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THE INCOMPLETE BAINITE REACTION : POSSIBLE REASONS FOR THE APPARENT DIFFERENCES IN TEM AND ATOM PROBE DETERMINATION OF AUSTENITE CARBON CONTENT

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Abstract. - Carbon segregation following the transformation of 0.43C 2.02Si 3.00Mn and 0.39C 2.05Si 4.09Ni (wt.pct.) steels to bainite has been studied by both atom probe and TEM lattice fringe techniques. The inferred carbon concentrations in the retained austenite are in general agreement with the theory that bainitic ferrite grows with the parent austenite carbon content (i.e. fully-supersaturated). However, "indirect" lattice fringe measurements suggest a broader spread for the carbon contents than the "direct" atom probe results. In this paper, we present further confirmatory data using the former approach and investigate the possible causes for the apparent inconsistency between the techniques. In particular we consider in detail the effect of the retained constrained elastic strains, associated with the transformation, on the TEM results.

1. Current Evidence for the Incomplete Bainite Reaction

The determination of the carbon content of bainitic ferrite directly during its formation would provide unequivocal evidence for the way in which it is formed in a steel. While this would not appear to be practicable, Bhadeshia and Edmonds (1,2) have shown that measurement of the carbon content of retained austenite, at the completion of the bainite reaction, can provide indirect evidence for the mode of transformation. The essential question to be answered is whether the bainite grows with a full supersaturation of carbon (with subsequent carbon rejection) or alternatively with either partial supersaturation or equilibrium carbon levels and diffusion controlled growth kinetics. Reaction by the former route (essentially martensitically) would only be thermodynamically possible below a temperature T_o (3) which can be defined as that at which the austenite and ferrite with the same composition have equal free energies. The enrichment of the residual austenite, as a product of the post-transformation redistribution of carbon, would then lead to reaction termination when the carbon content of the austenite reaches the T_o boundary. Because the T_o carbon level is well below the equilibrium level of carbon in austenite (Ae3' see ref.4), this apparently premature reaction termination is referred to as the "incomplete reaction phenomenon" (4).

Bhadeshia and Edmonds (1) originally provided indirect evidence based on dilatometric data (2), that the carbon content of the retained austenite at reaction termination can fall far short of that which might be expected (Ae3') on the assumption of bainitic growth with intersticial (but not substitutional) element partitioning, and on or about the values to be expected for an essentially martensitic growth process. Further indirect evidence for non-diffusional controlled kinetics has been obtained by Self et al. (5) who measured the relative lattice parameters of the austenite and ferrite from area to area using high resolution electron microscopy. It was also, however, shown (5) that the inferred carbon contents of the austenite showed considerable scatter between the T_o and Ae3' values. The complete way in which a bainite

sheaf develops (1,4) can be expected to lead to an inhomogeneous distribution of carbon (4,6) but the breadth of the inferred carbon contents (5) demands a critical study of the assumptions made in the TEM approach. Electron microscopical methods for measuring the carbon content are bound to rely, for example, on the assumed constancy of the ferrite lattice parameter, and the lack of retained elastic strains in the foils. Bhadeshia and Waugh (4,6) consequently undertook atom probe measurement of both the carbon and substitutional element segregation in the two steels previously examined by electron microscopy (5). The direct measurements of carbon contents obtained in this way showed somewhat less scatter than had been inferred from the previous preliminary results, but sufficient to prompt a further analysis of whether or not ferrite growth might occur with partitioning at partial supersaturation. This was, however, shown not to be justifiable, both on grounds of growth stability and on the basis of a detailed thermodynamic analysis of experimental results (4,6,7). Furthermore, comprehensive electron microscopical data have also now been obtained for one of the steels previously examined by this method (5). This was done with the aim of both making a fuller comparison of the results obtainable by improved techniques of indirect lattice measurement and the direct atom probe method, and to see whether or not the two approaches suggest substantially different carbon variability from place to place in the austenite. Our earlier work (5) using transmission electron microscopy was concerned primarily with the analysis of the accuracy with which the measurement of lattice fringes can give interplanar spacings and so specify spatial variation in the concentrations of alloying elements. It was noted that the best way of obtaining an accurate measure of a lattice spacing for a finite region involves averaging the lattice fringe spacings for a through focal series (a point which does not appear to have been appreciated in some earlier work, e.g. (8)). This is necessary because of the rapid variation of the objective lens transfer function, in the vicinity of the Bragg angle, with defocus. It is for this reason that non-axial imaging can provide lattice fringe spacing data showing less spread than values obtained axially. Here we present both the old (5) and new data obtained by transmission electron microscopy and compare them with the results obtained by atom probe techniques on the same steel (4,6). The results described were obtained for a steel of composition Fe-0.39C-2.05Si -4.08Ni, wt.pct. austenitised at 1100°C for ten minutes prior to it being isothermally transformed at 340°C for an hour. This heat-treatment ensures that the bainite reaction reaches termination (7). The values of the carbon contents of the austenite obtained by electron microscopy were inferred assuming both that the ferrite lattice can be taken as an internal standard (a_α = 0.28664nm) and that the austenite lattice parameter a_γ varies with carbon content in wt.pct (x_γ) as described by Roberts (9):

$$a_\gamma = 0.3555 + 0.0044x_\gamma \qquad (1)$$

It may be seen from figure 1 that while the new TEM values are consistent with the older data, the random errors for each of the TEM results are rather larger than those for the direct measurements using the atom probe technique. More interestingly, it is clear that the spread in the results obtained by electron microscopy is both greater than would be expected given the measured random error for each value and greater than for the atom probe results. Since the lattice fringe technique can be readily used to provide significantly more data than can be reasonably obtained using atom probe methods, it is important to analyse all possible reasons for any systematic differences between the approaches.

2. The Relative Spread of Atom Probe and Lattice Fringe Data

In comparing the relative spreads for the two sets of data it is immediately relevant that Bhadeshia and Waugh (4) demonstrated that the carbon content of the ferrite (as measured using the atom probe) can be well above its equilibrium value, and as high as ∪.8 wt.pct. This clearly casts doubt on the use of the ferrite lattice spacing as a reference standard in the indirect TEM approach. It would seem, however, that less than 1 at.pct. (or ∿0.3 wt.pct.) of the TEM inferred spread in carbon levels could have its origin in any such variability of ferrite lattice parameter. Indeed, it is likely that such high carbon levels in

the ferrite were obtained from regions where there were dislocations (4,10) and such regions are generally avoided in making lattice fringe spacing measurements (5). It should however be appreciated that the ferrite lattice fringe spacing measurements are more difficult to obtain than those for austenite (and could not be obtained by the potentially more accurate CBED technique because of the high dislocation density (5)). It is clear however that the ferrite here provides a far more reliable standard than has been used in earlier work (11) on a related carbon segregation problem in a steel when a martensite with an assumed carbon content was utilised. Barnard et al. (10) took the uncertainty in the martensite reflections used to be the reason for the broad spread of previous data (11) which they took to be consistent with their atom probe results (10).

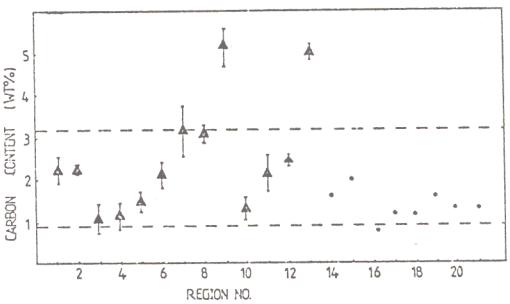

Fig.1 Comparison of lattice fringe (▲) and atom probe (●) determination of the carbon content of retained austenite in Fe-0.39C-2.05Si-4.08Ni(wt.pct.) isothermally transformed at 340°C. The dashed lines correspond to the T_o and Ae_3' carbon contents. The errors in the atom probe results are of comparable size to the circles. The new TEM results are 1-9, the old values are comparable, from (5), and are the values 10-13. The atom probe results, 14-21, are from (6) and included for comparison.

It will also be noted that two of the austenite carbon contents inferred from the lattice fringe measurements lie above that which should be possible on the basis of equilibrium partitioning assuming no substitutional element segregation. Neither result can be explained on the basis of either random error or any lack of constancy of the ferrite lattice spacing. In this connection it will be remembered (1,2) that silicon is added to the alloy examined to prevent the formation of carbides. However, the measured values of local (on an atom probe scale) silicon contents (6) showed scatter perhaps greater than that expected statistically. If there is local variation in the substitutional element level, then some variation in the appropriate Ae3' and T_o lines would be expected, but their movement is insignificant. There thus does not appear to be any consistent thermodynamic explanation for the two high carbon levels inferred from the TEM results. We do not wish to speculate on the potential mode of carbide formation in this material, but a single carbide was observed in one of the many foils examined. There are, in fact, two ways in which the inferred high carbon contents measured could have been obtained. The first of these is that some form of "carbide nucleus" of dimensions less than approximately $\frac{1}{4}$ of the foil thickness lay in the region examined (12). The second is that the local regions examined which were small and relatively equiaxed, retained constrained strains associated with the transformation greater than those which might be expected (see below) in which case the carbon levels inferred would be incorrect. It is also presumably significant that, because of the need for a comparison of ferrite and austenite lattice fringe spacings in a single micrograph, there is a systematic tendency to examine smaller regions of austenite than the average when using the TEM approach.

A more interesting potential reason for the greater spread of the indirectly (TEM) inferred carbon data lies in the possibility that the ferrite and austenite are relatively strained during the transformation, and that these strains are retained, in perhaps modified form, in the thin foils examined, thus invalidating the use of equation (1) for the inferred carbon contents. It should be noted

that random bending of foils does not provide a significant or systematic variability of the lattice fringe spacings which are necessarily obtained for regions of very uniform orientation (5). Limiting values for the elastic strains associated with the transformation can be obtained under a number of simplifying assumptions, provided that the stress free transformation strains, ε_{ij}^{T}, are known, using the prescriptions derived by Eshelby(13). Using his notation for the transformation of an oblate spheroid with a = b>>c and $\varepsilon_{11}^{T} = \varepsilon_{22}^{T} = \frac{\Delta}{3}$, $\varepsilon_{33}^{T} = \frac{\Delta}{3} + \zeta$ and $\varepsilon_{13}^{T} = \varepsilon_{31}^{T} = \frac{S}{2}$, the "constrained strains", ε_{ij}^{C}, may be obtained using a matrix of coupling constants, $S_{ijk\ell}$, from the ε_{ij}^{T}, since, using the repeated suffix notation:

$$\varepsilon_{ij}^{C} = S_{ijk\ell}\varepsilon_{k\ell}^{T} \qquad (2)$$

The appropriate values for the $S_{ijk\ell}$ for an oblate spheroid have been worked out by Christian (14). The elastic strains in the surrounding matrix fall away rapidly with distance from the transformed region, and for an infinite body have zero average value. The elastic strains within the inclusion, $\varepsilon_{ij}^{I} = \varepsilon_{ij}^{C} - \varepsilon_{ij}^{T}$, are however uniform for an inclusion of ellipsoidal shape and are necessarily associated with average strains in the matrix, in a finite body, of magnitude $\langle\varepsilon_{ij}\rangle_M$, which for our purposes (neglecting differences in the assumed isotropic elastic constants, and particle interactions important at high volume fraction (f)) may be taken to be given by:

$$\langle\varepsilon_{ij}\rangle_M \simeq -f\varepsilon_{ij}^{I} \qquad (3)$$

Thus for an oblate spheroid we find that:

$$\varepsilon_{11}^{C} = \varepsilon_{22}^{C} = \frac{\pi\Delta(1+\mu)}{12(1-\mu)}\frac{c}{a} - \frac{(1-2\mu)\pi\zeta}{8(1-\mu)}\frac{c}{a}$$

$$\varepsilon_{33}^{C} = \frac{\Delta(1+\mu)}{3(1-\mu)} - \frac{\pi\Delta(1+\mu)}{6(1-\mu)}\frac{c}{a} + \zeta - \frac{(1-2\mu)\pi\zeta}{4(1-\mu)}\frac{c}{a} \qquad (4)$$

$$\varepsilon_{13}^{C} = \varepsilon_{31}^{C} = S - \frac{(2-\mu)\pi S}{8(1-\mu)}\frac{c}{a}$$

whence:

$$\varepsilon_{11}^{I} = \varepsilon_{22}^{I} = \frac{\pi\Delta(1+\mu)}{12(1-\mu)}\frac{c}{a} - \frac{(1-2\mu)\pi\zeta}{8(1-\mu)}\frac{c}{a} - \frac{\Delta}{3}$$

$$\varepsilon_{33}^{I} = \frac{2\Delta\mu}{3(1-\mu)} - \frac{\pi\Delta(1+\mu)}{6(1-\mu)}\frac{c}{a} - \frac{\pi(1-2\mu)\zeta}{4(1-\mu)}\frac{c}{a} \qquad (5)$$

and $$\varepsilon_{13}^{I} = \varepsilon_{31}^{I} = \frac{-\pi S(2-\mu)}{8(1-\mu)}\frac{c}{a}$$

μ being Poisson's ratio.

It is generally assumed in invariant plane strain transformations of this type that $\Delta = 0$ and appropriate values for the other ε_{ij}^{T} are given by $S \simeq 0.24$ and $\zeta \simeq 0.016$ (15) and we thence find (taking $\frac{c}{a}$ as 0.02 (1) and $\mu \simeq 0.29$) that $\varepsilon_{11}^{I} = \varepsilon_{22}^{I} = -7.3 \times 10^{-5}$ and $\varepsilon_{33}^{I} = -14.6 \times 10^{-5}$. For a transformation which has proceeded to f = 0.5 the average matrix strains would be very approximately half the above values, and tensile in nature.

Several points are immediately apparent. Firstly, if these were in fact the principal elastic strains in a thin foil, the errors resulting from the use of equation (1) in assuming a relationship between the lattice parameter and the carbon content would amount to less than 0.01 wt.pct. and are thus negligible in comparison with the spread of values obtained experimentally. Even if, as is probable, the production of a thin foil leads to increases in the retained strain in the plane of the foil, it is unlikely that any errors from this origin could be greater than 0.1wt.pct. Secondly, it is worth noting that a transformation in which the scaler part of the dilatation, Δ, is zero results in elastic volume

changes of both inclusion and matrix, and the associated stresses would be expected to be partially relieved by carbon diffusion subsequent to the ferrite growth.

The retained values of the elastic strains in the inclusion are of course small in this analysis, precisely because the transformation proceeds in such a way that the shape of the resultant particle minimises the retained elastic energy as has been discussed by both Eshelby (16) and Christian (17). The conclusions arrived at above are, however, significantly altered if Δ were to have a finite value, since a low value of $\frac{c}{a}$ does not reduce strains in the particle associated with the scaler Δ. Indeed, as has been noted by Christian (17), the retained elastic energy is slightly reduced if Δ is negative. While there is no a-priori reason to assume that the transformation proceeds in such a way that the elastic energy is minimised, the value of Δ which would allow this would, again, not alter the accuracy of equation (1) significantly.

If we were to take the alternative approach of assuming that the transformation might proceed across an elastically unstrained plane, so that $\varepsilon_{11}^{I} = \varepsilon_{22}^{I} = 0$, this would require $\Delta \simeq -2 \times 10^{-4}$, under which circumstances the retained strain energy would be reduced by only about 0.01%. Again, minimal errors arise in the use of equation (1) for inferring carbon contents from lattice fringe measurements. It should be noted that, while considerable confusion remains in the literature on the interpretation of experimental measurements of Δ, necessarily made at free surfaces, Muddle et al. have concluded that Δ was not larger than 0.02% for the system they examined (18), though it would also appear that transformations in different steels can give significantly different values of Δ (18).

It will be clear that if plastic relaxation does not occur, $\varepsilon_{13}^{I} = \varepsilon_{31}^{I}$ would be considerably larger than the values of the strains perpendicular and parallel to the ellipsoid's face, and of the order of 1 pct. or more with comparable changes in lattice parameter locally around the transforming region. Analysis of the stresses associated with the transformation indicates, however, that plastic relaxation would occur during the growth of the ferrite to partially relieve the resultant stresses. The relaxation process would <u>not</u> be complete during growth in the incomplete bainite reaction in that the local forrest hardening of the austenite would progressively inhibit further relaxation (19) unless this could occur diffusionally. In the context of the measurement of the retained elastic strains and their effect on the accuracy of inferred carbon contents, diffusional relaxation of the shear strains would seem to be likely by interfacial shape changes only <u>after</u> the growth process is complete.

We may summarise this discussion by saying that it is extremely unlikely that the difference in spread between the inferred carbon contents from TEM data and those obtained directly by atom probe techniques can be explained by any elastic strains associated with the transformation. It would seem to be more likely that the differences in the two sets of results are real, and have their origin in the rather different non-random area sampling procedures associated with the two methods.

It should, however, be noted that the approach presented is not applicable to the effects which might occur at more equiaxed regions of retained austenite which can arise if termination is at high volume fractions of ferrite.

In conclusion, the above analysis has allowed us to calculate reasonably realistic values for the elastic strain energy retained during the growth process if this proceeds by the incomplete bainite reaction, for which only partial plastic stress relaxation is appropriate. The T_o' and T_o'' values shown in figure 2 are for zero and equilibrium plastic relaxation of the elastic strain energy, neglecting the effect of differences in the volume fraction of retained austenite on the stress systems.

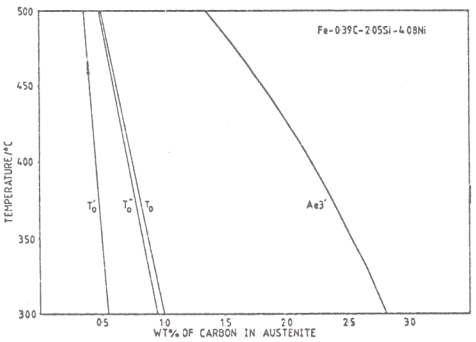

Fig.2 Phase diagram to show the relative positions of the T_o' (unrelaxed), T_o'' (relaxed) and Ae_3' lines.

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