CALCULATION OF THERMODYNAMIC PROPERTIES IN QUARTERNARY Ni-Cr-Co-Al SYSTEM

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Received 12 January 2011
Accepted 18 February 2011

ABSTRACT

The results of the calculation of thermodynamic properties in quaternary Ni-Cr-Co-Al system using general solution model are presented in this work. For twelve sections with different molar ratio of Cr:Co:Al investigated at a temperature of 2000K, integral molar excess Gibbs energies and activity coefficients for nickel were determined.

Keywords: thermodynamics of alloys, calculation, quaternary systems, Ni-Cr-Co-Al alloys.

INTRODUCTION

Alloys based on the Ni-Cr-Co-Al system [1-3] (Fig. 1) are of the great practical interest in the production of Ni-based super alloys, widely applied under high temperature conditions in different areas.

There are articles dealing with thermodynamics of Ni-Cr-Co-Al system [4, 5] and its phase equilibria [6,7], but still no complete thermodynamic data for that quaternary system in literature. The reasons are mainly difficulties in the experimental measuring, especially due to high investigation temperatures.

Having in mind the problems of a direct experimentation, there is a need for the application of theoretical calculations. The model developed for predicting thermodynamic properties of multicomponent systems from binaries, based on general solution model [8], was used for the thermodynamic calculations in the investigated Ni-Cr-Co-Al system, in order to give a contribution to the better knowledge of this system thermodynamics.

THEORETICAL FUNDAMENTALS

The general solution model for calculation of thermodynamic properties for ternary systems based on known binary thermodynamic data has been provided by Chou [9]. It breaks down the boundary between symmetrical and asymmetrical models, and has already been proved in some practical examples [10-12] as the correct and accurate model. This model has been derived for multicomponent systems [8] and it basic equations are given as follows [8]:

\[ \Delta G^E = \sum_{k=1}^{m} x_i x_j \left[ A_{ij}^{x} + A_{ij}^{y} \cdot ((x_i - x_j) + \sum_{k=1}^{m} A_{ik}^{y} x_k (2z_{ij} \xi_{ij}^{(k)} - 1) \right] \]  

(1)

where \( A_{ij}^{x}, A_{ij}^{y}, A_{ij}^{z} \) are regular-solution parameters for binary system \( ij \) independent of composition, only relying on temperature:

\[ \Delta G_{ij}^{E} = XX_{ij} \left( A_{ij}^{y} X_{ij} + A_{ij}^{z} (X_{ij} + X_{ij}^2) + \ldots + A_{ij}^{y} (X_{ij}^2) \right) \]

(2)

where \( X_{ij} \) and \( X_{ij} \) indicate the mole fraction of component \( i \) and \( j \) in \( ij \) binary system, expressed as:

\[ X_{ij} = x_i + \sum_{k=1}^{m} x_k \xi_{ij}^{(k)} \]

(3)

and where the coefficient signed as \( \xi_{ij}^{(k)} \) in Eq.(1) presents the similarity coefficient of component \( k \) to component \( i \) in \( ij \) system, defined as:
where \( h(ij,ik) \) is the function related to the excess Gibbs free energy of \( ij \) and \( ik \) binaries, given as:

\[
\eta(ij,ik) = \int_{X_i=0}^{X_i=1} (\Delta G_{ij}^E - \Delta G_{ik}^E)^2 \, dX_i \quad .
\]  

In all equations given, \( \Delta G^E \) and \( \Delta G_{ij}^E \) respond to the integral molar excess free energies for multicomponent and binary systems, respectively, while \( x_i, x_j, x_k \) respond to mole fraction of components in investigated multicomponent system.

**RESULTS AND DISCUSSION**

The thermodynamic calculations in the quaternary system Ni-Cr-Co-Al were carried out in twelve sections A-L, along the lines of a constant Cr:Co:Al molar ratio equal to A-8:1:1, B-6:2:2, C-4:3:3, D-2:4:4 (sections with constant ratio Co:Al=1:1), E-8:0.5:1.5, F-6:1:3, G-4:1.5:4.5, H-2:2:6 (sections with constant ratio Co:Al=1:3), and I-8:1.5:0.5, J-6:3:1, K-4:4.5:1.5, L-2:6:2 (sections with constant ratio Co:Al=3:1).

Data necessary for the calculation according to the Chou model [8] has been taken from the articles by Kaufman and Nesor [13-15]. The binary regular-solu-
Table 1. Binary regular-solution parameters for the constitutional binaries in the quaternary Ni-Cr-Co-Al system.

<table>
<thead>
<tr>
<th>System ij</th>
<th>$\Lambda_{ij}^c(T)$</th>
<th>$\Lambda_{ij}^t(T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Cr [13]</td>
<td>-8368</td>
<td>0</td>
</tr>
<tr>
<td>Ni-Co [13]</td>
<td>3347</td>
<td>0</td>
</tr>
<tr>
<td>Ni-Al [15]</td>
<td>$-147728.5-134.178T+0.13924T^2-2.7313 \times 10^{-5}T^3$</td>
<td>$-55647.5-3.972T$</td>
</tr>
<tr>
<td>Cr-Co [13]</td>
<td>-8368</td>
<td>0</td>
</tr>
<tr>
<td>Cr-Al [15]</td>
<td>-46442</td>
<td>0</td>
</tr>
<tr>
<td>Co-Al [14]</td>
<td>$-281347+118.003T$</td>
<td>$174264+0.379T+0.003612T^2$</td>
</tr>
</tbody>
</table>

Based on these starting data, similarity coefficients were determined by Eq.(4) and further calculations were carried out for 108 alloys in all of the selected cross sections in the investigated quaternary Ni-Cr-Co-Al system at the temperature of 2000K, according to the fundamentals of the general solution model, as was given by Eqs.(1-5). The results of the thermodynamic predictions including graphic illustration of the $\Delta G$ and $\ln \gamma_{Ni}$ are shown in Figs. 2 and 3, respectively.

Negative deviation from Raoult law was obtained for most investigated sections (Fig. 2), while the most
negative values of integral excess Gibbs molar energies, up to about -20 kJ/mol, were calculated for the section H. Only two sections - K and L, in the composition part with nickel molar content lower than 0.4, exhibit positive deviation from Raoult law. Described tendencies can be noticed similarly in ln $\gamma_{Ni}$ dependency on composition (Fig. 3). The results, obtained by calculation according to general solution model for multicomponent systems, indicate to prevalent existence of mixing tendencies between nickel and other three components in Ni-Cr-Co-Al system at investigated temperature 2000 K.

CONCLUSIONS

The calculation of thermodynamic properties in quaternary Ni-Cr-Co-Al system has been done applying general solution model for multicomponent systems. Based on starting thermodynamic data for constituent binary subsystems, the integral molar excess Gibbs energies were calculated in the whole system, in twelve section from its nickel corner. Obtained data showed mostly negative deviation from Raouls law, indicating to strong mutual mixing tendencies in the investigation system. Due to the fact that experimental determination at selected temperature is rather difficult and that there is a lack of relevant literature concerning that particular topic [16], these calculated results can be a good substitution for thermodynamic data of this multicomponent Ni-based system. That is more important, having in mind already proven accuracy of the model used in different cases, as cited in numerous literature works [17, 18].

Acknowledgements

The results of this paper are in the frame of Project OI 172037 financed by the Ministry of Science and Technological Development, Republic of Serbia.

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