

Kinetics of Martensitic Transformation in Partially Bainitic 300M Steel

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Abstract

The kinetics of athermal martensitic transformation have been studied in a high silicon steel (300M), beginning with samples which were first partially transformed to bainitic ferrite. It is found that the way in which the volume fraction of martensite increases with undercooling below the martensite start temperature is not greatly influenced by the presence of bainitic ferrite, when any carbon enrichment in the residual austenite is taken into account. The martensitic transformation obeys, within the limits of experimental errors, the same law irrespective of the presence or absence of bainitic ferrite prior to transformation. A new relationship, which takes some account of autocatalysis, has been derived to rationalize the athermal kinetics of martensitic reactions and, within the context of certain approximations, is found to be in reasonable agreement with experimental data. The role of chemical composition variations, of the type normally present in commercial steels, seems to be mainly to extend the temperature range over which most of the martensite reaction occurs in the heterogeneous samples, relative to samples which were given a homogenizing heat treatment.

1. Introduction

Mixed microstructures consisting of bainite and martensite are usually a consequence of inadequate heat treatment or the use of steels with insufficient martensite hardenability in applications involving heavy sections. Early research [1-3] suggested that the presence of bainite in an otherwise martensitic microstructure generally leads to a deterioration in ductility, toughness and strength.

Contrary to these generally pessimistic indications of the properties of mixed microstructures, more recent work by Tomita and Okabayashi [4,

5] has tended to indicate that in some circumstances the presence of bainite in a predominantly martensitic microstructure enhances both strength and toughness relative to the single-phase samples. They explained their results by postulating that, as the lower bainite subdivides regions of austenite, there is in effect a refinement of the austenite grain size and consequently a refinement of the martensite packet size on the subsequent transformation of austenite. This leads to a strengthening of the martensite via a grain size effect. In addition, the strength of the bainite is supposed to be enhanced by the constraint provided to its deformation by the stronger martensite.

Thus, mixed microstructures of bainite and martensite are bound to become more prominent commercially but are also of interest from a fundamental point of view, to reveal the influence of partial bainitic reaction on the subsequent formation of martensite. An attempt is therefore made here to model the development of martensitic transformation in a high silicon, medium carbon steel, with the commercial designation "300M", with the particular aim of rationalizing the formation of martensite in samples which already contain some bainitic ferrite. For this reason, some of the samples studied were quenched directly from the austenitization temperature, while others were first transformed isothermally to bainitic ferrite, before cooling to ambient temperature to allow some of the residual austenite to decompose to martensite. The studies were carried out both on chemically segregated "as-received" samples and, for comparison purposes, on samples homogenized by prolonged heat treatment at a high temperature.

The work presented here extends earlier research [6, 7], which focused on the development of the bainite reaction, to the modelling of the subsequent transformation of some of the residual austenite into martensite. The ultimate

aim of this research programme is to develop phase transformation theory which will permit the prediction of microstructural evolution in commercial steels which contain high silicon concentrations. Such steels have a demonstrated potential as far as good combinations of strength and toughness are concerned [8–12]. Commercial steels are usually chemically heterogeneous, and such segregation is known [13–21] to cause significant changes in the kinetics and thermodynamics of the phase transformations; it was also intended to investigate the effect of the segregation on martensitic transformation.

2. Experimental technique

The 300M steel used in the experiments was obtained in the form of bar 10 cm in diameter with an average chemical composition of Fe–0.44 wt.% C–1.74 wt.% Si–0.67 wt.% Mn–1.85 wt.% Ni–0.83 wt.% Cr–0.39 wt.% Mo–0.09wt.%V. Samples of the alloy were homogenized by holding at 1300 °C for 3 days, with the specimens sealed in quartz tubes containing argon. Microanalysis experiments were carried out using energy-dispersive X-ray analysis (interaction volume, approximately $4.5 \mu\text{m}^3$) on a scanning electron microscope. Dilatometric experiments using rods 3 mm in diameter, each of length 2 cm, were carried out on a Theta Industries high speed dilatometer. To avoid surface nucleation and surface degradation, all specimens were electroplated with nickel (plating thickness, about 0.08 mm) and austenitizing treatments were carried out in a helium environment. The dilatometer used was specially interfaced with a BBC/Acorn microcomputer so that length, time and temperature data could be recorded at millisecond intervals, and the data stored for further analysis.

3. Results and discussion

3.1. Dilatometry

The dilatometric specimens were quenched to room temperature after an appropriately long time at the isothermal temperatures T_b (until the bainite reaction ceased), for a variety of temperatures below the bainite start temperature B_s . Dilatometric curves showing the relative length change due to transformation as a function of temperature are shown in Fig. 1. In these curves, any deviation from a straight line as the specimen

cools represents the onset of martensitic transformation, so that a martensitic start temperature M_s can be determined. This relies on the experimental observation that the austenite in the 300M steel used has a constant thermal expansivity over the temperature range of interest [6, 7]. The expansion that occurs when austenite transforms to martensite is then detected as the deviation described earlier.

As expected, a higher martensite start temperature was observed when the sample had been transformed partially to bainite at a higher temperature T_b , since a lower maximum volume fraction of bainite is obtained as T_b is raised. It is also evident that M_s for the residual austenite* is higher for heterogeneous specimens when compared with the chemically homogeneous samples (Fig. 2). This is consistent with the fact that relatively less bainite forms in heterogeneous samples, so that the residual austenite then contains a lower carbon concentration relative to homogeneous specimens heat treated in an identical manner [7]. As a result, the tendency to form martensite is more pronounced in heterogeneous samples. This is also reflected in the calculated data presented in Fig. 2, since for identical transformation conditions it is established that more bainitic ferrite can be obtained in the homogeneous samples, giving a higher degree of carbon enrichment in the residual austenite in those samples, and hence lowering the martensite start temperature of the residual austenite. The carbon concentration x_γ of the residual austenite was calculated from the volume fraction of bainite, assuming a homogeneous distribution of carbon in austenite:

$$x_\gamma \approx \bar{x} + \frac{\bar{x} - V_{\alpha_b} x_\alpha}{1 - V_{\alpha_b}} \quad (1)$$

where \bar{x} is the average carbon concentration of the alloy and x_α is the carbon concentration of the bainitic ferrite. Since the latter is always rather small when compared with \bar{x} , it is assumed here to be given by the carbon concentration of ferrite which is in equilibrium with austenite in an Fe–C alloy, as calculated using the McLellan and Dunn quasi-chemical thermodynamic model [22].

*The term "residual austenite" refers to that which exists at the reaction temperature during isothermal transformation to bainite. "Retained austenite" refers to the austenite which remains untransformed after cooling the specimen to ambient temperature.

The calculations assume a homogeneous distribution of carbon in the residual austenite and hence underestimate the martensite start temperature (Fig. 2). The real distribution of carbon is known to be inhomogeneous following bainitic ferrite growth [23–26], so that the relatively dilute regions will tend to transform martensitically at a higher temperature. Consistent with this, the degree of underestimation is found to decrease as the volume fraction of bainitic ferrite decreases (*i.e.* T_b increases). Observation of occasional pockets of twinned martensite through electron microscopy confirms the presence of high carbon regions (Fig. 3).

As a check on the M_s calculations, a homogenized sample was quenched directly to ambient temperature; a martensite start temperature M_s of 280 °C was observed, and this agrees reasonably with the thermodynamically calculated [27, 28] M_s of 276 °C.

As expected, further length changes were observed as the samples were cooled below M_s as more of the residual austenite transformed martensitically. The relationship between the amount of martensite formed as a function of undercooling below M_s was, as expected, found to be non-linear. The volume fraction of martensite produced at first is small; the extent of transformation as a function of undercooling below M_s then increases, although it eventually begins to decrease towards zero as the amount of unreacted austenite decreases towards zero, or as the small quantity left untransformed stabilizes to further decomposition.

The “martensite finish temperature” M_f is not a meaningful concept from a fundamental point of view, because the reaction progresses with further and eventually decreasing increments of volume fraction as the temperature is reduced below M_s , in principle never reaching completion. Small amounts of retained austenite thus remain stable even at very low temperatures. The transformation of the last traces of austenite becomes more and more difficult as the amount of austenite decreases, probably owing to mechanical stabilization [29, 30] (Fig. 1).

The temperature range over which martensite forms is usually a characteristic of the specific alloy composition and in particular the carbon concentration. The range is generally greater when the residual austenite has a lower carbon content. It can be seen from Fig. 1 that the range from M_s to M_f is always greater in heterogeneous

specimens than in homogeneous samples, especially for low values of T_b . This is to be expected since each of the heterogeneous samples in effect consists of a composite of different alloys, each of which will have its own transformation range. The superposition of these ranges should consequently give a larger overall value of $M_s - M_f$ when compared with the homogeneous samples. Figure 1 shows that martensite formation starts at lower temperatures in the homogeneous samples and reaches apparent “completion” sooner than in the corresponding heterogeneous samples.

3.2. Calculation of volume fraction

Dilatometric data in the form of the relative length change $\Delta L/L$ (where L is the length of the sample at ambient temperature and ΔL is the change in length due to transformation) were converted into the fraction f of austenite which is transformed to martensite using the following relationship:

$$f = \frac{3 \Delta L a_\gamma^3}{V_\gamma L (2 a_\alpha^2 c_\alpha - a_\gamma^3)} \quad (2)$$

where a_γ is the lattice parameter of the carbon-enriched residual austenite, a_α and c_α are the lattice parameters of tetragonal martensite and V_γ is the volume fraction of austenite present in the sample prior to martensitic transformation. The absolute volume fraction $V_{a'}$ of martensite can be obtained by multiplying the fraction f of austenite transformed to martensite by the actual volume fraction V_γ of austenite initially present at T_b , *i.e.*

$$V_{a'} = f V_\gamma \quad (3)$$

A computer program was written and used for these calculations. The program takes full account of the changes in lattice parameters as a function of alloy composition and temperature, as described elsewhere [7, 31]. Figure 4 shows the volume fractions of martensite, obtained for homogeneous and heterogeneous specimens after the specimens had been transformed isothermally to bainite at the temperatures indicated, with enough time at the isothermal transformation temperatures to ensure cessation of bainite formation.

There is a rapid increase in the volume fraction $V_{a'}$ of martensite with an increase in the isothermal transformation temperature T_b , which is consistent with the respective measured and calculated M_s data (Fig. 2).

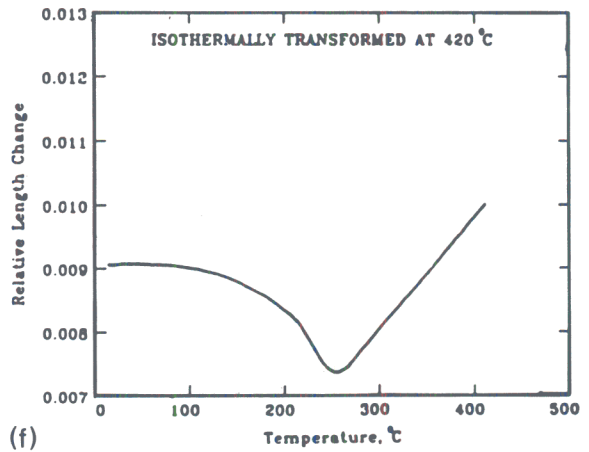
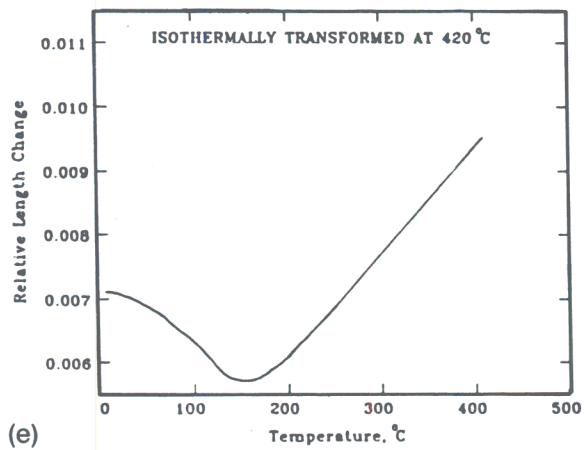
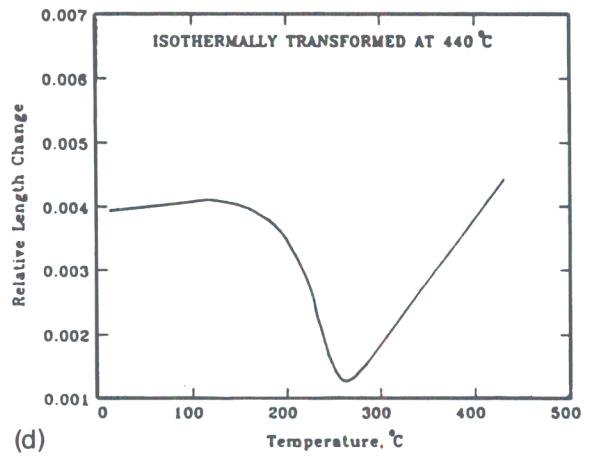
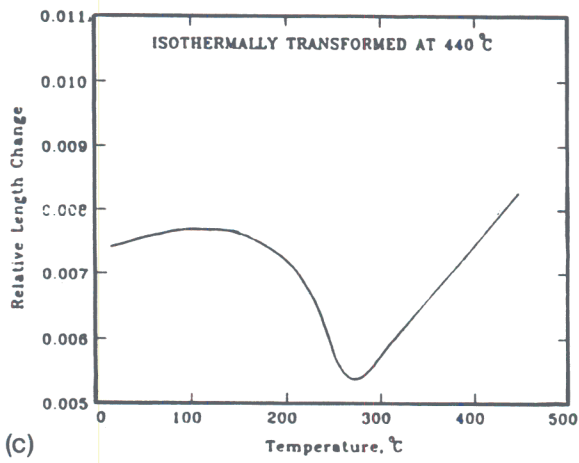
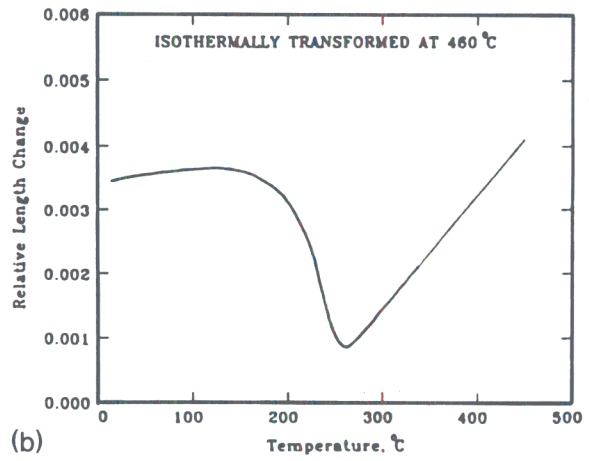
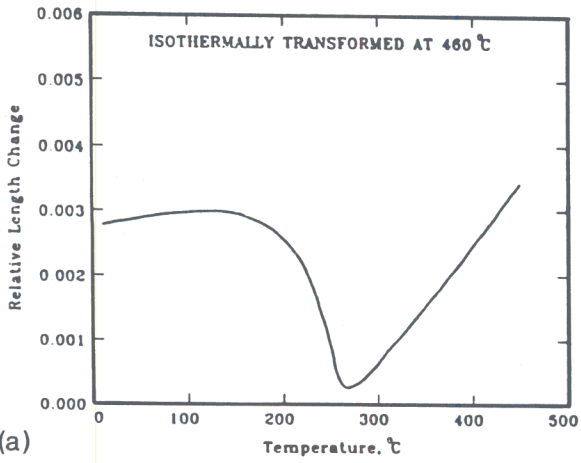


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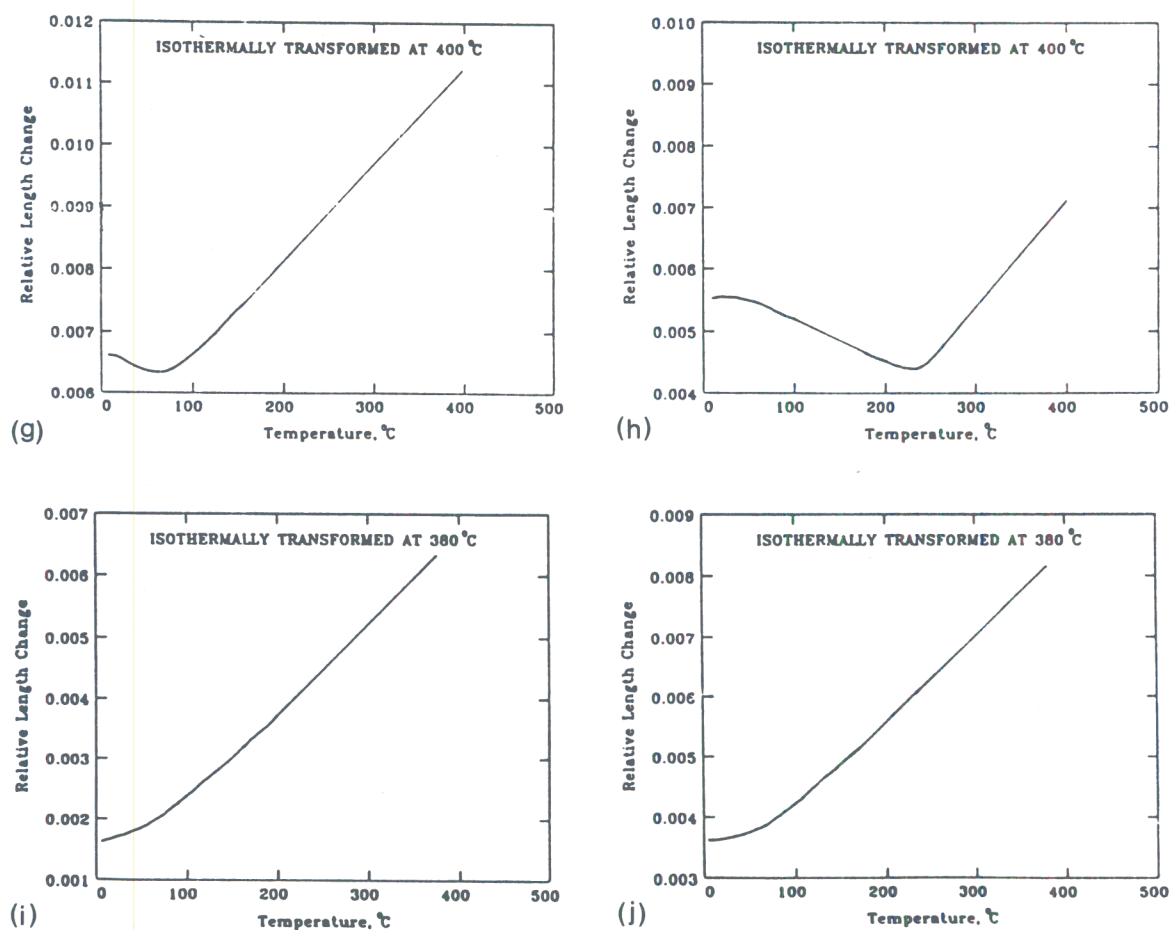


Fig. 1. Dilatometric curves showing the transformation to martensite in (a), (c), (e), (g) and (i) homogeneous steels and (b), (d), (f), (h) and (j) heterogeneous steels after the specimens were isothermally transformed to bainite at different temperatures, with enough time at each isothermal transformation temperature to ensure that bainitic ferrite formation stopped.

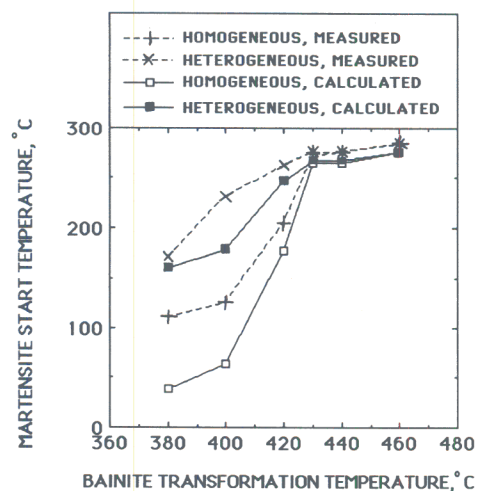


Fig. 2. Thermodynamically calculated [27, 28] and experimentally determined M_s for homogenized and heterogeneous samples, after partial isothermal transformation to bainite.

3.3. Retained austenite

Given that the volume fractions of bainite and martensite were determined by dilatometry, it is relatively easy to calculate the volume fraction V_{γ_r} of austenite retained at room temperature by the difference

$$V_{\gamma_r} = 1 - V_{\alpha_b} - V_{\alpha'} \quad (4)$$

It was found that for both homogeneous and heterogeneous specimens the volume fraction of retained austenite decreased at first and then increased with the isothermal transformation temperature T_b . At $T_b = 400^\circ\text{C}$, a relatively larger quantity of retained austenite was obtained for the homogeneous specimen (Fig. 5).

It is noted (Fig. 5) that in previous experiments a relatively higher volume fraction of bainite was obtained in the case of the homogeneous

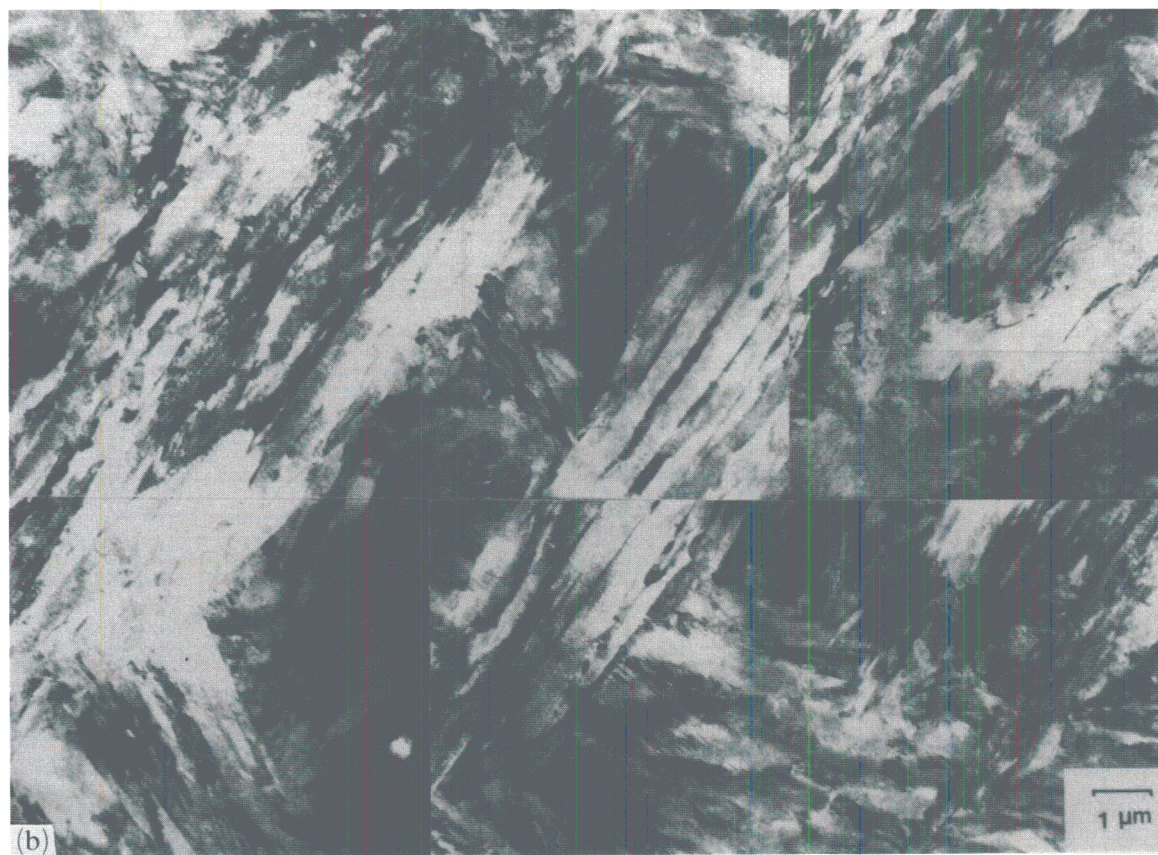
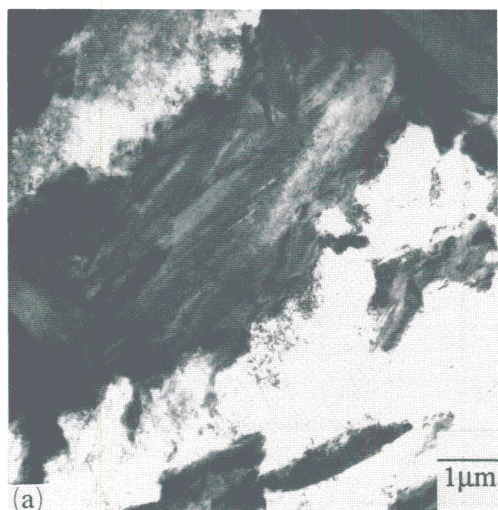


Fig. 3. Transmission electron micrographs showing twinned martensite in a homogenized 300M steel specimen which is isothermally transformed to bainite at 420 °C before quenching to room temperature: (a) bright field image; (b) untwinned martensite.

specimen relative to the heterogeneous sample transformed at 400 °C. This means that more film austenite* can be expected than the blocky morphology after the formation of bainite in a homogeneous sample. This film austenite, since it

*Film austenite is that retained between the subunits within a given sheaf of bainite while "blocky austenite" is the retained austenite, exhibiting a triangular shape in two-dimensional sections, bounded by different crystallographic variants of bainite sheaves [8, 9].

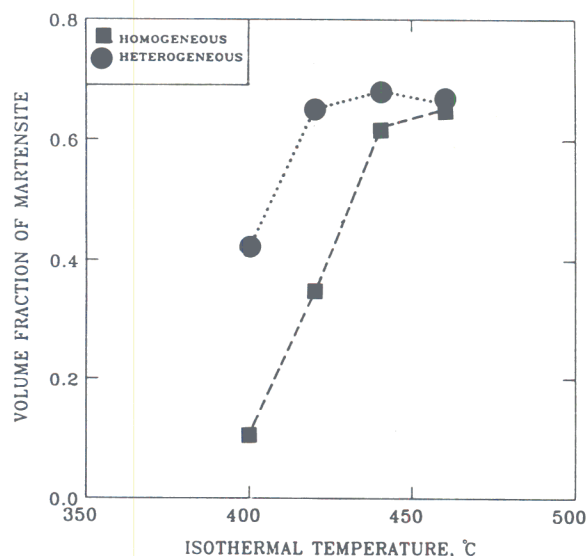


Fig. 4. Volume fraction of martensite obtained for homogeneous and heterogeneous specimens. The specimens were transformed initially to bainite at different isothermal temperatures, as indicated in the diagram. Hence, in each case the residual austenite, *i.e.* that left after transformation to bainite, had a different carbon concentration which decreases as the bainite transformation temperature increases.

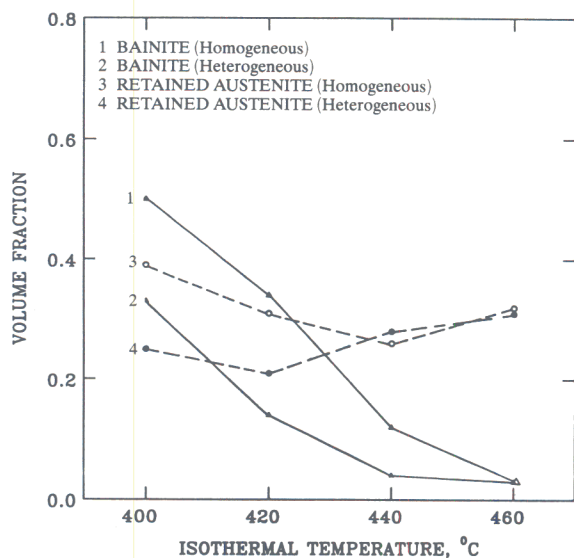


Fig. 5. Volume fraction of retained austenite obtained by difference and experimental volume fraction of bainite in samples partially transformed to bainite followed by quenching to room temperature.

is trapped in the immediate vicinity of bainite subunits, is known to contain a higher carbon content than the blocky austenite [32, 33] has and is difficult to transform to martensite. There is as a result a sudden rise in the volume fraction of

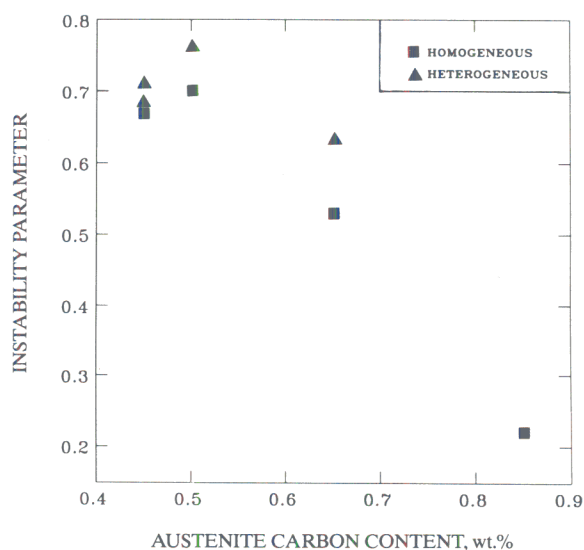


Fig. 6. Variation in the instability of the residual austenite which is left untransformed after the bainite reaction stops, with its carbon content.

austenite retained for the samples transformed to bainite at 400 °C. This also explains the marked drop in the volume fraction $V_{\alpha'}$ of martensite (Fig. 4). An increase in the calculated volume fraction of retained austenite with an increase in isothermal transformation temperature results as a higher amount of residual austenite with lower carbon content is being produced.

3.4. Instability of residual austenite

A parameter representing the stability of residual austenite can be defined by the ratio of volume fraction of martensite to the volume fraction of residual austenite at the isothermal bainite transformation temperature [8, 9], *i.e.* $V_{\alpha'}/(1 - V_{\alpha_b})$. Figure 6 shows a plot of the stability parameter as a function of carbon content x_{γ} of residual austenite for the homogeneous and heterogeneous specimens.

The instability of residual austenite at any isothermal transformation temperature is higher for the heterogeneous material, presumably because in all cases the degree of reaction to bainite was lower than in comparative homogeneous samples. As has been noted previously [8, 9], the observations also indicate that the enhanced stability arises from the finely divided state of the residual austenite whose carbon content is usually higher when compared with the rest of the austenite. The differences between instabilities in homogeneous and heterogeneous

specimens increase with increases in the maximum degree of bainitic transformation (*i.e.* with decrease in transformation temperature). It is interesting to note that the bainitic residual austenite becomes increasingly stable as the degree of transformation of bainitic ferrite becomes greater. The films of retained austenite separating the bainitic lenticular plates lead to high strength and they additionally break up the path of propagating cracks since not only has the crack to traverse interphase interfaces and varying crystal structures but also its motion can be dampened by transformation at the crack tip [34].

3.5. Kinetics of athermal martensitic transformation

Any assessment of the overall kinetics of transformations which are thermodynamically of first order in the Ehrenfest classification scheme must include a consideration of both the nucleation and the growth rates of the product phase. However, for martensitic transformation in steels, the growth rate of the plates can be very high, often limited by the speed of sound in the steel. Furthermore, because of the displacive character of the transformation, the martensite grows in the form of thin plates whose aspect ratio may be determined by the minimization of strain energy if the plates are elastically accommodated. Since the coordinated movement of atoms characteristic of displacive reactions cannot in general be sustained across austenite grains which are in different crystallographic orientations, the maximum dimension of each plate must in some way be limited by the austenite grain size. Considering all these factors together, it may as a first approximation be assumed that the volume of material transformed by each plate or lath of martensite is a constant value \bar{V} . In these circumstances, the growth part of the overall kinetics may be neglected, since each nucleus will transform \bar{V} of the parent phase.

It has been known for a long time [35] that the progress of the athermal martensitic transformation in a sample which is initially fully austenitic can be described empirically by an equation of the form

$$1 - f = \exp\{-C_1(M_s - T_q)\} \quad (5)$$

where f is the volume fraction of martensite divided by the volume fraction of austenite that exists prior to the formation of martensite, T_q is a temperature to which the sample is cooled

below M_s and C_1 is a constant obtained originally [35] by fitting to experimental data.

Magee [36] demonstrated that this relationship can be justified theoretically if it is assumed that the number of new plates of martensite that form per unit volume of austenite (*i.e.* dN) owing to the lowering of temperature below M_s is proportional to the consequential change $\Delta G^{\gamma\alpha'}$ in the driving force for diffusionless transformation:

$$dN = -C_2 d(\Delta G^{\gamma\alpha'}) \quad (6)$$

where C_2 is a positive proportionality constant. It should be noted that $\Delta G^{\gamma\alpha'}$ is given by $G^{\alpha'} - G^{\gamma}$, where $G^{\alpha'}$ and G^{γ} refer to the Gibbs free energies of unit volumes of martensite and austenite respectively. The change in the volume fraction of martensite is therefore given by

$$df = \bar{V} dN_V \quad (7)$$

where dN_V is the change in the number of new plates of martensite formed per unit volume of sample, with $dN_V = (1 - f)dN$ and \bar{V} is the average volume per newly formed plate. On combining eqns. (6) and (7) and substituting $\{d(\Delta G^{\gamma\alpha'})/dT\}dT$ for $d(\Delta G^{\gamma\alpha'})$, Magee showed that

$$df = -\bar{V}(1 - f) C_2 \frac{d(\Delta G^{\gamma\alpha'})}{dT} dT$$

which on integration between the limits M_s and T_q gives

$$\ln(1 - f) = \bar{V} C_2 \frac{d(\Delta G^{\gamma\alpha'})}{dT} (M_s - T_q)$$

or

$$1 - f = \exp\left\{\bar{V} C_2 \frac{d(\Delta G^{\gamma\alpha'})}{dT} (M_s - T_q)\right\} \quad (8)$$

The integration procedure used above assumes that the term $d(\Delta G^{\gamma\alpha'})/dT$ is constant with temperature. The form of the above equation is similar to that of the empirical relation used by Koistinen and Marburger [35], so that

$$C_1 = -\bar{V} C_2 \frac{d(\Delta G^{\gamma\alpha'})}{dT} \quad (9)$$

Graphs illustrating the variation in $\Delta G^{\gamma\alpha'}$ as a function of undercooling below M_s are illustrated in Fig. 7; they show that it is a good approxima-

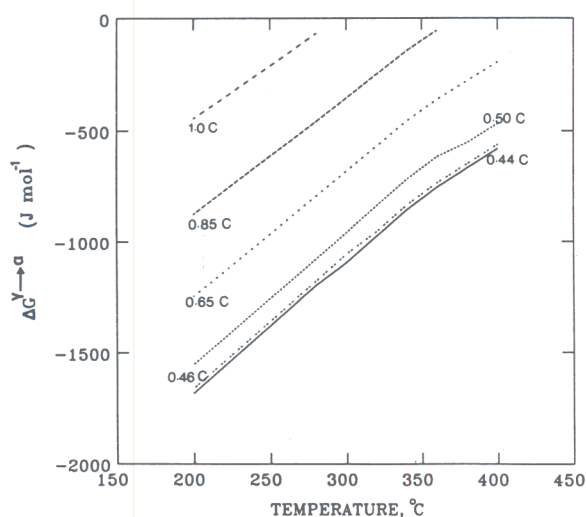


Fig. 7. Plots of $\Delta G^{\gamma \rightarrow \alpha}$ vs. $M_s - T_q$ for 300M steel containing a variety of carbon concentrations (in weight per cent).

tion to assume that the variation is linear so that C_1 should be approximately constant over the range of interest.

Data are presented in Fig. 7 for 300M steel containing a range of carbon concentrations, to simulate martensitic transformation following partial transformation to bainite. The formation of bainite leads to an enrichment of carbon in the residual austenite. The calculations use the thermodynamic theory and data detailed in refs. 37 and 38.

3.5.1. Results of kinetic analysis

An attempt was made to fit the data from dilatometric experiments to an empirical equation of the form

$$1 - f = \exp\{-C_1(M_s - T_q)\} \quad (10)$$

Graphs of $M_s - T_q$ vs. $\ln(1 - f)$ are shown in the Fig. 8. Comparison of the as-received heterogeneous and the homogenized samples revealed no obvious or systematic differences in the plots (Fig. 8). Results of the regression analysis, in which a line passing through the origin was best fitted to the data in each case, are given in the Table 1.

The data, when plotted according to eqn. (8), were usually found to deviate from linearity at the very early stages of reaction (Fig. 9). It was considered that this failure of the theory may be a consequence of the fact that it neglects the autocatalysis effect. When plates of martensite form, they induce new embryos which are then

available for further transformation, this is autocatalysis. Even Magee's interpretation (eqns. (6)–(8)) does not explicitly include the autocatalysis factor, although he clearly recognized and discussed the implications of autocatalytic nucleation. Table 1 also shows that, while the data corresponding to each isothermal transformation temperature can be correlated well using eqn. (10), the values of C_1 calculated from the regression analysis vary significantly when all the experimental data are considered together, again emphasizing the failure of the model. It is nevertheless found (Fig. 9) that the volume fraction of martensite at ambient temperature as predicted by an empirical application of the equation of Koistinen and Marburger is in good agreement with the experimental results, provided that a suitable value of the constant C_1 is used. However, the need to use a different value of C_1 in each case makes the procedure of little use for predictive purposes.

3.5.2. The role autocatalysis

As pointed out earlier, the model discussed above does not include the effects of autocatalysis. The nucleation of martensite is believed to begin at structural imperfections in the parent phase, such as arrays of dislocations. These are the pre-existing defects which, on cooling below M_s , dissociate into suitable partial dislocations in a way which leads to the operational nucleation of martensite [39]. The defects are not identical (they vary in potency) and are stimulated to grow into plates of martensite at different degrees of undercooling below M_s . Thus the volume fraction of martensite, in general, varies only with the degree of undercooling below M_s .

Detailed analysis reveals [39–41] that the initial number density of pre-existing defects typically found in austenite is not large enough to explain the kinetics of martensitic transformation. The extra defects necessary to account for the transformation rates which are faster than expected are attributed to autocatalysis; when plates of martensite form, they induce new embryos which are then available for further transformation. It has been proposed that the number of autocatalytic sites generated per unit volume at different temperatures can be calculated by integrating the following equation [42]:

$$dN = dN_i + d(f'p) \quad (11)$$

where N_i is the number of original nucleation

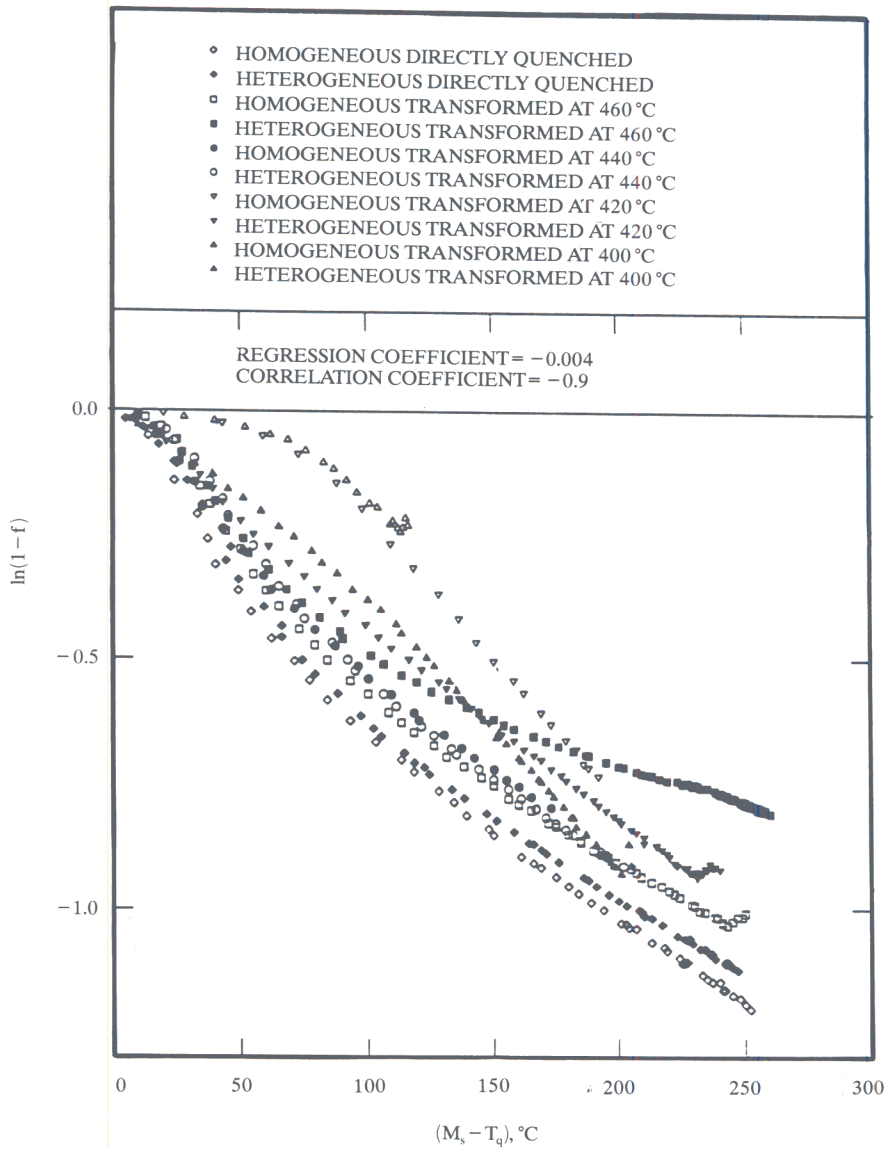


Fig. 8. Results of the regression analysis of the experimental data fitted to the empirical equation of Koistinen and Marburger.

TABLE 1 Regression constants for the curves shown in Fig. 8

Isothermal temperature (°C)	Homogenized samples		Heterogeneous samples	
	Correlation coefficient	Regression coefficient	Correlation coefficient	Regression coefficient
400	-0.98	-0.0019	-0.99	-0.0046
420	-0.98	-0.0031	-0.99	-0.0060
440	-0.99	-0.0051	-0.99	-0.0056
460	-0.98	-0.0050	-0.98	-0.0050
Directly quenched	-0.98	-0.0055	-0.98	-0.0052

sites per unit volume of sample, which remain after the formation of some martensite and is given [36] by

$$N_i = (1 - f') N_i^0$$

where N_i^0 is the number of original nucleation sites per unit volume of austenite. The term p represents the number of autocatalytic sites generated per unit volume of sample. We assume here that this autocatalytic factor is related linearly to the volume fraction of martensite and

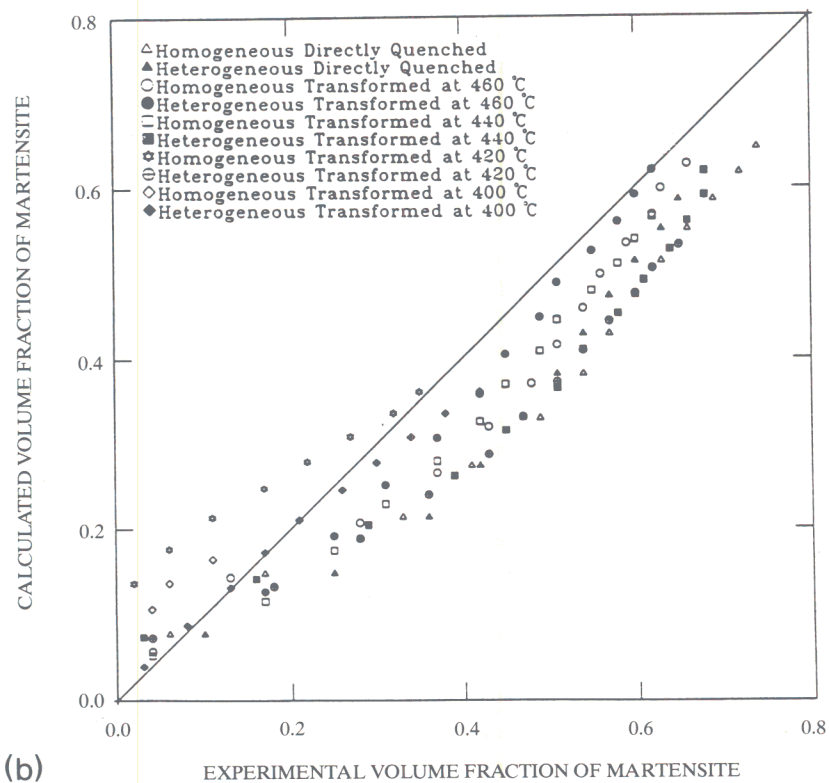
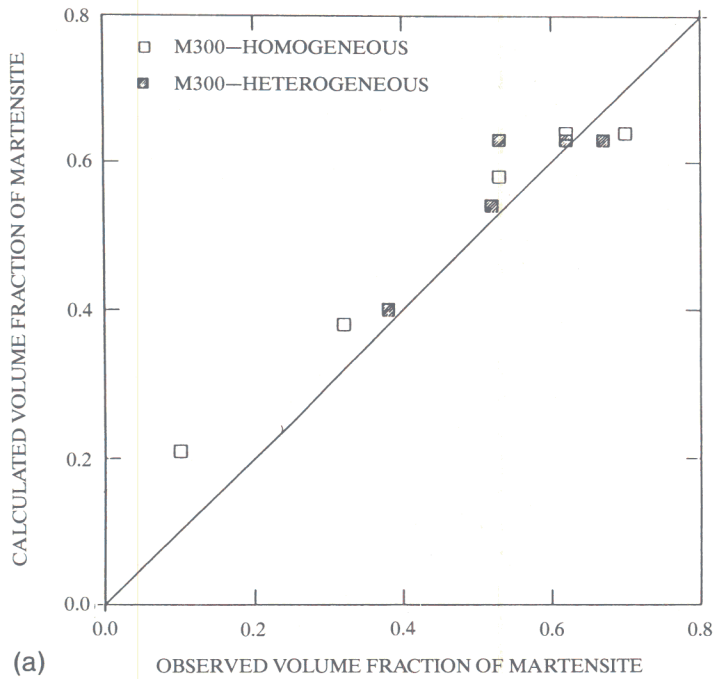


Fig. 9. Comparison of the observed and calculated volume fractions of martensite. The calculations utilize the equation of Koistinen and Marburger. A common value of 0.004 was assigned to C_1 for all these calculations. The true volume fraction of martensite (a) at 20 °C only and (b) at all temperatures where measurements were made.

hence to f' :

$$p = C_3 + C_4 f' \quad (12)$$

Then it follows that

$$dN = (-N_i^0 + C_3 + 2C_4 f') df' \quad (13)$$

Since \bar{V} is assumed to be constant in the present analysis, $df'/\bar{V} = (1-f') dN$ so that

$$\int_0^f \frac{df'}{\bar{V}(1-f')} = \int_0^f (-N_i^0 + C_3 + 2C_4 f') df' \quad (14)$$

On carrying out the integration, we get

$$p = N_i^0 - \frac{\ln(1-f)}{f\bar{V}} \quad (15)$$

It is noteworthy that, as $f \rightarrow 0$, $p \rightarrow N_i^0 + 1/\bar{V}$.

The value of \bar{V} can be estimated to be about $20 \mu\text{m}^3$ on the basis that a typical plate of martensite will have the approximate dimensions $0.2 \mu\text{m} \times 10 \mu\text{m} \times 10 \mu\text{m}$. With this assumed value, and the experimentally measured volume fraction of martensite, calculated values of $p - N_i^0$ were plotted against $M_s - T_q$, as illustrated in Fig. 10.

It is evident that the relationship between these variables is approximately linear and may be expressed as follows:

$$p - N_i^0 = C_5 + C_6(M_s - T_q) \quad (16)$$

where C_5 and C_6 are constants defining the best-fit line between the variables. On setting $M - T_q = 0$ or, in other words, $f = 0$, it is found that $p \rightarrow N_i^0 + 1/\bar{V}$ so that

$$C_5 = \frac{1}{\bar{V}}$$

and thus

$$p - N_i^0 = \frac{1}{\bar{V}} + C_6(M_s - T_q) \quad (17)$$

On combining this relationship with eqn. (13), it follows that

$$-\frac{\ln(1-f)}{f} = 1 + \bar{V}C_6(M_s - T_q) \quad (18)$$

or

$$-\frac{\ln(1-f)}{f} = 1 + C_7(M_s - T_q) \quad (19)$$

where $C_7 = \bar{V}C_6$. This equation represents a new law for the development of martensitic transformation as a function of undercooling below M_s . Its application is considered below. It should be noted that, in the analysis, homogeneous and heterogeneous samples are treated alike as previously no remarkable difference was observed in the development of martensite reaction in the two kinds of samples.

The experimental data as fitted to the above equation are represented in Fig. 11. A better correlation was obtained when compared with the previous model based on eqn. (8).

Figure 12 shows that the new model can accurately predict the kinetics of the martensite reaction at all stages. As the data include directly quenched samples as well as those partially transformed to bainite and quenched from this isothermal transformation temperature, it can be concluded further that the defects generated by bainitic transformation do not give rise to a large amount of autocatalytic nucleation of martensite.

3.5.3. Variation in \bar{V} with undercooling

Even with the new model developed above, it was assumed that \bar{V} is constant during the course of the reaction. The model of Fisher and co-workers [43-45] for plate martensite predicts that the average volume of martensite plates decreases strongly as the transformation proceeds. The theory assumes that the transformation is random throughout a specimen and that the plates partition the γ grains into smaller compartments. As a result, the plates forming later should tend to be smaller. However, the nucleation of martensite may not be random throughout [46], as most martensite plates nucleate in the vicinity of other martensite plates owing to the autocatalysis effect. It has been recognized [36] that the first observable transformation is due to several clusters of plates rather than to a random distribution of plates.

Magee *et al.* [47] have shown experimentally that, for Fe-23.8wt.%Ni-0.42wt.%C and Fe-28.5wt.%Ni-0.40wt.%C alloys, there is no significant decrease in \bar{V} at volume fractions up to 0.55. However, at high volume fractions, the geometrical partitioning* effect is expected to be important, and \bar{V} will be expected to decrease as

*Geometrical partitioning is based on the observation that the initial martensite plates divide the sample into progressively smaller compartments.

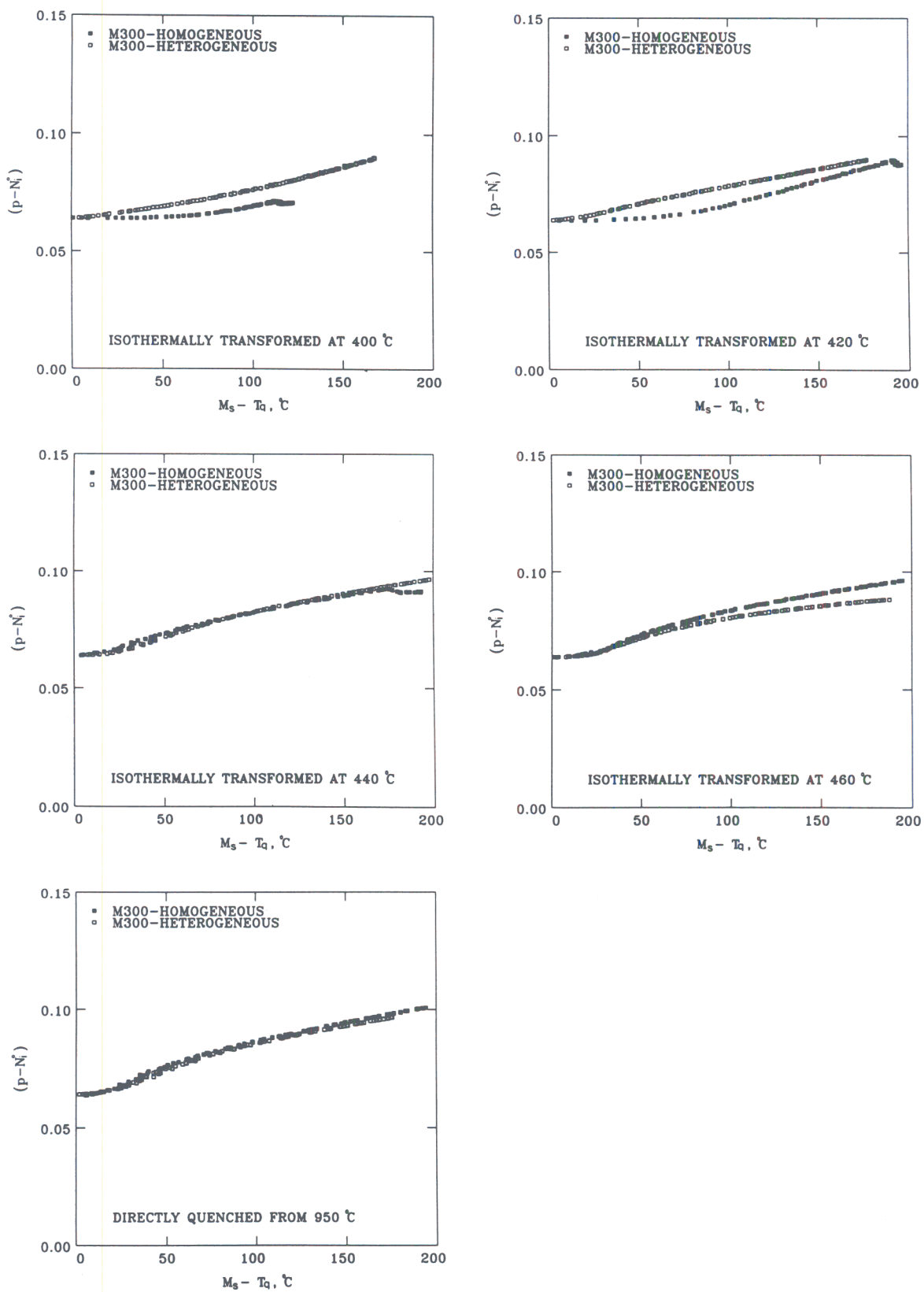


Fig. 10. Graphs illustrating the linear relationship between $p - N_i^0$ and $M_s - T_q$.

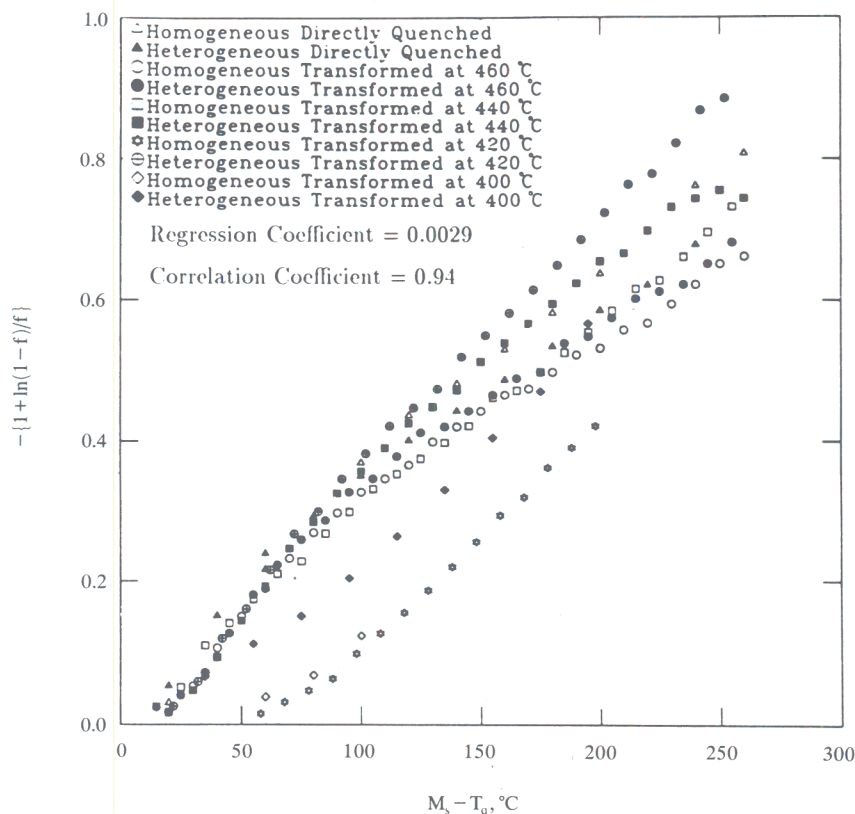


Fig. 11. Results of the regression analysis as the experimental data were fitted to an equation of the form $-[1 + \{\ln(1-f)\}/f] = C_7(M_s - T_q)$.

the volume fraction increases. Guimarães *et al.* [48] used Fullman's [49] stereographic method to determine both the mean plate radius \bar{r} and the volume \bar{V} . The mean plate thickness was estimated through the equation proposed by Chen and Winchell [50]:

$$\bar{t} = \frac{V_{\alpha'}}{S_V} \quad (20)$$

where $V_{\alpha'}$ is the volume fraction of martensite and S_V the mean density of martensite midplane in the material. The calculated aspect ratio \bar{t}/\bar{r} was found to reach a maximum at some intermediate fraction transformed. Guimarães and Saavedra [51], investigating the influence of austenite grain sizes on the mean volume of martensite plates in Fe-31.9wt.%Ni-0.02wt.%C, found that \bar{V} is constant in materials with a finer austenite grain size but that it noticeably decreases as the fraction transformed increases in samples with coarser austenite grain sizes. In the latter case, the partitioning effect found by Fisher and coworkers is probably more important when compared with

the situation for fine austenite grain structures. Their computer modelling shows that a fine grain size favours the formation of clusters of partially transformed grains and also enhances autocatalysis in the grains, so that \bar{V} is not sensitive to the volume fraction transformed.

In the present model, particularly good agreement has been observed between calculated and experimental volume fractions of martensite, although it slightly overestimates at low transformed fractions. This may be because the model assumes a constant value of \bar{V} at all stages of transformation. Moreover, the model assumes that all nucleation sites have the same activation energy. Magee [52] showed that there is a distribution of effectiveness of nucleation sites. These approximations require much further research and characterization.

4. Conclusions

The development of martensitic transformation has been studied using dilatometry, both from a fully austenitic starting microstructure and

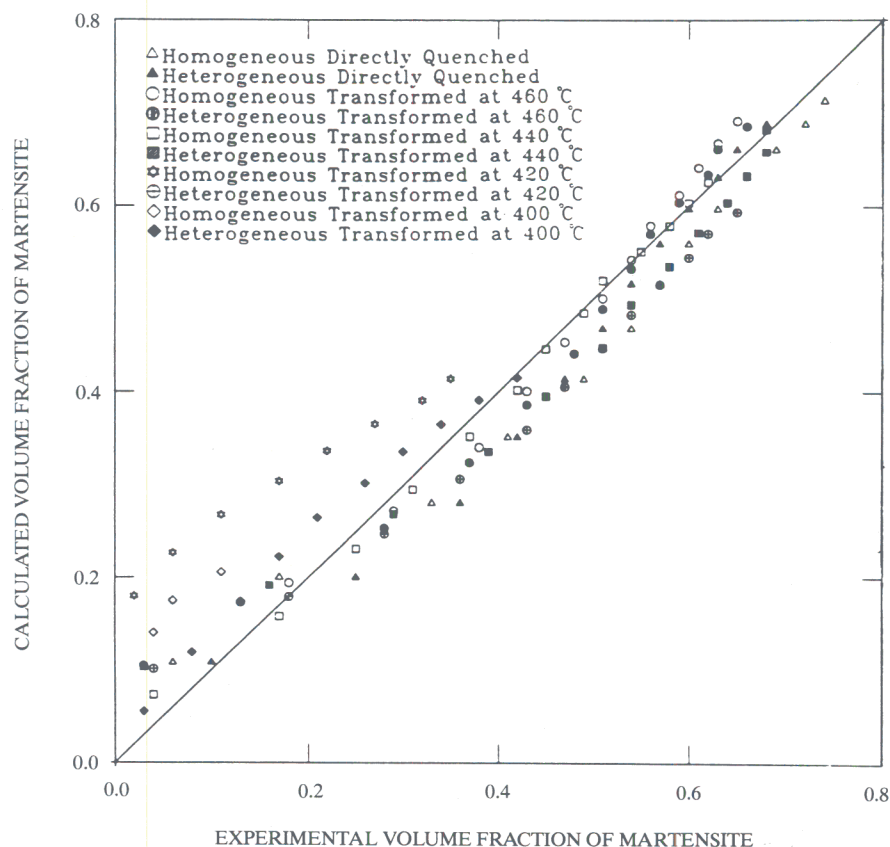


Fig. 12. Comparison of experimental results with those calculated by the new model based on eqn. (18).

from a microstructure containing a mixture of upper bainitic ferrite and carbon-enriched austenite. It is found that the presence of bainitic ferrite does not significantly alter the way in which the subsequent transformation to martensite occurs. In fact all the data can be rationalized using a new model of athermal martensite kinetics, which includes an effect of autocatalytic nucleation, subject to the approximation that all the plates of martensite have identical volumes.

For the levels of chemical segregation observed in the steel studied, the major effect on martensitic transformation is to extend the range over which the reaction occurs relative to homogenized samples. Otherwise, the same parameters can be used to predict martensitic reaction in all samples, within the limits of experimental error.

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Appendix A: Nomenclature and abbreviations

a_γ	lattice parameter of the carbon-enriched residual austenite
a_α, c_α	lattice parameters of tetragonal martensite
B_s	bainite start temperature
f	fraction of austenite transformed to martensite
M_s	martensite start temperature
M_f	martensite finish temperature
N_i	number of original nucleation sites for martensite per unit volume of sample
N	number of new martensite plates per unit volume of austenite
N_V	number of new martensite plates per unit volume of sample
T_b	temperature at which the sample is transformed to bainitic ferrite and carbon-enriched residual austenite
T_q	temperature to which the sample is cooled below M_s
$\Delta G^{\gamma\alpha'}$	driving force for diffusionless transformation
\bar{V}	average volume per newly formed plate
$V_{\alpha'}$	absolute volume fraction of martensite
V_γ	volume fraction of austenite present in the sample prior to martensitic transformation
V_{γ_r}	volume fraction of austenite retained at room temperature
V_{α_b}	volume fraction of bainitic ferrite