BAINITE: THE INCOMPLETE-REACTION PHENOMENON

AND THE APPROACH TO EQUILIBRIUM

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The existence of an incomplete-reaction phenomenon in a e-0.30C-4.08Cr (wt.pct.) alloy is demonstrated using dilatometric and metallographic techniques. The results show that the degree of transformation to bainite is well below that indicated by the extrapolated Ae$_3$ curve, and are interpreted in terms of the mechanism of bainite formation. It is found that the bainite-austenite interface which is responsible for the displacive transformation to bainite-ferrite becomes immobile after the initial rapid reaction corresponding to the incomplete-reaction effect. However, on prolonged holding at the isothermal transformation temperature, this interface develops perturbations which lead to the diffusional formation of ferrite. Thus, the incomplete-reaction phenomenon appears not to arise due to some restriction to diffusional growth.

An interesting feature of the isothermal bainite transformation is the existence of the "incomplete reaction phenomenon" (1,2). At any temperature within the bainite transformation range, and in the absence of any interfering secondary reactions, only a limited quantity of bainitic-ferrite forms before the reaction terminates. This apparently premature termination occurs before the carbon content of the remaining austenite reaches the equilibrium level indicated by the extrapolated Ae$_3$ curve. The maximum extent of transformation that can be achieved increases with undercooling below the bainite-start, (or Bs) temperature.

In discussing the incomplete-reaction phenomenon, it is pertinent to define the Ae$_3$', Ae$_3$'', T_o and T'_o curves. For alloy-steels, the Ae$_3$' curve separates the $\gamma/\gamma + \alpha$ phase field, when the austenite and ferrite are in a state of constrained equilibrium, such that substitutional alloying elements do not redistribute during transformation; the T_o curve delineates temperatures below which steels can undergo completely partitionless transformation. Both these curves refer to stress-free transformation, and differ from their counterparts, the Ae$_3$'' and T'_o curves, which additionally account for the stored energy (e.g. transformation strain energy) of ferrite (in plain carbon steels, the Ae$_3$' and Ae$_3$ curves are identical). The incomplete-reaction phenomenon can be useful in deducing the level of carbon-saturation that existed in the ferrite during growth (2), but there is some confusion as to whether such an effect occurs in chromium-containing steels; Lyman and Troiano (3) found such steels to exhibit an initial rapid reaction, that transforms only a very limited amount of austenite, indicating an incomplete-reaction. However, Boswell et al. (4) maintain that these experiments correlate badly with microstructural observations in the same alloys. It is believed that the present work helps to resolve these difficulties, and to show that the incomplete-reaction effect is not a manifestation of some restriction to diffusional growth.

Experimental Procedures

The alloy used was prepared as in Ref. 5, and the final composition (wt. pct.) was Fe-0.30C-4.08Cr. The dilatometry and transmission electron microscopy were carried out as stated in Ref. 6, but the dilatometric specimens were electroplated with a 70 micron layer of nickel, in order to avoid any surface transformation effects.

All specimens were austenitised at 1100°C for 10 minutes. Prolonged isothermal heat-treatments (e.g. 43 days) were carried out by sealing the specimens concerned in a quartz tube (containing a partial pressure of pure argon), quenching into a molten-tin bath set at the required temperature, and after a period of 30 minutes, rapidly transferring into a furnace operating at an identical temperature. At the end of the isothermal heat-treatment, the still intact quartz tube was plunged into iced-brine. Shorter isothermal heat-treatments were completed in the molten-tin bath. Some of the specimens were metallographically prepared before heat treatment so that any surface relief effects generated during transformation could be subsequently observed. A Philips EM400 electron microscope (with EDAX facilities) was used for obtaining compositional information from very small areas of interest in thin-foil specimens.

Results and Discussion

The dilatometric results and their interpretation (see appendix 1) are presented in Figs. 1a,b. The thermodynamic methods and data necessary for the calculation of the various curves illustrated in Fig. 1b have been described elsewhere (2), but the stored energy of bainite was taken to be 400 J/mol, according to Ref. 7. The experimental points refer to the carbon content of the residual austenite, following the rapid termination of the bainite reaction. They are calculated from experimentally measured length changes (appendix 1) and the size of the error bars reflects the uncertainty in x_γ due to a corresponding uncertainty in the parameter s, as indicated in the appendix 1. Metallographic examination confirmed that for the times taken to reach the upper flat portions of the transformation curves of Fig. 1a, the transformation product was solely bainite.

The results of Fig. 1 are consistent with the existence of an incomplete reaction phenomenon, (since transformation to bainite ceases well before the carbon content of the residual austenite reaches the Ae_3'' or Ae_3' curves) and with the rapid initial reaction observed by Lyman and Troiano. The analysis presented in Appendix 1 shows the low volume fractions of bainite involved in this initial stage of austenite decomposition. In steels such as the one used in the present work, where carbide precipitation cannot be avoided, it is important to conduct experiments at temperatures where little bainite can form, in order to minimise the role of carbides in removing carbon from the reaction system (see appendix 1).

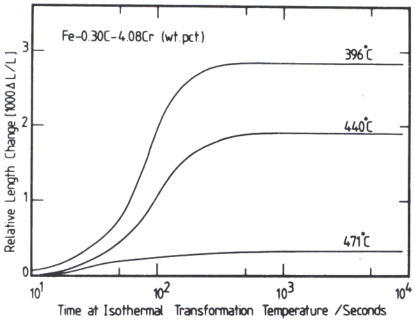

Fig. 1a - Isothermal Transformation curves

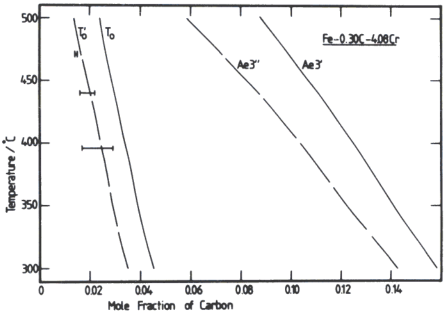

Fig. 1b - Extrapolated Phase boundaries

In none of the present experiments did the volume fraction of bainitic ferrite exceed 0.3. The experiments can be interpreted (Ref. 2) to be in agreement with the growth of bainite occurring by the propagation of martensitic sub-units, since the degree of transformation obtained complies approximately with the T_o or T_o' curves.

Examination of a specimen isothermally transformed at 478°C for 43 days (before finally quenching to ambient temperature) revealed that although the bainite transformation had ceased after about 30 minutes, at least two different diffusional transformations could be detected (one of these, the formation of alloy-pearlite from austenite grain boundaries is not further discussed). This is not unexpected, since Fig. 1 indicates that there is considerable scope for the diffusional decomposition of the austenite which remains untransformed following the termination of the displacive bainite reaction. Fig. 2 illustrates this effect very clearly; under the influence of the prolonged isothermal heat-treatment, the bainite-austenite interfaces degenerate into a series of perturbations, and accomplish diffusional transformation to ferrite - the formation of these regions did not lead to any invariant-plane strain shape change effects (Fig. 2 - the extent of the shape change as illustrated in Fig. 2b is smaller than the extent of the region of ferrite, as illustrated in Fig. 2c). EDAX analysis (See Ref. 8 for experimental details) in the electron microscope (Table I) indicated that the perturbations grew without any substitutional-element partitioning. The ferrite corresponding to the perturbations was found to be in the same crystallographic orientation as the original bainite itself. Despite all this, it took 43 days for the perturbations to develop (and accomplish roughly the same degree of transformation as the bainite, which formed very rapidly - see Fig. 1a), and the results indicate that the growth of the perturbations must be interface-reaction controlled. This is consistent with an earlier conclusion that there is insufficient thermal activation available at the temperatures where bainite forms to rapidly achieve diffusional growth, and also explains the very wavy morphology of the perturbations. Growth under diffusion control should give rise to uniform morphologies (e.g. cementite growth).

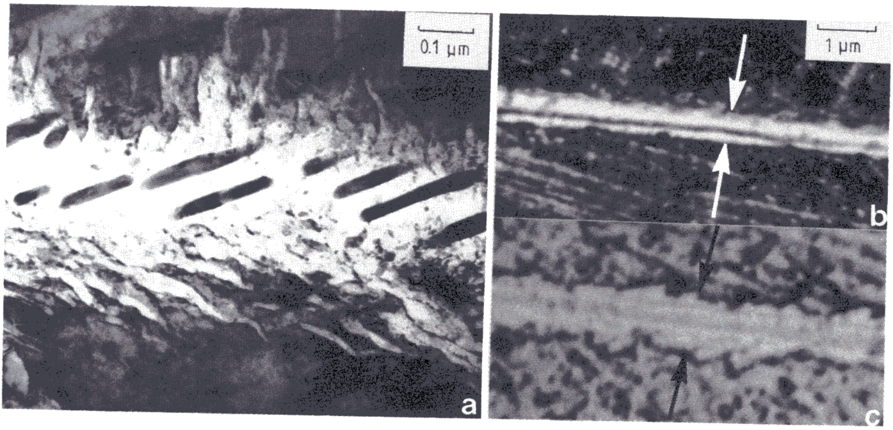

Fig. 2a - TEM micrograph of lower bainite whose original interface with the γ has degenerated into perturbations.

Fig. 2b - Normanski differential interference micrograph showing surface relief due to the bainite units.

Fig. 2c - corresponding optical micrograph showing that the relief effects of (b) do not extend to the perturbations.

Table I. EDAX analysis (Broadened beam diameter ∿ 40nm)

wt.pct.Cr in ferrite of perturbations	wt.pct.Cr in Adjacent Bainitic ferrite
3.8 ± 0.4	4.2 ± 0.4
4.3 ± 0.4	3.9 ± 0.5
4.3 ± 0.4	4.4 ± 0.3

Conclusions

The present results are consistent with those of Lyman and Troiano, and with the contention that bainite sub-units grow martensitically. The observation of diffusional transformation very much after the rapid termination of the bainite reaction shows that the incomplete-reaction phenomenon does not arise due to some restriction to diffusional growth.

The incomplete-reaction effect leads to the immobilisation of the original glissile bainite-austenite interfaces, since further transformation can only be achieved by the development of perturbations which grow 'normal' to the original bainite-austenite interfaces, and which accomplish diffusional transformation to ferrite (no accompanying surface-relief effects). Thus, diffusional transformation does not cease following the termination of the bainite reaction, and care has to be exercised in distinguishing between the various reactions in any study of the incomplete-reaction phenomenon.

Appendix 1. Interpretation of the Dilatometric Results

This appendix is concerned with the estimation of the carbon content of the residual austenite as a function of the experimentally determined dilatometric length changes. All concentrations are in wt.pct., and the following notation is used:

$\ell_{\alpha,\gamma}$ = Linear expansivities of α,γ, determined to be 1.1826×10^{-5} and 1.8431×10^{-5} respectively.
$\bar{x}, x_{Cr}$ = Average alloy carbon and chromium contents respectively.
x_γ = Carbon content of the austenite.
$\bar{a}_\gamma, a_\gamma$ = Lattice parameter of γ, at reaction temp., at the beginning of reaction and at any stage of the reaction, respectively.
$\bar{a}_\alpha$ = Lattice parameter of α, at ambient temp. (25°C) measured to be 2.861 - 2.866 A° (X-ray diffraction).
a_α = Lattice parameter of α at reaction temperature.

The ambient temp. γ lattice parameter was taken to be $(3.555 + 0.044x_\gamma)$ or $(3.573 + 0.033x_\gamma)$, according to Ref. 9. These are henceforth referred to as $(C_1 + C_2x_\gamma)$. C_3 = variation in a_γ with chromium content (Ref. 9).

S = carbon locked up in ferrite, either as carbides or in solution.
V = volume fraction of ferrite.
$d\ell/\ell$ = length change per unit length.
T = temperature in °C.

$$\text{Now, } (d\ell/\ell) = \left[2V(a_\alpha^3) + (1-V)(a_\gamma^3) - \bar{a}_\gamma^3\right] / \left[3\bar{a}_\gamma^3\right] \tag{1}$$

$$a_\alpha = \bar{a}_\alpha(1 + \ell_\alpha\left[T-25\right])$$
$$\bar{a}_\gamma = (C_2 + C_1\bar{x} + C_3x_{Cr})\;(1 + \ell_\gamma\left[T-25\right])$$
$$a_\gamma = (C_2 + C_1\;\{(\bar{x}-VS)/(1-V)\} + C_3x_{Cr})(1+\ell_\gamma\left[T-25\right])$$

Noting that $x_\gamma = \bar{x} + V(\bar{x}-S)/(1-V)$, (1) can be solved iteritively to give x_γ from $d\ell/\ell$ measurements. The value of S is uncertain, but was varied between 0.03 - 0.20. The error bars of Fig. 1b arise because of the various values of S, C_1,C_2 and a_α used in the calculations.

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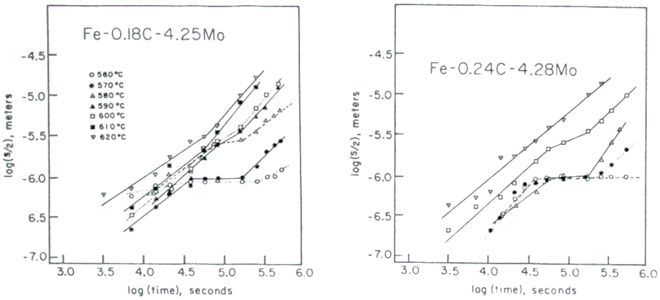
DISCUSSION

G. J. Shiflet (University of Virginia, Charlottesville, Virginia) and H. I. Aaronson (Carnegie-Mellon University, Pittsburgh, Pennsylvania): Inasmuch as one of the purposes of these Proceedings is to expose phase transformations researchers to a wide range of phenomena of current interest, it is important that compensation be made for the limited space available by providing readers with references to in-depth reviews of the particular phenomena under consideration. The references cited do not achieve this goal. However, refs. (10-12) do provide extensive access to the voluminous literature on incomplete transformation in steel. On a finer scale, we are pleased that Dr. Bhadeshia found our Lever Rule-based criterion for the occurrence of incomplete transformation (4) worth adopting as is, and our definitions of T'_o and Ae3' (13) useful, with some variations, for his purposes.

Although Dr. Bhadeshia expresses displeasure with our criticisms of dilatometry for delineating incomplete transformation (4), he nonetheless continues to use this technique with only the support of a suppositious analysis. A more satisfactory response would have been a comparison of the dilatometric data on fraction transformed to bainite with those obtained from quantitative metallography on specimens of the same alloy reacted within the same time range at one or more of the temperatures (particularly 471°C) utilized in the present study.

The evidence presented in this and in a previous paper (2) for the growth of bainite "by the propagation of martensitic sub-units" is not only highly indirect but is also based upon some curious thermodynamics; the latter will be the subject of a subsequent discussion. Such evidence can hardly be described as a contribution to critical testing of this mechanism (which was, incidentally, probably first proposed in this form by Oblak and Hehemann (14)). Kinsman and Aaronson (4), on the other hand, did attempt to test this mechanism directly through measurements of growth kinetics made with thermionic electron emission microscopy (THEEM). Their results provided no support for the mechanism. However, the resolution of THEEM is somewhat marginal for this purpose. A more thorough search for high-velocity growth kinetics with hot-stage TEM is now much in order.

Also on the basis of limited and indirect evidence, Dr. Bhadeshia concludes that "the incomplete-reaction effect is not a manifestation of some restriction to diffusional growth". Discussion Fig. 1, constructed from data obtained



Discussion Figure 1

Variation of the logarithm of the half-thickness of grain boundary allotriomorphs with the logarithm of the isothermal reaction time in two Fe-C-Mo alloys at various temperatures. Note temporary cessation of growth at some temperatures in both alloys. (ref. 17)

through application of a technique for measuring the growth kinetics of grain boundary allotriomorphs (15,16,) shows a temporary but complete cessation of the growth of ferrite allotriomorphs densely arrayed with carbides (17). Allotriomorphs were effectively the only ferrite morphology present. The allotriomorphic morphology usually does not yield invariant plane strain surface relief effects (18). Additionally, we do not accept the view that such relief effects, even if formed, provide sufficient evidence to prove that the transformation mechanism is shear (19,20). Nevertheless, an effort will be made to examine the surface reliefs associated with allotriomorphs whose growth kinetics are of the type shown in Discussion Fig. 1.

We remind Dr. Bhadeshia that there is no direct, i.e., TEM evidence presently available for a glissile misfit dislocation structure on the broad faces of ferrite (bainite) plates. The evidence of high resolution TEM is, instead, that these interfaces have a sessile dislocation structure (21). Dr. Bhadeshia's remarkable conjecture that this structure is glissile at temperature but changes (by means of an unspecified mechanism) to a sessile structure during quenching (2) is presently being considered, with conclusions to be reported soon.

Finally, we take note of the extraordinary suggestion that "growth under diffusion control should give rise to uniform morphologies". The author could surely peruse to advantage the paper by Sekerka and Marinis (22) in these Proceedings, wherein the "very wavy" morphologies which can arise from diffusion-controlled Mullins-Sekerka instability are reviewed in detail. This is not to question, of course, the very good possibility that the barrier to growth posed by a sessile misfit dislocation structure, which must be evaded through the ledge mechanism when the precipitate and matrix have significantly different crystal structures (19,23), has much to do with the observed waviness of bainite at late reaction times (Fig. 2).

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Author's Reply: The criticisms of Shiflet and Aaronson are in general rather vague, but the following points require comment:

1) There are no fundamental objections to the proper use of dilatometric techniques in the study of the incomplete reaction phenomenon. It should also be noted that such work has also been backed by atom-probe and lattice imaging measurements (24,25).

2) Detailed comment on the data presented in Discussion Fig. 1 is not possible until full publication. Among other things, it is not clear that the authors refer to transformation products which exhibit an invariant-plane strain surface relief (which has a significant shear component).

3) Rigsbee and Aaronson's conclusion that they observed sessile interfaces (21) is not justified - the curved interfaces they observed are necessarily glissile. Furthermore, the surface relief effects are consistent with the existence of glissile interfaces.

4) Shiflet and Aaronson seem to have missed the point that the growth rate of the perturbations discussed in the main paper is many orders of magnitude smaller than that expected under carbon diffusion control (43 days to grow a perturbation of length ∿ 0.5 microns) - the Mullins and Sekerka approach does not therefore apply. Actually, careful study of perturbation theory would demonstrate that perturbations need not develop even if growth is diffusion controlled (e.g. if capillarity effects dominate).

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