

Thermodynamic calculation of partial phase diagram of Al-Si alloy at high pressure

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Generally phase diagrams represent the relationship between temperature and composition under atmospheric pressure. However, the effect of pressure on the phase diagram is less well understood. In particular, metastable phases may occur at high pressures. Most often these phases are detected by experimental examination. Theoretical prediction of metastable phases appearing under conditions of high pressure is, at best, difficult.

Efforts towards determination of the phase diagram of Al-Si binary alloy at normal pressure are abundant and fruitful [1]; this alloy is of interest due to its ample applications in industry. In addition, rapid quenching processes were applied to achieve supersaturation in Al-Si alloys. The silicon contents of these metastable solid solutions were increased significantly from a maximum of 1.59 at % at equilibrium conditions to 11 at % [2, 3]. Subsequently, followed by an ageing treatment, very fine silicon precipitations possibly contribute to a dispersion-strengthened alloy [2]. Furthermore, a pressure effect on the solubility of Si in Al was studied experimentally [4]. They found that the solubility limit was extended beyond 15 at % at 5.4 MPa in comparison with 1.59 at % at atmospheric pressure. A thermodynamic analysis of high-pressure phase equilibria was also conducted [5]. Similar conclusions were drawn about the significant increases of Si solubility due to pressure. Their approach was based on the approximation of regular solutions and the independence of volume, energy and entropy on temperature, pressure and composition. The latter, which neglects thermal expansion and compressibility, may be inadequate.

Also, research by the author on the high-pressure effect in solidifying an Al-Si alloy revealed the potential importance of the rapid pressure solidification process over the more conventional quenching method [6]. The pressure effects on microstructures of the test alloy were found to be significant, whereas mechanical properties such as the yield strength and hardness showed only minor differences in samples solidified under atmospheric and pressurized conditions. This may be due to the competing effects of the dendritic and eutectic phases in the resultant structure [6].

In this study a partial phase diagram of Al-Si alloy at 0.69 MPa (10^5 lb in⁻²) was predicted on the basis of the Clapeyron equation and method of resolution into simple diagrams.

In general, the condition for the coexistence of

several phases is that the chemical potential of any species, i , is the same in all phases:

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots$$

For a three-dimensional phase diagram the slope of the fusion boundary in the pressure-temperature plane will be determined by the Clapeyron equation. For fixed compositions the phase boundary depends on the enthalpy change, volume change and temperature only. The thermodynamic data available are limited to a few specific temperatures and pressures. However, for phases that are stable at atmospheric pressure it is possible to use the thermodynamic data at atmospheric pressure to extrapolate approximate values of the free energies at high pressure.

The problem of interpreting and/or predicting phase equilibria at high pressures involves the calculation of changes in molar (one-component system) or partial molar (multi component system) free energies with changing pressure, temperature and composition. To determine the slope of the phase boundary in the pressure-temperature plane, the Clapeyron equation was used [7]

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \quad (1)$$

where ΔH is the enthalpy change of the phase transformation, ΔV is the volume change of the same transformation, P is the equilibrium pressure and T is the equilibrium temperature. Once ΔH and ΔV are calculated, the temperature shift can be determined for a given pressure change. The volume change is determined by the component's composition and density at a given temperature (since compressibility is considered to be secondary and is neglected), whereas the enthalpy change is generally dependent on pressure as well as temperature.

For a closed system of fixed composition undergoing a temperature change from T_1 to T_2 at constant pressure P , the enthalpy change will be [7, 8]

$$\Delta H = H(T_2, P) - H(T_1, P) = \int_{T_1}^{T_2} C_p dT$$

where C_p is the heat capacity at constant pressure. If this closed system undergoes a change of pressure at a constant temperature, since

$$dH = \left. \frac{dH}{dP} \right|_T dP \quad \text{and} \quad dH = T dS + V dP$$

$$\left. \frac{dH}{dP} \right|_T = T \left. \frac{dS}{dP} \right|_T + V$$

from Maxwell's relation

$$\left. \frac{dS}{dP} \right|_T = - \left. \frac{dV}{dT} \right|_P$$

$$\left. \frac{dH}{dP} \right|_T = -T \left. \frac{dV}{dT} \right|_P + V$$

$$= -T\alpha V + V$$

$$= V(1 - \alpha T)$$

where α is the isobaric coefficient of thermal expansion. That is,

$$\Delta H = H(P_2, T) - H(P_1, T) = \int_{P_1}^{P_2} V(1 - \alpha T) dP$$

Therefore, for a closed system of fixed composition undergoing both temperature and pressure change

$$\Delta H = H(P_2, T_2) - H(P_1, T_1) = \int_{T_1}^{T_2} C_P dT$$

$$+ \int_{P_1}^{P_2} V(1 - \alpha T) dP$$

Thus, the T - P diagram can be calculated (see Equation 1) if the specific heat, volume and compressibility data are available for each phase. Unfortunately, the equations of state for most materials in the liquid and solid phase are unknown. The development of these equations is still in progress by empirical or theoretical methods.

The following assumptions are adopted in this study to obtain a first-order approximation of the pressure effect on the phase diagram. First, equilibrium phases at atmospheric pressure are stable at high pressures. Secondly, thermodynamic data obtained at atmospheric pressure can be applied to high pressures, ignoring the pressure dependence as a second-order effect. The procedure used is as follows. First, treat each phase line separately (see Fig. 1). Calculate the enthalpy change of the phase transformation, ΔH , based on the phase data at atmospheric pressure. Secondly, estimate the temperature shift using the Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

Assuming ΔH and ΔV are independent of pressure,

$$\frac{\Delta V}{\Delta H} \int_{P_1}^{P_2} dP = \int_{T_1}^{T_2} \frac{dT}{T}$$

i.e.

$$\frac{\Delta V}{\Delta H} (P_2 - P_1) = \ln\left(\frac{T_2}{T_1}\right) \quad (2)$$

and

$$\Delta T = T_2 - T_1.$$

In summary, the enthalpy and volume changes are calculated first. Then for a given pressure increase

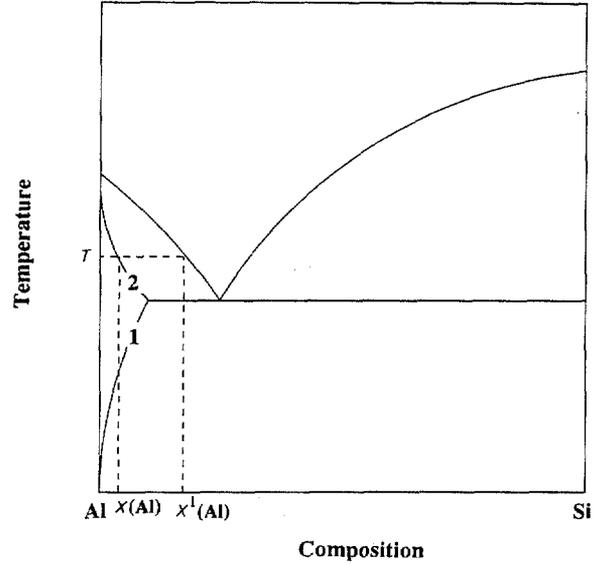


Figure 1 Schematic representation of Al-Si phase diagram.

the temperature shift is determined from Equation 2. In this manner, new phase diagrams at high pressures are constructed. Two phase boundaries (lines 1 and 2 in Fig. 1) have been analysed to determine the effect of high pressure on their position.

The Al-rich solvus line (line 1) represents the equilibrium between pure Si and dilute solid solution α . The dilute solution α was assumed to follow Henry's law [7]. Therefore, $\Delta H(\text{Si})$ can be determined from a plot of $\ln X$ versus $1/T$, and shown to be $60\,000 \text{ J mol}^{-1}$. The detailed calculation is given in Appendix A.

The Al-rich solidus line (line 2) is the equilibrium between liquid solution (liquidus line) and dilute solid solution (solidus line). It is assumed that the solution is regular and follows Raoult's law (for dilute solution, solvent follows Raoult's law [7]). The enthalpy change is calculated to be $-10\,550 \text{ J mol}^{-1}$ as shown in Appendix A.

After the determinations of the enthalpy changes of lines 1 and 2 and the volume changes of each phase transformation, the results were plugged into Equation 2 to compute the new position of the phase boundaries. A pressure of 0.69 MPa (10^5 lb in^{-3}) was analysed. The detailed calculations of volume changes and temperature shifts are given in Appendix B. Based on the above calculations, a partial phase diagram of the Al-Si alloy under 0.69 MPa (10^5 lb in^{-3}) was generated (Fig. 2). For phase line 1 the temperatures are shifted down by 15°C , whereas the temperatures of line 2 are raised by 50°C .

In the above discussions, a partial high-pressure phase diagram of Al-Si alloy was generated by calculating the temperature shift caused by pressure at constant compositions. Two significant conclusions can be observed from this phase diagram (Fig. 2). First, the maximum solubility limit of Si at the eutectic temperature is increased from 1.6 to 2.5 at % under 0.69 MPa pressure. This solubility extension is especially advantageous for a possible

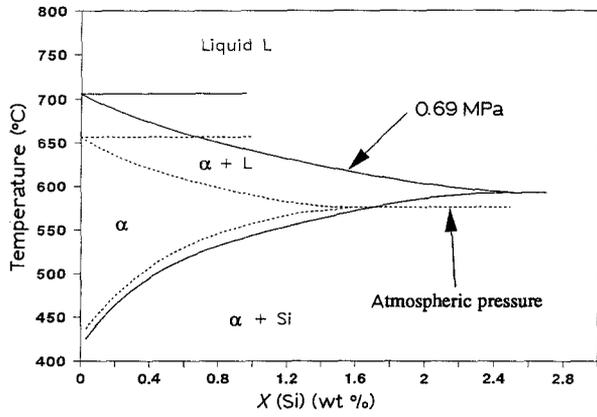


Figure 2 Predicted phase diagram of Al-Si alloy at 0.69 MPa.

dispersion-strengthened alloy (it is similar to the supersaturation by rapid quenching). Secondly, the eutectic temperature is increased from 577 to 591 °C under the same pressure. Compared with the predictions of Shinyaev *et al.* [5] of 3% solubility and 603 °C eutectic temperature at 1 MPa pressure, the current results appear reasonable.

Appendix A: Calculation of enthalpy changes

For line 1: pure Si to solid solution α

$$\text{Si}(s) = \text{Si}(X(\text{Si})_{\text{sat}}) \quad \Delta G = 0$$

where $X(\text{Si})_{\text{sat}}$ is the equilibrium saturation composition of Si in the solid solution

It is in equilibrium, so the chemical potential and activity are

$$\dot{\mu}(\text{Si}) = \mu(\text{Si}_{\text{sat}})$$

$$\dot{a}(\text{Si}) = a(\text{Si}_{\text{sat}})$$

since $\dot{a}(\text{Si}) = 1$ (pure solid Si), i.e. $a(\text{Si}_{\text{sat}}) = 1$, assume α solution is dilute (actually $X(\text{Si})_{\text{max}} = 0.0159$). Then it follows Henry's law

$$a(\text{Si}_{\text{sat}}) = 1 = \gamma(\text{Si})X(\text{Si})_{\text{sat}}$$

so the activity coefficient $\gamma(\text{Si}) = 1/X(\text{Si})_{\text{sat}}$.

But for the equilibrium case, $\Delta G = 0$. It is useless to calculate the enthalpy change. Let Si be transferred from the pure state to some arbitrary composition in α phase, say

$$X(\text{Si}) = 0.01 \text{ instead of to } X(\text{Si})_{\text{sat}}:$$

$$\text{Si}(s) = \text{Si}(X(\text{Si}) = 0.01) \quad \Delta G_1$$

$$\Delta G_1 = \mu(X(\text{Si})) - \dot{\mu}(\text{Si}) = RT \ln \left(\frac{a(X(\text{Si}))}{\dot{a}(\text{Si})} \right)$$

$\dot{a}(\text{Si}) = 1$ as before

$$a(X(\text{Si})) = \gamma(\text{Si}) \times 0.01 = \frac{0.01}{X(\text{Si})_{\text{sat}}}$$

so

$$\mu(X(\text{Si})) - \dot{\mu}(\text{Si}) = RT \ln 0.01 - RT \ln X(\text{Si})_{\text{sat}}$$

since

$$\frac{\partial(\mu(i)/T)}{\partial(1/T)} = H(i) \quad \text{Gibbs-Helmholtz equation}$$

$$\begin{aligned} \frac{\partial[\mu(X(\text{Si}))/T]}{\partial(1/T)} - \frac{\partial(\dot{\mu}(\text{Si}))/T}{\partial(1/T)} \\ = H(\text{Si}) - \dot{H}(\text{Si}) = \Delta H(\text{Si}) \end{aligned}$$

so

$$\frac{\partial[\ln X(\text{Si})_{\text{sat}}]}{\partial(1/T)} = -\frac{\Delta H(\text{Si})}{R}$$

where $\Delta H(\text{Si})$ is the enthalpy expended in transferring pure Si to the dilute solution α

A straight line is obtained by plotting $\ln X$ versus $1/T$, with a slope of $-\Delta H(\text{Si})/R$ as shown in Fig. A1. Therefore, $\Delta H(\text{Si})$ can be calculated from the slope measurement. Thus, the correspondent enthalpy change equals 60 000 J mol⁻¹.

For line 2, liquid solution to dilute solid solution α

$$\text{Al}(l) = \text{Al}(X(\text{Al}))$$

$$\mu(\text{Al}) - \mu'(\text{Al}) = RT \ln \left(\frac{a(\text{Al})}{a'(\text{Al})} \right)$$

where $a(\text{Al})$ and $a'(\text{Al})$ will be calculated in the following. It is reasonable to assume that the solution is regular and Al follows Raoult's law (for dilute solution, the solvent follows Raoult's law). So the activity can be derived [9] as

$$\begin{aligned} \ln a(T) &= -(T_0 - T_c)L_f/RTT_0 \\ &\quad + (T_c/T) \ln X' + (T - T_c)/T \ln X \\ \ln a'(T) &= (T - T_c)/T (\ln X - L_f/RT_0) \\ &\quad + T_c/T \ln X' \end{aligned} \quad (\text{A1})$$

where X , X' , a and a' are the molar fraction and activity at the liquidus and solidus compositions, respectively, at T_c (all quantities refer to solvent, see Fig. A2) and L_f is the heat of fusion of the pure solvent at its melting point T_0 .

Since $a(\text{Al}) = X(\text{Al})$ (Raoult's law),

$$\mu(\text{Al}) - \mu'(\text{Al}) = RT \ln [X(\text{Al})/a'(\text{Al})]$$

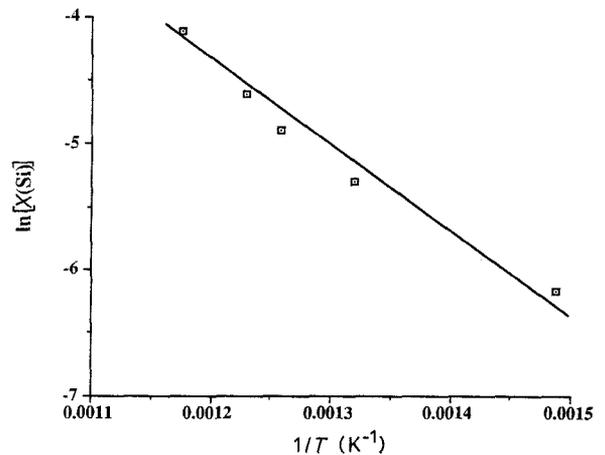


Figure A1 Plot of composition versus temperature for phase line 1.

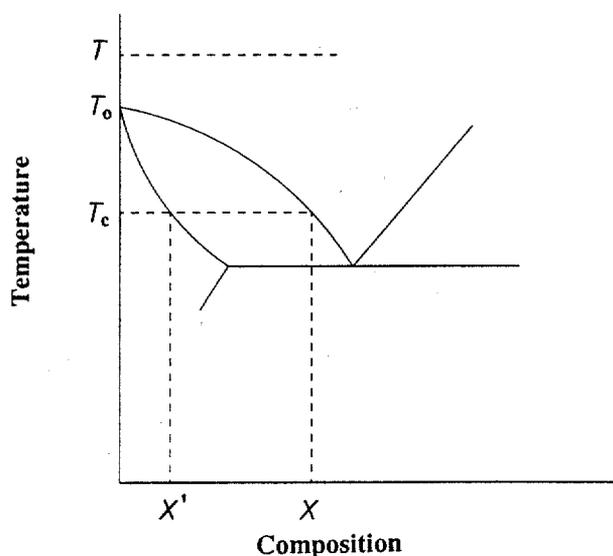


Figure A2 Schematic phase diagram of a binary system.

Similarly

$$\frac{\Delta H(\text{Al})}{R} = -\frac{\partial\{\ln[X(\text{Al})a^1(\text{Al})]\}}{\partial(1/T)}$$

from Equation A1

$$a^1(\text{Al}) = \exp[-(933 - T) \times 10500 / (8.3144 \times 933 \times T)] X(\text{Al})$$

Therefore, $-\Delta H(\text{Al})/R$ should be the slope of $\ln[X(\text{Al})/a^1(\text{Al})]$ versus $1/T$. Indeed, as shown in Fig. A3, a straight line is found with a slope of 1270 and $\Delta H(\text{Al})$ if found to be $-10550 \text{ J mol}^{-1}$. Compared with the enthalpy change of pure Al from solid

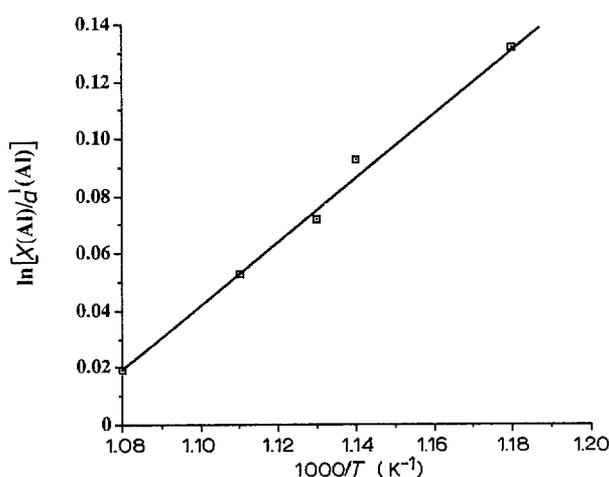


Figure A3 Plot of composition versus temperature for phase line 2.

TABLE BII Temperature shift of phase line 2

$T(\text{K})$	$X(\text{Al})$	$X_1(\text{Al})$	$V(\alpha)$ (ml mol^{-1})	$V(\text{l})$ (ml mol^{-1})	ΔV^a (ml mol^{-1})	$T_2(\text{K})$	$\Delta T(\text{K})$
920	0.998	0.979	10.54	11.33	-0.79	968.9	48.9
898	0.995	0.938	10.49	11.34	-0.84	948.9	50.9
886	0.992	0.921	10.49	11.35	-0.86	937.1	51.0
873	0.990	0.908	10.49	11.36	-0.86	923.6	50.6
850	0.984	0.883	10.48	11.37	-0.89	900.8	50.8

^a $\Delta V = V(\alpha) - V(\text{l})$.

to liquid as 10500 J mol^{-1} at its melting point 932 K, the above result agrees well.

Appendix B: Calculation of volume changes and temperature shifts by pressure

For line 1 pure Si to dilute solid solution α

$$\Delta V = 26.98/D_{\text{Al}}^s(T) - 28.09/D_{\text{Si}}^s(T)$$

where $D_{\text{Al}}^s(T)$ and $D_{\text{Si}}^s(T)$ are the densities of solid Al and Si at temperature T , respectively and 26.98 and 28.09 are the atomic weights of Al and Si, respectively. In the above calculation the volume change due to mixing as well as pressure is ignored.

$\Delta H = 60000 \text{ J mol}^{-1}$ from Appendix A. Let $\Delta P = 0.69 \text{ MPa} = 100000 \text{ lb in}^{-2} = 6800 \text{ atm}$. Then the temperature shift is calculated by Equation 2 and shown in Table B1.

For line 2 liquid solution to solid solution α , the molar volume of the α phase of the A-B solution is defined as

$$V = (1 - X)V(\text{A}) + XV(\text{B}) + V(\text{m})$$

where $V(\text{A})$ and $V(\text{B})$ are the molar volumes of pure A and B, respectively, $V(\text{m})$ is the mixing volume and X is the molar fraction of B. For simplicity, it is assumed that $V(\text{m}) = 0$ in the calculation. Thus

$$V(\text{l}) = X'(\text{Al}) \frac{26.98}{D_{\text{Al}}^{\text{l}}(T)} + [1 - X'(\text{Al})] \frac{28.09}{D_{\text{Si}}^{\text{l}}(T)}$$

$$V(\alpha) = X(\text{Al}) \frac{26.98}{D_{\text{Al}}^s(T)} + [1 - X(\text{Al})] \frac{28.09}{D_{\text{Si}}^s(T)}$$

where $X(\text{Al})$ and $X'(\text{Al})$ are shown in Fig. 1.

Table BII summarizes the data. Let us compare with the transformation from pure liquid aluminium to solid: $\text{Al}(\text{l}) = \text{Al}(\text{s})$, $\Delta V = 0.77 \times 10^{-3} \text{ l mol}^{-1}$, $\Delta H_{\text{m}} = 10500 \text{ J mol}^{-1}$, $T_1 = 933 \text{ K}$, from Equation 2, $T_2 = 981.4 \text{ K}$, i.e. $\Delta T = 48.4 \text{ K}$. The result agrees well with Table BII which range from 49 to 51 K.

TABLE BI Temperature shift of phase line 1

$T(\text{K})$	$\Delta V(\text{ml mol}^{-1})$	$T_2(\text{K})$	$\Delta T^a(\text{K})$
673	-1.778	659.4	-13.6
758	-1.719	743.2	-14.8
795	-1.679	779.8	-15.2
813	-1.647	797.8	-15.2
850	-1.598	834.5	-15.5

^a $\Delta T = T_2 - T$.

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