

Linking Ab Initio-Calphad for the Assessment of the Aluminium-Lutetium System.

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Abstract: First-principles calculations within density functional theory (DFT) were used to investigate intermetallics in the Al-Lu system at 0 K. The five compounds of the system were investigated in their observed experimental structures. Thermodynamic modelling of the Au-Lu system was carried out by means of the CALPHAD (calculation of phase diagrams) method. The liquid phase and the intermetallic compounds Al₃Lu, Al₂Lu, AlLu, Al₂Lu₃ and AlLu₂ are taken into consideration in this optimization. The substitutional solution model was used to describe the liquid phase. The five compounds are treated as stoichiometric phases. The enthalpies of formation of the compounds were found by the ab initio calculations and used in the optimization of the phase diagram.

Keywords: First principles calculations, CALPHAD, Al-Lu system, Thermodynamic assessment, Phase diagram.

I. INTRODUCTION

No phase diagram was found and has been developed in the literature for the Al-Lu system, therefore, the phase diagram of this system is not known. But, most binary phase diagrams of Al with rare earth metals are similar, so it can be assumed that the phase diagram of the Al-Lu system is of the same type. This prompted Moffat [1] to draw the phase diagram shown in figure 1. A survey of the system is given by Gschneidner jr et al.[2] We are based on this diagram to carry out a diagram optimization based on the Calphad method

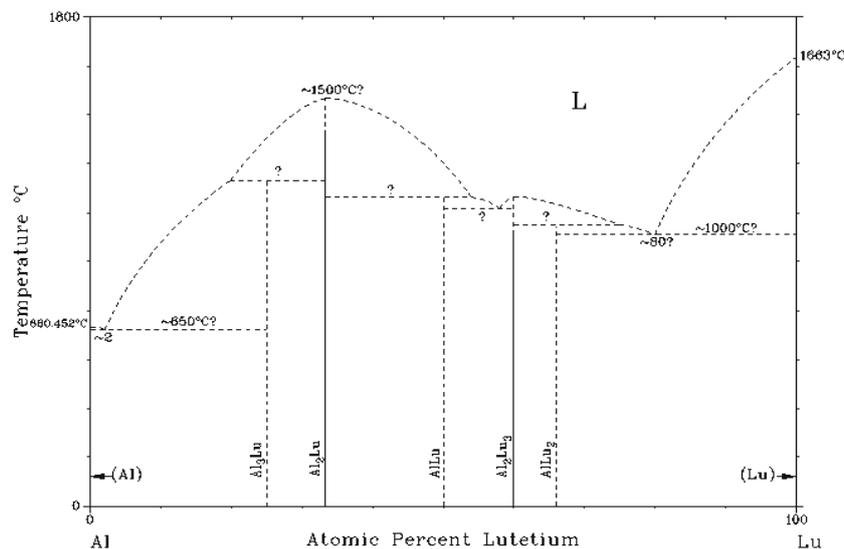


Fig. 1. Al-Lu proposed phase diagram by Moffat [1]

II. METHODOLOGY

1. First-principles

Our calculations were based on density functional theory (DFT) as implemented in the WIEN2k package [3]. We just considered generalized-gradient approximations (GGA). We employed the Perdew-Burke-Ernzerhof functional [4]. The Brillouin zone samplings were performed in such a way that the number of k-points multiplied by the number of atoms in the unit cell is greater than 10000. At 0 °K the thermodynamic stability criterion is the formation enthalpy $\Delta H_f(Al_p Lu_q)$. The formation enthalpies of the compounds were obtained through the following equation:

$$\Delta H_f(Al_pLu_q) = E_{tot}(Al_pLu_q) - \left[\frac{p}{p+q} E_{tot}^{fcc}(Al) + \frac{q}{p+q} E_{tot}^{hcp}(Lu) \right]$$

Where $\Delta H_f(Al_pLu_q)$ is the enthalpy of formation of the compound Al_pLu_q , and $E_{tot}(Al_pLu_q)$, $E_{tot}^{fcc}(Al)$ and $E_{tot}^{hcp}(Lu)$ are the ground state total energies (per atom) of the compound Al_pLu_q and its constituents Al and Lu, respectively, in fcc and hcp structures.

2. Calphad

a. Pure elements

The Gibbs energies functions used in the present work are those collected in the database compiled by Dinsdale [5]. We used the SGTE (Scientific Groupe Thermodata Europe) format for the Gibbs energy functions $G_i^\phi(T)$ for the elements i (Al and Lu) in the phase ϕ (liquid, fcc and hcp).

$G_i^\phi = {}^0G_i^\phi(T) - H_i^{SER}(298.15 K) = a + bT + cT \ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9}$ where ${}^0G_i^\phi(T)$ and G_i^ϕ are the relative and absolute Gibbs energy of the element i in the ϕ state. $H_i^{SER}(298.15 K)$ is the molar enthalpy of the element i at 298.15 K in its standard element reference (SER) state, fcc for Al and hcp for Lu. [6]

b. Liquid solution phase

The solution phases were treated by the substitutional solution model with Redlich-Kister equation [11]. The sum of reference (*ref*), ideal (*id*) and excess (*exc*) terms gives the Gibbs energy for 1 mol of atoms.

$$G^{Liq} = {}^{ref}G^{Liq} + {}^{id}G^{Liq} + {}^{exc}G^{Liq}$$

With

$${}^{ref}G^{Liq} = x_{Al}G_{Al}^{Liq} + x_{Lu}G_{Lu}^{Liq}$$

$${}^{id}G^{Liq} = RT[x_{Al} \ln(x_{Al}) + x_{Lu} \ln(x_{Lu})]$$

$${}^{exc}G^{Liq} = x_{Al}x_{Lu} \sum_{v=0}^n v L_{Al,Lu}^{Liq} (x_{Al} - x_{Lu})^v$$

Where $v L_{Al,Lu}^{Liq}$ is the v th-order binary interaction parameter which can be expressed as $\alpha_v + \beta_v T$ with α_v and β_v are the parameters to be optimized. [6]

c. Intermetallic compounds

All intermetallics are stoichiometric compounds. Their phases Gibbs energy per mol of atoms are given by the following expression : $G^{Al_pLu_q} = \frac{p}{p+q} H_{Al}^{SER} + \frac{q}{p+q} H_{Lu}^{SER} + \Delta H_f^{Al_pLu_q} - T\Delta S_f^{Al_pLu_q}$ with p and q : the number of Al and Lu in the intermetallic Al_pLu_q . The enthalpy and entropy of formation were considered as independent of temperature. [6]

III. OPTIMIZATION METHODOLOGY

A Calphad optimization requires the collection of a maximum number of information concerning the system studied. It is in this sense that we have calculated the enthalpies of formation of the compounds of this system by means of calculations ab-initio. The enthalpies of formation provided by the DFT were injected into the BATNABIN code in order to optimize the phase diagram. The calculation code BATNABIN [7] allows the optimization of the thermodynamic functions of each phase existing in the system and the restoration of the corresponding phase diagram. The calculation is based on the collection of a set of experimental and theoretical data concerning the equilibrium points of the phase diagram and the thermodynamic quantities. These data will allow us to make a linear least square fit to obtain a mathematical description that reproduces as closely as possible all the experimental data while allowing favoring certain results which may appear more reliable than others.

IV. RESULTS AND DISCUSSION

The enthalpies of formation of the intermetallic compounds Al_3Lu , Al_2Lu , $AlLu$, Al_2Lu_3 and $AlLu_2$ are summarized in table 1. There is good coherence between the values calculated during this work and the values found by previous ab-initio calculations [8] as well as experimental values. In this optimization, we took into consideration the proposed phase diagram of Moffat [1] with the five compounds reported. We have used as data some equilibrium points of this diagram as well as the enthalpies of formation of the five compounds that have already been calculated by the ab-initio method in this work. The optimization is obtained for a development of the free enthalpy of excess of the liquid phase to order 0. The calculated thermodynamic

quantities of all the phases are summarized in Table 2. In table 3, we summarized temperatures and compositions of the invariant reactions of the phase diagram shown in Figure 2. The calculated diagram is presented in Figure 2.

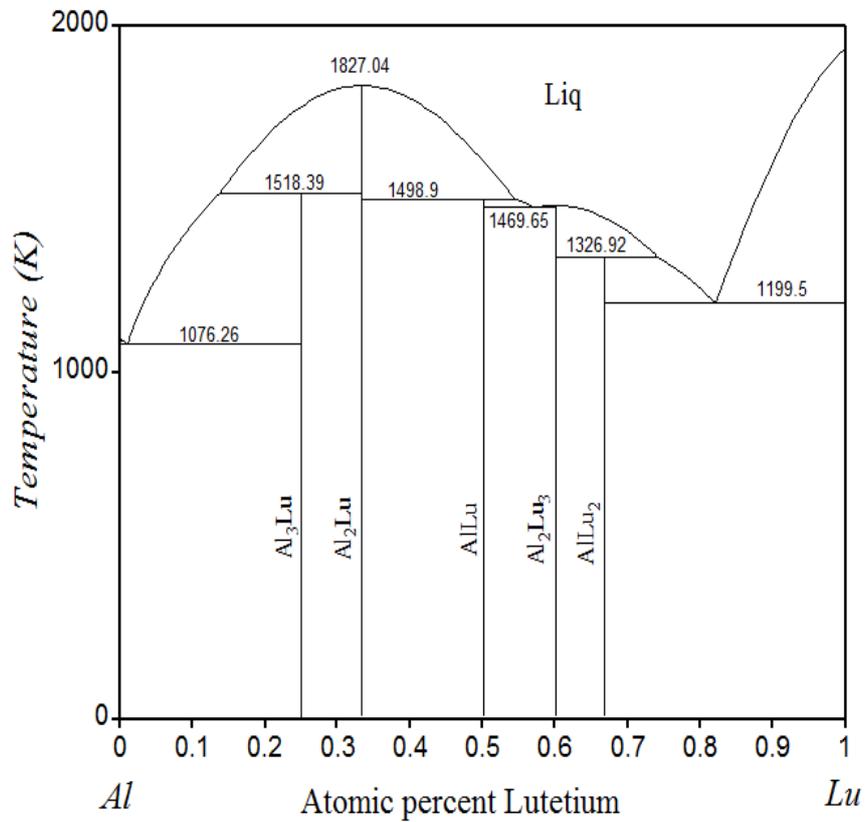


Fig. 2. Phase diagram computed by the CALPHAD modeling

Table 1. Calculated enthalpies of formation of Au-Sc intermetallics.

| Compound | Enthalpies of formation (kJ/mol-atom) | | | |
|---------------------------------|---------------------------------------|----------|---------|-----------------------|
| | This work (GHEM2K) | VASP [8] | Calphad | Experimental (110) |
| Al ₃ Lu | -43 | -38 | -36.8 | - |
| Al ₂ Lu | -50 | -46 | -45.9 | -52 |
| AlLu | -32 | -39 | -39.5 | - |
| Al ₂ Lu ₃ | -31.6 | -32 | -33.4 | - |
| AlLu ₂ | -24 | -28 | -29.1 | - |

Table 2. Parameters of the thermodynamic modeling of the phase diagram shown in Figure 3.

| Phase | Parameters |
|---------------------------------|--|
| Liquid | $L_0^{liquid} = -52414 - 69.798T$ |
| Al ₃ Lu | $G^{Al_3Lu} = -36800.078 - 2.630T + 0.75 H_{Al}^{SER} + 0.25 H_{Lu}^{SER}$ |
| Al ₂ Lu | $G^{Al_2Lu} = -45999.437 - 3.73T + 0.667 H_{Al}^{SER} + 0.333 H_{Lu}^{SER}$ |
| AlLu | $G^{AlLu} = -39500.345 - 5.508T + 0.5 H_{Al}^{SER} + 0.5 H_{Lu}^{SER}$ |
| Al ₂ Lu ₃ | $G^{Al_2Lu_3} = -33400.792 - 7.401T + 0.4 H_{Al}^{SER} + 0.6 H_{Lu}^{SER}$ |
| AlLu ₂ | $G^{AlLu_2} = -29100.117 - 6.159T + 0.333 H_{Al}^{SER} + 0.667 H_{Lu}^{SER}$ |

Table 2. Temperatures and compositions of the invariant reactions of the phase diagram shown in Figure 5.

| Reaction | Composition | Temperature | Type of reaction | Reference |
|---------------------------------------|-------------|-------------|------------------|-----------|
| $L \leftrightarrow Al_3Lu + Al$ | 0.010 | 1076.26 | Eutectic | This work |
| | 0.016 | 925.23 | | [9] |
| $L + Al_2Lu \leftrightarrow Al_3Lu$ | 0.139 | 1518.39 | Peritectic | This work |
| | 0.166 | 1448.67 | | [9] |
| $L + Al_2Lu \leftrightarrow AlLu$ | 0.545 | 1498.9 | Peritectic | This work |
| | 0.53 | 1396.33 | | [9] |
| $L \leftrightarrow AlLu + Al_2Lu_3$ | 0.571 | 1469.65 | Eutectic | This work |
| | 0.564 | 1364.92 | | [9] |
| $L + Al_2Lu_3 \leftrightarrow AlLu_2$ | 0.742 | 1326.92 | Peritectic | This work |
| | 0.747 | 1317.81 | | [9] |
| $L \leftrightarrow AlLu_2 + Lu$ | 0.819 | 1199.5 | Eutectic | This work |
| | 0.800 | 1265.47 | | [9] |

V. CONCLUSION

A thermodynamic assessment of the Al-Lu system is carried out using the results provided by ab-initio calculations. We have been able to reconstruct the phase diagram of the Al-Lu system. An optimal set of thermodynamic functions for the system has been obtained from the selected phase diagram and thermodynamic data by using the CALPHAD technique. There is good agreement between the calculated phase diagram and the proposed one.

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