

Thermodynamic optimization of the Al–Yb binary system

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Abstract

A thermodynamic description of the Al–Yb binary system was developed based on critically evaluated experimental data by using CALPHAD approach. Liquid (γ Yb) and (β Yb) were modeled as substitutional solution phases. Al_2Yb and Al_3Yb were treated as stoichiometric compounds. A set of self-consistent parameters for describing various phases in this system was obtained, with which most of the experimental data reported in the literatures were well reproduced.

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1. Introduction

Rare earth elements have been used in aluminum alloys for many years to improve the tensile strength, heat resistance and corrosion resistance, etc. [1]. For example, Sc has been added to Al alloys to form a thermo-stable L_{12} -type (AuCu_3) Al_3Sc phase and to obtain a significant strengthening improvement [2]. However, the research mainly focused on the application of the Sc, Y and the so-called ‘trivalent’ rare earth elements, such as La, Ce and Nd, etc. As for other RE elements, there is little investigation [3].

Ytterbium, with respect to its neighbouring lanthanide, exhibits different properties, such as melting point and density. Because of its electronic configuration, it can occur in the divalent or trivalent states. In the Al–Yb system, Yb can show a variable valence (passing from divalence, intermediate valence to trivalence) depending on the increasing concentration of the partner element Al [4]. The different properties may result in the different effects in aluminum alloys. For example, recent investigations show that the addition of Yb to A356.0 (Al–7%Si–Mg) alloy can cause modification to a well-refined plated-like eutectic silicon structure and the level of modification increased with increasing level of Yb [5]. But the mechanism is still unclear. It should be pointed out that further investigation on the effects of Yb in the aluminum alloys is needed.

The knowledge of the thermodynamics and phase diagram is one of the basic requirements in the field of materials research and process control of new alloy systems. The present work aims to evaluate the Al–Yb binary system and to develop a precise thermodynamic description of the system by means of the CALPHAD technique [6].

2. Experimental information

2.1. Phase diagram data

The earlier investigation of the Al–Yb phase diagram was carried out by Vengrenovich and Psarev [7] by thermal, metallographic, and X-ray diffraction analyses. Their results showed only one compound YbAl and one eutectic reaction between (Al), YbAl and liquid at 616 °C and 96.25 at.% Yb. The melting or decomposition of YbAl was not indicated in the phase diagram. In addition, it was found that Yb is nearly insoluble in (Al) up to 500 °C.

The first systematic investigation of the Al–Yb phase diagram was performed by Kulifeev et al. [8] using metallographic, X-ray diffraction, and differential thermal analyses and electrical resistance and micro-hardness measurements. The purity of the Al and the Yb used in their experiment were reported to be 99.99 and 99.9%, respectively. Only two intermediate phases, Al_2Yb and Al_3Yb were detected. The YbAl compound reported by Vengrenovich and Psarev [7] was not found. Al_2Yb was shown to melt congruently at 1450 °C and Al_3Yb to decompose peritectically at 1065 °C to the liquid phase and Al_2Yb . Moreover, two eutectic reactions were found—one at about 35 at.% Al and 665 °C between (Yb) and Al_2Yb , and the other between (Al) and Al_3Yb at 627 °C and 95 at.% Al. The liquidus between about 82 and 46 at.% Al and from about 35 to 0 at.% Al were not determined.

Later, the Al–Yb phase diagram was also systematically investigated by Palenzona et al. [9] using differential thermal, microscopic and X-ray analysis. The Al metal had a purity of 99.999% and the Yb metal had a claimed purity

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of 99.9+%. The obtained phase diagram was in general agreement with that of Kulifeev et al. [8], although some differences existed in the temperatures of the invariant reactions. Based on the experimental results, Palenzona et al. [9] ruled out the existence of YbAl in the Al–Yb system. The peritectic decomposition of Al₃Yb was found to be at 980 °C, instead of the 1065 °C claimed by Kulifeev et al. [8]. The melting point of Al₂Yb was shown to be 1360 °C, instead of 1450 °C. The Al-rich eutectic composition was micrographically estimated to be 96 at.% Al by Palenzona et al. [9]. The composition of Yb-rich eutectic was not given by Palenzona et al. [9]. The estimated value from their reported phase diagram is about 22.5 at.% Al. The two eutectic temperatures were shown by Palenzona et al. to occur at 625 and 675 °C, respectively, compared with 627 and 665 °C [8]. In addition, no significant solubility of Yb in (Al) was found by Palenzona et al., but the addition of Al to pure Yb resulted in a decrease in $\beta \leftrightarrow \gamma$ transformation temperature of Yb to 712 °C, at which an inverse peritectic reaction ($\gamma\text{Yb} \rightarrow \beta\text{Yb} + \text{L}$) occurs at 2.5 at.% Al. A little solid solution was found for compound Al₂Yb, lying on the Al-rich side, the extent of which was estimated to be less than 1 at.% Al at 900 °C. No solid solubility was found for compound Al₃Yb.

The analyses above show that the researches of two groups exist obvious discrepancies, especially for the peritectic decomposition temperature of Al₃Yb and the melting point of Al₂Yb. Gschneidner et al. [10] assessed the Al–Yb phase and mainly accepted the work of Palenzona et al. [9], but with some modification at the Yb-rich side. The accepted $\beta \leftrightarrow \gamma$ transformation temperature by Gschneidner et al. [10] was 795 °C, while the given value by Palenzona et al. [9] was 740 °C. There was a large difference between the two values. Therefore, Gschneidner et al. [10] raised the 712 °C peritectic temperature given by Palenzona et al. [9] to 770 °C. However, the $\beta \leftrightarrow \gamma$ transformation temperature from SGTE database [11] was 760 °C, instead of 795 °C. Consequently, the estimated peritectic temperature should be little higher than 712 °C since SGTE data were accepted in the present work.

The Al-rich portion of the phase diagram was also studied by Kononenko and Golubev [12] recently. They suggested that the eutectic reaction at 97.3 at.% Al and confirmed the 625 °C temperature.

2.2. Thermodynamic data

By vapor pressure measurements, Kulifeev et al. [13] measured vapor pressures at temperatures from 500 to 600 °C. From the results, thermodynamic activities were calculated.

The enthalpy of formation of Al₂Yb was also obtained as –24.4 kJ/mol by Kulifeev et al. [13] by extrapolation using the temperature dependence of the activity data. Enthalpies obtained by such a method have significant uncertainty so the value (–24.4 kJ/mol) is only introduced to compare with the optimized values in the present work. Almost the same value (–25.4 kJ/mol) was found by Palenzona et al. [14] using differential calorimetry and the Knudsen effusion method. More negative values were reported by Pasturel et al. [15] and Colinet et al. [16]. Pasturel et al. [15], who used a solution calorimetric method, reported the values of –36.4 kJ/mol for Al₂Yb and –32.5 kJ/mol for Al₃Yb. By the same method, Colinet et al. [16] found a value of –38.1 kJ/mol for Al₂Yb, which are in good agreement with the value from Pasturel et al. [15].

Recently, the standard enthalpies of formation for the different solid Yb–Al alloys at 300 K have been measured by direct calorimetry by Borzone et

al. [17]. The values for Al₂Yb and Al₃Yb compounds were -39.5 ± 2 and -32.5 ± 2 kJ/mol, respectively. Their results confirmed those obtained by Pasturel et al. [15] and Colinet et al. [16].

Ouyang et al. [18] calculated the enthalpy of formation of Al₂Yb and Al₃Yb compounds with Miedema's semi-empirical theory. But these calculated data show considerable discrepancies with the above-mentioned experimental data. The possible reason is that the enthalpies of formation predicted by Miedema's theory are for 0 K, while the experimental values are obtained at room temperature or at high temperature. In this paper, those from Miedema's theory are only introduced to compare with the optimized values.

3. Thermodynamic modeling

3.1. Solution phases: liquid (γYb) and (βYb)

The Gibbs energies of solution phases, liquid (γYb) and (βYb), are described with a substitutional solution model based on random mixing of the metallic atoms. They are expressed as follows:

$$G_m^\Phi = x_{\text{Al}} {}^0G_{\text{Al}}^\Phi + x_{\text{Yb}} {}^0G_{\text{Yb}}^\Phi + RT(x_{\text{Al}} \ln x_{\text{Al}} + x_{\text{Yb}} \ln x_{\text{Yb}}) + {}^E G^\Phi \quad (1)$$

where Φ denotes the phases, x_i the atom fraction of element i . ${}^0G_i^\Phi$ is the molar Gibbs energy of pure element i in the Φ state, which is taken from Dinsdale [11]. And ${}^E G^\Phi$ is the excess Gibbs energy, formulated with the Redlich–Kister polynomial:

$${}^E G^\Phi = x_{\text{Al}} x_{\text{Yb}} \sum_{j=0,1,\dots} {}^j L^\Phi (x_{\text{Al}} - x_{\text{Yb}})^j \quad (2)$$

where ${}^j L^\Phi$ ($j=0, 1, \dots$) are the interaction parameters between elements Al and Yb. The general form for ${}^j L^\Phi$ is:

$${}^j L^\Phi = A_j^\Phi + B_j^\Phi T \quad (3)$$

where A_j^Φ and B_j^Φ are parameters resulting from an optimization process.

3.2. Stoichiometric phases

The two intermetallic compounds, Al₂Yb and Al₃Yb, are all modeled as stoichiometric compounds, and their Gibbs energy functions are written as:

$$G^{\text{Al}_a\text{Yb}_b} = a {}^0G_{\text{Al}}^{\text{fcc}} + b {}^0G_{\text{Yb}}^{\text{fcc}} + D + ET \quad (4)$$

Table 1
Thermodynamic parameters for the Al–Yb system

Phases	Parameters
Liquid	${}^0L_{\text{Al,Yb}} = -62743.77 + 0.89367T$ ${}^1L_{\text{Al,Yb}} = -37607.14 + 6.29122T$
(γYb) or bcc_A2	${}^0L_{\text{Al,Yb}} = -25908.04$
fcc_A1 or (Al) or (βYb)	${}^0L_{\text{Al,Yb}} = -38173.22 + 15.89827T$ ${}^1L_{\text{Al,Yb}} = -7063.91$
Al ₂ Yb	$G^{\text{Al}_2\text{Yb}} - 0.66667 {}^0G_{\text{Al}}^{\text{fcc}} - 0.33333 {}^0G_{\text{Yb}}^{\text{fcc}} = -35350.36 + 2.53935T$
Al ₃ Yb	$G^{\text{Al}_3\text{Yb}} - 0.75 {}^0G_{\text{Al}}^{\text{fcc}} - 0.25 {}^0G_{\text{Yb}}^{\text{fcc}} = -31920.02 + 4.83054T$

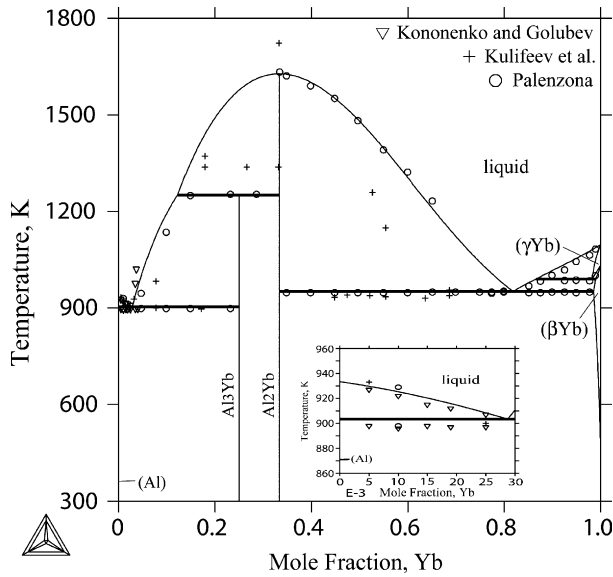


Fig. 1. Calculated Al–Yb phase diagram with the experimental data [8,9,12].

where *a* and *b* are the mole fraction of Al and Yb in the compound, respectively. *D* and *E* are the parameters to be assessed.

4. Results and discussion

The model parameters were optimized using the PARROT module in Thermo-Calc software [19] with experimental data. Each piece of the selected data is given a certain weight and the weight can be changed during the optimization until most of the selected data can be reproduced by the calculation within the uncertainty limits.

Thermodynamic parameters optimized in the present work are listed in Table 1. Comparison of the calculated Al–Yb phase diagram with the experimental data is shown in Fig. 1. The invariant equilibria in the Al–Yb system are listed in Table 2.

Table 2
Invariant reactions in the Al–Yb system

Reaction	<i>T</i> (K)		<i>X</i> (Yb)		Reference
Liquid → (Al) + Al ₃ Yb	903	0.029	0	0.25	This work
	898	0.04			[9]
	898	0.027			[12]
	900	0.05			[8]
Liquid + Al ₂ Yb → Al ₃ Yb	1251	0.122	0.333	0.25	This work
	1253				[9]
	1338				[8]
Liquid → Al ₂ Yb	1628				This work
	1633				[9]
	1723				[8]
Liquid → Al ₂ Yb + (βYb)	951	0.818	0.333	0.985	This work
	948	0.775			[9]
	938				[8]
(γYb) → liquid + (βYb)	989	0.982	0.866	0.989	This work
	985	0.975			[9]

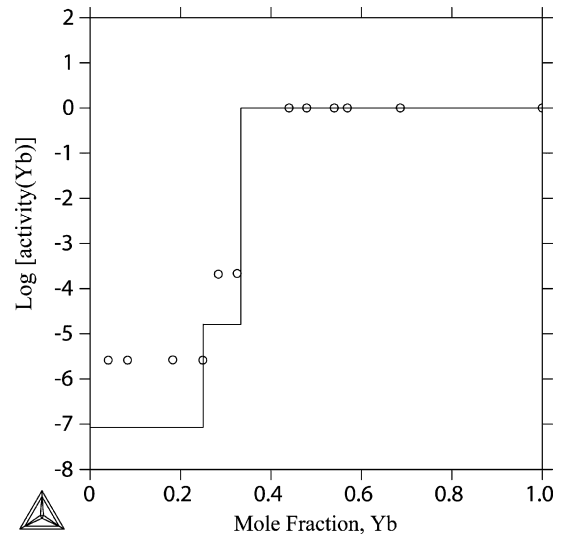


Fig. 2. Calculated thermodynamic activities of Yb in solid alloys at 823 K with the experimental data [13].

It is clear that the calculated results are in good agreement with most experimental data. The calculated temperature of the peritectic reaction (γYb) → liquid + (βYb) (989 K) is little higher than the experimental one (985 K), just as above assessment.

Calculated thermodynamic activities of Yb in solid alloys at 823 K are compared with the experimental data in Fig. 2. The calculated and experimental values are in general agreement.

Calculated enthalpies of formation of the solid Al–Yb alloys at 298 K with reported data are presented in Fig. 3. Our calculation agrees well with the experimental data from Borzone et al. [17], Colinet et al. [16] and Pasturel et al. [15]. From the calculated results, it also can be seen that the phase with the greatest relative stability is Al₂Yb, which is consistent with the phase diagram (Fig. 1).

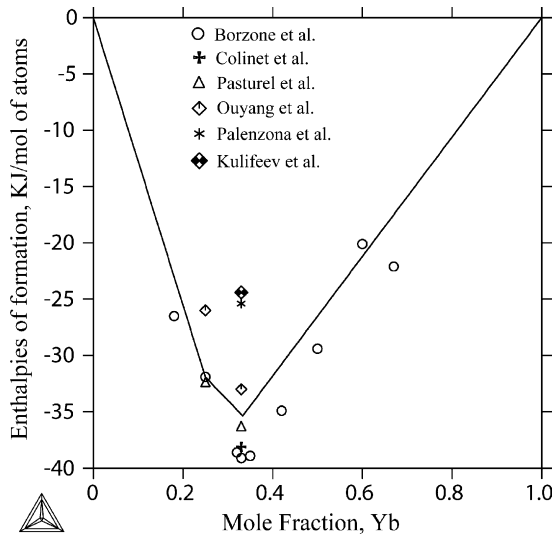


Fig. 3. Calculated enthalpy of formation in the Al–Yb system in comparison with the experimental data [13–18] (referred to the fcc state).

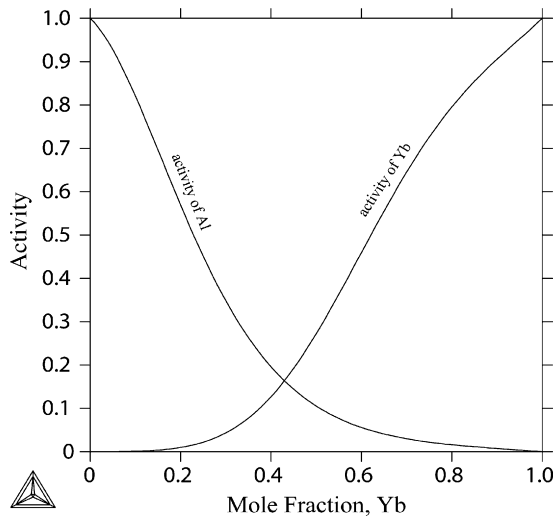


Fig. 4. Calculated activities at 1700 K.

Based on the obtained thermodynamic parameters, activities of Al and Yb in liquid alloys at 1700 K are further calculated as shown in Fig. 4. It can be seen that Al and Yb show negative deviation from ideal solution. Same behavior also occurs in other Al–RE systems, such as Al–La and Al–Pr [20].

5. Conclusion

The Al–Yb binary system has been critically assessed. A group of self-consistent thermodynamic parameters has been obtained, and the assessed phase diagram and thermodynamic properties agree well with most experimental data.

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