THE METASTABLE EUTECTIC GROWTH

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Abstract

The paper presents adaptation problem of metastable growth of eutectic. In the case of rapid solidification the ledeburite eutectic structure in Fe-C system is become. This cementite eutectic is one from the most commercial eutectic of quasi-regular eutectics group.

Keywords: eutectic, quasi-regular eutectic, cementite eutectic, ledeburite eutectic, kinetic, solidification,

1. Introduction

Normally in anomalous eutectics, the faceting of one of the phases leads to uncoupled growth and, as a result, a ragged (irregular) solid/liquid interface appears which produces an irregular (divorced) morphology as viewed in a transverse microsection. This is true not only when the volume fraction of the faceted phase is small, but also when it is large, i.e., 40% [1].

Growth of the austenite-iron carbide eutectic (ledeburite) (Fig.1) begins with the development of a cementite plate on which an austenite dendrite nucleates and grows. This destabilizes the Fe₃C, which then grows through the austenite. As a result, two types of eutectic structure develop: a lamellar eutectic with Fe₃C as a leading phase in the edgewise direction, and rod eutectic in the sidewise direction. Cooling rate significantly influences the morphology of the γ + Fe₃C eutectic [2].

![Fig.1. Scheme of cementite eutectic grain in eutectic cast iron [3]](image)

Data on the spacing of the ledeburite (Fe+Fe₃C) in pure Fe-C alloys has been extended to low solidification velocities. The data do not fit the standard theoretical model of \( \lambda^2V=\text{constant} \), and it
is suggested that this result may be related to the faceted nature of the Fe₃C component of the ledeburite eutectic [4].

2. The ledeburite eutectic growth

Eutectic growth characterized by the cooperative growth of two solid phases from a liquid is an important pattern in crystal growth, and has been attracting much attention [5].

Eutectic alloys can grow into the lamellar - or rod - like regular structures or other anomalous structures. The exact morphology of a eutectic alloy depends on the crystal features of the products and their relative volumes [6].

Theoretical treatments of eutectic growth give relationships between undercooling $\Delta T$, lamellar spacing $\lambda$, and growth velocity $V$ of the general form:

$$\Delta T = K_1 \lambda V + \frac{K_2}{\lambda}$$

where $K_1$ and $K_2$ are constants related to the material properties. Quasi-regular eutectics (like Fe-Fe₃C) are assumed to grow at the extreme, i.e. at maximum velocity or minimum undercooling. This leads to the well known relationships [7]:

$$\Delta T = 2\sqrt{K_1 + K_2} + \sqrt{V} = K_3 \sqrt{V}$$

$$\lambda = \frac{K_2}{K_1} \sqrt{\frac{V}{V}} = K_4 \sqrt{V}$$

Parameter, influencing the kind of eutectic received, is the fraction of the volume $g_\alpha$ occupied by one of eutectic phases. Quasi-regular eutectic solidification near the highest value of $g_\alpha$, which is over 0.4. They are characterized by lamellar-fibrous morphology. The typical feature of quasi-regular eutectics, is much about equal volumetric contribution of both eutectic phases and the growth of one of the phases in the shape of the wall crystal [3].

The characteristic of this group is that although they are in the anomalous (faceted/nonfaceted) class almost regular micro-structures can be observed in these eutectics. In the quasi-regular eutectics the high degree of regularity may result from the fact that the faceted phase forms the matrix. Therefore, despite a high entropy of solution value, faceting may be prevented and the unpredicted appearance of almost regular microstructures can be explained [1].

The growth kinetics (Fig.2) of the faceted phase activates a defect mechanism for growth, which produces a very anisotropic growth behavior. 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) [7].
The unidirectional solidification conditions with an apparent temperature gradient along heat conduction direction also influence the growth of eutectic cementite. As for the eutectic growth, the structures are controlled by the ratio of the temperature gradient \( G \) to the growth rate \( R \). A relatively high \( G/R \) value results in a quasi-regular lamellar structure with edgewise growth and a smaller \( G/R \) value leads to a ledeburite structure with cooperation growth of austenite and Fe₃C. Therefore, the straight eutectic cementite in a strip-cast specimen can be attributed to the domination of the edgewise growth. And the triangular prisms comprising one carbon atom and six surrounding iron atoms are arranged along the C-axis parallel to the heat conduction direction. Consequently, the cementite of the strip-cast specimen has straight interfaces and a distinct texture close to the close packed [001]_e direction [9].

3. Nucleation metastable eutectic

The grain density data are as follows for the white eutectic:

\[
N_w(\text{m}^{-2}) = 5.0 \times 10^5 + 1.0 \times 10^4 T
\]  
(4)

\( T \) is the cooling rate [10].

The research indicated that total number of nucleation was given by \( N = A \times (\Delta T)^n \) where \( \Delta T \) is the undercooling with respect to the equilibrium temperature of the phase transformation, \( A \) and \( n \) are constants reflecting the inoculation treatment.

The real volume fractions of cementite \( (f_c) \) eutectics can be described by:

\[
f_c = \frac{f_{ce}}{f_{ge} + f_{ce}} \left(1 - \exp[-(f_{ge} + f_{ce})]\right)
\]  
(5)

where \( f_{ce} \) are the extended volume fractions of cementite eutectics, which, in turn, can be given by:
Equation (6) assume spherical geometry, where \( R_c \) are the mean radii of either the cementite cells; \( N_c \) is the numbers of cementite eutectic cells, per volume or cell densities; and \( t \) is the time [11].

The growth rate for cementite eutectic (\( u_c \)) can be related to the degrees of undercooling through Eqs. (7), according to theoretical treatments on eutectic growth:

\[
u_c = \mu_c \Delta T_c^2
\]

where

\[
\Delta T_c = T_{mst} - T
\]

In Eqs. (7, 8) \( \Delta T_c \) is the undercooling for cementite eutectic, and \( \mu_c \) are their respective growth coefficients; and \( T_{mst} \) are the metastable equilibrium temperatures of the cementite eutectics [11].

As shown in Fig. 3, the distribution pattern of the eutectic cementite changes from the network-like form to a discontinuous plate-like form with increasing carbon content. Research has also confirmed that the morphology of Fe\(_3\)C changes from ledeburitic to plate like as the undercooling is increased. Studies of directional solidification have indicated that the cooling rate as the austenite begins to crystallize into a columnar dendrite increases and the local solidification time of the austenite crystallization decreases with increasing carbon content, respectively. As mentioned, the cooling rate of the cast iron strips produced by using strip casting ranged within 10\(^2\)-10\(^3\) °C s\(^{-1}\). This high cooling rate accompanied with high carbon content could lead to high undercooling which enhances the formation of discontinuous plate-like eutectic. Moreover, the growth direction of plate-like cementite of high carbon specimens, [001], also resulted from the edgewise growth along the heat conduction direction [9].

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**Fig. 3.** The morphology and microtexture of the eutectic cementite in strips with different compositions: (a) 2.6C–4.0Si; (b) 3.5C–2.1Si [9]
4. The microsegregation in white eutectic

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, white eutectics was approximately given by:

$$\langle X \rangle_{\text{white}} = K_{X,\text{white}} \langle X \rangle_{1...}$$  \hspace{1cm} (9)

where $\langle X \rangle_{\text{white}}$ are concentrations of $X$ element in white eutectic at time $t$, $K_{X,\text{white}}$ is partition coefficient of $X$ element in liquid and white eutectic, and $\langle X \rangle_{1...}$ is content of $X$ element in liquid at time $t$ [12].

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

$$k_{Si,g} = 1,70 - 0,31c_{Si} - 2,05c_{Si}^2$$  \hspace{1cm} (10)

$$k_{Si,w} = 0,88 - 0,05c_{Si}$$  \hspace{1cm} (11)

where $c_{Si}$ is the silicon concentration expressed in weight percent [8].

The eutectic temperatures white iron eutectics are obtained by:

$$T_w = 1147,2 - 6,93(c_{Si} + 2,5c_p) - 1,717(c_{Si} + 2,5c_p)^2$$  \hspace{1cm} (12)

Where $c_p$ is the concentration of phosphorus, which is assumed to be constant [8].

As for the silicon effect, the primary action of silicon in controlling the morphology of white cast irons is to produce the rod eutectic form of ledeburite. In other words, the morphology of cementite changes from a plate-like eutectic for plane front growth to a rod eutectic for cellular and dendritic growth due to the effect of silicon. The reason for this is that the solubility in Fe$_3$C, which is known to be extremely low, results in a significant solute buildup in the liquid at the Fe$_3$C - liquid interface and this could give rise to the rod facet formation. This cooperative eutectic growth occurs at right angles to the primary Fe$_3$C plate, that is, the rod-like structure grows perpendicular to the plate like cementite, and will result in curved interfaces and a random growth direction [9].

5. Discussion

Eutectic alloys can grow into the lamellar - or rod - like regular structures or other anomalous structures. The exact morphology of a eutectic alloy depends on the crystal features of the products and their relative volumes [13]. Evolution of solidification microstructures can be the strategic link between materials processing and materials behavior. The eutectic structure is the basis of most commercial casting alloys, and thus, the properties of these alloys strongly depend on the amount
and morphology of the eutectic phases, which, in turn, are affected by various variables, including cooling rate, modification, and faceted or nonfaceted nature of the constituent phases. In the quasi-regular eutectics the high degree of regularity may result from the fact that the faceted phase forms the matrix. Therefore, despite a high entropy of solution value, faceting may be prevented and the unpredicted appearance of almost regular microstructures can be explained.

References


