

Marcel Onink, Frans D. Tichelaar, Cornelis M. Brakman, Eric J. Mittemeijer and Sybrand van der Zwaag

(Delft University of Technology, Laboratory of Materials Science, Rotterdamseweg 137, 2628 AL Delft, The Netherlands)

Quantitative Analysis of the Dilatation by Decomposition of Fe-C Austenites; Calculation of Volume Change upon Transformation

A detailed analysis has been made of the length changes due to decomposition of iron-carbon austenites into ferrite and carbon enriched austenite above the A_1 temperature, and into ferrite and cementite below the A_1 temperature, using lattice-parameter data for the phases involved. The calculations have been performed as a function of carbon content, temperature and degree of transformation. A general definition for the total degree of transformation has been proposed for the case that more than one product phase develops. This definition also holds when the product phases develop consecutively, allowing an analysis of the kinetics of the austenite decomposition. Above the A_1 temperature, the relation between the degree of transformation and the dilatation is linear within good approximation. However, below the A_1 temperature a strong deviation from such a linear relationship occurs, as the result of subsequent decomposition of austenite into ferrite and carbon enriched austenite, and decomposition of the carbon enriched austenite into ferrite and cementite.

1 Introduction

To control the microstructure of steels much use is made of Transformation-Time-Temperature (TTT) diagrams and Continuous Cooling-Transformation (CCT) diagrams, which describe the phase composition of a specified steel with a specified grain size as a function of annealing temperature and time, and cooling rate respectively [1, 2]. Traditionally, dilatometry is used to obtain such diagrams. Strictly speaking, these diagrams are only valid for one composition, which implies that for each steel composition the dilatometric experiments have to be repeated. This time-consuming process can be avoided if the TTT and CCT diagrams could be predicted from knowledge of the kinetics of the nucleation and growth processes of the phase transformations involved. However, in spite of the extensive research performed until now, this knowledge is not available yet.

In order to study the transformation kinetics of the decomposition of austenite upon phase transformation, by dilatometry, a method to deduce the atom fraction of the product phase as a function of time and/or temperature from the

measured length changes is indispensable. In the literature, the relation between the atom fraction of the product phase at a certain stage of a transformation and the associated volume change is often taken to be linear, unjustly also for the case where the final reaction product is formed in separate, consecutive decompositions (see discussion). In this paper, a rigorous calculation is performed of the dilatation upon decomposition of Fe-C austenites as a function of temperature, carbon content and the total degree of transformation, on the basis of the lattice parameters of the constituting phases and their dependence on temperature and composition, and the phase diagram. The total degree of transformation is defined as the momentaneous number of Fe atoms in ferrite relative to the number of Fe atoms in ferrite after completed transformation(s).

Two types of decomposition have been studied in two different temperature regimes: the decomposition of austenite (γ) into ferrite (α) and carbon-enriched austenite for temperatures between the A_3 temperature¹⁾ [$\gamma/(\alpha + \gamma)$ equilibrium temperature] and the A_1 temperature [1000 K; the $(\alpha + \gamma)/(\alpha + \theta)$ equilibrium temperature; θ denotes cementite], and the decomposition of γ into α and θ between A_1 and 920 K. The different contributions of the various product phases to the total volume change on transformation, are analysed (see Section 2), and the use of dilatometry for kinetic analysis of the austenite decomposition is discussed (Section 3).

To our knowledge no similar work on pure Fe-C alloys has been reported earlier. A calculation of the volume fraction of ferrite formed in a bainitic transformation in an Fe-0.3 wt.% C-4.08 wt.% Cr steel, from measured length changes, has been reported in [3]. However, the calculations of the dilatation as presented in [3] are not correct. The correct formulas, according to the present analysis (Section 2), are presented in the appendix of this paper.

2 Calculation of the Dilatation on Phase Transformation

The relative volume change measured during a phase transformation is the consequence of a change in specific volume, i.e. a changing volume per atom which can be

¹⁾The A_1 and A_3 temperatures will further be denoted as A_1 and A_3 .

Table 1a. Lattice parameters of ferrite [4], austenite [4] and cementite [7, 8] as functions of the temperature T (in K) and the carbon concentration χ (in atom fraction). Data on the lattice parameters of cementite at room temperature [7] were extrapolated to elevated temperature using a temperature dependent mean thermal expansion coefficient taken from [8].

| Phase | Lattice parameter [nm] |
|----------|--|
| α | $a = 0.28863 \cdot (1 + 17.5 \cdot 10^{-6} \cdot [T - 800])$ |
| γ | $a = (0.36306 + 0.078 \cdot \chi) \cdot \{1 + (24.9 - 50 \cdot \chi) \cdot 10^{-6} [T - 1000]\}$ |
| θ | $a = 0.45234 \cdot \{1 + (5.311 \cdot 10^{-6} - 1.942 \cdot 10^{-9} \cdot T + 9.655 \cdot 10^{-12} \cdot T^2) \cdot [T - 293]\}$ $b = 0.50883 \cdot \{1 + (5.311 \cdot 10^{-6} - 1.942 \cdot 10^{-9} \cdot T + 9.655 \cdot 10^{-12} \cdot T^2) \cdot [T - 293]\}$ $c = 0.67426 \cdot \{1 + (5.311 \cdot 10^{-6} - 1.942 \cdot 10^{-9} \cdot T + 9.655 \cdot 10^{-12} \cdot T^2) \cdot [T - 293]\}$ |

Table 1b. Phase boundaries (PB's) in the Fe-C phase diagram [9]; see Fig. 1. Carbon concentration (in at. %) as a function of temperature T (in K). The carbon saturation concentration of austenite below A_1 was calculated from the criterion $\Delta\mu_C = 0$ (see text and [5]).

| Phase | PB | Carbon concentration [at. %] |
|----------|-------------------|---|
| α | GP | $\chi_{\alpha}^{\text{eq1}} = 6.5594 \cdot 10^{-1} - 5.5361 \cdot 10^{-4} \cdot T$ |
| γ | GS | $\chi_{\gamma}^{\text{eq1}} = 5.47472 \cdot 10^2 - 1.38709 \cdot T + 1.18089 \cdot 10^{-3} \cdot T^2 - 3.37774 \cdot 10^{-7} \cdot T^3$ |
| α | PQ | $\chi_{\alpha}^{\text{eq2}} = 100 \cdot 10^{(1.05 - 4040/T)}$ |
| γ | $\Delta\mu_C = 0$ | $\chi_{\gamma}^{\text{sat}} = -7.053 \cdot 10^{-1} - 3.450 \cdot 10^{-3} \cdot T + 7.609 \cdot 10^{-6} \cdot T^2$ |

caused by a) a change in the crystal structure(s) and/or b) an enrichment/depletion of the solute in solid solutions. The total relative volume change can be calculated using data for the lattice parameters of the various phases at the appropriate temperature. Thus, transformation strains are neglected.

For pure Fe the relative volume change for the transformation of austenite γ (fcc) to ferrite α (bcc), denoted as reaction 0, as a function of the degree of transformation reads:

$$\left[\frac{\Delta V}{V} \right]_{\text{Reaction 0}} = z_0 \cdot \left(\frac{\frac{V_{\alpha}}{2} - \frac{V_{\gamma}}{4}}{\frac{V_{\gamma}}{4}} \right) \quad (1)$$

Throughout this work the parameter z_i indicates the degree of transformation for reaction i and is defined as the atom fraction of ferrite at a certain stage of transformation divided by the final atom fraction of ferrite, i. e. after completed transformation; $0 \leq z_i \leq 1$. Because for pure Fe the austenite transforms completely, the equilibrium atom fraction of ferrite equals 1. The relative volume changes are given in terms of the specific volume per Fe atom in each phase, which is defined as the unit-cell volume, v_i of phase i divided by the number of Fe atoms in the unit cell, N_i . The unit-cell volumes are calculated from lattice-parameter data. Recent data for the lattice parameters for pure Fe ferrite and pure Fe austenite are given in [4]; see Table 1a.

For Fe-C alloys one has to take into account that the transformations lead to the presence of several phases, with equilibrium amounts and specific volumes per Fe atom that depend on temperature and composition. When a hypo-eutectoid Fe-C alloy is quenched from the austenitic state to an isothermal transformation temperature T_a below A_3 , different phase transformations can occur depending on the value of T_a . If T_a is between A_3 and A_1 , ferrite is formed, with a low solubility for carbon, and thus the untransformed austenite becomes enriched in carbon. If T_a is

below A_1 , the austenite is eventually transformed into ferrite and cementite. For the present dilatation calculations it is irrelevant whether a ferrite/cementite microstructure develops with cementite as grain-boundary precipitates or with ferrite and cementite in a lamellar fashion (pearlite).

2.1 Fe-C; above A_1

The decomposition of the initial austenite into ferrite with enrichment in carbon of the remaining austenite (for $A_1 < T_a < A_3$) is considered first:



The symbols α and γ refer to the different phases. The symbols χ_i^j denote the average carbon atom fractions in phase i for condition j , where $j = \text{in}$ and $j = \text{eq1}$ indicate the initial and equilibrium carbon atom fractions for Reaction 1, respectively. All carbon atom fractions denoted χ_i^j (except $\chi_{\gamma}^{\text{sat}}$, see Section 2.2) in this work are defined similarly and thus for $j = \text{eq}$ correspond to the carbon atom fractions as read from the usual Fe-C phase diagram; see lines indicated by χ_i^j in Fig. 1. The carbon atom fractions are defined as the number of C atoms in phase i divided by the total number of atoms, i. e. Fe and C, in phase i .

The equilibrium atom fraction of ferrite, with respect to the total number of atoms, i. e. Fe and C, in the specimen, for Reaction 1, x_{α}^{eq1} , is obtained by applying the lever rule to the Fe-C phase diagram at the relevant temperature ($B/(A+B)$ with A and B as the line segments as indicated in Fig. 1), using data for the carbon atom fractions in austenite and ferrite presented in Table 1b. The number of Fe atoms in phase i , n_i^{Fe} , is related to the relevant z_i , χ_i^j and χ_i^j by an atom balance for a total of N atoms, Fe and C, in the specimen; expressions for n_i^{Fe} are listed in Table 2a. The specific volumes per Fe atom are calculated from lattice-parameter data as a function of temperature and, for austenite, also as a function of carbon concentration. Such lattice-parameter

Table 2a. Expressions for the numbers of Fe and C atoms in the phases as indicated for a total number of N atoms, Fe and C, in the specimen, n_i^{Fe} and n_i^{C} , for decomposition Reaction 1, above A_1 . The equilibrium atom fraction of ferrite in the specimen is denoted by x_α^{eq1} . Atom fractions of carbon in each phase i are denoted by χ_i^j for the condition j , where $j = \text{in}$ and $j = \text{eq1}$ indicate the initial and equilibrium carbon atom fractions, respectively. The atom fraction of carbon in the initial austenite corresponds to the gross carbon concentration of the alloy. The degree of transformation, z_1 , is defined as the momentaneous atom fraction of ferrite relative to the equilibrium atom fraction of ferrite.

| Reaction 1 | n_i^{Fe} | n_i^{C} |
|--------------------|--|---|
| Ferrite | $Nz_1x_\alpha^{\text{eq1}}(1 - \chi_\alpha^{\text{eq1}})$ | $Nz_1x_\alpha^{\text{eq1}}\chi_\alpha^{\text{eq1}}$ |
| Enriched austenite | $N(1 - z_1x_\alpha^{\text{eq1}}) - (\chi_\gamma^{\text{in}} - z_1x_\alpha^{\text{eq1}}\chi_\alpha^{\text{eq1}})$ | $N(\chi_\gamma^{\text{in}} - z_1x_\alpha^{\text{eq1}}\chi_\alpha^{\text{eq1}})$ |
| Initial austenite | $N(1 - \chi_\gamma^{\text{in}})$ | $N\chi_\gamma^{\text{in}}$ |

Table 2b. Expression for the numbers of Fe and C atoms in the phases as indicated for a total number of N atoms, Fe and C, in the specimen, n_i^{Fe} and n_i^{C} , for decomposition Reaction 2a. The atom fraction of ferrite after completed decomposition 2a (Reaction 2a) is denoted by x_α^{2a} . χ_γ^{in} denotes the initial atom fraction of carbon in austenite, and χ_α^{eq2} denotes the equilibrium atom fraction of carbon in ferrite according to Fig. 1. The atom fraction of carbon in the initial austenite corresponds to the gross carbon concentration of the alloy. The degree of transformation, z_{2a} , is defined as the momentaneous atom fraction of ferrite divided by the equilibrium atom fraction of ferrite formed in Reaction 2a.

| Reaction 2a | n_i^{Fe} | n_i^{C} |
|--------------------|--|--|
| Ferrite | $Nz_{2a}x_\alpha^{2a}(1 - \chi_\alpha^{\text{eq2}})$ | $Nz_{2a}x_\alpha^{2a}\chi_\alpha^{\text{eq2}}$ |
| Enriched austenite | $N\{(1 - z_{2a}x_\alpha^{2a}) - (\chi_\gamma^{\text{in}} - z_{2a}x_\alpha^{2a}\chi_\alpha^{\text{eq2}})\}$ | $N(\chi_\gamma^{\text{in}} - z_{2a}x_\alpha^{2a}\chi_\alpha^{\text{eq2}})$ |
| Initial austenite | $N(1 - \chi_\gamma^{\text{in}})$ | $N\chi_\gamma^{\text{in}}$ |

Table 2c. Expressions for the numbers of Fe and C atoms in the phases as indicated for a total number of $N(1 - x_\alpha^{2a})$ atoms, Fe and C, n_i^{Fe} and n_i^{C} , for decomposition Reaction 2b, below A_1 . The initial austenite for Reaction 2b is the carbon enriched austenite resulting from Reaction 2a. The atom fraction of ferrite, with respect to all atoms, i. e. Fe and C, in the austenite remaining from Reaction 2a, for Reaction 2b is denoted as x_α^{2b} . The fraction of ferrite, with respect to all atoms, i. e. Fe and C, in the specimen, that occurs for completed Reaction 2b equals $(1 - x_\alpha^{2a}) \cdot x_\alpha^{2b}$. χ_γ^{in} denotes the initial atom fraction of carbon in austenite, χ_α^{eq2} denotes the equilibrium atom fraction of carbon in ferrite according to Fig. 1. The carbon concentration of the austenite remaining from Reaction 2a is indicated by χ_γ^{sat} . If Reaction 2a does not occur, substitute χ_γ^{in} for χ_γ^{sat} in the expressions given in the table. The degree of transformation, z_{2b} , is defined as the momentaneous atom fraction of ferrite formed in reaction 2b divided by the equilibrium atom fraction of ferrite formed in reaction 2b.

| Reaction 2b | n_i^{Fe} | n_i^{C} |
|-------------------------|--|--|
| Ferrite | $N(1 - x_\alpha^{2a})z_{2b}x_\alpha^{2b}(1 - \chi_\alpha^{\text{eq2}})$ | $N(1 - x_\alpha^{2a})z_{2b}x_\alpha^{2b}\chi_\alpha^{\text{eq2}}$ |
| Cementite | $3N(1 - x_\alpha^{2a})z_{2b}(1 - x_\alpha^{2b})/4$ | $N(1 - x_\alpha^{2a})z_{2b}(1 - x_\alpha^{2b})/4$ |
| Untransformed austenite | $N(1 - x_\alpha^{2a})\{(1 - \chi_\gamma^{\text{sat}}) - z_{2b}(x_\alpha^{2b}\chi_\alpha^{\text{eq2}} + (1 - x_\alpha^{2b})/4)\}$ | $N(1 - x_\alpha^{2a})\{\chi_\gamma^{\text{sat}} - z_{2b}(x_\alpha^{2b}\chi_\alpha^{\text{eq2}} + (1 - x_\alpha^{2b})/4)\}$ |
| Initial Austenite | $N(1 - x_\alpha^{2a})(1 - \chi_\gamma^{\text{sat}})$ | $N(1 - x_\alpha^{2a})\chi_\gamma^{\text{sat}}$ |

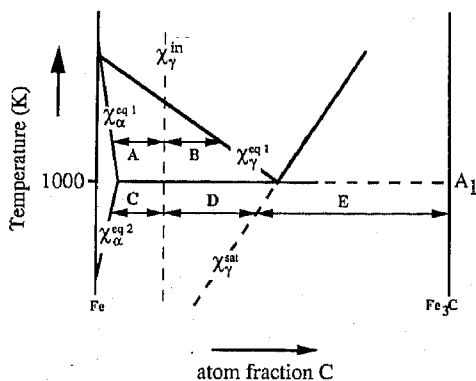


Fig. 1. Schematic drawing of the relevant part of the usual, metastable Fe-C phase diagram, indicating the notation for the carbon atom fractions used in Tables 1, 2, 7 and throughout the text. The line segments used to calculate the equilibrium atom fractions of ferrite for Reactions 1, 2a and 2b are denoted by "A" to "E".

data for α -Fe and γ -Fe-C were recently determined using neutron diffraction [4]; see Table 1a. Thus the relative volume change for Reaction 1, as a function of the degree of the transformation (z_1 ; see Table 2a), can be calculated from:

$$\left[\frac{\Delta V}{V} \right]_{\text{Reaction 1}} = \frac{V_{\text{final}} - V_{\text{initial}}}{V_{\text{initial}}} = \frac{n_{\alpha}^{\text{Fe}} \cdot \frac{V_{\alpha}^{\text{eq1}}}{2} + n_{\gamma}^{\text{Fe}} \cdot \frac{V_{\gamma}^{\text{eq1}}}{4} - n_{\gamma}^{\text{Fe}} \cdot \frac{V_{\gamma}^{\text{in}}}{4}}{n_{\gamma}^{\text{Fe}} \cdot \frac{V_{\gamma}^{\text{in}}}{4}} \quad (2)$$

where the ferrite is considered to have the equilibrium composition. The symbol χ_γ denotes the average atom fraction of carbon in the remaining austenite for a degree of trans-

formation z_1 (see below). The enrichment of the remaining austenite with carbon during the transformation starts at the transformation interface, while in the centre of the grain a delayed enrichment with carbon takes place, leading to a carbon concentration profile across the austenite grain. The relation between the lattice parameter of austenite and the carbon concentration is linear [4], so instead of calculating the expansion of an austenite grain containing a carbon-concentration profile across the grain, the overall expansion of the austenite grain can be calculated accurately for an austenite with the momentaneous average carbon concentration. The average atom fraction of carbon in the enriched austenitic phase during transformation, χ_γ , can be calculated according to:

$$\chi_\gamma(z_1) = \frac{\chi_\gamma^{\text{in}} - z_1 \cdot \chi_\alpha^{\text{eq1}} \cdot \chi_\alpha^{\text{eq1}}}{1 - z_1 \cdot \chi_\alpha^{\text{eq1}}} \quad (3)$$

For $z_1 = 0$, the atom fraction of carbon in austenite corresponds to the initial atom fraction of carbon in austenite, χ_γ^{in} . For $z_1 = 1$ the atom fraction of carbon on austenite corresponds to the equilibrium atom fraction of carbon in austenite, χ_γ^{eq1} .

Both the ferrite that forms and the remaining austenite that enriches in carbon contribute to the total relative change of the specimen. Their separate contributions to the total relative volume change are (following Eq. (2), with

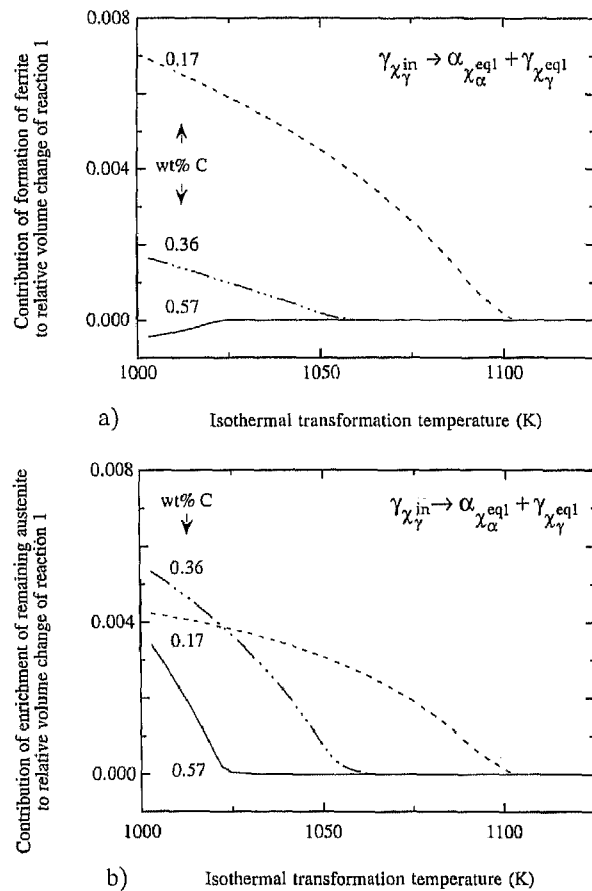
$$n_{\gamma_{\text{in}}}^{\text{Fe}} = n_{\gamma_{\text{xy}}}^{\text{Fe}} + n_{\alpha_{\text{eq1}}}^{\text{Fe}} :$$

$$\left[\frac{\Delta V}{V} \right]_{\text{Reaction 1}}^{\alpha_{\text{eq1}}} = \frac{n_{\alpha_{\text{eq1}}}^{\text{Fe}}}{n_{\alpha_{\text{eq1}}}^{\text{Fe}} + n_{\gamma_{\text{xy}}}^{\text{Fe}}} \cdot \frac{\frac{v_{\alpha_{\text{eq1}}}}{2} - \frac{v_{\gamma_{\text{in}}}}{4}}{\frac{v_{\gamma_{\text{in}}}}{4}} \quad (4a)$$

$$\left[\frac{\Delta V}{V} \right]_{\text{Reaction 1}}^{\gamma_{\text{xy}}} = \frac{n_{\gamma_{\text{xy}}}^{\text{Fe}}}{n_{\alpha_{\text{eq1}}}^{\text{Fe}} + n_{\gamma_{\text{xy}}}^{\text{Fe}}} \cdot \frac{\frac{v_{\gamma_{\text{xy}}}}{4} - \frac{v_{\gamma_{\text{in}}}}{4}}{\frac{v_{\gamma_{\text{in}}}}{4}} \quad (4b)$$

The separate contributions can be understood as the number of iron atoms in the appropriate phase with respect to the number of Fe atoms present in the total of N atoms, multiplied by the relative specific volume change of Fe in phase i with respect to Fe in the initial austenite. The partial contributions are shown for completed transformation ($z_1 = 1$) in Figs. 2a and 2b as a function of the isothermal transformation temperature, for different carbon concentrations of the initial austenite.

The contribution of the ferrite formation to the total relative volume change of Reaction 1 increases with decreasing isothermal transformation temperature and decreases with increasing carbon concentrations, see Fig. 2a. In terms of Eq. (4a), this is caused by variations of both the number of Fe atoms in ferrite and the difference in specific volume per Fe atom between ferrite and initial austenite with temperature and carbon concentration. The number of Fe atoms in ferrite depends on the equilibrium atom fraction of ferrite that increases with decreasing temperature and decreases with increasing carbon concentration. The difference in specific volume per Fe atom between ferrite and the initial austenite increases with decreasing temperature, because the thermal expansion coefficient of ferrite is smaller than that of austenite, and reduces with increasing atom



Figs. 2a and b. (a) Contribution of the formation of ferrite to the total relative volume change for Reaction 1, according to Eq. (4a), for temperatures above A_1 ($= 1000$ K) and (b) contribution of the enrichment of the remaining austenite to the total relative volume change for Reaction 1, according to Eq. (4b), for temperatures above A_1 . The numbers in the figure indicate the gross carbon concentration of the alloy concerned.

fraction of carbon in the initial austenite. For a carbon concentration of about 0.53 wt. % the difference in specific volume between the ferrite and the initial austenite is no longer significant in the temperature region investigated.

The contribution of the remaining austenite, that enriches with carbon, to the total relative volume change of Reaction 1 obviously decreases if the number of Fe atoms in the enriched austenite decreases, which is the case with increasing ferrite atom fraction (i. e. decreasing atom fraction of carbon of the initial austenite or decreasing temperature). The difference in specific volume per Fe atom of the enriched austenite and the initial austenite increases with decreasing temperature (because the carbon concentration in the enriched austenite then increases) and with decreasing carbon concentration of the initial austenite. The opposing effects, with decreasing carbon concentration of the initial austenite, explain why in Fig. 2b the curves for 0.17 wt. % C and 0.36 wt. % C intersect.

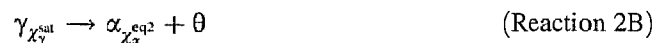
The total relative volume change for the decomposition of austenite according to Reaction 1 after completed transformation (combination of effects shown in Figs 2a and 2b) increases with decreasing temperature and decreases with increasing carbon concentration, see Fig. 5 for $T > A_1$.

2.2 Fe-C: below A_1

The decomposition of austenite into ferrite and cementite (for $T_a < A_1$) can be described as:



The symbols α , γ and θ refer to the different phases. The symbol $\chi_{\gamma}^{\text{in}}$ denotes the initial carbon atom fraction in phase γ , and the symbol $\chi_{\alpha}^{\text{eq2}}$ denotes the equilibrium atom fraction of carbon in ferrite, see Fig. 1. The cementite is considered to be of constant composition. Although Reaction 2 describes the final and initial phases for this temperature region, the final phases are formed in two consecutive reactions [5, 6]; a Reaction 1 like transformation of austenite into ferrite, enriching the remaining austenite with carbon up to saturation level (Reaction 2a), followed by the decomposition of the austenite saturated with carbon into ferrite and cementite (reaction 2b). The saturation carbon concentration in the enriched austenite ($\chi_{\gamma}^{\text{sat}}$) was calculated from the condition $\Delta\mu_C = 0$ [5], where $\Delta\mu_C$ is defined as the chemical potential of carbon in ferrite at the interface minus the chemical potential of carbon in austenite at the interface.



The atom fraction of ferrite, with respect to all atoms, i. e. Fe and C, in the specimen, produced according to Reaction 2a, x_{α}^{2a} , is obtained by applying the lever rule to the Fe-C phase diagram at the relevant temperature ($D/(C+D)$) with C and D as line segments as indicated in Fig. 1, using data for the carbon atom fractions of austenite and ferrite presented in Table 1b. The specific volumes per Fe atom for each phase are calculated similarly as for Reaction 1. The average atom fraction of carbon in the remaining austenite that enriches in carbon as a function of z_{2a} is calculated similar to Eq. (3). This average atom fraction of carbon in the remaining austenite, χ_{γ} , runs from $\chi_{\gamma}^{\text{in}}$ ($z_{2a} = 0$) to $\chi_{\gamma}^{\text{sat}}$ ($z_{2a} = 1$) in this case. The relative volume change for Reaction 2a, as a function of the degree of transformation, z_{2a} , can then be calculated using Eq. (2) applying expressions for the numbers of Fe atoms in each phase listed in Table 2b.

After completed Reaction 2a, the atom fraction of enriched austenite equals $(1 - x_{\alpha}^{2a})$. The atom fraction of ferrite, with respect to all atoms, i. e. Fe and C, in this austenite, produced according to Reaction 2b, x_{α}^{2b} , is obtained by applying the lever rule to the Fe-C phase diagram at the relevant temperature for the composition $\chi_{\gamma}^{\text{sat}}$ ($E/(C+D+E)$) with C , D and E as line segments as indicated in Fig. 1, using data for the carbon atom fractions in the cementite and ferrite presented in Table 1b. Hence the equilibrium atom fraction of ferrite, with respect to all atoms, i. e. Fe and C, in the specimen, that occurs for completed Reaction 2b, x_{α}^{eq2} , equals $x_{\alpha}^{2a} + (1 - x_{\alpha}^{2a}) \cdot x_{\alpha}^{2b}$, which is also obtained by applying the lever rule to the Fe-C phase diagram at the relevant temperature for the composition $\chi_{\gamma}^{\text{in}}$ ($(D+E)/(C+D+E)$) with C , D and E as line segments as indicated in Fig. 1. The specific volume per Fe atom for austenite, ferrite and cementite is calculated using data on the lattice parameters and the thermal expansion coefficients; see Table 1a. The relative volume change

for Reaction 2b as a function of the degree of transformation, z_{2b} , can then be calculated in a way similar to that for Eq. (2), applying expressions for the number of Fe atoms in each phase listed in Table 2c, which yields:

$$\left[\frac{\Delta V}{V} \right]_{\text{Reaction 2b}} = \frac{n_{\alpha_{\chi_{\alpha}^{\text{eq2}}}^{\text{Fe}}} \cdot \frac{V_{\alpha_{\chi_{\alpha}^{\text{eq2}}}^{\text{eq2}}}}{2} + n_{\theta}^{\text{Fe}} \cdot \frac{V_{\theta}}{12} + n_{\gamma_{\chi_{\gamma}^{\text{sat}}}^{\text{Fe}}} \cdot \frac{V_{\gamma_{\chi_{\gamma}^{\text{sat}}}^{\text{sat}}}}{4} - n_{\gamma_{\chi_{\gamma}^{\text{sat}}}^{\text{Fe}}} \cdot \frac{V_{\gamma_{\chi_{\gamma}^{\text{sat}}}^{\text{sat}}}}{4}}{n_{\gamma_{\chi_{\gamma}^{\text{sat}}}^{\text{Fe}}} \cdot \frac{V_{\gamma_{\chi_{\gamma}^{\text{sat}}}^{\text{sat}}}}{4}} \quad (5)$$

where the ferrite is considered to have the equilibrium composition and $n_{\gamma_{\chi_{\gamma}^{\text{sat}}}^{\text{Fe}}}$ denotes the number of Fe atoms in the as yet untransformed austenite. It should be noted that the equilibrium atom fraction of ferrite for Reaction 2b, x_{α}^{2b} refers to the part of the specimen present as the austenite remaining from Reaction 2a. In order to calculate the total relative volume change for Reaction 2, the absolute volume changes for Reaction 2a and Reaction 2b must be added and not the relative volume changes.

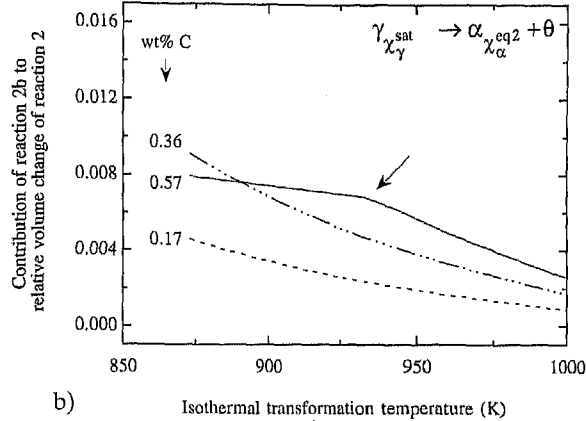
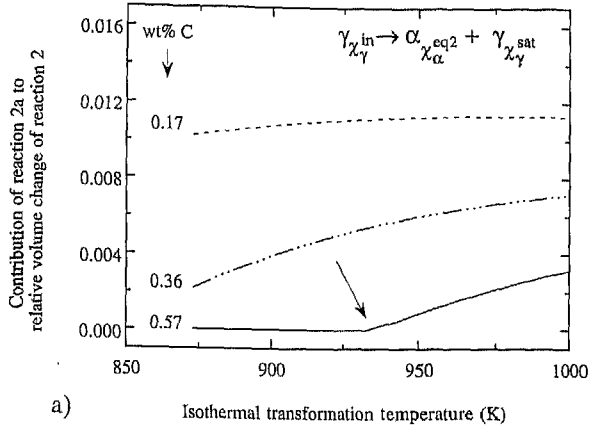
$$\left[\frac{\Delta V}{V} \right]_{\text{Reaction 2}} = \frac{V_{2a, \text{initial}} \left[\frac{\Delta V}{V} \right]_{\text{Reaction 2a}} + V_{2b, \text{initial}} \left[\frac{\Delta V}{V} \right]_{\text{Reaction 2b}}}{V_{\text{initial}}} \quad (6a)$$

where $V_{2a, \text{initial}}$ is the volume of the starting austenite for Reaction 2a, $V_{2b, \text{initial}}$ is the volume of the starting austenite for Reaction 2b, i. e. the austenite remaining from Reaction 2a and saturated with carbon according to the $\Delta\mu_C = 0$ criterion. All atoms are involved in Reaction 2a, therefore V_{initial} and $V_{2a, \text{initial}}$ are equal and Eq. (6a) reduces to Eq. (6b):

$$\left[\frac{\Delta V}{V} \right]_{\text{Reaction 2}} = \left[\frac{\Delta V}{V} \right]_{\text{Reaction 2a}} + \frac{V_{2b, \text{initial}}}{V_{\text{initial}}} \left[\frac{\Delta V}{V} \right]_{\text{Reaction 2b}} = \left[\frac{\Delta V}{V} \right]_{\text{Reaction 2a}} + \frac{n_{\gamma_{\chi_{\gamma}^{\text{sat}}}^{\text{Fe}}} \cdot V_{\gamma_{\chi_{\gamma}^{\text{sat}}}^{\text{sat}}}}{n_{\gamma_{\chi_{\gamma}^{\text{in}}}^{\text{Fe}}} \cdot V_{\gamma_{\chi_{\gamma}^{\text{in}}}^{\text{in}}}} \left[\frac{\Delta V}{V} \right]_{\text{Reaction 2b}} \quad (6b)$$

The value for the contribution of Reaction 2b as expressed by the second term at the righthand side of Eq. (6b) is shown in Fig. 3b. In the case that Reaction 2a does not occur, the total relative volume change for Reaction 2 is equal to the relative volume change for Reaction 2b.

The contributions of Reaction 2a and 2b to the total relative volume change of Reaction 2 for completed transformations ($z_{2a} = 1$; $z_{2b} = 1$) are illustrated in Figs. 3a and 3b. Clearly, for a low carbon concentration the largest contribution to the total relative volume change of Reaction 2 is due to Reaction 2a. With increasing carbon concentration this contribution diminishes and the formation of cementite with ferrite, Reaction 2b, becomes more important. For a carbon concentration of 0.57 wt. % C it is seen in Fig. 3a that the contribution of Reaction 2a is nil below a temperature of 932 K (see arrow in Fig. 3a). This occurs because, according to the $\Delta\mu_C = 0$ criterion (see above), austenite at 932 K is saturated if 0.57 wt. % C is dissolved. Then Reaction 2a is predicted not to occur and Reaction 2 only consists



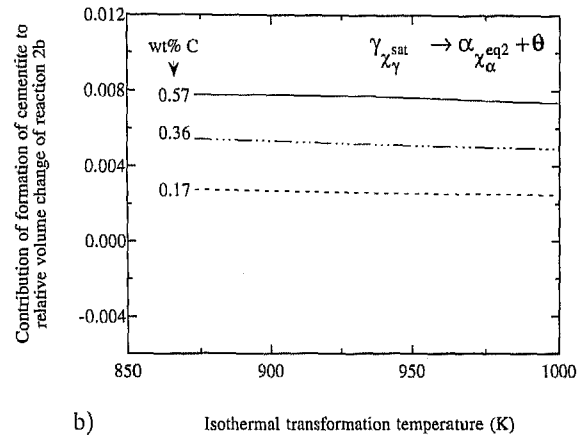
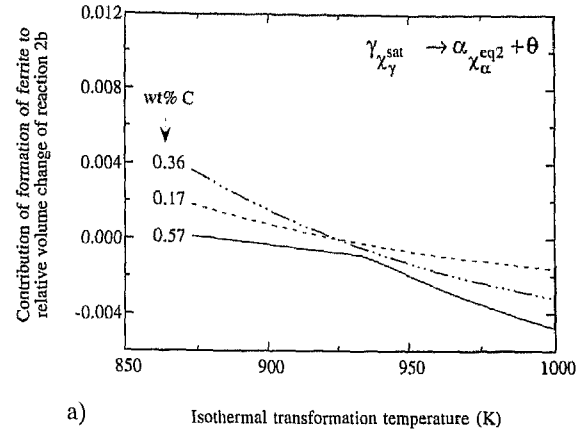
Figs. 3a and b. (a) Contribution of Reaction 2a to the total relative volume change for Reaction 2, for temperatures below A_1 (≈ 1000 K) and (b) contribution of Reaction 2b to the total relative volume change for Reaction 2, for temperatures below A_1 . The relative volume change of Reaction 2b is calculated according to the second term at the right-hand side of Eq. (6b) using Eq. (5). The arrows in the figure indicate the temperature for the Fe-0.57 C alloy below which Reaction 2a can not occur. The numbers in the figure indicate the gross carbon concentration of the alloy concerned.

of Reaction 2b. This leads to a discontinuity for the slope of the corresponding curve shown in Fig. 3b as well, because the composition of the initial austenite becomes equal to the gross composition of the alloy and thereby independent of temperature below 932 K (see arrow in Fig. 3b). For alloys with a lower carbon concentration of the initial austenite the same effect occurs, but at a lower temperature.

For each of the Reactions 2a and 2b a separation of the relative volume changes similar to Eqs. (4a) and (4b) can be performed. Thus, for Reaction 2a one can distinguish between the contributions of the ferrite that forms and that of the remaining austenite that enriches in carbon. As compared with Reaction 1 (see Fig. 2a), the temperature behaviour is reversed, because for Reaction 2a with decreasing temperature both the atom fraction of ferrite decrease and the carbon enrichment of the austenite diminishes as predicted from the $\Delta\mu_C = 0$ criterion. This explains that the relative volume change for Reaction 2a decreases with decreasing temperature (Fig. 3a).

Reaction 2b also includes two relative volume effects.

Thus (with $n_{\gamma_{\gamma}^{sat}}^{\text{Fe}} = n_{\alpha_{\alpha}^{eq2}}^{\text{Fe}} + n_{\theta}^{\text{Fe}} + n_{\gamma_{\gamma}^{sat}}^{\text{Fe}}$)



Figs. 4a and b. (a) Contribution of the formation of ferrite by Reaction 2b to the total relative volume change for Reaction 2 (see Eq. (7a) and text below it) for temperatures below A_1 (≈ 1000 K) and (b) contribution of the formation of cementite in Reaction 2b to the total relative volume change for Reaction 2 (see Eq. (7b) and text below it) for temperatures below A_1 . The numbers in the figure indicate the gross carbon concentration of the alloy concerned.

$$\left[\frac{\Delta V}{V} \right]_{\text{Reaction 2b}}^{\alpha_{\alpha}^{eq2}} = \frac{n_{\alpha_{\alpha}^{eq2}}^{\text{Fe}}}{n_{\alpha_{\alpha}^{eq2}}^{\text{Fe}} + n_{\theta}^{\text{Fe}} + n_{\gamma_{\gamma}^{sat}}^{\text{Fe}}} \cdot \frac{\frac{V_{\alpha_{\alpha}^{eq2}}}{2} - \frac{V_{\gamma_{\gamma}^{sat}}}{4}}{\frac{V_{\gamma_{\gamma}^{sat}}}{4}} \quad (7a)$$

$$\left[\frac{\Delta V}{V} \right]_{\text{Reaction 2b}}^{\theta} = \frac{n_{\theta}^{\text{Fe}}}{n_{\alpha_{\alpha}^{eq2}}^{\text{Fe}} + n_{\theta}^{\text{Fe}} + n_{\gamma_{\gamma}^{sat}}^{\text{Fe}}} \cdot \frac{\frac{V_{\theta}}{12} - \frac{V_{\gamma_{\gamma}^{sat}}}{4}}{\frac{V_{\gamma_{\gamma}^{sat}}}{4}} \quad (7b)$$

These effects are shown in Figs. 4 such that the relative volume changes as obtained from the above Eqs. (7a) and (7b) have been multiplied by the factor $V_{2b, \text{initial}} / V_{\text{initial}}$ (see Eq. (6b)).

First the formation of ferrite from austenite saturated with carbon is considered; see Fig. 4a. For temperatures near A_1 this effect is negative (i.e. relative volume decrease), because in the saturated austenite the specific volume per Fe atom is larger than in the ferrite. With decreasing temperature this volume change increases, i.e. becomes less negative, due to a thermal expansion coefficient that is larger for the austenite than for the ferrite. A linear dependence on temperature is expected for this volume change by only the difference in thermal expansion coefficient between austenite and ferrite. Instead a smooth curvature is observed because the ferrite atom fraction

decreases with decreasing temperature. As discussed above for Reaction 2a, for the carbon concentration of 0.57 wt. % C a discontinuous change of slope is noticed at 932 K in fig. 4a, because below 932 K Reaction 2a is not predicted to occur. Below such temperatures the atom fraction of ferrite is practically independent of temperature and the increase of volume change with decreasing temperature is therefore solely determined by the difference in thermal expansion coefficient between ferrite and the initial (saturated) austenite. The relative volume change due to formation of cementite shows a negligible influence of the temperature (see. Fig. 4b).

The total relative volume change for decomposition of austenite according to reaction 2 (combination of reactions shown in Figs. 3a and 3b) increase with decreasing temperature and decreases with increasing carbon concentration, see Fig. 5 for $T < A_1$, similarly as for Reaction 1 for $T > A_1$. Note that the discontinuity at 1000 K reflects that the total relative volume changes hold for different reactions for $T < A_1$ and $T > A_1$.

2.3 Parameter Sensitivity of the Calculations

The parameter sensitivity of the calculation of the volume changes upon phase transformation is assessed as follows. With respect to the application of Eqs. (2) and (5) two possible sources of error are recognised: (i) errors in the lattice-parameters values, (ii) an error in the value of the gross carbon concentration.

The uncertainties in the lattice-parameter data, for austenite and ferrite (about 0.01 %), are negligible with respect to the calculated total volume change.

The effect of an error in the gross carbon concentrations is more pronounced since in practice the absolute error in the determination of the carbon concentration is about 0.03 wt. % with the gross carbon concentration in the range 0.2–0.6 wt. % C. An error in the gross carbon concentration affects the calculated volume change directly via χ_γ^{in} , and indirectly via the atom fractions of ferrite, x_α^{eq1} and x_α^{2a} (x_α^{2b} is independent of the gross carbon concentration; see above Eq. (5)), and the lattice parameter of the initial austenite.

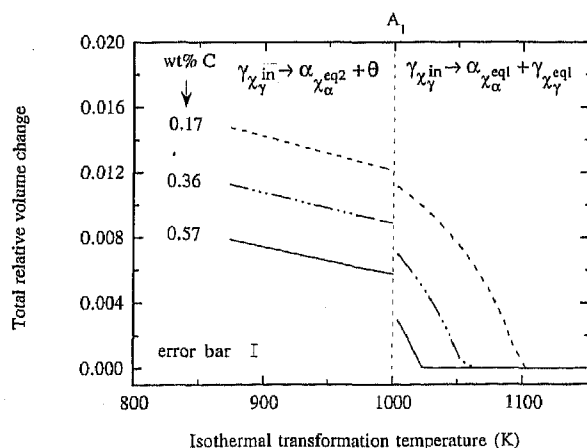


Fig. 5. The calculated total relative volume change for the decomposition of Fe-C austenites above and below A_1 ($= 1000$ K). The error bar indicates the inaccuracy due to the experimental uncertainty in the carbon concentration (≈ 0.03 wt. % C) of the initial austenite.

An absolute error in the carbon concentration of 0.03 wt. % gives rise to a possible variation of the relative volume change as indicated in Fig. 5 by the error bar.

3 The Total Degree of Transformation

To analyse transformation kinetics from dilatometer experiments, the relative length change measured as a function of time and/or temperature has to be expressed in terms of a (total) degree of transformation. For the isothermal decomposition of austenite the total degree of transformation, z_{tot} , is defined, similar to the degree of transformation for the different reactions (cf. Section 2), as the atom fraction of ferrite at a specified time, t_i , divided by the equilibrium atom fraction of ferrite, i.e. after completed total transformation at the appropriate temperature. This degree of transformation equals the number of Fe atoms in ferrite at a specified time t_i , divided by the total number of Fe atoms in ferrite after completed transformation. Thus (note that at constant temperature $n_\alpha^{\text{Fe}}/n_\alpha^{\text{C}}$ is constant):

$$z_{\text{tot}}(t = t_i) = \frac{x_\alpha(t = t_i)}{x_\alpha(t = \infty)} = \frac{n_\alpha^{\text{Fe}}(t = t_i) + n_\alpha^{\text{C}}(t = t_i)}{n_\alpha^{\text{Fe}}(t = \infty) + n_\alpha^{\text{C}}(t = \infty)} = \frac{n_\alpha^{\text{Fe}}(t = t_i)}{n_\alpha^{\text{Fe}}(t = \infty)} \quad (8)$$

If the product of transformation is a single phase, as in the case for the γ - α transformation in pure Fe (Reaction 0), the total degree of the transformation, z_{tot} , equal to z_0 , is deduced easily from the measured dilatation by dividing the measured relative length change at $t = t_i$ by the total relative length change at $t = \infty$.

If the products of transformation are two or more phases, the determination of the degree of the transformation becomes more complicated. If the two phases are formed in a single reaction, as in the case of Reaction 1, the total degree of the transformation equals the degree of transformation for Reaction 1, i.e. z_1 (see Eq. (2) and Table 2a). The relation between the degree of the transformation, z_1 , and the relative volume change, calculated from Eqs. (2) and (3) using Tables 1a and 2a, is practically linear. Hence, for Reaction 1, the degree of transformation, z_1 , is deduced easily from the measured length change, similar to the case for a single product phase (Reaction 0).

If the final phases form in two or more consecutive reactions, as holds for Reaction 2 (see Reaction 2a and 2b), it is not trivial to determine the total degree of transformation from the measured (total) length change. The degrees of transformations of the separate reactions, z_{2a} and z_{2b} , as defined in section 2.2 can be written as:

$$z_{2a} = \frac{\left(n_{\alpha_{\chi_\alpha^{\text{eq2}}}}^{\text{Fe}}\right)_{2a}(t = t_i)}{\left(n_{\alpha_{\chi_\alpha^{\text{eq2}}}}^{\text{Fe}}\right)_{2a}(t = \infty)} \quad (9a)$$

$$z_{2b} = \frac{\left(n_{\alpha_{\chi_\alpha^{\text{eq2}}}}^{\text{Fe}}\right)_{2b}(t = t_i)}{\left(n_{\alpha_{\chi_\alpha^{\text{eq2}}}}^{\text{Fe}}\right)_{2b}(t = \infty)} \quad (9b)$$

The total degree of transformation is then calculated by adding the number of Fe atoms in ferrite formed in Reac-

tion 2a, $(n_{\alpha_{\text{eq2}}}^{\text{Fe}})_{2a}$, and the number of Fe atoms in ferrite formed in Reaction 2b, $(n_{\alpha_{\text{eq2}}}^{\text{Fe}})_{2b}$, at the stage of transformation considered and dividing this sum, $(n_{\alpha_{\text{eq2}}}^{\text{Fe}})_{\text{tot}}$, by the total number of Fe atoms in ferrite after completed total transformation:

$$z_{\text{tot}} = \frac{(n_{\alpha_{\text{eq2}}}^{\text{Fe}})_{\text{tot}}(t = t_i)}{(n_{\alpha_{\text{eq2}}}^{\text{Fe}})_{2a}(t = \infty) + (n_{\alpha_{\text{eq2}}}^{\text{Fe}})_{2b}(t = \infty)} = \frac{z_{2a} \cdot (n_{\alpha_{\text{eq2}}}^{\text{Fe}})_{2a}(t = \infty) + z_{2b} \cdot (n_{\alpha_{\text{eq2}}}^{\text{Fe}})_{2b}(t = \infty)}{(n_{\alpha_{\text{eq2}}}^{\text{Fe}})_{2a}(t = \infty) + (n_{\alpha_{\text{eq2}}}^{\text{Fe}})_{2b}(t = \infty)} \quad (10)$$

where $(n_{\alpha_{\text{eq2}}}^{\text{Fe}})_{2a}$ and $(n_{\alpha_{\text{eq2}}}^{\text{Fe}})_{2b}$ are given by the expressions listed in Table 2b and 2c.

For the purpose of illustration, in the following the total relative volume change is calculated as a function of the total degree of transformation assuming that Reaction 2a is completed before Reaction 2b starts. For $0 \leq z_{2a} \leq 1$ and $z_{2b} = 0$, it holds that:

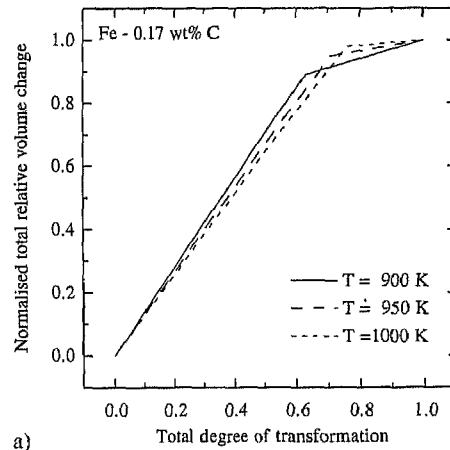
$$\left[\frac{\Delta V}{V} (z_{\text{tot}}) \right]_{\text{Reaction 2}} = \left[\frac{\Delta V}{V} (z_{2a}) \right]_{\text{Reaction 2a}} \quad (11)$$

Because the relative volume change according to Reaction 2a is practically a linear function of z_{2a} (see discussion above Eq. (9)), the relative volume change as a function of the total degree of the transformation, z_{tot} , is also practically linear (note that although $z_{2b} = 0$, $z_{\text{tot}} \neq z_{2a}$; cf. Eqs. (9a) and (10)).

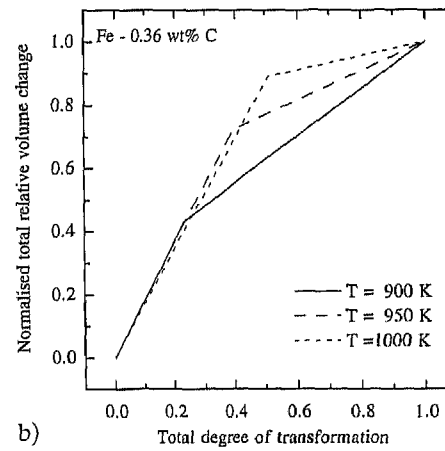
If Reaction 2b proceeds, in order to calculate the total volume change from the volume changes due to Reaction 2a and Reaction 2b, the absolute (and not the relative) volume changes due to Reactions 2a and 2b have to be added (cf. Section 2.2). Thus, for $z_{2a} = 1$ and $0 \leq z_{2b} \leq 1$ it holds that

$$\left[\frac{\Delta V}{V} (z_{\text{tot}}) \right]_{\text{Reaction 2}} = \left[\frac{\Delta V}{V} (z_{2a} = 1) \right]_{\text{Reaction 2a}} + \frac{V_{2b, \text{initial}}}{V_{\text{initial}}} \cdot \left[\frac{\Delta V}{V} (z_{2b}) \right]_{\text{Reaction 2b}} \quad (12)$$

The total relative volume change as a function of the total degree of transformation for Reaction 2 is shown in figs. 6a and 6b for a) the Fe-0.2 C alloy and b) the Fe-0.4 C alloy (note that $\left[\frac{\Delta V}{V} \right]_{\text{Reaction 2b}}$ is a truly linear function of its degree of transformation, z_{2b} ; see Eq. (5) and Table 2c). The striking conclusion from these calculations is that although the pearlite transformation (Reaction 2b) can correspond to more than 50 % of the total degree of transformation (as for the Fe-0.4 C alloy), it can contribute with only about 10 % to the total relative volume change. Clearly, in general no linear relation for Reaction 2 exists between the total relative volume change and the total degree of the transformation. Hence, if Reactions 2a and b occur, determination of the total degree of transformation (atom fraction ferrite) from the measured length change is not straightforward. This does not seem to be realised always; see e. g. [10] where the degree of transformation is taken equal to the



a)



b)

Fig. 6a and b. The normalised total relative volume change for Reaction 2 as a function of the total degree of transformation for different temperatures below A_1 for (a) the Fe-0.2 C alloy and (b) the Fe-0.4 C alloy.

measured relative length change. Only if the carbon concentration is that high or the isothermal transformation temperature is that low that Reaction 2a does not occur, the linear relationship between the degree of transformation and the relative volume change as reported in [3] holds. According to the criterion of Ref. [5], the minimal carbon concentration, above which Reaction 2a does not occur increases with temperature (from 1.40 at. % ($\hat{=}$ 0.31 wt. %) C at 800 K to 3.45 at. % ($\hat{=}$ 0.76 wt. %) C at 1000 K). The present proposal for a definition of the total degree of transformation incorporates correctly the contributions of Reaction 2a and 2b as functions of temperature and gross carbon concentration. An example of an in this sense incorrect treatment is provided by [11].

4 Conclusions

- (i) Defining the total degree of transformation during the isothermal decomposition of an austenitic Fe-C specimen, as the momentaneous number of Fe atoms in ferrite relative to the number of Fe atoms in ferrite after completed transformation, the dimensional change of the austenite specimen upon decomposition can be calculated on the basis of the lattice parameters of the constituting phases and their dependence on temperature and composition, and the phase diagram.

- (ii) During the isothermal decomposition of an austenitic Fe-C specimen, the total degree of transformation as a function of time can be deduced from the total relative volume change as a function of time provided that either a single transformation reaction occurs, such as the formation of ferrite from austenite in association with carbon enrichment of the remaining austenite, or multiple transformation reactions occur consecutively (separated in time), such as the formation of ferrite with carbon enrichment of the remaining austenite followed by the formation of pearlite from this remaining austenite. If the transition from the first to the second transformation does not occur at about the same time for the entire specimen, no unique relation can be given between the total degree of transformation and the relative volume change, as pertaining to a certain time.
- (iii) The relative length change is an approximately linear function of the degree of transformation for the decomposition of austenite into ferrite and carbon enriched austenite and it is a truly linear function of the degree of transformation for the decomposition of austenite into ferrite and cementite. However, the relative length change is not a linear function of the total degree of transformation incorporating both these reactions (i.e. decomposition of austenite below A_1). In many cases the formation of ferrite in association with carbon enrichment of the austenite prior to the formation of pearlite dominates the total relative length change measured in the dilatometer.

Financial support by Hoogovens Corporate Research, IJmuiden, The Netherlands, and the Innovative Research Project for Metals of the Dutch government (IOP-Metalen) is gratefully acknowledged.

Literature

1. Atkins, M.: Atlas of continuous cooling transformation diagrams for engineering steels, ASM, Metals Park, OH (1987).
2. Vandervoort, G.F.: Atlas of time-temperature diagrams for irons and steels, American Technical Publications, Hitchin (1992).
3. Takahashi, M.; Bhadeshia, H.K.D.H.: J. Mat. Sci. Letters 8 (1989) 477-478.
4. Onink, M.; Brakman, C.M.; Tichelaar, F.D.; Mittemeijer, E.J.; vd Zwaag, S.; Root, J.H.; Konyer, N.B.: Scripta Metall. Mater. 29 (1993) 1011-1016.
5. Krielaart, G.P.; Onink, M.; Brakman, C.M.; Tichelaar, F.D.; Mittemeijer, E.J.; vd Zwaag, S.: Z. Metallkd 85 (1994) 756-765.
6. Hawbolt, E.B.; Chau, B.; Brimacombe, J.K.: Metall. Trans. A 16A (1985) 565-578.
7. Powder Diffraction File, A.S.T.M. card 6-0688.
8. Stuart, H.; Ridley, N.: J. Iron Steel Inst. (1966) 711-717.
9. Kubaschewski, O.: Iron Binary Phase Diagrams, Springer, Berlin (1982) 23.
10. Constant, A.; Henry, G.: Trait. Thermique 155 (1981) 47-53.
11. Prado, J.M.; Catalan, J.J.; Marsal, M.: J. Mat. Sci. 25 (1990) 1939-1946.

(Received August 15, 1994)

Appendix

Volume Fractions of Ferrite and Cementite

For the decomposition of austenite into ferrite and carbon-enriched austenite, the following formulas have been given in [3]:

$$\frac{\Delta V}{V} = \frac{2V_{\alpha}^T \cdot a_{\alpha_{\chi_{\alpha}^{eq1}}}^3 + (1 - V_{\alpha}^T) \cdot a_{\chi_{\chi_{\gamma}}^3} - a_{\chi_{\chi_{\gamma}}^3}}{a_{\chi_{\gamma}^{in}}^3} \quad (A1)$$

where V_{α}^T denotes the "volume fraction" of ferrite and a_i represents the lattice parameter of phase i . A comparison of Eq. (A1) with Eq. (2) shows that the volume fraction of ferrite as employed in [3] is equal to:

$$V_{\alpha}^T = \frac{1}{1 - \chi_{\gamma}^{in}} \cdot \chi_{\alpha}^{eq1} \quad (A2)$$

Clearly, this is not a volume fraction since χ_{α}^{eq1} is an atom fraction of ferrite and χ_{γ}^{in} is an atom fraction of carbon.

The true volume fraction of ferrite follows straightforwardly from the Fe atom balance employed for the derivation of Eq. (2). It is obtained:

$$V_{\alpha} = \frac{n_{\alpha_{\chi_{\alpha}^{eq1}}}^{Fe} \cdot \frac{V_{\alpha_{\chi_{\alpha}^{eq1}}}^{eq1}}{2}}{n_{\alpha_{\chi_{\alpha}^{eq1}}}^{Fe} \cdot \frac{V_{\alpha_{\chi_{\alpha}^{eq1}}}^{eq1}}{2} + \left(N - \left(n_{\alpha_{\chi_{\alpha}^{eq1}}}^{Fe} + N_{\chi_{\gamma}^{in}} \right) \right) \cdot \frac{V_{\chi_{\gamma}}}{4}} \quad (A3)$$

with v_i/N_i as the unit cell volume of phase i , v_i , divided by the number of Fe atoms in the unit cell, N_i .

For the decomposition of austenite in ferrite and cementite, after re-arranging, the following formula has been given in [3] for the calculation of the volume fraction of cementite:

$$V_{\theta} = \frac{3\chi_{\gamma}^{in} \frac{V_{\theta}}{12}}{(1 - 3\chi_{\gamma}^{in}) \frac{V_{\alpha}}{2} + 3\chi_{\gamma}^{in} \frac{V_{\theta}}{12}} \quad (A4)$$

This equation is incorrect. The true volume fraction of cementite after completed transformation 2 follows straightforwardly from the Fe atom balance on which Eq. (5) is based; it is obtained:

$$V_{\theta} = \frac{3\chi_{\gamma}^{in} \frac{V_{\theta}}{12}}{(1 - 4\chi_{\gamma}^{in}) \frac{V_{\alpha}}{2} + 3\chi_{\gamma}^{in} \frac{V_{\theta}}{12}} \quad (A5)$$

Using the incorrect Eqs. (A 2) and (A 4), as in [3], leads to errors which can be of the order of 20 % for high-carbon alloys.