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Thermodynamic properties of liquid Ag-Li alloys

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ABSTRACT

The electrochemical concentration cell method was used in the measurements of the activities of Li in the Ag-Li liquid and solid alloys. Activity measurements were performed with the use of electrochemical cells with liquid LiCl-LiF and LiCl-KCl electrolytes for 9 alloys in the x_{Li} concentration range from 0.1 to 0.9 and at temperatures between 643 K and 916 K. The linear temperature dependencies of EMF of the Ag-Li alloys were observed and described by the equation $EMF(T) = a + bT$. The calculated partial thermodynamic functions of Li showed negative deviations from the ideal behaviour. With the application of all the available literature thermodynamic data, the interaction parameters of the Redlich-Kister equation for the liquid Ag-Li phase were worked out with the use of the least square method. The partial and integral Gibbs energies, entropies and enthalpies were calculated and presented in tables and figures. Additionally, the concentration-concentration partial structure factors for the ideal and real Ag-Li solutions were calculated and graphically presented.

1. Introduction

Silver-lithium alloys with a high concentration of lithium are not currently used by the industry in substantial quantities, due to their high reactivity with water (water vapor) and air. However, there is an important group among the silver brazing alloys of the Ag-Cu type which additionally contains lithium. They are used mainly for brazing without a flux, in controlled reduction atmospheres and in vacuum to obtain high quality connections of nickel-chrome and chrome stainless steels [1]. In the literature, one can find information on the study of the influence of small amounts of silver, lithium or both on the high temperature mechanical properties, corrosion resistance and castability of magnesium alloys which could be used as constructional materials. The knowledge of the thermodynamics of the Ag-Li system is important for the modeling of the thermodynamic properties of high order systems, the studies of the correlation between the physical and the thermodynamic properties and also for the prediction of the physical properties of liquid solutions, for example, the surface tension or viscosity.

The investigations of the Ag-Li system were initiated in 1930 by Pastorello [2,3], who used thermal and X-ray analyses. As a result, a phase diagram was proposed with two intermetallic phases, AgLi and $AgLi_3$, melting incongruently at 723 K and 955 K respectively. Freeth and Raynor, in 1954 [4], on the basis of the results of the thermal and X-ray analyses of alloys composed of high purity Ag and Li, proposed a completely different Ag-Li phase diagram, which has, ever since, been commonly accepted (Fig. 1).

The main differences between the phase diagram by Pastorello [2,3] and that by Freeth and Raynor [4] concerned the number of intermetallic phases and the liquidus and solidus lines. Pastorello [2,3] proposed the existence of two intermetallic compounds: AgLi and $AgLi_3$, melting congruently at 960 °C and 450 °C, eutectic transitions at 609 °C (x_{Li} = 0.28), 412 °C (x_{Li} = 0.7) and 180 °C (x_{Li} = ~1) and, in consequence, completely different liquidus and solidus lines in comparison to those by [4] (Fig. 1).

Based on the results of the microstructure, X-ray and thermal analysis investigations [4], it was suggested that the region of γ-brass should be divided into three γ_1, γ_2 and γ_3 separate phases. The concentration of the γ_3 phase in the homogeneity range was established between 63 and 73 at.% Li, that of the γ_2 phase – between 73 and 83 at.% and that of the γ_1 phase – between 87 and 93 at.% Li, all at 0 °C. Additionally, the β intermetallic phase was proposed instead of the AgLi intermetallic compound, as well as the (Ag) α and (Li) δ solid solutions: Li in Ag and Ag in Li, respectively.

The structure of the solid Ag(α) was analysed by Perlitz [5]. The lattice parameters were measured by Firth et al. [6] and by Kellington et al. [7], while Ruppersberg [8] and Migge and Andresen [9] studied the short range ordering in the Ag-Li alloys. In 1972, Arnberg and Westman [10,11] made an attempt to find the structure

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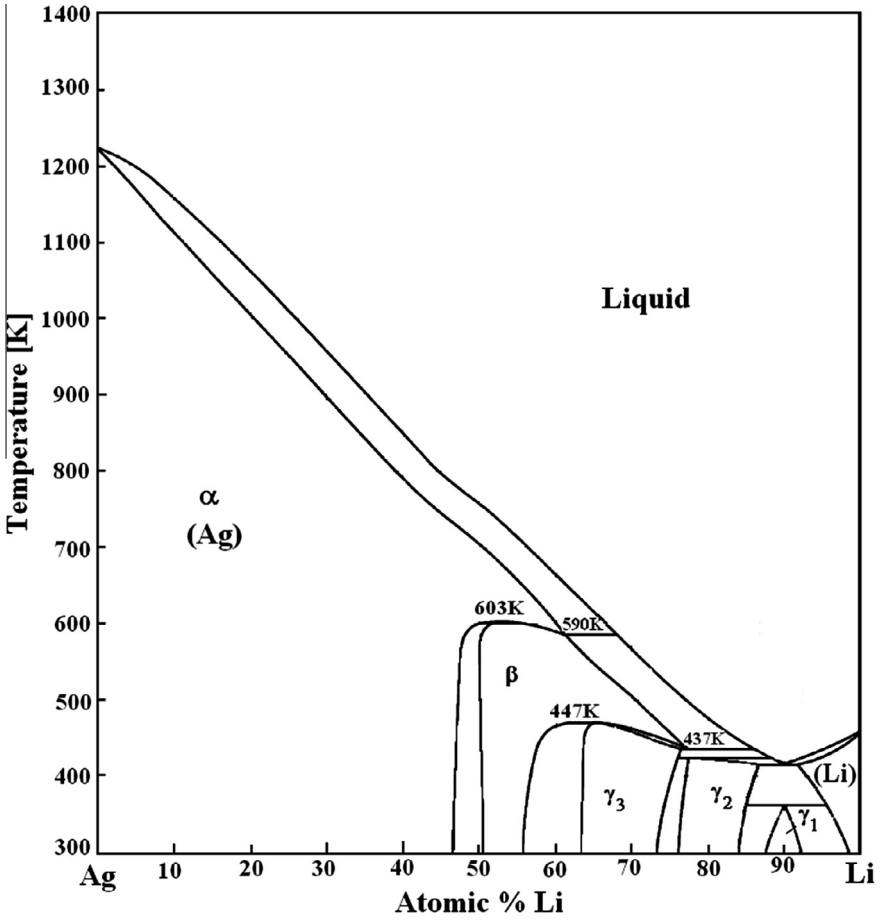

Fig. 1. The Ag-Li phase diagram proposed by Freeth and Reynor [4].

of the γ_3 phase ($Ag_{30.2}Li_{69.8}$) using X-ray phase analyses. Noritake and co-workers, in 2007 [12], on the basis of the Rietveld structure analysis, determined the structure of the γ-brass of $Ag_{36}Li_{64}$.

The phase diagram proposed by Okamoto [13] was practically the same as that proposed by Freeth and Raynor [4]. Pelton [14] presented an Ag-Li phase diagram based on calorimetric measurements, which concerned only the liquidus and solidus calculations. They adopted the results of the enthalpy of formation of liquid and solid alloys obtained by Predel et al. [15] at T = 1250 K and 623 K, respectively. Both the liquid or solid alloys were assumed to be regular solutions. It was practically impossible to calculate the equilibrium lines for the Ag-Li phase system with such an assumption.

The only EMF data for the liquid alloys at 830 K by Becker et al. [16] were published in 1981. They were applied, together with the earlier study of the Ag-Li system, by Wang et al. [17] for a new elaboration of thermodynamic properties and phase equilibria calculations. Before the publication of [17], in 2015, Dębski et al. [18] published the mixing enthalpy of the liquid Ag-Li alloys by means of drop calorimetry at two different temperatures, 1253 K and 873 K, in the whole concentration range.

Taking into consideration the very limited number of investigations of the Ag-Li system, especially of its thermodynamics, the authors concentrated on the activity measurements of the liquid and solid Ag-Li alloys (in the limited concentration range for the sake of the temperature range of the study) and used them, together with the earlier experimental calorimetric and EMF data [15,16,18], for the optimization of the thermodynamic functions of the liquid solutions.

2. Experimental

The electrochemical concentration cell, used for the investigation of the thermodynamic properties of the Ag-Li alloys, is schematically presented in Eq. (1) and shown in Fig. 2.

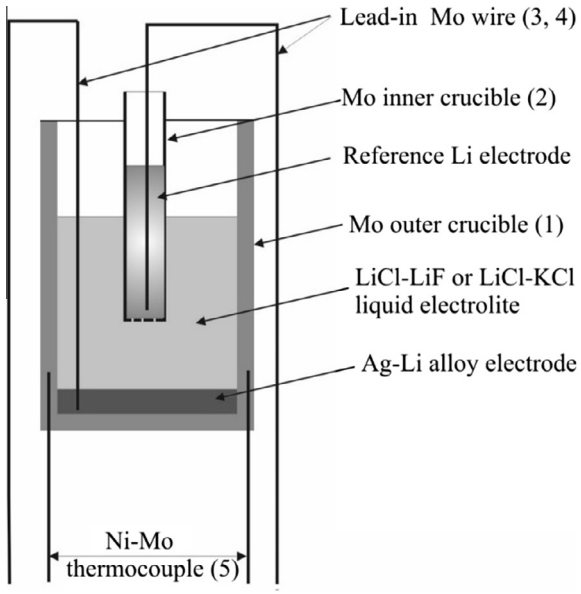

Fig. 2. The construction of the concentration cell for the electromotive force measurements of Ag-Li liquid and solid alloys.