MODELLING OF KINETICS OF ISOTHERMAL ALLOTRIOMORPHIC AND IDIOMORPHIC FERRITE FORMATION IN MEDIUM CARBON VANADIUM-TITANIUM MICROALLOYED STEEL

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Abstract

A theoretical model is presented in this work to calculate the evolution of austenite-to-allotriomorphic and idiomorphic ferrite transformation as a function of time in medium carbon vanadium-titanium microalloyed steel. At temperatures above the eutectoid temperature where allotriomorphic ferrite is the only austenite transformation product, the soft-impingement effect should be taken into account in the modelling. By contrast, at temperatures below the eutectoid temperature, the formation of pearlite avoids the carbon enrichment of austenite due to the previous ferrite formation, and therefore carbon concentration in austenite far from the $\alpha/\gamma$ interface remains the same as the overall carbon content of the steel. Hence, the soft-impingement effect should be neglected, and allotriomorphic and idiomorphic ferrite is considered to grow under a parabolic law. The nature, size and distribution of the inclusions which are responsible of the intragranular nucleation of idiomorphic ferrite have been considered in this study. An excellent agreement has been obtained between experimental and predicted values of volume fraction of ferrite in all the studied range of temperature.

**Key Words:** Modelling, Allotriomorphic and Idiomorphic Ferrite, Kinetics
1. Introduction

Ferrite which grows by a diffusional mechanism can be classified into two main forms: allotriomorphic ferrite and idiomorphic ferrite. The term *allotriomorphic* means that the phase is crystalline in internal structure but it does not show this appearance in microstructural form. In fact, allotriomorphic ferrite, which nucleates at the prior austenite grain boundaries, tends to grow along the austenite boundaries at a rate faster than in the direction normal to the boundary plane, so its shape is strongly influenced by the presence of the boundary and hence does not necessarily reflect the symmetry of its internal structure. The term idiomorphic implies that the phase concerned has faces resembling its crystalline structure; in steels, idiomorphic ferrite is taken to be that which has roughly equiaxed morphology. Idiomorphic ferrite usually forms intragranularly at inclusions.

A great number of attempts, from purely empirical to semi-empirical models, have been made to predict the kinetics of ferrite transformation. However, models recently developed are becoming less empirical since they rely on thermodynamic and phase transformation theories. Unemoto et al. developed a methodology to simulate the allotriomorphic ferrite transformation under isothermal conditions. Reed and Bhadeshia reported a thermodynamic model coupled with a simplified kinetic theory. This model can reproduce the C-curve behaviour typical of those parts of the time-temperature-transformation diagrams that are due to allotriomorphic ferrite in low-carbon multicomponent steel. In principle, most of these models are able to predict the kinetics of allotriomorphic ferrite for low-carbon low-alloy steels. But, the level of agreement between predicted and calculated allotriomorphic ferrite kinetics is less satisfactory for medium carbon microalloyed steels.
On the other hand, it is well established that idiomorphic and acicular ferrite are the microstructures that improve the strength and particularly the toughness of steels.\textsuperscript{7,8,9,10} There is a large amount of works on acicular ferrite formation,\textsuperscript{11,12,13,14} but, idiomorphic ferrite formation has been rarely studied. Some studies reported that idiomorphs may nucleate at precipitates of titanium oxide (Ti$_2$O$_3$), manganese sulphide (MnS), and vanadium nitride (VN).\textsuperscript{7,15,16} Those studies also analysed the reason for which such precipitates act as viable sites for intragranular ferrite nucleation, but the nucleation and growth kinetics for idiomorphic ferrite formation were not investigated. Furthermore, recent works have studied the role of the allotriomorphic ferrite to promote the formation of acicular ferrite to the detriment of bainite.\textsuperscript{17,18,19,20} Thus, the amount of acicular ferrite increases by the presence of allotriomorphic ferrite along the austenite grain boundaries and/or the reduction of the amount of ferrite intragranularly nucleated on inclusions (idiomorphic ferrite). Therefore, a deep understanding of the decomposition of austenite in allotriomorphic and idiomorphic ferrite is needed in order to control the total amount of acicular ferrite present in the microstructure.

The present paper is concerned with the theoretical and experimental description of the growth kinetics of allotriomorphic ferrite in medium carbon vanadium-titanium microalloyed steel. The theoretical models presented in this work allow calculation of the kinetics of isothermal austenite-to-allotriomorphic and idiomorphic ferrite transformation at temperatures at which these phases might not be the only austenite decomposition product.

2. Materials and Experimental Procedure
The chemical composition of the steel studied is presented in Table 1. The material was supplied in the form of 50 mm square bars, obtained by conventional casting as a square ingot (2500 kg) and hot rolling to bar.

The isothermal decomposition of austenite has been analysed by means of a high resolution dilatometer DT 1000 Adamel-Lhomargy described elsewhere.\(^{21}\) Cylindrical dilatometric samples of 2 mm in diameter and 12 mm in length, machined parallel to the rolling direction of the bar, were used for these tests. The change in length of the specimen is transmitted via amorphous silica push-rod. This variation is measured by a linear variable differential transformer (LVDT) sensor in a gas-tight enclosure enabling testing under vacuum or an inert atmosphere with accuracy lower than 0.1 \(\mu\)m. The dilatometric curve (relative change in length \((dL/L_0)\) vs. time \((t)\)) is monitored with the help of a computer assisted electronic device. The dilatometer is equipped with a very low thermal inertia radiation furnace. The power radiated by two tungsten filament lamps is focused on the specimen by means of a bi-elliptical reflector. The temperature is measured with a 0.1 mm diameter Chromel – Alumel (Type K) thermocouple spot-welded to the specimen. Cooling is carried out by blowing a jet of helium gas directly onto the specimen surface. The helium flow-rate during cooling is controlled by a proportional servovalve. Heating and cooling devices of this dilatometer ensure an excellent efficiency in controlling the temperature and holding time of isothermal treatments, as well as fast cooling in quenching processes (\(\approx 200\) K/s).

As it is well known, prior austenite grain size \((PAGS)\) exerts an important influence on the decomposition of austenite.\(^{22,23}\) The \(PAGS\) parameter directly affects the growth kinetics of allotriomorphic and idiomorphic ferrite obtained by isothermal decomposition of the austenite, but it does not affect the nucleation time of these phases.\(^{4,24}\) In this sense, austenitisation
conditions were fixed to avoid the influence of the austenite grain size on the kinetics of allotriomorphous and idiomorphic ferrite formation and to study specifically the effect of the isothermal decomposition temperature on the growth kinetics of those phases. Since the growth rate of allotriomorphous and idiomorphous is higher the finer the PAGS, a coarse PAGS of \( d_\gamma = 76 \, \mu m \) was selected to make easier the experimental study of the growth kinetic of these phases. Thus, specimens were austenitised at 1523 K for 1 min, and then isothermally transformed at 973, 913 and 873 K for different times. Finally, they were quenched under helium gas flow at a cooling rate of around 200 K/s. Specimens were ground and polished using standardised metallographic techniques, and subsequently etched with 2%-Nital solution to reveal the ferrite microstructure by optical microscopy.

The volume fraction of both allotriomorphic ferrite \( (\xi_\alpha) \) and idiomorphic ferrite \( (\xi_{IDI}) \) was statistically estimated by a systematic manual point counting procedure.\(^{25}\) A grid superimposed on the microstructure provides, after a suitable number of placements, an unbiased statistical estimation of \( \xi_\alpha \) and \( \xi_{IDI} \).

The equilibrium (or maximum) volume fraction of allotriomorphic \( (\xi_{EQ}^{\alpha}) \) and idiomorphic \( (\xi_{EQ}^{IDI}) \) ferrite formed during the isothermal decomposition of austenite at the three studied temperatures were determined by a combination of dilatometric and metallographic analysis. When the dilatometric curve reaches saturation, \( i.e. \) no further dilatation due to transformation is observed, the isothermal decomposition of austenite is completed, and this time represents approximately the minimum holding time needed to reach the equilibrium volume fraction of ferrite. Since dilatometric curves do not allow us to discriminate between allotriomorphous and idiomorphic ferrite formation, only the metallographic examination of the microstructure will enable an accurate determination of \( \xi_{EQ}^{\alpha} \) and \( \xi_{EQ}^{IDI} \). Figure 1 shows the microstructures obtained after
isothermal decomposition of austenite for three hours at 973, 913 and 873 K. From this figure could be observed that idiomorphic ferrite is not formed at temperatures close to $Ae_3$ (973 K). This is consistent with a inclusion/ferrite interface energy for nucleation higher than that for austenite/ferrite interface as was reported by Aaronson et al. The experimental $\xi_{\alpha}^{EQ}$ and $\xi_{IDI}^{EQ}$ values for allotriomorphic and idiomorphic ferrite obtained at those temperatures are listed in Table 2.

Finally, the morphology and nature of the inclusions were determined by means of scanning electron microscopy (SEM). Specimens were sectionalised longitudinally and transversally to the rolling direction, polished in the usual way and finished on 0.5 $\mu$m diamond paste. Samples were slightly etched in a 2%-Nital solution for SEM examination in a JEOL JXA 840 scanning electron microscope operating at 15 kV with an energy disperse X-ray analysis unit. Quantitative information on the size distribution of inclusions was obtained by means of an IBAS OPTIMAS 2.0 automatic image analyser. SEM images were digitised with a resolution of $512 \times 512$ pixel and 256 grey levels. After image enhancement processes, the size of the inclusions was determined through the measurement of the two perpendicular diameters in the transversal section ($d_1$ and $d_2$), and the highest diameter in the longitudinal section ($d_3$). For this purpose, a $512 \times 512$ points grid was used along with magnifications as high as 3000 times to characterise inclusions with a diameter lower than 0.1 $\mu$m. Minimum of 500 particles were counted to obtain a reliable result.

3. Results and Discussion
3.1 Incubation time of allotriomorphic ferrite

Lange et al.\textsuperscript{26}) proposed a model to calculate the classical nucleation rate of allotriomorphic ferrite based on a traditional disk-shaped 'pillbox' nucleus. In that case, the incubation time for allotriomorphic ferrite is estimated as:

\[
\tau = \frac{12k_B T \alpha^2 \sigma_{\alpha\gamma}}{D_{CG} \bar{x} \alpha \Delta G_v}
\]  

(1)

where \( k_B \) is Boltzmann constant; \( D_{CG} \) is the diffusivity of carbon in austenite; \( \nu_\alpha \) is the volume of an atom of iron in ferrite; \( \alpha \) is the average of the lattice parameters of both phases, ferrite and austenite; \( \bar{x} \) is the average carbon content in mole fraction; \( \Delta G_v \) is the volume free energy change associated with the formation of the nucleus; \( \sigma_{\alpha\gamma} \) is the interfacial energy of a disorder ferrite; and \( T \) is the isothermal temperature.

The theoretical determination of \( D_{CG} \), due to Siller and McLellan\textsuperscript{28}) and reviewed by Bhadeshia,\textsuperscript{29}) considers both the kinetic and equilibrium thermodynamic behaviour of carbon in austenite. Calculations of \( D_{CG} \) takes also into account the concentration dependence of the activity of carbon in austenite, and the repulsive interactions between the nearest neighbouring carbon atoms located in octahedral interstitial sites. Thus, the diffusivity \( D_{CG} \) is calculated by two factors: one of them is a concentration dependent factor and the other one is independent

\[
D_{CG} = \xi(\theta) \frac{k_B T}{h} \left( \frac{\lambda^2}{3\gamma_m} \right) \exp \left\{ -\frac{\Delta G^*}{k_B T} \right\}
\]

(2)
where $\xi(\theta)$ is the carbon concentration dependent factor obtained according to Bhadeshia’s calculations,$^{29}$ and takes values listed in Table 3; $\Delta G^*$ is the activation free energy for diffusion which is independent of composition and temperature; $\gamma_m$ is an activity coefficient assumed constant; $\lambda$ is the distance between the $\{002\}$ austenite planes and $h$ is the Planck’s constant. Bhadeshia$^{29}$ found that $\Delta G^*/k_B = 21230$ K and $\ln (\gamma_m / \lambda^2) = 31.84$. The values of $D_C^\gamma$ for temperatures ranging from 973 to 873 K are also listed in Table 3.

The volume free energy change, $\Delta G_v$, in equation (1) has been calculated with the help of commercial software denominated MTDATA,$^{30}$ which contains a large and rigorously evaluated thermodynamic database. The $\Delta G_v$ calculations take into account the effect of all the alloying elements in the decomposition of austenite. The values obtained for the studied steels are listed in Table 3. The value of $a$ in equation (1) has been calculated considering the influence of different alloying elements on ferrite and austenite lattice parameters. The ferrite lattice parameter has been calculated using the relations given by Bhadeshia,$^{31}$ whereas the austenite lattice parameter has been calculated as reported by Ridley et al.$^{32}$ and Dyson and Holmes.$^{33}$ The values of $a$ at temperatures ranging from 973 to 873 K are listed in Table 3. Likewise, a $\sigma_{xy}$ value of 0.705 J m$^{-2}$ and $\nu = 8.785 \times 10^{-30}$ m$^3$ have been considered in equation (1) for $\tau$ calculations.$^{26,34,35}$

The experimental determination of incubation time has been carried out by dilatometry and metallography. The experimental incubation time is defined as the minimum time at which it is possible to find some allotriomorphs nucleated on the austenite grain boundary. A detailed analysis of the dilatometric curve associated with the isothermal decomposition of austenite (Fig. 2) allows determination of an interval of time, $\Delta t$, in which it is more likely to find the incubation time. With the aim of carrying out an accurate determination, samples were isothermally treated
at different holding time within the $\Delta t$ interval and immediately quenched. A metallographic analysis of those samples determined the incubation time at which some allotriomorphs appear in the microstructure. Figure 3 shows an example of a microstructure with allotriomorphs at the initial stage of their formation.

Figure 4 shows a comparison between calculated (dashed line) and experimental (points) incubation time values for the studied steel. From this figure it can be concluded that calculated results for the incubation time are in good agreement with the predicted values from calculations proposed in this work.

### 3.2 Kinetics of austenite-to-allotriomorphic ferrite transformation

After nucleation occurs at the austenite grain boundaries, the thin layers of ferrite that decorate the austenite grain boundaries thicken at a rate controlled mainly by the diffusion of carbon in the austenite ahead of the advancing ferrite/austenite interface.\(^{36}\) The half-thickness of the allotriomorphs, $Z$, is generally calculated under parabolic growth conditions according to the following expression:\(^{37}\)

$$Z = \alpha_1 t^{1/2}$$

(3)

where $\alpha_1$ is the one – dimensional parabolic growth rate constant and $t$ is the growth time. The value of $\alpha_1$ can be obtained by numerical solution from the equation:\(^{38}\)
\[
\alpha_1 \exp\left(\frac{\alpha_1^2}{4D_C^\gamma}\right) \text{erfc}\left(\frac{\alpha_1}{2\sqrt{D_C^\gamma}}\right) = 2 \left(\frac{D_C^\gamma}{\pi}\right)^{1/2} \left(\frac{C_{\gamma\alpha} - \overline{C}}{C_{\gamma\alpha} - C_{\alpha\gamma}}\right) \tag{4}
\]

where \(D_C^\gamma\) is the diffusivity of carbon in austenite, \(\overline{C}\) is the overall carbon content, \(C_{\gamma\alpha}\) is the austenite solute content at the interface, and \(C_{\alpha\gamma}\) is the ferrite solute content at the interface. According to Bhadeshia,\(^{39}\) the consideration of \textit{paraequilibrium} is a good approach for the kinetics of this transformation. In that case, partitioning of substitutional solute atoms does not have time to occur and the adjoining phases have identical X/Fe atom ratios, where X represents the substitutional solute elements. Then, the substitutional lattice is configurationally frozen, but interstitial solutes such as carbon are able to partition and attain equilibration of chemical potential in both phases. Hence, the values of \(C_{\gamma\alpha}\) and \(C_{\alpha\gamma}\) in equation (4) refer to carbon concentrations and they were calculated according to the procedure reported by Shiflet \textit{et al.}\(^{40}\)

The \(C_{\gamma\alpha}\) and \(C_{\alpha\gamma}\) values as well as \(\alpha_1\) values are listed in Table 4.

**Kinetics of allotriomorphic ferrite formation at \(T>Ae_1\)**

At temperatures where allotriomorphic ferrite is the only austenite decomposition product, overlapping of carbon diffusion gradients occurs due to allotriomorphs growing from opposite sides of a grain. This effect, known as \textit{soft-impingement}, should be taken into account in the modelling of the growth kinetics of allotriomorphic ferrite. Soft impingement is considered in the model using an analytical treatment based on the work by Gilmour \textit{et al.}\(^{41}\)

The one-dimensional growth of planar grain boundary allotriomorphs from opposite sides of an austenite grain is illustrated schematically in Fig. 5.a. This process may be considered in two
stages. The first stage involves a parabolic growth from both sides of the grain according to the assumption that austenite has a semi-infinite extent with constant boundary conditions. In this stage, the carbon concentration in austenite far from the $\alpha/\gamma$ interface remains the same as the overall carbon content of the steel. During the second stage, soft-impingement occurs, the growth rate considerably decreases and the austenite is considered to have a finite extent beyond the $\alpha/\gamma$ interface. Therefore, the carbon concentration in the centre of the austenite grain is given by balancing the amount of carbon enrichment of the austenite against the corresponding depletion of the ferrite.$^{39,42}$ Figure 5.b shows a scheme of the carbon concentration profiles in austenite (dark lines) during the soft impingement stage. The calculations below are based on the assumption that the carbon concentration changes linearly from $\alpha/\gamma$ boundary to the centre of the grain. The carbon concentration in ferrite has been considered constant and negligibly small ($C^\alpha = 0$) (dark in X-axis). It is assumed that $\alpha/\gamma$ interface moves in z direction normal to the interface plane, and austenite is considered to have a finite size $L$ in that direction. The position of the interface at any time $t$ is defined by $z = Z$, being $Z = 0$ at $t = 0$. In this initial state, the carbon concentration in the austenite is uniform and corresponds to the overall carbon composition ($\overline{C}$). The position of the interface at the onset of soft impingement is defined by $z = Z_1$ and $t = t_1$. At that moment, carbon concentration rises at every point in the austenite located ahead of the interface. At a subsequent stage ($z=Z_2$ and $t=t_2$), the concentration of carbon in the centre of the austenite grain increases from $\overline{C}$ to $C_L$. Finally, when $z = Z_3$ and $t = t_3$, the carbon content in austenite is uniform and equal to that of austenite in the $\alpha/\gamma$ interface ($C^{\gamma\alpha}$).

At the onset of the soft impingement, when the position of the interface is $z = Z_1$, the carbon enrichment of the austenite is equal to the amount of carbon removed from the ferrite. Therefore,
according to Fig. 5.b, the mass balance allows calculation of the position of the interface $Z_1$, which is given by:

$$Z_1 = \frac{L(C_{\gamma a} - \bar{C})}{(C_{\gamma a} + \bar{C})}$$

where $L$ is the semi-extent of the austenite grain. Likewise, the position of the interface $Z_3$ when the carbon activity becomes uniform is calculated using the appropriate mass balance, and it is expressed as follows:

$$Z_3 = L \left( 1 - \frac{\bar{C}}{C_{\gamma a}} \right)$$

On the other hand, the carbon concentration in the centre of the austenite grain ($C_L$) can be calculated also by balancing the amount of carbon enrichment of austenite against the carbon depletion in the ferrite at an intermediate position $Z_2$ (Fig. 5.b) during the soft impingement process ($Z_1 < Z_2 < Z_3$),

$$C_L = \frac{2L\bar{C} - C_{\gamma a} \cdot (L - Z_2)}{L - Z_2}$$

The instantaneous interfacial carbon mass balance is described as follows:
\[ C^{\gamma_a} \frac{dZ_2}{dt} = -D_C^\gamma \frac{dC}{dz} \]  \hspace{1cm} (8)

where \( \frac{dC}{dz} \) represents the gradient of carbon ahead of the interface. Figure 5.b shows that, in position \( z=Z_2 \), this gradient can be expressed by:

\[ \frac{dC}{dz} = -\frac{C^{\gamma_a} - C_i}{L - Z_2} \]  \hspace{1cm} (9)

Finally, combining equations (7), (8), and (9) the following differential equation is obtained:

\[ \frac{dZ_2}{dt} = \frac{2D_C^\gamma (Z_3 - Z_2)}{(L - Z_2)^2} \]  \hspace{1cm} (10)

This velocity expression may then be integrated to yield the interface position (i.e. thickness of ferrite) as a function of time during isothermal decomposition of austenite. In one-dimensional model the calculated volume fraction of allotriomorph ferrite can be then approximated as:

\[ \xi_a = \frac{z}{L}; \quad (z = Z_2) \]  \hspace{1cm} (11)

According to equations (6) and (11) \( (z=Z_3) \), a maximum volume fraction of 26% is obtained during the isothermal decomposition of austenite into ferrite at 973 K, which is in excellent agreement with the experimental value listed in Table 2. Figure 6 shows the calculated and
measured $\xi_\alpha$ values under parabolic and soft impingement growth conditions. This figure suggests that care needs to be taken with the assumption of semi-infinite austenite grain extent and the modelling of allotriomorphic ferrite transformation under parabolic growth conditions in medium carbon microalloyed steels. It can be concluded that the soft impingement effect should be considered in the study of allotriomorphic ferrite growth kinetics of this steel. From Fig. 7 it is concluded that a great overall level of agreement between experiment and theory exists as soft impingement growth conditions are considered in calculations. Points lying on the line of unit slope show a perfect agreement between experimental and calculated values. $R^2$ in Fig. 7 is the square correlation factor of the experimental and calculated volume fraction of ferrite and quantifies the accuracy of the calculations. The accuracy of the model is 98%, which can be considered excellent for a thermodynamic and kinetics model.

*Kinetics of allotriomorphic ferrite formation at $T<Ae_1$*

At temperatures lower than $Ae_1$, the isothermal decomposition of austenite yields a ferrite-pearlite final microstructure. Pearlite is a lamellar product of eutectoid decomposition. A pearlite nodule is composed of multiple colonies; each colony has parallel lamellae of ferrite and cementite, which are orientated differently with respect to lamellae in adjacent colonies. The austenite transforms into pearlite by a reconstructive mechanism at temperatures below the eutectoid temperature $Ae_1$. The formation of allotriomorphic ferrite enriches the surrounding austenite in carbon promoting the formation of cementite nucleus at the $\alpha/\gamma$ interface and the local reduction of carbon content in the austenite that surrounds the cementite nucleus leads to the ferrite formation of pearlite aggregate (Fig. 8). The simultaneous ferrite and cementite formation
process yields the characteristic lamellar structure of pearlite.\textsuperscript{38) }As soon as pearlite surrounds a ferrite allotriomorph, its growth will finish, as is shown in Fig. 8. In addition, the carbon enrichment of austenite due to allotriomorphic ferrite formation is avoided, and carbon concentration in austenite far from the $\alpha/\gamma$ interface remains the same as the overall carbon content of the steel. Hence, the soft-impingement effect can be neglected. Allotriomorphic ferrite is considered to grow under a parabolic law, and the assumption of a semi-infinite extent austenite with constant boundary conditions is suitable for the kinetics of the isothermal decomposition of austenite at temperatures below $A_{e1}$.

Reed and Bhadeshia\textsuperscript{6) }proposed the following equation to describe the evolution of $\xi_\alpha$ with time ($t>\tau$) during the isothermal decomposition of austenite, assuming site saturation for nucleation of ferrite in austenite grain boundaries and within the framework of Johnson-Mehl-Avrami heterogeneous transformation kinetics theory:

$$\xi_\alpha = \xi^{EQ}_\alpha \left[ 1 - \exp \left( -\frac{2S_\gamma \alpha_1 (t - \tau)^{1/2}}{\phi} \right) \right]$$

(12)

where $t$ is the isothermal holding time; $\tau$ is the incubation time calculated according to equation (1); $\alpha_1$ is the one-dimensional parabolic rate constant; $S_\gamma$ is the austenite grain surface per unit volume; $\xi^{EQ}_\alpha$ is the equilibrium volume fraction of allotriomorphic ferrite and $\phi$ is the supersaturation in carbon, which can be estimated from the phase diagram as follows:

$$\phi = \frac{C^{\gamma\alpha} - C}{C^{\gamma\alpha} - C^{\alpha\gamma}}$$

(13)
Assuming austenite grains to be tetrakaidecahedra, $S_V$ in equation (12) can be expressed in terms of the average austenite grain diameter $d_γ$ by:

$$S_V = \frac{3.35}{d_γ}$$

(14)

with $d_γ = 2L$ (Fig. 5.a).

Figure 9 shows the experimental and predicted evolution of $ξ_α$ during the isothermal decomposition of austenite at 913 and 873 K. Likewise, Fig. 10 shows in more detail the $ξ_α$ values corresponding to the beginning of the allotriomorphic ferrite transformation at both temperatures. From both figures it is concluded that the lower the ferrite formation temperature, the slower allotriomorphic ferrite grows. That behaviour is consistent with the lower temperature, lower carbon mobility in austenite. A comparison of the calculated and experimental $ξ_α$ values for $T<Ae_1$ is shown in Fig. 11. This figure suggests that a good agreement (93% in $R^2$) between experiment and theory exists in the calculations.

3.3 Idiomorphic ferrite transformation kinetics

Idiomorphic ferrite nucleates intragranularly on the inclusions distributed inside the austenite grains. A detailed metallographic analysis on samples sectionalised longitudinally and transversally to the rolling direction, allowed determination of the shape and size of those inclusions. Their ellipsoidal shape is defined by three diameters ($d_1$ and $d_2$ in transverse direction...
and $d_3$ in longitudinal direction) which values are listed in Table 5. The EDX spectrum in Fig. 12 shows that all these inclusions are MnS.

The volume fraction of idiomorphic ferrite is related to the volume fraction of inclusions in the steel. Kluchen and Grong\textsuperscript{44}) proposed an equation to estimate the volume fraction of inclusions by converting the analytical oxygen and sulphur concentration in the steel into an equivalent inclusion volume fraction. Considering the solubility of sulphur in the steel equal to 0.003 mass \%,\textsuperscript{30}) the following equation has been derived:

$$V_v \approx 10^{-2} \left[5.0(\%O) + 5.4(\%S) - 0.003\right]$$

where $V_v$ is the volume fraction of inclusions in the steel and $O$ and $S$ are the oxygen and sulphur concentration of the steel, respectively, in mass \%. $V_v=2.34 \times 10^{-3}$ for the studied steel (see Table 1 for oxygen and sulphur composition).

In the studied steel, the austenite-to-idiomorphic ferrite transformation occurs at temperatures lower than $Ae_1$. Bearing in mind the above mentioned considerations for allotriomorphic ferrite transformation kinetics at those temperatures, the soft-impingement effect can be neglected. Therefore, idiomorphic ferrite is assumed to grow under a parabolic law with time, and the assumption of a semi-infinite extent austenite with constant boundary conditions is considered a sensible approach for the kinetics of the isothermal idiomorphic ferrite formation. Idiomorphic ferrite grows isotropically into the austenite grain and simultaneously in the three dimensions of the space. In this sense, the study of the austenite-to-idiomorphic ferrite transformation involves the calculation of the three-dimensional parabolic thickening rate ($\alpha_3$), which is given by:\textsuperscript{45)}
\[ \alpha_3 = \left[ \frac{2D^*_a (C^{\alpha_3} - \bar{C})}{C - C^{a_y}} \right]^{1/2} \]  \hspace{1cm} (16)

The values of \( \alpha_3 \) for the three studied temperatures were listed in Table 4.

Idiomorphs nucleate on inclusions randomly distributed in an existing austenite phase at a constant nucleation rate per unit area \((I)\) and subsequently, grow isotropically to form spherical particles. In diffusion-controlled growth, the radius of a particle formed after an incubation period \((\tau)\), will vary with the square root of time \((t)\) as follows:

\[ r = \alpha_3 (t - \tau)^{1/2} \]  \hspace{1cm} (17)

where \( \alpha_3 \) is considered constant at a given temperature as long as the far-field concentration in the matrix does not change. Therefore, the volume of an idiomorph after a time \(t\) is given by:

\[ v = \begin{cases} 4\pi \alpha_3^3 (t - \tau)^{3/2} & , \quad (t > \tau) \\ 0 & , \quad (t \leq \tau) \end{cases} \]  \hspace{1cm} (18)

Moreover, the number of idiomorphs \((N)\) formed in a time \(d\tau\) is:

\[ N = IS_{f^{\text{INC}}} V d\tau \]  \hspace{1cm} (19)
where $V$ is the volume of austenite before isothermal decomposition, $S_{V}^{INC}$ is the inclusion surface area per unit volume and $I$ is the nucleation rate per unit area of inclusion.

At the stages of transformation, when particles start to impinge, the above theory does not adequately describe the kinetics of idiomorphic ferrite formation. Avrami\textsuperscript{46} introduced the concept of an \textit{extended volume} to describe the volume of the particles whose growth is not impeded by impingement between particles. Particles are allowed to overlap and grow through each other. New nucleus forming in regions already transformed to idiomorphic ferrite, dubbed \textit{phantom nuclei}, are also included in the extended volume calculation. Thus, the contribution of all the particles nucleated in the interval between $\tau$ and $\tau + d\tau$ to the extended volume of idiomorphic ferrite ($V_{IDI}^{e}$) can be expressed as:

$$dV_{IDI}^{e} = vN = \frac{4\pi}{3}a_{3}^{\frac{1}{2}}(t - \tau)^{3/2}IS_{V}^{INC}Vd\tau$$

(20)

However, the \textit{actual} change in volume, $dV_{IDI}$, can be determined from the change in \textit{extended volume} just including the probability that some transformation to idiomorphic ferrite has already occurred. Thus, the volume of idiomorphic ferrite formed ($V_{IDI}$) could be expressed as:

$$dV_{IDI} = \left(1 - \frac{V_{IDI}}{V}\right)dV_{IDI}^{e}$$

(21)

Separating variables and integrating, the following expression can be obtained:
\[-\ln\left(1-\frac{V_{\text{IDI}}}{V}\right) = \frac{4\pi}{3} \int_{0}^{t} IS_{V}^{\text{INC}} \alpha_{3}^{3} (t-\tau)^{3/2} d\tau \] (22)

Finally, the volume fraction of idiomorphic ferrite, $\xi_{\text{IDI}}$, can be easily evaluated assuming that $I$ and $\alpha_{3}$ are constant with time, and $\xi_{\text{EQ}}^{\text{IDI}}$ is the maximum volume fraction of austenite that transforms to idiomorphic ferrite:

\[\xi_{\text{IDI}} = \frac{V_{\text{IDI}}}{V} = \xi_{\text{EQ}}^{\text{IDI}} \left[1 - \exp\left(-\frac{8\pi}{15} IS_{V}^{\text{INC}} \alpha_{3}^{3} t^{5/2}\right)\right] \] (23)

The nucleation rate ($I$) has been calculated according to Lange et al.\textsuperscript{26) and Reed and Bhadeshia,\textsuperscript{6) taking into account the chemical composition of the studied steel, and its values for a temperature of 913 and 873 K are $5.50\times10^{8}$ and $6.3\times10^{8}$ m\textsuperscript{-2} s\textsuperscript{-1}, respectively. Finally, $S_{V}^{\text{INC}}$ is given by:

\[S_{V}^{\text{INC}} = S_{V_{0}}^{\text{INC}} n^{\text{INC}} \] (24)

where $S_{V_{0}}^{\text{INC}}$ is the inclusion surface area per unit volume for a particular inclusion, and $n^{\text{INC}}$ is the total number of inclusions inside the austenite grain. In this sense, and assuming that all the inclusions are ellipsoids with the same size, $S_{V_{0}}^{\text{INC}}$ is written as $S_{V_{0}}^{\text{INC}} = 6/d_{5}$. Moreover, $n^{\text{INC}}$ could be expressed as the volume fraction of inclusions in the steel ($V_{V}$ ) modulated by the ratio between the austenite grain size and the inclusion size ($n^{\text{INC}} = \frac{d_{V}}{(d_{1} + d_{2})/2} V_{V}$). Therefore, $S_{V}^{\text{INC}}$ can be calculated as follows:
\[ S_V^{INC} = \frac{6 d_\gamma}{d_3 \left( d_1 + d_2 \right)/2} V_\gamma = \frac{12 d_\gamma}{d_3 \left( d_1 + d_2 \right)} V_\gamma \]  

(25)

where \( d_1, d_2, \) and \( d_3 \) are the inclusion diameters, and \( d_\gamma \) is the austenite grain diameter.

Figure 13 shows the evolution of the volume fraction of idiomorphic ferrite, \( \xi_{IDI} \), formed during the isothermal decomposition of austenite at 913 and 873 K. Figure 14 represents a comparison between the experimental and calculated values of \( \xi_{IDI} \). These figures suggest that a good agreement (85% in \( R^2 \)) between experimental and theoretical results exists.

4. Conclusions

1. The kinetics of austenite-to-allotriomorphic and idiomorphic ferrite transformations has been described in a wide temperature range for a 0.37C–1.45Mn–0.11V (in mass %) microalloyed steel. Experimental validation of these models has been carried out using dilatometric and metallographic analysis. An excellent agreement between the experimental and calculated volume fraction of allotriomorphic and idiomorphic ferrite has been found for the studied steel.

2. A mathematical process to calculate the incubation time for the isothermal formation of allotriomorphic ferrite has been described. Experimental validation of calculations has been also carried out using dilatometric and metallographic analysis. An excellent agreement between calculated and measured incubation time values for the isothermal formation of allotriomorphic ferrite has been found for the studied steel.
3. Gilmour et al. analysis considering the soft-impingement effect gives a very good representation of the kinetics of austenite-to-allotriomorphic ferrite transformation at temperatures above $Ae_1$ in the studied steel. Since pearlite is formed at temperatures below $Ae_1$, the soft-impingement effect should be neglected for the austenite-to-allotriomorphic and idiomorphic ferrite transformation kinetics. In that case, Reed and Bhadeshia analysis considering the growth of ferrite under a parabolic law, is the most suitable representation of ferrite transformation kinetics.

4. In this steel, idiomorphic ferrite nucleates intragranularly on ellipsoidal manganese sulfide inclusions homogeneously distributed inside the austenite grains. Since the excellent agreement between experimental and calculated results, it is concluded that, the equation reported by Kluken and Grong, which convert the analytical oxygen and sulfur concentration into an equivalent inclusion volume, is a sensible expression for calculation of the volume fraction of inclusions in the steel.

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References


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Table 1. Chemical composition (mass %)

Table 2. Equilibrium volume fraction of allotriomorphic and idiomorphic ferrite

Table 3. Calculated values of $\xi(\theta)$, $D_C^\gamma$, $\Delta G_v$, and $a$ parameters

Table 4. Calculated values of $C^{\alpha\gamma}$, $C^{\alpha\alpha}$, $\alpha_1$ and $\alpha_3$

Table 5. Diameters of ellipsoidal inclusions
Fig. 1. Microstructures obtained after isothermal heat treatment for 3 h at (a) 973 K, (b) 913 K and (c) 873 K.

Fig. 2. Dilatometric curve (relative change in length vs. time) obtained during isothermal decomposition of austenite at 873 K for 100 s for the studied steel.

Fig. 3. Optical micrograph of studied steel after isothermal heat treatment at 913 K for 18 s. F is allotriomorphic ferrite

Fig. 4. Experimental and calculated results for the incubation time of isothermally formed allotriomorphic ferrite.

Fig. 5. Diagram illustrating the soft-impingement process: (a) Schematic representation of the growth of grain boundary allotriomorphs, (b) carbon concentration profile for the calculation of impingement time. The dark lines represent the carbon profile in austenite and ferrite.

Fig. 6. Comparison between measured and calculated $\xi_\alpha$ values under parabolic and impingement considerations for the isothermal decomposition of austenite at 973 K.

Fig. 7. A comparison of the experimental and predicted ferrite volume fraction formed at a temperature higher than $Ae_1$. Soft impingement is considered in calculations.
Fig. 8. Early stage of pearlite transformation during the isothermal decomposition of austenite at 913 K for 60 s. P is pearlite and F is allotriomorphic ferrite.

Fig. 9. Comparison between calculated and measured $\xi_\alpha$ values during the isothermal decomposition of austenite at 913 and 873 K.

Fig. 10. Comparison between calculated and measured $\xi_\alpha$ values at the initial stages of isothermal decomposition of austenite in allotriomorphic ferrite at 913 and 873 K.

Fig. 11. A comparison of the experimental and predicted ferrite volume fraction formed at a temperature lower than $Ae_1$.

Fig. 12. EDX spectrum of an inclusion where idiomorphic ferrite nucleates.

Fig. 13. Evolution of the volume fraction of idiomorphic ferrite, $\xi_{IDI}$, during the isothermal decomposition of austenite at 913 and 873 K.

Fig. 14. A comparison of the experimental and calculated values of volume fraction of idiomorphic ferrite.
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Table 4  Calculated values of $C^\alpha\gamma$, $C^\gamma\alpha$, $\alpha_1$ and $\alpha_3$

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Table 5 Diameters of ellipsoidal inclusions

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<td>( d_2, \mu m )</td>
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</table>
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