Phase Diagrams of α -Phase Al-Li System

α 相Al-Li固溶体相の状態図

Toshinobu Soma*, Hiroko Kagaya*, Masaru Sato*, Mayumi Takaya*
相馬俊信、加賀屋弘子、佐藤 勝、高谷真弓

By taking into account the contributions of the band and local mode frequencies, the temperature- and pressure-dependent mean-square displacement in Al-Li solid solution was quantitatively calculated. Next, the concentration-dependence of the Debye temperature at higher and lower temperatures is estimated. The Debye temperature decreases with increasing the solubility of Li at low temperatures, while it increases at higher temperatures. Then, the compression effect on the solidus curves in the α -phase Al-Li solid solution is expressed by applying Lindeman's melting law to the alloy systems, and an increase of solubility exceeding 20 at. % Li in Al is predicted under pressure.

[Keywords: α -phase Al-Li alloy, Debye temperature, phase diagrams]

Al-Li固溶体中の原子の平均2乗変位の温度並びに圧縮依存性がバンド及び局所モード振動数の寄与を考慮することにより定量的に求められた。更に高温並びに低温領域でのデバイ温度の原子濃度依存性が算出され、低温部でのデバイ温度はLiの添加と伴に減少するが、高温部でのデバイ温度は逆に増加する。最後にリンデマンの融解則を本合金系に適用することにより α 相Al-Li固溶体の固相線への圧縮効果が求められ、圧縮下でAlへのLiの固溶度は原子濃度20%を上回ることが予測された。

1. INTRODUCTION

By rapid quenching from a liquid state under pressure, an increase of solubility limit of Si and Ge in Al has been observed [1-3]. Previously, we have calculated the solid solubility of Si and Ge [4] and Li [5] in Al under pressure by using the microscopic electron theory based on the pseudopotentials and the virtual crystal approximation. We [5] have predicted an increase of the solubility limit of Li in Al under pressure in the same manner as that of Si and Ge in Al. Then, we [6] have brought the simplified treatment where, as like those in pure Al, f.c.c. Li crystals, we considered apparently the lattice vibrations of Al, Li atoms in the solid solution with the equilibrium lattice constant and the electron density of the solid solution with f.c.c. phase. In the present work, taking into account the contributions of the band and local mode frequencies [6], we calculate the concentration- and pressure-dependent mean-square displacement in Al-Li solid solution. Next, the concentration-dependence of the Debye temperature at higher and lower temperatures is

calculated for Al-Li solid solution. Last, by applying Lindeman's melting law to the Al-Li alloy system in much the same way as Al-Si, Al-Ge alloy systems [7], we study the compression effect on the solidus curves of Al-Li alloy system.

2. MEAN-SQUARE DISPLACEMENT AND DEBYE TEMPERATURE

Taking into account the band and local mode frequencies $\nu_i^j(q, x)$ with the branch i , the wave vector q and concentration x of Li fixed [6] in the α -phase $\text{Al}_{1-x}\text{Li}_x$ solid solution, the mean-square displacement $\langle u^2 \rangle_x$ for this alloy system is given [7] by

$$\langle u^2 \rangle_x = (1-x) \frac{h}{NM^{\text{Al}}} U^{\text{Al}}(x) + x \frac{h}{NM^{\text{Li}}} U^{\text{Li}}(x) \quad (1)$$

where h , N , M are Planck's constant, Avogadro's number, atomic mass, respectively. Then, the contributions $U^j(x)$ with $j=\text{Al, Li}$ of the band and local mode.

$$U^j(x) = \sum_{i,q} \frac{1}{\nu_i^j(q, x)} \left[\frac{1}{\exp \{ h \nu_i^j(q, x) / kT \} - 1} + \frac{1}{2} \right] \quad (2)$$

where k is Boltzmann's constant. Using (1) and (2), we show the temperature dependence of the mean-square displacement $\langle u^2 \rangle$ under pressure for the

* Dept. of Computer Science and Engineering, Faculty of Engineering and Resource Science, Akita University, 1-1 Tegata Gakuen-machi, Akita 010-8502. FAX: 010-837-5788 秋田大学工学資源学部情報工学科, 〒010-8502 秋田市市形学園町 1-1.

$\text{Al}_{0.9}\text{Li}_{0.1}$ solid solution in Fig. 1. In this figure and what follows, the results calculated with Vashishta-Singwi screening function [4] are given, and our obtained mean-square displacement $\langle u^2 \rangle_x$ has a calculated accuracy $\langle u^2 \rangle_x \leq 10^{-20} \text{cm}^2$ at $T=0$ and $\leq 2 \times 10^{-19} \text{cm}^2$ at high temperatures which corresponds to variable interval of the calculated data due to other screening functions [4]. From Fig. 1, we see that the mean-square displacement for Al-Li alloy system decreases under pressure and its characteristic is similar to those for Al-Si and Al-Ge alloy systems [7].

In Debye's model, the mean-square displacement $\langle u^2 \rangle$ is related to the Debye temperature θ_D given (for example, see [8]) by

$$\langle u^2 \rangle = \frac{9\hbar^2 T}{Mk\theta_D^2} \quad \text{for } T > \theta_D \quad (3)$$

or

$$\langle u^2 \rangle = \frac{9\hbar^2}{4Mk\theta_D} \quad \text{for } T \ll \theta_D \quad (4)$$

Applying (3) and (4) to the Al-Li alloy system, we can estimate the Debye temperatures θ_D^{ht} and θ_D^{lt} at higher and lower temperatures, respectively. We obtained the concentration x -dependence of the Debye temperature θ_D^{ht} at the representative temperature 870K for the $\text{Al}_{1-x}\text{Li}_x$ solid solution, and θ_D^{lt} at the absolute zero as shown in Figs. 2 and 3, respectively. The Debye temperatures θ_D^{ht} and θ_D^{lt} in Figs. 2 and 3 have a calculated accuracy $|\Delta\theta_D|$ less than 4K. The relative change of the Debye temperature $\Delta\theta_D(x) = \theta_D(x) - \theta_D(x=0)$ from that for matrix Al

Fig.1 The calculated mean-square displacement $\langle u^2 \rangle$ under pressure versus temperature for $\text{Al}_{0.9}\text{Li}_{0.1}$ alloy.

have a reduced accuracy $|\Delta\theta_D| \leq 1.5\text{K}$. From Figs. 2 and 3, we see that the Debye temperature decreases with the solubility of Li i.e., the increase of x , at low temperatures, but increases at high temperatures. The concentration-dependence of θ_D^{lt} in Fig. 3 is consistent with those [6] from the specific heat and from the average elastic velocity.

Fig.2 The calculated Debye temperature θ_D^{ht} at 870K versus atomic fraction for $\text{Al}_{1-x}\text{Li}_x$ alloy.

Fig. 3 The calculated Debye temperature θ_D^{lt} at absolute zero K versus atomic fraction for $\text{Al}_{1-x}\text{Li}_x$ alloy. The open circle for matrix Al shows the experimental data [9]. The chain and dashed curves are the calculated those from the specific heat and from the average elastic velocity [6].

3. PHASE-DIAGRAMS UNDER PRESSURE OF α -PHASE AL-LI SYSTEM

Taking into account the pressure-dependence of the mean-square displacement $\langle u^2 \rangle_x$ in (1), (2) and the nearest-neighbor distance $R_1(x)$ for the α -phase $\text{Al}_{1-x}\text{Li}_x$ solid solution at a criterion for melting $X_m(x)$ to be constant, we can estimate the compression effect on the solidus curve for this alloy by satisfying the following relation [7]

$$X_m(x) = 2\sqrt{\langle u^2 \rangle_x} T_m(x, P) / R_1(x, P) \quad (5)$$

and

$$R_1(x, P) = \left\{ \frac{\Omega(x, P)}{\Omega_0(x)} \right\}^{1/3} R_1(x, \Omega_0) \quad (6)$$

where the conversion from the pressure $P(x)$ to the compressed volume $\Omega(x)$ is done with the help of the pressure-volume relation [5]. We show the obtained solidus curve for the $\text{Al}_{1-x}\text{Li}_x$ alloy system under pressure is calculated, as shown in Fig. 4. Our resultant solidus curve in Fig. 4 have a calculated accuracy $|\Delta x| \leq 0.01$ and $|\Delta T| \leq 5\text{K}$.

Fig. 4 The solidus curves under pressures of $P=0, 3, 5$ and 10 GPa for the α -phase $\text{Al}_{1-x}\text{Li}_x$ systems. The phase boundaries between α -phase solid solution (SS) and phase mixture (PM) under pressure are those previously calculated [5]. The dashed curves correspond to the observed data under $P=0\text{ GPa}$ [1].

4. CONCLUSIONS

We present the phase diagrams under pressure for the α -phase Al-Li alloy system based on the microscopic electronic theory. From Fig. 4, we see that the α -phase solid solution in Al-Li system is extended under pressure in the same manner as those in Al-Si and Al-Ge alloy systems [7]. And we hope that there will be further experimental researches in the mechanical and thermal properties of Al-based alloy systems.

ACKNOWLEDGEMENTS

The authors would like to thank Mr. S. Nito for his help in performing the preliminary calculations. The numerical calculations were carried out with ACOS 3900 operating system in the Computer Center of Tohoku University.

REFERENCES

- [1] M. Hansen; "Constitution of Binary Alloys", (McGraw-Hill, New York, 1958).
- [2] H. Mii, M. Senoo, I. Fujishiro; Japan J. Appl. Phys., **15**(1976)777.
- [3] V. F. Degtyareva, G. V. Chipenko, I. T. Belash, O. I. Barkalov, E. G. Ponyatovskii; Phys. Stat. Sol. (a), **89**(1985)K127.
- [4] T. Soma, Y. Funayama, H.-Matsuo Kagaya; J. Mater. Sci., **25**(1990)3917.
- [5] T. Soma, H. Kagaya, M. Sato; Jpn. J. Thermophys. Prop., **11**(1997)141.
- [6] T. Soma, H. Kagaya, S. Nito, M. Sato; Jpn. J. Thermophys. Prop., **13**(1999)13.
- [7] H.-Matsuo Kagaya, K. Imazawa, M. Sato, T. Soma; J. Mater. Sci., **33**(1998)2595.
- [8] J. M. Ziman; "Principles of the Theory of Solids", 2nd ed. Chap. 2 (Cambridge University Press, 1976).
- [9] C. Kittel; "Introduction to Solid State Physics", 6th ed. Chap. 5 (Wiley, New York, 1986).

[Received Nov. 17, 2000, Accepted Feb. 19, 2001]