

## Thermodynamic Assessment of the Fe-B System in the SSOL5 and User Databases

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### ABSTRACT

Thermodynamic assessment of Fe-B system, including phase diagram, Gibbs energy, enthalpy, heat capacity and activity, was performed in the ThermoCalc software ver. 4.1 (Sweden). Two databases were used: the commercial SSOL5 database for solid solutions (substitutional approach) and the USER made database based on work of T. Van Rompaey et al. (interstitial approach). Results obtained were compared with experimental data gathered from work of M. Van Ende et al. In low boron regime the curve of the Fe-B phase diagram is represented more reliable in the USER database. However, temperatures of the phase transformations are calculated with more accuracy in the SSOL5 database. For boron content higher than 0.3 mole fraction phase transformation temperatures are better assessed in the USER database, except for melting point of the Fe<sub>2</sub>B phase. Gibbs energy, enthalpy and heat capacity of the FeB and the Fe<sub>2</sub>B are difficult to evaluate because experimental data are spread and inaccurate. Activities of iron and boron in liquid Fe-B alloy, calculated at selected temperatures, are almost identical for both databases. paramount importance.

**Keywords:** thermocalc

### I. INTRODUCTION

Iron and Boron are important constituents of steels and magnetic materials. There is a need to simulate properties and behavior of these products. The milestone papers allowing for calculation of the Nd-Fe-B system were provided by Hallems et al. in 1994 [1] and 1995 [2]. Not so long ago, a significant article was published by Van Ende et al. who provided a critical review of all theoretical and experimental data available for the Nd-Fe-B system and proposed improved parameters for calculations [3]. Very recently Zhou et al. investigated thermodynamic description of the Nd-Fe-B system including metastable phases Fe<sub>3</sub>B, Fe<sub>17</sub>Nd<sub>2</sub>B and Fe<sub>23</sub>Nd<sub>2</sub>B<sub>3</sub> which have effect on magnetic properties of dual-nanoscale-phase nanocomposite magnets [4]. However, obtained phase diagrams cannot be easily compared because one must suspend stable phases from calculations, e.g. Fe<sub>2</sub>B phase, in order to display metastable one, e.g. Fe<sub>3</sub>B phase. In order to predict ternary system one has to properly assess binary one first [5]. Therefore, this work is focused on the Fe-B system which is calculated using different approaches. In the SSOL5 database iron and boron are recognized as substitutional solutions, while in the USER database boron is modelled as an interstitial element in the FCC and BCC solid solutions.

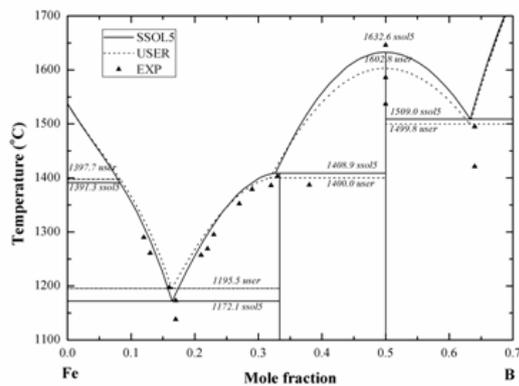
### II. EXPERIMENTAL

Calculations were performed using ThermoCalc ver. 4.1 software equipped with two

databases: commercial SSOL5 for solid solutions (substitutional approach) based on Hallems et al. [1,2] and USER made database with data from work of T. Van Rompaey [6]. Conditions used in calculations (reference states, temperatures etc.) were based on those used in Van Ende's et al. [3] thus allowing for easy comparison. Experimental data, gathered by various authors, were read from Van Ende's et al. paper using DataThief III software developed by B. Tummers [7].

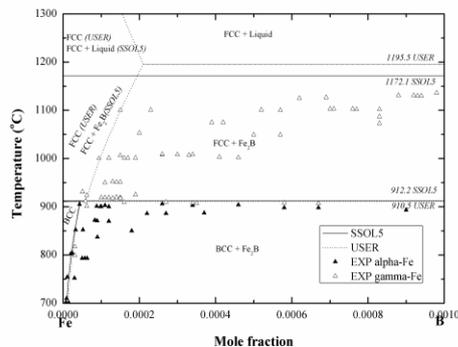
### III. RESULTS AND DISCUSSION

Boron-rich part of calculated Fe-B phase diagram is presented together with experimental data in Fig. 1. For boron content up to 0.3 mole fraction transformation temperatures are too high in USER database (e.g. difference in eutectic transformation at 0.16 B is higher by more than 20°C between the databases). In contrary, transformation temperatures for boron content more than 0.3 mole fraction are reduced in the USER database (e.g. melting point of FeB phase is almost 30°C lower comparing with the SSOL5) what fits better experimental data. Melting point of the FeB phase, calculated at 1651.1°C by Van Ende et al., is reduced in both databases: 1632.6°C in the SSOL5 and 1602.8°C in the USER. Unfortunately, experimental data for the FeB compound varies significantly and one has to choose among the results.



**Fig. 1** Phase diagrams of the Fe-B system calculated in the SSOL5 (solid line) and the USER (dotted line) database with experimental data (triangles) obtained by various authors [3].

An iron-rich corner of calculated the Fe-B phase diagram is presented together with experimental data in Fig. 2. A single phase region of the FCC phase is clearly visible only in the USER. Indeed, the FCC phase appears in the SSOL5 but has extremely narrow existence's range, making it practically invisible. This difference, including experimental results, should be considered in a favor of the USER database.

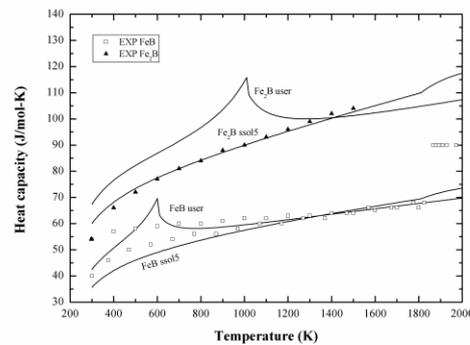


**Fig. 2** Fe-rich corner of the Fe-B binary phase diagrams calculated in the SSOL5 (solid line) and the USER (dotted line) database with experimental data (triangles) obtained by various authors [3]. Despite the FCC phase exists in the SSOL5 database, it is virtually invisible in the left side of the diagram.

The heat capacity of FeB and Fe<sub>2</sub>B versus temperature is presented together with experimental data in Fig. 3. Simulation for FeB calculated in the SSOL5 should be slightly elevated (around +5 J/mol-K) at temperatures below 1300 K and slightly reduced at higher temperatures in order to cover the experimental data. These adjustments are actually what the USER database provides. Peaks denote Curie temperature. Moreover, neither of the database fits experimental points measured above 1900 K.

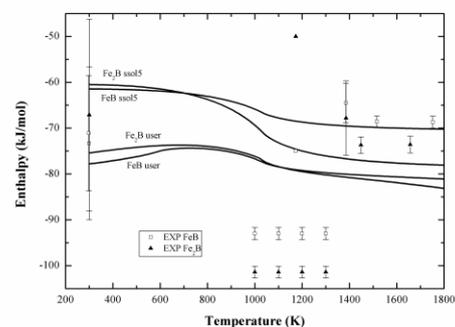
This part of curves should be elevated around +15 J/mol-K.

The heat capacity of Fe<sub>2</sub>B calculated in the SSOL5 covers experimental data well. Simulation performed in the USER lies too high and should be reduced. There are no experimental data for Fe<sub>2</sub>B at temperatures above 1500 K so this part of curves cannot be verified.



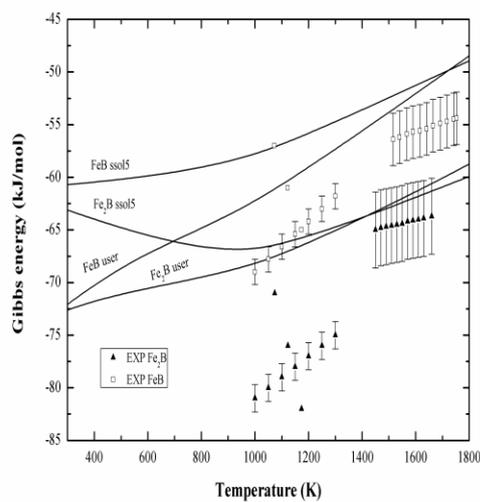
**Fig. 3** Heat capacity of FeB and Fe<sub>2</sub>B calculated in the SSOL5 and the USER database using hfr(phase).t formula at standard reference states (SER). Experimental data obtained by various authors (squares for FeB and asterisks for Fe<sub>2</sub>B) [3].

Enthalpy of formation of FeB and Fe<sub>2</sub>B calculated in the SSOL5 and the USER database is presented together with experimental data in Fig. 4. First of all, one should notice experimental points are spread and uncertain, hindering evaluation. Indeed, simulations obtained in the SSOL5 are closer to experimental data, both databases should be improved by elevating enthalpy values at temperatures above 1500 K for both FeB and Fe<sub>2</sub>B. Experimental points measured between 1000-1300K do not fit any calculation at all including database improved by Van Ende.



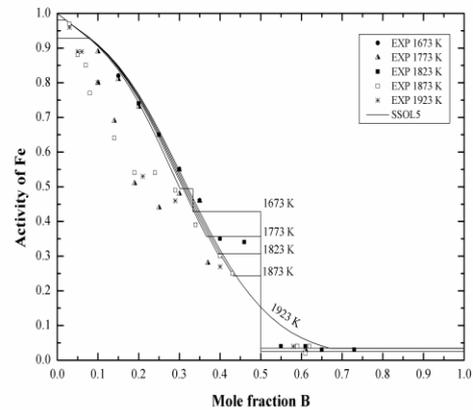
**Fig. 4** Enthalpy of formation of FeB and Fe<sub>2</sub>B calculated in the USER and the SSOL5 database with experimental data (squares for FeB and triangles for Fe<sub>2</sub>B) obtained by various authors [3]. The reference states are set as recommended: iron in BCC and boron in B<sub>beta</sub> at default temperature.

The Gibbs energy of FeB and Fe<sub>2</sub>B calculated in the USER and the SSOL5 database is presented together with experimental data in Fig. 5. Experimental data are spread, inaccurate and there are no measuring points below 1000 K. Calculations provided in both databases cover experimental data at temperatures between 1400-1700 K for Fe<sub>2</sub>B but not for FeB. At temperatures between 1000-1300 K simulations for both databases should be reduced by around -10 kJ/mol in order to fit experimental points for both phases. Although, calculated curves are generally lower for the USER database value's reduction should be greater.

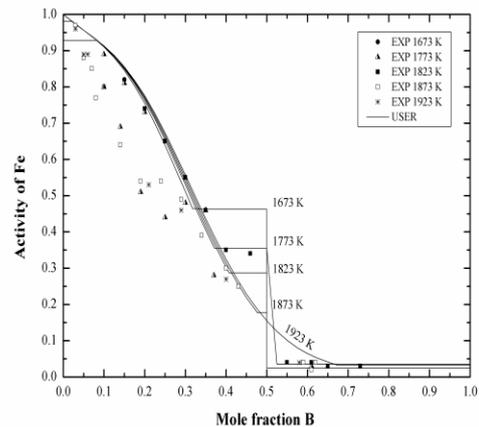


**Fig. 5** Gibbs free energy of FeB and Fe<sub>2</sub>B calculated in the SSOL5 and the USER database with experimental data (squares for FeB and triangles for Fe<sub>2</sub>B) obtained by various authors [3]. Reference states are: BCC for iron and BETA\_RHOMBO\_B for boron.

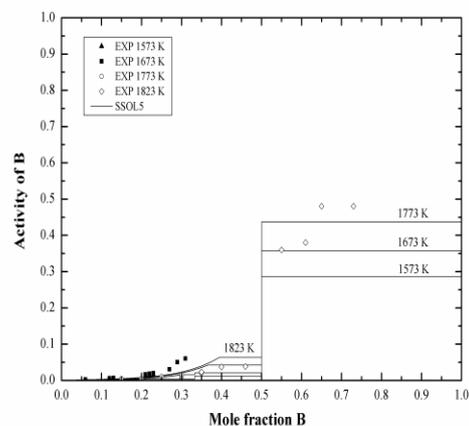
The activity of Fe and B in liquid Fe-B alloy calculated at selected temperatures is presented with experimental data in Fig. 6-8 for the SSOL5 and in Fig. 9-11 for the USER database, respectively. One could see the activities of Fe and B are calculated almost identically in the two databases. Activity of Fe calculated in the USER database for around 0.5 boron content is slightly elevated at lower temperature (1673 K) and slightly reduced at higher temperatures (1823 K and 1873 K). The iron's activity curve at 1923 K seems to be the same for both databases. On the other hand, activity of B calculated in the USER database is slightly elevated at higher temperatures (1773 K and 1823 K) and slightly reduced at lower temperature (1673 K).



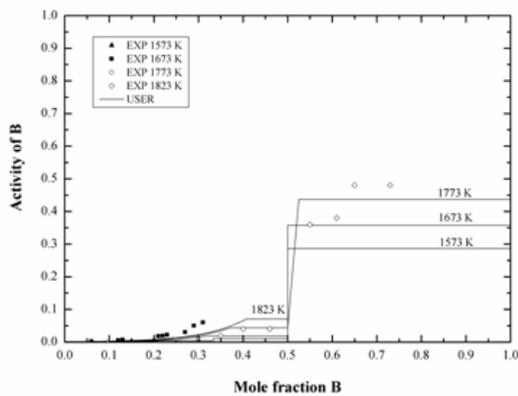
**Fig. 6** Activity of Fe in liquid Fe-B alloy calculated at selected temperatures in the SSOL5 database with experimental data [3].



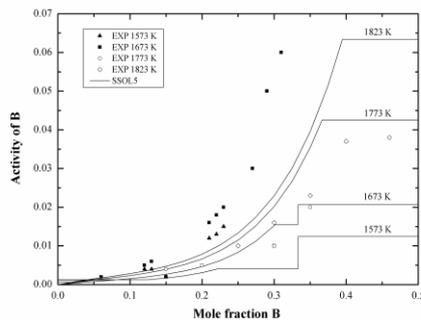
**Fig. 7** Activity of Fe in liquid Fe-B alloy calculated at selected temperatures in the USER database with experimental data [3].



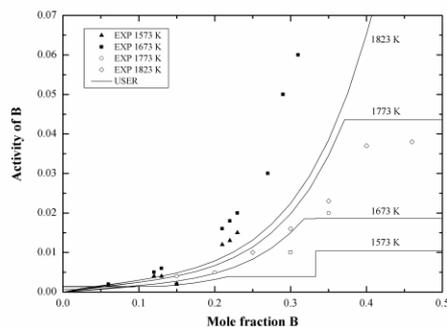
**Fig. 8** Activity of B in liquid Fe-B alloy calculated at selected temperatures in the SSOL5 database with experimental data [3].



**Fig. 9** Activity of B in liquid Fe-B alloy calculated at selected temperatures in the USER database with experimental data [3].



**Fig. 10** Activity of B at low boron content in liquid Fe-B alloy calculated at selected temperatures in the SSOL5 database with experimental data [3].



**Fig. 11** Activity of B at low boron content in liquid Fe-B alloy calculated at selected temperatures in the USER database with experimental data [3].

#### IV. CONCLUSION

The assessment of the Fe-B binary system, including calculation of phase diagrams and determining thermodynamic parameters, was carried out in the Thermo-Calc software ver. 4.1. Two databases were used: the commercial database for solid solutions SSOL5 (substitutional approach) and the USER database (interstitial approach). The assessments were compared each other and to experimental data collected by Van Ende et al. Each

of the database has some advantages and disadvantages, depending on the property calculated. Some differences are visible only in specific composition ranges. In addition, the experimental data is spread and inaccurate what hinders the evaluation. The following conclusions, referring to the Thermo-Calc calculations, could be drawn:

I. Phase diagram optimization might be in contrary to assessment of thermodynamic properties. One must improve both the shape of the curve (e.g. transformation temperatures) and the thermodynamic functions (Gibbs free energy, enthalpy of formation and heat capacity).

II. Instead of creating new databases it might be beneficial to modify current databases by amending selected parameters.

III. Reference states should be established in order to allow for unmistakable comparison between models and databases.

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