

THERMODYNAMIC MODELING OF THE AL–K SYSTEM

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Abstract

A thermodynamic modeling for the Al–K system is conducted. The thermodynamic parameters for liquid, (Al), and (K) are evaluated by using the experimental phase diagram data from the literature. The gas phase is described with an ideal gas model. The calculated Al–K phase diagram agrees well with the experimental data. In particular, the observed monotectic reaction is well described by the present calculation.

Keywords: Al–K phase diagram; Thermodynamic calculation; CALPHAD approach

1. Introduction

K is one of the common impurities in commercial Al and Mg alloys. It is among the detrimental impurities which yield high temperature embrittlement due to intergranular fracture and the formation of cracks during the hot-rolling process [1, 2].

Currently, a program to establish a thermodynamic database for commercial Al

alloys is in progress in our Science Center [3-6]. The Al–K phase diagram was measured by Smith [7] using thermal analysis method. According to Smith, the mutual solubility between Al and K is negligible, and there is one monotectic reaction at 656°C. The solubility of Na in molten Al at its melting point is 0.18 at.% [8], and the solubility of K in Al would thus be expected to be lower by a factor of ten, by

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analogy with many other binary systems involving alkali metals [9].

Since thermodynamic descriptions for binary systems are prerequisite for the development of a multi-component thermodynamic database, the present work is devoted to the thermodynamic modeling of the Al–K system. So far, a thermodynamic description for the Al–K system is not available in the literature.

2. Thermodynamic model

The Gibbs energy function ${}^0G_i^\Phi(T) = G_i^\Phi(T) - H_i^{\text{SER}}$ for the element i ($i = \text{Al}, \text{K}$) in the phase Φ is expressed by an equation of the form:

$$\begin{aligned} {}^0G_i^\Phi(T) = & a + b \cdot T + c \cdot T \cdot \ln T + \\ & + d \cdot T^2 + e \cdot T^{-1} + f \cdot T^3 + g \cdot T^7 + \\ & + h \cdot T^{-9} \end{aligned} \quad \dots(1)$$

where H_i^{SER} is the molar enthalpy of the element i at 298.15 K and 1 bar in its standard element reference (SER) state, and T is the absolute temperature. In the present work, the Gibbs energies for both Al and K are taken from the SGTE compilation [10].

The Gibbs energy of the liquid is described by the Redlich-Kister polynomial [11]:

$$\begin{aligned} G_m^L - H^{\text{SER}} = & x_{\text{Al}} \cdot {}^0G_{\text{Al}}^L + x_{\text{K}} \cdot {}^0G_{\text{K}}^L + \\ & + R \cdot T \cdot (x_{\text{Al}} \ln x_{\text{Al}} + x_{\text{K}} \ln x_{\text{K}}) + \\ & + x_{\text{Al}} \cdot x_{\text{K}} [a_0 + b_0 \cdot T + (x_{\text{Al}} - x_{\text{K}}) \cdot \\ & \cdot (a_1 + b_1 \cdot T) + \dots] \end{aligned} \quad \dots(2)$$

in which H^{SER} is the abbreviation of $x_{\text{Al}} \cdot H_{\text{Al}}^{\text{SER}} + x_{\text{K}} \cdot H_{\text{K}}^{\text{SER}}$, R is the gas constant, and x_{Al} and x_{K} are the mole fractions of Al and K, respectively. The coefficients a_j and

b_j ($j = 0, 1$) are the parameters to be optimized. Similar equations can be written for the phases (Al) and (K).

The gas phase is described as an ideal gas mixture of the species Al, Al₂, K, and K₂, and its Gibbs energy per mol of species in the gas is given by the following expression:

$$\begin{aligned} G^{\text{gas}} - H^{\text{SER}} = & \sum y_i [G_i^{\text{gas}} - H_i^{\text{SER}} + \\ & + R \cdot T \cdot \ln(y_i)] + R \cdot T \cdot \\ & \cdot \ln(0.98692 \cdot P / \text{bar}) \end{aligned} \quad \dots(3a)$$

$$\begin{aligned} (n_{\text{Al}}^0 + n_{\text{K}}^0) / n = & y_{\text{Al}} + 2 \cdot y_{\text{Al}_2} + \\ & + y_{\text{K}} + 2 \cdot y_{\text{K}_2} \end{aligned} \quad \dots(3b)$$

where n is the number of moles of the species in the gas in internal equilibrium, $(n_{\text{Al}}^0 + n_{\text{K}}^0)$ the number of moles of atoms in the gas, $y_i = n_i / n$ the mole fraction of species i , $G_i^{\text{gas}} - H_i^{\text{SER}}$ the Gibbs energy of species i , and P the pressure. The Gibbs energy functions of the individual gas species are taken from Ref. [12].

3. Results and discussion

The evaluation of the model parameters is attained by recurrent runs of the PARROT program [13], which works by minimizing the square sum of the differences between experimental values and computed ones. In the assessment procedure, each piece of experimental information is given a certain weight. The weights were varied systematically during the assessment until most of the experimental data were accounted for within the estimated uncertainty limits. The presently obtained thermodynamic parameters for the Al–K system are presented in Table 1.

Table 1 Optimized thermodynamic parameters in the Al-K System^{*}

Liquid: Model (Al, K) ₁
${}^{\text{ex}}G_{\text{Al,K}}^{\text{L}} = x_{\text{Al}} \cdot x_{\text{K}} (31615.7 + 8.70845 \cdot T)$
(Al): Model (Al,K) ₁
${}^0L_{\text{Al,K}}^{(\text{Al})} = 58179.1$
(K): Model (Al,K) ₁
${}^0L_{\text{Al,K}}^{(\text{K})} = 14835.3$
Gas: Model (Al, Al ₂ , K, K ₂)
${}^0G_{\text{Al}}^{\text{gas}} = R \cdot T \cdot \ln(0.98692 \cdot P) + \text{GASAL}(T)$
${}^0G_{\text{Al}_2}^{\text{gas}} = R \cdot T \cdot \ln(0.98692 \cdot P) + \text{GASAL2}(T)$
${}^0G_{\text{K}}^{\text{gas}} = R \cdot T \cdot \ln(0.98692 \cdot P) + \text{GASK}(T)$
${}^0G_{\text{K}_2}^{\text{gas}} = R \cdot T \cdot \ln(0.98692 \cdot P) + \text{GASK2}(T)$

^{*} In J/(mol of atom), and temperature (T) in Kelvin and pressure (P) in bar. The Gibbs energies for the pure elements are from the SGTE compilation [10], and the Gibbs energies for gas species are from Ref. [12].

Figure 1 shows the calculated Al–K phase diagram along with the experimental data [7]. The thermal effects from Smith [7] are well reproduced by the present calculations.

Since the mutual solubility between Al and K is negligible, only one regular parameter for each of (Al) and (K) phases is introduced in the modeling. One degenerated equilibrium L = (K), (Al) at 63.5°C is detected with the present calculation. The monotectic reaction Liquid #1 = (Al) +

Liquid #2 at 656°C observed experimentally [7] is also well reproduced by the calculation. A monotectic reaction is also observed in the similar Al–Na system [8]. The occurrence of such a monotectic reaction leads to a miscibility gap for liquid phase in both the Al–Na and Al–K systems.

Figure 2 presents the calculated Al–K phase with gas phase. According to the calculation, there is one invariant reaction Liquid #1 + gas = Liquid #2 at 762.3 °C.

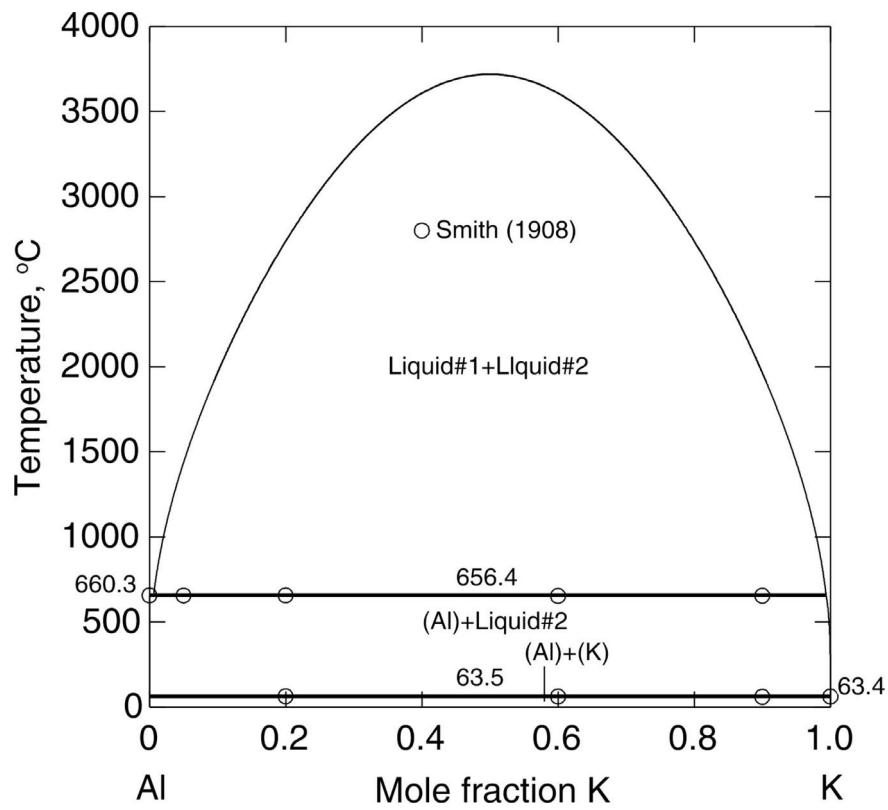


Fig. 1 Calculated Al-K phase diagram compared with the thermal effect data from Smith [7].

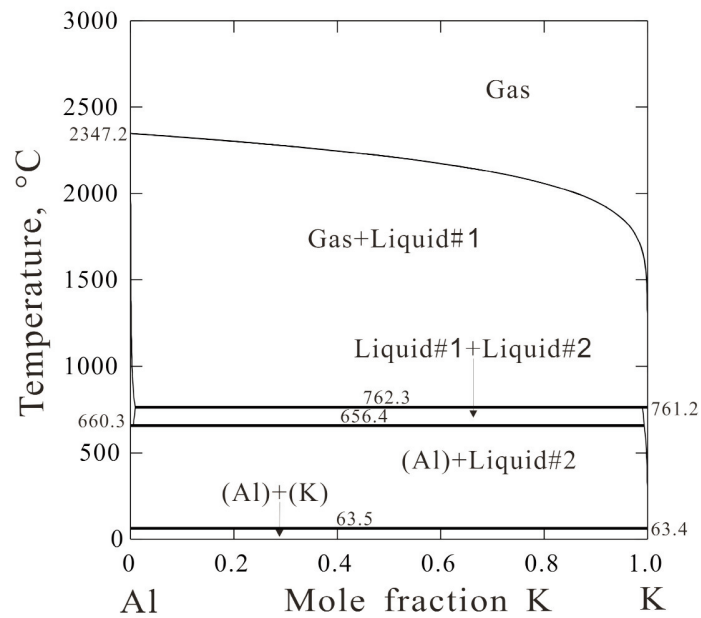


Fig. 2 Calculated Al-K phase diagram with solid phases, liquid and gas.

4. Summary

The Al–K system is assessed thermodynamically by considering the literature data.

The calculated phase relation is in a good agreement with the observed one. The Al–K phase diagram including solid phases, liquid, and gas is also presented.

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