

White and gray solidification of the Fe-C eutectic

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Abstract

The mechanism of structure transition from stable to metastable eutectic is the object of the publication. The influence of microsegregation elements on forming different phase, growth undercooling and growth rates was determined. Also competitive growth of both eutectic in alloys Fe-C was introduced.

Keywords: Solidification, Grey eutectic, White eutectic, Stable to metastable transition

1. Introduction

It is well known that one of the most important types of casting alloys, cast iron, solidifies in two different forms, gray and white (figure 1):

- Gray iron is predominantly obtained at low cooling rates. Its eutectic phases, γ - iron and graphite, are the equilibrium ones.
- White iron appears at high cooling rates and consists of γ - iron and the metastable Fe_3C [2].

In order to model the grey/white structural transition, the following phenomena should be described through appropriate physical and mathematical models:

- The nucleation and growth of both the stable and metastable eutectic.
- The growth competition between the same eutectics.
- The change in equilibrium temperatures and solubility limits because of the microsegregation of various elements occurring during solidification [3].

Theoretical treatments of eutectic growth give relationships between undercooling ΔT , lamellar spacing λ , and growth velocity V of the general form :

$$\Delta = \zeta_1 \lambda V + \frac{\zeta_2}{\lambda} \quad (1)$$

where K_1 and K_2 are constants related to the material properties. Regular eutectics (like Fe- Fe_3C) are assumed to grow at the extreme, i.e. at maximum velocity or minimum undercooling. This leads to the well known relationships [4]:

$$\Delta = \sqrt{K_1 + \zeta_2} + \sqrt{V} = \zeta_3 \sqrt{V} \quad (2)$$

$$\lambda = \sqrt{\frac{K_2}{K_1}} / \sqrt{V} = \zeta_4 \sqrt{V} \quad (3)$$

Growth of irregular eutectics (like Fe-C) is more complicated. The growth kinetics (fig.2.) of the faceted phase activates a defect mechanism for growth, which produces a very anisotropic growth behavior.

This means that branching of graphite, which is needed for growth at the optimum-lamellar spacing, is difficult. The lamella of graphite will then grow straight in a converging or diverging way, leading to a whole range of lamellar spacing (corresponding to a range of undercooling given by eq. (1)). It has been shown that growth cannot be achieved with a spacing lower than the extreme one. Growth of converging lamella will then stop when this spacing is reached. At the opposite, growth of diverging lamella will be stable only as long as λ is less than a critical spacing λ_{br} where branching occurs, as shown in fig. 3. It will be shown theoretically in a forthcoming paper that the

relationships (2) and (3) (with different constants) are still valid for irregular eutectics under usual conditions, with undercooling and lamellar spacing taken as average values over the whole interface [4].

Figure 3 shows growth temperature versus solidification rate for both Fe-C and Fe-Fe₃C eutectics. The undercooling of grey (Fe-C) eutectic is much higher than the one for white (Fe-Fe₃C) eutectic. This is so for two reasons:

- The concentration difference between the two phases is much higher in Fe-C than in Fe-Fe₃C (thus requiring a higher diffusion flux of carbon).
- The irregularity of growth is large in Fe-C, i.e. growth occurs at a larger mean spacing and therefore at a higher undercooling than the extreme one [4].

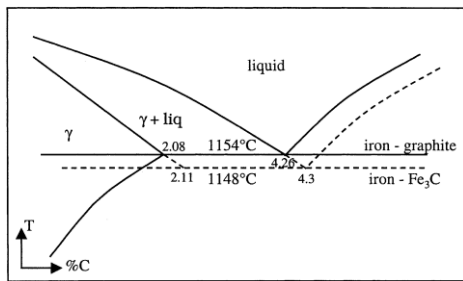


Fig. 1. Schematic of the iron-carbon phase diagram [1]

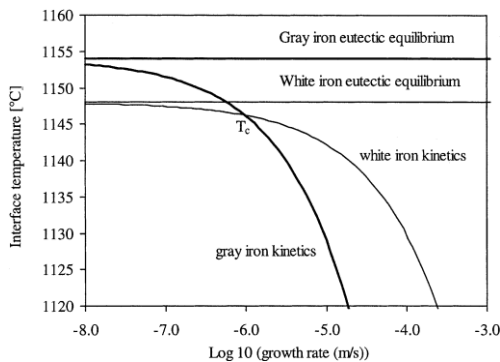


Fig. 2. Schematic of the growth kinetics of gray and white iron eutectics [1]

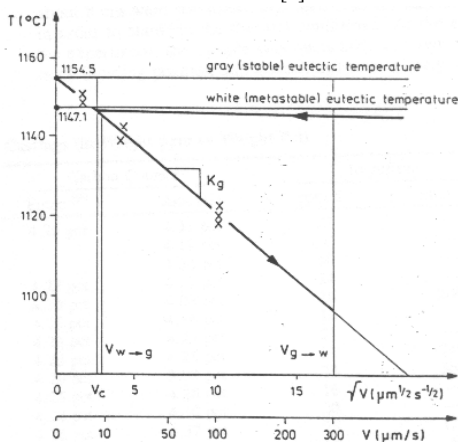


Fig. 3. Schematic diagram showing growth temperatures for white and gray eutectic [4, 5]

2. Nucleation of stable and metastable eutectics

The grain density data used in the present model are as follows:

- for the gray eutectic:

$$N_g(\text{m}^{-2}) = 1,0 \times 10^5 + 3,3 \times 10^4 \dot{T} \quad (4)$$

- for the white eutectic:

$$N_w(\text{m}^{-2}) = 5,0 \times 10^5 + 1,0 \times 10^4 \dot{T} \quad (5)$$

\dot{T} is the cooling rate [3].

The research indicated that total number of nucleation was given by $N = 4 \times (\Delta T)^n$ where ΔT is the undercooling with respect to the equilibrium temperature of the phase transformation, A and n are constants reflecting the inoculation treatment. The nucleation rate is expressed as eq. (6), and the number of nuclei appearing in liquid from calculation time t to $t+dt$ can be calculated by considering the available liquid volume of nucleation with eq. (7):

$$\frac{dN}{dt} = \nu A (\Delta T)^{n-1} \frac{d\Delta T}{dt} \quad (6)$$

$$N^{t \rightarrow t+dt} = \int_t^{t+dt} \left[f_l n A (\Delta T)^{n-1} \frac{d\Delta T}{dt} \right] dt \quad (7)$$

where f_l is volume fraction of liquid (%) [6].

In this work, the gray and white transformation under their equilibrium temperatures, T_{stable} and $T_{\text{metastable}}$ respectively, was considered and they were calculated by literature:

$$T_{\text{stable}}(^{\circ}\text{C}) = 154 + 1(Si\%) - 1(Mn\%) - 0(P\%) \quad (8)$$

$$T_{\text{metastable}}(^{\circ}\text{C}) = 148 - 5(Si\%) + 1(Mn\%) - 7(P\%) \quad (9)$$

where $(Si\%)$, $(Mn\%)$, and $(P\%)$ are weight percents of silicon, manganese, and phosphorus of liquid [6].

It is widely accepted that the nucleation of cementite eutectic is rather sluggish, requiring a certain degree of undercooling to temperatures in which $T_c < T_{\text{mst}}$. Below T_c , both graphite and cementite eutectic grow simultaneously, interfering with each other in giving rise to the final structure. The real volume fractions of graphite (f_g) and cementite (f_c) eutectics can be described by:

$$f_g = \frac{f_{ge}}{f_{ge} + f_{ce}} \{1 - \exp[-f_{ge} + f_{ce}]\} \quad (10)$$

$$f_c = \frac{f_{ce}}{f_{ge} + f_{ce}} \{1 - \exp[-f_{ge} + f_{ce}]\} \quad (11)$$

where f_{ge} and f_{ce} are the extended volume fractions of graphite and cementite eutectics, which, in turn, can be given by:

$$f_{ge} = \frac{4}{3} \pi N R^3 = \frac{4}{3} \pi V (u_g t)^3 = \frac{4}{3} \pi V [\mu_c (T_s - T_e)^2 t]^3 \quad (12)$$

$$f_{ce} = \frac{4}{3} \pi N_c R_c^3 = \frac{4}{3} \pi V_c (u_c t)^3 = \frac{4}{3} \pi V_c [\mu_c (T_{mst} - T_e)^2 t]^3 \quad (13)$$

Equations (12) and (13) assume spherical geometry, where R and R_c are the mean radii of either the graphite or cementite cells; N and N_c are the numbers of graphite and cementite eutectic cells, respectively, per volume or cell densities; and t is the time. Equations (10) and (11) are only valid for $f_{ge}/f_{ce} = \text{constant}$. After solidification, $f_g + f_c = 1$; this, in turn, indicates that the exponential components in eqs. (10) and (11) tend to zero. Thus, eqs. (10) and (11) can be rewritten as:

$$f_g = \frac{f_{ge}}{f_{ge} + f_{ce}} \quad (14)$$

$$f_c = \frac{f_{ce}}{f_{ge} + f_{ce}} \quad (15)$$

In order to estimate the fractions of graphite and cementite eutectics, it is assumed as a first approximation that isothermal conditions prevail for the eutectic transformation (figure 3) and that the nucleation of eutectic cells is instantaneous, with a constant density ratio of $N/N_c = 10$ [7].

3. Microsegregation

Many researchers have done significant effort to describe the microsegregation behavior during solidification of different alloys including SG iron. It was proved that microsegregation of various elements had a significant effect on stable to metastable transition as well as the solid-state transformation or heat treatment. The microsegregation behavior is quite different among various elements, for example, silicon segregates negatively during stable while positively in metastable solidification; manganese segregates positively in both reactions, which makes the content of manganese in liquid increase during solidification. Therefore, stable and metastable eutectic equilibrium temperature must be calculated as a function of silicon and manganese concentration in the liquid.

At any time t , the distribution of the element X in liquid, gray and white eutectics was approximately given by eqs. (16) and (17):

$$\langle X \rangle_{gray}^t = K_{X,gray} \langle X \rangle_{1...}^t \quad (16)$$

$$\langle X \rangle_{white}^t = K_{X,white} \langle X \rangle_{1...}^t \quad (17)$$

where

$\langle X \rangle_{gray}^t$ and $\langle X \rangle_{white}^t$ are concentrations of X element in gray and white eutectic at time t , $\langle X \rangle_{gray}^t$ is partition coefficient of X element in liquid and gray eutectic and $\langle X \rangle_{white}^t$ is partition coefficient of X element in liquid and white eutectic, and $\langle X \rangle_{1...}^t$ is content of X element in liquid at time t [5].

Neglecting macro convection, the total content of an element of any mesh was assumed unchanged (Eq. (18)), and then the concentration of an element in liquid was determined by Eq. (19):

$$\sum_{t=0}^t \langle X \rangle_{gray}^t \rho_{gray} df_{gray}^t + \sum_{t=0}^t \langle X \rangle_{white}^t \rho_{white} df_{white}^t + \langle X \rangle_0 \rho f_1^t = \langle X \rangle_0 \rho \quad (18)$$

$$\langle X \rangle_1^t = \langle X \rangle_0 / f_1^t - \left[\sum_{t=0}^t \langle X \rangle_{gray}^t \rho_{gray} df_{gray}^t + \sum_{t=0}^t \langle X \rangle_{white}^t \rho_{white} df_{white}^t \right] / (\rho \cdot f_1^t) \quad (19)$$

where $\langle X \rangle_0$ is initial content of X element in the melt, df_{gray}^t and df_{white}^t is volume increase of gray and white eutectic at calculation time t respectively [6].

The partition coefficients $k_{Si,g}$ and $k_{Si,w}$ are calculated using the following relationships:

$$k_{Si,g} = 0,70 - 0,31c_{Si} - 0,05c_{Si}^2 \quad (20)$$

$$k_{Si,w} = 0,88 - 0,05c_{Si} \quad (21)$$

where c_{Si} is the silicon concentration expressed in weight percent [1].

The eutectic temperatures of gray and white iron eutectics are obtained by:

$$T_g = 135,06 + 3,89c_{Si} - 0,05c_{Si} \quad (22)$$

$$T_w = 147,2 - 0,93(c_{Si} + 0,5c_p) - 0,717(c_{Si} + 0,5c_p)^2 \quad (23)$$

where c_p is the concentration of phosphorus, which is assumed to be constant [1].

4. Growth rates

The growth rates for graphite eutectic (u_g) and cementite eutectic (u_c) can be related to the degrees of undercooling through eqs. (24) and (25), according to theoretical treatments on eutectic growth:

$$u_g = \mu_c \Delta T_g^2 \quad (24)$$

$$u_c = \mu_g \Delta T_c^2 \quad (25)$$

where:

$$\Delta T_g = T_s - T^* \quad (26)$$

$$\Delta T_c = T_{mst} - T^* \quad (27)$$

In eqs. (24) through (27), ΔT_g is the undercooling for graphite eutectic and ΔT_c is the undercooling for cementite eutectic, and μ_g and μ_c are their respective growth coefficients; and T_s and T_{mst} are the stable and metastable equilibrium temperatures of the graphite and cementite eutectics, respectively [7].

One notices from figure 3 that there is a critical solidification rate V_c where the growth temperatures of white and grey eutectics are equal. It can be thought that the system will try to choose the eutectic which has - the minimum undercooling (or the maximum growth rate), i.e. grey as long as the growth rate is less than V_c and white for faster velocities. In fact, transitions from grey to white and white to grey exhibit a large hysteresis due to the difficulty of nucleation of the new phase. There are then two distinct critical velocities: with increasing growth rates, a grey eutectic will remain stable until the critical velocity $V_{g \rightarrow}$ is reached. This growth rate is associated with an undercooling ΔT_i^c required for the nucleation of cementite. At the opposite, transitions from white to grey occur at a solidification rate $V_{w \rightarrow}$ and an undercooling

ΔT_i^g . Note that the undercooling ΔT_i^c and ΔT_i^g are defined with respect to the eutectic temperature of γ Fe-cementite (white) and γ Fe-graphite (grey) [4].

As the white to gray transition occurs very close to the critical velocity V_c , $V_{w \rightarrow}$ will then be set equal to V_c in the subsequent analysis. From figure 2, one can deduce from geometrical considerations the following relationships:

$$V_{g \rightarrow w} = \left(\frac{\Delta T_e + \Delta T_n^c}{K_3^g} \right)^2 \quad (28)$$

$$V_{w \rightarrow g} = \left(\frac{\Delta T_e}{K_3^g} \right)^2 \quad (29)$$

where ΔT_e is the difference between stable and metastable eutectic temperatures. The transition velocities are then a function of the three parameters ΔT_e , K_3^g and ΔT_i^c . Modifications of these parameters by an alloying addition have different effects:

- ΔT_e is a measure of the thermodynamic stability of cementite with respect to graphite. An increase in ΔT_e by alloying will raise both $V_{g \rightarrow}$ and $V_{w \rightarrow}$ (i.e.

graphitizing effect) and decrease the hysteresis (if K_3^g and ΔT_i^c are unchanged).

- The growth undercooling of grey eutectic is markedly influenced by the growth conditions of graphite (i.e. Gibbs-Thomson coefficient and branching mechanism). Increasing K_3^g decreases $V_{g \rightarrow}$ and $V_{w \rightarrow}$ without changing the hysteresis. This carburizing effect is due to growth kinetics.
- The undercooling necessary to nucleate the cementite phase depends on the existence of clusters or heterogeneous phases in the liquid. In case of difficulties in nucleating cementite, ΔT_i^c will increase, thus increasing $V_{g \rightarrow}$ but leaving $V_{w \rightarrow}$ unchanged [4].

5. Conclusions

Transitions from grey to white and white to grey exhibit a large hysteresis due to the difficulty of nucleation of the new phase.

It was found that neglecting silicon microsegregation, if meta-stable transformation was advantageous to stable, the simulated carbide fraction is higher, and vice versa.

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