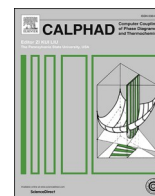




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Invited article

An assessment of Fe-Nb-B melts using the two-state liquid model

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A B S T R A C T

Amorphous alloys of the (Fe-Co-Ni)-(Cr-Mo-Nb)-B system are promising materials to supply the demands for higher wear resistance components in the petrochemical industry. Since the development of the CALPHAD method, the development of new metallic alloys has been accompanied by thermodynamic modelling and calculations. The prediction of the formation of amorphous alloys requires special care with the modeling of the liquid and or an amorphous phase. As a initial stage in the more complex system, the basic Fe-Nb-B ternary system was selected. In order to predict the stability and tendencies of transformations of these amorphous alloys, the Fe-Nb-B system was reassessed using Ågren's two-state model to describe the liquid phase. The results of the present assessment show very good agreement with the recently reported stable phase diagram. Furthermore, the use of the two-state model for the liquid is more accurate and physically consistent when evaluating transformations from supercooled liquid, as shown in the present work.

1. Introduction

The CALPHAD method is a very effective tool to study metastable equilibria as well as to perform extrapolation to higher order systems, based on proper assessment of binary and ternary systems [1,2]. On the other hand, the study of the formation of amorphous alloys as well as their crystallization benefits greatly from the understanding of possible metastable equilibria (see Ref. [3], for instance).

Furthermore, amorphous alloys are frequently produced in higher order systems (e.g. Ref. [4]). Thus, amorphous alloys seem to be perfect candidates to benefit from computational thermodynamics in the alloy design stage. However, properly modeling amorphous alloys via the CALPHAD method has so far proven to be somewhat elusive despite different degrees of success in various attempts [5–7]. First, the modeling of the liquid phase of pure substances has, in general, involved a discontinuity in $\frac{dC_p}{dT}$ at the substance melting point [8,9]. This contradicts physical evidence and leads to unreasonable discontinuities in $\frac{dC_p}{dT}$ in liquid solutions at the melting points of the pure elements [8,9]. However, this method leads to good results in the description of crystalline systems [2,10,11]. Second, the supercooled liquid Gibbs energy of pure elements and mixtures is usually fitted based mostly on information on low melting binary systems. Among the various attempts at modeling the liquid-amorphous phase in computational thermodynamics, Ågren's two-state liquid [9,12] seems to be the one that has a reasonable physical interpretation and is promising in real applications

[13–15].

In the present work we extend the previous CALPHAD assessment of the Fe-B system using the two-state liquid model [13] to the ternary Fe-Nb-B. We use Yoshitomi and co-workers [16] assessment of this system as a basis. The assessment procedure is described, and the results are presented. Furthermore, the new description of the ternary Fe-Nb-B employing the two-state liquid is used to evaluate previous experimental results in amorphous alloys both in this and in more complex systems containing Fe-Nb-B.

2. The Fe-Nb-B system

The main challenge in the present modeling of the Fe-Nb-B system resides in modeling the liquid. Schwarz, Nash and Turnbull [7] summarized the difficulties in modeling the liquid phase to include the amorphous (or glass) transition. For the liquid phase, there is a general lack of adequate experimental data for use in the assessments and there are inherent restrictions of fitting, since in general no low temperature thermodynamic data of the liquid phase are used in determining the model parameters in the thermodynamic assessments. Furthermore, they have observed the unsuitability of the thermodynamic models adopted, since the temperature dependence of thermodynamic quantities in the undercooled liquid is not properly considered [7]. In a series of papers Bormann and co-workers [6,17–19] described Zr, Ti and Nb systems considering that below the glass transition temperature (T_g) the specific heat of the amorphous phase is assumed to be equal to that of

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Table 1

Assessed parameters for the two state liquid (in J/mol formula unit).

Parameter	Source
$G_m^{sol,Fe} = {}^0 G_m^{fcc,Fe} + 6579.16 + 1.75 T \ln T - 0.0013T^2 - RT$	[13]
$G_m^{sol,B} = {}^0 G_m^{beta,B} + 47528.9 + 1.91T \ln T + 0.0019T^2 - RT$	[13]
$G_m^{sol,Nb} = {}^0 G_m^{bcc,Nb} + 16826 - 0.00197T^2 - RT$	This work
$\Delta H_{melting}^{Fe} = 13800$	[29]
$\Delta H_{melting}^B = 50200$	[29]
$\Delta G_m^{d,Nb} = 30040 + 8862.3 - RT$	[29] and this work
${}^0 L_{NbB}^{Li} = -168126 + 0.28T$	This work
${}^1 L_{NbB}^{Li} = 16048 + -28.1T$	This work
${}^2 L_{NbB}^{Li} = 4623.4$	This work
${}^0 L_{FeNb}^{Li} = -37756 + 3.8T$	This work
${}^1 L_{FeNb}^{Li} = -38.2$	This work
${}^0 L_{FeB}^{Li} = -140000 + 20.1T$	This work
${}^1 L_{FeB}^{Li} = +11016$	This work
${}^2 L_{FeB}^{Li} = +36971$	This work
${}^1 L_{B,Fe,Nb}^{Li} = -300000$	[16]
$T_{C,Fe}^{Li} = 520$	[13]/this work
$B_{C,Fe}^{Li} = 2.2$	[13]

crystalline phases while its enthalpy and entropy are the same as the undercooled liquid at T_g . This approach results, however, in discontinuities in the slopes of the enthalpy and entropy curves at T_g . Liu and co-workers [20] adapted the formalism proposed by Inden [21,22], Jarl and Hillert [23] for the magnetic transition to describe the second order transition at T_g . Palumbo and co-workers [5] described the Fe-B system considering glass transition as a second order transition, obtaining constraints relating the Gibbs energy function parameters. Palumbo and Battezzati [24] carefully reviewed these approaches and their thermodynamic limitations. They also proposed that kinetics should be considered when attempting to predict the glass transition. The reader is directed to their excellent review and to the work of Baricco and Palumbo [25] to further understand the thermodynamic limitations of these models.

In 1988 Ågren [12] proposed a phenomenological model for representing the properties of supercooled metallic liquids. In this model, the liquid is composed by “solid-like” and “liquid-like” atoms, which contribute differently to the thermodynamic properties of the liquid phase. As temperature increases, the fraction of “liquid-like” atoms increases. Some typical calculated values of this fraction, at melting temperature, are in the 0.30–0.55 range [9]. Conversely, as temperature decreases, the fraction of “solid-like” atoms increases. It is not the purpose of this paper to discuss in detail the model. The reader is referred to Refs. [9,12] for more details. Good agreement to experimental data has been obtained when applying this model to the pure Ga, Au [9], Sn [12] and Fe [15]. The model has also been successfully applied to the binaries Ag-Cu [14] and Fe-B [13].

In the present work we accepted the description of the solid phases for the Fe-Nb-B system given by Yoshitomi and co-workers [16] and reassessed the liquid phase CALPHAD description using Ågren's two-state liquid model.

2.1. The liquid phase

2.1.1. Unaries

In the two-state liquid model the molar Gibbs energy of the solid-like state is given by G_m^{sol} and that of the liquid-like state by G_m^{liq} , where the subscript ‘m’ denotes molar quantities.

The difference between these energies, given by ΔG_m^d (Eq. (1)) is an

important parameter in the model.

$$\Delta G_m^d = G_m^{liq} - G_m^{sol} = H_m^{liq} - H_m^{sol} - RT + \dots \quad (1)$$

The superscript “d” denotes the difference between the solid-like and liquid-like states in the liquid.

The model assumes a random mixture of solid-like and liquid-like atoms. This, the liquid phase Gibbs energy is obtained by Eq. (2) [12], where χ is the fraction of solid-like atoms in the liquid.

$$G_m^L = \chi G_m^{sol} + (1 - \chi) G_m^{liq} + RT(\chi \ln \chi + (1 - \chi) \ln(1 - \chi)) \quad (2)$$

In this equation, the superscript “L” denotes the liquid phase.

Becker et al. [9] have discussed the analytical solution of the liquid internal equilibrium, corresponding to the minimum of G_m^L associated to the value of χ at equilibrium at a given temperature. When the two-state liquid model is used with Thermo-calc [26], the software performs, for each temperature, the calculation of internal equilibrium, minimizing Equation (2), based on the given G_m^{sol} and G_m^{liq} values.

To model the liquid phase one has then to define the values of G_m^{sol} and G_m^{liq} . It is reasonable to assume that the difference between G_m^{sol} and the molar Gibbs energy of the crystalline phase of the pure element will not be very large.

Thus, for the pure elements Fe and B we followed the proposal of Ref. [13]:

$$G_m^{sol,Fe} = {}^0 G_m^{fcc,Fe} + A^{Fe} + B^{Fe} T \ln T + D^{Fe} T^2 - RT \quad (3)$$

In this equation, A^{Fe} , B^{Fe} , and D^{Fe} are parameters to be assessed. And

$$G_m^{sol,B} = {}^0 G_m^{beta,B} + A^B + B^B T \ln T + D^B T^2 - RT \quad (4)$$

A^B , B^B , and D^B are also parameters to be assessed.

The term ${}^0 G_m^{fcc,Fe}$ is the molar Gibbs energy of FCC Fe referred to HSERFe and ${}^0 G_m^{beta,B}$ is the molar Gibbs energy of Beta B referred to HSERB given by Dinsdale [26]. For both elements, the expressions used above the melting points of the elements by Ref. [26] were excluded from these terms. Both for Fe and B, we followed the approximation of Eq. (1) proposed in Ref 13. Hence,

$$\Delta G_m^{d,i} = \Delta H_{melting}^i - RT \quad (5)$$

where $\Delta H_{melting}^i$ is the molar equilibrium crystallization enthalpy for element “i”.

The values of all parameters adopted for pure Fe and B in the liquid phase are presented in Table 1.

There was no previous assessment of liquid Nb in the two-state model.

Initially we attempted the simplified solution for the parameters of the liquid phase proposed by Becker and co-workers [9]. In this approach, the difference between the molar Gibbs energy of the solid-like atoms $G_m^{sol,i}$ and that of the crystalline solid phase ${}^0 G_m^{cryst,i}$ of the element is assumed to be independent of the temperature, i.e. the solid-like atoms have the same c_p and the same entropy as the crystalline solid phase. Thus, it is assumed that this difference is simply an energy difference [9]. Hence instead of using an equation of the form of Equations (3) or (4), one would use:

$$G_m^{sol,i} = {}^0 G_m^{cryst,i} + A^i \quad (6)$$

where A^i is a constant energy difference to be calculated.

However, there was no solution for the system of non-linear equations formulated by Becker and co-workers based on this assumption. In their calculations, Becker and co-workers found that no solution was possible with elements that had entropy of melting larger than $\approx 11 \text{ Jmol}^{-1} \text{K}^{-1}$. As the entropy of melting of Nb is $10.8 \text{ Jmol}^{-1} \text{K}^{-1}$ [27] we found the result consistent with those of [9].

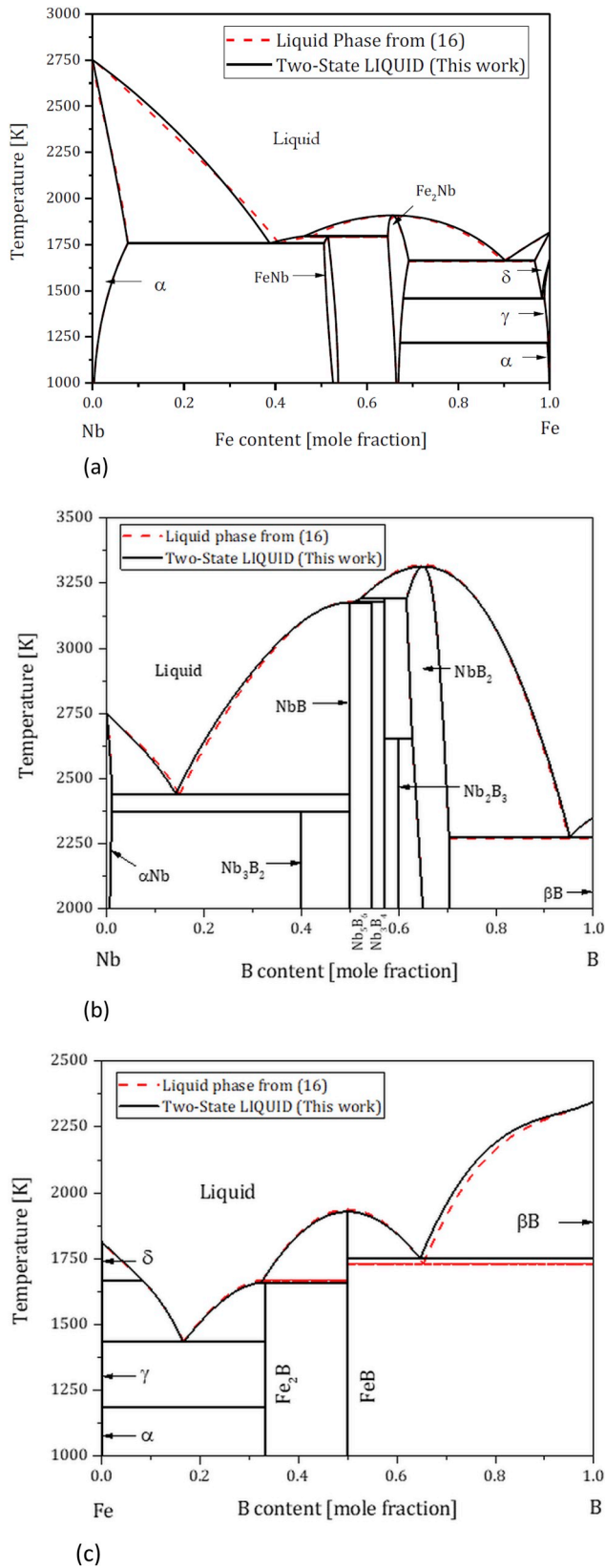


Fig. 1. (a). Nb-Fe binary diagram calculated by Yoshitomi and co-workers [16] compared to the results of the present work. (b). Nb-B binary diagram calculated by Yoshitomi and co-workers [16] compared to the results of the present work. (c). Fe-B binary diagram calculated by Yoshitomi and co-workers [16] compared to the results of the present work.

Table 2

Comparison of the invariant temperatures in equilibrium with liquid in the binaries. This work, Yoshitomi et al. assessment [16], experimental data. Temperature in K, composition in atom percent.

Equilibrium	This work, calculated	Yoshitomi [16], calculated	Experimental or assessed, for comparison	
System Nb-B	T (K); at.% B	T (K); at.% B	T (K); at.% B	Source
α -Nb = L	2750; 0	2750; 0	2748 ± 5	[30]
β B = L	2350; 100	2351; 100	2348 ± 5	[26]
α -Nb + NbB = L	2440; 14.3	2441; 15	2438 ± 10 ; ~16	[35]
NbB = L	3176; 50	3178; 50	3190 ± 10 ; ~50	[36]
NbB + Nb ₅ B ₆ = L	3176; 50.6	3177; 50.7	3133 ± 10 ; ~52	Estimated by Refs. [34,37]
Nb ₅ B ₆ = Nb ₃ B ₄ + L	3178; 54.5	3179; 54.5	3170 ± 10 ; ~54	Estimated by Ref. [34]
Nb ₃ B ₄ = NbB ₂ + L	3190; 57.1	3192; 57.1		
NbB ₂ = L	3314; 65	3320; 65	3309 ± 15 ; ~67	[36]
β B + NbB ₂ = L	2272; 95.7	2270; 95	2308 ± 20 ; ~98	[36]
System Fe-Nb	T (K); at.% Nb	T (K); at.% Nb	T (K); at.% Nb	
δ -Fe = L	1815.5; 0	1811; 0	1811; 0	[26]
δ -Fe + Laves = L	1660; 9.72	1660; 10.09	1647; 14.5	[32]
Laves = L	1904; 34.3	1905; 34.4	1903	[38]
Mu = Laves + L	1793.5; 48.5	1791.3; 48.4	1808; 53	[32]
Mu + α -Nb = L	1754; 61.1	1758; 59.3	1777; 60.1	[32]
System Fe-B	T (K); at.% B	T (K); at.% B	T (K); at.% B	
δ -Fe + Fe ₂ B = L	1432.5; 16.65	1435; 16.6	1444; 16.5	[33]
Fe ₂ B = FeB + L	1659.1; 33.3	1668; 33.3	1621; 33.7	[33]
FeB = L	1927.5; 50	1936.5; 50	1924; 50	[33]
FeB + β B = L	1750.5; 64.75	1730; 65.4	1752; 63.5	[33]

Table 3

Solid phases in the ternary Fe-Nb-B.

Phase Name	Modeled as
FCC_A1	$(Fe, Nb, B)_1 (Va)_1$
BCC_A2	$(Fe, Nb, B)_1 (Va)_3$
BETA_RHOMBO_B	(B)
FE1NB1B1	$(Fe)_1 (Nb)_1 (B)_1$
FE3NB3B4	$(Fe)_{0.3} (Nb)_{0.3} (B)_{0.4}$
FEB	$(Fe)_{0.5} (B)_{0.5}$
LAVES_PHASE	$(Fe, Va)_2 (Fe, Nb)_4 (Fe)_6$
M2B	$(Fe)_{0.667} (B)_{0.333}$
M3B2	$(Fe, Nb)_{0.6} (B)_{0.4}$
MU_PHASE	$(Fe, Nb)_1 (Fe, Nb)_2 (Fe)_6 (Nb)_4$
NB1B1	$(Nb)_{0.5} (B)_{0.5}$
NB1B2	$(Nb, Va)_{0.333} (B, Va)_{0.667}$
NB2B3	$(Nb)_{0.4} (B)_{0.6}$
NB3B4	$(Nb)_{0.429} (B)_{0.571}$
NB5B6	$(Nb)_{0.455} (B)_{0.545}$

Hence, instead of applying Eq. (5) directly to Nb we introduced a parameter to account for the enthalpy difference between the crystalline phase and the solid-like atoms, $\Delta H_{BCC-sol}^{Nb}$ as shown in Eq. (7). Both $\Delta H_{BCC-sol}^{Nb}$ and $G_m^{sol, Nb}$ must be assessed using the experimental data available. In the present assessment we used information on melting point,

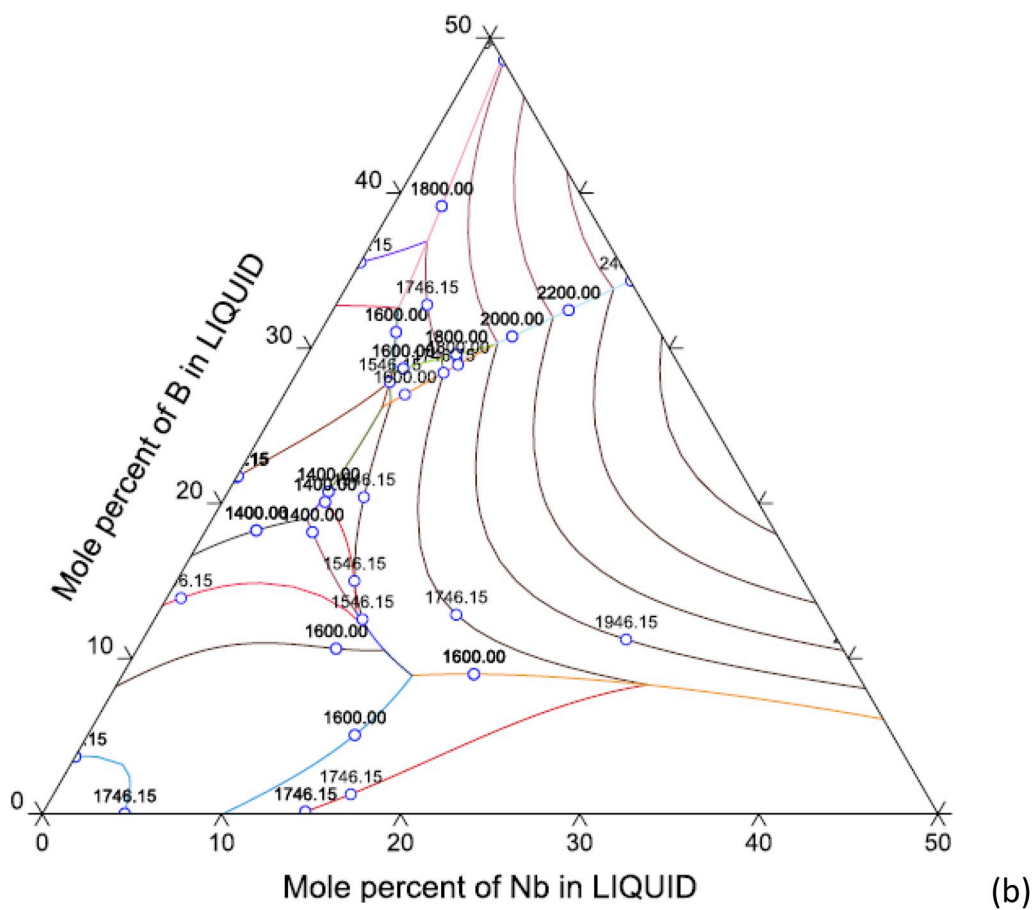
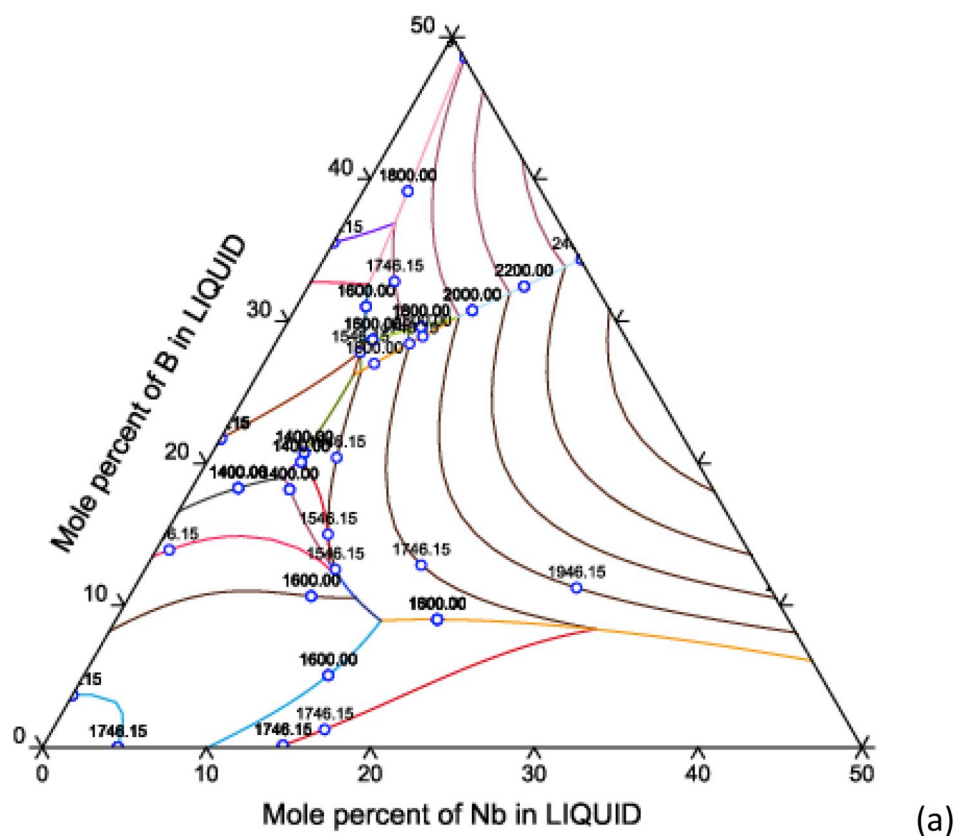


Fig. 2. Liquidus projection calculated (a) with data from this assessment and (b) with Yoshitomi and co-workers data [16].

Table 4

Calculated and experimental liquidus temperature for the composition Fe_{0.72}Nb_{0.04}B_{0.24}

Source	Liquidus T
This work	1513 K
Calculated using Yoshitomi and co-workers assessment [16]	1514 K
Measured by Li and co-workers [39]	1497 K

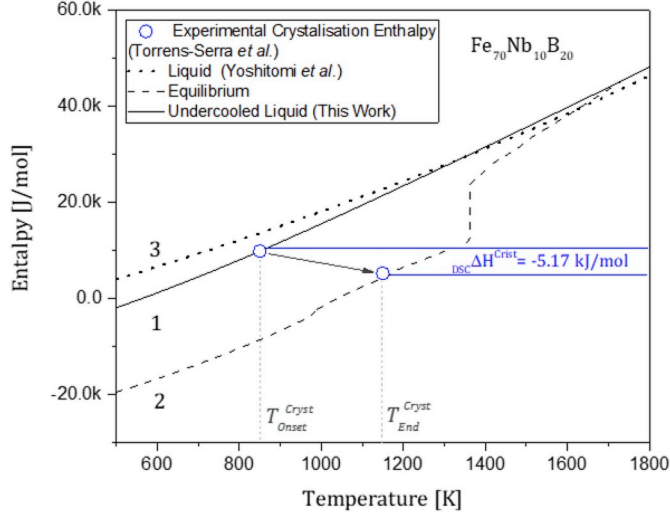


Fig. 3. Enthalpies for a Fe_{0.70}Nb_{0.10}B_{0.20} alloy. Line 1: Enthalpy of the liquid phase calculated with the present assessment. Line 2: Enthalpy of the equilibrium configuration calculated with the present assessment. Line 3: Enthalpy of the liquid phase calculated with Yoshitomi's assessment. Superimposed is the crystallization data from Torrens-Serra and co-workers [40].

T_m^{Nb} from Ref. [26], enthalpy change at the melting point, $\Delta H_{melting}^{Nb}$ from Ref. [29] and heat capacity data close to the melting point from Ref. [30]. Due to the limited experimental data available, however, the term on $T \ln T$, used to describe both $G_m^{sol,Nb}$ and $G_m^{sol,B}$ (Equations (3) and (4)) was not included in the equation for $G_m^{sol,Nb}$, as shown in Eq. (8).

$$\Delta G_m^{d,Nb} = \Delta H_{melting}^{Nb} + \Delta H_{BCC-sol}^{Nb} - RT \quad (7)$$

$$G_m^{sol,Nb} = G_m^{bcc,Nb} + A^{Nb} + D^{Nb}T^2 - RT \quad (8)$$

All parameters were assessed using Thermo-calc's optimization routine PARROT [28].

The assessed parameters are given in Table 1.

2.1.2. Binaries

To assess the two-state liquid thermodynamic description in the binaries, the following procedure was used. The solid phases (see section 3) modelling and parameters proposed by Yoshitomi and co-workers [16] were accepted. The binary liquid was described using the two state liquid model and a Redlich-Kister [31] polynomial. The solid-liquid invariants calculated by Yoshitomi and co-workers [16] were considered as experiments and Thermo-Calc [28] was used to assess the polynomial coefficients, with due care to limit the number of adjustable coefficients considering the number of data points, avoiding overfitting. Fig. 1 presents the calculated binaries, compared with those calculated by Yoshitomi and co-workers [16]. Table 1 presents the assessed coefficients and Table 2 compares the experimental invariant temperatures and compositions, calculated by Yoshitomi and co-workers [16], together with the invariants calculated using the presently assessed parameters (Table 1). As a reference, we included in Table 2 experimental data as well as the values calculated with the

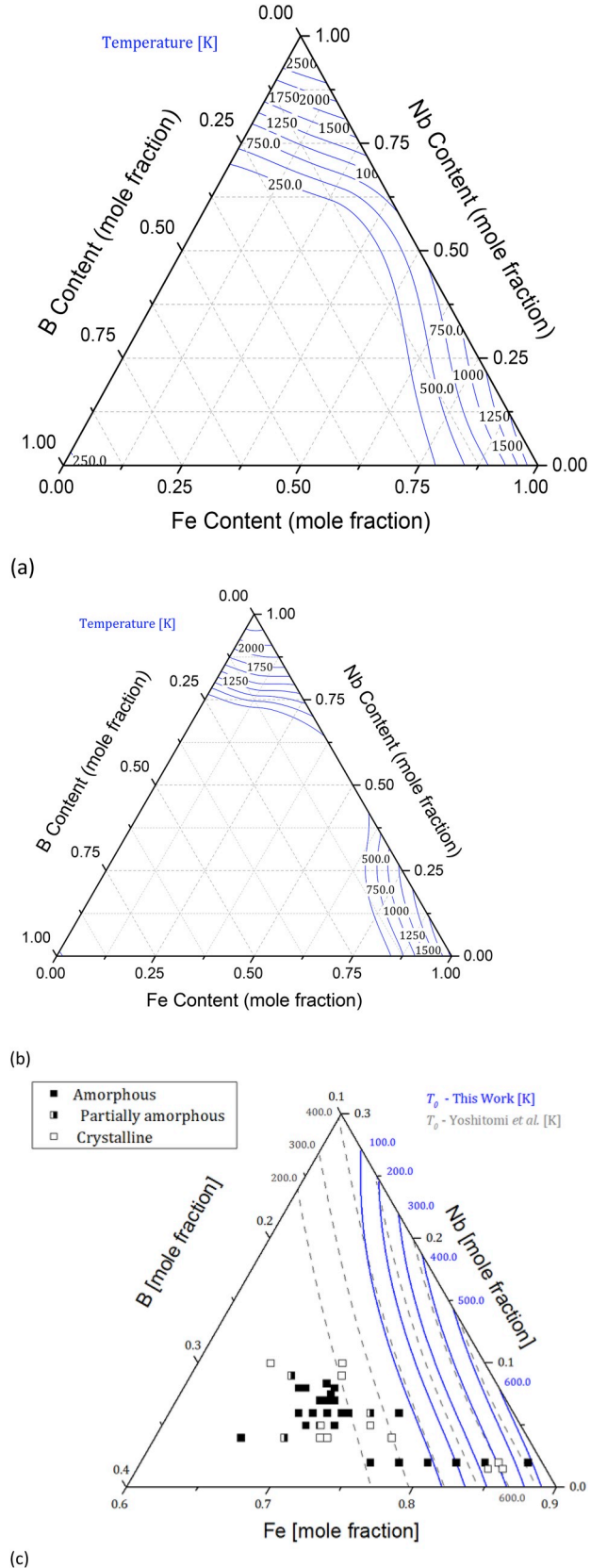


Fig. 4. T_0 curves (a) calculated using Yoshitomi's assessment. (b) Calculated using present assessment and (c) Superimposed, including experimental data on amorphization of alloys in this system from Refs. [44–48].

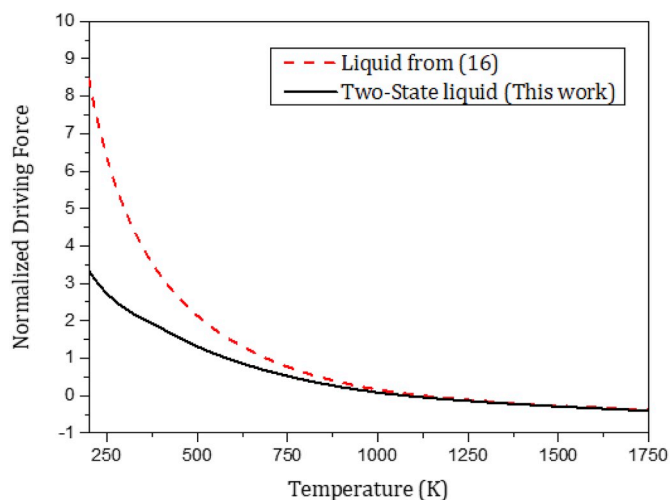


Fig. 5. Normalized driving force (see text for explanations) for the precipitation of BCC from the liquid as a function of temperature, calculated with the two-state liquid model and the substitutional liquid model [16].

recent assessments of Khvan and Hallstedt [32] for Fe-Nb, van Ende and Jung [33], for Fe-B and Peçanha and co-workers for Nb-B [34].

2.1.3. Ternary

As done by Yoshitomi and co-workers [16] a single ternary interaction parameter was used. We accepted the ternary interaction parameter proposed by Ref. [16] in view of the good agreement of the calculated results and the scarcity of experimental data.

The solid phases models as well as parameters proposed by Yoshitomi and co-workers for the solid phases [16] were accepted. Table 3 presents the models. The reader is referred to their original work for the parameters.

3. Results

3.1. Stable equilibria

There was good agreement in the calculated binary invariants, as presented in Table 2.

Calculations with the data of the present assessment reproduced very well the solid-solid relation presented in isotherms published by Yoshitomi and co-workers [16]. The liquidus projection also agreed quite well with Yoshitomi's [16] as shown in Fig. 2.

As a test of the ternary liquid behavior the liquidus point of the composition Fe_{0.72}Nb_{0.04}B_{0.24} was calculated and compared with available information. The results have shown good agreement and are presented in Table 4.

3.2. Glass formation

3.2.1. Crystallization enthalpy

Differential thermal analysis is frequently used to follow glass formation and crystallization reactions. In order to verify the enthalpy values calculated according to the present assessment, we compared them with the experimental value measured by Torrens-Serra and co-workers [40]. The change in enthalpy during crystallization of a Fe-Nb-B alloy was compared with the calculate value using the present assessment and the data of Yoshitomi and co-workers assessment [16]. The experimental results of Torrens-Serra and co-workers [40] are superimposed as shown in Fig. 3. The good agreement is evident.

3.2.2. T_0 (T_0) curves

Many criteria for glass formation ability depend on experimental

measurements of T_g . One of the predictive methods that does not rely on previous glass formation experiments is the use of T_0 curves. For two phases, compositions at the T_0 curve have equal Gibbs energies. Diffusionless transformations can occur at temperatures lower than T_0 [41]. The importance of the T_0 curve for the understanding of rapid solidification phenomena has been established for some decades [42,43]. It has been observed that the amorphous alloys in this system frequently crystallize to form BCC. (see, eg. Ref. [40]). In order to evaluate the possibility of BCC crystallization the T_0 curves for liquid-BCC were calculated and are presented in Fig. 4. For a given composition, the present assessment predicts considerably lower T_0 temperatures than Yoshitomi's [16], consistent with the glass formation ability of the alloys, as indicated in Fig. 4(c).

3.2.3. Driving force for precipitation of BCC phase

The driving force for crystallization from the metastable liquid phase can also be used to evaluate the stability of the amorphous phase [49]. Thermo-calc [28] calculates the driving force as the distance between the plane (in a ternary system) tangent to the Gibbs energy surface at the composition of the parent phase and the parallel plane tangent to the precipitating phase [50]. Thermo-calc normalizes the driving force by dividing the Gibbs energy difference by RT . As a convention, positive driving forces indicate the formation of stable phases. We selected an alloy with the composition Fe_{0.70}Nb_{0.08}B_{0.22}, in the range of the amorphous alloys cited by Ref. [45]. The driving force for the precipitation of the BCC phase from the liquid phase was calculated using the two-state model for the liquid and Yoshitomi's substitutional [16] liquid. The results are presented in Fig. 5. The driving force for crystallization for the two-state liquid become significantly smaller than that of the substitutional liquid as the temperature is lowered, as expected.

4. Conclusions

The Fe-Nb-B system was satisfactorily reassessed using the two-state liquid model for the liquid phase. It was possible to properly describe the system starting from the previous assessment of Yoshitomi and co-workers changing, mostly the parameters for the liquid phase. The parameters for the pure element liquid phases were taken directly from previous assessments, indicating the consistency of the model. The present assessment properly predicted the enthalpy change during the crystallization of a ternary alloy. The T_0 temperatures, frequently used to estimate glass forming ability were moved to lower values than when using a classical substitutional solution model for the liquid, more consistent with the observed composition region of amorphization in the system. In the next step of this work, we plan to explore other thermodynamic criteria to evaluate the glass forming ability of alloys in the Fe-Nb-B using the present two-phase liquid assessment.

Data availability statement

The raw data required to reproduce these findings are available to download from CALPHAD magazine site as supplemental material to this paper. The processed data required to reproduce these findings are available to download from CALPHAD magazine site as supplemental material to this paper.

Declaration of competing interest

The authors declare no conflicts of interest.

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