INTRODUCTION

Phase diagrams are the most concise representation of a given system, and are crucial for understanding phase transformations, interfacial reactions, solidification and related changes in microstructure. Therefore, they are essential for the development of new multicomponent materials. Phase diagrams are determined by experimental methods such as: thermal analysis, microstructure examination, pressure measurements and others. However, the experimental determination of phase diagrams is a time-consuming and costly task because the number of possible systems increases drastically with the number of elements. Experimental information for entire phase diagrams is available for most of the binary systems, but experimental information becomes increasingly sparse as the number of constituent elements increases (for ternary, quaternary and higher order systems) [1]. In this context, it is useful to estimate thermodynamic data of multicomponent systems from the constituent binary systems.

There are many methods of modelling thermodynamic properties and calculations of phase diagrams in complex systems on the basis of thermodynamic properties of binary alloys constituting the complex alloy. Geometrical models and thermochemical model may be used for prediction of excess Gibbs energies of a ternary homogenous solution from the corresponding binary data.

Methods of extrapolating thermodynamic properties of alloys into multicomponent systems are based on the summation of the binary and ternary excess parameters. The formulas for doing this are based on various geometrical weightings of the mole fractions. Binary compositions are chosen by using geometric correlations in the isothermal Gibbs triangle. Typically, the binary compositions are obtained from the intersection of an isogram, passing through the ternary composition of interest and the sides of the triangle. An isogram is a line of constant value of a given quantity, such as mole fraction, mole fraction ratio or mole fraction difference [2].

Geometrical models can be divided into symmetric and asymmetric ones. Models proposed by Kochler, Colinet, Muggianu et al., Jacob et al., Chou, Malakhov et al. and Ganesan et al. are of the symmetric type, whereas those proposed by Toop, Hillert and Li are asymmetric (Figure 1) [2].

The models proposed by Kohler, Colinet, Muggianu et al. and Jacob et al. are basic models and they use only fundamental isograms of similar nature. In a ternary i-j-k system isogram is a line passing through the ternary point of interest. Other models are combinations of these basic models, except the Malakhov’s model in which binary compositions are obtained from the circular arc, whereas in other models straight lines are used for this purpose. The ternary excess Gibbs energy is calculated as a sum of binary excess energies multiplied by weighting factors $\omega_{ij}$.

$$\Delta G_{\text{ex}} = \omega_{ij} \cdot \Delta G_{i} + \omega_{jk} \cdot \Delta G_{j} + \omega_{ik} \cdot \Delta G_{k}$$  (1)

The weighting factor $\omega_{ij}$ is given by:

$$\omega_{ij} = \frac{N_i \cdot N_j}{x_{i(j)} \cdot x_{j(i)}}$$  (2)

Where $N_i$ is the ternary mole fraction of component $i$ and $x_{i(j)}$ is the binary mole fraction of component $i$ in the $i-j$. Compositions of binary alloys are chosen using the models presented above.

The other approach is a semi-empirical Calphad method [3, 4]. It is a combination of experimental observation and theoretical modelling and depends on the quality of available experimental data. This approach is based on the modelling multicomponent systems starting from pure components followed by the more complex ones (binary and ternary). The basic mathematical method is a minimization of the Gibbs energy for a given temperature, pressure and overall composition. This approach is common to all currently available software packages for the modelling thermodynamic properties and phase diagrams of multicomponent systems [5].
This paper presents a numerical approach to modelling ternary Al-Ni-Zr system on the basis of thermodynamic properties of binary systems included in the investigated ternary system. The idea of predicting \( \Delta G_{ij} \) values is regarded as calculation of values of \( \Delta G \) function inside a certain area (a Gibbs triangle) unless all boundary conditions, that is values of \( \Delta G \) on all sides of the triangle, are known (\( \Delta G_{ij}, \Delta G_{ik}, \Delta G_{jk} \)). This approach is contrary to finding a function value outside a certain area, if the function value inside this area is known (this issue is well known in mathematics). In this approach, values of excess Gibbs functions for all concentrations of binary alloys are taken into consideration, not only the selected ones and there is no problem with choosing binary mole fractions and proper weighting, unlike in geometrical models. In this approach, weighting of each mole fraction is the same. This model was successfully applied to Cu-Sn-Zn and Bi-Cu-Ni alloys [6] and results stay in a good agreement with the values obtained by the Calphad method.

**Calculations**

The excess Gibbs energy \( \Delta G \) describes the influence of non-ideal mixing behaviour on the thermodynamic properties of a solution phase. The Muggianu [7] extension of the Redlich-Kister formalism [8] is a widely accepted description of the excess Gibbs energy:

\[
\Delta G = x_1 x_2 \sum_{i=0}^{m} \Delta L_i (x_i - x_i')^2 + x_1 x_2 \sum_{j=0}^{m} \Delta L_j (x_j - x_j')^2 + \sum_{i,j,k=0}^{m} \Delta L_{ijk} (x_i x_j x_k) + z = 0, 1, \ldots, m, \tag{3}
\]

where \( \Delta L_{ij} \) are binary and \( \Delta L_{ijk} \) is ternary temperature dependent on interaction parameters optimized on the basis of the available thermodynamic and phase diagram data.

\[
\Delta L_{ijk} = x_1 \Delta L_{ijk} + x_2 \Delta L_{ijk} + x_3 \Delta L_{ijk} \tag{4}
\]

Usually, binary systems are well investigated, so that \( \Delta L_{ij} \) parameters are known, but as not many ternary alloys have been investigated, so \( \Delta L_{ijk} \) parameters for many systems are unknown.

If the formula (3) and \( \Delta L_{ijk} \) parameters are known, the idea of calculating \( \Delta L_{ijk} \) parameters can be regarded as solving an equation (3), when all boundary conditions (binary alloys) are known. The approach proposed in this paper is as follows: if all boundary conditions, that is values of excess Gibbs functions on all sides of the Gibbs triangle (bold line) and for the corresponding point of the inner triangle (dotted line) (see Figure 2).

\[
\Delta G = \Delta G_{ij} \quad \text{for} \quad x_i = 0.1 \quad \tag{5}
\]

\[
\Delta G = \Delta G_{ij} \quad \text{for} \quad x_j = 0.1 \quad \tag{6}
\]

\[
\Delta G = \Delta G_{ij} \quad \text{for} \quad x_k = 0.1 \quad \tag{7}
\]

\( \Delta G_{ij} \) parameters were calculated numerically on the basis of this assumption using the Excel program and Solver. Thermodynamic parameters for binary alloys were accepted from Huang and Chang [9] for Al-Ni, Wang et al. [10] for Al-Zr and Wang et al. [11] for Ni-Zr.

Computations were performed using the Excel program and Solver. At first the \( \Delta G \) values on all legs of the triangle were calculated, and the concentration of the third component was 0. Next, an assumption was made that \( \Delta G \) value on the leg of the triangle and for the small concentration of the third component was the same. \( \Delta G \) was calculated on the basis of this assumption.

The concentration of the third component was assumed to be 0.1 mole fraction. In other words, \( \Delta G \) value was assumed to be the same for each point of the Gibbs triangle (bold line) and for the corresponding point of the inner triangle (dotted line) (see Figure 2).
Table 1. The calculated values of L parameters and the excess Gibbs energy

<table>
<thead>
<tr>
<th>x, Al</th>
<th>L_{AlNi} / J/mol</th>
<th>L_{AlNi} / J/mol</th>
<th>( \alpha G ) [J/mol] for ( x_{Al} = x_{Ni} = x_{Zr} = 1/3 )</th>
<th>( \alpha G ) [J/mol] for ( x_{Al} = x_{Ni} = 2/5, x_{Zr} = 1/5 )</th>
<th>( G^\alpha ) [J/mol] for ( x_{Al} = x_{Zr} = 1/10, x_{Ni} = 4/5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>-1.1·10^7</td>
<td>-4.3·10^6</td>
<td>-0.1·10^8</td>
<td>-4.0·10^7</td>
<td>3.3·10^6</td>
</tr>
<tr>
<td>0.02</td>
<td>-1.1·10^7</td>
<td>-3.6·10^6</td>
<td>-0.1·10^8</td>
<td>-3.8·10^7</td>
<td>3.1·10^7</td>
</tr>
<tr>
<td>0.03</td>
<td>-1.1·10^7</td>
<td>-2.8·10^6</td>
<td>-0.1·10^8</td>
<td>-3.6·10^7</td>
<td>3.0·10^7</td>
</tr>
<tr>
<td>0.04</td>
<td>-1.1·10^7</td>
<td>-2.1·10^6</td>
<td>-0.1·10^8</td>
<td>-3.5·10^7</td>
<td>2.9·10^7</td>
</tr>
<tr>
<td>0.05</td>
<td>-1.2·10^7</td>
<td>-1.3·10^6</td>
<td>-0.1·10^8</td>
<td>-3.3·10^7</td>
<td>2.7·10^7</td>
</tr>
<tr>
<td>0.06</td>
<td>-1.2·10^7</td>
<td>-4.5·10^6</td>
<td>-0.1·10^8</td>
<td>-3.1·10^7</td>
<td>2.6·10^7</td>
</tr>
<tr>
<td>0.07</td>
<td>-1.2·10^7</td>
<td>4.0·10^6</td>
<td>-0.1·10^8</td>
<td>-2.9·10^7</td>
<td>2.5·10^7</td>
</tr>
<tr>
<td>0.08</td>
<td>-1.3·10^7</td>
<td>1.3·10^6</td>
<td>-0.1·10^8</td>
<td>-2.7·10^7</td>
<td>2.3·10^7</td>
</tr>
<tr>
<td>0.09</td>
<td>-1.3·10^7</td>
<td>2.3·10^6</td>
<td>-0.1·10^8</td>
<td>-2.5·10^7</td>
<td>2.2·10^7</td>
</tr>
<tr>
<td>0.1</td>
<td>-1.3·10^7</td>
<td>3.3·10^6</td>
<td>-0.1·10^8</td>
<td>-2.3·10^7</td>
<td>2.1·10^7</td>
</tr>
</tbody>
</table>

Fig. 3. \( G_{AlNiZr} \) for \( x_{Zr} : x_{Ni} = 1:1 \) for different \( x_{Al} \) values

Fig. 4. \( G_{AlNiZr} \) for \( x_{Al} : x_{Ni} = 1:1 \) for different \( x_{Zr} \) values

Fig. 5. \( G_{AlNiZr} \) for \( x_{Zr} : x_{Al} = 1:1 \) for different \( x_{Ni} \) values

Fig. 6. Values of aluminium chemical potential in Al-Ni-Zr alloys

The results of calculations are presented in Figures 6-8.
CONCLUSIONS

The values of the excess Gibbs energy and chemical potentials of aluminum and zirconium in ternary Al-Ni-Zr alloys at 1273 K were predicted numerically for three cross-sections (x_{Zr}:x_{Ni} = 1:1, x_{Al}:x_{Ni} = 1:1, and for alloys with the following contents: x_{Al} = 1/3, x_{Ni} = 1/3, x_{Zr} = 2/5, x_{Ni} = 2/5, x_{Zr} = 1/5, x_{Al} = 1/10, x_{Ni} = 4/5, x_{Zr} = 1/10). The obtained values of the excess Gibbs energy do not change significantly with the change in the predicting procedure, namely the accepted x_i value, although values of $^1L$ and $^2L$ parameters change very much ($^1L$ from $-4.3 \times 10^6$ to $3.3 \times 10^6$ and $^2L$ from $-1.4 \times 10^7$ to $-5 \times 10^7$) for the $x_{Zr}:x_{Ni} = 1:1$, $x_{Al}:x_{Ni} = 1:1$ cross sections. The predicted values of chemical potentials change significantly with the change in the x_i value, along the examined cross-sections, especially for the small values of the third component.

The results obtained in this work will be used to model the diffusion process in the zirconium modified aluminide coatings, that is alloys of high nickel content and low zirconium and aluminum content. The smallest deviations of the predicted thermodynamic functions are present for these alloys.

ACKNOWLEDGMENT

This research was financially supported by the National Science Centre, Poland, project number 2011/01/ST8/05/036.

REFERENCES