

# ***The element redistribution associated with 'the incomplete-reaction phenomenon' in bainitic steels: An atom probe investigation***

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### SYNOPSIS

Atom-probe analyses of austenite at the end of transformation to bainite in high-silicon Fe-C-Si-Mn and Fe-C-Si alloys indicate that bainitic ferrite forms with a high carbon supersaturation. There is no evidence for a solute-drag like effect inhibiting transformation, but manganese redistribution near ferrite/austenite interfaces is observed after prolonged aging at the reaction temperature.

### INTRODUCTION

The determination of the carbon concentration of bainitic ferrite during growth has so far proved impossible due to the rapid decarburisation of the ferrite after transformation. However it is possible to determine the level indirectly by observing the carbon concentration in austenite at the end of the bainite transformation (1). A composition-invariant transformation is thermodynamically impossible if the carbon concentration of the austenite ( $x_{\gamma}$ ) exceeds that given by the  $T_0$  (the symbols  $T_0$ ,  $T_0'$ ,  $Ae3'$  and  $Ae3''$  are as defined by Christian and Edmonds, (2)) curve in the phase diagram (i.e.  $x_{T_0}$ ), whereas if para-equilibrium exists at the interface during growth, then the extent of the transformation is given by the lever rule as applied to the  $Ae1'$  and  $Ae3'$  paraequilibrium phase boundaries which determine the (ferrite and austenite) phase field. Bainite is not found to satisfy this lever rule (1,3) and this is termed the 'incomplete reaction phenomenon'.

The carbon content of austenite has previously been measured using atom-probe analysis (1), X-ray diffraction (4), Mossbauer spectroscopy (5), dilatometry (3) and lattice fringe spacing (6). Of these, atom-probe (AP) analysis is the most direct and is used in the present investigation. The atom-probe can also show fine-scale variations in carbon level.

It is noted that, although composition invariant transformation is impossible when  $x_{\gamma} > x_{T_0}$ , the austenite can still accommodate more carbon and the level can be expected to exceed  $x_{T_0}$  where austenite is surrounded by plates of bainite that physically restrict post-transformation carbon diffusion. However,  $x_{\gamma}$  is still expected to be closer to  $x_{T_0}$  than  $x_{Ae3'}$ . Previous

observations have shown levels between  $T_0$  and  $Ae3'$  with an average value significantly closer to  $T_0$  than  $Ae3'$  (1). These results have been taken as evidence that bainitic ferrite is fully supersaturated during growth. Alternatively, it has been proposed that a 'solute-drag-like effect' retards an essentially diffusive transformation (7). The intermediate hypothesis that the ferrite is partially supersaturated during growth has been shown to be unlikely in view of the expected instability of such an arrangement (1), although it might be stable given a particular interface configuration (2).

To observe whether the initial reaction does stop or whether it merely becomes very slow, it is essential that bainite formation clearly ceases before another decomposition process begins. Apparent uncertainties as to whether the effect exists have arisen through the use of alloys in which individual reactions are difficult to separate. A further condition that must be satisfied if the phenomenon is to be unambiguously identified, is that the product forming below the bay is bainitic ferrite and not Widmanstätten ferrite. The latter appears to be the case in Fe-C-Mo ternary alloys (8) and considerable confusion has arisen from failure to appreciate this.

There has been one previous atom-probe study of the incomplete reaction in which a Fe-0.43C-2.12Si-3.00Mn wt% alloy was used. The silicon prevented carbide formation at the temperatures of interest so that only ferrite and austenite are present, thereby simplifying interpretation. Manganese was added to ensure that no transformation temperature was reached. This study showed that the austenite carbon levels associated with incomplete reaction are significantly below  $Ae3'$  and that there is no silicon enrichment of the interface. However, the resolution of the instrument did not allow possible manganese effects to be investigated. The present study continues this work using a high-resolution atom-probe in which the manganese distribution can be unambiguously determined. The effect of an increased bulk carbon content on the level of carbon retained in the ferrite in a Fe-C-Si-Mn alloy is also investigated. Finally, the existence and character of the phenomenon in a Fe-C-Si ternary alloy is also investigated.

### EXPERIMENTAL

The alloys used were Fe-0.83C-3.05Si, Fe-0.81C-2.4Si-3Mn and Fe-0.43C-2.2Si-2.8Mn (all compositions in wt%). The latter is almost identical to the Fe-0.43C-2.12Si-3Mn wt% alloy used in the

previous study (1). Specimens were homogenised in evacuated silica tubes for three days at 1200°C and then quenched into brine. Subsequently they were re-austenitised at 1070°C before the silica tube was broken and the specimen quenched into a salt bath. After transformation, specimens were quenched into brine. All of the bars and discs were 1 mm thick. Decarburisation was not observed in any of the samples. The specimen preparation techniques and analysis conditions are detailed elsewhere in this conference (8). The preferential evaporation effects which arise with silicon-steels (9) were countered by use of a 20% pulse fraction.

## RESULTS

### Fe-C-Si-Mn alloys

Transformation to a carbide-free upper bainite is observed to be complete within two hours in the 0.43wt% C steel in agreement with previous studies (10). Optical microscopy shows that transformation of the 0.81wt% C alloy at 275°C is complete after 60 hours, hence the analyses in table 1 below are all from specimens in which the bainite reaction has finished. In no instance was there any indication of carbide formation.

Table 1 : Composition of ferrite and austenite (atomic %±σ). Where several analyses were obtained, the values given are the weighted mean and standard deviation. Analyses are from the 0.43wt% C alloy except that after transformation at 275°C which is from the 0.81wt% C alloy.

T <sub>0</sub> (°C)	Time at T (hours)	Ferrite			Austenite		
		C	Si	Mn	C	Si	Mn
396	17	—	—	—	2.1 0.1	4.1 0.2	2.7 0.1
358	2	0.5 0.08	6.1 0.2	2.4 0.1	4.6 0.5	5.1 0.3	2.0 0.2
"	17	0.4 0.09	5.9 0.3	1.5 0.1	3.2 0.2	4.3 0.1	2.8 0.1
326	17	0.2 0.04	4.9 0.1	2.4 0.1	3.6 0.3	4.0 0.2	2.1 0.2
"	64	0.4 0.03	4.6 0.1	2.8 0.1	4.2 0.2	4.5 0.2	2.8 0.2
"	264	0.2 0.1	4.2 0.3	3.1 0.2	3.6 0.2	3.7 0.1	2.4 0.1
300	14	0.7 0.08	4.5 0.2	2.4 0.1	2.5 0.2	6.4 0.4	3.6 0.3
275	60	0.6 0.04	5.1 0.1	2.0 0.1	12.0 0.8	3.9 0.5	2.2 0.4

Excepting the single analysis at 275°C which is discussed later, the austenite carbon contents are all close to the T<sub>0</sub> values and much lower than Ae<sub>3</sub>' (fig. 1a). The carbon levels in austenite at the ferrite/austenite interface are not higher than the levels away from the interface. The ferrite contains significant carbon supersaturations and  $\chi^2$ -testing of the distribution of carbon in suitably sized samples indicates that it is not random (table 2).

Table 2 : Observed carbon content (N) of 100-ion samples of ferrite formed at 275°C and that expected if carbon is randomly distributed.

N	0	1	2	3	4	5	6	7	8	9	10
Observed	665	148	64	40	18	8	7	5	4	7	3
Expected	463	343	126	30.4	5.5	$\sum > 4 = 1.1$					

Austenite and ferrite could easily be distinguished in the FIM as the former imaged dark whereas the crystallographic ring structure in

the ferrite was clearly visible. Figure 2a shows a ferrite/austenite interface after 17 hours at 358°C. There was no obvious silicon enrichment at the interface. This would have resulted in increased image brightness at the boundary (9). This was confirmed by the analyses obtained as the boundary moved across the probe hole. The analyses did however show high levels of manganese probing across the interface and corresponding manganese depletion in the adjacent ferrite (fig. 2b). This effect was observed on all of the ten separate occasions where an analysis was obtained across a ferrite/austenite interface after holding for 17 hours or longer at 358°C and 326°C. It was not apparent after 2 hours at 358°C.

In specimens aged for 17 hours or more, manganese levels 2-4 times higher than the bulk level were observed as the interface passed through the probed region. The peak levels are probably significantly higher as the analyses always contain contributions from non-boundary areas. The apparent extent of the manganese depletion in ferrite was observed to be sensitive to the angle of intersection between the boundary and the tip surface. Allowing for this, an approximate depletion-layer width in the ferrite of 3-5 Å was deduced. Depletion was more distinct after 11 days than after 17 hours at the isothermal aging temperature. A number of the interface profiles did show suggestions of a similar effect for silicon, although in this case it is the austenite that is solute depleted. Therefore, although FIM does not show this effect, its existence is tentatively proposed on the basis of the cumulative observation of composition profiles across ferrite/austenite interfaces. The bulk levels of manganese and silicon were found to be the same in both ferrite and austenite.

### Fe-0.83C-3.05Si wt% alloy

The overall transformation character of this alloy is expected to be similar to that of a Fe-0.9C-3.85Si wt% alloy studied by Papadimitriou and Genin (5) in which transformation to bainite is complete within one hour. Previous studies of high-silicon steels (5, 11, 12, 13) have also shown that, after transformation to bainitic ferrite has stopped, further decomposition may occur involving carbide formation in carbon supersaturated ferrite or in carbon-enriched austenite.

Table 3 below shows the carbon and silicon analyses obtained from this alloy. Where several analyses were obtained, the values were calculated as for the Fe-C-Mn-Si alloy.

T <sub>0</sub> (°C)	Time at T (hours)	Ferrite		Carbide		Austenite	
		at% C	at% Si	at% C	at% Si	at% C	at% Si
348	1.5	0.4 0.08	8.8 0.4	—	—	10.6 0.2	6.3 0.2
340	72	0.11 0.02	6.4 0.2	21 1.5	1.9 0.5	—	—
334	19	0.2 0.03	7.6 0.2	24 1.5	4.7 0.7	8.9 0.2	5.8 0.2
300	5	0.15 0.05	9.0 0.3	19 0.7	4.6 0.3	—	—

The existence of an incomplete reaction effect in this alloy could be observed using optical microscopy, as large regions of austenite remained untransformed after the initial rapid reaction. Transmission electron microscopy confirmed that 20-30% of the austenite remained

undecomposed after 4 days at 340°C. The austenite carbon levels at the end of bainite formation were all below Ae3' (fig. 1b), with an average value closer to To than Ae3'. The ferrite/austenite morphologies observed in the TEM indicate that carbon diffusion will frequently be restricted by adjacent ferrite (fig. 3a).

In all cases the carbon contents of the carbides were below the stoichiometric levels for cementite and epsilon carbide. In other alloys, after transformation at higher temperatures, it has proved possible to obtain the expected metal to carbon ratios for M<sub>3</sub>C and M<sub>2</sub>C. The size of the carbides and the consistency of the analyses obtained irrespective of whether the carbide plate was perpendicular to or parallel to the tip axis suggests that the low values do not result from substantial non-carbide contributions. The implication is that the analyses result from genuinely low carbon levels and are not an atom-probe artifact.

Silicon rejection from the carbide into the ferrite was observed for all of the carbides including those formed during transformation at 300°C. This effect is shown in the composition profile in figure 3b, where analyses were obtained successively from austenite, then carbide, then ferrite, after 19 hours at 340°C. The presence of a carbide at the ferrite/austenite interface is shown by the change from a carbon level of 8-9at% to one of 24at% and the rejection of silicon into the ferrite. The similar dark-imaging character of carbide and austenite made it impossible to distinguish them in the image. The four other interface analyses obtained after 1.5 and 19 hours at 340°C, showed no increase in austenite carbon content towards the boundary and a uniform silicon distribution.

## DISCUSSION

The extent of the initial reaction in both Fe-C-Si-Mn and Fe-C-Si alloys is significantly below the levels predicted by the lever-law calculation based on a final austenite carbon level of Ae3' or Ae3''.

The upper bainite transformation in a Fe-0.43 C-2.2Si-2.8Mn wt% alloy is complete within 2 hours at 326°C and there is no additional austenite decomposition apparent after 11 days at this temperature. This optical observation is confirmed by the similarity of the austenite carbon levels after the various reaction times.

The observation of the incomplete reaction effect in a high-purity Fe-C-Si alloy disproves the hypothesis that it is the result of a solute/interface interaction involving manganese (14). Incomplete reaction in a Fe-C-Si ternary has been seen before (5), but the present study provides the first complimentary direct analysis of the associated austenite carbon levels.

At the end of the bainite transformation the average austenite carbon level is closer to To than Ae3' in both systems (fig. 1). The single analysis from the higher carbon Fe-C-Si-Mn alloy was obtained from a 100A-wide band of austenite. Because diffusion is restricted by the surrounding ferrite, this high carbon level does not conflict with the diffusionless growth hypothesis.

The ferrite carbon supersaturations of 0.7at% are much higher than the calculated equilibrium levels (<0.06at% (15)) although they approach these in the Fe-C-Si alloy at 340°C as carbides form within the ferrite. The carbon distribution in carbide-free bainitic ferrite is non-random as shown in table 2. The observation of carbon levels up to 10at% and the high number of carbon-free regions is consistent with segregation at defects consistent with a defect density of  $\sim 10^{12} \text{ cm}^{-2}$ . This may be attributed either to retention at defects after rapid formation with a higher supersaturation, with the remaining carbon diffusing into the austenite, or to the incorporation into the ferrite of interface defects and their associated Cottrell atmospheres. Doubling the bulk carbon level, thereby decreasing the rate of carbon diffusion in ferrite, does not appear to significantly affect the amount retained.

The calculated diffusion distance of manganese in ferrite at 326°C is  $\sim 3\text{\AA}$  in 11 days (16) and less in austenite. Consequently, it is difficult to determine whether the high manganese levels are due to segregation to the interface or the onset of manganese redistribution as the system tends towards equilibrium. Whatever the effect, its absence after 2 hours at 358°C and its association with progressive manganese depletion of the adjacent ferrite, suggest that it happens after the ferrite has formed.

The consistency with which high interface manganese levels are observed might be considered unlikely to arise from segregation to a highly coherent bainite interface. An indication of whether it might represent an approach to equilibrium is provided by comparing the observed values with the calculated equilibrium ferrite and austenite compositions. The calculated compositions (atomic fractions) at 415°C are:

	Fe	C	Si	Mn
Ferrite	0.955	0.00007	0.043	0.002
Austenite	0.506	0.204	0.0000004	0.290

The data indicates that the mass flux of silicon from austenite to ferrite should be lower than that of manganese from ferrite to austenite and may explain why the latter is obvious whilst only suggestions of the former effect are observed. Allowing for non-boundary contributions, the observed levels of manganese are not inconsistent with the austenite immediately adjacent to the interface containing the equilibrium level of  $\sim 20\text{at}\%$ .

In the Fe-C-Si alloy, carbide formation accompanies transformation at 300°C and is a secondary process at 340°C. Previous studies (5, 11, 12, 13, 17) have shown a range of carbides in high-silicon alloys and the exact nature of those in the present study is not certain. The composition also changes during aging, as the carbide can form with at least 4-5at% silicon at 300-340°C, but then is observed to reject this into the adjacent ferrite. The value of 4-5at% is still below the bulk level and it appears that some degree of silicon rejection both accompanies carbide formation and then continues after growth has stopped.

## CONCLUSIONS

(1) The carbon levels at which austenite stops transforming to bainite in both the Fe-C-Si-Mn and Fe-C-Si alloys indicate that transformation to bainitic ferrite involves high, possibly full, carbon supersaturation. The level and range of austenite carbon concentrations detected provides strong evidence that the transformation involves shear at velocities greatly in excess of the carbon diffusion rates in austenite.

(2) The incomplete reaction phenomenon can be observed in Fe-C-Si ternary alloys if the alloying additions are sufficiently high. A uniform distribution of silicon is associated with this effect.

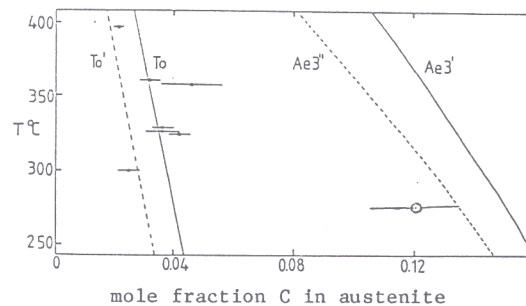
(3) The carbon supersaturations in carbide-free bainitic ferrite are greatly in excess of the calculated equilibrium levels and the distribution is consistent with carbon segregation at defects.

(4) Manganese redistribution occurs near ferrite/austenite interfaces during isothermal aging after transformation to bainite has stopped. The onset of bulk partitioning or of interface segregation are possible causes of this. Suggestions of similar silicon behaviour are also observed. Neither silicon nor manganese appear to be segregated at the interface during transformation.

(5) Silicon is rejected from the carbides formed in the range 300-340°C. This occurs both during and after carbide formation.

## REFERENCES

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(Curves for alloys containing 2.2wt%Si-2.8wt%Mn<sup>o</sup> and 2.4wt%Si-3wt%Mn<sup>o</sup> are very similar, only those for the former are shown.)

Figure 1a. 2.2wt%Si-2.8wt%Mn

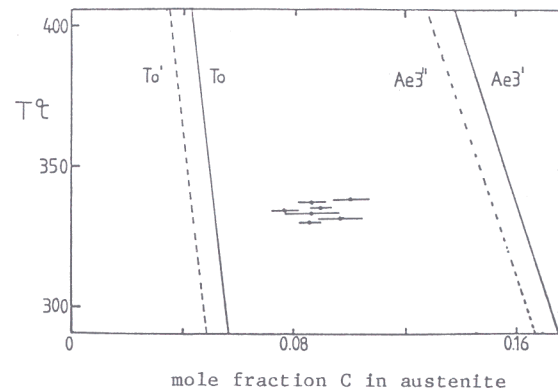


Figure 1b. 3.05wt%Si

Fig.1 Phase diagrams showing the calculated Ae3', Ae3'', To and To' values and the observed austenite carbon levels at the end of transformation to bainite.

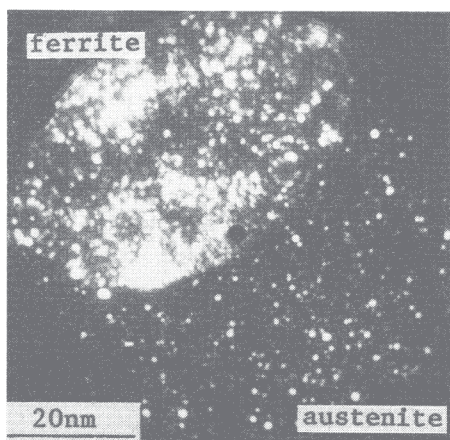


Figure 2a

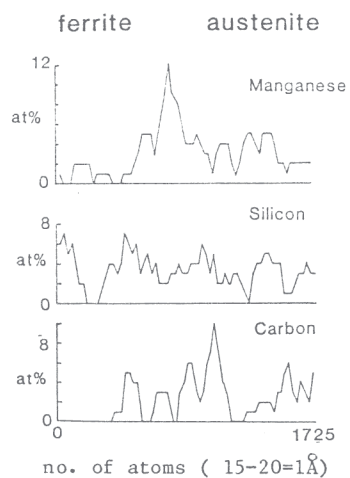


Figure 2b

Fig.2 Field-ion micrograph of a ferrite/austenite interface and the composition profile across this interface in a Fe-0.43C-2.2Si-2.8Mn wt% alloy after 17 hours at 358 C.

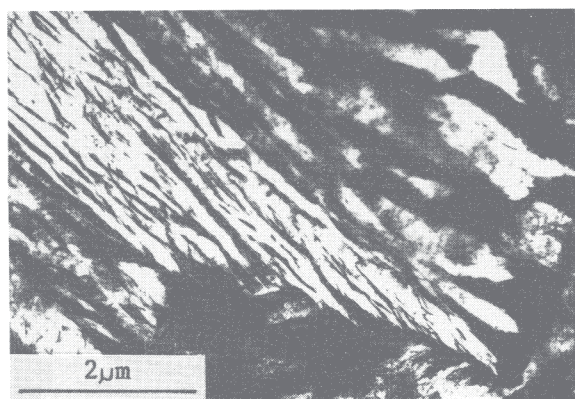


Figure 3a.  
TEM micrograph of a Fe-0.83C-3.05Si wt% alloy after 4 days at 340°C.

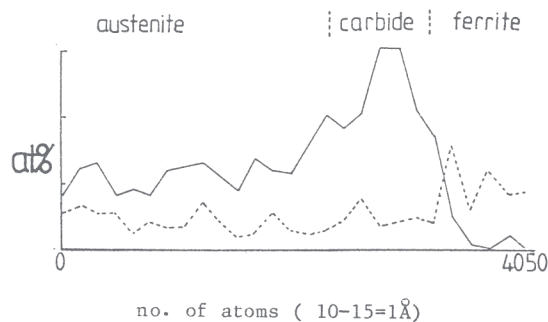


Figure 3b.  
Austenite → interface carbide → ferrite analysis in the same alloy after 19 hours at 334°C.