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Assessment of the ternary Fe–Si–B phase diagram

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ABSTRACT

An improvement of the thermodynamic description of the ternary Fe–Si–B system by means of Calphad method has been carried out in this work considering not only the equilibria involving the stable Fe_2B phase but also the metastable ternary equilibria in which the Fe_3B phase occurs. Furthermore, the glass transition is introduced in the Calphad framework as a second-order one using the tools provided by the Hillert–Jarl formalism of the ferromagnetic transitions not yet applied to Fe–B and Fe–Si–B. The assessments have been made using data available in the literature regarding both the amorphous and crystalline phases. The results improve the previous ones for the glassy phase while keeping the agreement with experimental data concerning stable equilibria.

1. Introduction

The most recent thermodynamic assessments of the Fe–B and Fe–Si–B glass forming systems were performed, respectively, by Palumbo and Tokunaga [1,2].

Fe–Si–B amorphous alloys are attractive technological materials both for their good magnetic properties and outstanding mechanical behavior [3]. $Fe_{78}Si_{13}B_9$ is one of the commercially available amorphous alloys [4] used as a core material in distribution transformers. A promising application of these materials concerns also the exploitation of their magnetoelastic properties to be employed in sensors [5,6] and bio-sensors [7]. Moreover the properties can be improved by tuning the composition of the alloy with the addition of other elements, therefore this ternary system is an important basis for more complex glass-forming alloys [8]. Examples include FINEMET, a nanocrystalline alloy with good soft magnetic properties obtained by adding to the Fe–Si–B system Copper and Niobium, while amorphous steels [9] are promising non magnetic Bulk Metallic Glasses with exceptional strength.

Amorphous alloys are metastable and it is well known that Fe–Si–B metallic glasses, similarly to binary Fe–B ones, crystallize in two different ways forming a mixture of *bcc* Fe with either the metastable Fe_3B phase or the stable Fe_2B one according to the metalloid content [10]. Moreover it is worthwhile to underline that Fe_3B can nucleate during quenching and competes with the formation of the glass. The ability of the alloy to glass formation is highest in the composition range where a metastable ternary eutectic is supposed to occur [11]. The above reasons motivate the interest in the metastable equilibria of this ternary system exploiting the potential of the Calphad method.

In the literature the most recent assessment of the ternary Fe–Si–B system has been provided, also using own experimental data, by Tokunaga [1] comparing the results with the ternary equilibria found experimentally by Aronsson [12], Efimov [13] and Chaban [14]. Although the issue of glass formation is clearly raised in [1], the metastable Fe_3B phase was not taken into account. On the other hand, Palumbo [2] provided an assessment of the binary Fe–B system comprehensive of both the stable and the metastable phase diagrams involving either Fe_2B or Fe_3B. In this work we propose an improvement of the description of the Fe–Si–B proposed by Tokunaga introducing the metastable Fe_3B compound in the Calphad description of the ternary system.

Furthermore, a treatment of the glass transition has been implemented both in the binary Fe–B and in the ternary Fe–Si–B systems according to the model proposed by Shao [15] where the amorphous phase is described by using the formalism developed by Hillert and Jarl [16] for the ferromagnetic transitions. This model also allows to consider the composition dependence of the glass transition temperature, T_g, and the introduction of experimental data on crystallization in the assessment process. In [2] the glass transition was already treated fixing the T_g at 800 K for every composition while in [1] the glass transition was not dealt with. Shao's model allows, although with some limitations, to model the heat capacity of the undercooled liquid in the region above T_g, reflecting the increase in short range order in the undercooled liquid needed for the formation of the glass.

2. Thermodynamic model

2.1. Solution phases and stoichiometric compounds

Aronsson [12], Efimov [13] and Chaban [14] studied the Fe–Si–B equilibria finding three ternary compounds: Fe_5Si_2B, $Fe_{4.7}SiB_2$ and

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Table 1
Calculated and experimental thermodynamic properties of intermetallic compounds in the Fe–B system obtained in this optimization and in [2].

Comp.	Property	Reference phase		T (°C)	Calculated	Palumbo [2]	Experimental	Ref.
		Fe	B		(J/mol of atoms)	(J/mol of atoms)	(J/mol of atoms)	
Fe_2B	Enthalpy of formation	α	β	25	−20,970	−21,000	−22,300	[46]
	Enthalpy of formation	γ	β	1112	−26,300	−26,344	−22,600	[47]
	Gibbs energy of formation	α	β	900	−25,580	−25,600	−26,000	[48]
	Gibbs Energy of formation	α	β	827	−25,600	−25,600	−26,400	[49]
FeB	Enthalpy of formation	α	β	25	−32,400	−29,600	−35,600	[46]
	Enthalpy of formation	γ	β	1112	−36,400	−33,600	−32,300	[47]
	Gibbs energy of formation	α	β	900	−32,700	−31,600	−31,800	[48]
	Gibbs Energy of formation	α	β	827	−32,940	−31,700	−33,300	[42]
	Enthalpy of fusion	–	–	1590	37,600	38,600	31,600	[50]
	Entropy of formation	–	–	25	17.96 (J/mol of atoms °C)	19.4 (J/mol of atoms °C)	18.1 (J/mol of atoms °C)	[50]
Fe_3B	Enthalpy of formation	γ	β	1112	−18,500	−18,300	−17,840	[37]

$Fe_2Si_{0.4}B_{0.6}$. In this study all these are described as stoichiometric phases expressing their free energy according to the formula

$$G^{Fe_aSi_bB_c} = a\,{}^0G_{Fe}^{bcc} + b\,{}^0G_{Si}^{diamond} + c\,{}^0G_{B}^{\beta-rhombohedral} + \Delta G^f_{Fe_aSi_bB_c} \tag{1}$$

where ${}^0G_{Fe}^{bcc}$, $G_{Si}^{diamond}$ and $G_B^{\beta-rhombohedral}$ are the lattice stability of the reference state respectively for Fe, Si and B.

The formation energy per mole of unit formula, $\Delta G^f_{Fe_aSi_bB_c}$, is expressed by

$$\Delta G^f_{Fe_aSi_bB_c} = A + BT \tag{2}$$

being A and B the enthalpy and the entropy of formation.

The Gibbs free energy of *fcc* and the *bcc* solid solutions and of the liquid are treated according to the conventional sub-regular solution model

$$G = {}^{ref}G + {}^{id}G + {}^{ex}G \tag{3}$$

$${}^{ref}G = x_B\,{}^0G_B^{\phi} + x_{Fe}\,{}^0G_{Fe}^{\phi} + x_{Si}\,{}^0G_{Si}^{\phi} \tag{4}$$

$${}^{id}G = RT(x_B \ln x_B + x_{Fe} \ln x_{Fe} + x_{Si} \ln x_{Si}) \tag{5}$$

$${}^{ex}G = x_Bx_{Fe}\,{}^{\phi}L_{B,Fe} + x_{Fe}x_{Si}\,{}^{\phi}L_{Fe,Si} + x_Bx_{Si}L_{B,Si} + x_Bx_{Fe}x_{Si}\,{}^{\phi}L_{B,Fe,Si} \tag{6}$$

where ${}^0G_i$ denotes the Gibbs free energy of the element i in the ϕ phase, x_i the molar fraction of the element i and R is the gas constant. The excess free energy ${}^{ex}G$ has been expressed with the Redlich–Kister–Muggianu polynomial and ${}^{\phi}L_{A,B}$, ${}^{\phi}L_{A,B,C}$ (Table 3) stand for the interaction parameters for the binary and ternary systems. The ${}^0G_i$ has been taken from SGTE data file [17]. A parameter of ternary interaction has been used in the description of the liquid but not for the ternary *fcc* and *bcc* solid solutions.

Table 2
Enthalpy and temperature of crystallization of the amorphous Fe–Si–B phase calculated in this work and experimental [41–43].

$x(Fe)$	$x(B)$	$x(Si)$	Exp. ΔH (J/mol)	Calc. ΔH (J/mol)	Exp. T_x (°C)	Ref.
0.75	0.1	0.15	5629	5763	548	[41]
0.78	0.13	0.09	7470	7370	542	[42]
0.8	0.18	0.02	6653	6749	493	[41]
0.8	0.16	0.04	7463	8057	515	[41]
0.8	0.12	0.08	7330	7309	538	[41]
0.8	0.1	0.1	6896	7263	539	[41]
0.8	0.14	0.06	7612	7580	532	[41]
0.805	0.173	0.022	6900	6805	487	[43]
0.805	0.129	0.066	8700	8518	517	[43]
0.81	0.106	0.084	7790	7312	537	[43]
0.81	0.085	0.105	7700	7625	527	[43]

Table 3
Assessed parameters of the ternary Fe–Si–B system.

Phase	Parameter (J/mol)		Amorphous phase parameter			
Liquid	${}^0L^L_{B,Fe}$	−122861 + 14.59T	${\Lambda_0}^{B,Fe}$	394	${\alpha_g}^{Fe}$	1.05
	${}^1L^L_{B,Fe}$	19523	${\Lambda_1}^{B,Fe}$	1152	${\alpha_g}^{Si}$	34.09.00
	${}^2L^L_{B,Fe}$	51070	${\Lambda_2}^{B,Fe}$	870	${\alpha_g}^{B}$	12
	${}^0L^L_{B,Fe,Si}$	0	${\Lambda_0}^{B,Fe,Si}$	−2039	${T_g}^{Fe}$	452.07.00
	${}^1L^L_{B,Fe,Si}$	−55686	${\Lambda_1}^{B,Fe,Si}$	662	${T_g}^{Si}$	422
	${}^2L^L_{B,Fe,Si}$	93217	${\Lambda_2}^{B,Fe,Si}$	−3483	${T_g}^{B}$	587.25.00
			${\Omega_0}^{B,Fe}$	471.06.00		
Fe_5SiB_2	A	−269801	${\Omega_0}^{B,Fe,Si}$	−77049		
	B	23.59	${\Omega_1}^{B,Fe,Si}$	40437		
$Fe_{4.7}Si_2B$	A	−248130	${\Omega_2}^{B,Fe,Si}$	−59909		
	B	5				
$Fe_2Si_{0.4}B_{0.6}$	A	−92665				
	B	0.296527778				
BCC	${}^0L^{bcc}_{B,Fe}$	−33092 + 15.6T				
FeB	A	−73933				
	B	0.307638889				
Fe_2B	A	−81226				
	B	3.01				
Fe_3B	A	−77749				
	B	2.59				

2.2. Accounting for the glass transition

In the temperature range from the glass transition temperature up to the melting point glass-formers display an excess heat capacity related to ordering at short range in the undercooling regime (expressed by both the associate solution model and the two state model [18,19]). Palumbo [2] proposed to model the glass transition as a second order one; this can be justified by the consideration that the behavior of the extensive and differential thermodynamic properties during it agree with Ehrenfest's classification of thermodynamic transitions [20]. Of course the amorphous phase cannot be considered as sitting in a single minimum in the free energy landscape of a multicomponent system but a wealth of local minima must be envisaged. Therefore, the glass transition temperature depends on the cooling rate and can be better defined as a range of temperatures where the formation of a glassy state occurs. With the aim to build a model capable of fitting experimental data in an assessment process, it can be assumed that the ordering in the undercooled liquid occurs until the entropy of the solid phase and that of the liquid are the same (Kauzmann paradox) at the Kauzmann temperature, T_K. Although this temperature point cannot be detected in experiments, it provides a thermodynamic definition of the glass transition temperature. In the framework of CALPHAD a formalism is used since long to represent