Mg-1	1.4Li-1.59A	l-0.02Ca-0.14Zr-0.0	15Si-0.018Na	-0.002K allo	oys
with different Na contents				1	54
Fig. 8.8. Calculated mole fraction	on of each el	ement in the liquid-2	2 phase vs. ten	nperature cu	rve
for the Mg-11.4Li-1.59Al-0.020	Ca-0.14Zr-0.0	015Si-0.018Na-0.00	2K alloy	1	55
Fig. 8.9. The enlarged view of	f Fig. 8.8 sh	owing the mole fra	ction of each	element in	the
liquid-2 phase	vs. te	emperature	curve	for	the
Mg-11.4Li-1.59Al-0.02Ca-0.14	Zr-0.015Si-0	0.018Na-0.002K allo	у	1	56

# LIST OF TABLES

Table 3.1. The results of first-principles calculation compared with experimental data	in the
K-Na system	21
Table 4.1. Thermodynamic parameters of the Al-K, Al-Na, Ca-K, Ca-Na, K-Li, K-Na, H	K-Mg,
Li-Na and Mg-Na systems in SI unit	45
Table 4.2. Invariant reactions and consolute points in the Al-Na, Ca-Na, Li-Na, K-N	a and
Mg-Na systems	47

#### ACKNOWLEDGEMENTS

I would first like to express my sincere gratitude and deep appreciation to my advisor, Dr. Zi-Kui Liu, for his patient and expert advice, guidance and encouragement during my Ph.D study. I also wish to express my gratitude to Dr. Long-Qing Chen, Dr. Earle R. Ryba and Dr. Robert C. Voigt for their help and serving in my thesis committee.

The assistance of Dr. Qingyou Han, Dr. Don M. Nicholson and Dr. Stan A. David of Oak Ridge National Laboratory in my thesis research is gratefully acknowledged.

I would also thank all the members of the Phase Research Lab, all the faculty and staff of the Department of Materials Science and Engineering in the Pennsylvania State University, as well as all the staff of Materials Processing Group of Materials Science and Technology Division in Oak Ridge National Laboratory, for their help and cooperation in the last four years.

Last but not least, I am grateful to my parents for their love, encouragement and support throughout my life, and I am deeply indebted to my grandmother. This thesis is my special gift for her 80<sup>th</sup> birthday.

To my grandma

# Chapter 1

## **INTRODUCTION**

Aluminum alloys are widely used in the automobile and aerospace industries as structural materials due to their low densities, high specific strengths and good formability. However, they suffer from poor hot rolling characteristics due to undesirable impurities like calcium, potassium, lithium and sodium. These impurities increase the hydrogen solubility in the melt and promote the formation of porosity in aluminum castings. During fabrication of aluminum alloys, they cause hot-shortness and embrittlement due to cracking [1, 2]. They also led to "blue haze" corrosion which promotes the discoloration of aluminum under humid conditions [3, 4]. The removal of these elements increases overall melt loss of aluminum alloys when aluminum products are remelted and recast [5].

Na is one of the common impurities in the Al and Mg alloys. In industry, primary Al is produced by the Hall-Héroult process, through the electrolysis of the mixture of molten alumina and cryolite ( $Al_2O_3+Na_3AlF_6$ ), the latter being added to lower the melting point [6]. Therefore Al without further treatment inevitably contains some Na (>0.002%), and Na content in Al is influenced by the thermodynamics and kinetics of the electrolysis. Similarly, in the electrolytic production and subsequent processing of Mg, Mg is commonly in contact with molten salt mixtures of NaCl and MgCl<sub>2</sub>. Because of the exchange reaction, Eq.1.1, 2-20 ppm Na (ppm is expressed as wt. ppm hereinafter, unless specified otherwise) is often found in Mg alloys [7].

$$2NaCl(l) + Mg(l) \rightarrow 2Na(l) + MgCl_2(l)$$
(1.1)

Besides origination from the industry production process, Na can also be introduced in laboratory experiments from alumina crucibles by the reaction between the molten Al-Mg alloys and the Na<sub>2</sub>O impurity in alumina crucibles [2].

The tracer element K plays a similar role in Al alloys although it is seldom discussed.

No systematic theoretical research has been carried out to investigate the behavior of these impurities during the processing of aluminum and magnesium alloys. The thermodynamic description of the Al-Ca-K-Li-Mg-Na senary system is needed to understand the effects of Ca, K, Li and Na on the phase stability of aluminum alloys.

As the first step of the thermodynamic description of the high-order system, the constitutive-binary systems were modeled in the present work using the CALPHAD technique combined with first-principles calculations. Then ternary and higher order systems can be modeled. For the ternary systems for which no without experimental data exist, the thermodynamic description is extrapolated by combining three constitutive-binary systems.

#### **1.1 Objectives**

The objective of this project is to study the effect of impurities on the processing of aluminum alloys systematically. These undesired impurities include alkali metals such as Li,

Na and K as well as alkali earth metal Ca. Mg is regarded as an important alloying element in Al alloys.

In this senary system, the thermodynamic descriptions of the pure Al, Ca, K, Li, Mg and Na elements were taken from the literature compiled in the Science Group Thermodata Europe (SGTE) database-PURE 4. There are 15 binary systems, 20 ternary system, 15 quaternary systems and 6 quinary systems involved as follows:

- Binary systems: Al-Ca, Al-K, Al-Li, Al-Na, Al-Mg, Ca-K, Ca-Li, Ca-Mg, Ca-Na, K-Li, K-Na, K-Mg, Li-Na, Li-Mg, Mg-Na.
- Ternary systems: Al-Ca-K, Al-Ca-Li, Al-Ca-Na, Al-Ca-Mg, Al-K-Li, Al-K-Na, Al-K-Mg, Al-Li-Na, Al-Li-Mg, Al-Mg-Na, Ca-K-Li, Ca-K-Na, Ca-K-Mg, Ca-Li-Na, Ca-Li-Mg, Ca-Mg-Na, K-Li-Na, K-Li-Mg, K-Mg-Na, Li-Mg-Na.
- Quternary systems: Al-Ca-K-Li, Al-Ca-K-Na, Al-Ca-K-Mg, Al-Ca-Li-Na, Al-Ca-Li-Mg, Al-Ca-Mg-Na, Al-K-Li-Na, Al-K-Li-Mg, Al-K-Mg-Na, Al-Li-Mg-Na, Ca-K-Li-Na, Ca-K-Li-Mg, Ca-K-Mg-Na, Ca-Li-Mg-Na, K-Li-Mg-Na.
- Quinary systems: Al-Ca-K-Li-Na, Al-Ca-K-Li-Mg, Al-Ca-Li-Mg-Na, Al-K-Li-Mg-Na, Ca-K-Li-Mg-Na.

Well-defined binary systems are the bases of the senary database. Some of them have already been modeled by previous investigations, and, the boldfaced systems listed above have not been done before. Only the Al-Ca-Mg ternary system, which was modeled by Yu [8-10], has experimental data in all the ternary systems. There are no experimental data available in all quaternary and quinary systems. The present work includes:

- Development of thermodynamic descriptions for the Al-K, Al-Na, Ca-K, Ca-Na, K-Li, K-Na, K-Mg, Li-Na and Mg-Na binaries which are absent and never done before.
- First-principles calculations for
  - Solid bcc solution phases in some of the binaries.
  - Laves phase KNa<sub>2</sub>
- Description of the Al-Ca-K-Li-Mg-Na senary system by combining all the binaries and ternaries together.
- Thermodynamic investigation of Na-induced high temperature embrittlement (HTE) in Al-Mg alloys and a fundamental understanding of its mechanism.
- Thermodynamic investigation of Na-induced HTE in Mg-Li alloys

# **1.2 Thesis Outline**

This thesis is organized into 8 chapters.

Chapter 1 describes the effects of the undesirable impurities elements (Ca, K, Li and Na) on the processing of Al and Mg alloys, followed by the research objectives and thesis outline.

Chapter 2 presents the approaches involved in this project. The CALPHAD approach and first-principles calculations were combined to develop the thermodynamic database for the Al-Ca-K-Li-Mg-Na senary system.

Chapter 3 describes the first-principles calculations results.

Chapter 4 presents the development of the thermodynamic database for the Al-Ca-K-Li-Mg-Na senary system. Thermodynamic databases of nine binary systems, Al-K, Al-Na, Ca-K, Ca-Na, K-Li, K-Na, K-Mg, Li-Na and Mg-Na, were constructed.

Chapter 5-8 presents a thermodynamic investigation of alkali-metal-induced HTE in Al-Li, Al-Mg, Mg-Li and multi-component Al and Mg alloys respectively.

Chapter 9 summarizes the contributions of the present work and gives suggestions for future work.

# Chapter 2

# METHOLOGY

#### **2.1 CALPHAD Approach**

Phase diagrams are a fundamental tool for materials scientists. They represent the equilibrium state of a system as a function of composition, temperature and pressure. They are useful "roadmaps" for material design and material processing. Nevertheless, experimental determinations of phase diagrams are very costly and time-consuming. CALPHAD is an acronym for CALculation of PHAse Diagram. The CALPHAD approach to model complex phase equilibria in multi-component alloys was pioneered by Kaufman [11], and was used to develop the Al-Ca-K-Li-Mg-Na senary system in the present work.

Its theoretical basis is modeling of individual phases: given the Gibbs energies of all the competing phases in a system, the final equilibrium state at a given composition, temperature and pressure can be calculated by minimizing the total Gibbs energy of the system:

$$G = \min\left(\sum_{p} n_{p} G_{p}\right)$$
(2.1)

where  $n_p$  is the number of moles of phase p and  $G_p$  is its molar Gibbs energy. By intentionally keeping stable phases from appearing, metastable phase equilibria can also be calculated. CALPHAD modeling of a multi-component system builds from lower order systems such as pure elements, binary and ternary systems as discussed below.

## 2.1.1 Pure elements

The Gibbs energies of pure elements in their stable, metastable or even unstable states, the so-called "lattice-stabilities", are taken from the Scientific Group Thermodata Europe (SGTE) pure element database [12]. The reference state is chosen to be the enthalpies of the pure elements in their stable states at 298.15 K and 1 bar, commonly referred to as Stable Element Reference (SER). In the SGTE pure elements database, the thermodynamic function of a pure element is usually described as follows.

$${}^{o}G_{i} - H_{i}^{SER} = a + bT + cT\ln T + \sum d_{n}T^{n}$$
(2.2)

The left-hand term is the Gibbs energy relative to the SER state where  $H_i^{SER}$  is the enthalpy of the element in its SER state at 298.15 K. *a*, *b*, *c* and *d<sub>n</sub>* are coefficients and *n* represents a set of integers, typically taking the values of 2, 3 and -1. From Eq. (2.2), other thermodynamic properties of interest can be obtained:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p} = -b - c - c \ln T - \sum n d_{n} T^{n-1}$$
(2.3)

$$H = G + TS = a - cT - \sum (n-1)d_{n}T^{n}$$
(2.4)

$$C_{p} = \left(\frac{\partial H}{\partial T}\right)_{p} = -c - \sum n(n-1)d_{n}T^{n-1}$$
(2.5)

### 4.1.2 Stoichiometric Compounds

For stoichiometric compounds, when experimental heat capacity data are available, it is preferable to express their Gibbs energies directly referred to the SER in a form similar to Eq. 2.1 as follows:

$${}^{o}G_{m}^{A_{1-x}B_{x}} - (1-x)H_{A}^{SER} - xH_{B}^{SER} = a + bT + cT\ln T + \sum d_{n}T^{n}$$
(2.6)

For compounds without heat capacity data, the Neumann-Kopp rule is used, i.e., assume  $\Delta C_p = 0$ . Their Gibbs energies can be expressed as:

$${}^{o}G_{m}^{A_{1-x}B_{x}} = (1-x)^{o}G_{A}^{\Phi_{A}} + x^{o}G_{B}^{\Phi_{B}} + a + bT$$
(2.7)

where  ${}^{o}G_{i}^{\Phi}$  is the molar Gibbs energy of pure element *i* in its structure  $\Phi$ , and *a* and *b* are the enthalpy and entropy of formation of the compound with respect to A and B in their structures  $\Phi_{A}$  and  $\Phi_{B}$ , respectively.

#### 4.1.3 Solution Phases

For solution phases such as liquids, many fcc, bcc and hcp phases, the substitutional random solution model is usually used. For a binary A-B solution phase  $\Phi$  for example, the Gibbs energy is:

$$G_{m}^{\Phi} = \sum_{i} x_{i}^{o} G_{i}^{\Phi} + RT \sum_{i} x_{i} \ln x_{i} + x_{i}^{x_{s}} G_{m}^{\Phi}$$
(2.8)

where  ${}^{o}G_{i}^{\Phi}$  is the molar Gibbs energy of the pure element *i* with the structure  $\Phi$  from Dinsdale [12], and R the gas constant. The first term on the right hand side is the contribution of the pure components of the phase to the Gibbs energy, the second term the ideal mixing contribution and  ${}^{xs}G_{m}^{\Phi}$  the excess Gibbs energy due to non-ideal interactions between the components, expressed in the Redlich-Kister polynomial [13] as:

$${}^{xs}G^{\Phi}_{m} = \sum_{i} \sum_{j>i} x_{i}x_{j} \sum_{k=0}^{n} {}^{k}L_{i,j}{}^{\Phi}(x_{i} - x_{j})^{k} + x_{i}x_{j}x_{h}I^{\Phi}$$
(2.9)

where  ${}^{k}L_{i,j}^{\Phi}$  is the *k*th binary interaction parameter between *i* and *j* and may depend on temperature as  ${}^{k}A_{k}^{\Phi} + {}^{k}B_{k}^{\Phi}T + {}^{k}C_{k}^{\Phi}\ln T$  with  ${}^{k}A_{k}^{\Phi}$ ,  ${}^{k}B_{k}^{\Phi}$  and  ${}^{k}C_{k}^{\Phi}$  being model parameters to be evaluated.  $I^{\Phi}$  is the ternary interaction parameter expressed as :

$$I^{\Phi} = x_i^{\ 0} L_i + x_j^{\ 1} L_j + x_h^{\ 2} L_h$$
(2.10)

where  ${}^{0}L_{i}$ ,  ${}^{1}L_{j}$  and  ${}^{2}L_{h}$  represent ternary interaction parameters.

# 2.1.4 Ionic Liquid Phase

The liquid phase with ionic species can be described by a two-sublattice ionic model, proposed by Hillert *et al.* [14], and modified by Sundman [15]. The formula for the sublattice ionic liquid is given by  $(C_i^{+\nu_i})_p (A_j^{-\nu_j}, Va, B_k^0)_Q$ , where *C* and *A* are cations and anions, respectively, *Va* and *B* are vacancies and neutral species, and *v* is the valence. *P* and *Q* are the number of sites of the sublattices and defined by electric neutrality as

$$P = \sum_{j} v_{j} y_{A_{j}} + Q y_{Va}$$
(2.11)

and

$$Q = \sum_{i} v_i y_{C_i} \tag{2.12}$$

In general, the total Gibbs energy for the two-sublattice ionic liquid model is represented by

$$G_{m}^{Liq} = \sum_{i} \sum_{j} y_{C_{i}} y_{A_{j}} G_{C_{i}:A_{j}}^{Liq} + Q y_{Va} \sum_{i} y_{C_{i}} G_{C_{i}}^{Liq} + Q \sum_{k} y_{B_{i}} G_{B_{i}}^{Liq} + RT \left[ P \sum_{i} y_{C_{i}} \ln y_{C_{i}} + Q \left( \sum_{j} y_{A_{j}} \ln y_{A_{j}} + y_{Va} \ln y_{Va} + \sum_{k} y_{B_{k}} \ln y_{B_{k}} \right) \right] + \sum_{i_{1}} \sum_{i_{2}} \sum_{j} y_{C_{i_{1}}} y_{C_{i_{2}}} y_{A_{j}} L_{c_{i_{1},C_{i_{2}:A_{j}}}} + \sum_{i_{1}} \sum_{i_{2}} y_{C_{i_{1}}} y_{C_{i_{2}}} y_{Va} L_{C_{i_{1},C_{i_{2}:Va}}}$$
(2.13)  
+  $\sum_{i} \sum_{j} \sum_{k} \sum_{j} y_{C_{i}} y_{A_{j}} y_{A_{j_{2}}} L_{C_{i:A_{j_{1}},A_{j_{2}}}} + \sum_{i} \sum_{j} \sum_{j} y_{C_{i}} y_{A_{j}} y_{Va} L_{C_{i:A_{j},Va}} + \sum_{i} \sum_{k} \sum_{j} y_{C_{i}} y_{A_{j}} y_{Va} L_{C_{i:A_{j},Va}}$ 

where  $G_X$  is the Gibbs energy of species X. The terms in the first row give the reference state, those in the second row the ideal Gibbs energy of mixing, and, in the rest of the row, the excess Gibbs energy of mixing. In the third row,  $L_{i_1,i_2;j}$ , is an interaction parameter representing the interaction between two cations (denoted by *i*) and a common anion (denoted by *j*).

The final term, summing interactions between neutral species, is of special note since it is the only term, which involves interactions in only one sublattice. For the calculation of the interaction parameter between neutral species, the effects of cations are ignored, and only interactions among the neutral species are considered.

## 2.1.5 Modeling Procedures

As illustrated in Fig.2.1, the development of thermodynamic databases using the CALPHAD approach is usually carried out in the following four steps:

The first step is collecting and categorising experimental information in the literature, e.g., crystal structure information about individual phases, phase equilibrium data, thermochemical data and first-principle calculation results. Crystal structure information is used to choose a proper model to describe a phase. Phase equilibrium and thermochemical data are used to evaluate the parameters. When experimental data are insufficient, first-principles results can be used as if they are experiments. The second step involves the critical evaluation of the collected data. Effort should be made to identify and exclude unreliable data. The validity of each piece of data are critically assessed and assigned a certain weight according to its experimental uncertainty and relative importance.

In the third step, based on the crystal structure information, a suitable thermodynamic model is chosen to represent each phase in the system. The models generally include some unknown phenomenological model parameters that need to be determined.

Finally, the evaluated model parameters are stored in computerized databases. Once the Gibbs energies of all the constituent subsystems have been assessed, the data can be combined to predict phase equilibria in higher-order systems.

# 2.2 First-Principles Method

#### 2.2.1 Fundamentals

Theoretically, an exact treatment of solids can be obtained by solving the many-body Schrödinger equation involving both the nuclei and the electrons:

$$\hat{H}\psi(\vec{R}_{1},\vec{R}_{2},\cdots\vec{R}_{N},\vec{r}_{1},\vec{r}_{2},\cdots\vec{r}_{n}) = E\psi(\vec{R}_{1},\vec{R}_{2},\cdots\vec{R}_{N},\vec{r}_{1},\vec{r}_{2},\cdots\vec{r}_{n})$$
(2.14)

where  $\vec{R}_{i}$  are the nuclei coordinates,  $\vec{r}_{i}$  the electron coordinates,  $\hat{H}$  the Hamiltonian operator, *E* the total energy of the system, *N* the total number of nuclei, and *n* the total number of electrons in the system.

However, although theoretically exact, it is impossible to solve Eq. (2.14) due to its many-body nature and the limitations of current computing power. In fact, the only system that can be solved analytically is the single-electron hydrogen atom. In general, the Schrödinger equation has to be solved numerically through a series of approximations. In the following, several levels of approximations will be briefly introduced.

#### 2.2.1.1. Born-Oppenheimer Approximation

Since the nuclei are much heavier than the electrons, it can be assumed that the electrons are always in an instantaneous ground state with the nuclei. In other words, we can fix the positions of the nuclei and only solve the many-body Schrödinger equation for the electrons:

$$\hat{H}\psi(\vec{r}_{1},\vec{r}_{2},\cdots\vec{r}_{n}) = E\psi(\vec{r}_{1},\vec{r}_{2},\cdots\vec{r}_{n})$$
 (2.15)

Since the nuclei are "frozen", they only contribute to an external potential for the electrons.

## 2.2.1.2. Density Functional Theory

Even after the simplification by the Born-Oppenheimer approximation, the Schrödinger equation in essence is still a many-body problem due to the interactions between electrons: each electron will interact with every other electron in the system. Most modern electronic calculations for solids are based on the density functional theory (DFT) proposed by Kohn and Sham [16]. According to DFT, the total energy of a system can be uniquely defined by the electron charge density, i.e.,  $E = E[\rho(\vec{r})]$ . The original many-electron Schrödinger equation is then converted into a set of one-electron Schrödinger equations, one for each electron in the system:

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{e^2}{4\pi\varepsilon_0} \sum_{I=1}^N \frac{Z_I}{\left| \vec{r} - \vec{R}_I \right|} + \frac{e^2}{4\pi\varepsilon_0} \int \frac{\rho(\vec{r}')}{\left| \vec{r} - \vec{r}' \right|} d^3\vec{r}' + V_{XC} \left[ \rho(\vec{r}') \right] \right] \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$$
(2.16)

The exchange correlation potential  $V_{XC}[\rho(\vec{r}')]$  is given by the functional derivative:

$$V_{XC}[\rho(\vec{r}')] = \frac{\delta}{\delta\rho(\vec{r}')} E_{XC}[\rho(\vec{r})]$$
(2.17)

Nevertheless, the exact form of the exchange correlation energy  $E_{xc}[\rho(\vec{r})]$  is unknown. The most widely used approximation is the so-called Local Density Approximation (LDA), which assumes that the exchange correlation energy  $E_{xc}[\rho(\vec{r})]$  is only a function of the local charge density:

$$E_{XC}[\rho(\vec{r})] = \int \rho(\vec{r}) \varepsilon_{XC}[\rho(\vec{r})] d^{3}\vec{r}$$
(2.18)

where  $\varepsilon_{xc}[\rho(\vec{r})]$  is the exchange-correlation energy of a homogeneous electron gas of the same charge density. LDA is expected to work well for systems with a slowly varying charge density, but, surprisingly, LDA works quite well for realistic systems as well.

One significant limitation of LDA is its overbinding of solids: lattice parameters are usually under-predicted while cohesive energies are usually over-predicted. In an effort to rectify the inaccuracies of LDA, the Generalized Gradient Approximation (GGA) was introduced. GGA is a natural improvement on LDA which considers not only the local charge density, but also its gradient. The lattice parameters calculated using GGA generally agree noticeably better with experimental values than those calculated from LDA. There is only one LDA exchange correlation functional, i.e. the one by Ceperley and Alder [17]. Nevertheless, there exist many versions of GGA due to the freedom in how to incorporate the gradient term in the exchange correlation energy.

The actual first-principles total energy calculations are performed in a self-consistent cycle. The initial charge density function is first "guessed". By solving Eq. (2.18), a new charge density is obtained. This is repeated until the new charge density (or the new total energy) does not differ much from the previous one, i.e., the iteration has converged. In practice, the nuclei also need to be relaxed into their equilibrium positions such that the quantum-mechanical forces acting on each of them vanish. Such structural relaxations are usually performed using a conjugate-gradient or a quasi-newton scheme. The final total

energies can be used to extract the formation enthalpies of stable, metastable or even unstable structures at T= 0 K using:

$$\Delta_{f} H(A_{1-x}B_{x}) = E_{TOT}(A_{1-x}B_{x}) - (1-x)E_{TOT}^{\Phi}(A) - xE_{TOT}^{\Phi}(B)$$
(2.19)

where the *E*'s are the first-principles calculated total energies of structure  $A_{1-x}B_x$  and pure elements A and B, each fully relaxed to their equilibrium (zero-pressure) geometries, respectively.

### 2.2.2 Treating Disordered Alloys via Special Quasirandom Structures (SQS's)

Since first-principles DFT calculations rely on the construction of cells with periodic boundary conditions, the calculations are fairly straightforward for perfectly-ordered stoichiometric compounds. However, the situation is more complicated when treating disordered alloys.

One way to treat random  $A_{1-x}B_x$  solid solutions is to directly construct a large supercell and randomly decorate the host lattice with A and B atoms. Such an approach would necessarily require very large supercells to adequately mimic the statistics of the random alloys. Density functional methods are computationally constrained by the number of atoms that one can treat; this brute-force approach could be computationally prohibitive. The concept of special quasirandom structures (SQS's) proposed by Zunger *et al.* [18-20] aims to overcome the limitations of mean-field theories, but without the prohibitive computational cost associated with directly constructing large supercells with random occupancy of atoms. SQS's are specially designed *small-unit-cell* periodic structures with only a few (2~32) atoms per unit cell, which closely mimic the most relevant, near-neighbor pair and multisite correlation functions of the random substitutional alloys. Since the SQS approach is not a mean-field approach, a distribution of distinct local environments is maintained, the average of which corresponds to the random alloy. Thus, a single DFT calculation of an SQS can give many important alloy properties (e.g. equilibrium bond lengths, charge transfer, formation enthalpies, etc.) which depend on the existence of those distinct local environments. Furthermore, since the SQS approach is geared towards relatively *small-unit-cells*, essentially any DFT method can be applied to this approach capable of accurately capturing the effects of atomic relaxation.

The SQS approach has been used extensively to study the enthalpies of formation, bond length distributions, density of states, band gaps and optical properties in semiconductor alloys [18-20]. They have also been applied to investigate the local lattice relaxations in size-mismatched transition metal alloys [21-24], and to predict the formation enthalpies of fcc Al-based alloys [25]. However, to date, most applications of the SQS methodology have been for systems in which the substitutional alloy problem is fcc-based (e.g., fcc-based metals, zinc-blende-based semiconductors, or rocksalt-based oxides). In the literature, the available SQSs exist for fcc [18, 19, 25, 26], bcc [27], hcp [28] and B2 [29] structures.


Fig. 2.1. The flowchart of computational materials science via CALPHAD and first-principles methods.

## Chapter 3

## **FIRST-PRINCIPLES CALCULATIONS**

The enthalpy of mixing for solid solutions is typically not available, particularly for binary systems with intermediate phases or a miscibility gap, where solubility ranges are usually rather limited. The corresponding interaction parameters in those solution phases have large uncertainties. In the present work, enthalpies of mixing of bcc phases in the Ca-Li, Ca-Na, Li-Na and K-Na systems were predicted from first-principles calculations. For the purpose of validation, the enthalpy of formation of KNa<sub>2</sub> was also calculated and compared with experimental data.

First-principles calculations were performed using Blöchl's projector augmented wave (PAW) approach [30, 31], as implemented in the highly-efficient Vienna *ab initio* simulation package (VASP) [32, 33]. The generalized gradient approximation (GGA) [34] was adopted in the present study. The *k*-point meshes for Brillouin zone sampling were constructed using the Monkhorst–Pack scheme [35] and the total number of *k*-points times the total number of atoms per unit cell was at least 6000.

The 16-atom bcc SQS's developed by Jiang *et al.* [27] were used. We fully relaxed the unit cell volume but preserved the symmetries of the SQS's in our calculations.

The enthalpies of mixing in bcc of an A-B system are calculated as follows:

$$\Delta H_{mix}^{bcc}(A_{1-x}B_x) = E^{bcc}(A_{1-x}B_x) - (1-x)E^{bcc}(A) - xE^{bcc}(B)$$
(3.1)

where x is the molar fraction of B (0.25, 0.50 and 0.75), the E's are the total energies of the bcc-SQS, bcc-A and bcc-B at 0 K, each relaxed to their unit cell volume to minimize their total energies, respectively. All the bcc-SQS results are shown in Table 3.1 and Fig. 3.1.

The enthalpy of formation of the compound KNa<sub>2</sub> was calculated as follows:

$$\Delta_{f} H^{KNa_{2}} = E(KNa_{2}) - E^{bcc}(K) - 2E^{bcc}(Na)$$
(3.2)

where the E's are the total energies of KNa<sub>2</sub>, bcc-K and bcc-Na at 0 K, each relaxed to its equilibrium geometry to minimize its total energy, respectively.

Table 3.1.	The results	of first-princip	ole calculations	compared with	experimental	data for the k	K-Na system.
		1 1		1	1		2

Phase	Composition	Energy				Lattice Constant (Å)		
		Total Energy (ev/atom)	Enthalpy (J/mol of atom)			Calculated	Experim	nental
		,	Calculated	Experimental			Value	Reference
				Value	Reference			
K	100 at. % K	-1.0384	0	-	-	5.271	5.328(298 K)	[36]
Na	100 at. % Na	-1.3165	0	-	-	4.197	4.2820± 0.0005(293 K)	[37]
KNa <sub>2</sub>	66.7 at. % Na	-1.2238	-699	-606.68	[38]	a=7.394 c=12.083	a=7.50 c=12.31	[39]
Bcc	25 at. % Na	-1.1589	1786	-	-	5.026	-	-
(K-INa)	50 at. % Na	-1.1464	2994	-	-	4.763	-	-
	75 at. % Na	-1.1525	2408	_	-	4.508	-	_



Fig. 3.1. The results from first-principles calculations on bcc solution phases.

## Chapter 4

# DEVELOPMENT OF THE THERMODYNAMIC DATABASE OF THE AL-CA-K-LI-MG-NA SENARY SYSTEM VIA CALPHAD APPROACH

#### **4.1 Introduction**

There are 15 binary subsystems in the Al-Ca-K-Li-Mg-Na senary system. Six of them were modeled by others: the Al-Ca system by Koray *et al.* [10]; the Al-Mg and Ca-Mg systems by Zhong *et al.* [8, 9]; the Ca-Li system by Grobner *et al.* [40]; and the Al-Li and Li-Mg systems taken from the COST2 database [41]. They are accepted in the present work. Five of them associated with Na (Al-Na, Ca-Na, K-Na, Li-Na and Mg-Na) and four of them associated with K (Al-K, Ca-K, K-Li and K-Mg) were modeled in the present work.

There exist 20 ternary subsystems in the Al-Ca-K-Li-Mg-Na system. Experimental data exists for only one, the Al-Mg-Ca ternary system, and has been modeled by others in our group. The ternary interactions are not considered in others ternary systems.

In this section, all available experimental data of the binary systems (Al-Na, Ca-Na, K-Na, Li-Na and Mg-Na) in the literature are critically reviewed, including both phase equilibrium data and thermochemical data.

#### 4.2 Experimental data and previous modeling

### 4.2.1 Al-K system

The Al-K system was first studied by Smith [42]. It was found that the melting points of Al and K are not affected by the addition of the other component.

## 4.2.2 Al-Na system

Emperimental phase-equilibrium experimental work on the Al-Na binary system focused on the Al-rich region. Great efforts were made to investigate the solubility of Na in liquid Al.

Heycock and Neville [43] investigated the lowering of the freezing point of Na by addition of many other metals and found that Al and Na do not mix together. Mathewson [44] found thermal arrests at temperatures indistinguishable from the melting points of pure Al and Na. The temperatures of invariant reactions were first determined to be 930 K and 370.5 K. However, the results were affected by the low-purity of Al (99.7% Al). Scheuer [45] measured the solubility of Na in liquid Al by heating Al with an excess of Na under hydrogen until equilibrium was attained, followed by quenching the melt and determining the Na content of the Al-rich layer. The solubility of Na was found to be 0.10 at. % at 973 K, 0.115 at. % at 1023 K, and 0.128 at. % at 1073 K. Due to hydrogen contamination, these results are rather uncertain as pointed out by Murray [46].

Fink *et al.* [47] determined the boundary of the liquid miscibility gap by a method similar to that of Scheuer [45], except under argon instead of hydrogen. They determined the monotectic temperature and the hypo-monotectic liquidus curve using both direct and differential thermal analysis (DTA) techniques. Their results show that the monotectic reation occurs at 932 K with the liquid composition being 0.18 at. % Na, and the solubility of Na in liquid Al decreases slightly with increasing temperature. They also found the maximum solubility of Na in solid Al to be less than 0.003 at. % using electrical resistivity measurements and metallographic examination. However, their results about the retrograde solubility of Na in liquid Al seem unreasonable.

Ransley and Neufeld [48] re-determined the boundary of the liquid miscibility gap and the solid solubility of Na in Al. They immersed high-purity Al (Al >99.99 at. %) in liquid Na and let it saturate (up to 650 hr) in a stout mild-steel bomb. Afterwards, the specimens were removed from the furnace and allowed to cool freely in air. The amount of Na dissolved in Al was investigated by chemical analysis. The solid solubility of Na in Al was found to be approximately 0.002 at. % in the range of 923-933 K. The monotectic composition was found to be 0.14 at. % Na at 932 K, and the solubility of Na in liquid Al increased smoothly with increasing temperature. Their results were given higher weight in present work because they avoided the drawbacks of the previous works [44, 45, 47].

More recently, Hansen *et al.* [49] determined the maximum solubility of Na in solid Al using electromotive force (EMF) measurements and quenching experiments. Their results showed that the composition of saturated Na in liquid Al is 1.348 at. % at

1023 K, 0.7639 at. % at 1073 K and 0.6610 at. % at 1123 K, which are more than 10 time greater than previously reported values [45, 47, 48]. Furthermore their results indicated that Al-Na exhibits a large retrograde solubility. Hansen et al. [49] derived an equation based on Fick's law by assuming saturation is controlled by diffusion of Na into liquid Al and concluded that saturation was probably never reached in previous attempts [45, 47, 48] to determine the solubility of Na in liquid Al.

The controversial work of Hansen et al. [49] was criticized by Motzfeldt [50] and Kaptay [51]. Motzfeldt [50] thought possible reactions between the Na and the sapphire crucible (Al<sub>2</sub>O<sub>3</sub>). According to the thermodynamic calculations, Kaptay [51] considered the reactions might exist between Al(g) and NaF(s) in Hansen's EMF experiments. But Hansen *et al.* [52, 53] stood by their results.

To further investigate this issue, Fellner *et al.* [54] carried out experiments at temperatures of 1023 K and 1233 K in which Na was deposited onto a molten Al cathode by the electrolysis of a molten mixture of 26.4% NaF + 73.6% NaCl. Their results did not confirm the high values of Na solubility in liquid Al published by Hansen *et al.* [49]. Further, Fellner *et al.* [55] achieved saturation of Na in liquid Al at 983, 1023, 1073, 1173 and 1233 K using the same method. Their results are close to the previous results [45, 47, 48].

Hansen is also doing new experiments now [56]. In his new experimental process, he has realized that his EMF-results were caused by a side-reaction between Na and sapphire and that the true solubility of Na in liquid Al is close to that determined by the previous authors [45, 47, 48]. The results from his quenching experiment may be caused by Na-inclusion [56].

All thermochemical investigations of the Al-Na system concentrated on measuring the activity and the activity coefficient of Na in Al. Mitchell and Samis [57] determined the distribution of Na by quenching samples and subsequent chemical analysis. They found that the activity coefficient of Na strongly increases with the Na content between 0-85ppm. Dewing [58] determined the Na content of Al in equilibrium with NaF(s) and Na<sub>3</sub>AlF<sub>6</sub>(s) over the temperature range from 952 K to 1149 K by measuring the vapor pressure of Na over a mixture of Al, Na fluorite and cryolite by a gas transference method. The activity coefficient of Na in liquid Al was expressed by the equation.

$$\frac{RT\ln\gamma_{Na}}{n_{Al}^2} = 8290 + 3.73T \tag{4.1}$$

where  $\gamma_{Na}$  is the Henry's activity coefficient of Na and  $n_{Al}$  is the molarity of liquid Al.

Later, Dewing [59] measured the Na content in liquid Al in contact with NaF-AlF<sub>3</sub> melts at 1293 K and 1353 K using the same method. Brisley and Fray [60] determined the Na activity in molten 99.99 a/o Al, commercial-purity Al (at. % Al = 99.41) and Al alloy LM6 using a Na  $\beta$ -alumina electrolyte at 998 K. They found that Na in liquid 99.99 a/o Al obeys Henry's law between 1-50 ppm, with  $\gamma_{Na} = 222 \sim 355$ 

and is, in agreement with the values obtained by Dewing [59] and Ransley and Neufeld [48]. Yao and Fray [61] investigated the activity of Na in liquid Al with 0.5 % impurities using a Na probe based on Nasicon (Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>-PO<sub>12</sub>) and air-sintered Na<sub>0.75</sub>CoO<sub>2</sub> solid solution electrode at 1023 K, 1068 K and 1098 K. They found that the activity coefficient of Na depends on the Na concentration strongly near the melting point of Al, and that Henry's law is obeyed at higher temperatures. Sun and Yang [62], who also used Na beta alumina sensors, measured the activities of Na in liquid Al containing 0.11 % Si at 1000 K and found that  $\gamma_{Na}$  increases from 0.16 to 22 with increasing Na concentration from 1 to 150 ppm. Henry's law was obeyed for Na contents less than 0.04 % in liquid Al. Dubreuil et al. [63] measured the potentials of a Na beta alumina sensor immersed in liquid Al with 1 to 100 ppm Na at 983 K to 1023 K. Hansen et al. [49] measured the activity data on Na in liquid Al-Na alloys by a coulometric titration technique using a galvanic cell employing CaF<sub>2</sub> as a solid electrolyte at 1023 K, 1073 K and 1123 K. They found that the activities exhibit strong negative deviation from Henry's law. This behavior was explained by the formation of Na clusters in the liquid. Their results are not used in this work due to the errors discussed above.

Given that the solubility of Na in Al is fairly low and that activities of Na in liquid Al are very sensitive to the Al purity, only part of the results of Brisley and Fray [60] in molten 99.99 a/o Al and of Dewing [59] were used in the evaluation of model parameters in the present work. Based on the experimental data in references [45, 47, 48], Murray [46] obtained the thermodynamic model parameters for the Al-Na system. The liquid was treated as a regular solution with excess entropy, and the fcc phase was treated as a Henrian solution. The results were in good agreement with the solubility of Na in liquid Al available at that time. However, thermochemical experimental data were not considered.

## 4.2.3 Ca-K system

The Ca-K system exhibits virtually complete immiscibility in the solid and liquid phases and no compounds were found by Klemm and Kunze [64] using x-ray diffraction (XRD).

## 4.2.4 Ca-Na system

The Ca-Na system was first studied by Metzger [65] who observed an upper and a lower layer in a solidified alloy. Due to the difficulty of separating the two immiscible liquid phases, Lorenz and Winzer [66, 67] and Rinck [68] made use of the reaction  $Ca + 2NaCl = CaCl_2 + 2Na$  at various temperatures to determine the miscibility gap indirectly. At the same time, they investigated the liquidus curve and the monotectic reaction using thermal analysis. However, Lorenz and Winzer [66, 67] reported an incorrect melting temperature of pure Ca due to nitride contamination, while the value of Rinck [68] is more reliable. No thermochemical data have been reported in the literature.

Based on the experimental data of Rinck et al. [68], Pelton [69] evaluated the thermodynamic model parameters for the Ca-Na system. The calculated Ca-Na phase diagram reproduced the experimental data for liquid miscibility gap very well, but no mutual solubilities were assumed between the solid Ca and Na phases.

## 4.2.5 K-Li system

Böhm and Klemm [70] found that Li and K do not alloy and there are neither intermetallic compounds nor solid solutions in the Li-K system using thermal analysis. Dotson and Hand [71] investigated the solubility of Li and K in mutual rich sides using a chemical analysis of the alloys after equilibrating pure K and Li for over 16 hours in an inert atmosphere. Smith [72] also measured the solubility in the condensed phases in equilibrium with vapors in an inert atmosphere. There are no thermochemical data available in the open literature.

#### 4.2.6 K-Na system

The K-Na binary system has been investigated using the freezing point method [73-78]. In these works, the liquidus curve and temperatures and compositions of the eutectic and peritectic reactions were established and the intermetallic compound KNa<sub>2</sub> was identified. However, no solubility of the bcc phases in one another was found. Moreover, their results lacked accuracy without chemicals of high purity, inert atmosphere protection, and high accuracy thermometry [79]. Further studies were carried

out by MacDonald et al. [80] using electrical resistance measurements and by Rimai and Bloembergen [81] using nuclear magnetic resonance. Their results showed the existence of a bcc solid solution.

Ott et al. [79] investigated the K-Na phase diagram using a freezing point apparatus and a cryogenic calorimeter. The melting points of the pure metals, the liquidus curve and the limits of solubility in the solution regions were determined with high precision ( $\pm 0.1$  K). No intermetallic compounds other than KNa<sub>2</sub> were found. The temperature and compositions for the eutectic and peritectic reactions were obtained as 260.53 K, 31.9 at. % Na and 280.07 K, 59.8 at. % Na, respectively.

The crystal structure of KNa<sub>2</sub> was determined by Laves and Wallbaum [39] using X-ray Diffraction. Krier et al. [82] measured the isobaric heat capacity of KNa<sub>2</sub> between 12 K and 320 K, and the temperature of the eutectic point and the incongruent melting point of KNa<sub>2</sub> using calorimetry. The formation enthalpy of KNa<sub>2</sub> was estimated to be -1802.04 J/mol at 280 K by Hultgren *et al.* [38].

The enthalpy of mixing in the liquid was measured by Joannis [73], Bichowsky and Rossini [83], Kawakami [84], and McKisson and Bromley [85] using rough calorimetric measurements. Their results are not used in this work due to the poor precision and the considerable scatter in their results. Yokokawa and Kleppa [86] determined the enthalpy of liquid mixing at  $384 \pm 2$  K with accurate reaction calorimetry. Their results are used in the present work.

There are considerable experimental data on the activities of Na and K in the liquid in the literature. The activities of Na and K in the liquid at 384 K were investigated by Cafasso *et al.* [87] using vapor-phase absorption spectrophotometry of atomic resonance lines. Kagan [88] measured the activities of K in the liquid at 400 K using an effusion method. Lokshin and Lgnatov [89] investigated the activity of K in the liquid state at 520 K using electromotive force (EMF) measurements. The results indicate that activities of Na and K show positive deviation from Raoult's law. Lantratov [90] measured the activity of K in the liquid state at 723 K and 773 K using EMF measurements. However, Lantratov's results, not used in the present work, are unreliable because of the reaction between molten alkali metals and silicic acid glass which was used as an electrolyte in the experiments [91]. All experimental activity data are compared with the calculated values later.

#### 4.2.7 K-Mg system

The Al-K system was first studied by Smith [42]. It was found that the melting points of Al and K are not affected by the addition of the other component. Klemm and Kunze [64] used an iron crucible and measured the solubility of Mg in liquid K by weight loss and chemical analysis techniques. No intermetallic phases were detected by X-ray diffraction (XRD) in this binary system.

Lantratov measured the activities of K in liquid by an electromotive force (EMF) method at 973 K over the entire concentration range. The activity of K exhibits very large positive deviation from Raoult's law due to phase separation.

## 4.2.8 Li-Na system

The Li-Na system has been investigated many times using different techniques, especially in the vicinity of the consolute point. The miscibility gap was investigated by Schurmann and Parks [92], Feistma et al. [93], Dowl et al. [94, 95] and Endo et al. [96] using electrical resistivity measurement technique; by Kanda et al. [97] using density measurement technique; and by Wu et al. [98] using light microscopy, X-ray diffraction and neutron scattering techniques. As shown in Table 4.1, their results are very closed to each other. No thermochemical data have been reported in the literature.

Bale [99] reviewed the available experimental data in the literature and made a qualitative thermodynamic analysis of the system assuming zero solubility in the bcc phases. The phase boundary of the liquid miscibility gap was represented by an analysical function of the temperature and the mole fraction of Na based on the experimental data summarized by Feistma et al. [93]. Pelton [100] thermodynamically modeled the liquid phase of the system based on Bale's review [99]. The solid solubility values at the monotectic and eutectic temperatures were estimated by applying Raoult's law. However, as shown by the dashed lines in Fig.3, the calculated phase diagram differs from

experimental data near the consolute point of the miscibility gap. Furthermore no model parameters of solid solution phases were given.

## 4.2.9 Mg-Na system

Mathewson [44] determined the solubility of Na in liquid Mg as 2 at % at the monotectic temperature of 911 K by thermal analysis. An almost identical value was found by Lantratov [101] for 2.1 at. % Na at 911 K. However, both of them used glass containers which usually react with Na and Mg and affect the results. Klemm and Kunze [64] used an iron crucible and measured the solubility of Mg in liquid Na by weight loss and chemical analysis techniques. No intermetallic phases were detected in X-ray investigations of this binary system.

Lantratov [101] measured the activities of Na and Mg in liquid by an electromotive force (EMF) method at 973 K over the entire concentration range. The activities of Na and Mg exhibit very large positive deviations from Raoult's law due to phase separation. Rosenkilde et al. [7] measured the concentration of Na in liquid Mg in equilibrium with NaCl-MgCl<sub>2</sub> melts of different compositions at temperatures from 923 K to 1063 K at very low Na concentrations.

Based on the experimental data in the literature [64, 101], Pelton [102] made a qualitative thermodynamic analysis of the Mg-Na system and used the van't Hoff

equation to analyze the liquid miscibility gap. No models or thermochemical data were considered.

## 4.3 Model Parameter Evaluation

All model parameters were evaluated using the Parrot module in Thermo-Calc [103]. This program is able to take various kinds of experimental data in one operation. It works by minimizing an error of sum with each of the selected data given a certain weight. The weights were chosen and adjusted based upon the uncertainties for the data given in the original publications and upon the authors' judgment by examining all experimental data simultaneously. All thermodynamic calculations were carried out using Thermo-Calc.

The complete and self-consistent thermodynamic descriptions for the Al-Ca, Al-Na, Ca-K, Ca-Na, K-Li, K-Na, K-Mg, Li-Na and Mg-Na binary systems thus obtained are listed in Table 4.1. The reference state of the Gibbs energy of the individual phases is the so-called Standard Element Reference (SER) state, i.e., the enthalpies of the pure elements in their stable states at 298.15K and 1 bar.

Since there are few experimental data available for the Al-K system, all the parameters are arbitrarily set positive value to generate liquid miscibility gap and the neglected solubilities in bcc and fcc phases. The gas phase is considered to be ideal at high temperatures. The parameter evaluation procedure in the Al-Na system started with the miscibility gap in the liquid phase with the selected experimental data on the solubility of Na in liquid Al and the activities of Na in liquid Al. The thermodynamic parameters of the fcc and bcc phases were then evaluated. Since there is an hcp phase in the Mg-Na binary system, the thermodynamic parameter of the metastable hcp phase was set to a large positive value so that it did not become stable in the system. Many iterations were necessary to reproduce all experimental data. Finally, the model parameters of all phases were adjusted simultaneously with all experimental data included.

Since there are few experimental data available for the Ca-K system, all the parameters are set arbitrarily positive value to generate liquid miscibility gap and the neglected solubilities in bcc and fcc phases. The gas phase is considered to be ideal at high temperatures.

In the Ca-Na system, the parameters of the liquid phase were taken from Pelton [69]. The thermodynamic parameters of the bcc phase were evaluated using the experimental liquid boundary data and the monotectic temperature and composition of the liquid phase. The parameters of the fcc phase were chosen arbitrarily due to the lack of data. The thermodynamic parameter of the metastable hcp phase, which will be present when Mg is added in the subsequent calculations, was set to an arbitrary positive value so it did not become stable in this system.

The parameter evaluation procedure in the K-Li system started with the miscibility gap in the liquid phase with the selected experimental data on the solubility of K and Li in the liquid state. The thermodynamic parameters of the bcc phase were then evaluated. The thermodynamic parameter of the metastable fcc and hcp phases were set to a large positive value so they did not become stable in the system. Many iterations were necessary to reproduce all experimental data. Finally, the model parameters of all phases were adjusted simultaneously with all experimental data included.

The evaluation of model parameters in the K-Na system started with the liquid phase followed by the bcc phase miscibility gap and the intermetallic compound KNa<sub>2</sub> using the experimental phase boundary data and thermodynamic data. Because the experimental data by Ott et al. [79] are more reliable than others [73-78, 80, 81], more weight was given to them. In the evaluation process, the enthalpies of mixing in bcc from first-principles calculations were considered as experimental data. Finally, all the model parameters were refined by simultaneous optimization of all the experimental and first-principles data.

In the K-Mg system, the parameter evaluation procedure started with the miscibility gap in the liquid phase with the selected experimental data on the solubility of Mg in liquid K and the activities of K in liquid. The thermodynamic parameters of the bcc and hcp phases were then evaluated.

The evaluation of model parameters in the Li-Na system started with the liquid miscibility gap followed by the bcc phase miscibility gap. Special attention was paid to the composition and temperature of the consolute point in the liquid miscibility gap to ensure the rational shape of the miscibility gap as it was not well reproduced by Pelton [100]. The thermodynamic parameters of the metastable fcc and hcp phases were set to an arbitrary positive value so they do not become stable in system. The miscibility gap in the liquid phase requires a positive  ${}^{o}L^{liq}{}_{Li,Na}$ . The consolute point of the liquid miscibility gap is Li-rich, therefore parameter  ${}^{1}L^{liq}{}_{Li,Na}$  is positive. The parameter  ${}^{2}L^{liq}{}_{Li,Na}$  and the temperature dependence of the parameter  ${}^{o}L^{bcc}{}_{Li,Na}$  are added to better reproduce the phase equilibrium data. The parameter  ${}^{o}L^{bcc}{}_{Li,Na}$  is also positive due to the miscibility gap in the bcc phase.

The evaluation procedure in the Mg-Na system started with the liquid miscibility gap followed by the bcc and hcp phases. The activities of Na in liquid Mg were used at the same time. The solubility of Na in solid Mg was taken as the solubility of Na in solid Al (0.002 %) since the atomic radii of Al and Mg (Al: 0.125 nm and Mg: 0.150 nm ) as well as the Al-Na and Mg-Na phase diagrams are similar and Al and Mg both have closely packed structures (Al: fcc and Mg: hcp).

Since there is a fcc phase in the Mg-Na binary system, the thermodynamic parameters of the metastable fcc phase were set to a large positive value so that they did

not become stable in the system. Finally, the model parameters of all phases were adjusted simultaneously with all experimental data included.

## 4.3 Results and discussion

## 4.3.1 Al-K system

A large positive interaction parameter in the liquid solution was obtained in the present work due to very low solubility of K in Al. The calculated phase diagram using the present thermodynamic description of the Al-K system is shown in Fig. 4.1.

#### 4.3.2 Al-Na system

A much more positive interaction parameter in the liquid phase than that of Murray [46],  ${}^{0}L_{Al,Na}^{Liq}$ , was obtained in the present work, due to using the more recent data which show a lower solubility of Na in liquid Al [55] (see Fig. 6.2). The calculated phase diagram using the present thermodynamic description of the Al-Na system is shown in Fig. 4.2.

Fig. 4.3 gives an enlarged view of the Al-rich part of the calculated phase diagram in comparison with previous work by Murray [46] (dashed lines) and all the available experimental data. The relative standard deviation are included in each figure caption, calculated from:

$$\sigma = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left(\frac{x_i^{cal} - x_i^{exp}}{x_i^{exp}}\right)^2}$$
(4.2)

where  $x_i^{cal}$  is a calculated result,  $x_i^{exp}$  an experimental datum, and *n* the number of experimental data. The calculated phase diagram shows excellent agreement with all the experimental data, especially the recent results. However, the results of Murray [46] only fit part of the experimental data and do not agree with the most recent data by Fellner *et al.* [55]. The invariant reactions in Al-Na system are listed and show good agreement with the experimental data.

Fig. 4.4 shows the calculated activities of Na in liquid Al at 998, 1293 and 1353 K, respectively, in comparison with experimental data. It shows that the activities of Na in liquid have a large temperature dependence. The calculated values do not fit the experimental data very well at 1353 K when the concentration of Na is  $\geq 0.03$  at. %. Dewing [104] pointed out that quenching may well have been inadequate in these experimental data.

## 4.3.3 Ca-K system

A large positive interaction parameter in the liquid was obtained in the present work due to very low solubilities of Ca and K in each other. The calculated phase diagram using the present thermodynamic description of the Ca-K system is shown in Fig. 4.5.

## 4.3.4 Ca-Na system

The phase diagram calculated using these parameters is shown in Fig. 4.6 with the experimental data superimposed. Most of the experimental liquidus data are well reproduced. The calculated values of the temperature and compositions in the invariant reactions in the Ca-Na system listed in Table 4.2 are identical to the experimental data.

#### 4.3.5 K-Li system

The calculated phase diagram using the present thermodynamic description of the K-Li system is shown in Fig. 4.7. Figs. 4.8 and 4.9 give enlarged views of the K-rich part and Li-rich part of the calculated phase diagram along with the available experimental data. Good agreement has been obtained.

## 4.3.6 K-Na system

The calculated K-Na phase diagram is shown in Fig. 4.10 with the experimental data superimposed. Fig. 4.11 and 4.12 depict the activities in the liquid and the calculated enthalpy of mixing in the liquid, respectively, compared to the experimental data. The calculated enthalpy of mixing in the bcc phase at 298 K is shown in Fig. 4.13 in comparison with the results from first-principles calculations. The calculated temperatures and compositions of the invariant reactions are listed in Table 4.2 along with the experimental data.

## 4.3.7 K-Mg system

The calculated phase diagram using the present thermodynamic description of the K-Mg system is shown in Fig. 4.14. The calculated activity of Mg in liquid is shown in Fig. 4.15 in comparison the available experimental data. Good agreement has been obtained.

#### 4.3.8 Li-Na system

Fig. 4.16 shows the calculated phase diagram using the present thermodynamic description in comparison with that of Pelton [100] and experimental data. The present calculation reproduces the experimental data better. The invariant equilibria and consolute point in Li-Na system are listed in Table 4.2 along with the experimental data included.

## 4.3.9 Mg-Na system

The calculated phase diagram using the present thermodynamic description is shown in Fig. 4.17 in comparison with the experimental. Fig. 4.18 shows a magnified view of the Na-rich part of the calculated phase diagram. The invariant equilibrium in the Mg-Na system is given in Table 4.2 and compared with the experimental data. Very good agreement is obtained. Fig. 4.19 shows the calculated activity of Na and Mg in the liquid state at 973 K along with the experimental data. Good agreement has been obtained, except for the activity of Na in the liquid miscibility gap in which the experimental data are almost equal to unity and seem unreasonable.

## 4.4 The binary systems in the literature

## 4.4.1 Al-Ca System

The Al-Ca system was modeled by Ozturk *et al.* [10] and accepted in the present work. It is shown in Fig. 4.20.

## 4.4.2 Al-Li System

The Al-Li system was taken from the COST2 database [41] and accepted in the present work. It is shown in Fig. 4.21

## 4.4.3 Al-Mg System

The Al-Mg system was modeled by Yu *et al.* [8] and accepted in the present work. It is shown in Fig. 4.22.

## 4.4.4 Ca-Li System

The Ca-Li system was modeled by Grobner et al. [40] and accepted in the present work. It is shown in Fig. 4.23.

# 4.4.5 Ca-Mg System

The Ca-Mg system was modeled by Yu *et al.* [9] and accepted in the present work. It is shown in Fig. 4.24.

## 4.4.6 Li-Mg System

The Li-Mg system was taken from COST2 database [41] and accepted in the present work. It is shown in Fig. 4.25.

System	Phase	Model	Parameter	Value (J/mol)
	Liquid	(Al, K)	${}^{0}L^{liq}_{{\scriptscriptstyle Al},K}$	65000
Al-K	Bcc	(Al, K)	${}^{0}L^{bcc}_{Al,K}$	20000
	Fcc	(Al, K)	${}^{0}L^{fcc}_{Al,K}$	50000
	Нср	(Al, K)	ModelParameterValue(Al, K) ${}^{0}L_{Al,K}^{liq}$ (Al, K) ${}^{0}L_{Al,K}^{bcc}$ (Al, K) ${}^{0}L_{Al,K}^{bcc}$ (Al, K) ${}^{0}L_{Al,K}^{hcp}$ (Al, K) ${}^{0}L_{Al,K}^{hcp}$ (Al, K) ${}^{0}L_{Al,Na}^{hcp}$ (Al, Na) ${}^{0}L_{Al,Na}^{hcp}$ 773'Al, Na) ${}^{0}L_{Al,Na}^{hcp}$ 773'Al, Na) ${}^{0}L_{Al,Na}^{hcp}$ 773'(Al, Na) ${}^{0}L_{Al,Na}^{hcp}$ 773'(Al, Na) ${}^{0}L_{Al,Na}^{hcp}$ 773'(Al, Na) ${}^{0}L_{Al,Na}^{hcp}$ 773'(Ca, K) ${}^{0}L_{Ca,K}^{hcp}$ 773'(Ca, Na) ${}^{0}L_{Ca,Na}^{hcp}$ 773'(Ca, Na) ${}^{0}L_{Ca,Na}^{hcp}$ 773'(Ca, Na) ${}^{0}L_{Ca,Na}^{hcp}$ 773'(K, Li) ${}^{0}L_{Ca,Na}^{hcp}$ 773'(K, Li) ${}^{0}L_{Ca,Na}^{hcp}$ 773'(K, Li) ${}^{0}L_{Ca,Na}^{hcp}$ 773'(K, Li) ${}^{0}L_{Ca,Na}^{hcp}$ 7562'(K, Li) ${}^{0}L_{Ca,Na}^{hcp}$ 773'(K, Li) ${}^{0}L_{Ca,Na}^{hcp}$ 773' <td>20000</td>	20000
	T · · 1		${}^{0}L^{liq}_{Al,Na}$	773708+20.277T
	Liquid	(AI, Na) $^{1}L^{liq}_{Al,Na}$		-745869
Al-Na	Bcc	(Al, Na)	${}^{0}L^{bcc}_{Al,Na}$	20000
	Fcc	(Al, Na)	${}^{0}L^{fcc}_{Al,Na}$	78765
	Нср	(Al, Na)	CI       1 aratificter $\hat{X}$ ${}^{0}L_{Al,K}^{liq}$ $\hat{X}$ ${}^{0}L_{Al,K}^{hcc}$ $\hat{X}$ ${}^{0}L_{Al,K}^{hcc}$ $\hat{X}$ ${}^{0}L_{Al,K}^{hcc}$ $\hat{X}$ ${}^{0}L_{Al,Na}^{hcc}$ $\hat{X}$ ${}^{0}L_{Al,Na}^{hcc}$ $\hat{X}$ ${}^{0}L_{Al,Na}^{hcc}$ $\hat{X}$ ${}^{0}L_{Al,Na}^{hcc}$ $\hat{X}$ ${}^{0}L_{Al,Na}^{hcc}$ $\hat{X}$ ${}^{0}L_{Ca,K}^{hcc}$ $\hat{X}$ ${}^{0}L_{Ca,K}^{hcc}$ $\hat{X}$ ${}^{0}L_{Ca,K}^{hcc}$ $\hat{X}$ ${}^{0}L_{Ca,Na}^{hcc}$ $\hat{X}$ ${}^{0}L_{Ca,$	20000
	Liquid	(Ca, K)	${}^{0}L^{liq}_{Ca,K}$	60000
Ca-K	Bcc	(Ca, K)	${}^{0}L^{bcc}_{Ca,K}$	60000
	Fcc	(Ca, K)	${}^{0}L^{fcc}_{Ca,K}$	40000
	Hcp	(Ca, K)	${}^{0}L^{hcp}_{Ca,K}$	30000
	Liquid	(Ca, Na)	${}^{0}L^{liq}_{Ca,Na}$	28896-8.35T
Ca-Na			${}^{1}L^{liq}_{Ca,Na}$	-33-7.03T
	Bcc	(Ca, Na)	${}^{0}L^{bcc}_{Ca,Na}$	56258-39.401T
	Fcc	(Ca, Na)	${}^{0}L^{fcc}_{Ca,Na}$	30000
	Нср	(Ca, Na)	${}^{0}L^{hcp}_{Ca,Na}$	15000
	T :: 1		${}^{0}L^{liq}_{Ca,Na}$	40849-15.723T
	Liquid	(K, Ll)	${}^{1}L^{liq}_{Ca,Na}$	-9583
K-Li	Bcc	(K, Li)	${}^{0}L^{bcc}_{Ca,Na}$	40000
	Fcc	(K, Li)	${}^{0}L^{fcc}_{Ca,Na}$	50000
	Нср	(K, Li)	${}^{0}L^{hcp}_{Ca,Na}$	60000
	т <sup>.</sup> .1		${}^{0}L^{liq}_{Li,Na}$	10684
	Liquid	(L1, Na)	${}^{1}L^{liq}_{Li,Na}$	3896-5.539T
Li-Na	Bcc	(Li, Na)	${}^{0}L^{bcc}_{Li,Na}$	1580

Table 4.1. Thermodynamic parameters of the Al-K, Al-Na, Ca-K, Ca-Na, K-Li, K-Na, K-Mg, Li-Na and Mg-Na systems in SI unit.

	Fcc	(Li, Na)	${}^{0}L^{fcc}_{Li,Na}$	16000
	Нср	(Li, Na)	${}^{0}L^{hcp}_{Li,Na}$	20000
	<b>T</b> · · · 1		${}^{0}L^{liq}_{K:Mg}$	37272
	Liquid	(K, Mg)	${}^{1}L^{liq}_{K:Mg}$	-1073
K-Mg	Bcc	(K, Mg)	${}^{0}L^{bcc}_{K,Mg}$	30000
	Fcc	(K, Mg)	${}^{0}L^{fcc}_{K,Mg}$	50000
	Нср	(K, Mg)	${}^{0}L^{hcp}_{KMga}$	38727
	T · · · 1		${}^{0}L^{liq}_{K:Na}$	2916-0.517T
	Liquid	(K, Na)	${}^{1}L^{liq}_{K:Na}$	-766+1.044T
	D		${}^{0}L^{bcc}_{K:Na}$	11445-10.037T
K-Na	Всс	(K, Na)	${}^{1}L^{bcc}_{K:Na}$	-1595-2.336T
	Fcc	(K, Na)	${}^{0}L^{fcc}_{K,Na}$	15000
	Нср	(K, Na)	${}^{0}L^{hcp}_{K,Na}$	15000
	KNa <sub>2</sub>	$(K)_1(Na)_2$	$G^{KNa_2}$	${}^{o}G_{K}^{bcc} + 2^{o}G_{Na}^{bcc} - 1949 + 3.866T$
	Liquid	$(M_{\alpha}, M_{\alpha})$	${}^{0}L^{liq}_{Mg,Na}$	26026
	Liquid	(Mg, Na)	${}^{1}L^{liq}_{Mg,Na}$	4510
Mg-Na	Bcc	(Mg, Na)	${}^{0}L^{bcc}_{Mg,Na}$	50000
	Fcc	(Mg, Na)	${}^{0}L^{fcc}_{Mg,Na}$	50000
	Нср	(Mg, Na)	${}^{0}L^{hcp}_{Mg,Na}$	75698

System	Reaction	Reference	Temperature	Conce	ntration of Na in	at. %
			(K)			
	$gas \rightarrow liquid1 + liquid2$	Present work	1157	100	0.238	100
		Present work	932	0.14	0.002	100
		Experiment [44]	930	-	-	-
	$liquid1 \rightarrow fcc(Al) + liquid2$	Experiment [47]	932	0.18	< 0.003	-
4137		Experiment[48]	932	0.14	0.002	-
Al-Na		Present work	371	99.99	7.03×10 <sup>-10</sup>	100
		Experiment [44]	371	-	-	-
	$liquid 2 \rightarrow fcc(Al) + bcc(Na)$	Present work	1157	100	0.238	100
		Present work	932	0.14	0.002	100
	$liquid1 \rightarrow bcc(Ca) + liquid2$	Present work	983.9	22.1	10.2	95.9
		Experiment [68]	$983 \pm 10$	0.221	-	95.9
Ca-Na	$bcc(Ca) \rightarrow fcc(Ca) + liquid 2$	Present work	707.3	0.563	0.363	99.5
	$liquid 2 \rightarrow fcc(Ca) + bcc(Na)$	Present work	370.9	99.998	5.180×10 <sup>-3</sup>	99.999
	consolute point	Present work	1470.3		71.275	
		Present work	280.053	59.3	99.3	66.7
		Experiment [74]	280.03	59.95	-	66.7
		Experiment [76]	280.05	58	-	66.7
		Experiment [77]	280.05	-	-	-
	$Liquid = Bcc(Na) + KNa_2$	Experiment [78]	279.75	-	-	-
		Experiment [79]	$280.07 \pm 0.05$	59.8	99.2	66.7
		Experiment [80]	$280.5 \pm 1$	60	97	66.7

Table 4.2. Invariant reactions and consolute points in the Al-Na, Ca-Na, Li-Na, K-Na and Mg-Na systems.

		Experiment [82]	$280.058\pm$	-	-	-	
K-Na			0.001				
		Present work	261.17	30.33	4.3	66.7	
		Experiment [74]	260.65	33.36	-	66.7	
		Experiment [76]	260.55	-	-	-	
	$Liquid + Bcc(K) = KNa_2$	Experiment [78]	260.65	-	-	-	
		Experiment [79]	$260.53 \pm 0.05$	31.9	4.6	66.7	
		Experiment [80]	$261 \pm 1$	33.4	4.5	66.7	
		Experiment [82]	$260.51 \pm 0.01$	-	-	-	
		Present work	444.5	3.4	1.2	90.0	
		Experiment [93]	443	3.4	-	90.2	
K-Na	$liquid1 \rightarrow bcc(Li) + liquid2$	Experiment [97]	443+1	3.4	-	87.87	
		Experiment [105]	444	3.4	-	91.6	
		Present work	360.2	96.5	0.5	99.5	
		Experiment [94, 95]	365.3	97.0	-	-	
<b>T</b> : <b>D</b> I	$liquid 2 \rightarrow bcc(Li) + bcc(Na)$	Experiment [106]	366.5	96.3	-	-	
L1-Na		Experiment [105]	365.4	96.3	-	-	
		Present work	581.5		33		
		Experiment [92]	$577 \pm 2$		$36\pm2$		
		Experiment [93]	576.4		35.7		
Li-Na gas	consolute point	Experiment [94, 95]	578	37			
		Experiment [96]	578	37			
		Experiment [97]	$579 \pm 1$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $			
		Experiment [98]	580		34		
	$gas \rightarrow liquid1 + liquid2$	Present work	1159	84.03	5.78	88.55	
	$gas \rightarrow liquid 2$	Present work	1157		97.31		
		Present work	908	2.0	0.002	92.70	
		Experiment [44]	911	2.0±0.1	-	-	
		Experiment [101]	911	2.1	-	98.6	

Mg-Na	$liquid1 \rightarrow hcp(Mg) + liquid2$	Experiment[64]	910	1.6	-	92.7
		Present work	371	99.98	1.76×10 <sup>-9</sup>	100.00
	$liquid 2 \rightarrow hcp(Mg) + bcc(Na)$	Experiment [44]	371	-	-	-
		Experiment[64]	371	-	-	-



Fig. 4.1. Calculated Al-K phase diagram.



Fig. 4.2. Calculated Al-Na phase diagram.



Fig. 4.3. The enlarged view of Fig. 4.2. at the Al-rich side in comparison with previous work by Murray [46] (dashed lines) and the experimental data  $\circ$  by Scheuer [45];  $\blacktriangle$  by Fink et al. [47];  $\Box$  by Ransley and Neufeid. [48];  $\blacklozenge$  by Hansen et al. [49] and by  $\diamond$  by Fellner et al. [55]. ( $\sigma$ =8.67%)



Fig. 4.4. Calculated activity of Na in liquid in comparison with the experimental data  $\diamond$  at 1293 K and  $\blacktriangle$  at 1353 K by Dewing [59] and  $\bullet$  at 998 K by Brisley and Fray [60] in the Al-Na system. ( $\sigma$ =5.42%)


Fig. 4.5. Calculated Ca-K phase diagram.



Fig. 4.6. Calculated Ca-Na phase diagram in comparison with the experimental data by Rinck *et al.*  $\circ$  [68].



Fig. 4.7. Calculated Li-K phase diagram in comparison with the experimental data  $\blacktriangle$  (liquid miscibility data) • (solubility data) by Smith [72].



Fig. 4.8. The enlarged view of Fig. 4.7. at the Li-rich side in comparison with the experimental data  $\blacktriangle \bullet$  by Smith [72].



Fig. 4.9. The enlarged view of Fig. 4.7. at the K-rich side in comparison with the experimental data  $\blacktriangle$  by Smith [72].



Fig. 4.10. Calculated K-Na phase diagram in comparison with the experimental data  $\triangle$  [74], $\Box$  [76], $\bigcirc$  [78],  $\bullet$  [79],  $\diamond$  [80]. ( $\sigma$ =3.71%)



Fig. 4.11. Calculated activity of K and Na in liquid in comparison with the experimental data  $\bigcirc \bullet$  [87],  $\triangle \blacktriangle$ [88],  $\blacksquare$ [89] in the K-Na system. ( $\sigma$ =9.28%)



Fig. 4.12. Calculated enthalpy of mixing in the liquid phase at 384 K in comparison with the experimental data  $\bullet$ [86] in the K-Na system. ( $\sigma$  =4.43%)



Fig. 4.13. Calculated enthalpy of mixing in the bcc phase at 298 K in comparison with the results from first-principles calculations  $\bullet$  in the Na-K system. ( $\sigma$ =7.75%)



Fig. 4.14. Calculated K-Mg phase diagram in comparison with the experimental data ▲ • by Klemm and Kunze [64].



Fig. 4.15. Calculated activity of Mg in liquid in comparison with the experimental data • by Lantratov [101] in the K-Mg system.



Fig. 4.16. Calculated Li-Na phase diagram in comparison with previous work by Pelton [100] (dashed lines) and the experimental data  $\Box$  [92];  $\diamond$  [93];  $\blacktriangle$ [94, 95];  $\diamond$ [96];  $\bigtriangleup$  [97];  $\blacksquare$ [98];  $\bullet$ [105] and  $\bigcirc$  [106].



Fig. 4.17. Calculated Mg-Na phase diagram in comparison with the experimental data O by Mathewson [44],  $\triangle$  by Lantratov [101] and  $\blacktriangle$  by Klemm and Kunze [64]. ( $\sigma$ =1.32%)



Fig. 4.18. The magnified view of Fig. 4.17 at the Na-rich side in the Mg-Na system.



Fig. 4.19. Calculated activities of Na and Mg in liquid at 973K in comparison with the experimental data  $O(a_{Na}^{liq})$  and  $\bullet(a_{Mg}^{liq})$  by Lantratov [101]. ( $\sigma$ =10.5%)



Fig. 4.20. Calculated Al-Ca phase diagram by Ozturk et al. [10].



Fig. 4.21. Calculated Al-Li phase diagram using COST2 database [41].



Fig. 4.22. Calculated Al-Mg phase diagram by Yu et al. [8].



Fig. 4.23. Calculated Ca-Li phase diagram Grobner et al. [40].



Fig. 4.24. Calculated Ca-Mg phase diagram Yu et al. [9].



Fig. 4.25. Calculated Li-Mg phase diagram using COST2 database [41].

### Chapter 5

# THERMODYNAMIC INVESTIGATION OF THE EFFECT OF ALKALI-METAL IMPURITIES ON THE PROPERTIES OF ALUMINUM-LITHIUM ALLOYS

# **5.1 Introduction**

Aluminum-lithium alloys are very important structural materials and widely used in aircraft and aerospace industries. Compared with other Al alloys, they have a lower density at the equivalent strength levels. The addition of 1 wt. % Li to an Al alloy results in a 6 % increase in the elastic modulus and a 3 % decrease in density. However, these alloys have a variable short-transverse fracture toughness in rolled, extruded and forged forms due to trace amounts of alkali-metal impurities like Na and K.

Alkali metals, such as sodium and potassium, are detrimental impurities in Al-Li alloys. Alkali-metal impurities are introduced into Al-Li alloys through feedback and pickup from refractories. Commercial grades Al-Li alloys usually contain 3-10 wt. ppm alkali-metal impurities.

Payne and Eynon [107] first mentioned Na-induced embrittlement of Al-Li alloys for Na content over 50 ppm. Vaynblat *et al.* [108, 109] found that the fracture toughness drops 16 % in the Al-2Li-0.13Zr alloy if the Na content increases from 31 to 76 ppm. Vasudevan *et al.* [110] observed a linear decrease as a function of Na content in the fracture toughness of Al-Li alloys containing up to 480 ppm Na. Webster [111] also found that toughness decreases in Al-Li alloys containing up to 434 ppm Na and 23 ppm K. Webster's further investigations [112, 113] indicated that alkali-metal impurities like Na, K, Cs and Rb in Al-Li alloys occur as grain boundary liquid phases which are responsible for the reduced toughness and ductility of alloysAlkali-metal-rich liquid particles occur along the grain boundaries in Al-Li alloys via TEM [112] and these liquid particles were highly Na- and K-rich via EDX, WDX and imaging secondary ion mass spectrometry (SIMS) [113]. Sweet *et al.* [114] studied the effects of alkali-metal impurities content on the fracture toughness of Al-Li-Cu alloys extrusions and found brittle islands resulting from liquid-metal embrittlement duo to the presence of discrete Na- and K-rich liquid phases in the grain boundaries.

The mechanisms of the alkali-metal-induced embrittlement in the Al-Li alloys has been proved that it is due to the formation of an intergranular alkali-metal-rich liquid phase that significantly weakens the strength of grain boundaries by TEM, EDX, WDX and SIMS techniques. The performance of Al-Li alloys can be substantially improved via a vacuum refining process [113] and high-purity Al and Li pigs. However, these methods are rather costly. How to suppress alkali-metal-induced HTE by the means of controlling industrial parameters is still not clear. In this chapter, efforts are made to understand the mechanism more deeply and to reveal the correlations between HTE, phase formation, temperature, and composition through thermodynamic calculations.

#### 5.2 Phase evolution and comparison with experimental information

In order to investigate the mechanism of alkali-metal-induced embrittlement in Al-Li alloys more deeply, it is very important to understand the correlations between HTE, phase relation, temperature, and constitution in Al-Li alloys. These correlations can be elucidated by understanding the thermodynamics of the Al-Li-Na-K system.

The thermodynamic database for the Al-Li-Na-K system was developed in Chapter 4 used the CALPHAD approach. In the CALPHAD thermodynamic modeling, the Gibbs energies of individual phase were modeled through the coupling of phase diagrams and thermochemistry, and the model parameters are collected in thermodynamic databases. Models for the Gibbs energy of binary and ternary phases are primarily based on the crystal structures of the phases. The Gibbs energies of individual phases are expressed as a function of composition and temperature that can be used to reveal the phase relations and phase compositions. In the present study, Thermo-Calc [103] was used for free energy minimization and the Al-Li-Na-K database [115] was used for phase description.

Fig. 5.1 shows the calculated isopleth section of Al-2.3Li-K (15 ppm)-Na alloys with respect to the Na content. Note that the Na content is plotted on logarithmic scale due to its low values. There is a liquid miscibility gap in this system originating from the Al-Na and Li-Na systems, denoted liquid-1 (Al-rich) and liquid-2 (Na-rich). Like the Al-Mg-Na system, there is a single phase (fcc) region and a two-phase region (liquid-2+fcc) at fairly low Na concentrations.

Further calculations were carried out to determine the relationship between the temperature and phase fractions for an Al-2.3Li-K (15 ppm)-Na alloy containing 476 ppm of Na. Fig. 5.2 shows phase evolution during cooling of the alloy. At the temperature above 929 K, two liquid phases exist. On cooling, the fcc phase begins to form at 929 K from the liquid-1 phase. Solidification is completed at 920 K and the phase

fraction of the fcc phase reaches unity which indicates that the temperature range of solidification is very shallow. When the fcc phase is cooled to 842 K, another liquid phase (liquid-2 phase) occurs. The amount of the liquid-2 phase increases with decreasing temperature and can be as high as  $5.28 \times 10^{-4}$  mole fraction. Most of the liquid-2 phase begins to transform to a bcc phase at 364 K. Below 280 K, the rest of the liquid-2 phase transforms to the KNa<sub>2</sub> phase.

Fig. 5.3 shows the calculated more fraction of liquid-2 phase vs. temperature, along with the experimental points of Webster [112]. The solid circle is at 394 K and was detected using TEM, EDX and WDX. As shown in Figs. 6.4 and 6.5 taken from the original reference, liquid particles were found along the grain boundaries and at the triple junction of grain boundaries using TEM. In Fig. 6.3, the calculated more fraction of the liquid-2 phase almost reaches a maximum at 394 K. Since the liquid-2 phase forms from the solid fcc grains, it most likely that the liquid-2 phase occures along grain boundaries or in other defect regions.

Fig. 5.6 shows the calculated values for the content of each element in the liquid-2 phase. The liquid-2 phase is highly Na- and K-rich. Al and Li have only the trace contents in the liquid-2 phase. With temperature decreasing, the K content increases, while the Al and Li contents decrease and the Na content decreases a little bit. The calculated results are consistent with the experimental observations of Webster through WDX [112] and SIMS [113]. Fig. 5.7 shows WDX results which indicate the Na and K distributions in the liquid particles. The trace contents of Li and Al as well as an amount of those Na and K can be seen in Fig. 5.8.

Any amount of liquid in the specimen is expected to reduce the ductility since the liquid phase serves as small cracks and the transport of impurity atoms to the crack tip can occur rapidly by capillary flow of liquid. The amount of the liquid-2 phase and experimental ultimate tensile strength (UTS) vs. the process temperatures are shown in Fig. 5.9. With increasing temperature, the amount of liquid-2 phase increases and the UTS decreases since the liquid-2 particles weaken the grain boundaries. Below 275 K, the UTS still increases with decreasing temperature even without the liquid-2 phase. This is due to the effects of the presence of H and Pb in this alloy.

# 5.3 Suppression of alkali-metal-induced HTE in Al-Li alloys

It is generally understood that alkali metal content has to be extremely low in order to completely suppress HTE and avoid cracking. On the other hand, alkali metal contamination is inevitable in the normal manufacturing process of Al-Li alloys. Since HTE is closely related to the liquid-2 phase formation, embrittlement can be suppressed by avoiding the liquid-2 phase formation in the alloy. The hot-rolling safe zone is defined as the region on the phase diagram where only the fcc phase exists and the HTE sensitive zone where the liquid-2 phase exists.

Fig. 5.10 is an enlarged view of Fig. 6.1. It shows the embrittlement sensitive and safe zones in a temperature vs Na content diagram for Al-2.3Li-K (15 ppm)-Na alloys alloys. The hot-rolling safe zone is bounded by the maximum hot-rolling temperature line and the critical hot-rolling temperature line shown in Fig. 6.10. The embrittlement

sensitive zone is bounded by the maximum hot-rolling temperature line, the bcc/liquid-2 transformation temperature line, and the critical hot-rolling temperature line.

The critical temperature line on Fig. 5.10 is also the boundary between the embrittlement safe zone and the embrittlement sensitive zone. In the embrittlement safe zone at the left side of the dashed line, no liquid-2 phase forms and the solid phases microstructure guarantees good hot-rolling characteristics. There are two regions in the embrittlement safe zone. One only has the fcc phase at higher temperatures, the other has the fcc and the intermetallic compound AlLi (B2 phase) at lower temperatures. Since a uniform microstructure guarantees good mechanical performance, Al-Li alloys should have better mechanical properties in the higher-temperature region where only the fcc phase exists. Embrittlement can be avoided when Al-2.3Li-K (15 ppm)-Na alloys are hot rolled in this zone. However, in the embrittlement sensitive zone at the right side of the critical temperature line, the liquid-2 phase occurs most likely at the grain boundaries and reduces hot-rolling formability. For Al-2.3Li-K (15 ppm)-Na alloys, the hot-rolling temperature should be chosen above the critical temperature line in order to suppress embrittlement and avoid cracking.

For a given Na content, there is a critical temperature above which high temperature cracking tends to occur during hot rolling. For instance, the critical temperature of an Al-2.3Li-K (15 ppm)-Na alloy containing 476 ppm Na is 841 K. The hot-rolling temperature should be higher than 841 K in order to avoid embrittlement and cracking. If the Na content decreases to 7.83 ppm, the critical temperature decreases to 575 K. Therefore, the lower the Na content, the lower the critical temperature. As a result, hot rolling can be performed at lower temperatures for alloys containing less Na.

The maximum hot-rolling temperature is 920 K, above which Al-rich liquid-1 and fcc phases coexist, i.e. the Al-2.3Li-K (15 ppm)-Na alloy begins to melt.

### 5.4 Discussion

# 5.4.1 Embrittlement mechanism

Experiments and calculations both indicate that alkali-metal impurities reduce the toughness and ductility in Al-Li alloys since they act as liquid phase in the grain boundaries. For a small grain boundary liquid phase in a fcc matrix, the grain boundary tension at equilibrium is

$$\gamma_{fcc-fcc} = 2\gamma_{fcc-liquid} \cdot \cos\frac{\theta}{2}$$
(5.1)

where  $\gamma_{fcc-fcc}$  and  $\gamma_{fcc-liquid}$  are the surface energies of the fcc grain boundary and the liquid-matrix interface, respectively, and  $\theta$  is the dihedral angle of the liquid-2 phase in the grain boundaries. At equilibrium, the grain boundary energy ( $\gamma_{fcc-fcc}$ ) is one-third of that of a free surface ( $\gamma_s$ ) in Al [116].

$$\gamma_{fcc-fcc} = \frac{\gamma_s}{3} = \frac{1200}{3} = 400 \, ergs \, / \, cm^2 \tag{5.2}$$

The dihedral angel of the lenticular Na-K particles at the grain boundaries was found to be in the range 100° to 120°. For an average of dihedral angel 110°, the surface energy of the liquid-matrix interface is 349 ergs/cm<sup>2</sup>. For grain boundary fracture, the energy required should be more than 2000 ergs/cm<sup>2</sup> ( $2\gamma_s - \gamma_{fcc-fcc}$ ). For grain boundary fracture

in the vicinity of a liquid particle, the energy required is only 298 ergs/cm<sup>2</sup>  $(2\gamma_{fcc-liquid} - \gamma_{fcc-fcc})$  which is much less than the energy required for normal grain boundary fracture. Therefore, embrittlement often occurs when the liquid-2 phase is present at the grain boundaries and the mechanical properties are affected by the liquid-2 phase.

# 5.4.2 Effect of grain size

For a given mole fraction of the liquid-2 phase, i.e., alloy composition and processing temperature, the cracking tendency of the alloy is dependent on the size of the fcc grains because the size of the liquid-2 phase film is dependent on the fcc grain size. The liquid-2 phase usually occurs at grain boundaries as discrete liquid particles.

### 5.4.2.1 Thin film model

For ease of analysis, it is assumed that the liquid-2 phase occurs at the grain boundaries as a continuous film. Thus, the thickness of the liquid film is a measure of cracking tendency since it is proportional to the size of the discontinuous liquid phase at the grain boundaries. Assuming that the mole fraction of the liquid-2 phase is equal to its volume fraction and that the grain boundaries are covered by a continuous layer of the liquid phase, the volume fraction of liquid-2 phase is:

$$f_{liquid-2} = \frac{V_{liquid-2}}{V_g + V_{liquid-2}} = \frac{\delta S_g}{V_g + \delta S_g}$$
(5.3)

where  $V_{liquid-2}$  is the volume of the liquid-2 phase,  $V_g$  the volume of the fcc grains,  $S_g$  the surface area of the grains, and  $\delta$  the average thickness of the liquid-2 film. In three dimensions, according to Tomkeieff's theorem [117], the volume of the grains can be expressed as

$$V_g = \frac{S_g L}{4} \tag{5.4}$$

where L is the average intercept length of grains, which is proportional to the grain size.

Substituting Eq. 5.4 to Eq. 5.3, we obtain

$$f_{liquid-2} = \frac{\delta S_g}{V_g + \delta S_g} = \frac{\delta S_g}{S_g L/4 + \delta S_g} = \frac{4\delta}{L + 4\delta} \approx \frac{4\delta}{L}$$
(5.5)

Thus, the thickness of the liquid-2 phase film can be calculated using the equation.

$$\delta = 0.25 \cdot L \cdot f_{liquid-2} \tag{5.6}$$

From Eq. 5.6, one can see that with increasing grain size, the thickness of the liquid-2 phase film increases and embrittlememt becomes more pronounced. As a result, alloys with small grains tend to have improved fracture resistance.

5.4.2.1 Discrete liquid particles model

According to experimental observations in Al-Li alloys, the liquid-2 phase is found to be lenticular discrete particles along the grain boundaries. In this model, we assume that the mole fraction of the liquid-2 phase is equal to its volume fraction, that the grain boundaries are covered by many lenticular discrete particles of the liquid phase, and that the grain is spherical. The volume of one lenticular liquid particle is as follows.

84

$$v = \frac{2\pi h^2}{3} (3R' - h)$$
(5.7)

where h is the height of the particle and R' is the radius of the sphere.

According to the geometrical relations, we know

$$h = R'(1 - \cos\frac{\theta}{2}) = 2R'\sin^2\frac{\theta}{4}$$
 (5.8)

where is the diheral angle. Substituting Eq. 5.8 to Eq. 5.7, we obtain

$$v = \frac{2\pi h^3}{3} \left( \frac{3}{2\sin^2 \frac{\theta}{4}} - 1 \right) = \pi h^3 \left( \frac{1}{\sin^2 \frac{\theta}{4}} - \frac{2}{3} \right)$$
(5.9)

The radius of the circle covering the grain boundary is

$$r = R'\sin\frac{\theta}{2} = \frac{h}{2\sin^2\frac{\theta}{4}} \cdot \sin\frac{\theta}{2} = h\cot\frac{\theta}{4}$$
(5.10)

The volume fraction of liquid-2 phase is given by:

$$f_{liquid-2} = \frac{V_{liquid-2}}{V_g} = \frac{nV}{2V_g} = \frac{n\pi\hbar^3 \left(\frac{1}{\sin^2\frac{\theta}{4}} - \frac{2}{3}\right)}{\frac{8}{3}\pi R^3} = \frac{3n\hbar^3}{8R^3} \left(\frac{1}{\sin^2\frac{\theta}{4}} - \frac{2}{3}\right)$$
(5.11)

where n is the number of the liquid particles along the grain boundary of one grain.

Then we can get

$$n = \frac{8r^3 f_{liquid-2}}{3h^3 \left(\frac{1}{\sin^2 \frac{\theta}{4}} - \frac{2}{3}\right)}$$
(5.12)

The coverage percent of the liquid particles along the grain boundaries is as follows.

$$K = \frac{nS}{4\pi R^2} = \frac{n\pi r^2}{4\pi R^2} = \frac{\frac{8R^3 f_{liquid-2}}{3h^3 \left(\frac{1}{\sin^2 \frac{\theta}{4}} - \frac{2}{3}\right)}}{4\pi R^2} = \frac{2R f_{liquid-2} \cot^2 \frac{\theta}{4}}{3h \left(\frac{1}{\sin^2 \frac{\theta}{4}} - \frac{2}{3}\right)} \times 100\% \quad (5.13)$$

where S is the area of the circle covering the grain boundaries and R is the radius of the grain.

We obtain the relation further.

$$Kh == R \cdot f_{liquid-2} \cdot g(\theta) \tag{5.14}$$

where

$$g(\theta) = \frac{2\cot^2\frac{\theta}{4}}{3\left(\frac{1}{\sin^2\frac{\theta}{4}} - \frac{2}{3}\right)}$$
(5.15)

In Eq. 5.14, the variables K and h on the left hand side indicate the degree of HTE, which should be minimized to avoid cracks. On the right hand side,  $g(\theta)$  is almost a constant for a given alloy. One can see that with increasing grain size, he degree of the HTE increases and embrittlement becomes more pronounced. As a result, alloys

with small grains tend to have improved fracture resistance. Comparing with Eq. 5.14 and Eq. 5.6, it is easy to see that they have the same physical meaning.

# 5.4.3 Effect of Na-K ratio

Since the amount of liquid-2 phase at a given temperature determines the extent of embrittlement, the transformation temperature of liquid-2/bcc is very important. Below that temperature, liquid-2 phase disappears and good mechanical properties recover. Because the liquid-2 phase is highly Na- and K-rich, the ratio of Na content to K content affect the transformation temperature greatly according to the Na-K phase diagram in Fig. 4.10. The effect of the ratio of the Na and K content on the amount of the liquid-2 phase is shown in Fig. 5.11. The amount of the liquid-2 phase increases with the ratio increasing. However, the amount of the liquid-2 phase is not very sensitive to ratio when it is much high or low. At 300 K, the ratio of the Na and K content influences the amount of liquid-2 phase very much. Fig. 5.12 shows that the amount of the liquid-2 phase reaches the maximum if the ratio is 1.64. However, when the ratio is more than 31.73, there is no liquid-2 phase.

## 5.5 Summary

Thermodynamic investigation was carried out to study the alkali-metal-induced embrittlement in Al-Li alloys. The calculated results indicate that the Na- and K-rich liquid-2 phase plays an important role on HTE. A liquid-2 phase forms from the solid fcc phase (most likely at grain boundaries) during cooling, resulting in the occurrence of the embrittlement and affecting the mechanical properties. The calculated results agree to the experimental data very well. Through thermodynamic simulation, the embrittlement safe and sensitive zone have been determined with different alkali metal content and temperature. The critical hot-rolling temperature was obtained which provides an important industrial parameter to suppress fracture and embrittlement.



Fig. 5.1. Calculated isopleth section of Al-2.3Li-K(15 ppm)-Na alloys.



Fig. 5.2. Calculated mole fraction of each phase vs. temperature curves during the solidification of the Al-2.3Li-Na (476 ppm)-K (15 ppm) alloy.


Fig. 5.3. Calculated mole fraction of liquid-2 phase vs temperature with experimental detect points  $\bullet$  (TEM, EDX and WDX),  $\blacktriangle$  (mechanical properties tests) by Webster [112].



Fig. 5.4. TEM picture showing discrete Na-K-rich liquid particles along the grain boundaries in the Al-2.3Li-Na (476 ppm)-K (15 ppm) alloy at 394 K [112].

(The caption in the original reference [112]: Fig. 5 -TEM of alloy 2BLKN aged 394 K showing density, lenticular grain boundary phases containing sodium and potassium. Dark circular particle inside each low density particle is rich in lead. )



Fig. 5.5. TEM picture showing discrete Na-K-rich liquid particles in a grain boundary triple junction in the Al-2.3Li-Na (476 ppm)-K (15 ppm) alloy at 394 K [112].

(The caption in the original reference [112]: Fig. 6 -TEM from alloy 2BLKN showing a low density particle at a grain boundary triple junction. A dark spherical rich in lead is contained within the low density article which contains sodium and potassium.)



Fig. 5.6. Calculated content of each element in the liquid-2 phase vs. temperature curve for the Al-2.3Li-Na (476 ppm)-K (15 ppm) alloy.



Fig. 5.7. Na and K content detected by WDX in the liquid-2 particles along the grain boundaries in the Al-2.3Li-Na (476 ppm)-K (15 ppm) alloy at 394 K [112].

(The caption in the original reference [112]: Fig. 4 -WDX scan for sodium and potassium across a grain boundary particle for alloy 2BLKN aged 394 K and fractured in the sgort transverse direction. )





(The caption in the original reference [113]: Fig. 2 –Distribution of elements in the grain boundary of an Al-Li alloy with high sodium (600 ppm).and potassium (9 ppm), but normal cesium and rubidium levels (less than 0.1 ppm). Colors represent concentration of indicated elements. Aged 16 h at 120 °C (250 °F). Alkali metal impurities sodium (a), potassium (b), rubidium (c), cesium (d), and hydrogen (e) are concentrated in three grain boundary particles. However, the grain boundaries show a denudation of lithium (f), and aluminum (g).)



Fig. 5.9. Experimental ultimate tensile strength ○ [112] and the calculated amount of the liquid-2 phase of the Al-2.3Li-Na (476 ppm)-K (15 ppm) alloy plotted as a function of the process temperature.



Fig. 5.10. HTE sensitive and safe zones as well as critical hot rolling temperatures and maximum Na content of Al-2.3Li-K (15 ppm)-Na alloys.



Fig. 5.11. The amount of liquid-2 phase vs the ratio of Na and K content in Al-2.3Li-Na-K alloys at 600 K.



Fig. 5.12. The amount of liquid-2 phase vs the ratio of Na and K content in Al-2.3Li-Na-K alloys at 300 K.

### Chapter 6

# THERMODYNAMIC INVESTIGATION OF NA-INDUCED HIGH TEMPERATURE EMBRITTLEMENT IN AL-MG ALLOYS

# **6.1 Introduction**

Due to its excellent formability, Al-Mg alloys are widely used in the automotive and aircraft industries. However, they suffer from poor hot rolling characteristics. Sodium is a common undesired impurity element in Al-Mg alloys of commercial grades. In spite of a trace amount, Sodium leads to high temperature embrittlement (HTE) at 473-673 K due to intergranular fracture and formation of cracks during the hot-rolling process [1, 2].

Ransley and Talbot [118] first investigated the embrittlement of Al-Mg-Si alloys by Na and suggested that hot ductility is severely impaired with a Na content higher than 20 ppm. A ternary compound NaAlSi was considered to be involved in the reaction of  $NaAlSi + 2Mg \rightarrow Mg_2Si + Na_{free}$ , resulting in free Na in the form of atoms. The embrittlement is related to the adsorption of free Na on internal surfaces generated in plastic flow and consequent modification of the growth of grain boundary cavities. When investigating the dependence of the hot ductility of Al-Mg alloys on temperature, strain rate, grain size and composition using tensile test, Otsuka and Horiuchi [119] found that the hot ductility trough shifts to higher temperatures with increasing strain rate and that hot ductility decreases with increasing grain size and bulk Mg concentration. However, the Na content was not determined. Talbot and Granger [1] studied the effects of Na and Bi on HTE in Al-5Mg-0.15Si (wt. %) and commercial Al-5Mg alloys by the use of a hydrogen absorption technique. They found that the solubility of Na in Al-Mg alloys was about 5 ppm, and that the excess Na was in the form of free Na atoms. However, Okada and Kanno's results [120] obtained in Al-5Mg and Al-5Mg-0.04Y alloys in the temperature range of 473 K to 673 K indicated that HTE was related both to hydrogen and Na concentrations [103]. A concentration of 0.1 ppm of Na was high enough to cause HTE.

Horikawa *et al.* [2, 121] examined the effect of Na on HTE by measuring the reduction of area during tensile testing of specimens of a high purity Al-5Mg alloy containing 0.01 ppm to 1.8 ppm of Na. The trace Na content was detected by glow discharge mass spectrometry (GD-MS). They reported that the HTE disappeared completely when the Na content was lower than 0.01 ppm. The trace Na was assumed to segregate to the grain boundaries in the form of free Na atoms and to reduce the grain boundary strength, although no Na was detected on intergranular fracture surface by auger electron spectroscopy (AES). However, Lynch [122] suggested that HTE is due to the formation of low melting point Na-rich phases or particles that precipitate at the grain boundaries of the alloys after comparing with embrittlement in other Al alloys.

Despite numerous previous investigations, the mechanisms of Na on HTE in Al-Mg alloys are still controversial [122, 123]. This is partly due to the fact that the trace amount of Na cannot be detected even by AES [121]. In the present work, efforts are

made to understand the mechanism and to reveal the correlations between HTE, phase formation, temperature, and composition by the use of thermodynamic modeling.

#### 6.2 Phase diagrams and phase evolution

In order to investigate the mechanism of Na-induced HTE in Al-Mg alloys, it is very important to understand the correlations between HTE, phase relation, temperature, and constitution in Al-Mg alloys. These correlations can be elucidated by understanding the thermodynamics of the Al-Mg-Na system.

The thermodynamic database of the Al-Mg-Na system has been developed by the present authors by the use of the CALPHAD approach [115]. In the CALPHAD thermodynamic modeling, the Gibbs energies of individual phase are modeled through the coupling of phase diagrams and thermochemistry and the model parameters are collected in thermodynamic databases. Models for the Gibbs energy of binary and ternary phases are primarily based on the crystal structure of the phases. The Gibbs energies of individual phases are expressed as a function of composition and temperature that can reveal the phase relations and phase compositions. In the present study, Thermo-Calc [103] was used for free energy minimization and the Al-Mg-Na database [115] was used for phase description.

Fig. 6.1 shows the calculated isopleth section of Al-5Mg alloys with respect to the Na content. Note that the Na content is plotted in the logarithmic scale due to its low

values. There is a liquid miscibility gap in this system originated from the Al-Na and Mg-Na systems, denoted by liquid-1 (Al-rich) and liquid-2 (Na-rich). There is a two-phase region (liquid-2+fcc) between 524 K and 853 K at fairly low Na concentrations. The temperature and the Na concentration range in this two-phase region coincides with the temperature and the Na concentration zones where HTE occurs as shown later.

Further calculations were carried out to determine the relationship between the temperature and phase fractions for an Al-5Mg alloy containing 1.8 ppm of Na. Fig. 5.2 shows phase evolution during cooling of the alloy. On cooling, the face centered cubic (fcc) phase begins to form at 908 K from the liquid-1 phase. Solidification is completed at 853 K and the phase fraction of the fcc phase reaches unity. When the fcc phase is cooled to 723 K, another liquid phase (liquid-2 phase) occurs. The amount of the liquid-2 phase increases with decreasing temperature and can be as high as  $2.1 \times 10^{-6}$  mole fraction. This liquid-2 phase transforms to a bcc phase at 371 K. Fig. 3 shows the Na content in the liquid-2 phase as a function of temperature depicting that the liquid-2 phase is highly Na-rich, and the Na content increases with decreasing temperature.

Figs. 6.2 and 6.3 indicate that Na is completely dissolved in the Al-rich fcc phase in the temperature range of 723 K to 853 K after solidification. As temperature decreases, the highly Na-rich liquid-2 phase forms from the solid fcc grains, most likely along grain boundaries or in other defect regions. Then, the liquid-2 phase transforms to Na-rich bcc phase at a low temperature.

### 5.3 Mechanism of Na-induced HTE

The mechanism of Na-induced HTE in Al-Mg alloys remains controversial. Talbot and Granger [1], Ransley and Talbot [118], and Horikawa *et al.* [2, 121] attributed HTE primarily to segregation of Na atoms to grain boundaries, although no Na was detected on intergranular fracture surfaces. Horikawa *et al.* [123] indicated that there is no possibility of forming enough Na-rich particles or Na-rich phases to cause HTE in view of the trace amount of Na. Lynch [122] concluded that Na-rich particles rather than Na atoms at grain boundaries induce HTE in comparison with the case in Al-Li alloys [112, 114]. In this section, the mechanism of Na-induced HTE is revealed by describing the correlations between HTE, phase relation, temperature, and constitution in Al-Mg alloys.

Fig. 6.4 shows the comparison between our calculated phase relations and the experimental data from the literature [2]. The calculated relationship between the temperature and the phase fraction for Al-5Mg-Na alloys under equilibrium conditions is shown in Fig. 6.4 (a). The effect of trace Na on the hot ductility of Al-5Mg alloys at different temperatures from the literature [2] is shown in Fig. 6.4 (b), where the reduction of area is defined as the percentage decrease in the cross-sectional area of a tensile specimen caused by wasting or necking of the specimen. It is expressed as a percentage of the original area of the test piece and is a measure of ductility. In Fig. 6.4 (a), it is evident that the Na content affects the formation temperature and the amount of liquid-2 significantly. With increasing Na content in Al-5Mg-Na alloys, the amount of liquid-2

and its formation temperature increase. However, the temperature of transformation from liquid-2 phase to body centered cubic (bcc) phase does not change. The temperature is approximately equal to the melting temperature of pure Na (371 K).

The ductility troughs in the temperature range of 400 K to 700 K shown in Fig. 6.4(b) can be explained by the use of data from Fig. 6.4(a). The troughs start at about 700 K at which point the liquid-2 phase starts to form. From 700 K to 600 K, as the amount of liquid-2 increases, the reduction of area decreases. At about 550 K, the amount of liquid-2 reaches the maximum, and the reduction of area reaches the minimum. At temperatures lower than 524 K, the formation of  $\beta$  (Al<sub>140</sub>Mg<sub>89</sub>) phase seems to improve the ductility. At about 380 K, the liquid-2 phase completely transforms to bcc and hot ductility recovers almost completely.

The relationship between HTE and the Na content can also been explained using Fig. 6.4. The mole fraction of the liquid-2 phase increases with increasing Na content. As a result, the reduction of area decreases with increasing Na in the temperature range of 400 K to 700 K.

The results of the thermodynamic simulation shown in Fig. 6.4(a) support Lynch's argument [122] that the HTE in Al-Mg alloy is due to the formation of a low melting point Na-rich phase that precipitates at the grain boundaries. They also clarify some of the doubts outlined in Lynch's article [122] on the hypothesis of embrittlement of Al-Mg alloys by Na-rich phases. Firstly, the liquid-2 phase precipitates out of the fcc phase at temperatures as high as 723 K. Secondly, the liquid-2 phase exists in the temperature range of 371 K (98 °C) to 723 K (450 °C), which is exactly the temperature range of the ductility trough reported in the literature. Thirdly, the maximum phase fraction under the equilibrium conditions is  $2.1 \times 10^{-6}$  in Al-5Mg alloy containing 1.8 ppm Na. Any amount of liquid fraction existing in the specimen is expected to reduce the ductility since the liquid phase serves as small cracks and the transport of impurity atoms to the crack tip can occur rapidly by capillary flow of liquid. However, the results shown in Fig. 5.4 cannot be used to explain the experimental observation on the effect of grain boundary inclination on the embrittlement reported by Otsuka and Horiuchi [119]. It is worth noting that the precipitation of the liquid-2 phase can occur both at the grain boundaries and other defects such as phase boundaries. It would be interesting to be able to detect the liquid phase distribution in the specimen of bi-crystal Al-Mg alloys.

# 6.4 Suppression of Na-induced HTE in Al-Mg alloys

It is generally understood that Na content has to be extremely low in order to completely suppress HTE and avoid cracking. On the other hand, contamination with Na is inevitable in the normal manufacturing process of Al-Mg alloys. Since HTE is closely related to the liquid-2 phase formation, HTE can be suppressed by avoiding the liquid-2 phase formation in the alloy. We define the hot-rolling safe zone as the region on the phase diagram where only fcc phase exists and the HTE sensitive zone where the liquid-2 phase exists.

Fig. 5.5 is an enlarged view of Fig. 5.1. It shows the HTE sensitive and safe zones in a temperature vs Na content diagram of Al-5Mg-Na alloys. The hot-rolling safe zone is bounded by the maximum hot-rolling temperature line and the dash line shown in Fig. 5. The HTE sensitive zone is bounded by the maximum temperature line, the bcc/liquid-2 transformation temperature line, and the dash line. The dash line on Fig. 5.5 is also the boundary between the hot-rolling safe zone and the HTE sensitive zone. In the hot-rolling safe zone at the left side of the dashed line, no liquid-2 phase forms and the single phase fcc microstructure guarantees good hot-rolling characteristics. HTE can be avoided when Al-5Mg-Na alloys are hot rolled in this zone. However, in the HTE sensitive zone at the right side of the dashed line, the liquid-2 phase occurs most likely at the grain boundaries and reduces hot-rolling formability. For Al-5Mg-Na alloys containing different Na contents, the hot-rolling temperature should be chosen above the dashed line in order to suppress HTE and avoid cracking. For a given Na content, there is a critical temperature above which high temperature cracking tends to occur during hot rolling. For instance, the critical temperature of the Al-5Mg alloy containing 1 ppm Na is 689 K. That is to say that the hot-rolling temperature should be higher than 689 K in order to avoid HTE. If the Na content decreases to 0.1 ppm, the critical temperature decreases to 583 K. Therefore, the lower the Na content, the lower the critical temperature. As a result, hot rolling can be performed at lower temperatures for alloys containing less Na than those containing more Na. The maximum hot-rolling temperature is 853 K above which Al-rich liquid-1 phase and fcc phase coexist, i.e. the Al-5Mg alloy begins to melt.

The boundaries that define the HTE zone shown in Fig. 5.5 include the critical hot-rolling temperature (dash line), the maximum hot-rolling temperature, and the maximum Na content. These boundaries can be affected by varying the Mg content of the alloy and can be determined using thermodynamic simulations with the Al-Mg-Na database and Thermo-Calc, a commercial simulation package.

The critical hot-rolling temperature is illustrated as the dash line separating the hot-rolling safe zone and the HTE sensitive zone in Fig. 5. An expression for the critical hot-rolling temperature, T, in the range of Mg content of  $0.01 \le w_{Mg} \le 0.10$  is given by the following equation by the use of regression analysis:

$$\frac{10^4}{T(K)} = -1.27 - 1.91 w_{Mg} - (1.09 + 1.19 w_{Mg}) \ln(w_{Na})$$
(6.1)

where  $w_{Na}$  and  $w_{Mg}$  are the weight fractions of Na and Mg. The logarithmic relationship shown in Eq.1 for the Na content indicates the critical role of Na in HTE.

The maximum hot-rolling temperature,  $T^{Max}$ , for Mg content in the range of  $0.01 \le w_{Mg} \le 0.10$  can be expressed as:

$$T^{Max}(K) = 931 - 1527 w_{Mg} \tag{6.2}$$

The maximum hot-rolling temperature is also the upper limit of the HTE zone shown in Fig. 5.5. The liquid-1 phase forms in the alloy when the temperature is higher than the maximum hot-rolling temperature.

The maximum Na content shown in Fig. 5.6 is a critical composition point above which the liquid-2 phase always forms at any hot-rolling temperatures. Therefore HTE cannot be avoided when the Na content is higher than the maximum Na content. The relationship between the maximum Na content,  $w_{Na}^{Max}$ , and the Mg content can be expressed by the following equation.

$$w_{Na}^{Max}(ppm) = 16.47 - 94.84 w_{Mg} \tag{6.3}$$

Also the maximum Na content decreases with increasing Mg content.

Eqs. 5.1, 5.2 and 5.3 can be used to determine the critical hot-rolling temperature, the maximum hot-rolling temperature, and the maximum Na content. The hot-rolling safe zone of the Al-Mg-Na alloys can be defined using these boundary equations.

Ideally the alloy should be hot rolled in the hot-rolling safe zone in order to avoid cracking formation. In case that the alloy has to be hot rolled at the temperature range corresponding to that of the HTE sensitive zone, the tendency of cracking formation can be evaluated by the use of the mole fraction of the liquid-2 phase because the reduction of area, a measure of ductility, decreases with increasing mole fraction of the liquid-2 phase

shown in Fig. 5.4. Factors affecting HTE include the strain rate, grain size, and alloy composition [122]. The strain rate is related to the response of the liquid phase/particles to strain. The effect of grain size and alloy composition can be evaluated using thermodynamic simulations.

For a given mole fraction of the liquid-2 phase, i.e., alloy composition and processing temperature, the cracking tendency of the alloy is dependent on the size of the fcc grains because the size of the liquid-2 phase film is dependent on the fcc grain size. The liquid-2 phase usually occurs at grain boundaries as discrete liquid particles. For the easiness of analysis, we assume that the liquid-2 phase occurs at the grain boundaries as a continuous film. Thus the thickness of the liquid film is a measure of cracking tendency since it is proportional to the size of the discontinuous liquid phase at the grain boundaries. Assuming that the mole fraction of the liquid-2 phase is equal to its volume fraction and that the grain boundaries are covered by a continuous layer of the liquid phase, the volume fraction of liquid-2 phase is given by:

$$f_{liquid-2} = \frac{V_{liquid-2}}{V_g + V_{liquid-2}} = \frac{\delta S_g}{V_g + \delta S_g}$$
(6.4)

where  $V_{liquid-2}$  is the volume of the liquid-2 phase,  $V_g$  the volume of the fcc grains,  $S_g$  the surface area of the grains, and  $\delta$  the average thickness of the liquid-2 film. In three dimensions, according to Tomkeieff's theorem [117], the volume of the grains can be expressed as

$$V_g = \frac{S_g L}{4} \tag{6.5}$$

where L is the average intercept length of grains, which is proportional to the grain size.

Substituting Eq. 5.6 to Eq. 5.5, we obtain

$$f_{liquid-2} = \frac{\delta S_g}{V_g + \delta S_g} = \frac{\delta S_g}{S_g L/4 + \delta S_g} = \frac{4\delta}{L + 4\delta} \approx \frac{4\delta}{L}$$
(6.6)

Thus the thickness of the liquid-2 phase film can be calculated by the following equation.

$$\delta = 0.25 \cdot L \cdot f_{\text{liauid-2}} \tag{6.7}$$

where  $f_{liquid-2}$  is the mole fraction of the liquid-2 phase and is approximately equal to the Na content as shown in Fig. 6.4(a). From Eq. 6.8, one can see that with increasing grain size, the thickness of the liquid-2 phase film increases and HTE becomes more pronounced. As a result, alloys with small grains tend to have improved HTE resistance. This is in good agreement with the experimental results reported by Otsuka and Horiuchi [119].

The effect of alloy composition is partly shown in Fig. 6.4 and Fig. 6.6. Fig. 5.4 (a) shows that mole fraction of the liquid-2 phase as a function of Na concentration and

temperature. The mole fraction of the liquid-2 phase increases with increasing Na concentration in Al-5Mg-Na alloy, indicating the HTE tendency increases with increasing Na.

The effect of Mg concentration on HTE is more complex. Fig. 6.6 shows the relationship between the mole fraction of the liquid-2 and the weight fraction of Mg in Al-Mg-Na alloys at various Na concentrations at a temperature T=573 K at which the reduction of area reaches the minimum in the experiments by Horikawa et al. [2, 121]. For a given Na concentration in the alloy, there is a critical Mg concentration,  $C_{Mg}$ , below which the variation in Mg concentration has a little effect on the mole fraction of the liquid-2 phase since the alloy is in the HTE safe zone. Immediately above the critical Mg concentration, the alloy composition enters into the HTE sensitive zone and a slight increase in Mg concentration leads to a sharp increase in the mole fraction of the liquid-2 phase. The mole fraction of liquid-2 phase keeps increasing in the composition range between  $C_{Mg}$  and  $C_{Mg}$  + 2 wt. %. With a further increase in Mg composition more than  $C_{Mg}$  + 2 wt. %, the mole fraction of the liquid-2 phase almost remains a constant. Therefore HTE is sensitive to the Mg concentration only if the magnesium concentration at a certain range which varies with the Na concentration. Out of this Mg content range, HTE is insensitive to the variation on magnesium concentration.

The critical Mg concentration,  $C_{Mg}$ , can be expressed by the following equation at 573 K.

$$C_{Mg}(wt.\%) = -0.6486\ln[w(Na)](ppm) + 3.3281$$
(6.8)

113

 $C_{Mg}$  increases with the Na concentration decreasing.  $C_{Mg}$  is 4.8 wt. % at Na=0.01ppm and is 2.9 wt. % at Na=1.8 ppm. For an Al-5Mg alloys, the HTE could be sensitive with a slight variation on Mg concentration if the Na concentration is about 0.1 ppm. The understanding of the Mg content on Na-induced HTE tell us that changing the Mg content can suppress HTE when the Na content cannot be changed.

The curves in Fig. 6.7 are the calculated results using Eqs. 1 to 3 respectively. The symbols are the date points calculated using Thermo-Calc software and the Al-Mg-Na database. It is clear that the results obtained using Eqs. 6.1, and 6.3 agree with the thermodynamic simulation results well. Thus, Eqs. 6.1, 6.2 and 6.3 can be used to determine the critical hot-rolling temperature, the maximum hot-rolling temperature, and the maximum Na content. The hot-rolling safe zone of the Al-Mg-Na alloys can be defined using these boundary equations.

Fig. 6.8 is a contour map of the critical hot-rolling temperature and the maximum Na content (dashed line) of Al-Mg-Na alloys with respect to Mg and Na contents. The contour map can serve as a roadmap for Al-Mg alloys processing by enabling one to choose the proper hot-rolling temperature according to various Mg and Na contents. In order to avoid cracking formation during hot rolling operation, the rolling temperature has to be higher than the critical hot-rolling temperature illustrated in Fig. 6.8.

# 6.6 Summary

Fundamental understanding of Na-induced HTE in Al-Mg-Na alloys is revealed by performing a thermodynamic investigation. The results indicate that the liquid miscibility gap due to Na plays an important role on HTE. A liquid-2 phase forms from the solid fcc phase (most likely at grain boundaries) during cooling, resulting in the occurrence of the HTE. Comparison of the thermodynamic simulation results with experimental measurements on the high temperature ductility of Al-5Mg-Na alloy shows that the HTE occurs in the temperature range where the liquid-2 phase exists.

A hot-rolling safe zone is defined in which no liquid-2 phase will occur. Also an HTE sensitive zone is defined on the phase diagram where the liquid-2 phase forms. The hot rolling safe zone is within the temperature and composition ranges described using the following two equations:

$$\frac{10^4}{T(K)} = -1.27 - 1.91 w_{Mg} - (1.09 + 1.19 w_{Mg}) \ln(w_{Na})$$
$$T^{Max}(K) = 931 - 1527 w_{Mg}$$

where T(K) is the critical hot-rolling temperature and  $T^{Max}$  is the maximum hot-rolling temperature. The hot-rolling safe zone lies at the left side of the T(K) vs  $w_{Mg}$  and  $w_{Na}$  and the HTE sensitive zone on the right side. HTE should not occur when the hot-rolling temperature and the composition of the alloy falls in the safe zone. In the HTE sensitive zone, the tendency of crack formation is proportional to the mole fraction of the liquid-2 phase and the size of the fcc grains. The cracking tendency decreases with decreasing Na content, increasing hot-rolling temperature (in the temperature range between 371 and  $T^{Max}$ ), and decreasing grain size.



Fig. 6.1. Calculated isopleth section (Al-5Mg-Na).



Fig. 6.2. Calculated mole fraction of each phase vs. temperature curves during the solidification of the Al-5Mg-Na (1.8 ppm) alloy.



Fig. 6.3. Na content in the liquid-2 phase vs. temperature curve for the Al-5Mg-Na (1.8 ppm) alloy.





Effect of Na on hot ductility of Al-5Mg alloys at different temperatures [2].



Fig. 6.5. HTE sensitive and safe zones as well as critical hot rolling temperatures (the dashed line) and maximum Na content of Al-5Mg-Na alloys.



Fig. 6.6. Calculated mole fraction of liquid-2 phase vs. the Mg content.



Fig. 6.7. Experimental hot ductility • [2] and the calculated amount of the liquid-2 phase of Al-5Mg-Na alloys plotted as a function of the Na content.



Fig. 6.8. HTE sensitive and safe zones as well as critical hot rolling temperatures and maximum Na content of the Al-Mg-Na alloys with different Mg contents.



Fig. 6.9. Contour map of the critical hot-rolling temperature and the highest Na content (the dashed line) of Al-Mg alloys with respect to Mg and Na content (a), and with the y axis enlarged (b).

# Chapter 7

# FUNDAMENTAL UNDERSTANDING OF NA-INDUCED HIGH TEMPERATURE EMBRITTLEMENT IN MG-LI ALLOYS

# 7.1 Introduction

Magnesium is the eighth most abundant element in the Earth's crust and the third most plentiful element dissolved in seawater. It is the lightest structural metal with a density of 1.741 g/cm<sup>3</sup>, in comparison with the densities of Al (2.70 g/cm<sup>3</sup>) and Fe (7.86 g/cm<sup>3</sup>). Lithium is the lightest metal with a density of 0.53 g/cm<sup>3</sup> of all metals and has extensive solid solubility in Mg. This makes magnesium-lithium alloys particularly attractive in aircraft and aerospace industries for weight reduction and higher fuel efficiency. Furthermore, the hcp structure of magnesium can be changed to more ductile and workable bcc structure by adding 11 wt. % lithium.

However, the ductility of Mg-Li alloys is destroyed by even trace quantities of Na which is introduced through feedback and pickup from refractories. Payne and Eynon [124] found that the ductility of Mg-Li alloy containing 12-13.5 wt. % Li was reduced if the Na content is over 20 ppm. Frost *et al.* [125] found that the trace amount of Na reduces the elongation and reduction of area of Mg-9Li-4Zn alloy. They suggested that the effects of Na can be minimized by using a flux consisting of 75 wt. % LiCl and 25 wt. % LiF. Bubbling nitrogen through the melt also helps remove Na. The effects of Na on the mechanical properties of 01420 alloy (Al-Mg-Li alloy) was investigated by Vaynblat *et al.* [108, 109]. Toaz and Ripling [126] investigated the tensile properties of three
Mg-Li alloys having respectively 3.6 wt. %, 5.8 wt. % and 10.6 wt. % Li. The intergranular cracks result from the localized diffusion of Na to the grain boundaries. Singh [127] measured the ductility troughs of Mg-Li-Al alloy containing some alloy elements.

#### 7.2 Phase evolution and comparison with experimental information

In order to investigate the mechanism of Na-induced HTE in Mg-Li alloys, it is very important to understand the correlations between HTE, phase relation, temperature, and constitution in Mg-Li alloys. These correlations can be elucidated by understanding the thermodynamics of the Mg-Li-Na system.

The thermodynamic database of the Mg-Li-Na system has been developed by the present authors by the use of the CALPHAD approach in Chapter 3. In the CALPHAD thermodynamic modeling, the Gibbs energies of individual phase are modeled through the coupling of phase diagrams and thermochemistry and the model parameters are collected in thermodynamic databases. Models for the Gibbs energy of binary and ternary phases are primarily based on the crystal structure of the phases. The Gibbs energies of individual phases are expressed as a function of composition and temperature that can reveal the phase relations and phase compositions. In the present study, Thermo-Calc [103] was used for free energy minimization and the Mg-Li-Na database was used for phase description.

The calculated liquidus projection of the Mg-Li-Na ternary system is presented in Fig. 7.1 with the primary phases forming from the liquid phase during solidification shown. The dotted lines are isotherms, with the numbers indicating the temperature in Kelvin. It shows that the liquid miscibility gap at high temperatures in the Mg-Na system smoothly connects to the liquid miscibility gap at low temperatures in the Li-Na system. Unlike the Al-Mg-Na and Al-Li-Na ternary system, there is no intermetallic compound in the Mg-Li-Na system.

Similar to the Al-Li and Al-Mg alloys, the liquid-2 phase is presented after the solidification process of Mg-Li alloys. However, the big difference is there is no intermetallic compound in the Mg-Li-Na system and the majority of solid phase after solidification can be hep or bee according to the Li content.

Figs. 7.2, 7.6 and 7.10 show the calculated isopleth sections of Mg-3.6Li-Na, Mg-5.8Li-Na, and Mg-10.6Li-Na alloys respectively with respect to the Na content. Note that the Na content is plotted in the logarithmic scale due to its low values. There is a liquid miscibility gap in this system originated from the Mg-Na and Li-Na systems, denoted by liquid-1 (Mg-rich) and liquid-2 (Na-rich). There is a phase region containing liquid-2 and hcp/bcc-1 phase at fairly low Na concentrations.

Further calculations were carried out to determine the relationship between the temperature and phase fractions for three Mg-Li-Na alloy containing different Na. Fig. 7.3(b), 7.7(b) and 7.11(b) show phase evolution during cooling of the alloys.

For Mg-3.6Li-Na alloys, on cooling, the liquid-1 phase transforms to an hcp phase and liquid-2 phase at 1050 K. The amount of the liquid-2 phase increases with decreasing temperature and can be as high as  $1.57 \times 10^{-4}$  mole fraction. This liquid-2 phase ransforms to a bcc phase at 371 K. Fig. 7.4 shows the each element content in the liquid-2

phase as a function of temperature depicting that the liquid-2 phase is highly Na-rich, and the Na content increases with decreasing temperature.

For Mg-5.8Li-Na alloys, the phase evolution during cooling is similar. The bigger difference is the solid phase is the major hcp and minor bcc-1 (Mg-rich) after solidification. For Mg-10.6Li-Na alloys, the solid phase is the bcc-1 after solidification.

The calculated phase relations in comparison with the experimental data on the reduction of area [126] are shown in Figs 3-4, 7-8 11-12. They show that the ductility properties of these three alloys become bad when the liquid-2 phase form from the solid phase after the solidification. When the amount of liquid-2 phase reaches the maximum, the reduction of area and 0.2 % offset yield strength reach the minimum. The close relationship between the liquid-2 and mechanical properties of Mg-Li alloys indict that the Na-induced bad mechanical properties have the same mechanism as those in Al-Li and Al-Mg alloys.

As discussed in the previous two chapters, the HTE sensitive and safe zoon, the maximum and critical hot-rolling temperature and the maximum Na content are determined through thermodynamic calculations and marked in Figs. 7.2, 7.6 and 7.10.



Fig. 7.1. Calculated liquid projection of the Mg-Li-Na system.



Fig. 7.2. Calculated isopleth section of Mg-3.6Li-Na alloys showing the HTE safe and sensitive zone, the critical and maximum hot-rolling temperature as well as the maximum Na content.



Fig. 7.3. Calculated phase relations in comparison with the experimental data on the reduction of area [126]. (a) Effect of Na on hot ductility of Mg-3.6Li-Na alloys at different temperatures and strain rate. (b) The calculated mole fraction of each phase vs. temperature curves during the solidification of Mg-3.6Li-Na alloys with different Na contents



Fig. 7.4. Calculated phase relations in comparison with the experimental data on the 0.2 % offset yield strength [126]. (a) Effect of Na on hot ductility of Mg-3.6Li-Na alloys at different temperatures and strain rate. (b) The calculated mole fraction of each phase vs. temperature curves during the solidification of Mg-3.6Li-Na alloys with different Na contents



Fig. 7.5. Calculated mole fraction of each element in the liquid-2 phase vs. temperature curve for Mg-3.6Li-Na (160 ppm) alloy.



Fig. 7.6. Calculated isopleth section of Mg-5.8Li-Na alloys showing the HTE safe and sensitive zone, the critical and maximum hot-rolling temperature as well as the maximum Na content.



Fig. 7.7. Calculated phase relations in comparison with the experimental data on the reduction of area [126]. (a) Effect of Na on hot ductility of Mg-5.8Li-Na alloys at different temperatures and strain rate. (b) The calculated mole fraction of each phase vs. temperature curves during the solidification of Mg-5.8Li-Na alloys with different Na contents.



Fig. 7.8. Calculated phase relations in comparison with the experimental data on the 0.2 % offset yield strength [126]. (a) Effect of Na on hot ductility of Mg-5.8Li-Na alloys at different temperatures and strain rate. (b) The calculated mole fraction of each phase vs. temperature curves during the solidification of Mg-5.8Li-Na alloys with different Na contents.



Fig. 7.9. Calculated mole fraction of each element in the liquid-2 phase vs. temperature curve for Mg-5.8Li-Na (300 ppm) alloy.



Fig. 7.10. Calculated isopleth section of Mg-10.6Li-Na alloys showing the HTE safe and sensitive zone, the critical and maximum hot-rolling temperature as well as the maximum Na content.



Fig. 7.11. Calculated phase relations in comparison with the experimental data on the reduction of area [126]. (a) Effect of Na on hot ductility of Mg-10.6Li-Na alloys at different temperatures and strain rate. (b) The calculated mole fraction of each phase vs. temperature curves during the solidification of Mg-10.6Li-Na alloys with different Na contents.



Fig. 7.12. Calculated phase relations in comparison with the experimental data on the 0.2 % offset yield strength [126]. (a) Effect of Na on hot ductility of Mg-10.6Li-Na alloys at different temperatures and strain rate. (b) The calculated mole fraction of each phase vs. temperature curves during the solidification of Mg-10.6Li-Na alloys with different Na contents.



Fig. 7.13. Calculated mole fraction of each element in the liquid-2 phase vs. temperature curve for Mg-11.6Li-Na (680 ppm) alloy.

#### Chapter 8

# THERMODYNAMIC INVESTIGATION OF ALKALI-METAL-INDUCED HIGH TEMPERATURE EMBRITTLEMENT IN MULTI-COMPONENT AL AND MG ALLOYS

# 8.1 Introduction

It is a general phenomenon that alkali metals induce poor mechanical properties in Al and Mg alloy. However, the case becomes more complicated in multi-component systems. The alloy elements induce many intermetallic compounds which might affect the mechanical properties of the alloy.

Vasudevan *et al.* [128] investigated the effect of alkali metals on the mechanical properties in Al-11.4Li-0.09Mn alloys containing different Na. They detected Na on the fracture surface using ion scattering spectroscopy (ISS). They found the elongation of these Al alloys decrease with increasing the Na content. Alkali metals segregate to the grain boundaries and affect mechanical properties.

Singh [127] studied the ductility trough in multi-component Mg-Li alloys. At high temperature range 373-423 K, an intergranular fracture is observed. Localized diffusion of Na and other alkali metals toward the grain boundaries induced high temperature intergranular cracking. After the previous discussions about alkali-metal-induced HTE in Al-Li, Al-Mg and Mg-Li alloys, the mechanism of alkali-metal-induced HTE has been understood. How to avoid and suppress HTE and maintain good mechanical properties of

there alloys is very clear. In this chapter, the afford is made to understand alkali-metal-induced HTE problems for a multi-component alloy system.

## 8.2 Phase evolution

The phase evolution in multi-component system is similar to the case in Al-Li, Al-Mg and Mg-Li alloy. After solidification from liquid-1 phase to  $\alpha$  phase ( $\alpha$  phase is fcc for Al-based alloys or hcp for Mg-based alloys), liquid-2 phase and other intermetallic phases present from the  $\alpha$  phase. Usually, the liquid-2 phase is alkali-metal-rich and also has some trace alloy elements content. The intermetallic precipitates is closely related to the alloy elements.

The calculated relationship between the temperature and the phase fraction for Mg-11.4Li-0.09Mn-Na (564 ppm) alloys under equilibrium conditions is shown in Fig. 8.1. On cooling, the fcc phase begins to form at 923 K from the liquid-1 phase. Solidification is completed at 902 K and the phase fraction of the fcc phase reaches unity. When the fcc phase is cooled to 840 K, another liquid phase (liquid-2 phase) occurs. The amount of the liquid-2 phase increases with decreasing temperature and can be as high as  $5.64 \times 10^{-4}$  mole fraction. This liquid-2 phase transforms to a bcc phase at 371 K. The intermetallic compounds AlLi and Al<sub>6</sub>Mn also precipitate from fcc during cooling.

Fig. 8.2 shows the each element content in the liquid-2 phase as a function of temperature depicting that the liquid-2 phase is highly Na-rich, and the Na content increases with decreasing temperature.

#### 8.3 Alkali-metals-induced HTE in multi-component Al-based and Mg-based alloys

Since the database developed in these work only contains six elements and a lot of important alloy elements like Ti, Si, and Zr are not included, these alloys elements can be obtained from the commercial Al-based and Mg-based thermodynamic database.

The commercial Al-based alloys database (version 3.0) contains 15 elements, namely Al, B, C, Cr, Cu, Fe, Mg, Mn, Ni, Si, Sr, Ti, V, Zn and Zr. The commercial Mg-based alloys database (version 2.0) contains 9 elements, namely Mg, Al, Cu, Ce, La, Mn, Si, Zn and Zr. The database combining these two databases and the database developed in this work can be used to investigation of alkali-metal-induced HTE problems for a multi-component alloy system.

From these two commercial Al and Mg database, the Gibbs energies of the liquid,  $\alpha$  phase and many intermetallic compounds can be obtained. However, the bcc phase is omitted in these two databases. The Gibbs energy of bcc should be added. In this chapter, the bcc Gibbs energy of pure element is taken from SGTE pure element database. The interaction parameters between the alloy element and Na are determined via first-principles calculations. Fig. 8.3 shows the experimental elongation [128] and the calculated amount of the liquid-2 phase (the dashed line) of Mg-11.4Li-0.09Mn-Na alloys plotted as a function of the Na content at 477 K. The elongation decreases when the amount of liquid-2 increases. The elongation decreases at fairly low temperature without liquid-2 phase probably because of many intermetallic compounds along the grain boundaries.

Fig. 8.4. shows the Na content detected by the initial ISS spectra at the fracture surface in the Al-11.4Li-0.09Mn-Na alloys. These experimental results are inconsistent with the calculated results in Fig. 8.2. Lithium is not detected in these spectra because the ISS sensitivity for the low atomic number elements is poor.

The experimental elongation [127] and the calculated amount of teach phase of the Mg-11.2Li-1.52Al-0.03Ca-0.018Na-0.002K alloys plotted as a function of the processing temperature in Fig. 8.5. The Mg-11.2Li-1.52Al-0.03Ca-0.018Na-0.002K alloys contains all six elements in the senary database developed in this work. The temperature range of the loss of ductility is in consistent with the temperature range where liquid-2 phase exists. This indicates that liquid-2 phase induces the loss of ductility. The elongation decreases at fairly low temperature without liquid-2 phase probably because of many intermetallic compounds along the grain bounadaiers. Fig. 8.6 shows that the liquid-2 phase is still highly alkali-metal-rich. The experimental elongation [127] and the calculated amount of each phase of the Mg-11.4Li-1.59Al-0.02Ca-0.14Zr-0.015Si-0.018Na-0.002K alloys plotted as a function of the processing temperature in Fig. 8.7. The temperature range of the loss of ductility is in consistent with the temperature range where liquid-2 phase exists. This indicates that liquid-2 phase induces the loss of ductility. The elongation decreases at fairly low temperature without liquid-2 phase probably because of many intermetallic compounds along the grain bounadaiers. Figs. 8.8 and 8.9 show that the liquid-2 phase is still highly alkali-metal-rich and other elements are in trace.

#### 8.4 Summary

The senary database developed in this work can be used to handle investigation of alkali-metal-induced loss of ductility in multi-component Al and Mg alloys by combined with commercial Al and Mg alloys databases and first-principles calculations. The industrial parameters can be obtained through calculations.



Fig. 8.1. Calculated mole fraction of each phase vs. temperature curves during the solidification of the Mg-11.4Li-0.09Mn-Na (564 ppm) alloy.



Fig. 8.2. Each element content in the liquid-2 phase vs. temperature curve for the Mg-11.4Li-0.09Mn-Na (564 ppm) alloy.



Fig. 8.3. Experimental elongation  $\circ$  [128] and the calculated amount of the liquid-2 phase (the dashed line) of Mg-11.4Li-0.09Mn-Na alloys plotted as a function of the Na content at 477 K.



Fig. 8.4. Na content detected by the initial ISS spectra at the fracture surface in the Al-11.4Li-0.09Mn-Na alloys.

(The caption in the original reference [128]: Fig. 10 –Comparison of the initial ISS spectra of the fracture surface of 53, 112, 176, and 564 at. ppm Na alloys in the peak aged conditions)



Fig. 8.5. Calculated phase relations in comparison with the experimental data on the reduction of area [127]. (a) Experimental elongation of the Mg-11.2Li-1.52Al-0.03Ca-0.018Na-0.002K alloys at different temperatures and strain rates. (b) The calculated mole fraction of each phase vs. temperature curves during the solidification of Mg-11.2Li-1.52Al-0.03Ca-0.018Na-0.002K alloys with different Na contents.



Fig. 8.6. Calculated mole fraction of each element in the liquid-2 phase vs. temperature curve for the Mg-11.2Li-1.52Al-0.03Ca-0.018Na-0.002K alloy.



Fig. 8.7. Calculated phase relations in comparison with the experimental data on the reduction of area [127]. (a) Experimental elongation of the Mg-11.4Li-1.59Al-0.02Ca-0.14Zr-0.015Si-0.018Na-0.002K alloys at different temperatures and strain rates. (b) The calculated mole fraction of each phase vs. temperature curves during the solidification of the Mg-11.4Li-1.59Al-0.02Ca-0.14Zr-0.015Si-0.018Na-0.002K alloys with different Na contents.



Fig. 8.8. Calculated mole fraction of each element in the liquid-2 phase vs. temperature curve for the Mg-11.4Li-1.59Al-0.02Ca-0.14Zr-0.015Si-0.018Na-0.002K alloy.



Fig. 8.9. The enlarged view of Fig. 8.8 showing the mole fraction of each element in the liquid-2 phase vs. temperature curve for the Mg-11.4Li-1.59Al-0.02Ca-0.14Zr-0.015Si-0.018Na-0.002K alloy.

#### Chapter 9

# **CONCLUSIONS AND FUTURE WORKS**

# 9.1 Conclusions

The major accomplishments achieved in the present Ph.D. study can be summarized as follows:

- (1) The Al-Ca-K-Li-Mg-Na senary database was developed via a combined CALPHAD and first-principles calculations method. This database contains the major elements Al and Mg and alkali-metal impurity elements K, Li, Na and alkali earth metal element Ca.
- (2) Alkali-metal induced HTE and loss of ductility were investigated in Al-Li and Mg-Li alloys. It is discovered that alkali-metal-rich liquid-2 phase weakens grain boundaries strength. Liquid-2 phase causes HTE and loss of ductility. The calculated results are consistent with the experimental observations. Calculation results are used to determine HTE safe and sensitive zones, maximum and critical hot-rolling temperaturea and the maximum Na content in the alloy. These parameters can be used to understand and improve industrial processing of Al and Mg alloys.
- (3) A fundamental understanding of Na-induced HTE in Al-Mg alloys is obtained via thermodynamic calculations. It was found (i) HTE is related to the formation of an intergranular Na-rich liquid phase that significantly weakens the strength of grain boundaries; (ii) for a given Mg content, there exists a maximum Na content above

which HTE cannot be avoided; and (iii) for a given alloy, a proper hot-rolling temperature should be chosen with respect to Na and Mg contents in order to suppress HTE. The HTE sensitive zone and a hot-rolling safe zone of the Al-Mg-Na alloys are defined as functions of processing temperature and alloy composition. The tendency of HTE formation was evaluated based on thermodynamic simulations of phase fraction of the intergranular Na-rich liquid phase.

(4) The Al-Ca-K-Li-Mg-Na senary database can be combined with commercial Al and Mg databases to understand alkali-metal-induced HTE and loss of ductility in multi-component Al and Mg alloy system and provide proper industrial controlling parameters.

#### 9.2 Future works

- (1) Bi and Sn can be used to trap Na and suppress Na-induced HTE. Bi and Sn should be added to the database in the future.
- (2) The constitutive-binary systems including Al-K, Al-Na, Ca-K, Li-K and K-Mg need more investigations via first-principles calculation due to very scarce experimental data.
- (3) The interaction parameter of bcc phase between Na and other alloy element in the commercial Al and Mg database should be determined via first-principles calculations.

# Appendix A

# THERMODYNAMIC DATABASE OF THE AL-CA-K-LI-MG-NA SENARY SYSTEM

\$ The compiled Al-Ca-K-Li-Mg-Na Senary Sy \$ Database file written 6- 6-21 \$	ystem
ELEMENT /- ELECTRON GAS	0 0000E+00 0 0000E+00 0 0000E+00!
ELEMENT VA VACUUM	0.0000E+00 = 0.0000E+00 = 0.0000E+001
ELEMENT AL $ECC(A1)$	2 6982F+01 0 0000F+00 6 7690F+00!
ELEMENT CA $FCC(A1)$	4.0080E+01 = 0.0000E+00 = 9.9320E+001
ELEMENT K $BCC(A2)$	3.9098E+01 = 0.0000E+00 = 1.526E+011
ELEMENT LI BCC(A2)	6 9400E+00 0 0000E+00 6 9540E+00!
ELEMENT MG HCP(A3)	2 4305E+01 0 0000E+00 7 8140E+00!
ELEMENT NA BCC(A2)	2 2990E+01 0 0000E+00 1 2260E+01!
	2.27701.01 0.00001.00 1.22001.01.
SPECIES AL1	AL!
SPECIES AL1L11	AL1L11!
SPECIES AL2	AL2!
SPECIES AL2CA1	AL2CA1!
SPECIES AL4CA1	AL4CA1!
SPECIES CA1MG2	CA1MG2!
SPECIES CA2	CA2!
SPECIES K1LI1	K1LI1!
SPECIES K1NA1	K1NA1!
SPECIES K2	K2!
SPECIES LI1NA1	LI1NA1!
SPECIES LI2	LI2!
SPECIES MG1	MG!
SPECIES MG2	MG2!
SPECIES NA2	NA2!
EUNCTION E110T 2 98140E+02 +	323947 58-25 1480943*T-20 859*T*I N(T)
+4 5665E-05*T**2-3 942E-09*T**3-2	42755*T**(-1)· 4 30000E+03 Y
$+342017\ 233-54\ 0526109*T-17\ 7891*T*LN(T)+6\ 822E-05*T**2$	
-1 91111667E-08*T**3-14782200*T**(-1)· 8 20000E+03 Y	
+54239607-411214335*T+222419*T*LN(T)-00349619*T**2+40491E-08*T**3	
-2.0366965E+08*T**(-1): 1.00000E+04 N!	
FUNCTION F566T 2.98140E+02 +496408.232+35.479739*T-41.6397*T*LN(T)	
+.00249636*T**2-4.90507333E-07*T**3+85390.3*T**(-1): 9.00000E+02 Y	
+497613.221+17.368131*T-38.85476*T*LN(T)-2.249805E-04*T**2	
-9.49003167E-09*T**3-5287.23*T**(-1); 2.80000E+03 N !	
FUNCTION F5174T 2.98140E+02 +171531.61-14.4704726*T-20.97219*T*LN(T)	
+1.78157E-04*T**2-2.74831667E-08*T**3+4459.1005*T**(-1); 1.90000E+03 Y	
+133942.047+211.942959*T-51.03146*T*LN(T)+.01095733*T**2	
-7.58329333E-07*T**3+8900275*T**(-1); 3.60000E+03 Y	
+803006.637-2023.14842*T+221.2015*T*LN(T)03849748*T**2	
+9.34346333E-07*T**3-3.007237E+08*T**(-1); 5.90000E+03 Y	

-1015607.92+1951.8583\*T-236.1074\*T\*LN(T)+.012768595\*T\*\*2 -1.46631567E-07\*T\*\*3+1.0593555E+09\*T\*\*(-1); 1.00000E+04 N ! FUNCTION F5393T 2.98140E+02 +328351.638+100.727906\*T-57.06096\*T\*LN(T) +.043881965\*T\*\*2-1.00131433E-05\*T\*\*3-34035.885\*T\*\*(-1); 5.00000E+02 Y +341516.759-125.927776\*T-21.13135\*T\*LN(T)+2.0114005E-04\*T\*\*2 -1.72831E-08\*T\*\*3-939425\*T\*\*(-1); 2.40000E+03 Y +341937.684-129.505067\*T-20.63507\*T\*LN(T)-3.0526885E-05\*T\*\*2 +1.18918867E-09\*T\*\*3-1003665\*T\*\*(-1); 3.00000E+03 N! FUNCTION F11301T 2.98140E+02 +82666.7286-18.8597114\*T-21.13652\*T\*LN(T) +3.263815E-04\*T\*\*2-4.88193833E-08\*T\*\*3+8623\*T\*\*(-1); 2.10000E+03 Y +95214.8988-58.7763871\*T-16.47469\*T\*LN(T)+1.8283925E-04\*T\*\*2 -1.181286E-07\*T\*\*3-4900225.5\*T\*\*(-1); 4.50000E+03 Y +330899.458-746.725542\*T+65.78716\*T\*LN(T)-.012648195\*T\*\*2 +2.58849667E-07\*T\*\*3-1.323186E+08\*T\*\*(-1); 7.40000E+03 Y -586517.642+917.252815\*T-121.1246\*T\*LN(T)+.0043326875\*T\*\*2 -3.13419333E-08\*T\*\*3+7.14826E+08\*T\*\*(-1); 1.00000E+04 N! FUNCTION F11311T 2.98140E+02 +159708.142+13.3177748\*T-36.16766\*T\*LN(T) -.002080635\*T\*\*2+2.01223167E-07\*T\*\*3+5542.825\*T\*\*(-1); 9.00000E+02 Y +152464.636+65.2173366\*T-43.07486\*T\*LN(T)-4.1793015E-04\*T\*\*2 +3.981725E-07\*T\*\*3+1202979\*T\*\*(-1); 1.70000E+03 Y +130505.04+261.203731\*T-70.48822\*T\*LN(T)+.0133959\*T\*\*2 -8.36289667E-07\*T\*\*3+3879652.5\*T\*\*(-1); 3.10000E+03 Y +412695.288-899.517606\*T+75.04089\*T\*LN(T)-.01992972\*T\*\*2 +5.93207667E-07\*T\*\*3-98632550\*T\*\*(-1); 5.50000E+03 Y -302016.554+900.324372\*T-135.8796\*T\*LN(T)+.00774844\*T\*\*2 -8.77728E-08\*T\*\*3+3.5598985E+08\*T\*\*(-1); 6.00000E+03 N! FUNCTION F11338T 2.98140E+02 +122242.069-17.7329212\*T-33.66411\*T\*LN(T) -.0057727\*T\*\*2+8.57839833E-07\*T\*\*3-50940\*T\*\*(-1); 8.00000E+02 Y +109122.155+100.248471\*T-50.15795\*T\*LN(T)+.0018502215\*T\*\*2 +5.24156333E-07\*T\*\*3+1733788\*T\*\*(-1); 1.40000E+03 Y +88354.4451+304.04821\*T-79.20345\*T\*LN(T)+.01874343\*T\*\*2 -1.24203683E-06\*T\*\*3+4199069.5\*T\*\*(-1); 2.70000E+03 Y +423048.302-1120.71314\*T+100.4292\*T\*LN(T)-.024460385\*T\*\*2 +7.237585E-07\*T\*\*3-1.1359655E+08\*T\*\*(-1); 5.40000E+03 Y -407096.036+981.040607\*T-146.0493\*T\*LN(T)+.008087385\*T\*\*2 -8.23452833E-08\*T\*\*3+4.112531E+08\*T\*\*(-1); 6.00000E+03 N! FUNCTION F11372T 2.98140E+02 +116830.132-35.2572172\*T-31.24845\*T\*LN(T) -.011272125\*T\*\*2+2.82333833E-06\*T\*\*3-67414.35\*T\*\*(-1); 9.00000E+02 Y +80568.4035+357.696336\*T-88.60734\*T\*LN(T)+.02938261\*T\*\*2 -2.63023167E-06\*T\*\*3+4260576.5\*T\*\*(-1); 2.20000E+03 Y +639659.157-2443.85825\*T+272.9801\*T\*LN(T)-.074798\*T\*\*2 +3.01408333E-06\*T\*\*3-1.5813375E+08\*T\*\*(-1); 3.30000E+03 Υ -487725.534+1421.21034\*T-199.1774\*T\*LN(T)+.012645665\*T\*\*2 -4.84245E-09\*T\*\*3+3.4436415E+08\*T\*\*(-1); 4.50000E+03 Y -775041.605 + 2444.94874 \* T - 324.4177 \* T \* LN(T) + .035652475 \* T \* \* 2000 + .00000 + .00000 + .0000 + .0000 + .0-7.70021667E-07\*T\*\*3+4.5724375E+08\*T\*\*(-1); 6.00000E+03 N ! 2.98140E+02 +152984.64+2.33568548\*T-21.07772\*T\*LN(T) FUNCTION F11525T +2.515552E-04\*T\*\*2-3.41354333E-08\*T\*\*3+7690.735\*T\*\*(-1); 2.40000E+03 Y +183390.413-110.69493\*T-7.20516\*T\*LN(T)-.002217371\*T\*\*2 +2.443155E-08\*T\*\*3-11648370\*T\*\*(-1); 4.80000E+03 Y +109652.446+17.244513\*T-21.24264\*T\*LN(T)-.0015038825\*T\*\*2 +3.76717667E-08\*T\*\*3+50092500\*T\*\*(-1); 8.80000E+03 Y -72231.6407+344.035356\*T-57.87689\*T\*LN(T)+.0017448465\*T\*\*2 -1.58650733E-08\*T\*\*3+2.178053E+08\*T\*\*(-1); 1.00000E+04 N!

FUNCTION F11561T 2.98140E+02 +167499.139+24.0768959\*T-36.1274\*T\*LN(T) -.002313599\*T\*\*2+2.498375E-07\*T\*\*3+20282.63\*T\*\*(-1); 1.00000E+03 Y +158805.041+82.82398\*T-43.89188\*T\*LN(T)-4.3518875E-04\*T\*\*2 +3.99696E-07\*T\*\*3+1574155\*T\*\*(-1); 1.80000E+03 Y +130225.898+304.895232\*T-74.39618\*T\*LN(T)+.01325589\*T\*\*2 -7.11431167E-07\*T\*\*3+6137435\*T\*\*(-1); 3.50000E+03 Y +514976.598-1062.26261\*T+93.58793\*T\*LN(T)-.019554065\*T\*\*2 +4.97396E-07\*T\*\*3-1.602374E+08\*T\*\*(-1); 6.00000E+03 N! FUNCTION F11601T 2.98140E+02 +203319.119+52.2617048\*T-37.02637\*T\*LN(T) -8.421915E-04\*T\*\*2-1.078653E-07\*T\*\*3+65874.15\*T\*\*(-1); 1.10000E+03 Y +200885.055+48.6776399\*T-35.9057\*T\*LN(T)-.0039990175\*T\*\*2 +5.08151333E-07\*T\*\*3+883657\*T\*\*(-1); 1.90000E+03 Y +137315.894+473.019388\*T-93.02457\*T\*LN(T)+.018440525\*T\*\*2 -1.12358533E-06\*T\*\*3+13866255\*T\*\*(-1); 3.10000E+03 Y +638944.289-1507.74849\*T+153.9314\*T\*LN(T)-.035715045\*T\*\*2 +1.10781833E-06\*T\*\*3-1.776338E+08\*T\*\*(-1); 5.10000E+03 Y -624845.178+1789.13827\*T-234.2722\*T\*LN(T)+.0173718\*T\*\*2 -2.55232167E-07\*T\*\*3+5.95322E+08\*T\*\*(-1); 6.00000E+03 N ! FUNCTION F11716T 2.98140E+02 +140825.883-8.26177982\*T-20.96302\*T\*LN(T) +1.331861E-04\*T\*\*2-1.51554617E-08\*T\*\*3+5221.91\*T\*\*(-1); 2.90000E+03 Y + 141959.02 + 20.1923541 \* T - 25.1271 \* T \* LN(T) + .002179723 \* T \* \* 2-1.502275E-07\*T\*\*3-3744678\*T\*\*(-1); 5.40000E+03 Y +458455.469-794.05688\*T+70.54811\*T\*LN(T)-.010649025\*T\*\*2 +1.716475E-07\*T\*\*3-1.996814E+08\*T\*\*(-1); 9.20000E+03 Y -315972.848+423.179252\*T-63.73726\*T\*LN(T)-2.847232E-04\*T\*\*2 +2.15099667E-08\*T\*\*3+6.39436E+08\*T\*\*(-1); 1.00000E+04 N! FUNCTION F11802T 2.98140E+02 +281408.793-104.38489\*T-20.63169\*T\*LN(T) -6.14869E-05\*T\*\*2+4.25457833E-09\*T\*\*3-156733.25\*T\*\*(-1); 3.00000E+03 N ! 2.98140E+02 +101202.044-12.9290068\*T-21.02539\*T\*LN(T) FUNCTION F12299T +1.9194285E-04\*T\*\*2-2.37558167E-08\*T\*\*3+6714.165\*T\*\*(-1); 2.70000E+03 Υ +123818.458-80.8203215\*T-13.00233\*T\*LN(T)-6.87485E-04\*T\*\*2 -3.3153E-08\*T\*\*3-10435685\*T\*\*(-1); 5.50000E+03 Y +200317.377-314.322311\*T+14.94379\*T\*LN(T)-.0049580625\*T\*\*2 +8.45444167E-08\*T\*\*3-45680820\*T\*\*(-1); 9.60000E+03 Y -248549.945+382.618817\*T-61.81729\*T\*LN(T)+8.73722E-04\*T\*\*2 +1.54938383E-09\*T\*\*3+4.4661115E+08\*T\*\*(-1); 1.00000E+04 N! 2.98140E+02 +131697.685+6.55101085\*T-35.05636\*T\*LN(T) FUNCTION F12339T -.0039954535\*T\*\*2+5.82776667E-07\*T\*\*3-20127.66\*T\*\*(-1); 8.00000E+02 Y +123510.411+75.1001481\*T-44.47351\*T\*LN(T)-5.345085E-04\*T\*\*2 +6.400745E-07\*T\*\*3+1150765\*T\*\*(-1); 1.50000E+03 Y +79657.0271 + 417.408691 \* T - 91.76357 \* T \* LN(T) + .022097085 \* T \* \* 2-1.3875195E-06\*T\*\*3+8765605\*T\*\*(-1); 3.10000E+03 Y +841444.171-2436.16812\*T+261.4099\*T\*LN(T)-.0509968\*T\*\*2+1.46319E-06\*T\*\*3-3.005069E+08\*T\*\*(-1); 4.80000E+03 Y -471200.866+911.74126\*T-131.5149\*T\*LN(T)+.0011608825\*T\*\*2 +1.68225167E-07\*T\*\*3+5.200375E+08\*T\*\*(-1); 6.00000E+03 N ! FUNCTION UN ASS 298.15 0.0; 6000.00 N! FUNCTION GHSERAL 2.98140E+02 -7976.15+137.093038\*T-24.3671976\*T\*LN(T) -.001884662\*T\*\*2-8.77664E-07\*T\*\*3+74092\*T\*\*(-1); 7.00000E+02 Y -11276.24+223.048446\*T-38.5844296\*T\*LN(T)+.018531982\*T\*\*2 -5.764227E-06\*T\*\*3+74092\*T\*\*(-1); 9.33470E+02 Y -11278.378+188.684153\*T-31.748192\*T\*LN(T)-1.230524E+28\*T\*\*(-9);

2.90000E+03 N! FUNCTION GHSERBB 2.98140E+02 -7735.284+107.111864\*T-15.6641\*T\*LN(T) -.006864515\*T\*\*2+6.18878E-07\*T\*\*3+370843\*T\*\*(-1); 1.10000E+03 Y -16649.474+184.801744\*T-26.6047\*T\*LN(T)-7.9809E-04\*T\*\*2-2.556E-08\*T\*\*3 +1748270\*T\*\*(-1); 2.34800E+03 Y -36667.582+231.336244\*T-31.5957527\*T\*LN(T)-.00159488\*T\*\*2 +1.34719E-07\*T\*\*3+11205883\*T\*\*(-1); 3.00000E+03 Y -21530.653+222.396264\*T-31.4\*T\*LN(T); 6.00000E+03 N ! FUNCTION GHSERCE 2.98140E+02 -7160.519+84.23022\*T-22.3664\*T\*LN(T) -.0067103\*T\*\*2-3.20773E-07\*T\*\*3-18117\*T\*\*(-1); 1.00000E+03 Y -79678.506+659.4604\*T-101.32248\*T\*LN(T)+.026046487\*T\*\*2 -1.9302976E-06\*T\*\*3+11531707\*T\*\*(-1); 2.00000E+03 Y -14198.639+190.370192\*T-37.6978\*T\*LN(T); 4.00000E+03 N ! FUNCTION GHSERCR 2.98140E+02 -8856.94+157.48\*T-26.908\*T\*LN(T) +.00189435\*T\*\*2-1.47721E-06\*T\*\*3+139250\*T\*\*(-1); 2.18000E+03 Y -34869.344+344.18\*T-50\*T\*LN(T)-2.88526E+32\*T\*\*(-9); 6.00000E+03 N ! 2.98140E+02 -7770.458+130.485235\*T-24.112392\*T\*LN(T) FUNCTION GHSERCU -.00265684\*T\*\*2+1.29223E-07\*T\*\*3+52478\*T\*\*(-1); 1.35777E+03 Y -13542.026+183.803828\*T-31.38\*T\*LN(T)+3.64167E+29\*T\*\*(-9); 3.20000E+03 N! FUNCTION GHSERCC 2.98150E+02 -17368.441+170.73\*T-24.3\*T\*LN(T) -4.723E-04\*T\*\*2+2562600\*T\*\*(-1)-2.643E+08\*T\*\*(-2)+1.2E+10\*T\*\*(-3); 6.00000E+03 N ! 2.98140E+02 +1225.7+124.134\*T-23.5143\*T\*LN(T) FUNCTION GHSERFE -.00439752\*T\*\*2-5.8927E-08\*T\*\*3+77359\*T\*\*(-1); 1.81100E+03 Y -25383.581+299.31255\*T-46\*T\*LN(T)+2.29603E+31\*T\*\*(-9); 6.00000E+03 N 1 FUNCTION GHSERHF 2.98140E+02 -6987.297+110.744026\*T-22.7075\*T\*LN(T) -.004146145\*T\*\*2-4.77E-10\*T\*\*3-22590\*T\*\*(-1); 2.50600E+03 Y -1446776.33+6193.60999\*T-787.536383\*T\*LN(T)+.1735215\*T\*\*2 -7.575759E-06\*T\*\*3+5.01742495E+08\*T\*\*(-1); 6.00000E+03 N! FUNCTION GHSERLI 2.00000E+02 -10583.817+217.637482\*T-38.940488\*T\*LN(T) +.035466931\*T\*\*2-1.9869816E-05\*T\*\*3+159994\*T\*\*(-1); 4.53600E+02 Y -559579.123+10547.8799\*T-1702.88865\*T\*LN(T)+2.25832944\*T\*\*2 -5.71066077E-04\*T\*\*3+33885874\*T\*\*(-1); 5.00000E+02 Y -9062.994+179.278285\*T-31.2283718\*T\*LN(T)+.002633221\*T\*\*2 -4.38058E-07\*T\*\*3-102387\*T\*\*(-1); 3.00000E+03 N ! FUNCTION GHSERMG 2.98140E+02 -8367.34+143.675547\*T-26.1849782\*T\*LN(T) +4.858E-04\*T\*\*2-1.393669E-06\*T\*\*3+78950\*T\*\*(-1); 9.23000E+02 Y -14130.185+204.716215\*T-34.3088\*T\*LN(T)+1.038192E+28\*T\*\*(-9); 3.00000E+03 N! FUNCTION GHSERMN 2.98140E+02 -8115.28+130.059\*T-23.4582\*T\*LN(T) -.00734768\*T\*\*2+69827\*T\*\*(-1); 1.51900E+03 Y -28733.41+312.2648\*T-48\*T\*LN(T)+1.656847E+30\*T\*\*(-9); 6.00000E+03 N ! FUNCTION GHSERMO 2.98140E+02 -7746.302+131.9197\*T-23.56414\*T\*LN(T) -.003443396\*T\*\*2+5.66283E-07\*T\*\*3+65812\*T\*\*(-1)-1.30927E-10\*T\*\*4; 2.89600E+03 Y -30556.41+283.559746\*T-42.63829\*T\*LN(T)-4.849315E+33\*T\*\*(-9); 5.00000E+03 N! FUNCTION GHSERNN 2.98140E+02 -3750.675-9.45425\*T-12.7819\*T\*LN(T) -.00176686\*T\*\*2+2.681E-09\*T\*\*3-32374\*T\*\*(-1); 9.50000E+02 Y -7358.85+17.2003\*T-16.3699\*T\*LN(T)-6.5107E-04\*T\*\*2+3.0097E-08\*T\*\*3 +563070\*T\*\*(-1); 3.35000E+03 Y -16392.8+50.26\*T-20.4695\*T\*LN(T)+2.39754E-04\*T\*\*2-8.333E-09\*T\*\*3
+4596375\*T\*\*(-1); 6.00000E+03 N! 2.98140E+02 -8402.93+111.10239\*T-27.0858\*T\*LN(T) FUNCTION GHSERND +5.56125E-04\*T\*\*2-2.6923E-06\*T\*\*3+34887\*T\*\*(-1); 9.00000E+02 Y -6984.083+83.662617\*T-22.7536\*T\*LN(T)-.00420402\*T\*\*2-1.802E-06\*T\*\*3; 1.12800E+03 Y -225610.846+1673.04075\*T-238.182873\*T\*LN(T)+.078615997\*T\*\*2 -6.048207E-06\*T\*\*3+38810350\*T\*\*(-1); 1.80000E+03 N ! FUNCTION GHSERNB 2.98140E+02 -8519.353+142.045475\*T-26.4711\*T\*LN(T) +2.03475E-04\*T\*\*2-3.5012E-07\*T\*\*3+93399\*T\*\*(-1); 2.75000E+03 Y -37669.3+271.720843\*T-41.77\*T\*LN(T)+1.528238E+32\*T\*\*(-9); 6.0000E+03 N ! FUNCTION GHSERNI 2.98140E+02 -5179.159+117.854\*T-22.096\*T\*LN(T) -.0048407\*T\*\*2; 1.72800E+03 Y -27840.655+279.135\*T-43.1\*T\*LN(T)+1.12754E+31\*T\*\*(-9); 6.00000E+03 N ! FUNCTION GHSEROO 2.98140E+02 -3480.87-25.503038\*T-11.136\*T\*LN(T) -.005098888\*T\*\*2+6.61846E-07\*T\*\*3-38365\*T\*\*(-1); 1.00000E+03 Y -6568.763+12.65988\*T-16.8138\*T\*LN(T)-5.95798E-04\*T\*\*2+6.781E-09\*T\*\*3 +262905\*T\*\*(-1); 3.30000E+03 Y -13986.728+31.259625\*T-18.9536\*T\*LN(T)-4.25243E-04\*T\*\*2 +1.0721E-08\*T\*\*3+4383200\*T\*\*(-1); 6.00000E+03 N ! FUNCTION GHSERSI 2.98140E+02 -8162.609+137.236859\*T-22.8317533\*T\*LN(T) -.001912904\*T\*\*2-3.552E-09\*T\*\*3+176667\*T\*\*(-1); 1.68700E+03 Y -9457.642+167.281367\*T-27.196\*T\*LN(T)-4.20369E+30\*T\*\*(-9); 3.60000E+03 N! FUNCTION GHSERTA 2.98140E+02 -7285.889+119.139858\*T-23.7592624\*T\*LN(T) -.002623033\*T\*\*2+1.70109E-07\*T\*\*3-3293\*T\*\*(-1); 1.30000E+03 Y -22389.955+243.88676\*T-41.137088\*T\*LN(T)+.006167572\*T\*\*2 -6.55136E-07\*T\*\*3+2429586\*T\*\*(-1); 2.50000E+03 Y +229382.886-722.59722\*T+78.5244752\*T\*LN(T)-.017983376\*T\*\*2 +1.95033E-07\*T\*\*3-93813648\*T\*\*(-1); 3.25800E+03 Y -963392.734+2773.7774\*T-337.227976\*T\*LN(T)+.039791303\*T\*\*2 -9.74251E-07\*T\*\*3+5.09949511E+08\*T\*\*(-1); 6.00000E+03 N! 1.00000E+02 -7958.517+122.765451\*T-25.858\*T\*LN(T) FUNCTION GHSERSN +5.1185E-04\*T\*\*2-3.192767E-06\*T\*\*3+18440\*T\*\*(-1); 2.50000E+02 Y -5855.135+65.443315\*T-15.961\*T\*LN(T)-.0188702\*T\*\*2+3.121167E-06\*T\*\*3 -61960\*T\*\*(-1); 5.05080E+02 Y +2524.724+4.005269\*T-8.2590486\*T\*LN(T)-.016814429\*T\*\*2 +2.623131E-06\*T\*\*3-1081244\*T\*\*(-1)-1.2307E+25\*T\*\*(-9); 8.00000E+02 Y -8256.959+138.99688\*T-28.4512\*T\*LN(T)-1.2307E+25\*T\*\*(-9); 3.00000E+03 NI FUNCTION GHSERTI 2.98140E+02 -8059.921+133.615208\*T-23.9933\*T\*LN(T) -.004777975\*T\*\*2+1.06716E-07\*T\*\*3+72636\*T\*\*(-1); 9.00000E+02 Y -7811.815+132.988068\*T-23.9887\*T\*LN(T)-.0042033\*T\*\*2-9.0876E-08\*T\*\*3 +42680\*T\*\*(-1); 1.15500E+03 Y +908.837+66.976538\*T-14.9466\*T\*LN(T)-.0081465\*T\*\*2+2.02715E-07\*T\*\*3 -1477660\*T\*\*(-1); 1.94099E+03 Y -124526.786+638.806871\*T-87.2182461\*T\*LN(T)+.008204849\*T\*\*2 -3.04747E-07\*T\*\*3+36699805\*T\*\*(-1); 4.00000E+03 N! FUNCTION GHSERV 2.98140E+02 -7930.43+133.346053\*T-24.134\*T\*LN(T) -.003098\*T\*\*2+1.2175E-07\*T\*\*3+69460\*T\*\*(-1); 7.90000E+02 Y -7967.842+143.291093\*T-25.9\*T\*LN(T)+6.25E-05\*T\*\*2-6.8E-07\*T\*\*3; 2.18300E+03 Y -41689.864+321.140783\*T-47.43\*T\*LN(T)+6.44389E+31\*T\*\*(-9);

6.0000E+03 N ! FUNCTION GHSERW 2.98140E+02 -7646.311+130.4\*T-24.1\*T\*LN(T) -.001936\*T\*\*2+2.07E-07\*T\*\*3+44500\*T\*\*(-1)-5.33E-11\*T\*\*4; 3.69500E+03 Y -82868.801+389.362335\*T-54\*T\*LN(T)+1.528621E+33\*T\*\*(-9); 6.00000E+03 N ! FUNCTION GHSERY 2.98140E+02 -7347.055+117.532124\*T-23.8685\*T\*LN(T) -.003845475\*T\*\*2+1.1125E-08\*T\*\*3-16486\*T\*\*(-1); 1.50000E+03 Y -15802.62+229.831717\*T-40.2851\*T\*LN(T)+.0068095\*T\*\*2-1.14182E-06\*T\*\*3; 1.79900E+03 Y -72946.216+393.885821\*T-58.2078433\*T\*LN(T)+.002436461\*T\*\*2 -7.2627E-08\*T\*\*3+20866567\*T\*\*(-1); 3.70000E+03 N !

FUNCTION GHSERZN 2.98140E+02 -7285.787+118.470069\*T-23.701314\*T\*LN(T) -.001712034\*T\*\*2-1.264963E-06\*T\*\*3; 6.92680E+02 Y -11070.559+172.34566\*T-31.38\*T\*LN(T)+4.70514E+26\*T\*\*(-9); 1.70000E+03 N !

FUNCTION GHSERZR 1.30000E+02 -7827.595+125.64905\*T-24.1618\*T\*LN(T) -.00437791\*T\*\*2+34971\*T\*\*(-1); 2.12800E+03 Y -26085.921+262.724183\*T-42.144\*T\*LN(T)-1.342895E+31\*T\*\*(-9);

6.00000E+03 N!

FUNCTION F57T 2.98130E+02 +323947.58-25.1480943\*T-20.859\*T\*LN(T) +4.5665E-05\*T\*\*2-3.942E-09\*T\*\*3-24275.5\*T\*\*(-1); 4.30000E+03 Y +342017.233-54.0526109\*T-17.7891\*T\*LN(T)+6.822E-05\*T\*\*2 -1.91111667E-08\*T\*\*3-14782200\*T\*\*(-1); 8.20000E+03 Y

-1.9111166/E-08\*1\*\*3-14/82200\*1\*\*(-1); 8.20000E+03 Y +542396.07-411.214335\*T+22.2419\*T\*LN(T)-.00349619\*T\*\*2+4.0491E-08\*T\*\*3 -2.0366965E+08\*T\*\*(-1); 1.00000E+04 N !

FUNCTION F346T 2.98130E+02 +496860.479+26.9906218\*T-40.26491\*T\*LN(T) +8.38355E-04\*T\*\*2-1.4850915E-07\*T\*\*3+59807.45\*T\*\*(-1); 1.40000E+03 Y +497564.417+17.7705096\*T-38.89205\*T\*LN(T)-2.1144975E-04\*T\*\*2 -1.0357225E-08\*T\*\*3+2845.8125\*T\*\*(-1); 3.00000E+03 N !

FUNCTION F8433T 2.98130E+02 +466676.993-100677.291\*T\*\*(-1) -25.5431898\*T-23.4738718\*T\*LN(T)+.002633828\*T\*\*2-4.85754729E-07\*T\*\*3; 1.80000E+03 Y

+488277.593-4788253.28\*T\*\*(-1)-166.8867\*T-4.45587632\*T\*LN(T)

-.00492684828\*T\*\*2+8.4922648E-08\*T\*\*3; 3.90000E+03 Y +485410.035+2258606.88\*T\*\*(-1)-190.892757\*T-.994064008\*T\*LN(T)

-.00631737976\*T\*\*2+1.55685245E-07\*T\*\*3; 6.00000E+03 N !

FUNCTION F1559T 2.98140E+02 +564913.402-13.9693124\*T

-20.8085801\*T\*LN(T)+1.6646044E-05\*T\*\*2; 7.00000E+02 Y +564920.973-14.1156663\*T-20.786112\*T\*LN(T); 2.80000E+03 Y +565086.023-15.0515115\*T-20.6682069\*T\*LN(T)-2.10566076E-05\*T\*\*2;

4.07500E+03 N ! FUNCTION F1786T 2.98140E+02 +469920.773-69873.2184\*T\*\*(-1) -57.4937871\*T-22.339422\*T\*LN(T)-.0105569014\*T\*\*2+1.41488236E-06\*T\*\*3;

1.00000E+03 Y +462619.822+719942.972\*T\*\*(-1)+28.1899597\*T-35.0100802\*T\*LN(T)

-7.99851096E-04\*T\*\*2+1.10267925E-08\*T\*\*3; 3.50000E+03 Y +449529.29+7491452\*T\*\*(-1)+65.7741362\*T-39.4662494\*T\*LN(T)

-1.95814338E-04\*T\*\*2-9.14385307E-10\*T\*\*3; 6.00000E+03 N !

FUNCTION F1835T 2.98140E+02 +824867.604-136465.972\*T\*\*(-1) -125.766398\*T-8.16800062\*T\*LN(T)-.0430888612\*T\*\*2+1.00098016E-05\*T\*\*3;

5.50000E+02 Y

+809306.765+980387.558\*T\*\*(-1)+132.643168\*T-48.851589\*T\*LN(T) +.00423205742\*T\*\*2-3.22751598E-07\*T\*\*3; 2.15000E+03 Y

+826793.716-3665441.32\*T\*\*(-1)+32.6504991\*T-35.6295549\*T\*LN(T)

```
-4.58209505E-04*T**2+1.70149264E-10*T**3; 6.00000E+03 N!
FUNCTION F7202T
                     2.98140E+02 +466446.153+2788.78662*T**(-1)
    -13.2660528*T-20.8939295*T*LN(T)+8.4552092E-05*T**2-1.00186856E-08*T**3;
      2.95000E+03 Y
     +481259.023-7559107.28*T**(-1)-52.4348889*T-16.3761342*T*LN(T)
    -2.28373808E-04*T**2-2.78997209E-08*T**3; 6.00000E+03 N!
                     2.98140E+02 -8000.12601-38326.6952*T**(-1)
FUNCTION F7307T
    -8.70687347*T-27.2233215*T*LN(T)-.00125991746*T**2-5.39381057E-07*T**3;
     8.00000E+02 Y
     -10569.6428+416969.072*T**(-1)+2.88463409*T-28.4238366*T*LN(T)
    -.00318927492*T**2+2.06637997E-07*T**3; 2.20000E+03 Y
     -22468.6452+3427511.88*T**(-1)+71.9269909*T-37.5501448*T*LN(T)
    -6.15899444E-06*T**2-4.22547041E-09*T**3; 6.00000E+03 N!
FUNCTION F7363T
                     2.98140E+02 +403075.636+55714.144*T**(-1)-14.3245228*T
    -29.5595416*T*LN(T)-.02413122*T**2+3.6156036E-06*T**3; 8.00000E+02 Y
    +388937.207+1536448.48*T**(-1)+158.809275*T-55.404528*T*LN(T)
    -.0026570492*T**2+1.9365644E-07*T**3; 2.00000E+03 Y
    +380898.006+3336949.2*T**(-1)+210.207464*T-62.295576*T*LN(T)
    +6.5726456E-06*T**2-7.868012E-10*T**3; 6.00000E+03 N!
FUNCTION F1780T
                     2.98140E+02 -254468.017+68652.118*T**(-1)-2.01673169*T
    +2.02130295*T*LN(T)-.0466239856*T**2+8.4686252E-06*T**3; 7.00000E+02 Y
     -252837.33-464549.52*T**(-1)+31.8460931*T-4.77377664*T*LN(T)
    -.0296618404*T**2+3.442909E-06*T**3; 1.20000E+03 Y
    -305197.766+7712952.96*T**(-1)+485.722721*T-68.6456328*T*LN(T)
    +.00556601704*T**2-2.64600344E-07*T**3: 1.90000E+03 Y
    -276126.047+17.7193237*T**(-1)+333.505404*T-48.9528*T*LN(T)
    -4.05854276E-09*T**2+3.84088411E-13*T**3; 6.00000E+03 N!
FUNCTION GBCCAL
                       2.98150E+02 +10083-4.813*T+GHSERAL#:
                                                                6 00000E+03
                                                                              Ν
FUNCTION GBCCCU
                       2.98150E+02 +4017-1.255*T+GHSERCU#;
                                                               6.00000E+03
                                                                             N !
FUNCTION GBCCHF
                       2.98140E+02 +5370.703+103.836026*T-22.8995*T*LN(T)
    -.004206605*T**2+8.71923E-07*T**3-22590*T**(-1)-1.446E-10*T**4;
    2.50600E+03 Y
    +1912456.77-8624.20573*T+1087.61412*T*LN(T)-.286857065*T**2
    +1.3427829E-05*T**3-6.10085091E+08*T**(-1); 6.00000E+03 N!
FUNCTION GBCCMG
                        2.98150E+02 +3100-2.1*T+GHSERMG#; 6.00000E+03
                                                                            N !
FUNCTION GBCCMN
                        2.98140E+02 -3235.3+127.85*T-23.7*T*LN(T)
    -.00744271*T**2+60000*T**(-1); 1.51900E+03 Y
    -23188.83+307.7043*T-48*T*LN(T)+1.265152E+30*T**(-9); 6.00000E+03 N !
FUNCTION GBCCNI
                      2.98150E+02 +8715.084-3.556*T+GHSERNI#;
                                                                 6.00000E+03
    N!
FUNCTION GBCCSI
                      2.98150E+02 +47000-22.5*T+GHSERSI#;
                                                             6.00000E+03
                                                                           N!
                      2.98140E+02 -1272.064+134.71418*T-25.5768*T*LN(T)
FUNCTION GBCCTI
    -6.63845E-04*T**2-2.78803E-07*T**3+7208*T**(-1); 1.15500E+03 Y
     +6667.385+105.366379*T-22.3771*T*LN(T)+.00121707*T**2-8.4534E-07*T**3
    -2002750*T**(-1); 1.94099E+03 Y
    +26483.26-182.426471*T+19.0900905*T*LN(T)-.02200832*T**2
    +1.228863E-06*T**3+1400501*T**(-1); 4.00000E+03 N !
FUNCTION GBCCZN
                       2.98150E+02 +2886.96-2.5104*T+GHSERZN#:
                                                                   6.00000E+03
    N !
FUNCTION GFCCCR
                       2.98150E+02 +7284+.163*T+GHSERCR#;
                                                              6.00000E+03
                                                                            N!
FUNCTION GFCCHF
                       2.98150E+02 +10000-2.2*T+GHSERHF#;
                                                              6.00000E+03
                                                                           N !
FUNCTION GECCMO
                       2.98140E+02 +7453.698+132.5497*T-23.56414*T*LN(T)
    -.003443396*T**2+5.66283E-07*T**3+65812*T**(-1)-1.30927E-10*T**4;
```

2.89600E+03 Y -15356.41+284.189746\*T-42.63829\*T\*LN(T)-4.849315E+33\*T\*\*(-9); 5.00000E+03 N! FUNCTION GFCCMN 2.98140E+02 -3439.3+131.884\*T-24.5177\*T\*LN(T) -.006\*T\*\*2+69600\*T\*\*(-1); 1.51900E+03 Y -26070.1+309.6664\*T-48\*T\*LN(T)+3.86196E+30\*T\*\*(-9); 6.00000E+03 N ! 2.98150E+02 +13500+1.7\*T+GHSERNB#; 6.00000E+03 FUNCTION GFCCNB N ! FUNCTION GECCTA 2.98150E+02 +16000+1.7\*T+GHSERTA#; 6.0000E+03 N! FUNCTION GFCCTI 2.98150E+02 +6000-.1\*T+GHSERTI#; 6.00000E+03 NI 2.98150E+02 +7500+1.7\*T+GHSERV#; FUNCTION GFCCV 6.00000E+03 N ! 2.98140E+02 +11653.689+131.03\*T-24.1\*T\*LN(T) FUNCTION GFCCW -.001936\*T\*\*2+2.07E-07\*T\*\*3+44500\*T\*\*(-1)-5.33E-11\*T\*\*4; 3.69500E+03 Y -63568.801+389.992335\*T-54\*T\*LN(T)+1.528621E+33\*T\*\*(-9); 6.00000E+03 N ! FUNCTION GFCCZN 2.98150E+02 +2969.82-1.56968\*T+GHSERZN#; 6.00000E+03 N ! FUNCTION GHCPAL 2.98150E+02 +5481-1.8\*T+GHSERAL#; 6.00000E+03 N! 2.98150E+02 +4438+GHSERCR#; 6.00000E+03 FUNCTION GHCPCR N ! FUNCTION GHCPMO 2.98140E+02 +3803.698+131.9197\*T-23.56414\*T\*LN(T) -.003443396\*T\*\*2+5.66283E-07\*T\*\*3+65812\*T\*\*(-1)-1.30927E-10\*T\*\*4; 2.89600E+03 Y -19006.41+283.559746\*T-42.63829\*T\*LN(T)-4.849315E+33\*T\*\*(-9); 5.00000E+03 N! 2.98140E+02 +10000+2.4\*T+GHSERNB#; 5.00000E+03 N! FUNCTION GHCPNB FUNCTION GHCPTA 2.98150E+02 +12000+2.4\*T+GHSERTA#; 6.00000E+03 N ! 2.98150E+02 +4000+2.4\*T+GHSERV#; 6.00000E+03 FUNCTION GHCPV N! 2.98140E+02 +7103.689+130.4\*T-24.1\*T\*LN(T) FUNCTION GHCPW -.001936\*T\*\*2+2.07E-07\*T\*\*3+44500\*T\*\*(-1)-5.33E-11\*T\*\*4; 3.69500E+03 Y -68118.801+389.362335\*T-54\*T\*LN(T)+1.528621E+33\*T\*\*(-9); 6.00000E+03 N! FUNCTION GLIQAL 2.98140E+02 +11005.029-11.841867\*T+7.934E-20\*T\*\*7 +GHSERAL#; 9.33470E+02 Y +10482.382-11.253974\*T+1.231E+28\*T\*\*(-9)+GHSERAL#; 6.00000E+03 N ! 2.98150E+02 +117369-24.63\*T+GHSERCC#; FUNCTION GLIQCC 6.00000E+03 N ! FUNCTION GLIQCE 2.98140E+02 +4117.865-11.423898\*T-7.5383948\*T\*LN(T) -.02936407\*T\*\*2+4.827734E-06\*T\*\*3-198834\*T\*\*(-1); 1.00000E+03 Y -6730.605+183.023193\*T-37.6978\*T\*LN(T); 4.00000E+03 N ! 1.00000E+02 -855.425+108.677684\*T-25.858\*T\*LN(T) FUNCTION GLIOSN +5.1185E-04\*T\*\*2-3.192767E-06\*T\*\*3+18440\*T\*\*(-1)+1.47031E-18\*T\*\*7; 2.50000E+02 Y +1247.957+51.355548\*T-15.961\*T\*LN(T)-.0188702\*T\*\*2+3.121167E-06\*T\*\*3 -61960\*T\*\*(-1)+1.47031E-18\*T\*\*7; 5.05080E+02 Y +9496.31-9.809114\*T-8.2590486\*T\*LN(T)-.016814429\*T\*\*2 +2.623131E-06\*T\*\*3-1081244\*T\*\*(-1); 8.00000E+02 Y -1285.372+125.182498\*T-28.4512\*T\*LN(T); 3.00000E+03 N ! FUNCTION GLIOTA 2.98140E+02 +29160.975-7.578729\*T+GHSERTA#; 1.00000E+03 Y +51170.228-181.121652\*T+23.7872147\*T\*LN(T)-.009707033\*T\*\*2 +4.4449E-07\*T\*\*3-3520045\*T\*\*(-1)+GHSERTA#; 1.30000E+03 Y +66274.294-305.868555\*T+41.1650403\*T\*LN(T)-.018497638\*T\*\*2 +1.269735E-06\*T\*\*3-5952924\*T\*\*(-1)+GHSERTA#; 2.50000E+03 Y -185498.547+660.615425\*T-78.4965229\*T\*LN(T)+.00565331\*T\*\*2 +4.19566E-07\*T\*\*3+90290310\*T\*\*(-1)+GHSERTA#; 3.29000E+03 Y

+1036069.47-2727.38037\*T+320.319132\*T\*LN(T)-.043117795\*T\*\*2 +1.055148E-06\*T\*\*3-5.54714342E+08\*T\*\*(-1)+GHSERTA#; 6.00000E+03 N ! FUNCTION GLIQTI 2.98140E+02 +12194.415-6.980938\*T+GHSERTI#; 1.30000E+03 Y +368610.36-2620.99904\*T+357.005867\*T\*LN(T)-.155262855\*T\*\*2 +1.2254402E-05\*T\*\*3-65556856\*T\*\*(-1)+GHSERTI#; 1.94099E+03 Υ +104639.72-340.070171\*T+40.9282461\*T\*LN(T)-.008204849\*T\*\*2 +3.04747E-07\*T\*\*3-36699805\*T\*\*(-1)+GHSERTI#; 6.00000E+03 N ! FUNCTION GLIQV 2.98140E+02 +20764.117-9.455552\*T-5.19136E-22\*T\*\*7 +GHSERV#; 7.90000E+02 Y +20764.117-9.455552\*T-5.19136E-22\*T\*\*7+GHSERV#; 2.18300E+03 Y +22072.354-10.0848\*T-6.44389E+31\*T\*\*(-9)+GHSERV#; 6.00000E+03 N ! FUNCTION GLIQZR 1.30000E+02 +18147.703-9.080762\*T+1.6275E-22\*T\*\*7 +GHSERZR#; 2.12800E+03 Y +17804.649-8.91153\*T+1.343E+31\*T\*\*(-9)+GHSERZR#; 6.00000E+03 N ! FUNCTION ALCRW1 2.98150E+02 -1300\*R#: 6.00000E+03 NI FUNCTION ALFEW1 2.98150E+02 +860\*R#; 6.00000E+03 N ! 2.98150E+02 -30740+7.9972\*T+ALFEW1#; 6.00000E+03 Ν **FUNCTION LALFEB0** 1 FUNCTION LALFEB1 2.98150E+02 368.15; 6.00000E+03 N ! FUNCTION ETCALFE 2.98150E+02 63; 6.00000E+03 N ! FUNCTION W1 2.98150E+02 +860\*R#; 6.00000E+03 N ! FUNCTION L0BCC 2.98150E+02 -30740.04+7.9972\*T+W1#; 6.00000E+03 N ! FUNCTION L1BCC 2.98150E+02 368.15; 6.00000E+03 N ! 2.98150E+02 -8650+T; **FUNCTION ALNBB2** 6.00000E+03 N ! 2.98150E+02 -8750+1.25\*T; N ! **FUNCTION ALTIB2** 6.00000E+03 FUNCTION U1ALTI 2.98150E+02 -16755+3.5\*T; 6.00000E+03 N! **FUNCTION GAL2TI** 2.98150E+02 -121500+31.2\*T; 6.00000E+03 N 2.98150E+02 17000; 6.00000E+03 FUNCTION LAVAL2TI N ! 2.98150E+02 **FUNCTION ALVB2** -700\*R#; 6.00000E+03 N ! 2.98150E+02 -207709+307.438\*T-48.0195\*T\*LN(T) FUNCTION GHSERTIC -.00272\*T\*\*2+819000\*T\*\*(-1)-2.03E+09\*T\*\*(-3); 6.00000E+03 N ! FUNCTION GLAVCR 2.98150E+02 +5000+GHSERCR#; 6.00000E+03 N ! 2.98150E+02 +5000+GHSERTI#; 6.00000E+03 FUNCTION GLAVTI N ! FUNCTION CRTIW1 298.15 0.0; 6000.00 N! FUNCTION U1CRTI 2.98150E+02 1E-04; 6.00000E+03 N ! FUNCTION L0 2.98150E+02 -51595.87+13.06392\*T; 6.00000E+03 N ! **FUNCTION P1** 2.98150E+02 -3085; 6.00000E+03 N! 2.98150E+02 +.5\*L0#+2\*P1#+GBCCCU#+GBCCZN#; FUNCTION GCZBCC 6.00000E+03 N ! FUNCTION L0CZ 2.98150E+02 -12898.97+3.26598\*T; 6.00000E+03 N ! FUNCTION L1CZ 2.98150E+02 +945.265-.80679\*T; 6.00000E+03 N ! 2.98150E+02 +1921.485-1.86969\*T; **FUNCTION L2CZ** 6.00000E+03 NI 2.98150E+02 -3085; 6.00000E+03 **FUNCTION A1CZ** N ! FUNCTION K4 2.98150E+02 -11552.71-1.67824\*T; 6.00000E+03 N! 2.98150E+02 +15732.3-10.26575\*T; **FUNCTION K5** 6.00000E+03 N ! FUNCTION K6 2.98150E+02 +37289.2-13.05259\*T; 6.00000E+03 N ! 2.98150E+02 -27809+11.62\*T; 6.00000E+03 FUNCTION FSL0BCC N ! 6.00000E+03 N ! FUNCTION FESIW1 2.98150E+02 +1260\*R#: FUNCTION FSL1BCC 2.98150E+02 -11544; 6.00000E+03 N ! FUNCTION FSL2BCC 2.98150E+02 3890; 6.00000E+03 N ! FUNCTION ETCFESI 2.98150E+02 63; 6.00000E+03 N ! FUNCTION GHSERTIN 2.98150E+02 -357905+330.498\*T-52.4587\*T\*LN(T) -9.28E-04\*T\*\*2+871000\*T\*\*(-1)+1.48976561E-08\*T\*\*3; 6.00000E+03 N !

FUNCTION NBTIB2 2.98150E+02 5500; 6.00000E+03 N ! **FUNCTION TATIB2** 2.98150E+02 2500; 6.00000E+03 N ! 2.98150E+02 -221500+18.46\*T; 6.00000E+03 N! FUNCTION OPHA FUNCTION SPHA 2.98150E+02 -63200+4.13\*T: 6.00000E+03 N ! FUNCTION T3CU 2.98150E+02 -220000+440\*T: 6.0000E+03 N ! FUNCTION T2AL3CU 2.98150E+02 243000; 6.00000E+03 N! 2.98150E+02 -4649190+2261.86\*T; 6.00000E+03 FUNCTION TRK N ! **FUNCTION T2ALRK** 298.15 0.0; 6000.00 N! FUNCTION T3CUMGRK 2.98150E+02 -220000; 6.00000E+03 N ! FUNCTION VPHA 2.98150E+02 -274527.45+13\*T; 6.00000E+03 NI 2.00000E+02 -11989.434+260.548732\*T-51.0393608\*T\*LN(T) FUNCTION GHSERNA +.072306633\*T\*\*2-4.3638283E-05\*T\*\*3+132154\*T\*\*(-1); 3.70870E+02 Y -11009.884+199.619999\*T-38.1198801\*T\*LN(T)+.009745854\*T\*\*2 -1.70664E-06\*T\*\*3+34342\*T\*\*(-1)+1.65071E+23\*T\*\*(-9); 2.30000E+03 N ! 2.98140E+02 -4955.062+72.794266\*T-16.3138\*T\*LN(T) FUNCTION GHSERCA -.01110455\*T\*\*2-133574\*T\*\*(-1): 1.11500E+03 Y -107304.428+799.982066\*T-114.292247\*T\*LN(T)+.023733814\*T\*\*2 -1.2438E-06\*T\*\*3+18245540\*T\*\*(-1); 3.00000E+03 N ! FUNCTION GHSERSR 2.98140E+02 -7532.367+107.183879\*T-23.905\*T\*LN(T) -.00461225\*T\*\*2-1.67477E-07\*T\*\*3-2055\*T\*\*(-1); 8.19990E+02 Y -13380.102+153.196104\*T-30.0905432\*T\*LN(T)-.003251266\*T\*\*2 +1.84189E-07\*T\*\*3+850134\*T\*\*(-1); 3.00000E+03 N ! FUNCTION GALLIQ 2.98130E+02 +11005.553-11.840873\*T+7.9401E-20\*T\*\*7 +GHSERAL#; 9.33600E+02 Y +10481.974-11.252014\*T+1.234264E+28\*T\*\*(-9)+GHSERAL#; 2.90000E+03 N ! 2.98130E+02 +12964.84-9.510243\*T-5.83932E-21\*T\*\*7 FUNCTION GCULIO +GHSERCU#; 1.35801E+03 Y +13495.4-9.920463\*T-3.64643E+29\*T\*\*(-9)+GHSERCU#; 3.20000E+03 N ! 2.98130E+02 +8202.24-8.83693\*T-8.01759E-20\*T\*\*7 FUNCTION GMGLIO +GHSERMG#: 9.23000E+02 Y +8690.32-9.39216\*T-1.03819E+28\*T\*\*(-9)+GHSERMG#; 3.00000E+03 N ! FUNCTION GZNLIO 2.70000E+02 -128.517+108.176926\*T-23.701314\*T\*LN(T) -.001712034\*T\*\*2-1.264963E-06\*T\*\*3-3.58652E-19\*T\*\*7; 6.92730E+02 Y -3620.474+161.608677\*T-31.38\*T\*LN(T); 2.90000E+03 N ! FUNCTION GFCCMG 2.98150E+02 +2600-.9\*T+GHSERMG#; 6.00000E+03 N ! **FUNCTION ALCUK4** 2.98150E+02 -48025.3+14.55872\*T; 6.00000E+03 N ! **FUNCTION ALCUK5** 2.98150E+02 +187178+3.02112\*T; 6.00000E+03 N ! **FUNCTION ALCUK6** 2.98150E+02 +254993.9-8.16271\*T; 6.00000E+03 N ! **FUNCTION CUZNK4** 2.98150E+02 -39470.1+9.43583\*T; 6.00000E+03 N! 2.98150E+02 +36675.1-5.19593\*T; **FUNCTION CUZNK5** 6.00000E+03 N ! FUNCTION CUZNK6 2.98150E+02 +90162.6-32.61986\*T; 6.00000E+03 NI FUNCTION CUZNL0 2.98150E+02 -51595.87+13.06392\*T; 6.00000E+03 N! 2.98150E+02 +7562.13-6.45432\*T; FUNCTION CUZNL1 6.00000E+03 N ! **FUNCTION CUZNL2** 2.98150E+02 +30743.74-29.91503\*T; 6.00000E+03 N ! FUNCTION CUZNP1 2.98150E+02 -3085; 6.00000E+03 N ! **FUNCTION CUZNP2** 2.98150E+02 -CUZNP1#; 6.00000E+03 N ! FUNCTION FIVEK 2.98150E+02 5000; 6.00000E+03 N ! 2.00000E+02 -16112.929+389.624197\*T-77.0571464\*T\*LN(T) FUNCTION GHSERKK +.146211135\*T\*\*2-8.4949147E-05\*T\*\*3+243385\*T\*\*(-1): 3.36530E+02 Y -11122.441+192.586544\*T-39.2885968\*T\*LN(T)+.012167386\*T\*\*2 -2.64387E-06\*T\*\*3+43251\*T\*\*(-1)+1.19223E+22\*T\*\*(-9); 2.20000E+03 N! FUNCTION F11716T 2.98140E+02 +140825.883-8.26177982\*T-20.96302\*T\*LN(T) +1.331861E-04\*T\*\*2-1.51554617E-08\*T\*\*3+5221.91\*T\*\*(-1); 2.90000E+03 Y +141959.02+20.1923541\*T-25.1271\*T\*LN(T)+.002179723\*T\*\*2

-1.502275E-07\*T\*\*3-3744678\*T\*\*(-1); 5.40000E+03 Y +458455.469-794.05688\*T+70.54811\*T\*LN(T)-.010649025\*T\*\*2 +1.716475E-07\*T\*\*3-1.996814E+08\*T\*\*(-1); 9.20000E+03 Y -315972.848+423.179252\*T-63.73726\*T\*LN(T)-2.847232E-04\*T\*\*2 +2.15099667E-08\*T\*\*3+6.39436E+08\*T\*\*(-1); 1.00000E+04 N! FUNCTION F154T 2.98140E+02 +323947.58-25.1480943\*T-20.859\*T\*LN(T) +4.5665E-05\*T\*\*2-3.942E-09\*T\*\*3-24275.5\*T\*\*(-1); 4.30000E+03 Y +342017.233-54.0526109\*T-17.7891\*T\*LN(T)+6.822E-05\*T\*\*2 -1.91111667E-08\*T\*\*3-14782200\*T\*\*(-1); 8.20000E+03 Y +542396.07-411.214335\*T+22.2419\*T\*LN(T)-.00349619\*T\*\*2+4.0491E-08\*T\*\*3 -2.0366965E+08\*T\*\*(-1); 1.00000E+04 N ! 2.98140E+02 +496408.232+35.479739\*T-41.6397\*T\*LN(T) FUNCTION F625T +.00249636\*T\*\*2-4.90507333E-07\*T\*\*3+85390.3\*T\*\*(-1); 9.00000E+02 Y +497613.221+17.368131\*T-38.85476\*T\*LN(T)-2.249805E-04\*T\*\*2 -9.49003167E-09\*T\*\*3-5287.23\*T\*\*(-1); 2.80000E+03 N ! FUNCTION F12933T 2.98140E+02 +101202.044-12.9290068\*T-21.02539\*T\*LN(T) +1.9194285E-04\*T\*\*2-2.37558167E-08\*T\*\*3+6714.165\*T\*\*(-1); 2.70000E+03 Y +123818.458-80.8203215\*T-13.00233\*T\*LN(T)-6.87485E-04\*T\*\*2 -3.3153E-08\*T\*\*3-10435685\*T\*\*(-1); 5.50000E+03 Y +200317.377-314.322311\*T+14.94379\*T\*LN(T)-.0049580625\*T\*\*2 +8.45444167E-08\*T\*\*3-45680820\*T\*\*(-1); 9.60000E+03 Y -248549.945+382.618817\*T-61.81729\*T\*LN(T)+8.73722E-04\*T\*\*2 +1.54938383E-09\*T\*\*3+4.4661115E+08\*T\*\*(-1); 1.00000E+04 N! 2.98140E+02 +131697.685+6.55101085\*T-35.05636\*T\*LN(T) FUNCTION F12977T -.0039954535\*T\*\*2+5.82776667E-07\*T\*\*3-20127.66\*T\*\*(-1); 8.00000E+02 Y +123510.411+75.1001481\*T-44.47351\*T\*LN(T)-5.345085E-04\*T\*\*2 +6.400745E-07\*T\*\*3+1150765\*T\*\*(-1); 1.50000E+03 Y +79657.0271+417.408691\*T-91.76357\*T\*LN(T)+.022097085\*T\*\*2 -1.3875195E-06\*T\*\*3+8765605\*T\*\*(-1); 3.10000E+03 Y +841444.171-2436.16812\*T+261.4099\*T\*LN(T)-.0509968\*T\*\*2 +1.46319E-06\*T\*\*3-3.005069E+08\*T\*\*(-1); 4.80000E+03 Y -471200.866+911.74126\*T-131.5149\*T\*LN(T)+.0011608825\*T\*\*2 +1.68225167E-07\*T\*\*3+5.200375E+08\*T\*\*(-1); 6.00000E+03 N! 2.98140E+02 -7976.1511+137.093055\*T-24.3672\*T\*LN(T) FUNCTION F150T -.001884662\*T\*\*2-8.77663667E-07\*T\*\*3+74092.35\*T\*\*(-1); 7.00000E+02 Y -11276.2397+223.048449\*T-38.58443\*T\*LN(T)+.01853198\*T\*\*2 -5.76422667E-06\*T\*\*3+74092.35\*T\*\*(-1); 9.33400E+02 Y -11507.1871+188.90476\*T-31.74819\*T\*LN(T); 2.90000E+03 N ! FUNCTION F12929T 2.00000E+02 -11989.4322+260.548717\*T-51.03936\*T\*LN(T) +.07230665\*T\*\*2-4.36382833E-05\*T\*\*3+132153.75\*T\*\*(-1); 3.70800E+02 Y -10997.4282+199.589766\*T-38.11988\*T\*LN(T)+.009745855\*T\*\*2 -1.70664E-06\*T\*\*3+34342.48\*T\*\*(-1); 2.30000E+03 N! FUNCTION F12309T 2.98140E+02 +140825.883-8.26177982\*T-20.96302\*T\*LN(T) +1.331861E-04\*T\*\*2-1.51554617E-08\*T\*\*3+5221.91\*T\*\*(-1); 2.90000E+03 Y +141959.02+20.1923541\*T-25.1271\*T\*LN(T)+.002179723\*T\*\*2 -1.502275E-07\*T\*\*3-3744678\*T\*\*(-1); 5.40000E+03 Y +458455.469-794.05688\*T+70.54811\*T\*LN(T)-.010649025\*T\*\*2 +1.716475E-07\*T\*\*3-1.996814E+08\*T\*\*(-1); 9.20000E+03 Y -315972.848+423.179252\*T-63.73726\*T\*LN(T)-2.847232E-04\*T\*\*2 +2.15099667E-08\*T\*\*3+6.39436E+08\*T\*\*(-1); 1.00000E+04 N! FUNCTION F12397T 2.98140E+02 +281408.793-104.38489\*T-20.63169\*T\*LN(T) -6.14869E-05\*T\*\*2+4.25457833E-09\*T\*\*3-156733.25\*T\*\*(-1); 3.00000E+03 N !

**TYPE DEFINITION % SEO \*! DEFINE SYSTEM DEFAULT SPECIE 2!** DEFAULT COMMAND DEF SYS ELEMENT VA ! PHASE GAS:G % 1 1.0 ! CONSTITUENT GAS:G :AL,AL2,CA,CA2,K,K1L11,K1NA1,K2,LI,L11NA1,L12,MG,MG2, NA, NA2 : !PARAMETER G(GAS,AL;0) 2.98150E+02 +F154T#+R#\*T\*LN(1E-05\*P); N REF:92 ! 6.00000E+03 PARAMETER G(GAS,AL2;0) 2.98150E+02 +F625T#+R#\*T\*LN(1E-05\*P); 6.00000E+03 N REF:310 ! PARAMETER G(GAS,CA;0) 2.98150E+02 +F5174T#+R#\*T\*LN(1E-05\*P); 6.0000E+03 N REF:2410 ! PARAMETER G(GAS,CA2;0) 2.98150E+02 +F5393T#+R#\*T\*LN(1E-05\*P); 6.00000E+03 N REF:2530 ! PARAMETER G(GAS,K;0) 2.98150E+02 +F11301T#+R#\*T\*LN(1E-05\*P); 6.00000E+03 N REF:5217 ! PARAMETER G(GAS,K1LI1;0) 2.98150E+02 +F11311T#+R#\*T\*LN(1E-05\*P); N REF:5222 ! 6.0000E+03 PARAMETER G(GAS,K1NA1;0) 2.98150E+02 +F11338T#+R#\*T\*LN(1E-05\*P); 6.0000E+03 N REF:5227 ! PARAMETER G(GAS,K2;0) 2.98150E+02 +F11372T#+R#\*T\*LN(1E-05\*P); 6.00000E+03 N REF:5235 ! PARAMETER G(GAS,LI:0) 2.98150E+02 +F11525T#+R#\*T\*LN(1E-05\*P); 6.0000E+03 N REF:5297 ! PARAMETER G(GAS,LI1NA1;0) 2.98150E+02 +F11561T#+R#\*T\*LN(1E-05\*P); 6.00000E+03 N REF:5311 ! PARAMETER G(GAS,LI2;0) 2.98150E+02 +F11601T#+R#\*T\*LN(1E-05\*P); N REF:5320 ! 6.0000E+03 PARAMETER G(GAS,MG;0) 2.98150E+02 +F12309T#+R#\*T\*LN(1E-05\*P); 6.00000E+03 N REF:6959 ! PARAMETER G(GAS,MG2;0) 2.98150E+02 +F12397T#+R#\*T\*LN(1E-05\*P); 6.00000E+03 N REF:7012 ! PARAMETER G(GAS,NA;0) 2.98150E+02 +F12933T#+R#\*T\*LN(1E-05\*P); 6.00000E+03 N REF:7345 ! PARAMETER G(GAS,NA2;0) 2.98150E+02 +F12977T#+R#\*T\*LN(1E-05\*P); 6.00000E+03 N REF:7374 !

PHASE LIQUID:L % 1 1.0 ! CONSTITUENT LIQUID:L :AL,CA,K,LI,MG,NA% : !

PARAMETER G(LIQUID,AL;0) 2.98140E+02 +11005.029-11.841867\*T+GHSERAL# +7.9337E-20\*T\*\*7; 7.00000E+02 Y +11005.03-11.841867\*T+GHSERAL#+7.9337E-20\*T\*\*7; 9.33470E+02 Y -795.996+177.430178\*T-31.748192\*T\*LN(T); 2.90000E+03 N REF:0 ! PARAMETER G(LIQUID,CA;0) 2.98140E+02 +10799.908-10.310466\*T+GHSERCA#; 5.00000E+02 Y +7838.856+18.2979\*T-8.9874787\*T\*LN(T)-.02266537\*T\*\*2+3.338303E-06\*T\*\*3 -230193\*T\*\*(-1); 1.11500E+03 Y

-2654.938+188.9223\*T-35\*T\*LN(T); 3.00000E+03 N REF:0!

PARAMETER G(LIQUID,K;0) 2.00000E+02 +2318.096-6.886859\*T+GHSERKK# -9.44E-19\*T\*\*7; 3.36530E+02 Y +2323.019-6.902217\*T+GHSERKK#-1.19223E+22\*T\*\*(-9); 2.20000E+03 N REF:0 ! PARAMETER G(LIQUID,LI;0) 2.00000E+02 +2700.205-5.795621\*T+GHSERLI#; 2.50000E+02 Y +12015.027-362.187078\*T+61.6104424\*T\*LN(T)-.182426463\*T\*\*2 +6.3955671E-05\*T\*\*3-559968\*T\*\*(-1); 4.53600E+02 Y -6057.31+172.652183\*T-31.2283718\*T\*LN(T)+.002633221\*T\*\*2-4.38058E-07\*T\*\*3 -102387\*T\*\*(-1); 5.00000E+02 Y +3005.684-6.626102\*T+GHSERLI#; 3.00000E+03 N REF:0 ! PARAMETER G(LIQUID,MG;0) 2.98140E+02 +8202.243-8.83693\*T+GHSERMG# -8.0176E-20\*T\*\*7; 9.23000E+02 Y -5439.869+195.324057\*T-34.3088\*T\*LN(T); 3.00000E+03 N REF:0 ! PARAMETER G(LIQUID,NA;0) 2.00000E+02 +2581.02-6.95218\*T+GHSERNA# -2.76132E-18\*T\*\*7; 3.70870E+02 Y +2609.444-7.032656\*T+GHSERNA#-1.65071E+23\*T\*\*(-9); 2.30000E+03 N REF:0 ! PARAMETER G(LIQUID,AL,LI;0) 2.98150E+02 -41500+20.96\*T; 6.00000E+03 N REF:0 ! PARAMETER G(LIQUID, AL, LI; 1) 2.98150E+02 +10000-5.8\*T; 6.00000E+03 Ν **REF:0**! PARAMETER G(LIQUID,AL,LI;2) 2.98150E+02 +15902-9.368\*T; 6.00000E+03 N REF:0 ! PARAMETER G(LIQUID,AL,LI;3) 2.98150E+02 -250; 6.00000E+03 N REF:0 ! PARAMETER G(LIQUID,AL,CA;0) 2.98140E+02 -89545+26.368\*T; 2.00000E+03 N REF:0 ! PARAMETER G(LIOUID,AL,CA;1) 2.98140E+02 -21847+11.769\*T; 2.00000E+03 N REF:0 ! PARAMETER G(LIQUID,AL,CA;2) 2.98140E+02 +4780+5.03\*T; 2.00000E+03 N REF:0 ! PARAMETER G(LIOUID,AL,MG;0) 2.98150E+02 -9031.5816+4.8547124\*T; 6.0000E+03 N REF:0 ! PARAMETER G(LIQUID,AL,MG;1) 2.98150E+02 -891.11184+1.1368285\*T; 6.00000E+03 N REF:0 ! PARAMETER G(LIQUID,AL,MG;2) 2.98150E+02 434.02777; 6.00000E+03 Ν REF:0 ! PARAMETER G(LIQUID,AL,K;0) 2.98150E+02 65000; 6.00000E+03 N REF:0 ! PARAMETER G(LIQUID,AL,NA;0) 2.98150E+02 +773867.87+20.270738\*T; 6.00000E+03 N REF:0 ! PARAMETER G(LIQUID,AL,NA;1) 2.98150E+02 -746012.77; 6.00000E+03 Ν REF:0 ! PARAMETER G(LIQUID,CA,LI;0) 2.98150E+02 -5641.2-3.2065\*T; 6.00000E+03 N REF:0 ! PARAMETER G(LIQUID,CA,NA;0) 2.98150E+02 +28896-8.35\*T; 6.00000E+03 N REF:0 ! PARAMETER G(LIQUID,CA,NA;1) 2.98150E+02 -33-7.03\*T; 6.00000E+03 Ν **REF:0** ! PARAMETER G(LIQUID,CA,MG;0) 2.98150E+02 -32322.4+16.7211\*T; 6.00000E+03 N REF:0 ! PARAMETER G(LIQUID,CA,MG;1) 2.98150E+02 +60.3+6.549\*T; 6.00000E+03 N REF:0 ! PARAMETER G(LIQUID,CA,MG;2) 2.98150E+02 -5742.3+2.7596\*T; 6.00000E+03 N REF:0 ! PARAMETER G(LIQUID,CA,K;0) 2.98150E+02 60000; 6.00000E+03 N REF:0 ! PARAMETER G(LIQUID,K,MG;0) 2.98150E+02 37272.243; 6.00000E+03 Ν

REF:0 !

PARAMETER G(LIQUID,K,MG;1) 2.98150E+02	2 -1072.5519; 6.00000E+03 N
REF:0 !	
PARAMETER G(LIQUID,K,LI;0) 2.00000E+02	+40849.0649-15.7234801*T;
2.20000E+03 N REF:0 !	
PARAMETER G(LIQUID,K,LI;1) 2.00000E+02	-9583.48979; 2.20000E+03 N
REF:0 !	
PARAMETER G(LIQUID,K,NA;0) 2.98150E+02	2 +2987.1394627679*T;
6.00000E+03 N REF:0 !	
PARAMETER G(LIQUID,K,NA;1) 2.98150E+02	2 -687.71141+1.0120956*T;
6.00000E+03 N REF:0 !	
PARAMETER G(LIQUID,LI,MG;0) 2.98150E+0	02 -14935+10.371*T; 6.00000E+03
N REF:0 !	
PARAMETER G(LIQUID,LI,MG;1) 2.98150E+0	02 -1789+1.143*T; 6.00000E+03
N REF:0 !	
PARAMETER G(LIQUID,LI,MG;2) 2.98150E+0	02 +6533-6.6915*T; 6.00000E+03
N REF:0 !	
PARAMETER G(LIQUID,LI,NA;0) 2.98150E+02	2 10684.3678; 6.00000E+03 N
REF:0 !	
PARAMETER G(LIQUID,LI,NA;1) 2.98150E+02	2 +3896.41952-5.46265483*T;
6.00000E+03 N REF:0 !	
PARAMETER G(LIQUID,LI,NA;2) 2.98150E+02	2 1580.34389; 6.00000E+03 N
REF:0 !	
PARAMETER G(LIQUID,MG,NA;0) 2.98150E+	-02 26025.7787; 6.00000E+03 N
REF:0 !	
PARAMETER G(LIQUID,MG,NA;1) 2.98150E+	-02 4509.96384; 6.00000E+03 N
REF:0 !	

PHASE AL12MG17 % 3 24 10 24 ! CONSTITUENT AL12MG17 :LI,MG : LI,MG : MG : !

PARAMETER G(AL12MG17,LI:LI:MG;0) 2.98150E+02 +290000+34\*GHSERLI# +24\*GHSERMG#; 6.00000E+03 N REF:0 ! PARAMETER G(AL12MG17,MG:LI:MG;0) 2.98150E+02 +290000+10\*GHSERLI# +48\*GHSERMG#; 6.00000E+03 N REF:0 ! PARAMETER G(AL12MG17,LI:MG:MG;0) 2.98150E+02 +290000+24\*GHSERLI# +34\*GHSERLI#; 6.00000E+03 N REF:0 ! PARA G(AL12MG17,MG:MG:MG;0) 298.15 0; 6000 N!

PHASE AL14CA13 % 2 14 13 ! CONSTITUENT AL14CA13 :AL : CA : !

PARAMETER G(AL14CA13,AL:CA;0) 2.98140E+02 -747604+161.632\*T+14\*GHSERAL# +13\*GHSERCA#; 2.00000E+03 N REF:0 !

PHASE AL2LI3 % 2 2 3 ! CONSTITUENT AL2LI3 :AL : LI : !

PARAMETER G(AL2LI3,AL:LI;0) 2.98150E+02 -89640+32.79\*T+2\*GHSERAL# +3\*GHSERLI#; 6.00000E+03 N REF:0 ! PHASE AL3CA8 % 23 8! CONSTITUENT AL3CA8 :AL : CA : ! PARAMETER G(AL3CA8,AL:CA:0) 2.98140E+02 -194475+44.784\*T+8\*GHSERCA# +3\*GHSERAL#; 2.00000E+03 N REF:0 ! PHASE AL4CA % 24 1! CONSTITUENT AL4CA : AL : CA : ! PARAMETER G(AL4CA,AL:CA;0) 2.98140E+02 -100170+20.197\*T+4\*GHSERAL# +GHSERCA#; 2.00000E+03 N REF:0 ! PHASE AL4LI9 % 24 91 CONSTITUENT AL4LI9 :AL : LI : ! PARAMETER G(AL4LI9,AL:LI;0) 2.98150E+02 -185250+67.8\*T+4\*GHSERAL# +9\*GHSERLI#; 6.00000E+03 N REF:0 ! PHASE ALLI % 21 1! CONSTITUENT ALLI :AL,LI,MG : LI,MG,VA : ! PARAMETER G(ALLI,AL:LI:0) 2.98150E+02 -41300+16.86\*T+GHSERAL#+GHSERLI#; 6.00000E+03 N REF:0 ! PARAMETER G(ALLI,LI:LI;0) 2.98150E+02 +2+2\*GHSERLI#; 6.00000E+03 N REF:0 ! PARAMETER G(ALLI,MG:LI;0) 2.98150E+02 -9168+4.2\*T+GBCCMG#+GHSERLI#; 6.00000E+03 N REF:0 ! PARA G(ALLI,AL:MG;0) 298.15 0; 6000 N! PARAMETER G(ALLI,LI:MG;0) 2.98150E+02 -9168+4.2\*T+GBCCMG#+GHSERLI#; N REF:0 ! 6.00000E+03 PARA G(ALLI,MG:MG;0) 298.15 0; 6000 N! PARAMETER G(ALLI,AL:VA;0) 2.98150E+02 +24000+GHSERAL#; 6.00000E+03 N REF:0 ! PARAMETER G(ALLI,LI:VA;0) 2.98150E+02 +50000+GHSERLI#; 6.00000E+03 N REF:0 ! PARA G(ALLI,MG:VA;0) 298.15 0; 6000 N! PARAMETER G(ALLI, AL, LI:LI;0) 2.98150E+02 20000; 6.00000E+03 N REF:0 ! 6.00000E+03 PARAMETER G(ALLI,AL,LI:LI;1) 2.98150E+02 -26000; Ν **REF:0**! PARAMETER G(ALLI,AL:LI,VA;0) 2.98150E+02 -24000+10\*T; 6.00000E+03 Ν REF:0 ! PARAMETER G(ALLI, AL, LI: VA; 0) 2.98150E+02 2000; 6.00000E+03 N REF:0 ! PHASE ALMG BETA % 289 140 ! CONSTITUENT ALMG BETA :MG: AL%: ! PARAMETER G(ALMG BETA,MG:AL;0) 2.98150E+02 -809136.27+115.01663\*T

PHASE ALMG EPS % 2 23 30! CONSTITUENT ALMG EPS :MG:AL%: !

PARAMETER G(ALMG EPS,MG:AL;0) 2.98150E+02 -172080.69-5.8490582\*T +23\*GHSERMG#+30\*GHSERAL#; 6.00000E+03 N REF:0 !

PHASE ALMG GAMMA % 35 12 12! CONSTITUENT ALMG GAMMA :MG : AL,MG% : AL%,MG : !

PARAMETER G(ALMG GAMMA,MG:AL:AL;0) 2.98150E+02 +8360+20.338857\*T +5\*GHSERMG#+24\*GHSERAL#; 6.00000E+03 N REF:3 ! PARAMETER G(ALMG GAMMA,MG:MG:AL;0) 2.98150E+02 -104308.83+23.495281\*T +17\*GHSERMG#+12\*GHSERAL#; 6.00000E+03 N REF:3 ! PARAMETER G(ALMG GAMMA,MG:AL:MG:0) 2.98150E+02 +180556-138.069\*T +17\*GHSERMG#+12\*GHSERAL#; 6.00000E+03 N REF:3 ! PARAMETER G(ALMG GAMMA,MG:MG:MG;0) 2.98150E+02 +139371-87.319\*T +29\*GHSERMG#; 6.00000E+03 N REF:0 ! PARAMETER G(ALMG GAMMA,MG:AL:AL,MG;0) 2.98150E+02 +113100-14.5\*T; 6.00000E+03 N REF:0 ! PARAMETER G(ALMG GAMMA,MG:MG:AL,MG;0) 2.98150E+02 +113100-14.5\*T; 6.00000E+03 N REF:0 !

TYPE DEFINITION & GES A P D ALM D019 MAGNETIC -3.0 2.80000E-01 ! PHASE ALM D019 %& 23 1! CONSTITUENT ALM D019 :AL : AL% : !

PARAMETER G(ALM D019,AL:AL;0) 2.98150E+02 +4\*GHCPAL#; 6.00000E+03 Ν REF:0 !

TYPE DEFINITION 'GES A P D BCC A2 MAGNETIC -1.0 4.00000E-01 ! PHASE BCC A2 %' 21 3! CONSTITUENT BCC A2 :AL,CA,K,LI,MG,NA : VA% : !

PARAMETER G(BCC A2,AL:VA;0) 2.98140E+02 +10083-4.813\*T+GHSERAL#; 2.90000E+03 N REF:0 !

PARAMETER G(BCC A2,CA:VA;0) 2.98140E+02 -7020.852+142.970155\*T -28.2541\*T\*LN(T)+.0072326\*T\*\*2-4.500217E-06\*T\*\*3+60578\*T\*\*(-1); 7.16000E+02 Y

+1640.475+1.999694\*T-6.276\*T\*LN(T)-.0161921\*T\*\*2-523000\*T\*\*(-1); 1.11500E+03 Y

-142331.096+1023.54905\*T-143.872698\*T\*LN(T)+.032543127\*T\*\*2

-1.704079E-06\*T\*\*3+25353771\*T\*\*(-1); 3.00000E+03 N REF:0 !

PARAMETER G(BCC\_A2,K:VA;0) 2.00000E+02 +GHSERKK#; 2.20000E+03 N REF:0 ! PARAMETER G(BCC A2,LI:VA;0) 2.00000E+02 +GHSERLI#; 3.00000E+03 N **REF:0**!

PARAMETER G(BCC A2,MG:VA;0) 2.98140E+02 +3100-2.1\*T+GHSERMG#; 3.00000E+03 N REF:0!

PARAMETER G(BCC A2,NA:VA;0) 2.00000E+02 +GHSERNA#; 2.30000E+03 N **REF:0** !

PARAMETER G(BCC A2,AL,LI:VA;0) 2.98150E+02 -27000+8\*T; 6.00000E+03 N REF:0 ! PARAMETER G(BCC A2,AL,LI:VA;1) 2.98150E+02 1E-06; 6.00000E+03 Ν **REF:0** ! PARAMETER G(BCC A2,AL,LI:VA;2) 2.98150E+02 3000; 6.00000E+03 Ν **REF:0** ! PARAMETER G(BCC A2,AL,K:VA;0) 2.98150E+02 20000; 6.00000E+03 Ν **REF:0** ! PARAMETER G(BCC A2,AL,NA:VA;0) 2.98150E+02 15000; 6.00000E+03 Ν **REF:0**! PARAMETER G(BCC A2,CA,LI:VA;0) 2.98150E+02 5918.9; 6.00000E+03 Ν **REF:0**! PARAMETER G(BCC A2,CA,NA:VA;0) 2.98150E+02 +56258.1161-39.401314\*T; 6.00000E+03 N REF:0 ! PARAMETER G(BCC A2,CA,MG:VA;0) 5.00000E+02 100000; 2.00000E+03 N **REF:0** ! PARAMETER G(BCC A2,CA,K:VA;0) 2.98150E+02 60000; 6.00000E+03 Ν **REF:0** ! PARAMETER G(BCC A2,K,MG:VA;0) 2.98150E+02 30000; 6.00000E+03 Ν **REF:0**! PARAMETER G(BCC A2,K,LI:VA;0) 2.00000E+02 39914.8369; 3.00000E+03 N **REF:0** ! PARAMETER G(BCC A2,K,NA:VA;0) 2.98150E+02 +11350.857-10.390631\*T; 6.00000E+03 N REF:0 ! PARAMETER G(BCC A2,K,NA:VA;1) 2.98150E+02 -1488.4794-2.2363528\*T; 6.00000E+03 N REF:0 ! PARAMETER G(BCC\_A2,LI,MG:VA;0) 2.98150E+02 -18335+8.49\*T; 6.00000E+03 N REF:0 ! PARAMETER G(BCC A2,LI,MG:VA;1) 2.98150E+02 3481; 6.00000E+03 Ν REF:0 ! PARAMETER G(BCC A2,LI,MG:VA;2) 2.98150E+02 +2658-.114\*T; 6.00000E+03 N REF:0 ! PARAMETER G(BCC A2,LI,NA:VA;0) 2.98150E+02 16000; 6.00000E+03 Ν REF:0 ! PARAMETER G(BCC A2,MG,NA:VA;0) 2.98150E+02 50000; 6.00000E+03 Ν REF:0 !

\$ THIS PHASE HAS A DISORDERED CONTRIBUTION FROM BCC\_A2 TYPE\_DEFINITION ( GES AMEND\_PHASE\_DESCRIPTION BCC\_B2 DIS\_PART BCC\_A2,,,! PHASE BCC\_B2 %( 3.5 .5 3! CONSTITUENT BCC\_B2 :AL%,LI,MG : AL,LI,MG : VA : ! PARA G(BCC\_B2,AL:AL:VA;0) 298.15 0; 6000 N! PARA G(BCC\_B2,LI:AL:VA;0) 298.15 0; 6000 N! PARA G(BCC\_B2,MG:AL:VA;0) 298.15 0; 6000 N! PARA G(BCC\_B2,AL:LI:VA;0) 298.15 0; 6000 N! PARA G(BCC\_B2,AL:LI:VA;0) 298.15 0; 6000 N! PARA G(BCC\_B2,LI:LI:VA;0) 298.15 0; 6000 N! PARA G(BCC\_B2,LI:LI:VA;0) 298.15 0; 6000 N!

PARA G(BCC\_B2,AL:MG:VA;0) 298.15 0; 6000 N! PARA G(BCC\_B2,LI:MG:VA;0) 298.15 0; 6000 N! PARAMETER G(BCC\_B2,MG:MG:VA;0) 2.98150E+02 +GBCCMG#; 6.00000E+03 N REF:0 ! PHASE CALI2 % 21 2! CONSTITUENT CALI2 :CA:LI: ! PARAMETER G(CALI2,CA:LI:0) 2.98150E+02 +2\*GHSERLI#+GHSERCA#-11681.91 +6.396\*T: 6.0000E+03 N REF:0 ! TYPE DEFINITION) GES A P D FCC A1 MAGNETIC -3.0 2.80000E-01 ! PHASE FCC A1 %) 21 1! CONSTITUENT FCC\_A1 :AL%,CA,K,LI,MG,NA : VA% : ! PARAMETER G(FCC A1,AL:VA;0) 2.98140E+02 +GHSERAL#; 2.90000E+03 N **REF:0**! PARAMETER G(FCC A1,CA:VA;0) 2.98140E+02 +GHSERCA#; 3.00000E+03 N REF:0 ! PARAMETER G(FCC A1,K:VA;0) 2.00000E+02 +50+1.3\*T+GHSERKK#; 2.20000E+03 N REF:0 ! PARAMETER G(FCC A1,LI:VA;0) 2.00000E+02 -108+1.3\*T+GHSERLI#; 4.53600E+02 Y -108+1.3\*T+GHSERLI#; 5.00000E+02 Y -108+1.3\*T+GHSERLI#: 3.00000E+03 N REF:0 ! PARAMETER G(FCC A1,MG:VA;0) 2.98140E+02 +2600-.9\*T+GHSERMG#; 3.00000E+03 N REF:0 ! PARAMETER G(FCC A1,NA:VA;0) 2.00000E+02 -50+1.3\*T+GHSERNA#; 2.30000E+03 N REF:0 ! PARAMETER G(FCC A1,AL,LI:VA;0) 2.98150E+02 -27000+8\*T; 6.00000E+03 N REF:0 ! PARAMETER G(FCC A1,AL,LI:VA;1) 2.98150E+02 1E-06; 6.00000E+03 Ν REF:0 ! PARAMETER G(FCC A1,AL,LI:VA;2) 2.98150E+02 +3000+T; 6.00000E+03 Ν **REF:0** ! PARAMETER G(FCC A1,AL,MG:VA;0) 2.98150E+02 +1587.61+2.1413324\*T; 6.00000E+03 N REF:0 ! PARAMETER G(FCC A1.AL,MG:VA:1) 2.98150E+02 +1179.5327-.69523422\*T; 6.00000E+03 N REF:0 ! PARAMETER G(FCC A1,AL,MG:VA;2) 2.98150E+02 -866.82189; 6.00000E+03 N REF:0 ! PARAMETER G(FCC A1,AL,K:VA;0) 2.98150E+02 50000; 6.00000E+03 Ν **REF:0** ! PARAMETER G(FCC A1,AL,NA:VA;0) 2.98150E+02 50000; 6.00000E+03 Ν **REF:0**! PARAMETER G(FCC A1,CA,LI:VA;0) 2.98150E+02 6458.3; 6.00000E+03 Ν **REF:0** ! PARAMETER G(FCC\_A1,CA,NA:VA;0) 2.98150E+02 30000; 6.00000E+03 Ν **REF:0** ! PARAMETER G(FCC A1,CA,MG;VA;0) 5.00000E+02 100000; 2.00000E+03 N **REF:0**! PARAMETER G(FCC A1,CA,K:VA;0) 2.98150E+02 40000; 6.00000E+03 Ν **REF:0** ! PARAMETER G(FCC A1,K,MG:VA;0) 2.98150E+02 50000; 6.00000E+03 Ν **REF:0**! PARAMETER G(FCC\_A1,K,LI:VA;0) 2.00000E+02 50000; 3.00000E+03 N REF:0 ! PARAMETER G(FCC A1,K,NA:VA;0) 2.98150E+02 10000; 6.00000E+03 N

REF:0 ! PARAMETER G(FCC A1,LI,MG:VA;0) 2.98150E+02 7500; 6.00000E+03 Ν **REF:0** ! PARAMETER G(FCC A1,LI,NA:VA;0) 2.98150E+02 20000; 6.00000E+03 Ν **REF:0** ! PARAMETER G(FCC A1,MG,NA:VA;0) 2.98150E+02 50000; 6.00000E+03 Ν REF:0 ! TYPE DEFINITION \* GES A P D HCP A3 MAGNETIC -3.0 2.80000E-01 ! PHASE HCP\_A3 %\* 21 .5! CONSTITUENT HCP A3 :AL,CA,K,LI,MG%,NA : VA% : ! PARAMETER G(HCP A3,AL:VA;0) 2,98140E+02 +5481-1.8\*T+GHSERAL#; 2.90000E+03 N REF:0 ! PARAMETER G(HCP A3,CA:VA;0) 2.98140E+02 +500+.7\*T+GHSERCA#; 3.00000E+03 N REF:0 ! PARAMETER G(HCP A3,K:VA;0) 2.00000E+02 +50+2\*T+GHSERKK#; 2.20000E+03 N REF:0 ! PARAMETER G(HCP A3,LI:VA;0) 2.00000E+02 -154+2\*T+GHSERLI#; 3.00000E+03 N REF:0 ! PARAMETER G(HCP A3,MG:VA;0) 2.98140E+02 +GHSERMG#; 3.00000E+03 N REF:0 ! PARAMETER G(HCP A3,NA:VA;0) 2.00000E+02 -104+2\*T+GHSERNA#; 2.30000E+03 N REF:0! PARAMETER G(HCP A3,AL,LI:VA;0) 2.98150E+02 -27000+8\*T; 6.00000E+03 N REF:0 ! PARAMETER G(HCP A3,AL,MG:VA;0) 2.98150E+02 +4271.9648-2.1898692\*T; N REF:0 ! 6.00000E+03 PARAMETER G(HCP\_A3,AL,MG:VA;1) 2.98150E+02 -1.076864+1.014848\*T; 6.0000E+03 N REF:0 ! PARAMETER G(HCP A3,AL,MG:VA;2) 2.98150E+02 -965.93125; 6.00000E+03 N REF:0 ! PARAMETER G(HCP A3,AL,K:VA;0) 2.98150E+02 20000; 6.00000E+03 Ν REF:0 ! PARAMETER G(HCP A3,AL,NA:VA;0) 2.98150E+02 20000; 6.00000E+03 Ν **REF:0**! PARAMETER G(HCP A3,CA,LI:VA;0) 2.98150E+02 5000; 6.00000E+03 Ν **REF:0** ! PARAMETER G(HCP\_A3,CA,NA:VA;0) 2.98150E+02 15000; 6.00000E+03 Ν **REF:0**! PARAMETER G(HCP\_A3,CA,MG:VA;0) 2.98150E+02 -9183.2+16.981\*T; N REF:0 ! 6.00000E+03 PARAMETER G(HCP A3,CA,K:VA;0) 2.98150E+02 30000; 6.00000E+03 Ν **REF:0**! PARAMETER G(HCP A3,K,MG:VA;0) 2.98150E+02 38727.091; 6.00000E+03 Ν REF:0 ! PARAMETER G(HCP A3,K,LI:VA;0) 2.00000E+02 60000; 3.00000E+03 N REF:0 ! PARAMETER G(HCP A3,K,NA:VA;0) 2.98150E+02 5000; 6.00000E+03 N REF:0 ! PARAMETER G(HCP\_A3,LI,MG:VA;0) 2.98150E+02 -6856; 6.00000E+03 Ν REF:0 ! PARAMETER G(HCP A3,LI,MG:VA;1) 2.98150E+02 4000; 6.00000E+03 Ν **REF:0** ! PARAMETER G(HCP A3,LI,MG:VA;2) 2.98150E+02 4000; 6.00000E+03 Ν

REF:0 !

PARAMETER G(HCP\_A3,LI,NA:VA;0) 2.98150E+02 20000; 6.00000E+03 N REF:0 !

PARAMETER G(HCP\_A3,MG,NA:VA;0) 2.98150E+02 75698.3133; 6.00000E+03 N REF:0 !

PHASE HCP\_ZN % 21 .5 ! CONSTITUENT HCP ZN :AL,MG : VA% : !

PARAMETER G(HCP\_ZN,AL:VA;0) 2.98150E+02 +5482-1.8\*T+GHSERAL#; 6.00000E+03 N REF:0 ! PARAMETER G(HCP\_ZN,MG:VA;0) 2.98150E+02 +100+GHSERMG#; 6.00000E+03 N REF:0 ! PARAMETER G(HCP\_ZN,AL,MG:VA;0) 2.98150E+02 +1950-2\*T; 6.00000E+03 N REF:0 ! PARAMETER G(HCP\_ZN,AL,MG:VA;1) 2.98150E+02 +1480-2.08\*T; 6.00000E+03 N REF:0 ! PARAMETER G(HCP\_ZN,AL,MG:VA;2) 2.98150E+02 3500; 6.00000E+03 N REF:0 !

PHASE KNA2 % 21 2! CONSTITUENT KNA2 :K : NA : !

PARAMETER G(KNA2,K:NA;0) 2.98150E+02 +2\*GHSERNA#+GHSERKK#+230.29056 -3.8663294\*T; 6.00000E+03 N REF:0 !

PHASE LAVES C14 % 22 1! CONSTITUENT LAVES C14 :AL,CA,MG: AL,CA,MG%: ! PARAMETER G(LAVES C14,AL:AL;0) 2.98150E+02 +5000+GHSERAL#; 6.00000E+03 N REF:0 ! PARA G(LAVES C14,CA:AL;0) 298.15 0; 6000 N! PARAMETER G(LAVES C14,MG:AL;0) 2.98150E+02 +5776.333-5.6\*T +.33333\*GHSERAL#+.66667\*GHSERMG#; 6.00000E+03 N REF:0 ! PARA G(LAVES C14, AL:CA;0) 298.15 0; 6000 N! PARAMETER G(LAVES C14,CA:CA;0) 2.98150E+02 +12330+4.333\*T+GHSERCA#; N REF:0 ! 6.00000E+03 PARAMETER G(LAVES C14,MG:CA;0) 2.98150E+02 -22624.9+155.073\*T -27.57338\*T\*LN(T)-.00158741\*T\*\*2+210000\*T\*\*(-2)+690; 6.00000E+03 N **REF:0**! PARAMETER G(LAVES C14, AL:MG;0) 2.98150E+02 +4223.7+5.6\*T +.33333\*GHSERMG#+.666667\*GHSERAL#; 6.00000E+03 N REF:0 ! PARAMETER G(LAVES\_C14,CA:MG;0) 2.98150E+02 +26650+4.333\*T +.33333\*GHSERMG#+.66667\*GHSERCA#; 6.00000E+03 N REF:0 ! PARAMETER G(LAVES\_C14,MG:MG;0) 2.98150E+02 +7720+4.333\*T+GHSERMG#; 6.0000E+03 N REF:0 ! 6.00000E+03 PARAMETER G(LAVES\_C14,AL,MG:AL;0) 2.98150E+02 5000; Ν REF:0 ! PARAMETER G(LAVES C14,AL:AL,MG;0) 2.98150E+02 2666.7; 6.00000E+03 Ν **REF:0** ! PARAMETER G(LAVES C14,MG:AL,MG;0) 2.98150E+02 2666.7; 6.00000E+03 Ν

REF:0 ! PARAMETER G(LAVES C14,CA,MG:CA;0) 2.98150E+02 16000; 6.00000E+03 Ν **REF:0** ! PARAMETER G(LAVES C14,CA:CA,MG;0) 2.98150E+02 16000; 6.00000E+03 Ν **REF:0** ! PARAMETER G(LAVES C14,MG:CA,MG;0) 2.98150E+02 16000; 6.00000E+03 Ν **REF:0** ! PARAMETER G(LAVES C14,AL,MG:MG;0) 2.98150E+02 5000; 6.00000E+03 Ν **REF:0**! PARAMETER G(LAVES C14,CA,MG:MG;0) 2.98150E+02 16000; 6.00000E+03 Ν REF:0 ! PHASE LAVES C15 % 22 1! CONSTITUENT LAVES C15 :AL,CA,MG: AL,CA,MG%: ! PARAMETER G(LAVES C15,AL:AL;0) 2.98140E+02 +15391+6.528\*T+GHSERAL#; 2.00000E+03 N REF:0 ! PARAMETER G(LAVES C15, CA: AL; 0) 2.98140E+02 +46508+6.528\*T +.666667\*GHSERCA#+.33333\*GHSERAL#; 2.00000E+03 N REF:0! PARAMETER G(LAVES C15,MG:AL;0) 2.98150E+02 +34990.32-5.48816\*T +.666667\*GHSERMG#+.33333\*GHSERAL#; 6.00000E+03 N REF:0 ! PARAMETER G(LAVES\_C15,AL:CA;0) 2.98140E+02 -32047.667+6.528\*T +.666667\*GHSERAL#+.33333\*GHSERCA#; 2.00000E+03 N REF:0 ! PARAMETER G(LAVES\_C15,CA:CA;0) 2.98140E+02 +8201+6.528\*T+GHSERCA#; 2.00000E+03 N REF:0 ! PARA G(LAVES C15,MG:CA:0) 298.15 0; 6000 N! PARAMETER G(LAVES C15, AL:MG;0) 2.98150E+02 +10000+1.333\*T +.666667\*GHSERAL#+.33333\*GHSERMG#; 6.00000E+03 N REF:0 ! PARA G(LAVES C15,CA:MG;0) 298.15 0; 6000 N! PARAMETER G(LAVES C15,MG:MG;0) 2.98150E+02 +5000+GHSERMG#; 6.00000E+03 N REF:0 ! PARAMETER G(LAVES C15,AL,MG:AL;0) 2.98150E+02 5000; 6.00000E+03 Ν **REF:0** ! PARAMETER G(LAVES C15,AL:AL,MG;0) 2.98150E+02 2666.7; 6.00000E+03 Ν **REF:0** ! PARAMETER G(LAVES C15,MG:AL,MG;0) 2.98150E+02 2666.7; 6.00000E+03 Ν **REF:0** ! PARAMETER G(LAVES C15,AL,MG:MG;0) 2.98150E+02 5000; 6.0000E+03 Ν **REF:0**! PHASE LAVES C36 % 22 1! CONSTITUENT LAVES C36 :AL,MG : AL,CA,MG% : ! PARAMETER G(LAVES C36,AL:AL;0) 2.98150E+02 +5000+GHSERAL#; 6.00000E+03 N REF:0 ! PARAMETER G(LAVES C36,MG:AL;0) 2.98150E+02 +28323.653-5.48816\*T +.66667\*GHSERMG#+.33333\*GHSERAL#; 6.00000E+03 N REF:0 ! PARAMETER G(LAVES C36,AL:CA:0) 2.98140E+02 -31684.667+11.667\*T +.666667\*GHSERAL#+.33333\*GHSERCA#; 2.00000E+03 N REF:0 ! PARAMETER G(LAVES C36,MG:CA;0) 2.98150E+02 -13795+5.333\*T

+.666667\*GHSERAL#+.33333\*GHSERMG#; 6.00000E+03 N REF:0! PARAMETER G(LAVES C36,MG:MG;0) 2.98150E+02 +5000+GHSERMG#; 6.00000E+03 N REF:0 ! PARAMETER G(LAVES C36,AL,MG:AL;0) 2.98150E+02 5000; 6.00000E+03 N **REF:0** ! PARAMETER G(LAVES C36,AL:AL,MG;0) 2.98150E+02 2666.7; 6.00000E+03 N **REF:0** ! PARAMETER G(LAVES C36,MG:AL,MG;0) 2.98150E+02 2666.7; 6.00000E+03 Ν **REF:0**! PARAMETER G(LAVES C36,AL,MG:CA;0) 2.98150E+02 3333.333; 6.00000E+03 N REF:0 ! PARAMETER G(LAVES C36,AL,MG:MG;0) 2.98150E+02 5000; 6.00000E+03 N REF:0 ! PHASE MG24Y5 % 2 24 5 ! CONSTITUENT MG24Y5 :MG : MG : ! PARAMETER G(MG24Y5,MG:MG;0) 2.98150E+02 +44506.01+29\*GHSERMG#; 6.00000E+03 N REF:0 ! PHASE MG2Y % 22 1! CONSTITUENT MG2Y :MG:MG: ! PARA G(MG2Y,MG:MG;0) 298.15 0; 6000 N! PHASE MG2ZN11 % 2.153846 .846154 ! CONSTITUENT MG2ZN11 :MG:AL: ! PARAMETER G(MG2ZN11,MG:AL;0) 2.98150E+02 +10000-2\*T+.153846\*GHSERMG# +.846154\*GHSERAL#; 6.00000E+03 N REF:0 ! PHASE MG2ZN3 % 2.4 .6 ! CONSTITUENT MG2ZN3 :MG : AL : ! PARAMETER G(MG2ZN3.MG:AL;0) 2.98150E+02 +200-.04\*T+.4\*GHSERMG# +.6\*GHSERAL#; 6.00000E+03 N REF:0 ! PHASE MGY GAMMA % 21 1! CONSTITUENT MGY GAMMA :MG: MG: ! PARAMETER G(MGY GAMMA,MG:MG;0) 2.98150E+02 +9891.48+2\*GHSERMG#; 6.00000E+03 N REF:0 ! PHASE MGZN % 2.48 .52 ! CONSTITUENT MGZN :MG : AL : ! PARAMETER G(MGZN,MG:AL;0) 2.98150E+02 -400+.1\*T+.48\*GHSERMG# +.52\*GHSERAL#; 6.00000E+03 N REF:0 !

<sup>179</sup> 

PHASE PHI % 26 5! CONSTITUENT PHI :MG : AL : ! PARAMETER G(PHI,MG:AL;0) 2.98150E+02 -15400-16.5\*T+5\*GHSERAL# +6\*GHSERMG#; 6.00000E+03 N REF:0 ! PHASE TAU % 4 26 6 48 1 ! CONSTITUENT TAU :MG : AL,MG% : AL%,MG : AL : ! PARAMETER G(TAU,MG:AL:AL:AL:0) 2.98150E+02 -105.3\*T+55\*GHSERAL# +26\*GHSERMG#; 6.00000E+03 N REF:0 ! PARAMETER G(TAU,MG:MG:AL:AL;0) 2.98150E+02 -81000-186.3\*T+49\*GHSERAL# +32\*GHSERMG#; 6.00000E+03 N REF:0 ! PARAMETER G(TAU,MG:AL:MG:AL;0) 2.98150E+02 +1053000+405\*T+7\*GHSERAL# +74\*GHSERMG#; 6.00000E+03 N REF:0 ! PARAMETER G(TAU,MG:MG:MG:AL;0) 2.98150E+02 +405000+243\*T+GHSERAL# +80\*GHSERMG#; 6.00000E+03 N REF:0 ! PARAMETER G(TAU,MG:AL:AL,MG:AL;0) 2.98150E+02 -202500-40.5\*T; 6.0000E+03 N REF:0 ! PARAMETER G(TAU,MG:MG:AL,MG:AL;0) 2.98150E+02 -202500-40.5\*T; 6.00000E+03 N REF:0 ! LIST OF REFERENCES NUMBER SOURCE

1

## **Appendix B**

## THE ORIGINAL INPUT FILES USED IN THERMO-CALC

### The Al-Na system

\$\$ POP FILE FOE AL-NA BINARY SYSTEM E-SYM CON P0=1E5 R0=8.314

\$\$ The phase bounary of left side of liquid miscibility gap\$\$ These eperimenatl data come from Ransley and Neufeid (1950)

TABLE 100 C-N @@,1 CH P LIQ,LIQ#2=F 1 S-C X(liq,NA)=@2 P=P0 EXPERIMENT T=@1:1% LABEL ALL1 TABLE\_VALUE 938 0.001642686 943 0.00175999 943 0.00175999 973 0.002111878 998 0.002581005 998 0.00234645 1023 0.002698277 1023 0.002581005 1048 0.002932808 TABLE END

\$\$ The monotectic reaction\$\$ These eperimenatl data come from Ransley and Neufeid (1950)

TABLE 200 C-N @@,1 CH P LIQ,LIQ#2,FCC=F 1 S-C P=P0 EXPERIMENT T=@2:1% EXPERIMENT X(liq,NA)=@1:1% EXPERIMENT X(fcc,NA)=0.00002:1% EXPERIMENT X(liq#2,NA)=1:1% LABEL ALL2 TABLE\_VALUE 0.0014 932

#### TABLE\_END

\$\$ Activity of Na in liquid Al in 998K\$\$ These experimental data come from Brisley and Fray (1983)

**TABLE 300** C-N @@,1 CH P LIQ=F 1 S-C T=998 X(NA)=@1 P=P0 EXPERIMENT ACR(na,liq)=@2:1% LABEL ALL3 TABLE VALUE 1.17363E-06 0.000261 0.00189 5.86816E-06 1.17363E-05 0.00337 5.86811E-05 0.0205 TABLE\_END

\$\$ Activity of Na in liquid Al in 1293K\$\$ These experimental data come from Dewing (1972)

TABLE 400 C-N @@,1 CH P LIQ=F 1 S-C T=1293 X(NA)=@1 P=P0 EXPERIMENT ACR(na,liq)=@2:1% LABEL ALL4 TABLE VALUE 0.000199512 0.03280 0.000258189 0.04260 7.86325E-05 0.01300 0.000363806 0.06000 5.16394E-05 0.00849 2.93407E-05 0.00483 1.52572E-05 0.00251 8.21542E-06 0.00135 9.97587E-07 0.00016 6.68964E-05 0.01100 4.45977E-05 0.00734 8.09797E-05 0.01330 7.98061E-05 0.01310 4.92922E-05 0.00811 4.57714E-05 0.00751 TABLE\_END

\$\$ Activity of Na in liquid Al in 1353K\$\$ These experimental data come from Dewing (1972)

TABLE 500

C-N @@,1	
CH P LIQ=F 1	
S-C T=1353 X(NA	A)=@1 P=P0
EXPERIMENT A	CR(na,liq)=@2:1%
LABEL ALL5	
TABLE_VALUE	
1.40836E-05	0.00201
1.29099E-05	0.00184
4.69453E-06	0.00067
3.5209E-06	0.0005
0.000334469	0.0477
0.000310998	0.0443
0.000399011	0.057
0.000528093	0.0757
0.000569164	0.0811
0.000193644	0.0276
0.000164305	0.0234
0.000117361	0.0167
0.000125576	0.0179
9.03685E-05	0.0129
9.38893E-05	0.0134
5.63339E-05	0.00803
6.22019E-05	0.00887
5.01137E-05	0.00703
4.57714E-05	0.00652
1.76044E-05	0.00251
1.76044E-05	0.00251
1.17363E-05	0.00167
8.21542E-06	0.00117
0.000675945	0.0965
0.000592632	0.0844

## SAVE

TABLE\_END

## The Ca-Na system

### \$\$ POP FILE FOR CA-NA BINARY SYSTEM E-SYM CON P0=101325 R0=8.314

\$\$ THIS TABLE TAKES CARE OF LIQUIDUS LINE OF CA-RICH AREA TABLE 100 C-N @@,1 CH P LIQUID,BCC=FIX 1 S-C X(LIQ,NA)=@2 p=p0 EXPERIMENT T=@1:0.1% LABEL ALL1 \$SET-ALL-START 998.523,,,,,, TABLE\_VALUE 997.031 0.207181 998.523 0.195356 1017.926 0.179328 1026.881 0.164529 1034.34 0.14663 1047.777 0.129707 1052.25 0.11617 1065.687 0.0948822 1074.64 0.0865877 1085.09 0.0600588 1094.046 0.0417753 1104.493 0.0234933 TABLE\_END

\$\$ INVARIANT POINT AT 22.1% NI \$\$ MONOTECTIC REACTION WILL TAKE PLACE THIS POINT \$\$ LIQUID1 -> BCC + LIQUID2 C-N 200,1 CH P LIQUID,BCC,LIQ#2=FIX 1 S-C P=P0 EXPERIMENT T=983.15:1% EXPERIMENT T=983.15:1% EXPERIMENT X(LIQUID,NA)=0.221:1%, X(LIQUID#2,NA)=0.959:1% LABEL ALL2 \$SET-ALL-START 986.15,,,,,

\$\$ THIS TABLE TAKES CARE OF MISCIBILITY GAP OF L->L1+L2 TABLE 300 C-N @@,1 CH P LIQUID, LIQ#2=FIX 1 S-C P=P0 X(LIQ,NA)=@2EXPERIMENT T=@1:1% X(LIQ#2,NA)=@3:1% LABEL ALL3 \$SET-ALL-START 1124.64,,,,, TABLE VALUE 1040.314 0.265588 0.949383 1088.075 0.30135 0.938979 1124.64 0.291363 0.933351 1139.568 0.339729 0.926837 1189.568 0.380722 0.914692 1250.77 0.431797 0.897831 1286.58 0.462701 0.883432 1335.09 0.507177 0.862575 1376.89 0.606208 0.842271 1385.835 0.55862 0.836495 1433.595 0.61616 0.80083 TABLE\_END

SAVE

#### The Li-K system

\$\$ POP FILE FOE LI-K BINARY SYSTEM E-SYM CON P0=1E5 R0=8.314

\$\$ MONOTECTIC REACTION WILL TAKE PLACE IN THIS POINT

\$\$ LIQUID1--->BCC#1(LI)+LIQUID2 TABLE 100 C-N @@,1 CH P LIQ,LIQ#2,BCC=F 1 S-C P=P0 EXPERIMENT T=@1:1% EXPERIMENT X(BCC#1,K)=@2:1% LABEL ALL1 TABLE\_VALUE 454.75 1.00 TABLE\_END

#### \$\$ THIS TABLE TAKE CARE OF LIQUIDUS LINE

**TABLE 200** C-N @@,1 CH P LIQUID, LIQUID#2=F 1 S-C X(LIQUID,K)=@1 P=P0 EXPERIMENT T=@2:0.001 EXPERIMENT X(LIQUID#2,K)=0.999:1% LABEL ALL2 TABLE VALUE 0.000566219 668.7979026 0.000225359 599.401797 0.000203508 610.9743207 0.000139616 563.3675861 0.000123004 564.8760097 8.96389E-05 565.0771048 7.82787E-05 515.5011186 3.41069E-05 467.2766184 3.00503E-05 468.3138827 2.61435E-05 469.3601682 2.24542E-05 472.4111867 TABLE END

TABLE 300 C-N @@.1 CH P LIQUID,LIQUID#2=F 1 S-C X(LIQUID#2,K)=@1 P=P0 EXPERIMENT T=@2:0.001 EXPERIMENT X(LIQUID,K)=0.00:1% LABEL ALL3 TABLE VALUE 0.95671613 799.7824592 0.945952216 705.8308688 0.964740059 715.3382835 0.978980566 670.6503296 0.987199566 610.4558885 0.99331722 565.962986 0.993701588 516.2009674 0.997416255 470.8430445 TABLE\_END

\$\$ EUTECTIC REACTION WILL TAKE PLACE IN THIS POINT \$\$ LIQUID2--->BCC(LI)+BCC(K) TABLE 400 C-N @@,1 CH P LIQUID#2,BCC,BCC#2=F 1 S-C P=P0 EXPERIMENT X(LIQ,K)=@2:1%, T=@1:1 LABEL ALL4 TABLE\_VALUE 336.7 0 TABLE\_END

TABLE 500 C-N @@,1 CH P LIQUID#2,BCC#1=F 1 S-C X(BCC#1,K)=@1 P=P0 EXPERIMENT T=@2:0.001 LABEL ALL5 TABLE VALUE 1.58006E-05 445.1983136 1.15162E-05 445.3232156 6.53692E-06 419.5528406 6.64207E-06 394.3171019 3.08056E-06 371.5400334 1.13957E-06 342.6664245 343.238039 9.42512E-07 TABLE END

SAVE

### The K-Na system

E-SYM CON P0=1E5 R0=8.314

\$\$ SOLIDUS K LINE TABLE 100 C-N @@,1 CH P LIQ BCC=F 1 S-C X(BCC,NA)=@2, P=P0 EXPERIMENT X(LIQ,NA)<0.5:1e-2 EXPERIMENT T=@1:1% S-S-V X(BCC,NA)=0.01 LABEL ALL1 TABLE\_VALUE 334.88 0.0017 333.19 0.0035 331.31 0.0056 326.80 0.0102 315.50 0.0210 303.71 0.0311 289.4 0.0400 283.4 0.0432 TABLE\_END

TABLE\_END

**\$\$** LIQUIDUS K LINE TABLE 200 C-N @@,1 CH P LIQ BCC=F 1 S-C X(LIQ,NA)=@2, P=P0 EXPERIMENT T=@1:1% EXPERIMENT X(BCC,NA)<@2:1E-2 S-S-V X(BCC,NA)=0.01 LABEL ALL2 TABLE VALUE 323.40 .0500 312.52 .0893 301.80.1325 297.30 .1501 291.35 .1747 285.93 .1980 279.01 .2284 271.32 .2648 265.57 .2952 264.60.3000 263.42.3050 261.31.3150

\$\$ LIQUIDUS, TWO PHASE EQUILBRIUM OF L+KNA2 TABLE 300 C-N @@,1 CH P LIQ KNA2=F 1 S-C X(LIQ,NA)=@2, P=P0 EXPERIMENT T=@1:1% LABEL ALL3 TABLE\_VALUE 264.28 .3501 269.62 .4033 273.50 .4517 276.56 .5006 278.76 .5505 280.09 .5992 TABLE END

\$\$ LIQUIDUS NA LINE TABLE 400 C-N @@,1 CH P LIQ BCC=F 1 S-C X(LIQ,NA)=@2, P=P0 EXPERIMENT T=@1:1%

EXPERIMENT X(BCC,NA)>0.90:1E-2 S-S-V X(BCC,NA)=0.99 LABEL ALL4 TABLE VALUE 283.12 .6142 285.51 .6285 288.04 .6428 292.43 .6698 296.75 .6952 300.30.7167 303.19.7334 309.09 .7649 315.65.7898 324.95 .8428 339.00 .9002 352.61.9470 366.64 .9880 371.05 1.000 TABLE\_END **\$\$ SOLIDUS NA LINE** TABLE 500 C-N @@,1 CH P LIQ BCC=F 1 S-C X(BCC,NA)=@2, P=P0 EXPERIMENT X(LIQ,NA)>0.5:1e-2 EXPERIMENT T=@1:1% S-S-V X(BCC,NA)=0.99 LABEL ALL5 TABLE\_VALUE 367.25 0.9988 364.98 0.9980 355.0 0.9950

**\$\$ EUTECTIC POINT AT K SIDE** 

344.8 0.9936 329.0 0.9927 TABLE\_END

TABLE 600 C-N @@,1 CH P LIQ,KNA2,BCC=F 1 S-C P=P0 EXPERIMENT T=260.53:0.05 EXPERIMENT X(BCC,NA)=@1:1%, X(LIQ,NA)=@2:1% LABEL ALL6 TABLE\_VALUE 0.046 0.319 TABLE\_END

\$\$ PERITECTIC POINT AT NA SIDE TABLE 700 C-N @@,1 CH P LIQ,KNA2,BCC=F 1 S-C P=P0 EXPERIMENT T=280.07:0.05 EXPERIMENT X(BCC,NA)=@1:1%, X(LIQ,NA)=@2:1% LABEL ALL7 TABLE\_VALUE 0.992 0.598 TABLE\_END

\$\$ ENTHALPY OF mixing in liquid **TABLE 800** C-N @@,1 CH P LIQ=F 1 S-R-S K LIQ,,,,, S-R-S NA LIQ,,,, S-C T=384 X(LIQ,NA)=@1 P=P0 EXPERIMENT HMR=@2:10% LABEL ALL8 TABLE\_VALUE 0.190 401.66 0.238 464.42 0.263 510.45 0.382 669.44 0.403 665.26 0.450 677.81 0.559 761.49 0.646 711.28 0.756 627.6 0.853 435.14 0.927 238.49 TABLE\_END \$\$ activity in liquid TABLE 900 C-N @@,1 CH P LIQ=F 1 S-R-S K LIQ,,,,, S-R-S NA LIQ,,,, S-C T=384 X(LIQ,NA)=@1 P=P0 EXPERIMENT ACR(K)=@2:10% \$\$ EXPERIMENT ACR(NA)=@3:10% LABEL ALL9 TABLE VALUE 0.125 0.928 0.263 0.182 0.887 0.328 0.32 0.764 0.517 0.594 0.578 0.694 0.654 0.527 0.748 0.826 0.359 0.856 TABLE\_END

\$\$ ENTHALPY OF mixing in BCC TABLE 10 C-N @@,1 CH P BCC=F 1 S-R-S K BCC,,,,, S-R-S NA BCC,,,,, S-C T=384 X(BCC,NA)=@1 P=P0 EXPERIMENT HMR=@2:10% LABEL ALL0 TABLE\_VALUE 0.25 1786.07 0.50 2993.89 0.75 2407.58 TABLE END

SAVE

## The K-Mg system

\$\$ POP FILE FOE K-MG BINARY SYSTEM E-SYM CON P0=1E5 R0=8.314

\$\$ MONOTECTIC REACTION WILL TAKE PLACE IN THIS POINT \$\$ LIQUID2--->HCP(MG)+LIQUID1 TABLE 100 C-N @@,1 CH P LIQ,LIQ#2,HCP=F 1 S-C P=P0 EXPERIMENT X(LIQUID,MG)=@2:5% X(HCP,MG)=@3:1% EXPERIMENT T=@1:1% LABEL ALL1 TABLE\_VALUE 923 0.0095 1.00 TABLE\_END

\$\$ THIS TABLE TAKE CARE OF LIQUIDUS LINE

TABLE 200 C-N @@,1 CH P LIQUID,LIQUID#2=F 1 S-C X(LIQUID,MG)=@1 P=P0 EXPERIMENT T=@2:1% EXPERIMENT X(LIQUID#2,MG)=0.999:1% LABEL ALL2 TABLE\_VALUE 0.01027510 979.493 TABLE\_END

\$\$ EUTECTIC REACTION WILL TAKE PLACE IN THIS POINT \$\$ LIQUID1--->BCC(K)+HCP(MG) TABLE 300 C-N @@,1 CH P LIQ,BCC,HCP=F 1 S-C P=P0 EXPERIMENT X(LIQ,MG)=@2:1%, T=@1:1 LABEL ALL3 TABLE\_VALUE 336.2 0.0002 TABLE\_END

\$\$ ENTHALPY OF mixing in liquid TABLE 400 C-N @@,1 CH P LIQ=F 1 S-R-S K LIQ,,,,, S-R-S MG LIQ,,,, S-C T=973 X(LIQ,MG)=@1 P=P0 EXPERIMENT ACR(K,liq)=@2:0.001 LABEL ALL4 TABLE\_VALUE 0.9998 0.116 0.9982 0.238 0.9972 0.311 0.9958 0.489 0.9953 0.522 0.9922 0.789 0.9920 0.800 0.9900 0.995 0.9500 0.996 0.9000 0.996 0.8000 0.995 0.998 0.2000 TABLE END

TABLE 500 C-N @@.1 CH P LIQUID, HCP=F 1 S-C X(LIQUID,MG)=@1 P=P0 EXPERIMENT T=@2:1% LABEL ALL5 TABLE VALUE 0.00110285 422.229 0.00469984 575.383 724.466 0.00521012 0.00774540 877.358 TABLE\_END

SAVE

#### The Li-Na system

#### \$\$ POP FILE FOE LI-NA BINARY SYSTEM E-SYM CON P0=1E5 R0=8.314

\$\$ INVARIANT POINT AT ABOUT 0.034% NA \$\$ MONOTECTIC REACTION WILL TAKE PLACE IN THIS POINT \$\$ LIQUID1--->BCC(LI)+LIQUID2 TABLE 100 C-N @@,1 CH P LIQ,LIQ#2,BCC=F 1 S-C P=P0 EXPERIMENT X(LIQ,NA)=@2:5% X(LIQ#2,NA)=@3:1% EXPERIMENT T=@1:1 LABEL ALL1 TABLE\_VALUE 443.75 0.03 0.899 TABLE\_END

#### \$\$ THIS TABLE TAKE CARE OF LIQUIDUS LINE

TABLE 200 C-N @@,1 CH P LIQ,LIQ#2=F 1 S-C T=@1 P=P0 EXPERIMENT X(liq,NA)=@2:1% LABEL ALL2 TABLE VALUE 462.916 0.0448221 463.585 0.0448249 481.66 0.0517057 488.35 0.0585374 500.396 0.0670928 511.1 0.0790438 525.82 0.0927128 533.844 0.106353 551.902 0.131941 562.587 0.1643 571.921 0.21196 574.58 0.23408 573.211 0.268088 575.859 0.302113 576.494 0.341231 TABLE\_END

TABLE 300 C-N @@,1 CH P LIQ,LIQ#2=F 1 S-C T=@1 P=P0 EXPERIMENT X(liq#2,NA)=@2:1%

LABEL ALL3 TABLE VALUE 576.494 0.341231 579.164 0.351447 574.429 0.405848 575.744 0.433065 574.364 0.478977 573.678 0.497682 571.666 0.501074 568.282 0.541876 564.907 0.572474 563.541 0.60308 552.776 0.660857 544.703 0.703339 533.282 0.745807 508.454 0.803523 462.194 0.866248 TABLE END

\$\$ INVARIANT POINT AT ABOUT 0.96% NA \$\$ EUTECTIC REACTION WILL TAKE PLACE IN THIS POINT \$\$ LIQUID2--->BCC(LI)+BCC(NA) TABLE 400 C-N @@,1 CH P LIQ#2,BCC,BCC#2=F 1 S-C P=P0 EXPERIMENT X(LIQ#2,NA)=@2:1%, T=@1:1 LABEL ALL4 TABLE\_VALUE 365.2 0.962 TABLE END

SAVE

### The Na-Mg system

### \$\$ POP FILE FOE Mg-NA BINARY SYSTEM E-SYM CON P0=1E5 R0=8.314

### \$\$ THIS TABLE TAKE CARE OF LIQUIDUS LINE

\$\$ INVARIANT POINT AT ABOUT 0.034% NA \$\$ MONOTECTIC REACTION WILL TAKE PLACE IN THIS POINT \$\$ LIQUID1--->HCP(Mg)+LIQUID2 TABLE 100 C-N @@,1 CH P LIQ,LIQ#2,hcp=F 1 S-C P=P0 EXPERIMENT T=@1:1, X(LIQ,NA)=@2:1% EXPERIMENT T=@1:1, X(LIQ,NA)=0.927:1% LABEL ALL1 TABLE\_VALUE 910 0.021 \$911.15 0.020 TABLE END

TABLE 200 C-N @@,1 CH P LIQ,LIQ#2=F 1 S-C X(LIQ,Na)=@1 P=P0 EXPERIMENT T=@2:1% LABEL ALL2 TABLE\_VALUE \$\$ These eperimenatl data come from Lan 0.0293963 972.74 TABLE\_END

TABLE 300 C-N @@,1 CH P LIQ,HCP=F 1 S-C X(liq,NA)=@1 P=P0 EXPERIMENT T=@2:1% LABEL ALL3 \$\$ These eperimenatl data come from Kle TABLE\_VALUE 0.994521 579.153 0.983256 678.699 0.970229 753.573 0.954707 829.325 0.944080 879.533 TABLE\_END

TABLE 400 C-N @@,1 CH P LIQ=F 1 S-C X(liq,NA)=@1 P=P0 T=973 SET\_REFERENCE\_STATE Na liq,,,, SET REFERENCE STATE Mg liq,,,, EXPERIMENT ACR(Na,liq)=@2:1% LABEL ALL4 TABLE VALUE \$\$ These eperimenatl data come from Lantratov ACR(Na,liq) \$ X(liq,Na) 0.005 0.123 0.010 0.248 0.012 0.450 0.020 0.800 0.027 0.963 0.050 0.985 0.100 0.989 0.200 0.990 0.300 0.994

0.400	0.995
0.500	0.995
0.600	0.995
0.700	0.992
0.800	0.992
0.900	0.992
0.950	0.992
0.990	0.990
1.000	1.000
TABL	E_END

TABLE 500 C-N @@,1 CH P LIQ=F 1 S-C X(liq,NA)=@1 P=P0 T=973 SET\_REFERENCE\_STATE Mg liq,,,, EXPERIMENT ACR(Mg,liq)=@2:1% LABEL ALL5 TABLE\_VALUE \$\$ These eperimenatl data come from Rosenkilde \$ X(liq,Na) ACR(Mg,liq) 0.100 0.972 0.200 0.970 0.300 0.971 0.400 0.967 0.500 0.974 0.600 0.970 0.700 0.968 0.800 0.980 0.900 0.970 TABLE\_END

\$\$ INVARIANT POINT AT ABOUT 0.034% NA \$\$ MONOTECTIC REACTION WILL TAKE PLACE IN THIS POINT \$\$ LIQUID2--->HCP(Mg)+BCC(NA) TABLE 700 C-N @@,1 CH P BCC,LIQ#2,HCP=F 1 S-C P=P0 EXPERIMENT T=@1:1 LABEL ALL7 TABLE\_VALUE 370.9 TABLE END

SAVE

## Appendix C

## EXPERIMENTAL MECHANICAL PROPERTIES DATA OF AL AND MG ALLOYS IN THE LITERATURE

# Al-Li alloys

## Al-2.3Li-Na(476 ppm)-K(15 ppm) Alloy

Temperature, K	Ultimate Tensile Strength (UTS), MPa
77	333
200	267
295	250

## **Al-Mg alloys**

## Al-5Mg-Na Alloys

Na content, ppm	Temperature, K	Reduction of Area, %
	306	74.51
	425	63.98
1.0	475	23.10
	526	6.46
1.8	577	5.48
	625	23.69
	677	73.21
	727	100.26
	306	78.30
	425	69.03
	475	31.43
1.3	526	6.97
	577	5.99
	625	26.47
	677	97.46
	306	77.54
F	425	89.74
	475	79.92
0.5	526	34.74
	577	30.73
	625	80.00
	677	99.98
0.1	306	78.05
	425	93.02
	475	91.78

	526	69.09
	577	79.72
	625	95.15
	677	100.23
0.01	306	76.79
	425	91.75
	475	93.05
	526	88.03
	577	91.09
	625	100.00
	677	100.00
	727	100.00

# Mg-Li alloys

## Mg-3.6Li-Na(160 ppm) Alloy

Strain Rate, in/min	Temperature, K	Reduction of Area,	Temperature, K	0.2 % Offset Yield
	•	%	•	Strength, MPa
-	76	24.24	75	27.32
	136	29.32	131	24.61
	190	32.37	191	17.17
0.05	255	32.37	254	11.01
	295	30.85	298	8.76
	363	24.75	363	8.59
	420	41.02	422	7.16
	74	28.81	75	28.18
	128	32.88	138	26.73
	191	37.46	189	21.46
10	253	40.51	252	15.30
10	293	42.54	295	12.19
	363	37.46	366	9.45
	420	30.34	422	8.02
	477	39.49	75	28.18
	74	30.34		
	142	35.42		
	171	37.46		
	202	41.52		
100	256	47.12		
	296	50.68		
	364	49.15		
	423	41.53		
	474	35.42		
	591	59.83		
19000	77	26.78		
	125	30.85		
	145	33.39		
	171	36.44		
	196	40.51		
	222	45.08		

197
253.7526944	51.6949	
293.9227222	60.339	
365.3266667	70	
475.7144444	67.4576	
590.9611111	50.678	

## Mg-5.8Li-Na(300 ppm) Alloy

Strain Rate, in/min	Temperature, K	Reduction of Area,	Temperature, K	0.2 % Offset Yield
		%		Strength, MPa
	75	34.14	76	23.14
	137	36.67	133	18.00
	193	36.67	193	13.29
0.05	254	35.66	253	10.71
0.05	299	30.10	296	10.29
	338	27.07	368	9.00
-	366	26.06	422	7.29
	423	47.27		
	78	38.18	76	24.43
	131	44.24	138	20.14
	190	48.28	193	15.00
	254	40.20	253	12.00
10	296	35.15	298	11.14
	364	29.09	367	10.29
	423	26.06	422	9.00
ŀ	465	32.63		
ŀ	481	43.23		
	72	39.19		
ŀ	142	46.77		
	170	49.29		
	198	51.82		
100	224	53.33		
100	288	47.78		
ŀ	366	36.16		
	451	28.59		
	515	32.62		
	549	37.17		
	78	37.68		
19000	126	41.71		
	140	43.2323		
	170.	51.8182		
	198	54.8485		
	229	59.3939		
	299	61.9192		
	366	59.899		
	479	54.3434		
	535	45.2525		
	593	30.101		
	647	30.6061		

Strain Rate, in/min	Temperature, K	Reduction of Area,	Temperature, K	0.2 % Offset Yield
		%		Strength, MPa
0.05	76	67.10	73	15.74
	134	55.93	130	11.06
	195	26.22	192	11.06
	253	19.80	252	11.06
	303	43.36	298	11.06
	376	72.57	367	5.96
	76	60.03	76	18.72
	132	54.70	135	12.34
	18	46.21	197	11.49
10	252	28.57	257	11.49
10	299	24.58	300	11.91
	342	32.54	365	11.06
	366	50.97		
	387	70.26		
	77	68.69		
	144	66.30		
	199	63.41		
100	227	60.02		
100	295	47.26		
	329	31.07		
	365	26.21		
	424	62.11		
19000	76	67.22		
	123	64.21		
	173	62.66		
	212	62.45		
	294	53.36		
	363	31.46		
ļ Ē	393	22.95		
ļ Ē	424	31.51		
	475	44.59		

# Multi-component Al and Mg alloys

#### Al-11.4Li-0.09Mn-Na Alloys 477.15K

Na Content, (at. ppm)	Elongation, %
0	1.6
7	0.8
53	0.9
564	0.1

### Mg-11.2Li-1.52Al-0.03Ca-0.018Na-0.002K Alloy

Temperature, K	Elongation, %
233	20.02
273	30.00
299	40.00
373	78.36
423	50.23
471	99.98

### Mg-11.4Li-1.59Al-0.02Ca-0.14Zr-0.015Si-0.018Na-0.002K Alloy

Temperature K	Elongation %
233	7.65
274	12.62
299	16.60
373	59.97
424	55.57
472	89.61

#### BIBLIOGRAPHY

- 1. D. E. J. Talbot and D. A. Granger, *JOM*, **47** (1995) 44-46.
- 2. K. Horikawa, S. Kuramoto and M. Kanno, *Light Met. Rev.*, 7 (2000) 18-23.
- 3. X. Li, X. Rao, D. Zhang and P. Si, *Transaction of Nonferrous Metals Society of China (English Edition)*, **10** (2000) 224-227.
- 4. J. E. Hatch, *Aluminum: Properties and Physical Metallurgy* (American Society for Metals, Metal Park, Ohio, 1984).
- R. Narayanan and Y. Sahai, *Metal Loss in Aluminium Alloys in Molten Salt Fluxes*. L. M. 1995, Ed. (Las Vegas, NV,USA, TMS, Warrendale, PA, USA, 1995).
- G. D. Parkes, *Mellor's Modern Inorganic Chemistry* (John Wiley and Sons Inc., 1967).
- C. Rosenkilde, L. H. Arnesen and O. Wallevik, *Journal of Phase Equilibria*, 21 (2000) 521-527.
- 8. Y. Zhong, M. Yang and Z. K. Liu, *Calphad*, **29** (2005) 303-311.
- Y. Zhong, K. Ozturk, J. O. Sofo and Z. K. Liu, J. Alloy. Compd., 420 (2006) 98-106.
- K. Ozturk, Y. Zhong, L. Q. Chen, C. Wolverton, J. O. Sofo and Z. K. Liu, *Metall. Trans. A*, 36A (2005) 5-13.
- 11. L. Kaufman and H. Bernstein, *Computer Calculation of Phase Diagram with Special Reference to Refractory Metals* (Academic Press, New York, 1970).

- 12. A. T. Dinsdale, *CALPHAD*, **15** (1991) 317-425.
- 13. O. Redlich and A. Kister, *Indust. Eng. Chem.*, 40 (1948) 345-350.
- M. Hillert, B. Jansson, B. Sundman and J. Agren, *Metall. Trans. A*, 16A (1985) 261-266.
- 15. B. Sundman, *CALPHAD*, **15** (1991) 109-119.
- 16. W. Kohn and L. Sham, J. Phys. Rev. A, 140 (1965) 1133.
- 17. D. W. Ceperley and B. J. Alder, *Phys.Rev.Lett.*, **45** (1980) 566.
- A. Zunger, S. H. Wei, L. G. Ferreira and J. E. Bernard, *Phys. Rev. Lett.*, 65 (1990)
   353-356.
- S. H. Wei, L. G. Ferreira, J. E. Bernard and A. Zunger, *Phys. Rev. B*, 42 (1990) 9622-9649.
- 20. K. C. Hass, L. C. Davis and A. Zunger, *Phys. Rev. B*, 42 (1990) 3757-3760.
- 21. Z. W. Lu, S. H. Wei and A. Zunger, *Phys. Rev. B*, 44 (1991) 3387-3390.
- 22. Z. W. Lu, S. H. Wei and A. Zunger, *Phys. Rev. B*, **45** (1992) 10314-10330.
- A. V. Ruban, S. I. Simak, S. Shallcross and H. L. Skriver, *Phys. Rev. B*, 67 (2003) 214302.
- 24. V. Ozolins, C. Wolverton and A. Zunger, *Phys. Rev. B*, **57** (1998) 6427-6443.
- 25. C. Wolverton, Acta Mater., 49 (2001) 3129-3142.
- A. V. Ruban, S. I. Simak, S. Shallcross and H. L. Skriver, *Phys. Rev. B*, 67 (2003) 214302.
- C. Jiang, C. Wolverton, J. Sofo, L. Q. Chen and Z. K. Liu, *Phys. Rev. B*, 69 (2004) 214202.
- 28. D. Shin, R. Arroyave, Z. K. Liu and v. d. Walle, *Phys. Rev. B*, (2006) in press.

- 29. C. Jiang, L. Q. Chen and Z. K. Liu, Acta Mater., 53 (2005) 2643-2652.
- 30. P. E. Blochl, *Phys. Rev. B*, **50** (1994) 17953.
- 31. G. Kresse and J. Joubert, *Phys. Rev. B*, **59** (1999) 1758.
- 32. G. Kresse and J. Furthmuller, *Phys. Rev. B*, **54** (1996) 11169-11186.
- 33. G. Kresse and J. Furthmuller, *Comput. Mater. Sci.*, **6** (1996) 15-50.
- J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J.
   Singh and C. Fiolhais, *Phys. Rev. B*, 46 (1992) 6671-6687.
- 35. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, **13** (1972) 5188.
- 36. L.-G. Liu, J. Phys. Chem. Solids, 47 (1986) 1067-1072.
- 37. E. Aruja and H. Perlitz, Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.,
  100 (1939) 195-200.
- R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley, Selected Values of Thermodynamic Properties of Metals and Alloys (Wiley, New York, 1963).
- 39. F. Laves and H. J. Wallbaum, Z. Anorg. Chem., 250 (1943) 110.
- J. Grobner, R. Schmid-Fetzer, A. Pisch, C. Colinet, V. V. Pavlyuk, G. S. Dmytriv,
  D. G. Kevorkov and O. I. Bodak, *Thermochim. Acta*, 389 (2002) 85-94.
- 41. I. Ansara, A. T. Dinsdale and M. H. Rand, COST 507: Thermochemical Database for Light Metal Alloys (European Commission, 1998), vol. 2.
- 42. D. P. Smith, Z. Anorg. Chem., 56 (1907) 109-142.
- 43. C. T. Heycock and F. H. Neville, J. Chem. Soc., 55 (1889) 666-676.
- 44. C. H. Mathewson, Z. Anorg. Chem, 48 (1906) 191-200.
- 45. E. Scheuer, Z. Metallkd., 27 (1935) 83-85.
- 46. J. L. Murray, Bull. Alloy Phase Diag., 4 (1983) 407-410.

- 47. W. L. Fink, L. A. Willey and H. C. Stumpf, *Trans. AIME*, **175** (1948) 364-371.
- 48. C. E. Ransley and H. Neufeld, J. Inst. Met., 78 (1950) 25-46.
- 49. S. G. Hansen, J. K. Tuset and G. M. Haarberg, *Metall. Trans. B*, **33B** (2002) 577-588.
- 50. K. Motzfeldt, Metall. Trans. B, 34B (2003) 744-746.
- 51. G. Kaptay, Metall. Trans. B, **35B** (2004) 393-398.
- 52. S. G. Hansen, J. K. Tuset and G. M. Haarberg, *Metall. Trans. B*, **34B** (2003) 746-748.
- 53. S. G. Hansen, J. K. Tuset and G. M. Haarberg, *Metall. Trans. B*, **35B** (2004) 398-400.
- 54. P. Fellner, M. Korenko and V. Danielik, Comments on the Solubility and Activity of Sodium in Molten Aluminium, G. M. Haarberg, Ed., The International Jomar Thonstad Symposium, Trondheim, Norway (2002), pp. 199-206.
- 55. P. Fellner, M. Korenko, V. Danielik and J. Thonstad, *Electrochimica Acta*, **49** (2004) 1505-1511.
- 56. S. G. Hansen, Personal Communication, (2004)
- 57. J. C. Mitchell and C. S. Samis, *Trans. TMS-AIME.*, **245** (1969) 1227-1234.
- 58. E. W. Dewing, Metall. Trans., 1 (1970) 1691-1694.
- 59. E. W. Dewing, Metall. Trans., 3 (1972) 495-501.
- 60. R. J. Brisley and D. J. Fray, *Metall. Trans. B.*, **14B** (1983) 435-440.
- 61. P. C. Yao and D. J. Fray, J. Appl. Electrochem, 15 (1985) 379-386.
- 62. M. Sun and S. Yang, J. Central-South Inst. Mining Metall., 23 (1992) 99-104.
- 63. A. A. Dubreuil and A. D. Pelton, *Light Met.*, (1985)

- 64. W. Klemm and D. Kunze, *London Chem. Soc.*, **22** (1967) 3-22.
- 65. J. Metzger, *Liebigs Annalen*, **355** (1907) 141-143.
- 66. R. Lorenz and R. Winzer, Z. Anorg.und Allg. Chem., 179 (1929) 281-286.
- 67. R. Lorenz and R. Winzer, Z. Anorg.und Allg. Chem., 181 (1929) 193-202.
- 68. E. Rinck, Compt. Rend., 192 (1931) 1378-1381.
- 69. A. D. Pelton, Bull. Alloy Phase Diag., 6 (1985) 35-37.
- 70. B. Bohm and W. Klemm, Z. Anorg. Chem., 243 (1939) 69-85.
- 71. L. E. Dotson and R. B. Hand, *The Mutual Solubilities Of Lithium and Potassium at 610F(321C) to 1230F(666C)*, Patent GESP-603-R-71-NSP-2, 1970
- 72. F. J. Smith, J. Less-Common Met., 35 (1974) 147-151.
- 73. M. A. Joannis, Ann. Chem. Phys., 12 (1887) 358-384.
- 74. N. S. Kurnakow and N. A. Puschin, Z. Anorg. Chem., 30 (1902) 109-112.
- 75. K. Bornemann, Metallurgie, 6 (1909) 239-243.
- 76. G. L. C. M. v. Rossen and H. v. Bleiswijk, Z. Anorg. Chem., 74 (1912) 152-156.
- 77. E. Janecke, Z. Metallk., 20 (1928) 113-117.
- 78. E. Rinck, Compt.Rend., 197 (1933) 49-51.
- J. B. Ott, J. R. Goates, D. R. Anderson and H. T. Hall, Jr., *Trans. Fara. Soc.*, 65 (1969) 2870-2878.
- D. K. C. MacDonald, W. B. Pearson and T. Towle, *Can. J. Phys.*, **34** (1956) 389-394.
- 81. L. Rimai and H. Bloembergen, J. Phys. Chem. Solids., 13 (1960) 257-270.
- 82. C. A. Krier, R. S. Craig and W. E. Wallace, J. Phys. Chem., 61 (1957) 522-529.

- Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corp., New York, 1936).
- 84. M. Kawakami, Sci. Rept. Tohoku Univ. First Ser., 16 (1927) 915-935.
- 85. R. L. McKisson and L. A. Bromley, J. Am. Chem. Soc., 73 (1951) 314-315.
- 86. T. Yokokawa and O. J. Kleppa, J. Chem. Phys., 40 (1964) 46-54.
- F. A. Cafasso, V. M. Khanna and H. M. Feder, Thermodynamic Properties and Ordering in Liquid NaK Alloys, Int. Conf. on the Props. of Liquid Metals (1966), pp. 535-543.
- 88. D. N. Kagan, Teplofiz. Vys. Temp., 26 (1988) 478-491.
- 89. E. P. Lokshin and O. S. Ignatov, *Teplofiz. Vys. Temp.*, 9 (1971) 94-98.
- 90. M. F. Lantratov, Zh. Prikl. Khim., 46 (1973) 1484-1587.
- 91. E. E. Shpil'rain, V. I. Shkermontov, S. N. Skovorod'ko and A. G. Mozgovoi, *High Temperature*, **40** (2002) 33-43.
- 92. H. K. Schurmann and R. D. Parks, *Phy. Rev. Lett.*, **27** (1971) 1790-1793.
- M. G. Feistma, J. J. Hallers, F. V. D. Werff and W. V. Lugt, *Pysica B*, **79** (1975) 35-52.
- M. G. Down, P. Hubberstey and R. J. Pulman, J. Chem. Soc. Dalton Trans., 14 (1975) 1490-1492.
- 95. M. G. Down, P. Hubberstey and R. J. Pulman, *JCS Faraday I*, **71** (1975) 1387-1391.
- 96. H. Endo, H. Hoshino, K. Tamura and M. Mushiage, *Solid State Sci.*, **32** (1979)
   1243-1246.

- 97. F. A. Kandan, R. C. Faxon and D. V. Keller, *Phys. and Chem. of Liquids*, 1 (1968) 61-73.
- 98. E. S. Wu and Brumberger, *Phy. Lett. A*, **53** (1975) 475-477.
- 99. C. W. Bale, Bull. Alloy Phase Diag., 10 (1989) 265-268.
- 100. A. D. Pelton, Z. Metallkd., 84 (1993) 767-772.
- 101. M. F. Lantratov, J. Appl. Chem. USSR., 46 (1973) 2107-2110.
- 102. A. D. Pelton, Bull. Alloy Phase Diag., 5 (1984) 454-456.
- 103. J. O. Andersson, T. Helander, L. H. Hoglund, P. F. Shi and B. Sundman, *CALPHAD*, **26** (2002) 273-312.
- 104. E. W. Dewing, Metall. Trans. B, 21B (1990) 285-294.
- 105. W. H. Howland and L. F. Epstein, Advan. Chem. Ser., 19 (1957) 34-41.
- 106. O. N. Salmon and D. H. Ahmann, J. Phy. Chem., 60 (1956) 13-16.
- 107. R. J. M. Payne and J. D. L. Eynon, Patent 787665, 1957
- Y. M. Vaynblat, B. A. Kopeliovich and Y. G. Gol'der, *Phys. Metal. Metall.*, 42 (1976) 105-112.
- Y. M. Vaynblat, B. A. Kopeliovich and Y. G. Gol'der, *Fiz. Metalloved.*, 42 (1976) 1021-1028.
- 110. A. K. Vasudevan, A. C. Miller and M. M. Kersker, Proceeding of the Second International Aluminum-Lithium Conference (AIME, 1984), pp. 181-199.
- D. Webster, Proceeding of the Third International Aluminum-Lithium Conference, London (Institute of Metals, 1986), pp. 602-609.
- 112. D. Webster, Metall. Trans. A, 18A (1987) 2181-2193.
- 113. D. Webster, Adv. Mater. Process., 145 (1994) 18-24.

- 114. E. D. Sweet, S. P. Lynch, C. G. Bennett, R. B. Nethercott and I. Musulin, *Metall. Trans. A*, **27A** (1996) 3530-3541.
- 115. S. Zhang, Q. Han and Z.-K. Liu, J. Alloy. Compd., 419 (2006) 91-97.
- 116. J. W. Taylor, J. Inst. Met., 86 (1957-1958) 456-458.
- 117. S. I. Tomkeieff, Nature, 155 (1945) 24.
- 118. C. E. Ransley and D. E. J. Talbot, J. Inst. Met., 88 (1959) 150-158.
- 119. M. Otsuka and R. Horiuchi, J. Jpn Inst. Met., 48 (1981) 688-693.
- 120. H. Okada and M. Kanno, Scr. Mater., 37 (1997) 781-786.
- 121. K. Horikawa, S. Kuramoto and M. Kanno, Acta Materialia, 49 (2001) 3981-3989.
- 122. S. P. Lynch, Scr. Mater., 47 (2002) 125-129.
- 123. K. Horikawa, S. Kuramoto and M. Kanno, Scr. Mater., 47 (2002) 131-135.
- 124. R. J. M. Payne and J. D. L. Eynon, J. Inst. Met., 86 (1957-1958) 351-352.
- 125. P. D. Frost, J. H. Jackson, A. C. Loonam and C. H. Lorig, *JOM*, **188** (1950) 1171-1172.
- 126. M. W. Toaz and E. J. Ripling, J. Inst. Met., 85 (1956-1957) 137-144.
- 127. R. K. Singh, J. Mater. Sci. Let., 13 (1994) 744-745.
- 128. A. K. Vasudevan, A. C. Miller and M. M. Kersker, E. A. Starke Jr, T. H. Sanders, Eds., Proceedings of the Second International Alimunum-Lithium Conference (AIME, 1984), pp. 181-199.

### VITA

### Shengjun Zhang

Shengjun Zhang was born on October 11<sup>th</sup>, 1977 in Yueyang city, Hunan province, China, a beautiful place rich in fish and rice. After graduating with honors in 1995 from the No. one middle school, he began his collegiate career in Beijing, China, enrolling at University of Science and Technology Beijing where he obtained a B.S. degree in Metallurgical Engineering in 1999 and a M.S. degree in Physical Chemistry of Metallurgy in 2002. He then joined the Pennsylvania State University, University Park, PA, to pursue his Ph.D. degree in Materials Science and Engineering. From June 2004 to June 2006, he worked in Oak Ridge National Laboratory. Listed below are his publications during his Ph.D. study:

- 1. <u>Shengjun Zhang</u>, Dongwon Shin and Zi-Kui Liu. *Thermodynamic modeling of the Ca-Li-Na system*, CALPHAD, Vol.27, 2003, 235-241.
- <u>Shengjun Zhang</u>, Carl Brubaker, Chao Jiang, Mei Yang, Yu Zhong, Qingyou Han and Zi-Kui Liu. *A combined first-principles calculations and thermodynamic modeling of the F-K-Na system*, Mater. Sci. Eng. A, Vol.418, 2006, 161-171.
- 3. <u>Shengjun Zhang</u>, Qingyou Han and Zi-Kui Liu. *Thermodynamic modeling of the Al-Mg-Na system*, J. Alloy. Compd., Vol.419, 2006, 91-97.
- 4. H. Xu, L. D. Xu, <u>S. J. Zhang</u>, and Q. Han. *Effect of the composition on the grain refinement of aluminum alloys*. Scrip. Mater., Vol.54, 2006, 2191-2196.
- 5. <u>Shengjun Zhang</u>, Qingyou Han and Zi-Kui Liu. *Fundamental understanding of Na-induced high temperature embrittlement in Al-Mg alloys*, Philo. Mag., in press.