Stress induced transformation to bainite in Fe–Cr–Mo–C pressure vessel steel

H. K. D. H. Bhadeshia, S. A. David, J. M. Vitek, and R. W. Reed

The kinetics of the bainitic transformation in a polycrystalline Fe–Cr–Mo–C alloy designed for applications in energy generation systems has been studied, with particular attention to the influence of mild tensile stresses on transformation behaviour. The steel was found to exhibit the incomplete reaction phenomenon, in which transformation to bainite stops well before the residual austenite acquires its paraequilibrium carbon concentration. It was found that even in the absence of an applied stress, the growth of bainitic ferrite caused anisotropic changes in specimen dimensions, consistent with the existence of crystallographic texture in its austenitic condition and, significantly, with the nature of the invariant-plane strain shape change that accompanies the growth of bainitic ferrite. Thus, transformation induced plasticity could be detected in fine grained polycrystalline samples, even in the absence of applied stress. The application of an external stress was found to alter radically the transformation behaviour, with clear evidence that the stress tends to favour the development of certain crystallographic variants of bainite, even though the stress may be well below the single phase yield strength. It is concluded that the transformation is influenced significantly by stresses as low as $45 \, MN \, m^{-2}$, even though the effect may not be obvious in metallographic studies. The results are analysed and discussed in terms of the mechanism of the bainite transformation.

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Introduction

Many attempts have been made to improve the properties of steels used in energy systems, especially for pressure vessel applications at elevated temperatures and in hydrogen environments. However, there is a very large expense involved in creep testing, welding procedure development, and validation of such steels. For this reason, any new alloy must have significant advantages over those already in service before extensive research is undertaken.

In the low alloy content sector of steels, attention has been focused on the further development of the much used bainitic 2·25Cr–Mo steel, the main objective of the research being to extend the temperature range over which the alloy can be utilised, while maintaining the bainitic microstructure. The ability to operate at higher temperatures leads to an increase in the thermodynamic or process efficiency. The modifications that have been proposed to the standard 2·25Cr–Mo steel include increased concentration of chromium for improved resistance to hydrogen attack; carbide stabilising additions, such as vanadium and niobium; and nickel, boron, and carbon additions for improved bainitic hardenability.[1-9] For example, Wada and co-workers[1-3] have developed a successful alternative alloy (approx. composition (wt-%) Fe–3Cr–1·5Mo–0·1V–1Mn–0·1C) which seems to be the focus of much research.

After austenitisation at ∼1000°C for ∼2 h followed by air cooling (the details depending on section size), the alloy has a microstructure which is essentially a mixture of bainitic ferrite, austenite, and a small amount of martensite; the microstructure is therefore similar to that of the classic 2·25Cr–Mo steel. Arc welding using filler metal of matching composition gives a similar microstructure in the fusion zone, although the heat affected zone may also contain carbide precipitation in some regions, which have been tempered as a result of the temperature increase due to the heat input. Autogenous electron beam welding at power levels sufficient to fuse 100 mm thick plates was originally thought to lead to predominantly martensitic fusion and heat affected zone microstructures owing to the relatively high cooling rates compared with conventional arc welding.[10] However, later higher resolution observations[11,12] confirmed that the microstructure consists of a mixture of bainitic ferrite and retained austenite*, with small amounts of high carbon martensite. The welded assembly is usually post-weld heat treated at about 690°C for 9 h, giving a tempered microstructure with $M_{23}C_6$ carbides and little variation in hardness across the weld and parent plate.[12,13]

The present research is a part of a programme aimed at modelling the development of microstructure and mechanical properties in the fusion zone of welded Cr–Mo steels. To achieve this, it is necessary to be able to predict the thermodynamics and kinetics of the bainite transformation under the influence of the types of stress that arise naturally during welding. The Fe–Cr–Mo–C alloys described above are ideal for this purpose, since the formation of bainitic ferrite can be studied in isolation, without interference from any secondary carbide precipitation reaction. Carbide precipitation during bainitic transformation is rather sluggish in these alloys. The specific aim of the work reported here, is to investigate from a fundamental point of view, the effect of applied stress on the kinetics of bainitic transformation.

Previous work on stress induced bainitic transformation

There are several independent observations which indicate that stress has a significant effect on the progress of the bainite reaction. The degree of transformation to bainite at any temperature is restricted by the incomplete reaction phenomenon,[14] but the application of a tensile stress during

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* Throughout this work, the term 'residual austenite' refers to the austenite remaining after the formation of bainitic ferrite. Some of this residual austenite may decompose by martensitic transformation on cooling below its martensite start M_s temperature and any that remains untransformed at ambient temperature is referred to as 'retained austenite'. In the present context, both residual and retained austenite are enriched in carbon.
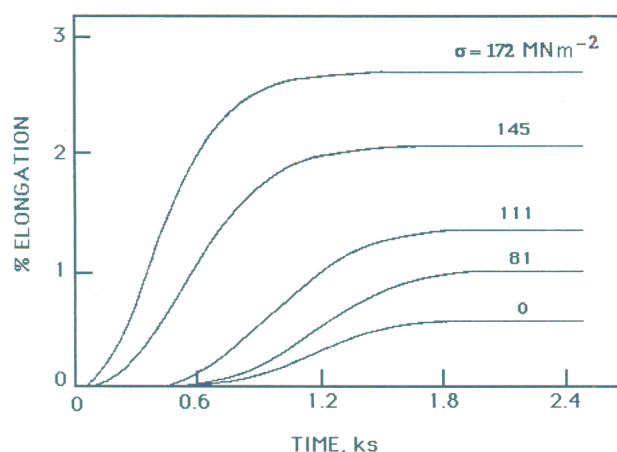
1 **Longitudinal strain recorded during bainitic transformation at 360°C as function of time at isothermal transformation temperature: data from Ref.19**

transformation has been reported to lead to an increase in the extent of reaction.[15] In the context of thermomechanical processing, it is well known that general deformation accelerates the overall rate of the bainite reaction.[16,17] The overall transformation kinetics is also accelerated by the application of a uniaxial tensile stress, provided that the stress exceeds a certain threshold value whose magnitude decreases with increasing temperature.[18] However, the existence of such a threshold stress is doubtful and may be an experimental artefact resulting from the difficulty in resolving any acceleration of transformation at low applied stresses. Umemoto *et al.*[19] claimed that the bainitic transformation is not accelerated by stresses less than the yield stress, but this is inconsistent with their experimental data (reproduced here in Fig. 1), which show an increase in the rate of transformation even when the applied stress is less than the yield stress. In fact, Umemoto *et al.* unusually define the yield stress not in terms of the stress required to propagate slip across grain boundaries in polycrystalline austenite or ferrite, but instead as the stress at which a specified degree of *transformation* plasticity is observed.

The stress influencing transformation need not be applied externally; internal stresses generated by the presence of other products also have an effect. Early studies of overall reaction kinetics indicated an acceleration in the rate at which upper bainite forms in specimens which are first transformed partially at a lower temperature.[20,21] Howard and Cohen[22] demonstrated that on cooling a steel below the M_s temperature, martensite forms first, but that after a suitable incubation period, the austenite (which is somewhat deformed by the formation of martensite) undergoes accelerated transformation to bainite. Similar results have been obtained by Radcliffe and Rollason[23] and it has also been demonstrated[24] that the upper bainite reaction is accelerated by first forming some lower bainite.

In principle, these experiments can be understood in terms of the invariant-plane strain shape change associated with the formation of bainite. The shape deformation is, in all respects, a physical deformation which differs from the more usual lattice-invariant deformations only in that it is associated with the change in crystal structure during transformation. An externally applied stress may assist or oppose the shape deformation associated with the transformation, depending on how it resolves with respect to the crystallography of the plate habit planes. When a uniaxial tensile stress is applied, transformation is expected to be enhanced since, for steels, both the shear and normal components of the stress of the habit plane should interact

favourably with the shear and dilatational components of the shape change. Since stress may also be generated internally, it is not surprising that the bainite transformation is accelerated in samples previously partially transformed to martensite.

Another revealing observation is that the nucleation and growth rates of bainite are both accelerated by the proximity of a free surface,[25,26] where the shape change can occur with the least degree of constraint. In the absence of such mitigating circumstances, the matrix sometimes cannot tolerate the large displacements associated with the formation of bainite. It then relaxes by plastic deformation driven by the shape change.[27]

The highest temperature at which martensite can form during the cooling of austenite is the M_s temperature. It has been found[28] that this can be increased by the application of a suitable stress, to a maximum value termed the M_d temperature. Similar experiments have not been carried out for bainite, but Goodenow and Hehemann[24] showed that the transformation stresses associated with the formation of lower bainite stimulated the growth of upper bainite at temperatures just above the bainite start temperature B_s. In principle, it should therefore be possible to define a B_d temperature. Early work by Cottrell[15] gives some support to the B_d concept; he found that the maximum amount of bainite obtainable by isothermal transformation of unstressed samples, can be increased with the application of a tensile stress during transformation, but that the effect of the applied stress diminishes as (what is now known as) the bainite start temperature is approached.

Deformation does not always accelerate transformation; it is well established for martensitic transformations that severe deformation causes mechanical stabilisation of the austenite. Mechanical stabilisation is due to the work hardening of the austenite and the increase in its defect density. The defects interfere with the motion of transformation interfaces. Experiments to find a similar effect for bainite have not yet been carried out. Vlad[29] reported that during the continuous cooling transformation of some low alloy steels into a mixed microstructure, the decomposition of austenite to bainite is retarded if the austenite is deformed before transformation. The effect was correlated with a change in the crystallographic texture of the austenite. However, a more plausible explanation, which is consistent with the reported microstructural data, is that the deformation accelerates the formation of allotriomorphic ferrite, thereby causing a greater degree of carbon enrichment in the residual austenite and consequently retarding both the bainite and martensite reactions.

Given that welded fabrications usually develop residual stresses having magnitudes that may approach the yield stress of the steel concerned, it is possible that these stresses have an effect on the development of microstructure during the cooling of the weld to ambient temperature. To the authors' knowledge, the only study dealing directly with the influence of applied stresses on the formation of acicular ferrite (intragranularly nucleated bainite) is that of Dallum and Olson.[30] They studied the microstructure obtained by transformation under the influence of stress generated during the cooling of constrained samples of reaustenitised steel weld metal. The level of stress therefore varied from zero at the austenitisation temperature to a maximum at ambient temperature, although the absolute magnitude of the stresses involved were not stated. Other tests involving compression were also carried out.

Dallum and Olson found that with the types of stress typical during welding, there was very little influence on the volume fraction of acicular ferrite obtained. However, their results are difficult to interpret because the samples contained mixed microstructures. More significantly, the tests were based on continuous cooling experiments in

which transformation was allowed, in all cases, to proceed to its maximum extent during cooling to ambient temperature. Since the extent of transformation was not measured, the tests are probably not capable of detecting the influence of stress on either the volume fraction or kinetics of transformation. Given that there is an invariant-plane strain shape change associated with the growth of acicular ferrite, experiments involving isothermal reaction under the influence of a constant tensile stress should demonstrate an acceleration of transformation.

An applied stress will tend to favour the development of crystallographic variants which comply with that stress. Given that the shear component of the shape deformation is much larger than the dilatational component, it is likely that those variants having displacement vectors inclined at about 45° to the tensile axis in a tension test will tend to be favoured,[28] so that the overall microstructure should exhibit such alignment. This has been confirmed for martensitic transformations (e.g. *see* Ref. 31), although similar evidence is lacking for bainitic transformations. Umemoto *et al.*[19] have reported that alignment of bainite platelets was observed only when the stress exceeded the yield stress, there being no significant changes in microstructure for lower stresses. The details of the alignment, such as the inclination with respect to the applied stress, have not been reported. The insensitivity of the microstructure to elastic stresses contrasts with the behaviour of martensite under stress and may be a consequence of the low stresses at which the experiments must be conducted for bainite, since at the temperatures concerned, the yield stress of the steel can be relatively low.

Judging from the work discussed above, there is little doubt that the stress response of the bainite reaction is similar to that of martensitic reactions. Nevertheless, some discrepancies are also evident and detailed experiments involving the monitoring of transformation strain along orthogonal directions have not been carried out. Furthermore, all the experiments to date have been carried out on steels in which carbide precipitation reactions overlap the formation of bainitic ferrite. Consequently, the aim of this work is to re-examine the effects of stress on bainitic transformation in an Fe–Cr–Mo–C steel in which upper bainite grows without the precipitation of carbides. A study of this steel is also particularly relevant because of its potential applications in the energy industry, where it is used in structures fabricated by welding and where residual stresses generated by the welding process itself can be rather large. The ultimate aim is to be able to model the development of microstructure in such welds for the electron beam and submerged arc welding processes.
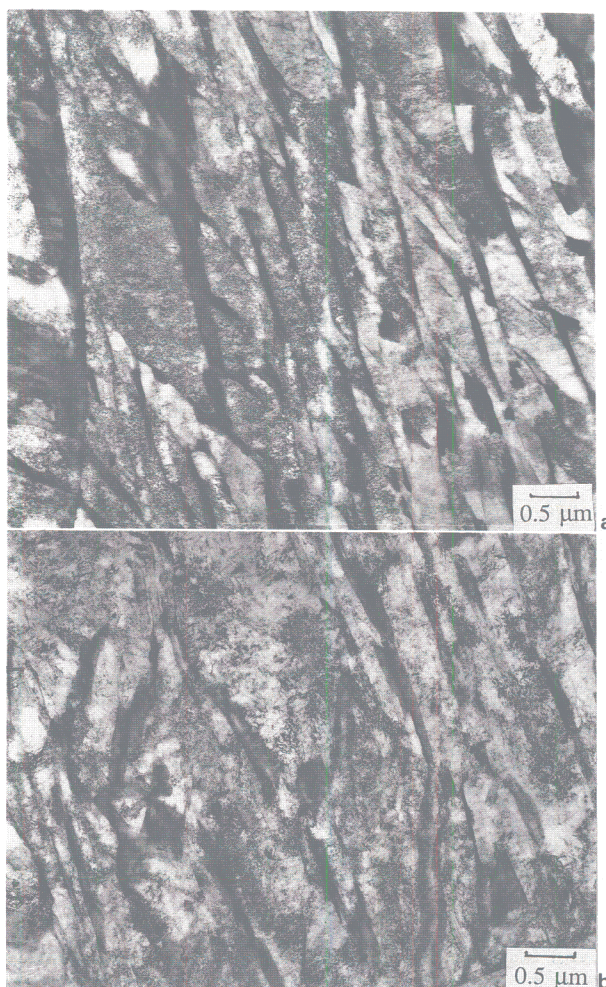
Experimental techniques

ALLOY COMPOSITION

The alloy used was a part of an experimental steel manufactured by Lukens Steel (Coatesville, PA); the chemical composition and relevant transformation temperatures are given in Table 1. The steel was available as a block of approximate dimensions $25 \times 100 \times 340$ mm, the longest direction being parallel to the rolling direction.
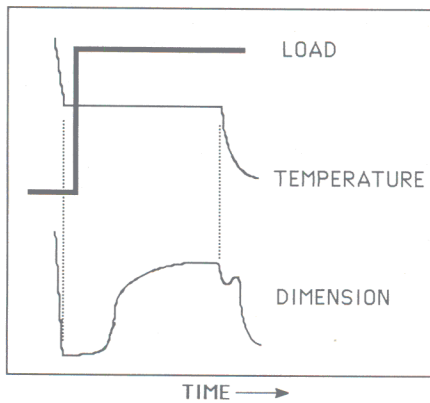

2   **Bright field TEMs obtained from specimens isothermally transformed at** *a* **440°C and** *b* **400°C, then gas quenched to ambient temperature: microstructure consists of bainitic ferrite platelets separated by regions of retained austenite and martensite**

Rod shaped samples were machined from the block, the rod axes being parallel to the rolling direction. Separate samples were used for each transformation temperature–stress combination; in each case, anisotropy was characterised by measuring strain along different directions of the same sample. Transmission electron micrographs (TEMs) confirming the typical bainitic ferrite and residual austenite (and martensite formed by decomposition of the residual austenite) obtained by isothermal transformation are shown in Fig. 2.

GLEEBLE EXPERIMENTS

The samples used to study transformation kinetics were cylindrical, $6\cdot35$ mm (dia.) $\times$ 110 mm (length), and had a 10 mm region at each end threaded to fit into the water cooled copper jaws of a Gleeble 1500 simulator. The equipment utilises resistive heating so that the hot zone

Table 1   Chemical composition, wt-% and at.-%*, (mole fraction is given by at.-%/100) and transformation temperatures of steel used

C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu	V
0·12	0·27	0·84	0·011	0·002	2·86	1·48	0·14	0·004	0·006	0·01
0·56*	0·54*	0·85*	0·020*	0·004*	3·06*	0·86*	0·13*	0·008*	0·005*	0·01*

Transformation temperatures (calculated as in Refs. 32–34) are: martensite start $M_s = 386$°C, bainite start $B_s = 460$°C, and temperature on $\gamma/\alpha + \gamma$ paraequilibrium phase boundary $Ae_3' = 730$°C, where γ is austenite and α is bainitic ferrite.

3 Schematic illustration of design of isothermal transformation experiments: specimens were austenitised before isothermal transformation to bainite

on the cylindrical samples is limited to ~10 mm gauge length about the centre of the sample. The dimensional changes accompanying transformation or straining were measured using an extensometer located at the thermocouple position, across the specimen diameter. For some of the experiments, it was necessary to measure dimensional changes along the length of the specimen. Another extensometer was used for that purpose, with a gauge length of 5 mm across the quartz wedges which were in contact with fiducial marks on the specimen. The short gauge length was necessary to ensure that the data collected originated from a region of the specimen at uniform temperature. The difference in temperature between the centre and edges of the gauge length was measured to be not greater than ~10 K during isothermal heat treatment at temperatures in the range 400–480°C.

Most of the experiments involved isothermal transformation to bainite after austenitisation at 950°C for 2 min, which gave an austenite grain size, as represented by the mean lineal intercept, of 0.18 ± 0.08 mm based on 26 measurements. The error term represents one standard deviation about the mean. Following isothermal transformation, the samples were quenched to ambient temperature using an argon gas quench. Dimensional, temperature, time, and load data were collected simultaneously throughout the course of the experiments (Fig. 3). It was established from these observations that in most cases no transformation occurred at temperatures above the intended isothermal reaction temperature; this is not surprising given the high hardenability of the alloy. However, a small degree of bainitic reaction could not be avoided during cooling to the lowest isothermal reaction temperature used, 400°C, although even at that level, the vast majority of the reaction occurred at the intended temperature.

When the transformation was intended to occur under the influence of an applied stress (0 to ~100 MN m^{-2}), the load was applied about 2·4 s after the specimen reached the transformation temperature and was maintained constant (under computer control) throughout the remainder of the test. This caused problems only during transformation at 400°C, when a small amount of reaction occurred before the load could be applied. The heat treatments were carried out with the specimen assembly in a chamber purged with argon.

As mentioned above, two different extensometers were used to monitor the dimensional changes across the diameter and axis of the cylindrical specimens. The output from each was confirmed to be correct within experimental error, by measuring the expansion coefficient of a pure nickel sample of geometry identical to that of the steel samples used. A further check was carried out on the

measurements made along the axial direction, to ensure the absence of unknown constraints due to the grips holding the specimen. In experiments not involving applied tensile stresses, the grips were decoupled from the hydraulic drives, but there remained the possibility of a small constraint imposed by the mass of the grips. To test for this, two experiments were conducted, one with the grips decoupled and another in which they were driven to maintain a *constant* very small stress of about 4 MN m^{-2}. The latter, in effect, allows the grips to become free floating. The two experiments revealed essentially identical results during isothermal transformation to bainite, indicating the absence of any constraint along the length direction for experiments involving transformation at zero applied stress.

X-RAY ANALYSIS OF FERRITE

A knowledge of the lattice parameters of the phases involved is important in interpreting the dilatometric experiments, since the relationships between dimensional changes due to transformation and the volume fraction of ferrite depend on the lattice parameters and thermal expansivities of the parent and product phases (*see* below).

The ferrite lattice parameter was investigated using a precision X-ray diffractometer with Cu $K\alpha_1$ radiation. The experiment was conducted on a disc 6 mm in diameter, which had been annealed at 600°C for 30 min, metallographically polished to 0·25 μm finish, and finally etched in nital to remove any smeared surface. The results included the {1 1 0}, {2 0 0}, {2 1 1}, {2 2 0}, {3 1 0}, and {2 2 2} peaks, the positions of which were located by computer fitting to standard profiles. The data were then analysed using a least squares analysis from which the lattice parameter most compatible with information from all the peaks was deduced.

Results and discussion

EXPANSION COEFFICIENTS

Known values of the linear expansion coefficients (in K^{-1}) of austenite and ferrite (e_γ and e_α respectively) are required to interpret the experimental data from the Gleeble 1500 experiments. For ferrite, specimens annealed for 10 min at 600°C were cooled slowly at a rate of 1 K s^{-1} over the temperature range 580–230°C. For austenite, the samples were cooled at the same rate over the temperature range 1200–900°C; data were also obtained for the range 540–485°C where the austenite could be cooled at a rate of 0·15 K s^{-1} without transformation taking place. The results from three experiments for each phase are

$$e_\gamma = 2 \cdot 03 \times 10^{-5} \pm 0 \cdot 11 \times 10^{-5}$$

and

$$e_\alpha = 1 \cdot 59 \times 10^{-5} \pm 0 \cdot 10 \times 10^{-5}$$

The error terms represent one standard deviation from the mean. The expansion coefficients were found not to vary with temperature within the limits of experimental error.

LATTICE PARAMETER OF FERRITE

The X-ray analysis yielded a room temperature (298 K) value of the ferrite lattice parameter of $a_{0\alpha} = 0 \cdot 2873 \pm 0 \cdot 0001$ nm, where the error term represents one standard error in the least squares analysis mentioned above. An attempt was made to ascertain whether this is compatible with published data on the effect of alloying elements on the lattice parameter of pure iron a_{Fe}. The following equation ($a_{0\alpha}$ in nm) was deduced using data

from various publications[35-38]

$$a_{0\alpha} = 0.28664 + (3a_{Fe}^2)^{-1}$$
$$\times [(a_{Fe} - 0.0279x_C^\alpha)^2(a_{Fe} + 0.2496x_C^\alpha) - a_{Fe}^3]$$
$$- 0.003x_{Si}^\alpha + 0.006x_{Mn}^\alpha + 0.007x_{Ni}^\alpha$$
$$+ 0.031x_{Mo}^\alpha + 0.005x_{Cr}^\alpha + 0.0096x_V^\alpha \quad \dots \quad (1)$$

where x_i^α represents the mole fraction of the species i in phase α. Substitution of the appropriate concentrations (the amount of carbon in bainitic ferrite was assumed to be 0.03 wt-%, equivalent to $x_C^\alpha = 0.00139$) and taking the lattice parameter of pure ferrite as $a_{Fe} = 0.28664$ nm (Ref. 35), gives $a_{0\alpha} = 0.2872$ nm, in good agreement with the experimental measurement.

LATTICE PARAMETER OF AUSTENITE

The room temperature (298 K) lattice parameter of austenite ($a_{0\gamma}$ in nm) can be estimated using the following equation[39]

$$a_{0\gamma} = 0.3573 + \sum_{i=1}^n c_i w_i^\gamma \quad \dots \dots \quad (2)$$

where the subscript i defines a solute element having an average concentration (weight fraction) in the alloy as a whole of $\bar{w}_i$ and w_i^γ is the weight fraction of component i in phase γ. For iron, $i = 0$, and for carbon, $i = 1$, so that values of $i > 1$ represent substitutional solutes. The term c_i represents the change in the austenite lattice parameter caused by the addition of a unit concentration of alloying addition i; using data from Dyson and Holmes,[39] the summation is given by

$$\sum_{i=1}^n c_i w_i^\gamma = 3.3 \times 10^{-1} w_C^\gamma + 9.5 \times 10^{-3} w_{Mn}^\gamma$$
$$- 2.0 \times 10^{-3} w_{Ni}^\gamma + 6.0 \times 10^{-3} w_{Cr}^\gamma$$
$$+ 3.1 \times 10^{-2} w_{Mo}^\gamma + 1.8 \times 10^{-2} w_V^\gamma$$

To check the accuracy of the above equations, an experiment was conducted in which a ferritic sample (heat treated at 600°C for 10 min and cooled to ambient temperature) was heated continuously to 950°C at 1 K s⁻¹ while monitoring the change in specimen diameter. The part of the dimension change curve corresponding to a fully austenitic state was then extrapolated to 453°C, where the specimen was previously fully ferritic. The difference between the heating and cooling stages of the cycle thus yielded a value of the dimensional change accompanying the complete transformation of ferrite to austenite, which can be related to the lattice parameter as follows

$$a_\gamma^3 = 2(1 + 3[\Delta L/L])a_\alpha^3 \quad \dots \dots \quad (3)$$

where a_γ and a_α are respectively the lattice parameters of austenite and ferrite at the transformation temperature, L is the specimen dimension (longitudinal or transverse), and $\Delta L = L_{final} - L_{initial}$ (with $L = L_{final}$) and is negative for the transformation of ferrite to austenite. At 453°C, the value of a_α for ferrite which has the overall alloy composition but with $x_C^\alpha = 0.00139$ (0.03 wt-%), is 0.2893 nm. The value of $\Delta L/L$ at 453°C was measured to be -0.7936×10^{-3}, giving (for austenite of average carbon concentration 0.12 wt-%) $a_{0\gamma} = 0.36152$ nm at room temperature, which compares well with the value of 0.36153 nm estimated using the empirical relationship given in equation (2). The calculation assumes that the expansion coefficient of austenite as determined over the range 485–1200°C can be applied.

DETERMINATION OF VOLUME FRACTIONS

During the experiments carried out using the Gleeble 1500 simulator, the transformation kinetics was monitored by

following the change in specimen length or diameter as a function of isothermal heat treatment. Since, for the present steel, the bainite reaction generates a microstructure which contains only bainitic ferrite and residual austenite, it should be possible to convert these dimensional changes into the volume fraction of transformation. The analysis presented below is more rigorous than earlier methods (e.g. Ref. 40) and results in a slight improvement in accuracy. The relative volume change is given by

$$\frac{\Delta V}{V} = \frac{V_{final} - V_{initial}}{V_{final}} = 1 - \frac{a_\gamma^3}{\beta + a_{e\gamma}^3} \quad \dots \dots \quad (4)$$

where V_{final} and $V_{initial}$ are the final and initial volumes of the sample, $a_{e\gamma}$ is the lattice parameter of carbon enriched austenite at the transformation temperature, and

$$\beta = \frac{2a_\alpha^3 - a_{e\gamma}^3}{1 + [(2V_\gamma a_\alpha^3)/(V_\alpha a_{e\gamma}^3)]}$$

where V_γ and V_α are respectively the volume fraction of residual austenite and bainitic ferrite.

The lattice parameter of austenite after transformation $a_{e\gamma}$ is a function of the volume fraction of bainitic ferrite, since the carbon concentration of the austenite increases as carbon is partitioned from the bainitic ferrite. The lattice parameters of untransformed austenite and bainitic ferrite, a_γ and a_α respectively, are calculated from the room temperature (298 K) lattice parameters using the thermal expansion coefficients e_α and e_γ

$$a_\gamma = a_{0\gamma}[1 + e_\gamma(T - 298)] \quad \dots \dots \quad (5)$$

and

$$a_\alpha = a_{0\alpha}[1 + e_\alpha(T - 298)] \quad \dots \dots \quad (6)$$

where T is the absolute temperature.

As a consequence of bainitic transformation, the carbon concentration of the residual austenite increases to x_1^γ. If the final microstructure consists of only bainitic ferrite and carbon enriched residual austenite, it is possible to show that mass conservation requires that

$$x_1^\gamma = \frac{2a_\alpha^3 \bar{x}_1(1 - x_1^\alpha)(1 - V_\alpha) + a_{e\gamma}^3(\bar{x}_1 - x_1^\alpha)V_\alpha}{2a_\alpha^3(1 - x_1^\alpha)(1 - V_\alpha) + a_{e\gamma}^3(\bar{x}_1 - x_1^\alpha)V_\alpha} \quad \dots \quad (7)$$

or in terms of weight fractions w_i

$$w_1^\gamma = \frac{V_\alpha \rho_\alpha}{(1 - V_\alpha)\rho_\gamma}(\bar{w}_1 - w_1^\alpha) + \bar{w}_1 \quad \dots \dots \quad (8)$$

where ρ represents the density of the phase concerned. Equations (7) and (8) must be solved iteratively, since ρ_γ and $a_{e\gamma}$ are functions of x_1^γ. In fact, the relationship between volume change and volume fraction of bainitic ferrite is also not explicit and must be solved using iterative procedures.

The experimental measurements correspond to dimensional changes ΔL rather than volume changes ΔV. The relationship between these quantities, assuming isotropic strain, is given by

$$\frac{\Delta V}{V} \approx 3\frac{\Delta L}{L} \quad \dots \dots \quad (9)$$

where L is the dimension of the specimen at the transformation temperature. Once the volume change is experimentally determined, the data can be substituted into equation (4) to deduce by iteration the volume fraction of bainitic ferrite and the lattice parameter of the carbon enriched austenite. With these results, equation (7) can be solved to yield the carbon concentration of the enriched austenite.

INCOMPLETE REACTION PHENOMENON

It is well established that the 2·25Cr–Mo steels and their derivatives all exhibit a bainitic microstructure consisting

of a mixture of bainitic ferrite, retained austenite, and high carbon martensite after either continuous cooling from austenite at rates consistent with industrial practice or after isothermal transformation at temperatures below the bainite start temperature (e.g. Refs. 41–43). The martensite forms subsequent to bainite as some of the carbon enriched residual austenite transforms martensitically on cooling below its martensite start temperature. The microstructure that forms by continuous cooling transformation, when observed using light microscopy, appears to consist of relatively coarse ferritic regions in a mixture of austenite and martensite and is often referred to as 'granular bainite'.[41,44–47] The observation of these coarse regions is unexpected and, in addition, the cementite which usually accompanies conventional bainite transformation is absent, presumably because the alloy chemistry retards its precipitation.

There is now considerable evidence that the granular bainite is not different from conventional bainite, the morphology simply being altered by continuous cooling transformation.[43,48] In fact, transmission electron microscopy has revealed that the apparently coarse ferritic regions correspond to sheaves of small platelets of bainitic ferrite.[48] The absence of carbide precipitation is also not unusual; it is well established that the formation of carbides during the bainitic reaction is a secondary event which may lag far behind the formation of bainitic ferrite, and carbide free bainite has been reported in a wide range of steels.[14]

Given that the microstructure is primarily bainitic, it should exhibit an incomplete reaction phenomenon,[14,49] in which the maximum degree of reaction increases from zero at the B_s temperature to some other finite value at lower temperatures, which is always less than would be expected from an application of the lever rule to the equilibrium or paraequilibrium phase diagram. Experiments were therefore carried out to confirm the incomplete reaction phenomenon for the alloy used in the present study. The lack of carbide precipitation during bainitic transformation makes the alloy ideal for the study, allowing the carbon concentration of the residual austenite to be determined by a mass balance procedure and permitting the study of the formation of bainitic ferrite without interference from an overlapping carbide precipitation reaction.

For experimental verification of the incomplete reaction phenomenon, isothermal transformation to bainite was allowed to continue until the reaction ceased. It is evident from the data presented in Fig. 4a that the extent of the reaction only becomes significant below the calculated B_s temperature of 460°C, even though the alloy is by then well below the Ae_3' (730°C) temperature. The degree of reaction was also found to increase with decreasing reaction temperature. The maximum dimensional change at each temperature was used to estimate the volume fraction of bainitic ferrite and the carbon concentration of the residual austenite (assuming uniform distribution in the austenite), as discussed above (equations (4) and (7)). The results were plotted on a phase diagram (Fig. 4b), which was calculated using thermodynamic data and a quasichemical solution model, as described elsewhere.[50] In Fig. 4b, a $(\alpha + \gamma)/\gamma$ paraequilibrium (Ae_3') phase boundary and a T_0' curve are illustrated. The T_0' curve represents the locus of all points (as a function of temperature) for which austenite and ferrite of the same composition have equal free energy, after allowing for 400 J mol^{-1} of stored energy in the ferrite, owing to the invariant-plane strain shape change accompanying the growth of bainitic ferrite.[51]

The data presented as open circles on Fig. 4b show that in all cases, the carbon concentration of the austenite x_1^γ when bainitic transformation ceases is much less than would be expected from paraequilibrium transformation. In fact, the reaction appears to stop when x_1^γ approaches
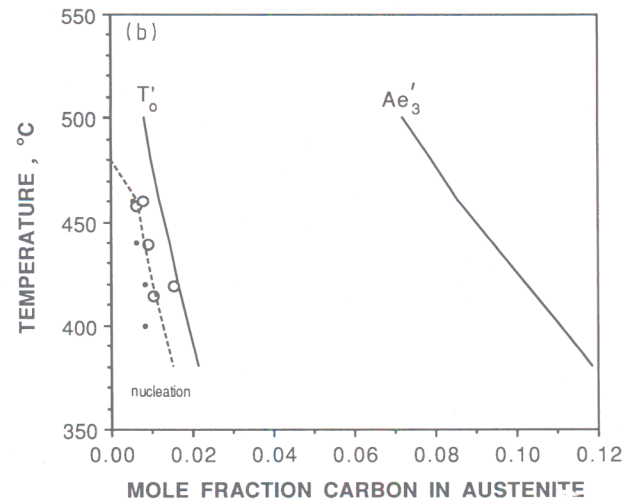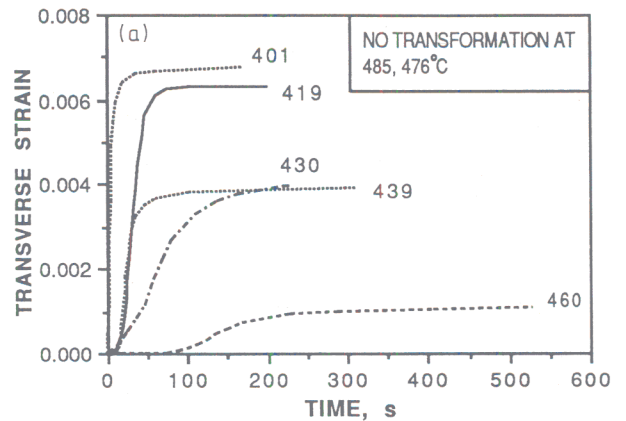

a representative data from large number of isothermal transformation experiments, illustrating increase from zero in extent of transformation on cooling below bainite start temperature; *b* experimental data for present steel, representing carbon concentration of residual austenite after cessation of isothermal bainitic transformation plotted on calculated phase diagram (open circles represent data obtained from measurement of single diameteral strain, whereas other points are derived using strains measured along three orthogonal directions for any given isothermal transformation temperature)

4 Incomplete reaction phenomenon for steel used in present study

the T_0' curve for the alloy. The reaction is, in this context, found always to be incomplete. The results are consistent with published data on other alloys and can be interpreted to imply that bainitic ferrite grows by a diffusionless transformation, the excess carbon being partitioned from each platelet into the residual austenite, shortly after its growth is terminated.[14,49] The data plotted as open circles were derived by monitoring dimensional changes along a single direction; the analysis thus assumes that the transformation in the polycrystalline samples produces isotropic strains.

Also included in Fig. 4b are data from the experiments described below, in which the transformation strains were measured along three orthogonal directions. These data should be more reliable, given that the samples had a tendency to be sensitive to the austenite crystallographic texture when reacted at relatively low temperatures (discussed below). The dilatational component of strain was in each case calculated as the mean of the maximum values of the three orthogonal strains. In fact, since there is little difference between the two sets of experiments, the assumption of isotropy for the zero stress state is certainly justified to distinguish whether the transformation stops in the proximity of the T_0' curve or the Ae_3' curve on the phase diagram.

ISOTROPIC EXPANSION

GENERAL INVARIANT-PLANE
STRAIN

(a)

(b)
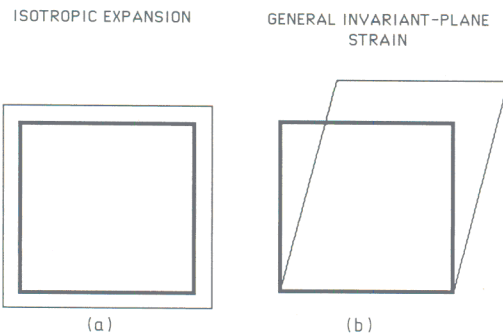
a isotropic volume expansion; *b* general invariant-plane strain

5 Schematic diagram of shape changes due to transformation

A more detailed examination of Fig. 4 reveals that bainitic transformation in the present alloy ceases somewhat *before* the carbon concentration in the residual austenite reaches the T_0' curve in all instances but one. This may be because the strain energy term of $400 \, \text{J mol}^{-1}$ is an underestimate in the T_0' calculations. Alternatively, it may more probably be because the transformation is nucleation limited. To obtain a detectable rate of nucleation, the driving force available for nucleation (a negative quantity) must become less than a value defined[51,52] by the function $G_N\{T\}$; i.e.

$$\Delta G_{max} \leqslant G_N\{T\} \qquad \ldots \ldots \ldots \ldots (10)$$

where ΔG_{max} is the driving force available and G_N is the driving force required for nucleation of bainite or Widmanstätten ferrite.

As the carbon concentration of the residual austenite increases, ΔG_{max} becomes smaller in magnitude and nucleation then can be considered effectively to cease. In Fig. 4b, the curve marked 'nucleation' is derived by calculating the value of x_1^γ at which $\Delta G_{max} = G_N\{T\}$, and appears to fit the experimental data rather well. It should be emphasised that for the alloy used in the present study, the nucleation curve occurs at lower carbon concentrations relative to the T_0' curve. This is not generally true; for example, it is the T_0' curve that occurs at lower carbon concentrations when compared with the nucleation curve for the alloy (Fe–0·2C–1·8Mn–0·44Si, wt-%) utilised in the study by Strangwood and Bhadeshia,[53] where abundant nucleation sites were presumably available.

INFLUENCE OF CRYSTALLOGRAPHIC TEXTURE

The experiments reported in this section were conducted after the studies of the influence of stress on transformation behaviour, but are presented first for clarity. As is discussed below, the full interpretation of data from the stress induced transformation experiments requires strain to be monitored along the stress axis and along a direction normal to that axis. During transformation under a tensile stress (which is well below the single phase yield stress), the total strain along the stress direction is expected to be larger than that along the transverse direction. However, the experimental data (discussed below) demonstrated otherwise, indicating the presence of crystallographic texture in the austenite.

In a stress free transformation, if the volume change due to transformation is isotropic (Fig. 5a), then the strain monitored is expected to be independent of the direction in which it is measured. The change in shape due to the displacive formation of bainitic ferrite is, however, an invariant-plane strain (Fig. 5b) on the habit plane, so that the dilatational component of the strain (which determines the volume change) is directed along the habit plane

normal; strain monitored along different directions may therefore vary in magnitude and/or sign. On the other hand, if in a fine grained polycrystalline sample of the type used here, the austenite grains are randomly oriented, the directions of the displacement vectors should average out, leading to the same amount of expansion in all directions. If that is not found, then the austenite grains cannot be randomly orientated and the sample is said to exhibit crystallographic texture.

To test for the presence of texture, isothermal transformation experiments were conducted in which the dimensional changes were monitored along the longitudinal axis and along two mutually perpendicular transverse directions. One of the transverse strain directions was arbitrarily fixed as the 0° orientation and the other the 90° orientation. With the equipment available, the strains could not be monitored simultaneously, so that for a given transformation temperature, the experiment was repeated three times on the same specimen to monitor each strain individually.

The results (Fig. 6) demonstrate that during transformation without externally applied stress, there may be significant differences between the three strains at any given stage of reaction. The differences are also a function of temperature, the transverse strains being much larger than the longitudinal strain as the transformation temperature decreases or the total volume fraction of transformation increases. The alloy behaves more or less isotropically for the two higher transformation temperatures, indicating that the variants which nucleate most readily for the given austenite grain structure are isotropically distributed in the polycrystalline sample. At relatively higher undercoolings, the variants which nucleate are far from isotropically distributed since for both of the lower transformation temperatures, $\varepsilon_L \ll \varepsilon_T$, where ε_L and ε_T are the longitudinal and transverse plastic strains, respectively, as measured from experiments.

The results can be explained satisfactorily only if two conditions are satisfied simultaneously: that the transformation is accompanied by an invariant-plane strain shape change with a significant shear component and that the distribution of the parent austenite grains is not random. An isotropic expansion, for example of the type due to the volume change during the growth of allotriomorphic ferrite, cannot produce differences in dimensional change as a function of direction even if the austenite is textured, or if the transformation occurs in a single crystal of austenite.

The nucleation of bainite begins at the austenite grain surfaces and the crystallography of the austenite grain boundaries must influence their nucleation potency. The results, particularly the anisotropy of transformation strain, indicate that the texture favours the nucleation of particular crystallographic variants of bainite. If all the 24 possible crystallographic variants could form in equal proportions, then the corresponding orientation variants of the invariant-plane strain displacement vectors might be expected to lead to an overall averaging effect, thus giving the appearance of isotropy on a macroscopic scale, in contradiction to the experimental observations.

The results demonstrate uniquely the transformation plasticity associated with the bainitic reaction in polycrystalline samples, despite the absence of an applied stress. The observed large differences between the longitudinal and transverse strains cannot be explained by the dilatational component of the shape change alone, since that would require almost all the bainite sheaves to have their habit plane normals parallel to the radial directions of the sample. It is shown below, that the microstructure does not exhibit such strong alignment. On the other hand, there is no difficulty in explaining the magnitudes of the differences observed if transformation plasticity, arising from the shear component of the shape change, is also included in the analysis.
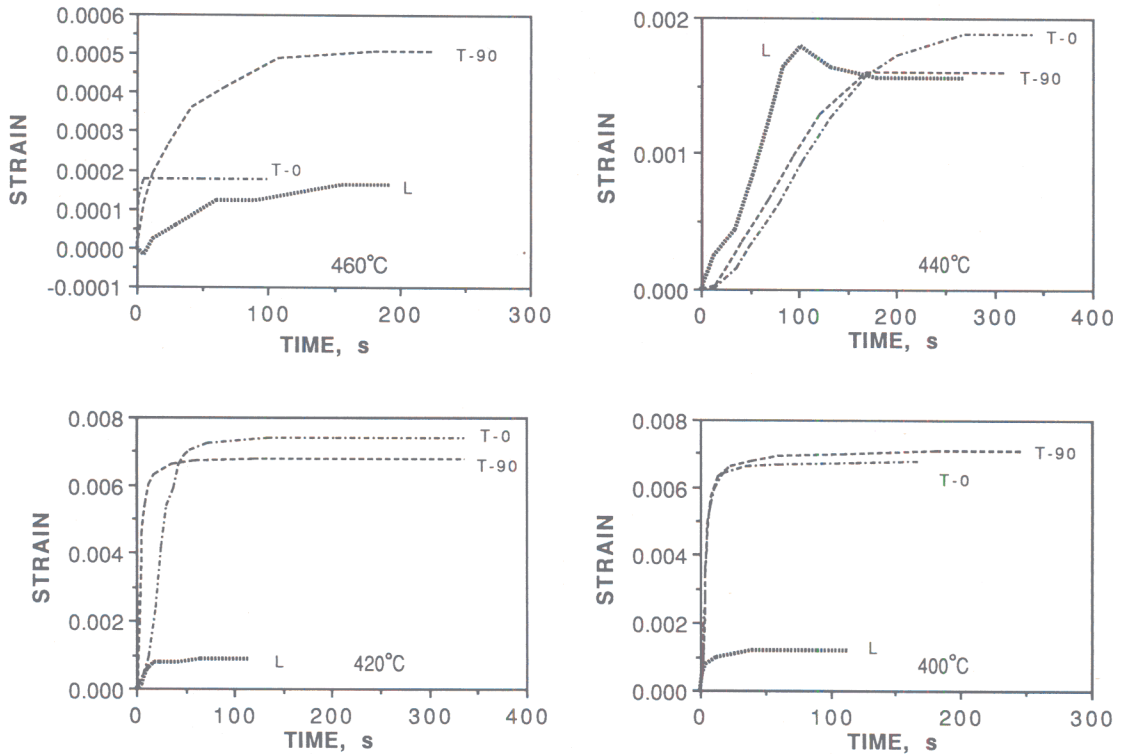
6 Isothermal transformation experiments in which strains were measured along two orthogonal transverse directions (T-0 and T-90) and along longitudinal direction (L); experiments were conducted without externally applied stress and indicate presence of crystallographic texture in austenite phase

TRANSFORMATION UNDER STRESS

Tensile stresses of approximately 45 and 95 MN m^{-2}, i.e. much lower than the measured yield stress of the ferrite at temperature (829 MN m^{-2} at 433°C), were applied soon after the sample reached the isothermal transformation temperature (Fig. 3). The strength of austenite should be lower than that of ferrite, but certainly not as low as the applied stresses. The effects on strain measured in the longitudinal and transverse directions are shown in Figs. 7 and 8 . (The actual values of stress used are given in the subcaption key to Fig. 7; values of ~45 and ~95 MN m^{-2} are referred to below as low and high, respectively.) The results demonstrate a strong tendency of the stress to favour the growth of bainite variants which contribute to elongation along the longitudinal direction. The longitudinal strain was consistently found to become larger relative to the transverse strain as the applied stress was increased from zero, for any stage of reaction. The results do not include any elastic components of strain, since the data were collected isothermally and at constant load.

The transformation strain monitored along the transverse direction was found generally to decrease when the reaction was carried out under the influence of a tensile stress. This is because of the Poisson effect, which for plastic deformation follows from the conservation of volume; elongation along the stress axis therefore leads to a corresponding contraction in orthogonal directions. In addition, variants which would ordinarily contribute to ε_T would not be favoured when the stress axis is parallel to the longitudinal axis of the cylindrical sample. At the higher stress, in particular, the transverse strain was often found to be negative during the initial stages of reaction, but began to recover as the rate of change of ε_L decreased with time. In terms of the microstructure, this means that the transverse strain begins to recover when the rate of growth of variants favoured by the stress decreases owing to the exhaustion of suitable nucleation sites. In some cases, the total transverse strain was found to remain negative throughout

the reaction. That the longitudinal strain was sometimes found to be less than the transverse strain (for the low stress experiments) is due to the crystallographic texture, which also caused ε_T to be greater than ε_L in the absence of applied stress.

These data constitute a dramatic demonstration of the transformation plasticity associated with the bainitic reaction. The anisotropic strains and their relative magnitudes cannot be interpreted in terms of any reconstructive transformation mechanism. On the other hand, there is no difficulty in rationalising the observations in terms of the shape deformation accompanying the growth of bainitic ferrite. The data (especially the changes in the relative magnitudes of ε_L and ε_T) also show quantitatively that the microstructure responds significantly to stresses as low as 45 MN m^{-2}.

For a tensile stress applied along the longitudinal axis, and assuming that the volume change due to transformation is isotropic, the longitudinal and transverse strains are given by

$$\varepsilon_L = \frac{1}{3}\frac{\Delta V}{V} + \varepsilon_P \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$\varepsilon_T = \frac{1}{3}\frac{\Delta V}{V} - 0.5\varepsilon_P \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where ε_P is the plastic strain due to transformation (i.e. transformation induced plasticity) and $\Delta V/V$ is the corresponding fractional change in volume. The data obtained by deconvoluting the maximum values of recorded strains according to these equations are shown in Fig. 9. At the highest transformation temperature of 460°C (and to a lesser extent at 440°C), where the steel behaves more or less isotropically for the zero and low stress experiments, the effect of an increase in applied stress is, as expected, to increase the degree of transformation. (If the shape change due to transformation complies with the applied stress, then there is, in effect, an increased driving force for
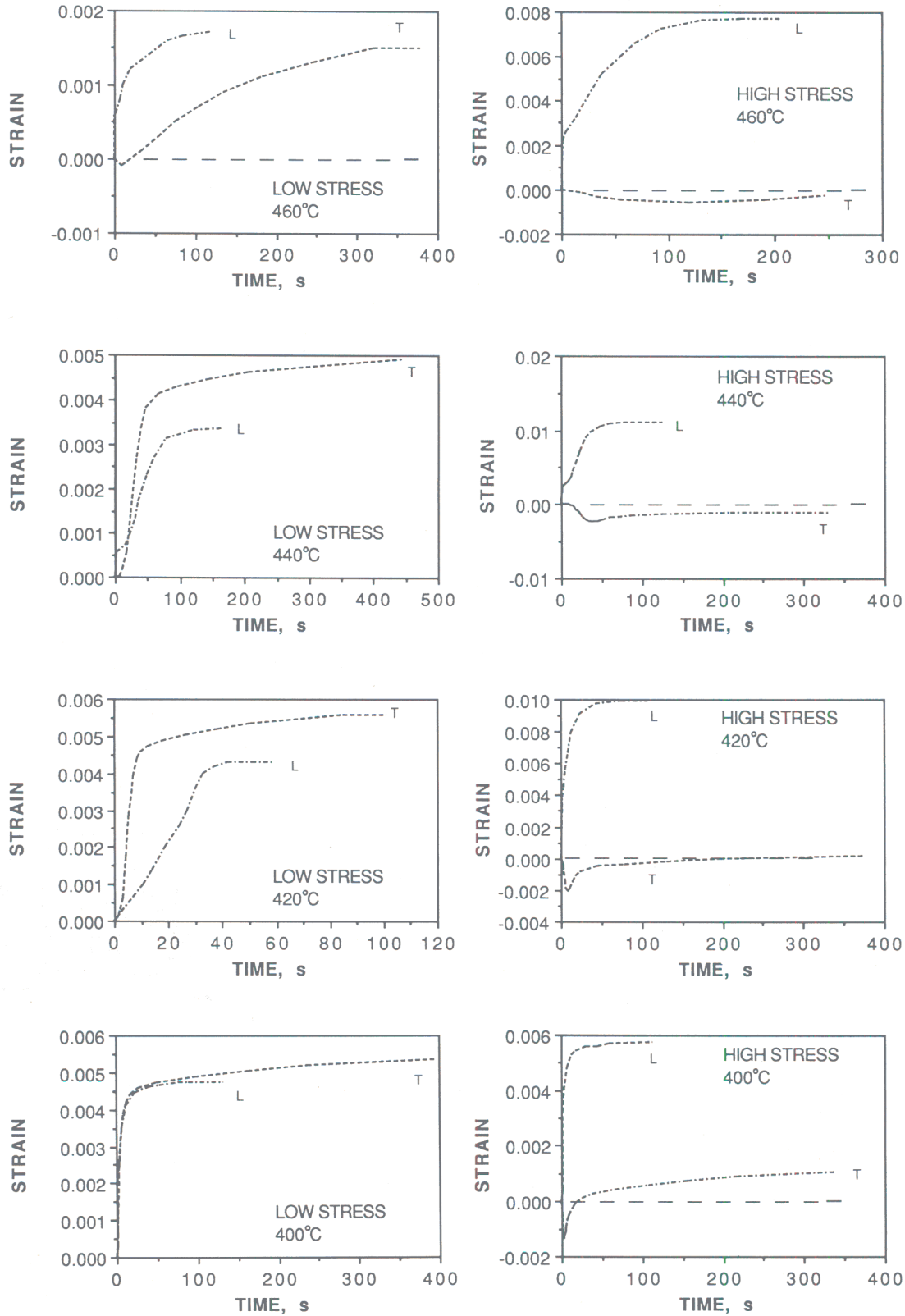
Temperature, °C	Actual stress, MN m^{-2}	
	Low	High
460	47·8	···
460	···	96·5
440	41·4	···
440	···	98·4
420	41·6	···
419	···	98·4
399	41·5	···
398	···	98·4

7 Isothermal transformation under influence of externally applied tensile stress along longitudinal axis of sample: L and T denote longitudinal and transverse strains, respectively
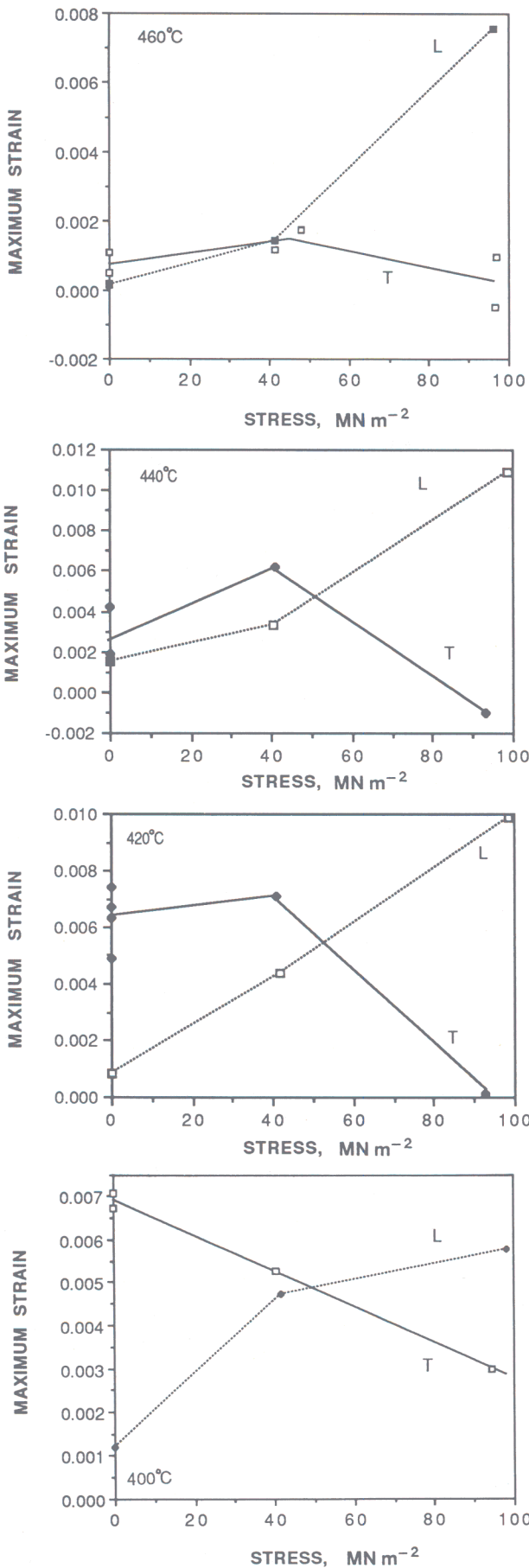
8 Maximum values of strain recorded during isothermal transformation to bainitic ferrite: reaction at each temperature was allowed to go to completion
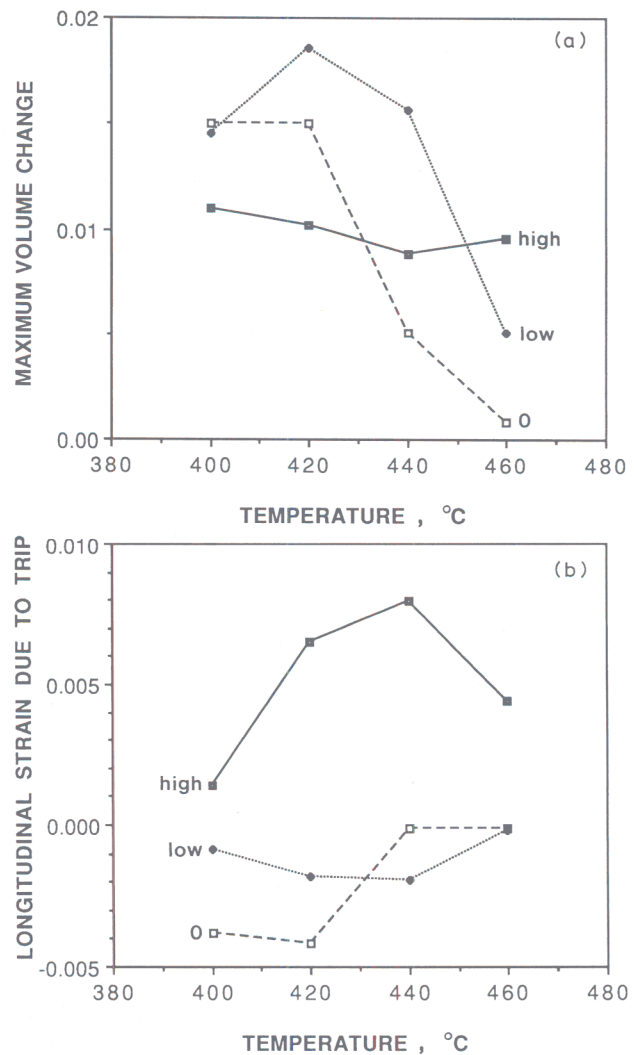
a maximum volume change due to transformation; *b* calculated transformation induced plasticity (TRIP) ε_P

9 Deconvolution of strains recorded during transformation (Fig. 8) into dilatational and deviatoric components: 0, low, and high denote experiments carried out at zero, ~ 45 MN m^{-2} and ~ 95 MN m^{-2} stress, respectively

transformation.[28]) For the other transformation temperatures ($<440°C$), the effect of stress is complicated by the fact that the crystallographic texture favours the growth of variants which make a greater contribution to transverse than to longitudinal strain. Since the stress is applied along the longitudinal direction, its effect is first to remove the influence of the crystallographic texture and to make the transformation more random. Thus, the transformation induced plasticity as measured along the longitudinal axis tends towards zero (from lower values) when the applied stress is low. As the stress is increased, the variants that produce a longitudinal strain are favoured and they grow to a greater extent, increasing the transformation induced plasticity considerably as the longitudinal strain becomes dominant (Fig. 9).
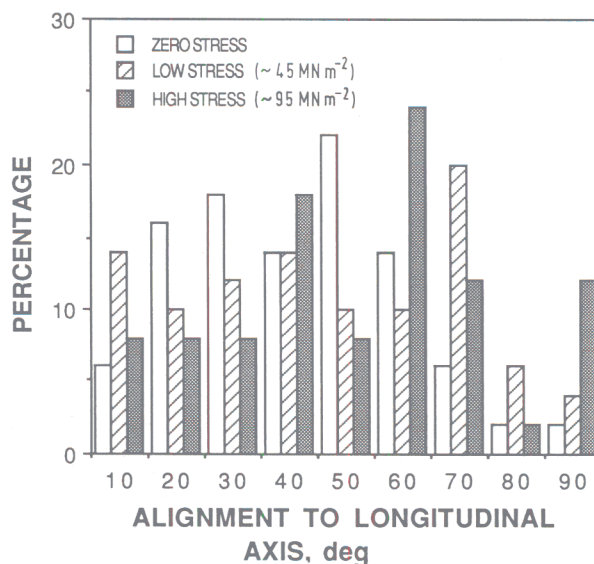
METALLOGRAPHY

Light microscopy was carried out to reveal the response of the microstructure to the applied stress. The stress should favour the formation of variants with habit planes at approximately 45° to the stress axis.[28] A comparison of

a

b

c

a zero stress; *b* low stress (~45 MN m⁻²); high stress (~95 MN m⁻²)

10   Light micrographs of bainitic microstructures generated by isothermal transformation at 400°C under tensile stress: stress axis horizontal

11   Approximate distribution of bainite sheaf traces (at 400°C) with respect to longitudinal axes of samples: completely random distribution would correspond to constant frequency at all angles

blocky and less random appearance. This effect also leads to a very clear definition of the austenite grain structure as the stress increases, since a few favoured variants dominate the microstructure and grow completely across the austenite grains (Figs. 10*a*–10*c*); at lower stresses, there are more sheaves nucleated, thereby giving at first sight, the appearance of a smaller austenite grain size. Caution must be exercised in interpreting the micrographs, because in all cases, further transformation to bainite was found to occur during cooling from the isothermal reaction temperature.

The angular distributions of bainite sheaves with respect to the longitudinal axis were measured for each sample, using a goniometer scale on the microscope stage. Fifty such measurements were made on each sample, the locations being chosen by random translations of the stage. Given that further bainite formation could not be avoided during the quench from the isothermal reaction temperature, only the data from experiments carried out at the lowest isothermal transformation temperature (400°C) are used, since the largest volume fraction of bainite is obtained during transformation at that temperature. A histogram of the results is shown in Fig. 11. There are several approximations in this method. Owing to the limited resolution of the light microscope, it is the bainite sheaves that are examined rather than the subunits. The measurements also refer to the traces of the habit planes rather than the orientation of the habit planes relative to the stress axis. The sheaf traces themselves were often not clearly defined; during the random counting procedure, regions where the microstructure could not be easily resolved were therefore ignored. The accuracy of each measurement is not likely to be better than ~5°.

The results (Fig. 11) show that there is a slight change in the distribution of bainite sheaves with the application of stress. This contrasts with the relatively large degree of anisotropy in the dimensional changes recorded during transformation. Without detailed data on the distribution of the shape deformations associated with individual platelets in the polycrystalline samples, the data cannot be explained quantitatively. None the less, given the large value of the shear component of the shape deformation, it is not surprising that small changes in microstructure correspond to significant anisotropy in transformation strains.

the zero and high stress samples (Fig. 10) indicates a discernible increase in the proportion of such variants in the samples transformed under stress. A further qualitative observation is that each austenite grain appears to transform to fewer variants of bainite in the specimens transformed under stress, giving the microstructure a

It is of interest that the application of a small stress actually makes the microstructure rather more random (Fig. 11), since, in the absence of stress, crystallographic texture ensures a non-random distribution in which there is a dearth of variants at the low and high angle orientations. The application of a small stress during the reaction appears to make the distribution more random, effectively reducing the structural anisotropy, consistent with the data presented in Fig. 9 (calculated using equations (11) and (12)), where it is apparent that the transformation induced plasticity ε_P is close to zero for the low stress experiments, at all temperatures. The more random distribution at low stress is also evident in Fig. 7, which shows that the most isotropic behaviour at all temperatures occurs for the low stress. As the stress is increased, ε_P also increases; this should mean also that the frequency of variants about the 45° orientation increases, but that is difficult to judge from Fig. 11. Such effects should become more detectable as the stress level is increased further; this will be investigated in future work.

It is also shown in Fig. 9 that the effect of low stress is to increase the maximum volume fraction of bainite; this is not unexpected, since there is in effect an increase in the magnitude of the free energy of formation for the favoured variants.[28] However, in addition, it is also shown that at the lower transformation temperatures, there is in fact a decrease in the maximum volume fraction obtained under high stress, relative to the zero stress or low stress data. This observation is consistent with the earlier conclusion that the bainite reaction in this steel is nucleation limited. The stress can only enhance the formation of favoured variants and it opposes the formation of others. If there existed an indefinite supply of suitable nuclei, then there should always be an increase in the maximum allowable degree of reaction and the loss of those variants not favoured by the stress could be more than compensated by the formation of those variants which comply with the stress. However, if it is assumed that the supply of nuclei is limited, then it is expected that the suppression of unfavourable orientations by stress cannot be matched by an increase in the favoured variants, leading to a drop in the observed maximum degree of reaction. Consistent with the experimental data, this 'negative' effect of stress on the extent of reaction can be significant only when the extent of transformation is large, i.e. when the supply of nuclei is close to exhaustion. Thus, at the higher transformation temperatures, where the maximum volume fraction of bainite that can form is lower, a higher degree of reaction is obtained as the stress is increased. (Fig. 9).

Summary

The growth of bainitic ferrite has been studied in an Fe–Cr–Mo–C alloy using quantitative dilatometric methods and metallography. Consistent with published data, the maximum volume fraction of bainitic ferrite obtained during isothermal transformation is found to depend on the undercooling below the bainite start temperature B_s. The degree of reaction is found to increase from zero at the B_s temperature to a value which is always far less than expected from a paraequilibrium growth model. The results can be understood on the basis that bainite grows without diffusion, with the excess carbon partitioning into the residual austenite subsequent to transformation; in such circumstances, transformations cannot be sustained if the carbon concentration of the austenite exceeds the T_0' curve on the phase diagram. On the other hand, the observation that, in fact, the reaction ceases at a somewhat lower austenite carbon concentration, could indicate that the transformation stops when the nucleation of bainite becomes impossible.

Experimental measurements of transformation strains along orthogonal axes were found to reveal anisotropic dimensional changes. These observations can be attributed to the presence of crystallographic texture in the austenite, and the invariant-plane strain shape deformation (with a large shear component) accompanying the displacive growth of bainitic ferrite. The results are inconsistent with a reconstructive transformation mechanism and provide direct evidence for transformation induced plasticity in textured polycrystalline samples.

Isothermal transformation experiments conducted under the influence of tensile stresses not exceeding 95 MN m^{-2} (with strain being monitored along both the longitudinal and transverse directions) prove conclusively that the microstructure responds significantly to the applied stress. However, the effect may not be apparent when the microstructure is examined using light microscopy. The details of the response are complicated by the presence of texture, but are consistent with the nature of the shape deformation accompanying the formation of bainite.

Future work will be focused on bainitic transformation using higher applied stresses and in regimes where the austenite undergoes plastic deformation before transformation.

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