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Czestochowa, 27.04.2015

R e v i e w

of a doctoral thesis by MSc Marcela Trybuła:

„Thermodynamic, structural and thermophysical properties of liquid Al-Li-Zn alloys”.

The review was prepared upon a request of Director of the Aleksander Krupkowski Institute of Metallurgy and Materials Science, Polish Academy of Sciences in Kraków, prof. dr Paweł Zięba, enclosed in formal letter N^o IMIM/DP/728/2015, sent on 16.03.2015.

1. General evaluation.

The thesis is focused on the thermodynamic properties of ternary systems, with particular emphasis on analyzing the influence of ternary interactions, which in the thesis are connected to the existence of so-called “associates” and their influence on the thermodynamic, structural and termophysical properties of three investigated alloys Al-Li-Zn. These alloys may find potential application as hydrogen storage metallic materials for ecological energy sources and further applications in light metals industry, such as aerospace or automotive industries.

The investigated alloys are an interesting research subject due to the existence of three intermetallic phases, only partially investigated in the liquid state and phase transitions. The aims of the thesis have been achieved by complex experimental investigation and numerical calculations starting from macroscopic size and coming down to the atomic level, which allowed the Author to obtain interesting and innovative results, concerning the liquid phase of the Al-Li-Zn alloys.

Therefore, I state that the thesis under review presents original research and is characterized by a high level of complexity. The research methods applied are adequate

for the undertaken scientific problem. The scope of research performed within this thesis corresponds to that usually present in doctoral dissertations.

The thesis should be qualified as basic research, however, the obtained results may find practical applications. It is important to note the diversity of applied theories, which provide complementary results. These allowed the Author to fully characterize the close-range ordering phenomenon in liquid Al-Li-Zn alloys. An important point in the doctoral thesis was the development of ternary interaction parameters, based on measurements of electromotive force and calorimetric measurements taken from the literature. These parameters were applied for the Redlich-Kister-Muggianu (RKM) equation, which allowed to reproduce the experimental mixing enthalpy values obtained by Kim and Sommer with high accuracy.

Within the thesis, the remaining molar functions were determined: Gibbs energy and entropy, which later are used by the Author for surface tension and viscosity determination, respectively. An important positive aspect of the thesis is the confrontation of each investigated quantity with available literature data and the results obtained using semiempirical thermodynamic models, and molecular dynamics (MD and AIMD) simulations. Each of the considered quantities is also discussed in relation to the undertaken scientific problem, which raises the importance of the thesis and shows that there exists a correlation between the properties and that the Author perfectly understands the scientific problem, at the same time being able to explain it clearly. A good example is the confrontation of viscosity or surface tension measured within the doctoral thesis to the values obtained using semiempirical thermodynamic models as well as MD and AIMD simulations. A further advantage of the performer investigation is the comparison with pure metals and reference binary alloys: Al-Li, Li-Zn and Al-Zn.

An important element of the thesis is the computation of self-diffusion coefficients which are difficult to determine experimentally for pure elements, but even more problematic in the case of binary and ternary systems. Their discussion with previously computed viscosity and structural properties allows to understand and explain the interesting observations emerging from chemical and topological short-range order analysis performed for three Al-Li-Zn alloys, which are correctly discussed in the last part of the thesis. It is important to note that, performing three-dimensional pair analysis and Voronoi analysis, the Author has found dominant contribution of icosahedral short-range order in ternary liquid alloys in comparison to pure liquid aluminium (Jakse and Pasturel data) as well as binary Al-Zn alloys. Whereas, for two remaining binary systems, i.e Al-Li and Li-Zn this tendency is

less pronounced. The last aspect to be mentioned in general evaluation is that the thesis was prepared within a project co-financed by the European Union and in cooperation with a French research team (University of Grenoble, France). It also received support within Preludium and Etiuda programmes financed by the National Science Centre. Therefore, it can be presumed that the obtained results were discussed and presented in wider research teams.

2. Detailed evaluation.

The doctoral thesis under review consists of 10 chapters, including the bibliography. Apart from these, it also includes three annexes. Generally, the thesis can be divided into four main parts.

The first part concerns:

- general review of the literature, including an essential outline of the physicochemical properties examined within the doctoral thesis (density, viscosity and surface tension), thermodynamic and structural properties;
- an introduction to the thermodynamics of metallic solutions, including the definition of interaction parameter and characteristics of solutions according to their deviations from Raoult's law;
- brief and concise characteristics of liquid Al-Li-Zn alloys (chapter 3), introducing the reader to the gaps in the existing literature concerning the Al-Li-Zn alloys.

It is important that in this part, the Author has underlined the presence of three identifiable intermetallic phases in the Al-Li-Zn system, mentioned by previously cited authors. **The state of knowledge presented in this part of the thesis indicates the timeliness of the undertaken topic, the desirability of the research and correct selection of research methods used in the dissertation.**

The second part (chapter 4) presents a clearly formulated thesis, which was stated by the Author basing on the previously presented state of knowledge and detailed aims of the thesis, enabling to verify the stated thesis. **I state that the thesis and aims formulated by the Author present high scientific value and contain an innovative connection of experimental and computational investigations. The scope of undertaken research is very ambitious.**

In the third part (including chapters 6 and 7), the Author described the experimental methods: the concentration cell method – for the electromotive force measurement, the draining crucible method as well as classical and *ab initio* molecular dynamics. Each of the applied methods was described precisely, but without going into too much details, which are well

described in the appended bibliography. The molecular dynamics methods are presented concisely and in accessible language. The third part also presents a wide range of theories, used by the Author to analyze the structural and thermophysical properties. In the end of the third part (chapter 7), the Author presents semiempirical models used for estimating surface tension and viscosity of liquid binary alloys and extension of these models to ternary alloys. The last, fourth part of the thesis (chapter 8), describes the obtained results, both experimental and computational. It is divided into subchapters, introduced by short overview passages for the discussed analyses. First, the results of electrochemical measurements were presented, providing a thermodynamic characteristics of the liquid alloys for three Al/Zn molar fraction ratios (3, 1 and 0.136) and compared to literature data. Next subchapter (8.2) concerns physicochemical properties (density and surface tension). Subchapter (8.3) contains a complete analysis of structural properties of three liquid Al-Li-Zn alloys, including the description of chemical and topological short-range ordering. Subchapter (8.4) is devoted to the analysis of transport properties (viscosity and diffusion). The last subchapter (8.5) summarizes the most important conclusions drawn from the analyses presented earlier, which finally lead to the statement that the hypothesis was proven. Chapter 9 is a short and concise summary of the thesis, containing the most important general conclusions drawn from the research.

3. Critical and polemic remarks

The thesis is written clearly and communicatively, the graphical layout and text editing are attentively done and minor spelling, style and language errors do not diminish the significance and readability of the thesis. The editorial remarks were given to the author, but they do not influence the highly positive grade of the thesis. The main editorial remarks include:

- Using various fonts e.g. for the designation of ternary Al-Li-Zn alloys, sometimes marked as functions or as names, particularly in the part concerning structural properties analysis,
- the fonts in some graphs are too large, e.g. radial distribution function for the gamma phase, and of variable size, e.g. Figure 8.4, 8.10 and 8.11.

The issues that should be explained by the Author during public defense, are:

1. Why the computations were performed for only one temperature? This has not been satisfactorily explained in the Discussion chapter.

2. What kinds of ordering exist in liquid metallic solutions? Is medium- or long-range ordering possible? Can the icosahedral short-range ordering in liquid be connected to diffusion and viscosity and why is it so important?
3. Please explain the selection of thermodynamic viscosity models.
4. How can we assess the usefulness of the obtained results for the applications briefly mentioned in the thesis?

4. Conclusion

To summarize, I think that the thesis presented for review is an individual solution of a complex research problem of a basic and utilitarian nature. The Author has made an **original contribution to the field of multicomponent system thermodynamics** and the obtained results are of high cognitive and partially practical value. Taking the above into consideration, **I state that the doctoral thesis of MSc Marcela Trybula 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 Trybula to the public defense of the thesis and further stages of the dissertation process.**

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