AN ATOM-PROBE STUDY OF BAINITE

H.K.D.H. Bhadeshia and A.R. Waugh

Department of Metallurgy and Materials Science
University of Cambridge
Pembroke Street, Cambridge CB2 3QZ, U.K.

An imaging atom-probe combined with a high mass-resolution energy-
compensated time-of-flight spectrometer has been used to study localised
composition changes at the interfaces whose motion leads to the formation of
bainite in steels. 'Bulk' compositional analysis of the retained austenite
and bainitic-ferrite has also been carried out, and the results are inter-
preted in terms of a new thermodynamic analysis, which allows better dis-
tinction between diffusion-controlled growth involving the formation of
bainitic-ferrite with a partial supersaturation of carbon, and that in which
the ferrite grows with the precise composition of the parent austenite (i.e.
in essence martensitic). The fine scale distribution of substitutional
alloying elements (Si,Ni) has also been examined. It is believed that the
results can be best understood in terms of the martensitic growth of bainite
sub-units.

In considering the bainite reaction, it does not seem possible to
directly measure the carbon supersaturation that existed in the bainitic-
ferrite during growth, since carbon can be rapidly redistributed immediately
after transformation. The carbon concentration can, however, be indirectly
deduced by measuring the composition of the austenite that remains un-
transformed after the cessation of the bainite reaction (1). The details
have been discussed elsewhere (1,2), but it is pertinent to define the Ae3',
Ae3'', T_o and T' curves. The Ae3' curve represents paraequilibrium between
the alpha and gamma phases, whose substitutional (though not the inter-
stitial) alloying element content is identical. The T_o curve defines the
temperature below which completely partitionless transformation becomes
possible; the Ae3'' and T'$_o$ curves differ from their counterparts the Ae3'
and T_o curves respectively since some energy (e.g. due to strain) is
assumed to be stored in the ferrite, to a level of 400 J/mol (2). If
reaction terminates when the carbon content of the austenite (x_γ) reaches
the Ae3'' curve, then the bainite must have grown with a near paraequilibrium
(as modified by stored energy) carbon content. Bainite growth involving the
propagation of martensitic sub-units (the size of each sub-unit is limited,
for reasons discussed in Refs. 1,2), with the rejection of excess carbon
into the austenite occurring after the transformation event, would lead to
reaction termination when x_γ approximately reaches the T'$_o$ line (1). In the

present work, an imaging atom-probe (3) is used to measure the compositions
of the bainitic-ferrite and austenite in specimens where the bainite re-
action had been allowed to reach its maximum extent; because of space
restrictions, only quantitative data (rather than compositional maps, etc.)
is presented in the present work. Experimental details are similar to those
given elsewhere (4), but the alloy used (Fe-0.39C-2.05Si-4.08Ni, wt.pct.)
was isothermally transformed at 340°C for 10 hours after austenitising at
1100°C for 15 mins; the microstructure then consists of bainitic-ferrite
and carbon-enriched retained austenite (1,2).

Results and Discussion

The results of Fig. 1a demonstrate the non-uniform distribution of
carbon in the retained austenite (Fig. 1b is discussed later). The carbon
concentration in many cases exceeds that given by the T' curve, although
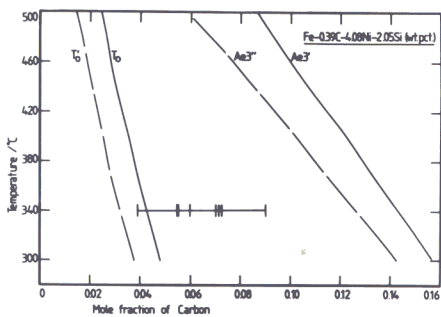the results fall below the level of the Ae3'' calculations.

Fig. 1a – Phase diagram with
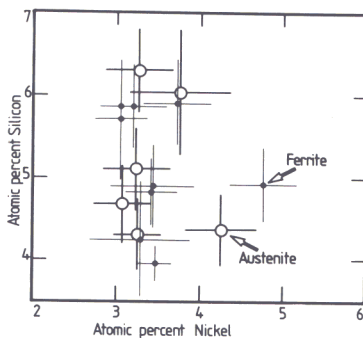   experimental x_γ values

Fig. 1b – Atom probe results on
       Si and Ni

The data can still be interpreted to be in accord with the contention that
bainite initially forms with a full supersaturation of carbon (1,2), despite
the apparent disagreement with the T' criterion. This becomes clear when it
is realised that the austenite can continue to accumulate carbon from
suitable sources, up to a maximum corresponding to the Ae3'' limit, although
it cannot then transform to fully supersaturated ferrite (5). A small
region of austenite which has already been affected by the dumping of carbon
from an extant bainite plate may become isolated by the formation of further
supersaturated platelets in close proximity. The subsequent rejection of
carbon from the latter can then raise the carbon content of the entrapped
austenite to levels beyond the T' curve. The probability of such a
sequence of events is high because of the nature of bainite sheaf develop-
ment (1).

An alternative interpretation would involve bainite growth, with only
a partial supersaturation of carbon, the rest being pushed ahead of the
transformation interface, giving diffusion-controlled kinetics. It might
be assumed that the experimental data (Fig. 1a) falls between the T' and
Ae3'' boundaries because the level of carbon in the ferrite during growth
must have been less than the average alloy carbon content ($\bar{x}$), although
greater than the corresponding equilibrium concentration. Hence some

partitioning of carbon may be assumed to occur even at the beginning of transformation, so that the actual level of excess carbon in the ferrite must, at any stage of the reaction, be less than or equal to the initial level of supersaturation (i.e. $< \bar{x}$). This is because the driving force for reaction decreases with the progress of transformation, and it becomes increasingly difficult for the ferrite to maintain the starting level of supersaturation.

Referring to Fig. 2a, it is possible (4) to calculate the interface tie-line compositions (i.e. $x_\alpha^I \rightarrow x_\gamma^I$) for growth involving partial supersaturation. The tie-line $x_\alpha^l \rightarrow x_\gamma^l$ refers to the formation of bainitic-ferrite with a carbon excess of $(x_\alpha^l - x_\alpha^{\alpha\gamma})$, with reaction termination occurring when x_γ reaches x_γ^l. If the supersaturation in the ferrite is now allowed to
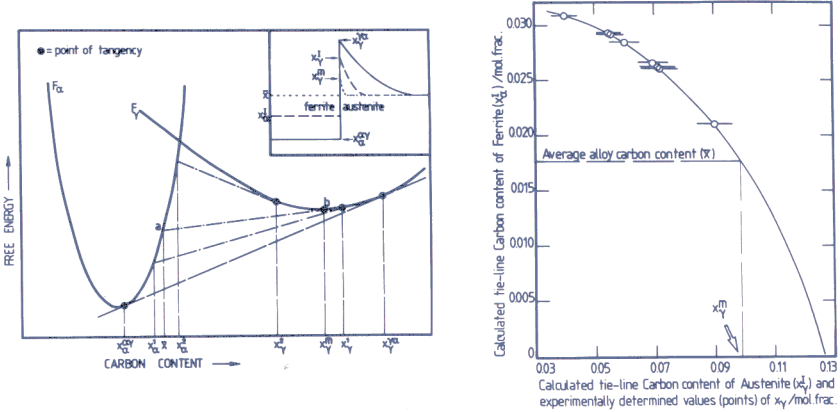

Fig. 2a – Schematic free energy curves for the analysis of growth involving partial supersaturation. Inset shows composition profiles at the interface.

Fig. 2b – Graph of x_α^I versus x_γ^I

approach $\bar{x}$, then x_γ^l tends towards x_γ^m. In the limit that $x_\alpha^l = \bar{x}$ we obtain the unexpected result that growth involving partial supersaturation must have a minimum terminal carbon level in the austenite, given by x_γ^m. Clearly, for diffusion-controlled growth, an austenite tie-line composition less than x_γ^m (e.g. x_γ^2) is physically unreasonable since it corresponds to a ferrite supersaturation exceeding $\bar{x}$! Calculations were carried out to determine sets of tie-line compositions; the results are plotted (as a curve) in Fig. 2b - the stored energy of bainite was taken to be 400 J/mol. The experimentally determined values of x_γ are also plotted in Fig. 2b such that they coincide with the theoretical curve. It is evident that the experimental data falls below x_γ^m; this would imply higher levels of carbon supersaturation in the ferrite than is physically possible, and the results must therefore be taken to be inconsistent with the hypothesis that bainitic-ferrite formation occurs with some partitioning of carbon during growth. Other reasons against such a hypothesis are discussed in Refs.2,4.

While bainitic-ferrite growth involving supersaturations less than $(\bar{x} - x_\alpha^{\alpha\gamma})$ does not seem reasonable, there is yet a third possible interpretation. In this, the sub-units of bainite may first grow martensitically, with subsequent carbon rejection into the residual austenite, until the

carbon content of the latter reaches the T'_o line. At this point, the bainite <u>could</u> start growing with a lower carbon content than the now enriched remaining austenite (although the level of carbon in the ferrite could exceed $\bar{x}$). However, such an interpretation seems unsatisfactory since there is then no clear reason why the bainitic-ferrite should not <u>continue</u> to grow with successively decreasing levels of excess carbon, until reaction stops when the austenite carbon content reaches the Ae3'' line. The latter clearly does not occur, and hence it is believed that bainite growth involving full supersaturation (i.e. each sub-unit growing martensitically) is still the most reasonable interpretation of the incomplete-reaction phenomenon, with the apparent discrepancy between the measured austenite carbon contents and the T'_o curves arising due to the incidental kinetic factors mentioned earlier. It should be noted that in considering diffusion-controlled growth, no direct account has been taken of the reduction in available driving force due to capillarity (Gibbs-Thompson) or interface reaction effects, since these should not only be small compared with the stored-energy, but would be included in the latter (Refs. 2,4).

Field-evaporation experiments were also carried out in order to study the compositional variations across the α/γ interfaces. Fig. 3 illustrates the results of one such experiment; the data are plotted as concentrations averaged over 400 ions (changing this to 100 or 200 did not alter the form of the curves, but simply increased the noise levels), versus the total number of ions collected. As expected, Fig. 3 shows that substitutional alloying elements do not redistribute during the bainite transformation, consistent with the data of Fig. 1b. Furthermore, there are no significant peaks in the levels of any of the alloying elements at the position of the interface, in agreement with some recent (4) and more detailed imaging atom-probe work on an Fe-Mn-Si-C alloy.

Conclusions

The existence of an incomplete-reaction (1,2) connected with the bainite reaction has been directly confirmed, as has the inhomogeneous distribution of carbon in the residual austenite – this latter effect had been previously (6) predicted to exist, on the basis of metallographic evidence. The measured carbon concentrations in the residual austenite have been found (using a new thermodynamic analysis) to be best understood in terms of the formation of <u>fully</u> supersaturated bainitic-ferrite, with the excess carbon being rejected into the remaining austenite <u>after</u> the transformation event.
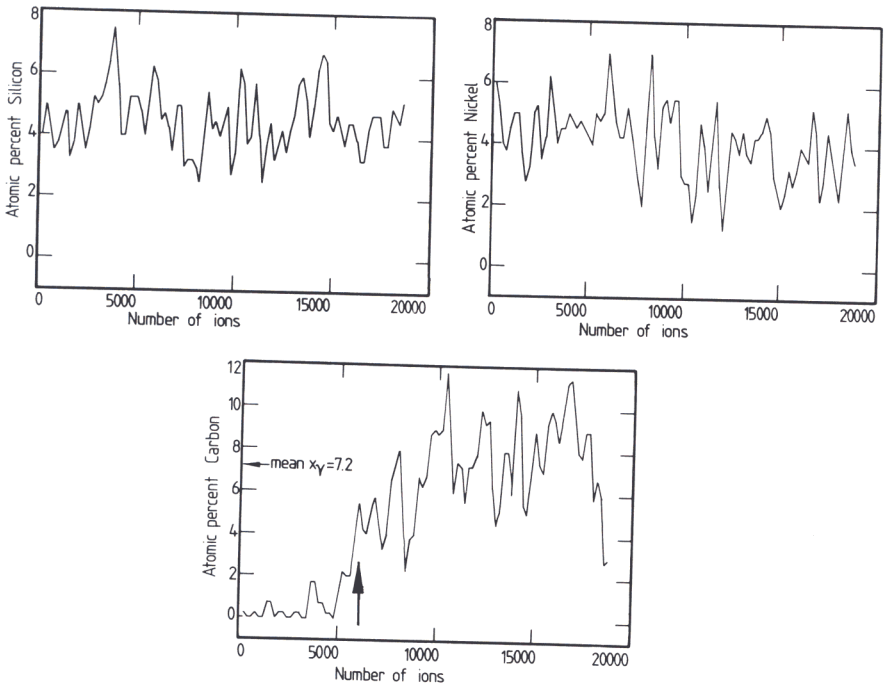
Fig. 3 - Field evaporation experiments across an α/γ interface
(approximate position of interface indicated by arrow)

Acknowledgements

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Proceedings of an International Conference on
Solid ➤ Solid Phase Transformations
sponsored by the Phase Transformations Committee
of the Materials Science Division of American Society for Metals,
and Carnegie-Mellon University,
and cosponsored by the U.S. National Science Foundation
and The Metallurgical Society of AIME,
held at Carnegie-Mellon University, Pittsburgh, Pennsylvania, U.S.A.,
August 10-14, 1981.

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