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Verification of ab-initio mixing enthalpy using thermodynamic simulation of phase equilibrium and the temperature dependences of the heat capacity of the bcc Fe-Cr alloys

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Abstract. The paper deals with application of physical-empirical models for the thermodynamic description of the bcc Fe-Cr alloys and phase equilibrium, as well as prediction of behavior of the temperature dependences of the specific heat of alloys. This approach allowed performing verification of ab-initio calculations results obtained by different authors for the mixing enthalpy at 0K which were used to assess the chemical part of the mixing enthalpy. Analysis of calculated phase diagram fragments and the temperature dependences of heat capacities for two alloy compositions and their comparison with experimental data, has allowed us to estimate the degree of reliability of various approximations used in ab-initio calculations, and thereby realize their verification for further practical use.

1. Introduction

Ferritic steels are considered as promising for use as reactor fuel element cladding of the new generation IV, as well as the first wall of future fusion reactors. This is due to their low creep and good corrosion resistance at elevated temperatures [1]. Long duration of the material exploitation under irradiation and elevated temperatures is responsible for kinetic processes, due to diffusion, which lead to the changes of its structural and physical properties that in turn can lead to cracking and fracture of the material. For understanding the diffusion processes taking place in those materials is expedient to conduct the computer simulations. In its turn the suitable interatomic potentials (IP) which are used, for example, in the embedded atom model (EAM) are needed to simulate the kinetic processes. IP parameters are frequently calculated by fitting to the ab-initio calculations. The Fe-Cr system is a base for development of ferritic steels, therefore great attempts of obtaining reliable IP for ferromagnetic bcc Fe-Cr alloys are carried out for a long time. In recent 10 years ab-initio calculations of the mixing enthalpy (ΔH) of ferromagnetic bcc alloys at 0K were carried out in many works, see for example [3-5] and Figures 1 – 3. In particular, in the work [6] “a fitting” to values of ab-initio calculations of ΔH calculated in [4] was made for obtaining the IP.

Calculation of ΔH differs between ΔH obtained in [4, 6] and ΔH obtained in [3]. In this work, a verification of ab-initio calculations of ΔH conducted in [3-5] is carried out by the thermodynamical simulation.

2. Description of the model

According to [7], the Gibbs energy of mixing of bcc Fe-Cr alloys depending on composition and temperature without taking into account a short range order was formulated as a partition function of non-interacting subsystems:

$$^{\alpha\alpha}\Delta G^{\alpha}(x,T) = \Delta G^{\alpha}_{chem}(x,0) + \sum_{j}^{4} {}^{\alpha\alpha}\Delta G^{\alpha}_{j}(x,T) + RT\sum_{i}^{2} x_i \ln(x_i) \ , \quad (1)$$

where the molar mixing energy of bcc alloys is described with respect to the bcc phase of the pure components by the formula:

$$^{\alpha\alpha}\Delta G^{\alpha}_{j}(x,T) = G^{\alpha}_{j}(x,T) - \left((1-x)G^{\alpha}_{j,Fe}(T) + x\cdot G^{\alpha}_{j,Cr}(T)\right). \quad (2)$$

In the formulas (1) and (2) x is the mole fraction of Cr, T – temperature, R – the gas constant, j – index runs on all those non-interacting statistical subsystems: 1 - elastic, 2 - vibration, 3 - electronic and 4 - magnetic parts of the Gibbs energy of mixing.

$\Delta G^{\alpha}_{chem}(x,0)$ – the chemical part of the mixing energy at 0K was described as a difference between the free mixing energy of alloys calculated by ab-initio calculation at 0K and the energy sum caused by the static displacements of atoms from their ideal lattice nodes formulated in a frame of the elastic theory, and the magnetic part of the free mixing energy, see the following formula.

$$\Delta G^{\alpha}_{chem}(x,0) = \Delta H(x,0) - \Delta G_{elast}(x,0) - \Delta G_{mag}(x,0) \ . \quad (3)$$

Details of used physical - empirical models are described in [7].

3. Calculated results

The concentration dependencies of physical properties of bcc Fe-Cr alloys which were approximated according to experimental data of the alloys taken from literature, namely, heat capacity electronic coefficients, thermally expansion coefficients and the mean magnetic moments, Debye and Curie temperatures, were used for calculating the energy parts (2).

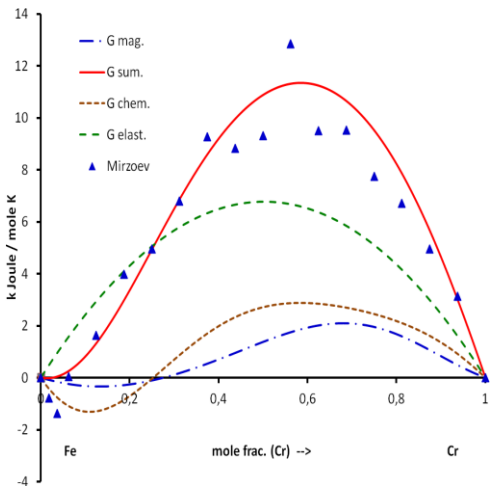

Figure 1. The calculated concentration dependences: ▲ - the mixing enthalpy ΔH of ferromagnetic bcc Fe-Cr alloys at 0K, according to [3]; G_{elast} - the energy of elastic distortions of the crystal lattice; G_{mag} , G_{chem} – the magnetic and the chemical energy parts.

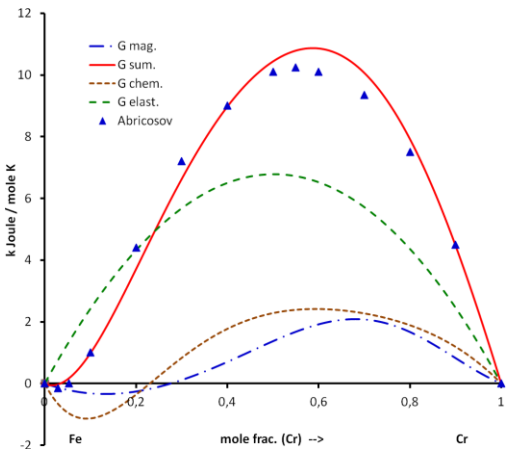

Figure 2. The calculated concentration dependences: ▲ - ΔH of ferromagnetic bcc Fe-Cr alloys at 0K, according to [4]; G_{elast} - the energy of elastic distortions of the crystal lattice; G_{mag}, G_{chem} – the magnetic and the chemical energy parts.

Calculated Gibbs mixing energy was used for calculation boundaries of bcc Fe-Cr alloys (a more detailed description is given in [7]) and the temperature dependence of the isobaric heat capacity. In contrast to the work [7], in this paper, various options to describe the enthalpy of mixing solutions, ΔH, obtained using ab-initio calculations by different authors: Mirzoev, Abrikosov and Korzhavyi [3-5] have been discussed.

The graphs of enthalpy of mixing alloys obtained by those authors and corresponding calculated mixing energy of chemical interaction, $\Delta G^{\alpha}_{chem}(x,0)$, are shown in figures 1-3. The bcc Fe-Cr alloy boundaries and spinodal line calculated in this work using different input data of enthalpy of mixing alloys ΔH at 0 K obtained in [3-5], are shown in Figure 4 in comparison with experimental data taken from [9-11].

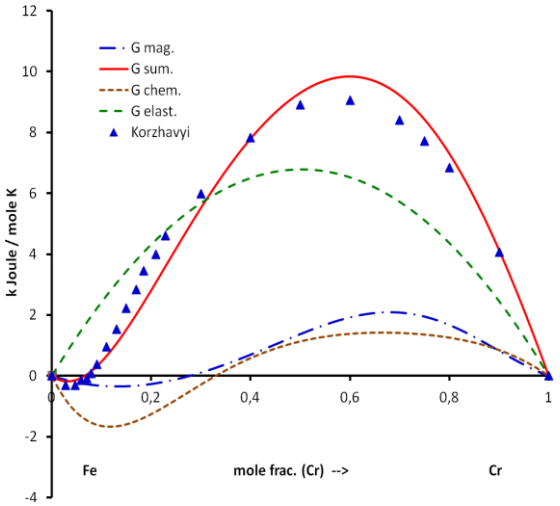

Figure 3. The calculated concentration dependences: ▲ - ΔH of ferromagnetic bcc Fe-Cr alloys at 0K, according to [5]; G_{elast} - the energy of elastic distortions of the crystal lattice; G_{mag}, G_{chem} – the magnetic and the chemical energy parts.

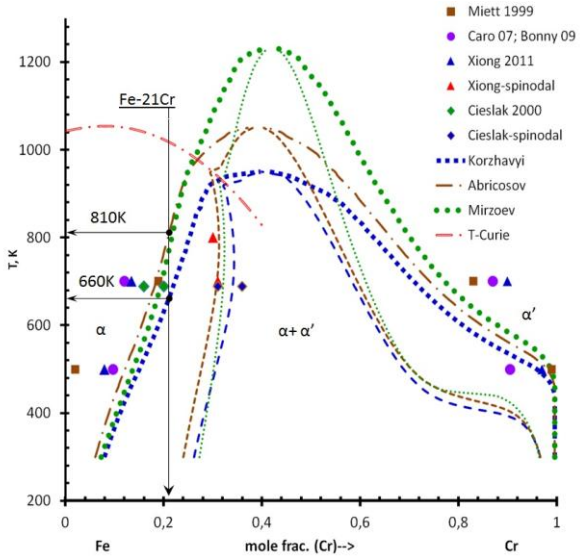

Figure 4. The calculated solubility and spinodal curve of bcc Fe-Cr alloys obtained by ab-initio calculations, shown in Figures 1-3, in comparison with the experimental data taken from [9-11]; the arrows show coordinates of configurational points of the Fe-21 at.% Cr alloy.

4. Discussion

The boundaries of bcc Fe-Cr alloys are shown in Figure 4 without the σ - phase which exist in the experimental phase diagram [8]. Namely, the upper part of the calculated phase boundaries, being above 748K is in a metastable state. If the $\Delta H(x,0\ \mathrm{K})$ dependence obtained by Mirzoev will be used for bcc Fe-Cr alloy boundary calculations then the critical point becomes above 1200 K and therefore the results of work [3] can not be considered as reliable evidence.

The critical point of the curve of bcc alloys boundary obtained by the data calculated in work [4] is about coincided with the critical point of the experimental diagram [8]. But because of the present the σ- phase in the equilibrium diagram such critical point location can not be trusted as well. Therefore, in our opinion, the data obtained in [5] should be preferred.

The calculated dependencies of isobaric heat capacity of Fe-6.7 at.% Cr and Fe-21 at.% Cr alloys are shown in Figure 5 in comparison with experimental data taken from [9]. The two-phase area (α+α') of the phase diagram is calculated by the formula (4) [12]:

$$C_p^{\alpha+\beta}(x,T) = \alpha(x,T)\left(C_P^{\alpha}(x^{\alpha}) + T\left(\frac{\partial x^{\alpha}}{\partial T}\right)^2 \left(\frac{\partial^2 G^{\alpha}}{\partial x^2}\right)_{x^{\alpha}} \right) + \beta(x,T)\left(C_P^{\beta}(x^{\beta}) + T\left(\frac{\partial x^{\beta}}{\partial T}\right)^2 \left(\frac{\partial^2 G^{\beta}}{\partial x^2}\right)_{x^{\beta}} \right), \quad (4)$$

where β - the mole fraction of bcc - phase of the Cr-rich alloys (or α'- phase).

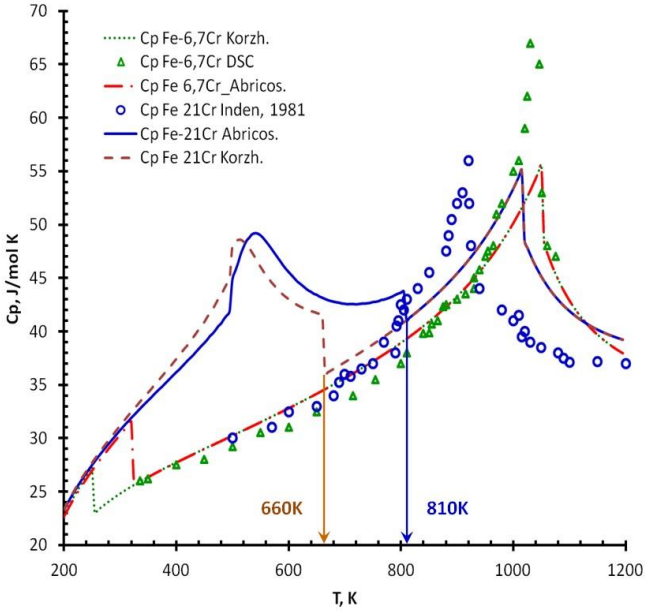

Figure 5. The temperature dependences of isobaric heat capacities for Fe-6.7 at.% Cr and Fe-21 at.% Cr alloys calculated using the results of ab-initio calculations of the mixing enthalpy at 0K [4, 5] in comparison with the experimental data (Δ -Xiong, ○ -Inden) taken from [9]. The temperatures of the heat capacity jumps of Fe-21 at.% Cr alloy are shown by arrows.

One can learn from those graphs that when "moving" down by temperature from the high temperature area to the lower area the first heat capacity jumps could be seen when the alloys transit from paramagnetic to ferromagnetic state. The difference in heat capacity jumps between experimental and calculated data of the Fe-21at.% Cr alloy is due to insufficiently accurate approximation of Curie temperature, it can be expected that a more accurate description would eliminate this misleading.

By the further lowering temperature, the second jumps could be seen (at 660K or 810K- figure 5 using data of work [5] or [4] accordingly) when the configuration point for composition of the Fe-21 at.% Cr alloy transits from one phase area (α) to the two phase area (α+α') of the phase diagram (shown by arrows in figure 4).

This obtained result can be used for verification of models employed in ab-initio calculations of the mixing enthalpies at 0K. For example, if one will take the Fe-6.7 at.% Cr or Fe-21 at.% Cr alloy and carry out the heat capacity measurements at 280K or 780K correspondingly then according to the obtained results in the present study the heat capacity jumps don't be expected at these temperatures.

5. Conclusions

The calculated boundary of bcc Fe-Cr alloys and temperature dependencies of heat capacity of two alloys were accomplished by using ab-initio calculations of the mixing enthalpy [3-5] and presented in Figures 4 and 5. The calculated results of alloy heat capacities can be recommended the experimenters for accurate definition of the phase boundaries of bcc Fe-Cr alloys, in particular for the Fe- rich alloys. The obtained result allows to conduct verification of those ab-initio data by caring out the experimental researches and thus to help researchers involved in the kinetic simulations in the choice of the inter-atomic potentials.

Acknowledgments

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