

A correction to “parallel tangent” method for modelling segregation to grain boundaries and other interfaces for components of different atomic sizes

George KAPTAY

Dep Nanotechnology, University of Miskolc, Egyetemvaros, Miskolc, 3515 Hungary

Dep Materials Development, BAY-ENG, 2 Igloi, Miskolc, 3519 Hungary

MTA ME Materials Science Research Group, Egyetemvaros, Miskolc, 3515 Hungary

phone: +36 30 415 0002, e-mail: kaptay@hotmail.com

Abstract

Hillert showed an elegant way to obtain the equilibrium composition of interfaces (including grain boundaries) and the equilibrium interfacial energy for binary solutions using his “parallel tangent construction”. However, this method is correct only for equal sizes of atoms of the components. A corrected equation is derived here from the two fundamental equations of Gibbs. Our resulting non-parallel tangent construction is less elegant, but more correct compared to the parallel tangent construction of Hillert. Our method is also extended to multi-component solid solutions. Our method is equivalent to the Butler equations, without a need to introduce partial interfacial energies.

Keywords: segregation; grain boundary; parallel tangent construction; Butler equation.

Interfaces and particularly grain boundaries (GB) play an important role in materials science [1-4]. Therefore modelling equilibrium interface composition (segregation) and equilibrium interfacial energy in binary and multi-component solutions is one of the important tasks of materials science [5-10].

An elegant method was introduced by Hillert [11], demonstrated in Fig.1 for a binary A-B solid solution α at a fixed temperature and at a fixed pressure. Suppose its integral molar Gibbs energy (denoted as $G_{m,\alpha}$, J/mol) is known as function of bulk mole fraction of component B (denoted as $x_{B,\alpha}$, dimensionless) at given temperature and pressure for a macroscopic solution. The chemical potentials of its components can be found by drawing a tangent line to the curve of the integral molar Gibbs energy at the selected composition, as shown in Fig.1. Suppose the integral molar Gibbs energy of the grain boundary (denoted as $G_{m,gb}$, J/mole) is also known as function of the composition of the interfacial region (denoted as $x_{B,gb}$, dimensionless) at the same temperature and pressure. Hillert suggests drawing a

parallel tangent line to the above explained tangent line, but this time being a tangent to the integral molar Gibbs energy line of the GB. He has two important claims regarding to this parallel tangent construction:

- i. the mole fraction at which the new tangent line touches the molar integral Gibbs energy line of the GB corresponds to the equilibrium composition of the GB,
- ii. the vertical distance (measured in J/mole) between the two parallel lines corresponds to the equilibrium interfacial energy, multiplied by $V_{m,i}/t$, where $V_{m,i}$ (m^3/mole) is the molar volume of the interfacial region and t (m) is its thickness.

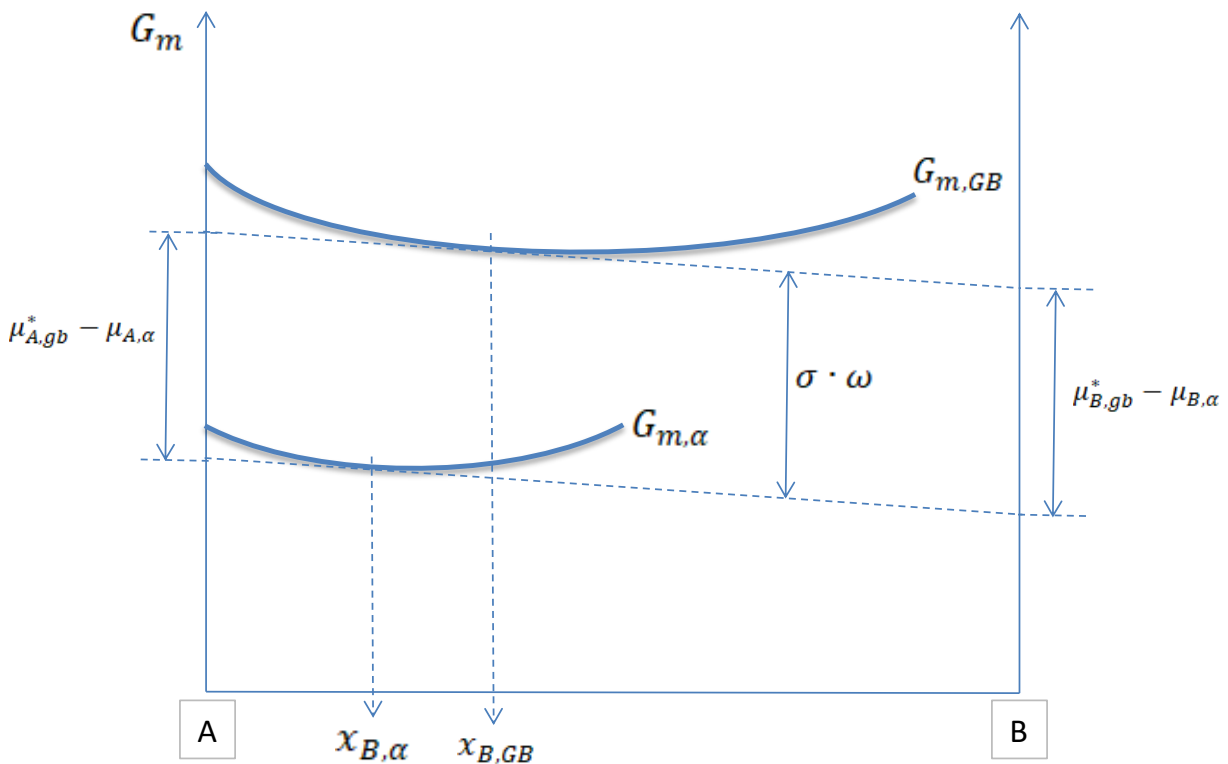


Fig.1. Schematic representation of the parallel tangent construction by Hillert at constant temperature and pressure (similar to Fig.16.5 of his book [11]). From the figure one can easily read the equilibrium values of $x_{B,GB}$ and $\sigma \cdot \omega$ as function of bulk composition ($x_{B,\alpha}$). If the value of ω ($= V_{m,GB}/t$ after Hillert) is known, the equilibrium value of σ follows. This parallel tangent construction is valid only at $\omega_A = \omega_B = \omega$.

Let us mention that the expression $V_{m,i}/t$ is equivalent to the partial molar GB area of component i as used by this author (denoted as ω_i , m^2/mol) – for more details see below. The distance between the two parallel tangents in the construction of Hillert is the excess partial molar interfacial Gibbs energy ($\sigma \cdot \omega_i$, J/mole). When $\omega_A = \omega_B = \omega$ for the binary A-B solution, the correct result $\sigma = \sigma$ follows from the parallel tangent construction as shown in Fig.1. However, if $\omega_A \neq \omega_B$, then the incorrect result $\sigma \neq \sigma$ follows from the same parallel

tangent construction of Hillert. The goal of this paper is to derive a correct equation for the general case from the fundamental equations of Gibbs [12].

The parallel tangent construction of Hillert is frequently used in the literature for GBs of binary and multi-component systems [13-19] and even to anti phase boundaries [20]. However, there is some confusion in the literature as a method under the same name “parallel tangent” is applied to find equilibrium composition of nuclei [21-28]. However, despite the same name of the two methods, the two problems are different and should not be confused or treated together. The first problem relates to adsorption / segregation of components from bulk phases to interfaces, while the second problem relates to nano-thermodynamics, extensively discussed by the author recently [3, 29-31]. In this paper only the problem of GB segregation, or more generally, the problem of interfacial segregation will be discussed.

Let us first write the first fundamental equation of Gibbs [12] for the case of bulk phase α , neglecting the role of any interface:

$$dG_{\alpha} = \sum_i \mu_{i,\alpha} \cdot dn_{i,\alpha} \quad (1)$$

where G_{α} (J) is the Gibbs energy of bulk phase α , $\mu_{i,\alpha}$ (J/mole) is the chemical potential of component i in the same phase and $n_{i,\alpha}$ (mole) is the amount of component i in the same phase. Now, let us define the chemical potential in the bulk phase from Eq.(1):

$$\mu_{i,\alpha} \equiv \left(\frac{dG_{\alpha}}{dn_{i,\alpha}} \right)_{p,T,n_{j \neq i,\alpha}} \quad (2a)$$

Now, let us divide the right hand side of Eq.(2a) by the ratio $1 = n_{\alpha}/n_{\alpha}$ (with n_{α} , mole, the total amount of matter in bulk phase α). Then, an alternative for of Eq.(2a) is obtained, taking into account that the molar Gibbs energy of bulk phase α is defined as $G_{m,\alpha} \equiv G_{\alpha}/n_{\alpha}$ and the mole fraction of component i in bulk phase α is defined as: $x_{i,\alpha} \equiv n_{i,\alpha}/n_{\alpha}$:

$$\mu_{i,\alpha} \equiv \left(\frac{dG_{m,\alpha}}{dx_{i,\alpha}} \right)_{p,T,x_{j \neq i,\alpha}} \quad (2b)$$

Eq.(2b) is equivalent with Eq.(2a), but Eq.(2b) is written using quantities of Fig.1. Now, let us write the second fundamental equation of Gibbs [12] for the bulk phase with an interface, particularly with a grain boundary (GB):

$$dG_{GB} = \sum_i \mu_{i,gb} \cdot dn_{i,gb} + \sigma \cdot A \quad (3)$$

where G_{GB} (J) is the Gibbs energy of the grain boundary, $\mu_{i,gb}$ (J/mole) is the chemical potential of component i in the GB, $n_{i,gb}$ (mole) is the amount of component i in the GB, σ (J/m²) is the GB energy (or more generally the interfacial energy), A (m²) is the interfacial

area of the GB. Now, let us express the chemical potential from Eq.(3) similarly as done above:

$$\mu_{i,gb} \equiv \left(\frac{dG_{gb}}{dn_{i,gb}} \right)_{p,T,n_{j \neq i,gb}} - \sigma \cdot \left(\frac{dA}{dn_{i,gb}} \right)_{p,T,n_{j \neq i,gb}} \quad (4a)$$

The partial molar surface area of component i in the GB is denoted as ω_i (m²/mole) and is defined as:

$$\omega_i \equiv \left(\frac{dA}{dn_{i,gb}} \right)_{p,T,n_{j \neq i,gb}} \quad (4b)$$

Now, let us define the reduced chemical potential of component i in the GB (it is called “reduced “ as it does not contain the $\sigma \cdot \omega_i$ term), denote $\mu_{i,gb}^*$ (J/mole):

$$\mu_{i,gb}^* \equiv \left(\frac{dG_{m,gb}}{dx_{i,gb}} \right)_{p,T,x_{j \neq i,gb}} \quad (4c)$$

Eq.(4c) was obtained by multiplying the first term on the right hand side of Eq.(4a) by the ratio $1 = n_{gb}/n_{gb}$ (with n_{gb} , mole, the total amount of matter in the GB) and taking into account that the molar Gibbs energy of GB is defined as $G_{m,gb} \equiv G_{gb}/n_{gb}$ and the mole fraction of component i in GB is defined as: $x_{i,gb} \equiv n_{i,gb}/n_{gb}$. In this way Eq.(4c) is written using quantities of Fig.1. Now, let us substitute Eq-s (4b-c) into Eq.(4a):

$$\mu_{i,gb} = \mu_{i,gb}^* - \sigma \cdot \omega_i \quad (4d)$$

Following Gibbs [12], the condition of equilibrium between a bulk phase α and the GB follows as:

$$\mu_{i,\alpha} = \mu_{i,gb} \quad (5)$$

Substituting Eq.(4d) into Eq.(5), the GB energy can be expressed as:

$$\sigma = \frac{\mu_{i,gb}^* - \mu_{i,\alpha}}{\omega_i} \quad (6a)$$

As Eq.(6a) is valid for each component, the following equations are valid for a multi-component solution A-B-C...:

$$\sigma = \frac{\mu_{A,gb}^* - \mu_{A,\alpha}}{\omega_A} = \frac{\mu_{B,gb}^* - \mu_{B,\alpha}}{\omega_B} = \frac{\mu_{C,gb}^* - \mu_{C,\alpha}}{\omega_C} = \dots \quad (6b)$$

As follows from Eq.(6b), the differences of chemical potentials of different components will equal ($\mu_{A,gb}^* - \mu_{A,\alpha} = \mu_{B,gb}^* - \mu_{B,\alpha} = \mu_{C,gb}^* - \mu_{C,\alpha} = \dots$) only, if the partial GB areas of the components have the same values: $\omega_A = \omega_B = \omega_C = \dots$. Thus, only under this latter condition the parallel tangent construction of Hillert is valid. For all other cases the tangents to the molar Gibbs energy of the bulk phase and the tangent to the molar Gibbs

energy of the GB should not be parallel, rather they should obey Eq.(6b). For a binary A-B system, the following equation follows from Eq.(6b):

$$\frac{\mu_{A,gb}^* - \mu_{A,\alpha}}{\mu_{B,gb}^* - \mu_{B,\alpha}} = \frac{\omega_A}{\omega_B} \quad (6c)$$

The case of $\omega_A/\omega_B = 1$ is shown in Fig.1. As another example, Fig.1 is repeated in Fig. 2 for $\omega_A/\omega_B = 0.5$. As follows from Fig.2, in this case segregation of component B is enhanced compared to the case shown in Fig.1. This is a general rule for the case when the interface active solute B has a larger atomic size compared to the solvent atom A.

Now, let us write the simplest model for the partial GB area supposing spherical atoms [3, 10]:

$$\omega_i = \pi \cdot r_{i,a}^2 \cdot \frac{N_{Av}}{f_{gb}} \quad (7a)$$

where $r_{i,a}$ (m) is the atomic radius of component i, $N_{Av} \cong 6.02 \cdot 10^{23}$ 1/mol is the Avogadro number, f_{gb} (dimensionless) is the 2-D packing fraction of atoms along the GB. The latter is a complex function of the structure of the grain, the structure of the grain boundary and the crystal planes of the two grains around the GB. For the same GB between the same two grains it can be supposed that f_{gb} is not a function of the composition of the GB and the grains, and therefore Eq.(6c) can be re-written using Eq.(7a) as:

$$\frac{\mu_{A,gb}^* - \mu_{A,\alpha}}{\mu_{B,gb}^* - \mu_{B,\alpha}} = \left(\frac{r_{A,a}}{r_{B,a}} \right)^2 \quad (7b)$$

As the molar volume is proportional to the cube of the atomic radii, alternatively also the following equation can be written:

$$\frac{\mu_{A,gb}^* - \mu_{A,\alpha}}{\mu_{B,gb}^* - \mu_{B,\alpha}} = \left(\frac{V_{m,A\alpha}}{V_{m,B\alpha}} \right)^{2/3} \quad (7c)$$

where $V_{m,A\alpha}$ (m^3/mol) is the partial molar volume of component A in phase α and $V_{m,B\alpha}$ (m^3/mol) is the partial molar volume of component B in phase α . As follows from Eq-s.(7b-c), the deviation from the parallel tangent rule of Hillert depends on the square of the ratios of the atomic radii of the two components of the binary solution, or alternatively it depends on the 2/3 power of the ratio of the partial molar volumes of the two components. Eq.(7b) is more transparent to understand, but Eq.(7c) is more useful as it can take into account the T-dependence through the T-dependences of the partial molar volumes of the components.

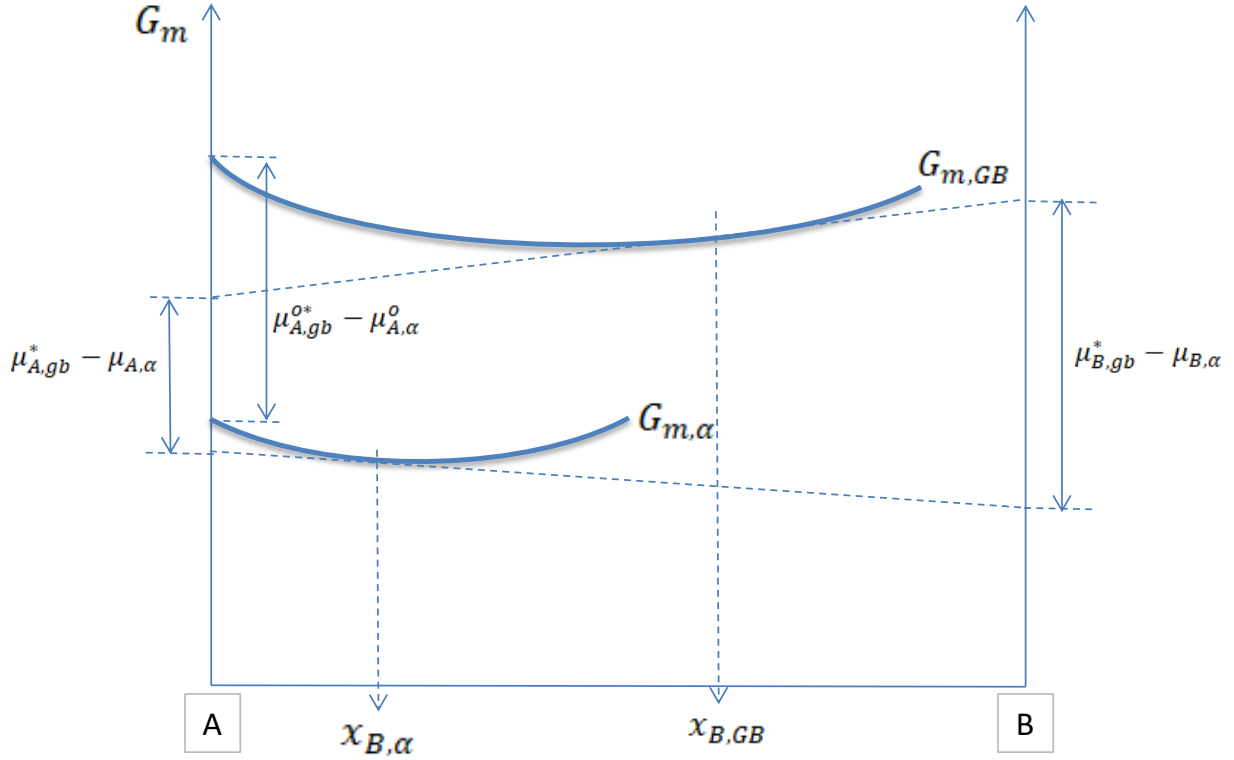


Fig.2. Same as Fig.1, but valid for $\omega_A/\omega_B = 0.5$ in accordance with Eq.(6c). Note that in equilibrium the two tangents lines are not parallel, in contrary to the case of Fig.1 valid for

$$\omega_A/\omega_B = 1$$

Now, let us write an equation for the integral molar Gibbs energy of the bulk phase α ($G_{m,\alpha}$, J/mole):

$$G_{m,\alpha} = G_{m,\alpha}^o + \Delta G_{m,\alpha}^{id} + G_{m,\alpha}^E \quad (8a)$$

where $G_{m,\alpha}^o$ (J/mole) is the standard integral molar Gibbs energy of the mechanical mixture, $\Delta G_{m,\alpha}^{id}$ (J/mole) is the molar Gibbs energy change accompanying the formation of the ideal solution from the mechanical mixture, $G_{m,\alpha}^E$ (J/mole) is the molar integral excess Gibbs energy of the bulk solution, written as:

$$G_{m,\alpha}^o = (1 - x_{B,\alpha}) \cdot \mu_{A,\alpha}^o + x_{B,\alpha} \cdot \mu_{B,\alpha}^o \quad (8b)$$

$$\Delta G_{m,\alpha}^{id} = R \cdot T \cdot [x_{B,\alpha} \cdot \ln x_{B,\alpha} + (1 - x_{B,\alpha}) \cdot \ln (1 - x_{B,\alpha})] \quad (8c)$$

$$G_{m,\alpha}^E = L_o \cdot x_{B,\alpha} \cdot (1 - x_{B,\alpha}) \quad (8d)$$

where $\mu_{A,\alpha}^o$ (J/mole) is the standard chemical potential of phase α made of only component A, $\mu_{B,\alpha}^o$ (J/mole) is the same when phase α is made of only component B, $R = 8.314$ J/molK is the universal gas constant, T (K) is absolute temperature, L_o (J/mole) is the interaction energy of

the regular solution model. Now, let us substitute $x_{B,\alpha} = x_{B,gb} = 0$ into Eq.(6a) and express from the resulting equation $\mu_{A,gb}^{*o}$:

$$\mu_{A,gb}^{o*} = \mu_{A,\alpha}^o + \omega_A^o \cdot \sigma_A^o \quad (9a)$$

where all the quantities are defined similarly as above, but the upper index “o” and the lower index “A” mean that all quantities belong to a pure phase made of only component A. For example, σ_A^o (J/m²) is the GB energy of a pure system made of only component A. A similar equation can also be written for component B by substituting $x_{B,\alpha} = x_{B,gb} = 1$ into Eq.(6a) as:

$$\mu_{B,gb}^{o*} = \mu_{B,\alpha}^o + \omega_B^o \cdot \sigma_B^o \quad (9b)$$

Now, let us write the integral molar Gibbs energy of the GB ($G_{m,gb}$, J/mole), in analogy with Eq.(8a):

$$G_{m,gb} = G_{m,gb}^o + \Delta G_{m,gb}^{id} + G_{m,gb}^E \quad (10a)$$

where the quantities are the same as in Eq.(8a), but they all belong to the GB and can be written by equations similar to Eq-s (8b-d):

$$G_{m,gb}^o = (1 - x_{B,gb}) \cdot \mu_{A,gb}^{o*} + x_{B,gb} \cdot \mu_{B,gb}^{o*} \quad (10b)$$

$$\Delta G_{m,gb}^{id} = R \cdot T \cdot [x_{B,gb} \cdot \ln x_{B,gb} + (1 - x_{B,gb}) \cdot \ln (1 - x_{B,gb})] \quad (10c)$$

$$G_{m,gb}^E = \frac{z_{gb}}{z_\alpha} \cdot L_o \cdot x_{B,gb} \cdot (1 - x_{B,gb}) \quad (10d)$$

where z_{gb} (dimensionless) is the coordination number in GB, z_α (dimensionless) is the coordination number in the bulk of the α grain. As follows from Eq-s (8-10), if the model parameters for the molar Gibbs energy of the bulk phase α are known, then the molar Gibbs energy of the GB can be modelled if the following additional parameters are known: σ_A^o , σ_B^o , ω_A^o , ω_B^o and z_{gb}/z_α . In the first approximation: $\omega_i = \omega_i^o$. Now, let us write the ratio of the differences of the two chemical potentials from Eq-s (6a, 9a):

$$\frac{\mu_{A,gb}^* - \mu_{A,\alpha}}{\mu_{A,gb}^{o*} - \mu_{A,\alpha}^o} = \frac{\omega_A \cdot \sigma}{\omega_A^o \cdot \sigma_A^o} \quad (11a)$$

If the above approximation $\omega_A = \omega_A^o$ is valid, then σ can be expressed from Eq.(11a) as:

$$\sigma = \sigma_A^o \cdot \frac{\mu_{A,gb}^* - \mu_{A,\alpha}}{\mu_{A,gb}^{o*} - \mu_{A,\alpha}^o} \quad (11b)$$

Similar equations are valid for all other components. As follows from Eq.(11b), in this case the molar interfacial areas and therefore the value of f_{gb} fall out from the calculation of σ . As follows from Fig.2, the ratio in the right hand side of Eq.(11b) is smaller than unity and

so $\sigma < \sigma_A^0$. This is generally valid when component B is GB-active, i.e. when $\sigma_B^0 < \sigma_A^0$, i.e. when component B segregates preferentially to GB.

As a conclusion it is claimed here that the parallel tangent construction of Hillert is just a simplified case of our generally valid Eq-s (6-7). The parallel tangent construction can be used only if the atomic sizes of all components are the same. In all other cases our Eq-s (6-7) should be used and the two tangent lines are not parallel. It should be also mentioned that Eq-s (6) are identical with the Butler equations applied to GBs [10] (see also [15]), but without the need to introduce partial GB energies.

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References

1. L.Zhang, Q.Zheng, H.Jiang, J.Zhao, Scripta Mater 160 (2019) 25.
2. J.Pinkas, J.Sopousek, P.Broz, V.Vykoukal, J.Bursik, J.Vrestal, Calphad 64 (2019) 139.
3. G.Kaptay, Adv Colloid Interface Sci 256 (2018) 163.
4. P.Lejcek, Grain Boundary Segregation in Metals. Springer-Verlag Berlin, 2010.
5. Y.Liu, S.Liu, Y.Du, Y.Peng, C.Zhang, S.Yao, Calphad 65 (2019) 225.
6. V.M.Samsonov, A.G.Bembel, A.Yu. Kartoshkin, S.A.Vasilyev, I.V.Talyzin, J Thermal Anal Calorimetry 133 (2018) 1207.
7. P.Lejcek, M.Vsianska, M.Sob, J Mater Res, 33 (2018) 2647.
8. G.Kaptay, J Mater Sci 53 (2018) 3767.
9. Y.Yang, S.L.Chen, Calphad 52 (2017) 134.
10. G.Kaptay, J Mater Sci 51 (2016) 1738.
11. M.Hillert, Phase equilibria, phase diagrams and phase transformations – their thermodynamic basis. 2nd edition, Cambridge University Press, Cambridge, UK. 2007.
12. J.W.Gibbs, Trans. Conn. Acad. Arts Sci. 3 (1875-1878) 108 and 343.
13. N.Goukon, T.Ikeda, M.Kajihara, Acta Mater 48 (2000) 1551.
14. T. Nishizawa, ISIJ Int 40 (2000) 1269.
15. Y.B. Kang, Calphad 50 (2015) 23.
16. S.G. Kim, J.S. Lee, B.J. Lee, Acta Mater 112 (2016) 150.
17. M.M. Gong, F.Liu, Y.Z.Chen, J Alloys Compounds 682 (2016) 89.
18. F. Abdeljawad, P. Lu, N.A. Blythe, G.C. Brad, L.B. Stephen, M. Foiles, Acta Mater 126 (2017) 528.
19. A. Kwiatkowski da Silva, R. D. Kamachali, D. Ponge, B. Gault, J. Neugebauer, D. Raabe, Acta Mater 168 (2019) 109.
20. K.Niitsu, K.Minakuchi, X.Xu, M.Nagasako, I.Ohnuma, T.Tanigaki, Y.Murakami, D.Shindo, R.Kainuma, Acta Mater 122 (2017) 166.
21. E. Kozeschnik, Calphad 24 (2000) 245.
22. M.Hillert, M. Rettenmayr, Acta Mater 51 (2003) 2803.
23. B. Rheingans, E.J. Mittemeijer, Calphad 50 (2015) 49.

24. A.Malik, J.Odqvist, L.Höglund, S.Hertzman, J.Agren, *Metal Mater Trans A* 48A (2017) 4919.
25. F.S. Spear, O.M. Wolfe, *Chem Geology* 491 (2018) 39.
26. X. Kang, L. Zhang, S. Sobolev, *Sci Rep* 8 (2018) 5348.
27. W.K.Che, J.B.Zhang, L.K.Huang, S.Y.Duan, F.Liu, S.J.Song, *J Mater Sci Technol* 35 (2019) 1753.
28. M. Bonvalet-Rolland, T. Philippe, J. Ågren, *Acta Mater* 171 (2019) 1.
29. G.Kaptay, *J Mater Sci* 47 (2012) 8320.
30. G.Kaptay, *RSC Adv* 7 (2017) 4124.
31. A.Vegh, G.Kaptay, *Calphad* 63 (2018) 37.