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Discussion on “Stable Eutectoid Transformation in Nodular Cast Iron: Modeling and Validation”*

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Given that cast irons are multicomponent alloys, the decomposition of the high temperature austenite into ferrite and graphite happens within a finite temperature range and not at an invariant point, as often described schematically. Only a few models explicitly consider the existence of such an austenite–ferrite–graphite range: the contribution under discussion,[1] those that inspired it[2,3] and one previous study from the present author.[4] For kinetics reasons, this latter work explained that ferrite could not grow within the equilibrium three-phase field under continuous cooling; this is in contradiction with the other three reports. The aim of this discussion is first to recall the experimental evidence about ferrite formation during eutectoid transformation of cast iron and then to provide an explanation as to why ferrite starts forming upon cooling only when the temperature of the material is below the equilibrium three-phase field range, as observed experimentally.

It has long been recognized in the literature that the eutectoid transformation in cast irons occurs at very different temperatures upon cooling and upon heating, with the transformation temperature range being much lower upon cooling than that upon heating. Some authors called this behavior the eutectoid hysteresis[5] which can be studied by dilatometry or (differential) thermal analysis. Attempts to understand this phenomenon in relation to the general understanding of phase transformations led to a number of experimental studies looking for the actual equilibrium austenite–ferrite–graphite three-phase field, *e.g.*, works by Rehder,[5] Maitland and Hughes,[6] and Ekpoom and Heine[7] which are the most extensive reports available as reviewed in a former study.[8]

To illustrate this hysteresis, focus can be laid on the data from Ekpoom and Heine.[7] This work is of special interest as those authors plotted in one single graph the experimental temperature ranges for eutectoid transformation upon heating (at a rate of 11 K/min), at equilibrium, and upon cooling (at a rate of 7 K/min) as a function of the alloys’ silicon content. Figure 1 shows some of their experimental values, namely the start of the eutectoid transformation upon heating and upon cooling (solid symbols), and the upper limit of the equilibrium three-phase field (open symbols). Ekpoom and Heine mentioned that they unfortunately could not determine the exact lower limit of the equilibrium three-phase field because in the low-temperature range they always observed the formation of pearlite during the 1-hour holding time they scheduled for equilibration. It is worth noting that the experimental upper limit of the equilibrium three-phase field and the experimental temperature for the start of the eutectoid transformation upon heating appear superimposed. If Ekpoom and Heine had used a significantly higher heating rate, the formation of austenite would have started at a higher temperature, as it has been well established experimentally.[9]

Moreover, in Figure 1, the solid lines represent the calculated upper (denoted T_α^0) and lower (denoted T_α)

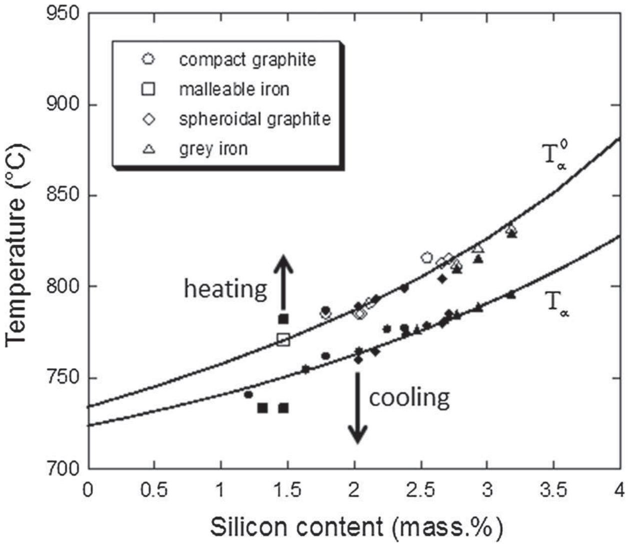

Fig. 1—Symbols represent experimental results from Ekpoom and Heine[7] showing the start of the eutectoid transformation upon heating and upon cooling (solid symbols), and the upper limit of the equilibrium three-phase field (open symbols). The solid lines are the upper (T_α^0) and lower (T_α) limits of the equilibrium three-phase field as calculated using the SSOL databank. The various symbols enable one to differentiate cast irons according to graphite shape: see insert. Note that the opening of the three-phase field at 0 mass pct Si is due to the fact that calculations were performed for alloys containing 0.3 mass pct Mn (see text).

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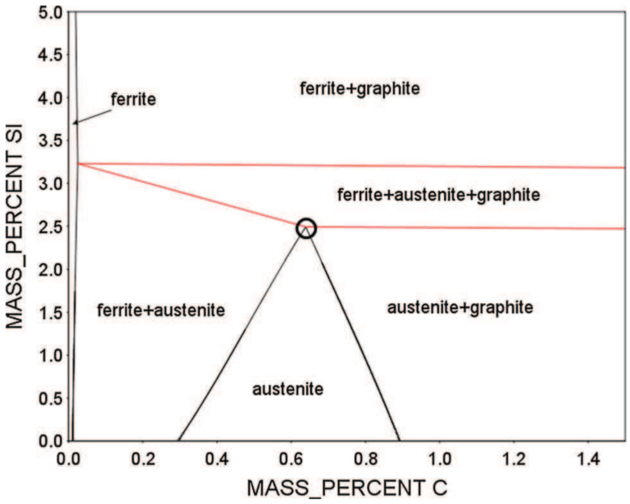

Fig. 2—Isothermal section of the Fe-C-Si system at 1084.3 K (811.2 °C) corresponding to the upper temperature limit of the equilibrium austenite–ferrite–graphite three-phase field (T_α^0) for an alloy with 2.5 mass pct Si. The eutectoid composition is indicated by an open circle which corresponds to the austenite composition. The composition of the ferrite in equilibrium with this eutectoid austenite is represented in the upper left corner of the three-phase field.

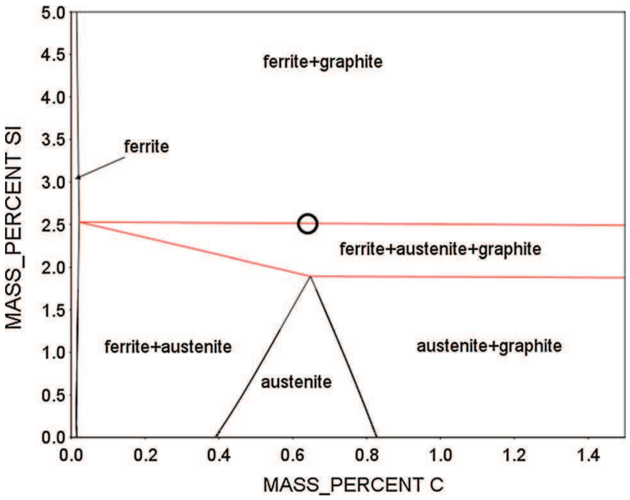

Fig. 3—Isothermal section of the Fe-C-Si system at 1062.4 K (789.2 °C) corresponding to the lower temperature limit of the equilibrium austenite–ferrite–graphite three-phase field (T_α) for an alloy with 2.5 mass pct Si. The eutectoid composition in Fig. 2 is indicated by an open circle.

limits of the three-phase field as a function of Si content for alloys containing 0.3 mass pct Mn (the average value indicated by Ekpoom and Heine for their alloys). Calculations have been carried out using the available SSOL database which includes the assessment of the Fe-C-Si phase diagram performed by Lacaze and Sundman.[10] It is observed that calculated and experimental upper limits of the equilibrium three-phase field are in close agreement. Symmetrically, the experimental temperature at which ferrite appears upon cooling closely matches the lower limit of the calculated equilibrium three-phase field. If Ekpoom and Heine had used a higher cooling rate, the formation of ferrite would have started at a lower temperature, as is clearly shown in continuous cooling transformation diagrams of cast irons.[11]

In summary, the above-mentioned hysteresis is strongly related to the equilibrium three-phase field, and Figure 1 shows that (i) upon continuous heating, austenite appears from ferrite above the equilibrium three-phase field; and (ii) upon cooling, ferrite appears from austenite at temperatures below the equilibrium three-phase field. In other words, upon continuous cooling, the eutectoid transformation does not occur within the temperature range of the equilibrium three-phase field. This has been detailed in works based on differential thermal analysis,[12,13] and this experimental evidence was recognized by Suarez and Loper in their discussion[14] of a previous paper on the effect of copper on the eutectoid transformation of steel and spheroidal graphite cast iron.[15]

It is worth noting that the above statements seem to apply to all types of graphitic irons: in Figure 1, the various symbols relate to different forms of graphite, and findings show that form has no effect on recorded temperatures. The fact that graphite shape has no influence on the start of the eutectoid transformation upon cooling was also demonstrated experimentally by Pan *et al.*[16] Consequently, this means that the conditions for ferrite formation during eutectoid transformation of cast irons are equivalent, whatever the graphite shape may be, even though the overall kinetics of the transformation are different.

It is well established that upon continuous cooling, the formation of ferrite occurs at the graphite–austenite interface, which suggests that ferrite growth is controlled by carbon redistribution. Accordingly, models for ferrite growth during eutectoid transformation rely on carbon redistribution and diffusion. Among the numerous works performed in this area, one finds models for lamellar graphite irons,[17] compact graphite irons,[3] and spheroidal graphite irons.[1,2,4,18] In contradistinction with the experimental evidence mentioned above, there is a long-lasting controversy on when ferrite can nucleate and initiate the eutectoid transformation in relation to the equilibrium three-phase field. As mentioned previously, there are very few works where the opening of the austenite–ferrite–graphite equilibrium three-phase field due to silicon and other substitutional solutes is actually taken into account. The study discussed herein[1] assumes that ferrite may nucleate and grow as soon as the upper limit of the equilibrium three-phase field is reached and that the ferrite then grows by rejecting carbon into austenite. Figure 2 shows the isothermal section of the Fe-C-Si phase diagram at 1084.3 K that is the temperature of the upper limit of the equilibrium three-phase field for an alloy with 2.5 mass pct Si. It is clear that the ferrite appearing under the equilibrium contains much more silicon than the austenite matrix it should form from. In other words, if ferrite were to grow within the temperature range of the equilibrium three-phase field, not only should carbon diffusion be taken into account but also silicon redistribution and diffusion in the parent austenite. Simple arguments based on diffusion length have been repeated recently[19–21] showing that such a long-range redistribution of substitutional solutes (Si, Mn, Cu,..) is unmistakably impossible due to the slow diffusion of these elements in austenite at temperatures corresponding to the eutectoid transformation of cast iron.

If long-range redistribution of substitutional solutes at such low temperatures is not possible, the only way ferrite can grow is by keeping the content in substitutional solutes of the parent austenite. These growth conditions are similar to those of the para-equilibrium which has been described at length for steels and was already considered by Venugopalan in the case of cast irons.[19] The highest temperature at which this may occur is the lower limit of the equilibrium three-phase field as seen in Figure 3 which represents the calculated isotherm corresponding toT_α. In this figure, the open circle represents the original composition of the eutectoid parent austenite shown in Figure 2. Below T_α, ferrite can grow simply by rejecting carbon into both austenite and graphite which process is much faster than the diffusion of substitutional solutes.

In summary, the growth of ferrite at any temperature above the lower limit of the equilibrium three-phase field, as assumed by Carazo *et al*.[1] and in the studies that inspired it[2,3] is impossible upon continuous cooling of a cast iron because it would need long-range diffusion of substitutional solutes ahead of the supposedly growing ferrite. This is true for any cooling rate higher than about 1.2 K/min[8] and for any shape of graphite. Figure 1, based on experimental results by Ekpoom and Heine,[7] clearly proves the validity of this statement, and none of the results previously reviewed contradicted this.[8]

It is worth stressing here that it is not surprising that a phase, supposedly stable according to equilibrium thermodynamics, is not observed for kinetics reasons. This phenomenon is well known in diffusion couple experiments where interface kinetics may hinder the appearance of stable phases. In the present case, the diffusion kinetics of substitutional solutes is far too slow for any compositional change in the product phase (ferrite) compared with the parent phase (austenite) during continuous cooling.[20–22]

Finally, it is interesting to note that during isothermal holding or at very slow cooling rate, near-equilibrium ferrite can be formed with a composition that is different from that of the parent austenite. For a long time, such equilibrium ferrite has been shown to appear at austenite grain boundaries and not close to graphite nodules.[5,7] Under such isothermal conditions, since carbon activity is the same everywhere in the material, the growth of ferrite has to be explained by means of diffusion of substitutional solutes and not by carbon transfer as stated by Carazo *et al*.[1]

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