



Calorimetric measurements of liquid (Al + Li + Zn) alloys



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ABSTRACT

The integral molar enthalpies of mixing are described by drop calorimetry for liquid alloys based on the (Al + Li) and (Al + Li + Zn) system, with the use of the Setaram MHTC 96 Line Evo calorimeter.

The measurements for the (Al + Li) system were carried out at two temperatures, 1023 K and 1027 K, and compared with the literature data. The integral molar enthalpies of mixing of the liquid binary system over the entire concentration range have negative values. Moreover, for the mole fraction of lithium ($X_{\text{Li}} = 0.5053$), the minimum value of the integral enthalpy of mixing of the (Al + Li) system is equal to $\Delta_{\text{mix}}H_{\text{m}} = -12.1 \text{ kJ} \cdot \text{mol}^{-1}$.

The experimental studies for the (Al + Li + Zn) system involved measurements at three different temperatures: 942 K for the $(\text{Al}_{0.90}\text{Li}_{0.10})_{1-x}\text{Zn}_x$ alloy composition; 978 K for the $(\text{Al}_{0.35}\text{Li}_{0.65})_{1-x}\text{Zn}_x$ and $(\text{Al}_{0.65}\text{Li}_{0.35})_{1-x}\text{Zn}_x$ alloy composition and finally, 1014 K for the $(\text{Al}_{0.50}\text{Li}_{0.50})_{1-x}\text{Zn}_x$ alloy composition.

This work presents a complete study of mixing enthalpies in (Al + Li) and (Al + Li + Zn) systems and may therefore provide reference for earlier attempts on calorimetric measurements of the (Al + Li + Zn) system.

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1. Introduction

1.1. (Al + Li) system

The (Al + Li) alloys are promising materials because of the low density and high specific strength, especially as construction materials in the aerospace, military and automobile industry. Moreover, they can be used as new environmentally friendly energy storage materials, e.g. for safe hydrogen storage in hydrogen power engineering and also as the negative electrodes in high temperature batteries.

The thermodynamic studies of the alloy set based on the (Al + Li) system were started in 1971 by Yao *et al.* [1], who used EMF measurements in the region of $X_{\text{Li}} = (0.069 \text{ to } 0.5)$ within the temperature range of 555 K to 662 K. Later Selman *et al.* [2] examined electrochemically liquid (Al + Li) alloys with a high Li concentration and the $(\alpha + \beta)$, β , $(\beta + \gamma)$ regions over the temperature range of 663 K to 823 K. In 1979 and in 1980, Wen *et al.* [3,4] measured the mass transport and the thermodynamic properties of α (AlLi) solutions and the β phase at $T = 678 \text{ K}$ to $T = 873 \text{ K}$ by using the coulometric titration technique. Then Amezawa *et al.* [5] defined the thermodynamics of the two-phase regions, that is $\{\alpha(\text{Al}) + \beta(\text{AlLi})\}$, $\{\beta(\text{AlLi}) + \gamma(\text{Al}_2\text{Li}_3)\}$ and $\{\gamma(\text{Al}_2\text{Li}_3) + \text{liquid}\}$ within

the temperature range of $T = 560 \text{ K}$ to $T = 760 \text{ K}$, with the use of the EMF studies. Zaitsev *et al.* [6] determined the solid alloys from the α phase and from the $(\alpha + \beta)$ two-phase region by using the Knudsen mass spectrometry. The β phase was investigated by Veleckis [7] by the hydrogen titration method. The mixing enthalpies of liquid (Al + Li) alloys were measured by Bushmanov and Yatsenko [8] at $T = 1023 \text{ K}$ over the concentration range between 0.3 and 0.8 mol fraction Li and by Moser *et al.* [9], over the whole range of composition at $T = 879 \text{ K}$ and $T = 973 \text{ K}$.

Furthermore, the lithium activity in liquid alloys and the partial enthalpy were measured by Hicter *et al.* [10] and Lee and Sommer [11], respectively. The first phase diagram was defined by Saboungi and Hsu [12], and it was then further advanced by McAlister [13] in 1982, Sigl and Sanchez [14] in 1986, Saunders [15] and Chen *et al.* [16] in 1989. The most recent phase diagram was created in 2007 by Hallstedt and Kim [17]. For the first time, in 2014 Gašior *et al.* [18] experimentally determined the formation enthalpy of the intermetallic phases occurring in the (Al + Li) system by means of solution calorimetry and also determined the formation enthalpy of the phase AlLi with the use of the direct reaction method.

1.2. (Al + Zn) system

Recently, the alloys based on the (Al + Zn) system have been widely studied because of their low density and good ability to be cast. The zinc addition increases the mechanical properties, so

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the field of application of this binary system is still growing. These materials could be used in various industries, such as the automotive, military or aerospace industry.

The *liquidus* and *solidus* have been investigated extensively by many researchers [19–31]. Furthermore Batalin and Beloborodova [32], Predel and Schallner [33] and also Sebkova and Beranek [34] measured the activity of Al at various temperatures within (960 to 1100) K range in the liquid alloys based on the (Al + Zn) system, with the use of the EMF studies. Moreover, the activity of Zn in (Al + Zn) liquid alloys was defined by Bolsaitis and Sullivan [35] at $T = 1076$ K, by means of the isopiestic technique, and by Lutz and Voigt [36] at $T = 950$ K and $T = 1050$ K and Yazawa and Lee [37] at $T = 1073$ K, with the use of the dew point method. In 1973, Connell and Downie [38] began the experimental work on the (Al + Zn) system and defined the formation enthalpies of the fcc alloys at three different temperatures, namely: (599, 637 and 648) K. Next, in 1983, Murray [39] calculated the phase diagram of (Al + Zn) which is inconsistent with the literature data. Three years later, Mey and Effenberg [40] presented a new thermodynamic description of this binary system, by using the computer program written by Lukas *et al.* [41]. However, these calculations showed differences in the invariant temperatures for the eutectic equilibrium, the critical point and the monotectoid equilibrium by $T = (2.9, 13.3$ and $5.0)$ K, respectively. In addition, there were also differences between the literature values and those values obtained by the authors for the phase boundaries of the fcc phase in the two-phase region (fcc + hcp) and also those for the miscibility gap of the fcc phase. In 1987, Shaarbafe *et al.* [42] measured the enthalpy change associated with the dissociation of a 29.5 at.% Zn alloy into Al (fcc) and Zn (hcp) phases, by using Differential Scanning Calorimetry (DSC). These results were in agreement with those obtained by Lyashenko [43], Wittig and Schöffl [44], but inconsistent with the results of the EMF studies of solid alloys published by several authors [45–50]. In 1990, Holender and Soltys [51] measured the eutectoid temperature at 549 K. Later, the thermodynamic phase diagram of the (Al + Zn) system was calculated by Mey [52], Chen and Chang [53] and Mathon *et al.* [54]. These three optimisations have given very similar phase diagrams. In 2014, Balanović *et al.* [55] defined such thermodynamic properties as activities, activity coefficients, partial and integral excess Gibbs free energy and mixing energies at $T = 1000$ K by using the Olsen calorimetric method.

1.3. (Li + Zn) system

Due to some very attractive properties, such as low density, high rigidity and good machine cutting workability, the (Li + Zn) system is a promising material, especially in the military industry and the aerospace applications. In spite of these impressive characteristics of the (Li + Zn) alloys, their thermodynamic properties are not well known. This is probably due to the very high reactivity of lithium with the oxygen, nitrogen, and steam contained in the air, which poses serious problems for thermodynamic studies of such alloys.

The first measurements of alloys based on the (Li + Zn) system were initiated in 1931 by Fraenkel and Hahn [56], who determined the *liquidus* and *solidus* lines of the (Li + Zn) system for the concentration range of (60 to 100) at.% Zn by using thermal analysis. They found that the intermetallic phase Li_2Zn_3 has a wide homogeneity range. In 1933, Grube and Vosskühler [57], and in 1934, Baroni [58], with the use of the thermal and X-ray analyses established the existence of the intermetallic phases such as Li_2Zn_3 and LiZn_4 , which were both stoichiometric. They noticed the presence of three high temperature phases: $\beta\text{Li}_2\text{Zn}_3$, $\beta\text{Li}_2\text{Zn}_5$ and βLiZn_4 , two infinitely dilute solid solutions: βLi and Zn, as well as five intermetallic phases existing at room temperature: LiZn , $\alpha\text{Li}_2\text{Zn}_3$, LiZn_2 ,

$\alpha\text{Li}_2\text{Zn}_5$ and αLiZn_4 . Next, in 1935, Zintl and Schneider [59] and later, in 1976, Schonemann and Schuster [60] corroborated the presence of the intermetallic phases mentioned above. Furthermore, Zintl and Schneider [59] confirmed that the βLiZn_4 phase has a compact hexagonal structure and the LiZn_2 phase has a narrow homogeneity range. The αLiZn_4 phase (with an oriented structure), was determined by Schonemann and Schuster in 1976 [60], as a result of a very slow cooling of the sample. Farrar and King [61] measured the solubility of Li in Zn at $T = 423$ K. The activity of Li in liquid alloys was measured for the concentration range between (70.37 and 99.26) at.% Zn at $T = 773$ K by Hoshino *et al.* [62] in 1973, and also by Moser *et al.* [63] in 1986, over the whole concentration range at $T = 803$ K to $T = 833$ K, as well as by Gąsior and Moser [64] in 1993, within the concentration range between (0.12 and 0.975) at.% Zn at $T = 733$ K to $T = 850$ K. All the results of the activity of Li in liquid alloys were in good agreement. In 1989, Moser *et al.* [65] defined the mixing enthalpies of liquid (Li + Zn) alloys over the whole concentration range and at three different temperatures: (816, 818 and 820) K by means of calorimetric methods. Pelton [66], and Liang *et al.* [67] optimised the phase diagram of the (Li + Zn) system.

1.4. (Al + Li + Zn) system

Research on the (Al + Li + Zn) system was initiated by Weisse *et al.* [68] in 1942, who defined the temperature and the triple eutectic in the Zn corner. Later Badaeva and Sal'dau [69], with the use of thermal and microscopic analysis, confirmed the existence of two triple intermetallic compounds τ_1 and τ_3 in the (Al + Li + Zn) area. In 1964, Cherkashinn *et al.* [70] proved the existence of τ_1 phase and determined its homogeneity range. However, while finding the τ_1 phase, which is actually in equilibrium with the Zn phase, the authors [70] missed the τ_3 phase. Next, in 1987, and 1989,

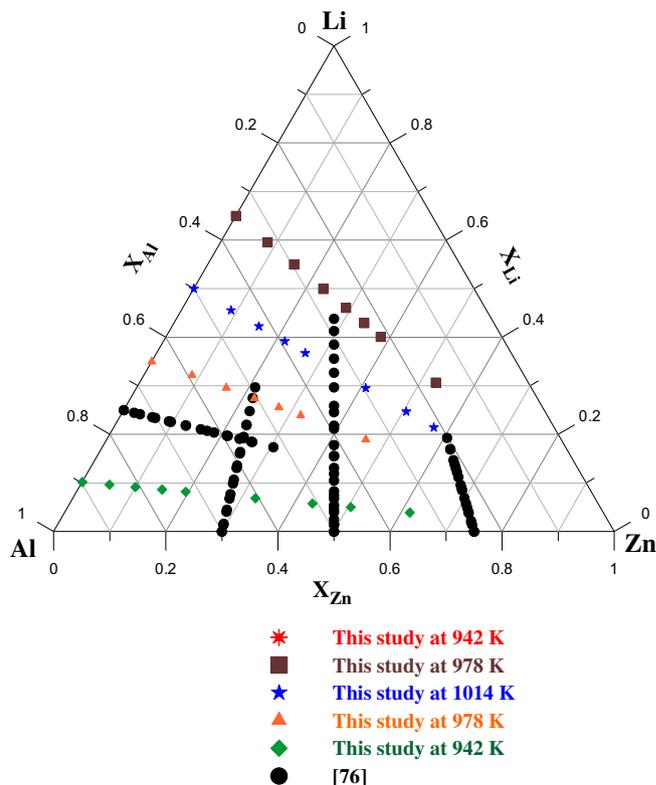


FIGURE 1. Points corresponding to compositions studied by Kim and Sommer compositions [76].

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