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Review

Of the PhD thesis of MSc Marcela Trybuła

" Thermodynamic, structural and thermophysical properties of liquid Al-Li-Zn alloys"

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The doctoral thesis was completed at the Institute of Metallurgy and Materials Science of the Polish Academy of Science in Cracow within the "Interdisciplinary PhD Studies in Materials engineering with English as the language of institution" co-financed by the European Union within the European Social Fund. Some research were performed at the Institute of Technology in Grenoble. The thesis was supervised by prof. Władysław Gąsior from Cracow and prof. Alan Pasturel from Grenoble as well as dr Przemysław Fima and prof. Noel Jaksee as assistant supervisors. The research presented in this thesis focus on the description of liquid Al-Li-Zn alloys and involve both experiments and simulation. I assume, that prof. Gąsior and dr Fima supervised the experimental part of the research, whereas prof Pasturel and Jaske, the theoretical one.

The thesis consists of 10 chapters, the list of publications, 3 appendixes and summaries in Polish and French. List of references contains 197 items. Results obtained by the author are presented in 31 figures and 11 tables.

In the introduction, the Author outlines the role of the knowledge of thermophysical, physical and structural properties and relationships between them in understanding the properties of liquid metals, as they reflect in the liquid to solid phase transformation and characteristics of solid metals. Than the scope of the thesis is presented which covers the determination of thermophysical, physical and structural properties of liquid Al-Li-Zn alloys using a variety of experimental and computational methods, such as: the galvanic cell method,

the draining crucible method, *ab initio* calculations, classical molecular dynamics and semi-empirical methods.

In the next chapters the Author presentes fundamentals of thermodynamics of metallic solutions, thermodynamic functions, types of solutions and relations between thermodynamic and structural or thermophysical properties. Moreover, the available information about the Al-Li-Zn system and binary systems constituting the investigated ternary system is presented. Al-Li and Li-Zn systems indicate the negative deviation from the Raoult's law, due to the large number of intermetallic compounds, whereas the positive deviation from the Raoult's law suggests the miscibility gap in Al-Zn alloys. In the Al-Li-Zn system, three ternary compounds $\rho - Li_{26}Al_6(Zn_{1-x}Al_x)_{49}$ and $\gamma - LiAlZn_3$ and a stable phase τ- Li_3ZnAl_5 in the solid phase and short range ordering in the liquid phase are reported. The number of available thermodynamic experimental data is limited (only mixing enthalpy measured by the calorimetric method) and there is no evidence of any structural and physicochemical data.

Therefore, the aim of this work was to determine experimentally density, viscosity and surface tension by the draining crucible method (DC) and Li activity by the emf method and, compare the experimental values with the calculated ones. This procedure proved the stated hypothesis that *" Associates related to intermetallic phases in the Al-Li-Zn system affect the thermodynamic, structural and thermophysical properties of the liquid phase"*

Experiments performed by the galvanic cell method and the draining crucible method and the data analysis are outlined in chapter 5 whereas results and discussion in chapter 8. The emf measurements were performed for three cross-section of the constant mole fractions ratio of Al to Zn, namely 3, 1 and 0.136 at the temperature range from 793 to 1021 K. The Li activity calculations followed by the determination of the ternary interaction parameters in the Redlich–Kister equation, excess Gibbs energy, mixing enthalpy and entropy calculations were performed twice, on the basis of the literature data and the experimental data obtained within this thesis. In all cases the model that includes ternary interaction, that has been proposed by the Author, better describes the experimental results. The S-shaped dependencies of activity and partial excess Gibbs energy of lithium versus Li concentration (for cross sections equal 3 and 1) indicate the tendency of compound formation in the solid state and associate forming tendency in the liquid state. The position of the inflection point indicates that the stoichiometry of the compound corresponds to one of the τ- Li_3ZnAl_5 or $\rho - Li_{26}Al_6(Zn_{1-x}Al_x)_{49}$ phases. The lack of S-shaped dependency for the third cross-section ($x_{Al}/x_{Zn} = 0.136$) suggests the lack of associates in the liquid alloy of the composition corresponding to the $\gamma -$

$LiAlZn_3$ phase. It indicates that τ- Li_3ZnAl_5 or ρ – $Li_{26}Al_6(Zn_{1-x}Al_x)_{49}$ phases may be the most energetically favored.

Three thermophysical properties: density, surface tension and viscosity were determined for three liquid alloys. The chemical composition of these alloys corresponds to three intermetallic phases ρ – $Li_{26}Al_6(Zn_{1-x}Al_x)_{49}$, γ – $LiAlZn_3$ and τ- Li_3ZnAl_5. The dependencies of these properties on temperature and alloys' content were analyzed. Experimental data of the surface tension were compared with the ones calculated on the basis of the Butler model. Better agreement between calculated and experimental data was observed when ternary parameters determined within this thesis were applied.

Computational methods applied within this thesis are presented in chapter 6 whereas physical properties models in chapter 7. Results of simulations of chemical short-range ordering, viscosity and diffusivity modeling presented in chapter 8 are compatible with the experimental data. Chapter 9 includes conclusions and chapter 10 references.

Editorial remarks

1. The dissertation is written in English. Although the Author is not a native speaker of English, the dissertation is well written, both from the linguistic and pertaining to the content points of view. Gramatical mistakes such as the lack of articles or Polish words order that occur in the PhD thesis do not lower the overall quality of dissertation
2. Symbols in Figure 3.1 (τ_1, τ_2, τ_3) do not correspond with the description in text (τ, ρ, γ)
3. The description in Figure 5.1 is not clear, some descriptions are numbered and some are not and. What is more, the word "wire" substitutes for "thermocouple", whereas both words are not synonymous.

Merits:

1. The justification why the Al-Li-Zn system was chosen for examination is not sufficient. The statement that it "remains a mystery until today" is very nice, but not convincing enough.
2. The reason why the Bi, $Li_3Bi_{(l)}+Li_3Bi_{3(s)}$ |9LiCl-LiF)$_{eut}$| Al-Li-$Zn_{(l)}$ galvanic cell is used for lithium concentration from 0.1 to 0.4 and $Li_{(l)}$ | (LiCl-LiF) | Al-Li-$Zn_{(l)}$ for Li concentration from 0.5 to 0.9 is not explained.
3. The draining crucible method was tested on pure aluminum to obtain DC method parameters, but there is no information which parameters were obtained–page 22

4. The second similarity arising from thermodynamic and structural analysis of Al_5Li_3Zn and $AlLiZn_3$ alloys is presented in reference 180, but to my mind, it might be presented in the thesis as well.
5. It seems to me, that diffusion is induced by the gradient of chemical potential. The statement presented on page 44, that diffusion is induced by the gradient of concentration is a kind of simlification.

MSc Marcela Trybula submitted the doctoral thesis in which she presented a broad description of ternary liquid Al-Li-Zn alloys. This description is based mainly on the results of experiments performed by the author and on theoretical calculations and simulations. The obtained results will significantly contribute to the complete multi-scale description of these alloys. The dissertation fulfills the requirements of the Act of 14th of March 2003 on academic degrees and academic title and degrees and title in the scope of art (J. of Laws no 65 item 595) and I apply to admit MSc Marcela Trybyła to the public defense of the thesis and further stages of the dissertation process.

Moreover, I would like to emphasize the broad scope of the research work presented in the thesis. The pioneering measurements of density, surface tension, viscosity and activity in Al-Li-Zn alloys were followed by the extensive theoretical analysis performed by many techniques: classical molecular dynamics, *ab initio* calculations, analysis of chemical short-range order, surface tension and viscosity modeling (three models). The presentation of results is followed by the detailed discussion. The results of experimental work and theoretical calculations fully support the accepted hypothesis and are a significant contribution to the multi-scale description of this alloy. In my opinion, this is an excellent scientific research material, well written, logically organized and clearly presented in English, despite the fact, that it is not the native language of the Author. What is more, the scope of the thesis is extensive. Therefore, I would like to recommend this thesis to be awarded with distinction.

Jolanta Romaniec