Averaged Voronoi polyhedron in the peritectic transformation modelling

INTRODUCTION

Peritectic solidification of the alloys is in the centre of attention of researchers. This is a mechanism of the structure formation for many technical alloys. Peritectic solidification is believed to be the major cause of crack formation during the solidification of many steels [1].

During the peritectic solidification primary solid phase vanishes simultaneously along with liquid phase and new secondary (peritectic) phase grows as a solidification product. In the carbon steel γ-phase (austenite) appears, replacing δ-phase (ferrite) and liquid. Two separate mechanisms of peritectic solidification are known as:

- peritectic reaction: when dissolution of primary phase, directly in liquid phase, is possible independently from the secondary one [2],
- peritectic transformation; when primary phase is completely separated from liquid by the layer of secondary phase [3].

An analytical model of the kinetics of peritectic transformation, based on the linearized concentration gradient of the solute, has been presented by Das et al. [4]. The results shown in this paper exhibit a good agreement with the experimental results, but the difference between rates obtained by the computer modelling and relevant experimental data increase at the later stages of transformation. According to authors of [4] one of the reasons of this disagreement is the deviation from the idealized geometry.

The idealized geometry of the elementary peritectic cell is usually used in the known numerical models. Furthermore, the idealized initial concentration profile of the solute in the pre-peritectic phase is assumed. Spherically symmetrical cell of radius \( (3/4n)^{1/3} \) was applied in [5], where \( n \) is the number of peritectic cells per unit volume. In the Ref. [6] only a plane spatial segment of the melt pool was used as the simulation domain.

According to the analysis of diffusion transformations presented in [7], a single common mathematical model allows for interpretation of the mechanisms of peritectic transformation and the growth of globular eutectic. For the modelling of the diffusion-limited growth of the globular eutectics, the spherical Elementary MicroDiffusion Field (EMDF) was usually used [8–13] similarly to EMDF used in [5] for investigations into peritectic transformation. Real shapes of the grains in the solidifying alloys are quite different from the sphere, even considering instantaneous nucleation and symmetrical growth, due to stochastic spatial nuclei distribution.

One of the assumptions of the model [5] is the initial concentration profile of the solute in the primary phase described by Scheil’s equation. Matsuura et al. [14] used linear distribution of solute in the peritectic phase and uniform solute distribution in the primary and liquid phases (full mixing). The same assumption was applied in Ref. [15].

In the presented study, a mathematical micromodel of peritectic transformation was investigated. The model takes into account back diffusion of solute in the primary solid phase both during solidification from liquid and peritectic transformation under the condition of continuous cooling. In addition, changes in the spatial shape of EMDF were considered during the late stage of transformation, when the effect of collision of the diffusion fields should not be neglected. For that the concept of Averaged Voronoi Polyhedrons (AVP) was used.

MODEL DESCRIPTION

Spatial patterns of EMDF

For a description of the polycrystalline structure of metals and alloys, the Voronoi polyhedrons are often used. In the space with random distribution of nuclei, the Voronoi polyhedrons divide the space into multiple regions, each containing single nucleus along with all the nearest points – with shortest distance to this particular nucleus.

The boundaries of these polyhedrons are fragments of planes perpendicular to the segments joining the nuclei and dividing these segments into two equal parts. The specific shape and volume of this polyhedron as well as the number of faces and edges depend on the positions of the nearest neighbouring nuclei. This type of structure is formed when nucleation occurs simultaneously and grains are considered spherical, having equal growth rate.

Two-dimensional solidification model was introduced by Mathier et al. [16]. The globular grain structure of the alloy in this model has been approximated by the Voronoi tessellation with limited number of straight segments representing the grain boundaries. Solidification and microsegregation were analysed in the triangular domains generated by two segments connecting the nucleation centre and the Voronoi cell’s vertices. The geometrical approach like above can be easily extended to three dimensions where, as the result of the Voronoi tessellation, one will obtain tetrahedral shapes of EMDF [17]. Solidification model based on the Voronoi diagrams was used also in [18]. The final grain structure and the shapes of the triangular/tetrahedral EMDF in these cases are the results of the preliminary Voronoi tessellation.

The subject and aim of this study is to create a mathematical model describing the three-dimensional field of solute concentration in non-spherical elementary microdiffusion field during the primary solidification and following peritectic transformation in the simultaneous nucleated equiaxed grains in the two-component alloy. The model assumes that EMDF has non-spherical shape as a result of random contacts between the grains growing around the individual nuclei. To determine the geometry of a three-dimensional EMDF, the principles of the statistical theory of crystallization [19] are used.

The numerical model of the diffusion-limited growth of the globular eutectic, using the geometry of the averaged Voronoi cell, was proposed in [20]. The diffusion equation was solved numerically by the elementary balance method. The method used
to determine the geometry of EMDF as well as equations used in the solution are shown below.

On the basis of [19], in the case of a simultaneous nucleation of the all \(n\) grains presented in a unit volume and their spherical growth at the same (not necessarily constant) speed, the average volume of the material of one grain at a maximum distance \(r\) from the nucleation site can be determined by the following equation:

\[ V(r) = \frac{1}{n} \left( 1 - \exp \left( -\frac{4}{3} \pi n r^3 \right) \right) \]  

where: \(n\) is number of grains in unit volume, \(m^3\)

The random-shaped body of volume given by the above equation, on which the EMDF bases, will be denoted as the Averaged Voronoi Polyhedra.

The field of the surface separating the volume \(V(r)\) from the material of this grain more remote from the nucleation site is given by:

\[ F(r) = \frac{dV(r)}{dr} = 4\pi n^2 \cdot \exp \left( -\frac{4}{3} \pi n r^3 \right) \]  

The surface of the contact with adjacent grains is not taken into account in the above equation. It means that diffusion flux between the neighbouring EMDF across the common boundary is neglected.

The volume of AVP layer contained between two concentric surfaces centred in the nucleation site, with distance from the centre of \(r\) and \((r + \Delta r)\), can be computed as:

\[ \Delta V(r, \Delta r) = \frac{1}{n} \left( \exp \left( -\frac{4}{3} \pi n r^3 \right) - \exp \left( -\frac{4}{3} \pi n (r + \Delta r)^3 \right) \right) \]  

In the modelling one assumes that within the area of EMDF, carbon concentration can be described as a relation of the distance from the nuclei \((r)\) and time \((r)\):

\[ C(r, r) = f(r, r) \]  

It means that direction of the diffusion fluxes is identical to the grain radius, while the side flux is negligible. A zero diffusion flux through the Voronoi cell boundary was also adopted.

**Governing equations for numerical solution**

Taking into account the above spatial relations the difference equation for the elementary balance method can be written as:

\[ \mathbf{W}(\eta, \Delta r) \frac{C(r + \Delta r) - C(r, r)}{\Delta r} = \mathbf{D}(\eta) \cdot \text{grad} \{ C(r, r) \} \cdot F(r) \]

where: \(D(\eta)\) – average diffusion coefficient of material in a layer of EMDF, \(r_2 = r_1 + \Delta r, r = (r_1 + r_2)/2\).

If the concentration gradient is approximated with the central differential quotient and the explicit scheme is used, then in the case of constant grid step \(\Delta r\) the concentration in the \(i\)-th area of an elementary balance can be computed as:

\[ C_i(r + \Delta r) = (1 - A) C_i(r) + AC_j(r) + BC_m(r) \]

where:

\[ A = \frac{D(r)}{\mathbf{W}(\eta, \Delta r) \cdot \Delta r}, \quad B_i = \frac{D_i(r + \Delta r)}{\mathbf{W}(\eta, \Delta r) \cdot \Delta r}, \quad B_j = \frac{D_j(r + \Delta r)}{\mathbf{W}(\eta, \Delta r) \cdot \Delta r} \]

It has been assumed that the \(i\)-th area is located within the distance range from \(r\) to \(r + \Delta r\) from the centre of EMDF.

From equation (1) it arises that the fraction of the EMDF space distant from the centre by a value exceeding \(R_{VP}\) is as follows:

\[ f(R_{VP}) = \exp \left( -\frac{4}{3} \pi n R_{VP}^3 \right) \]

Assuming a small value of this fraction (in order of \(e = 10^{-3}\)), denoted hereafter the rounding constant, the EMDF radius for which the computations will be performed now can be determined:

\[ R_{VP} = \sqrt[3]{\frac{3ln e}{4\pi n}} \]

For an averaged Voronoi cell, the probability that a random point in the structure of grain will be located at a distance from the nucleus centre smaller than \(r\) is described by a cumulative distribution function:

\[ P(r) = 1 - \exp \left( -\frac{4}{3} \pi n r^3 \right) \]

The probability density function

\[ p(r) = 4\pi n^2 \cdot r^2 \cdot \exp \left( -\frac{4}{3} \pi n r^3 \right) \]

has its maximum at the point

\[ R_{VP} = \left( \frac{2}{\pi} \right)^{1/3} \]

The value of \(R_{VP}\) can be called a characteristic radius of the AVP. Among the random points selected in the supposed volume composed of Voronoi polyhedra, the greatest number of these points will be located at the distance of \(R_{VP}\) from the nucleus centre. In addition, according to (10), almost 49% of the grain's volume will be located at a distance not exceeding the value of \(R_{VP}\) from the nucleus centre, while areas further than 2\(R_{VP}\) from the centre will contain up to 0.5% of the grain’s volume.

In the known works the EMDF radius has been chosen arbitrary of order of \(-n^{-3}\) [5, 21, 22]. In this case the relative volume of EMDF (EMDF volume to average grain volume ratio) may be appreciably greater than 1.

The Voronoi polyhedrons are convex but not necessarily bounded [23]. Internal volume of the AVP converges to 1/\(n\) and always will be smaller than 1/\(n\). Probability of locating a random point out of AVP of radius \(r\) vanishes when this radius exceeds 2\(R_{VP}\). As it follows from Eq. (9), for the specified rounded constant \(f\), the bounding value of EMDF radius may be calculated.

The computations were performed on a differential grid with constant space step (with the exception of elements in areas adjacent to the phase boundaries). In the two boundary elements with a combined length of 2\(\Delta r\) containing the interface between adjacent phases a variable spatial step has been used. As the interface progresses through the boundary couple so does the edges of elements themselves. The width of the boundary elements varies in the range from 0.5\(\Delta r\) to 1.5\(\Delta r\). When this range is exceeded, the computed grid is subjected to local modifications to move the boundary elements, while preserving the mass balance of constituents.

The speed of the phase boundaries migration is determined from the mass balance at the interfaces:

\[ u_i \left( C_i \cdot \rho_i - C_j \cdot \rho_j \right) = \frac{D_i \rho_i}{\frac{dr}{dt}} \frac{dC_i}{dt} - \frac{D_j \rho_j}{\frac{dr}{dt}} \frac{dC_j}{dt} \]

where: \(u_i\) is the migration speed of the interphase \(i\) between \(i\) and \(j\) phases; \(C_i, C_j\) are the solute concentration in the growing and vanishing phases at the transformation interface; \(\rho_i, \rho_j\) are the densities of these phases, and \(D_i, D_j\) are the diffusion coefficients of the solute in these phases, respectively.

Latent heat released upon transformation during one time iteration was calculated using equation (3):

\[ \Delta Q_i = \Delta H_i \cdot \left[ \exp \left( -\frac{4}{3} \pi n r^3 \right) - \exp \left( -\frac{4}{3} \pi n (r + \Delta r)^3 \right) \right] \]

where \(\Delta H_i\) is the volumetric enthalpy of phase transformation. Proper values of transformation enthalpy obtained by means of the Thermo-Calc software are given in Table 1.

**Table 1. Enthalpy of the phase transformations**

<table>
<thead>
<tr>
<th>Phase transformation</th>
<th>(\Delta H_0) (kJ/m^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid-austenite</td>
<td>1.97·10^6</td>
</tr>
<tr>
<td>Liquid-ferrite</td>
<td>1.72·10^6</td>
</tr>
<tr>
<td>Ferrite-austenite</td>
<td>0.988</td>
</tr>
</tbody>
</table>
Modelling conditions

Computation of the equation (6) has been performed for the liquid phase \((L)\), ferrite grain \((\delta)\) and austenite layer \((\gamma)\) with moving boundaries between these phases. It was assumed that austenite layer nucleates on the ferrite surface at the time step when the temperature decreases below the temperature of peritectic equilibrium. Primary width of this layer is assumed to be equal to one grid step.

A binary alloy with the properties similar to Fe-C was used in the modelling. For the sake of simplicity, the solidus and liquidus lines, as well as the solvus lines, were obtained by linearization of the appropriate lines of the Fe-C phase equilibrium diagram [24] between 0 and 2 wt % of carbon. Simulations were performed for the 5 alloys with peritectic solidification: two hypoperitectic (0.1 and 0.135 wt %C), one with the peritectic composition (0.17% C) and two hyper-peritectic (0.35 and 0.5%). It was assumed that interphase compositions, used in the equation (13), are equal to equilibrium ones.

Rate of external cooling of the sample in the simulation was approximated by relation:

\[
T_{\text{ext}} = -5.134 + 0.725 \log(t)
\]  

(15)

The above relation was obtained on the basis of experimental cooling curve measured in the middle part of 30 mm thick casting. This industrial casting was produced from the 18Cr-9Ni-1Mo peritectic steel.

The changes in the sample temperature in time were calculated taking into consideration internal heat source of the phase transformations:

\[
\Delta T = \Delta T_{\text{ext}} + \sum \Delta Q_i
\]  

(16)

The data used in the computations are given in Table 2 and should be considered only as approximate values.

RESULTS OF SIMULATION

The influence of the carbon concentration on the shapes of cooling curves and cooling rates of steel is shown in Figures 1 and 2a. The comparison of the simulated cooling rate for peritectic composition with experimental one is shown in Figure 2b – confirming qualitatively the accuracy of the model’s assumptions.

Changes in the phase interface distances from the AVP centre during primary solidification for the growing ferrite grain \((\alpha-L)\), and during peritectic transformation for the dissolving ferrite grain \((\gamma-\alpha)\), and for the growing austenite layer \((\gamma-L)\), are shown in Fig. 3. Migration rate of the ferrite-liquid interface has the maximal value in the beginning of solidification and becomes slower over the time of about 50 s; at the same time the volumetric solidification rate of primary ferrite is only slightly moderated (Fig. 4).

After initialization of peritectic transformation the migration rate of both interfaces: solid-liquid \((\gamma-L)\) and austenite-ferrite \((\gamma-\alpha)\) is increased. As illustrated in Figure 4, it is not followed by the increase in the volume rate of solidification. Rate of the solid fraction evolution descents up to the end of solidification (Fig. 4). The reason for such behaviour is due to constant decrease of surface between austenite and liquid phases caused by contacts with adjacent grains.

![Fig. 1. Cooling curves of the steels with a carbon concentration, wt %C: 1) 0.1, 2) 0.135, 3) 0.17, 4) 0.35 and 5) 0.5](image1)

![Fig. 2. Simulated cooling rates (a) of the steels with different carbon concentration (the same value as in Fig. 1) and experimental cooling rate (b) of the industrial casting with wall thickness of 30 mm, produced from the 18Cr-9Ni-1Mo peritectic steel](image2)

| Table 2. Computation parameters (typical for Fe-C) |
| Tabela 2. Parametry zastosowane w obliczeniach (typowe dla Fe-C) |

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon diffusion coefficient [25], m²/s:</td>
<td></td>
</tr>
<tr>
<td>– in the liquid phase</td>
<td>(2 \times 10^{-8})</td>
</tr>
<tr>
<td>– in the austenite</td>
<td>(1 \times 10^{-9})</td>
</tr>
<tr>
<td>– in the ferrite</td>
<td>(6 \times 10^{-9})</td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>7000</td>
</tr>
<tr>
<td>Number of grains, m⁻³</td>
<td>(10^7)</td>
</tr>
<tr>
<td>Rounding constant</td>
<td>(10^{-3})</td>
</tr>
<tr>
<td>EMDF radius, μm</td>
<td>1198</td>
</tr>
<tr>
<td>Characteristic radius of the AVP, μm</td>
<td>542</td>
</tr>
<tr>
<td>Grid spatial step, μm</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 5 shows carbon distribution versus EMDF radius (solid line). In the same figure dashed line presents volume fraction of the part of the AVP with the distance from nucleation site not exceeding $R$ (cumulative distribution of AVP volume).

Data analysis (Fig. 5) indicates that 2.5% of AVP volume, with minimal carbon concentration (0.11–0.12 wt %), remains in the middle of the grain – not further than 182 μm from the nucleus. Carbon-rich remote sites of the grain, which also contain 2.5% of AVP volume, are located further than 959 μm from the nucleus. Carbon concentration in this most distant regions is greater than 0.28 wt % and increases dramatically with distance due to segregation, but equally rapidly decreases probability of occurrence of such regions.

CONCLUSIONS

The mathematical model of solute diffusion in the elementary microdiffusion field has been introduced for the modelling of solidification with peritectic, diffusion-controlled transformation. For the geometry of the EMDF, the averaged Voronoi cell was adopted. Usage of the proposed geometry of the EMDF reduces the considered volume fraction of remote (far from nuclei) grains regions due to grains collision.

The results of the solidification modelling have been presented. Comparison of the simulated cooling rate for peritectic carbon concentration to the experiment qualitatively confirms the accuracy of the model’s assumptions.

The data for space distribution of solute in a grain right after completion of the peritectic transformation have been shown.

ACKNOWLEDGEMENTS

The author wishes to thank Prof. W. Kapturkiewicz for valuable assistance in preparing the paper. This work was supported by Polish NCN project DEC-2011/01/B/ST8/01689.

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