Reply to Comments on Comments on Kinetics Model of Isothermal Pearlite Formation in a 0.4C-1.6Mn Steel

C. Capdevila^{*}, F.G. Caballero and C. García de Andrés

Dept. Physical Metallurgy, Centro Nacional de Investigaciones Metalúrgicas (CENIM),
Consejo Superior de Investigaciones Metalúrgicas (CSIC), Avda. Gregorio del Amo 8,
E-28040 Madrid, Spain

Abstract

A theoretical model to calculate the evolution of austenite-to-pearlite transformation with time at a very wide temperature range is presented. The model is based on thermodynamic calculations under partitioning local equilibrium (LE) and non-partitioning local equilibrium (NPLE) consideration.

The manuscript replies to comments [1] on our previous work [2].

Pearlite transformation is reconstructive and known to show a constant growth rate because the composition of untransformed matrix remains unchanged except near the transformation front [3]. The growth rate of pearlite is believed to be controlled by either volume diffusion of carbon [4-5] or by boundary diffusion of substitutional alloying elements [6-7]. When the growth rate of pearlite in Fe-C-Mn steels is controlled by the diffusion of carbon in austenite ahead of the interface between pearlite and austenite, it is natural to assume that there is no redistribution of Mn between matrix and precipitate phases. Therefore, the interface composition may be determined by the NPLE condition.

When the redistribution of Mn can occur during the growth event of pearlite, on the other hand, the LE condition is maintained at the interfaces. Under such condition, the activity of carbon in austenite at the austenite-ferrite (g_a) and austenite-cementite (g_q) interfaces are identical so that the flux of carbon ahead of the interfaces is negligible, thus allowing the diffusion of Mn catch up with that of carbon.

Recently Capdevila *et al* presented a theoretical model to calculate the evolution of pearlite volume fraction formed during the isothermal decomposition of austenite. The nucleation of pearlite was considered as a cementite precipitation process on a moving g_a interface, meanwhile the expression for pearlite growth rate is different depending on volume diffusion of carbon or boundary diffusion of Mn as the rate controlling mechanism.

In their discussion of Ref. [2] to which this reply is a companion, Hillert and Höglund [1] point out that the results of the reported thermodynamic calculations shows “an impossible situation”. They show, rightly so, that the solubility limit of ferrite under NPLE condition should fall below the tie line for partitioning equilibrium condition. Thus an error is introduced into calculations of the set of interface compositions by Capdevila *et al* [2]. As it is shown below, the error is minor for the aim of the work presented in Ref. [2] of describing the kinetics of pearlite formation during isothermal decomposition of austenite.

In their discussion paper [1], Hillert and Höglund describe an alternative procedure to calculate the interface compositions. In the following paragraphs a new set of interface

---

^{*} Corresponding author: Tel. +34-915538900; fax: +34-915347425; e-mail: ccm@cenim.csic.es

compositions are re-calculated, and it is shown that the results obtained with the method described in Ref. [2] are similar to those presented by Hillert and Höglund obtained with Thermocalc.

In the case of the ga interface, the equilibrium condition can be expressed by the equality of the chemical potentials of each element (iron, carbon and manganese) between ferrite and austenite phases, which lead to three different equations (equations (6) in Ref. [2], the subscripts 0, 1 and 2 denote iron, carbon, and manganese, respectively). However, there are four unknown variables, *i.e.* the carbon and manganese concentration in austenite and ferrite at the ga interface. Therefore, a fourth equation is needed. In this sense, points (x_1^a, x_2^a) and (x_1^g, x_2^g) in the phase diagram are on a tie-line going through the alloy composition $(\bar{x}_1, \bar{x}_2)$. Thus this coordinates are related by

$$x_2^g - \bar{x}_2 = \frac{x_2^g - x_2^a}{x_1^g - x_1^a} (x_1^g - \bar{x}_1) \quad (1)$$

Substitution of equations (9) and (10) in Ref. [2], which relate the carbon and manganese concentrations in ferrite with those in austenite ($x_1^{ag} = A_1 x_1^{ga}$ and $x_2^{ag} = A_2 x_2^{ga}$), into equation (1) yields

$$x_2^{ga} = \frac{\bar{x}_2 (1 - A_1) x_1^{ga}}{(1 - A_2) \bar{x}_1 + (A_2 - A_1) x_1^{ga}} \quad (2)$$

This is equation (11) in Ref. [2] about which some concerns are expressed by Hillert and Höglund [1]. Therefore, combining these four equation, it is yield an equation only function of x_1^{ga} (equation (12) in Ref. [2]), which can be solved easily using numerical analysis methods.

Nevertheless, the main concern of Hillert and Höglund in the discussion paper [1] are focussed on calculation procedure of interface compositions under NPLe condition. In this sense, the calculation procedure is detailed below. By the definition of NPLe, x_2^{ag} and x_2^{ga} (subscript N denotes NPLe) are set equal to the alloy composition $(\bar{x}_2)$. Thus, one obtains $x_{2E}^{ga} = \bar{x}_2 / A_2$ (subscript E denotes LE). Introducing these two conditions in the equation (12) in Ref. [2], a value of x_{1E}^{ga} is obtained. This step is clearly indicated in Ref. [2].

Moreover, in reference to Fig. 1, points E and N are related by the carbon iso- activity condition. Therefore $\ln a_{1E}^g = \ln a_{1N}^g$. The value of $\ln a_1^g$ could be expressed as $\ln a_1^g = \ln x_1^g + c_1$ where x_1^g is the mole fraction of carbon in austenite, and c_1 is the activity coefficient. The activity coefficients for dilute solutions may be expressed in the

familiar Wagner formalism, which for a ternary system become $c_1 = e_{11}^g x_1^g + e_{12}^g x_2^g$. Thus, the iso- activity condition yields,

$$\ln \frac{e_{11}^g x_{1E}^g}{e_{11}^g x_{1N}^g} = e_{11}^g (x_{1N}^g - x_{1E}^g) + e_{12}^g (x_{2N}^g - x_{2E}^g) \quad (3)$$

Setting $\Delta x_1 = x_{1E}^g - x_{1N}^g$, and noting the condition $\Delta x_1 \ll x_{1E}^g$, the expression $\ln(x_{1E}^g/x_{1N}^g)$ could be approximated by $1 - (x_{1N}^g/x_{1E}^g)$. Therefore, the carbon concentration under NPLE condition could be expressed as a function of x_{1E}^g by means of the following equation:

$$x_{1N}^g = x_{1E}^g \frac{e_{12}^g x_2 (1 - 1/A_2)}{1 + e_{11}^g x_{1E}^g} \quad (4)$$

The procedure above described in this reply was also carried out in calculations presented in Ref. [2], but some error were introduced during calculations.

On the other hand, in the case of the gq interface, only three equations are need to calculate the interface composition under the equilibrium condition, since the carbon concentration in cementite at the gq interface is fixed. In this sense, and restricting attention to low alloy steels where $x_2 \ll 1$, $y_2 \ll 1$, $x_0 \gg 1$ and $y_0 \gg 1$, subtracting equation (8) to equation (7) in Ref. [2], one then obtains:

$$y_2 = B_2 x_2^g = x_2^g \exp \left[\frac{DG_0^g - DG_2^g - w_{02}}{RT} + e_{12} x_1^g + e_{11} x_1^g / 2 \right] \quad (5)$$

It is worth noting that this expression for B_2 is different than the expressed by equation (13) in Ref. [2].

The manganese concentration in austenite at the gq interface (value of x_2^g) is calculated by the tie line indicated in Ref. [2]. However, a third equation is still needed. Alternatively to the procedure reported in Ref. [2], expanding the expression for the chemical potentials in equation (8) in Ref. [2] (instead of in equation (7) as indicated in Ref. [2]), this equation results in

$$DG_2^{gg} = RT \ln \frac{x_2}{y_2} + \frac{1}{3} \ln x_1^g + x_1^g e_{12}^g + \frac{1}{3} e_{11}^g x_2^g + x_2^g e_{22}^g + \frac{1}{3} e_{12}^g x_1^g - w_{02} (1 - y_2) \quad (6)$$

Since x_2^g and y_2 are expressed as a functions of x_1^g , equation (6) can be solved in the same way as for ga interface under LE condition.

For the case of gq interface under NPLe condition, by the definition of NPLe, $y_2 = 4\bar{x}_2/3$ and hence $x_2^{gq} = 4\bar{x}_2/3B_2$. Substituting these two conditions in equation (15) in Ref. [2], one might obtain a value of x_{1E}^{gq} . Then, the carbon concentration in austenite at the gq interface, in a similar procedure as for ga interface, is expressed by

$$x_{1N}^{gq} = x_{1E}^{gq} \frac{\dot{\epsilon}}{\dot{\epsilon}_1} - \frac{e_{12}^g \bar{x}_2 (1 - 4/3B_2) \dot{U}}{1 + e_{11}^g x_{1E}^{gq} \dot{U}} \quad (7)$$

Figure 2 shows the new calculated isopleth of the Fe-C-Mn phase diagram for 1.6 wt.-% Mn. It is clear that result is very similar to that obtained by Hillert and Höglund, which indicates that the procedure reported in Ref. [2], and slightly modified above, allows to calculate the interface compositions.

As was pointed out above, the aim of the kinetics model presented is to calculate the evolution of pearlite volume fraction formed during the isothermal decomposition of austenite. To assess the error that is introduced into the pearlite volume fraction calculations of Capdevila *et al* in Ref. [2], new calculations were evaluated as it is shown in Fig. 3. The above calculated interface compositions are introduced in the corresponding equation for pearlite growth rate (depending on carbon bulk diffusion or manganese boundary diffusion are the rate controlling mechanism), and then the extent of the pearlite reaction can be calculated as described in section 8 of Ref. [2].

Furthermore, some concerns about the equation used by Capdevila *et al* [2] to calculate the volume fraction of pearlite from the solubility limits are reported by Hillert and Höglund [1]. Such equation should reproduce the experimental fact that the lower isothermal temperature, the higher amount of pearlite is formed. Likewise, the isothermal transformation of a hypoeutectoid steel such as the studied will occur in two stages, the first being the separation of pro-eutectoid ferrite and the second the pearlite reaction itself. Between the temperatures Ae_3 and Ae_1 only pro-eutectoid ferrite is formed. As the temperature is lowered below Ae_1 the formation of pro-eutectoid phase gradually diminishes and is replaced by the pearlite reaction, and eventually, at a certain temperature T^* (the temperature at which the average carbon content set equal to the extrapolated gq interface) the whole product consists of the finely divided ferrite - cementite mixture [3]. The equation proposed by the authors deals with both situations. Figure 4 shows a comparison between the experimental values of pearlite volume fraction as compare with the calculated by equation (16) in Ref. [2] (interface composition values calculated as above). No significant changes with Fig. 3(b) in Ref. [2] are observed.

One final word should be made regarding the nucleation of pearlite which is two fold. Firstly, the austenite- ferrite (pro-eutectoid) interface should advance at a velocity slow enough to allow cementite precipitation, and latter the carbon content in the vicinity of the interface should fall inside the Hultgren's extrapolation. Of course, both conditions are only applied to the vicinity of the interface which nucleation is taking place. Likewise, both condition are considered in equation (19) in Ref. [2] for nucleation of pearlite, and therefore, we agree with the assessment that pearlite start to form well before that the average carbon content reaches such value.

Acknowledgements

The authors acknowledge financial support from Spanish Ministerio de Ciencia y Tecnología (MAT2001-1617). F.G. Caballero would like to thank the Spanish Ministerio de Ciencia y Tecnología and the Consejo Superior de Investigaciones Científicas for the financial support in the form of a Ramon y Cajal contract. C. Capdevila would like to express his gratitude to the Consejo Superior de Investigaciones Científicas for financial support as a Post-Doctoral contract (I3P PC-2001-1).

References

1. M Hillert and L Höglund, Scripta Materialia, (2003), this issue.
2. C Capdevila, F G Caballero and C García de Andrés, Acta Materialia, 50 (2002) 4629.
3. J W Christian, The theory of Transformations in Metals and Alloys (Part II), 3rd edition, Pergamon Press, Elsevier Science Ltd., Oxford 2002, p.802
4. C Zener, Trans. AIME, 167 (1946) 550.
5. M Hillert, Jernkont Ann., 141 (1957) 757.
6. J M Shapio and J S Kirkaldy, Acta Metall. 16 (1968) 579.
7. B E Sandquist, Acta Metall., 16 (1968) 1413.

Figure captions

Figure 1.- Schematic relationship between LE and NPLE for a ternary system

Figure 2.- Isopleth of the Fe-C-Mn phase diagram for Mn = 1.6 wt.-%.

Figure 3.- Comparison between old and new calculations for the extent of pearlite reaction at (a) 913 and (b) 873 K.

Figure 4.- New calculated evolution of pearlite volume fraction under LE and NPLE.

Figure 1.- Schematic relationship between LE and NPLE for a ternary system

Figure 2.- Isopleth of the Fe-C-Mn phase diagram for Mn = 1.6 wt.-%.

(a)

(b)

Figure 3.- Comparison between old and new calculations for the extent of pearlite reaction at (a) 913 and (b) 873 K.

Figure 4.- New calculation for the evolution of pearlite volume fraction under LE and NPLE.