

# Changes in chemical composition of carbides in 2·25Cr–1Mo power plant steel

## Part 2 Mixed microstructure

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*It is found that the carbide chemistry changes at a slower rate in a mixed microstructure of bainite and allotriomorphic ferrite when compared with carbides in a fully bainitic microstructure. These results are expected intuitively and confirmed theoretically.*

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### Introduction

It has been predicted<sup>1</sup> that in theory the aging behaviour of carbides in a fully bainitic microstructure should be different from that in carbides in a mixed microstructure of bainite and allotriomorphic ferrite. This is because the bainite in the specimens containing allotriomorphic ferrite forms from carbon enriched austenite. The cementite particles should then be more closely spaced relative to a fully bainitic microstructure, so that interference between the diffusion fields of adjacent particles is expected to occur sooner. In addition, the high carbon concentration may locally modify the equilibrium state, favouring for example, a lesser saturation chromium concentration in the cementite. The enrichment kinetics of the cementite are therefore expected to be different from those in the fully bainitic microstructure.

Power plant components tend to be large in size and have to be heat treated using continuous cooling processes. This inevitably leads to variations in microstructure through the section of the component. It is common therefore, to find a variety of mixtures of allotriomorphic ferrite, bainite, and martensite in any given component. The purpose of the present work was to investigate how the changes in cementite chemical composition depend on gross variations in the starting microstructure. Experimental results from a mixed allotriomorphic ferrite–bainite microstructure are therefore compared against equivalent data on fully bainitic microstructures (reported in Part 1 of the present work<sup>2</sup>). The fully bainitic microstructure also contains small regions of martensite because the bainite reaction does not go to completion, however, it is henceforth referred to as 'fully bainitic' for brevity, following the convention used in Part 1.

### Experimental

Most of the experimental details have been reported in Part 1 of the present work,<sup>2</sup> therefore only those points specific to the mixed microstructure are dealt with here.

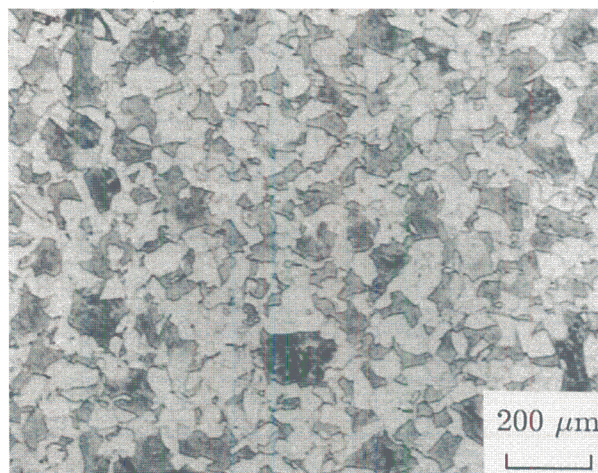
The heat treatment necessary to produce the mixed microstructure was deduced using the calculated time–temperature–transformation (TTT) diagram (Part 1). It involved austenitisation at 1050°C for 15 min, followed by holding at 700°C for 1 h to produce allotriomorphic ferrite, then further transformation at 480°C for 30 min to allow bainite to form in the residual austenite, before finally quenching to room temperature. The time for isothermal transformation at 700°C was estimated using the method

of Bhadeshia.<sup>3</sup> Thus, the thickness of allotriomorphic ferrite layers located at the austenite grain boundaries is calculated and converted into a volume fraction by relating the thickness to the austenite grain structure. Using this method, the volume fraction of allotriomorphic ferrite for the transformation conditions described above was estimated to be 0·6.

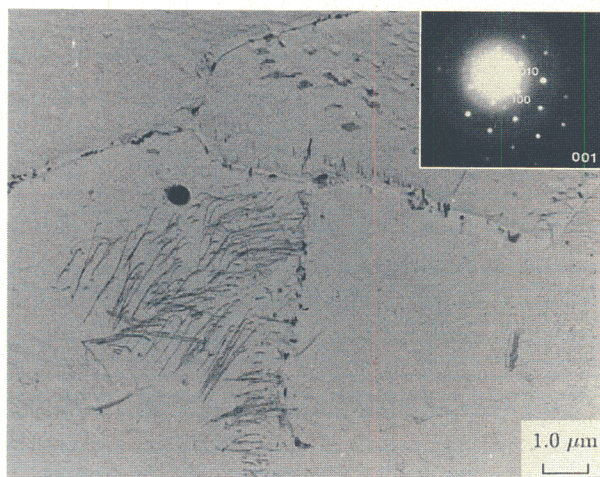
Heat treatments to generate the initial mixed microstructure were performed on the smaller 8 × 12 mm cylindrical specimens in a thermomechanical simulator. This enabled the exact heating cycle and cooling rates to be accurately programmed and recorded. The experiments were performed in vacuum; however, nitrogen gas was introduced into the chamber to quench the specimen between the transformation temperatures. An optical micrograph of the mixed microstructure specimen is shown in Fig. 1. It can be seen that the observed volume fraction of allotriomorphic ferrite is approximately 0·5, in good agreement with the predicted value.

### TEMPERING TIMES

The samples were tempered at 565°C only, because the purpose of this investigation was to determine any changes in the rate of enrichment compared with the fully bainitic microstructures rather than the effect of temperature. Tempering was carried out for times of 1, 46·5, 80, 128, and 180 h covering the range during which cementite was known to exist in the fully bainitic specimens.



1 Optical micrograph of mixed microstructure specimen – heat treated in thermomechanical simulator (austenitised 1050°C/15 min, 700°C/1 h and 480°C/30 min and gas cooled)



2 Carbon extraction replica from as transformed mixed microstructure showing fibrous  $M_2C$  carbides at ferritic/ferritic grain boundaries: inset is selected area electron diffraction pattern from cluster of  $M_2C$  fibres showing that single spot pattern is obtained

## Results and discussion

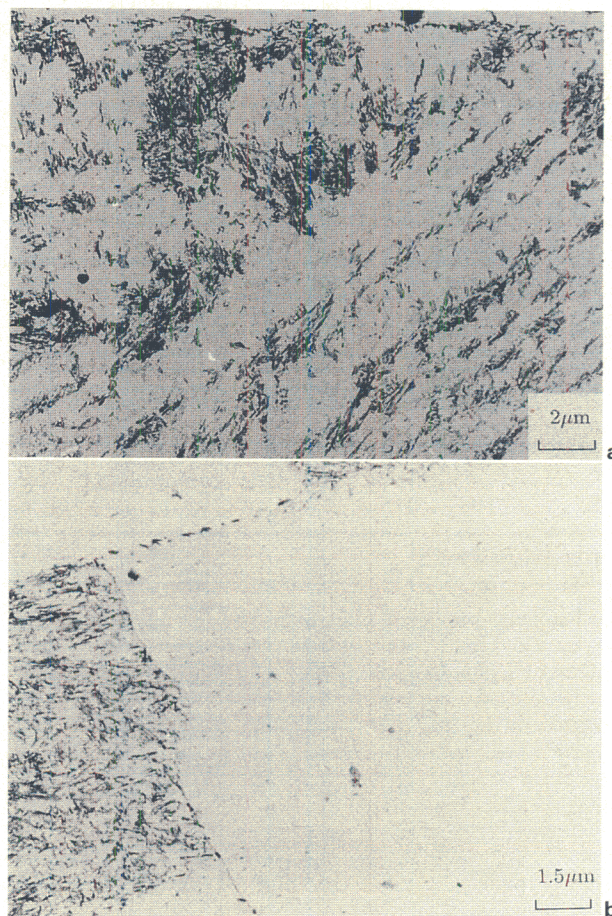
### PRECIPITATION IN ALLOTRIOMORPHIC FERRITE

Although there was no precipitation before tempering in the bainitic regions of the microstructure, extensive precipitation was observed in the allotriomorphic ferrite regions of the untempered initial microstructure. Fibrous carbides were found in the allotriomorphic ferrite, both at grain boundaries with other ferrite grains and at the ferrite/bainite grain boundaries (Fig. 2). Electron diffraction from individual clusters of the fibrous carbides showed that all the fibres within each cluster have the same crystallographic orientation. The carbides were identified as hexagonal  $M_2C$ . The fibres were approximately 30 nm in thickness and up to 2  $\mu\text{m}$  in length. Clusters of fibres were analysed using energy dispersive X-ray (EDX) and were found to have a chemical composition (wt-%) of 50Mo-40Cr with small amounts of iron and manganese consistent with the electron diffraction results.

A second morphology of  $M_2C$  clusters was also observed in the ferrite. These particles were much smaller than the fibres ( $\sim 60$  nm in length and  $\sim 20$  nm in thickness) and precipitated in a Widmanstätten array usually parallel to the prior austenite grain boundaries. The  $M_2C$  fibres and small particles present in the as transformed microstructure persisted throughout tempering, also being observed in the specimens tempered for 180 h at 565°C. Larger precipitates, identified by EDX as both  $M_2C$  and  $M_6C$ , were also found on ferrite/ferrite grain boundaries. The  $M_6C$  precipitates became larger during tempering at the expense of some of the smaller  $M_2C$  particles.

### PRECIPITATION IN BAINITIC REGIONS

The characteristics of precipitation in the bainitic regions of the mixed microstructures were found to be broadly the same as those in the fully bainitic specimens (Part 1). However, cementite precipitation in the bainitic regions of the mixed microstructure specimens was very dense compared with that in the fully bainitic specimens. This is to be expected because of the increased carbon concentration in the bainitic regions due to the rejection of carbon into the austenite as the allotriomorphic ferrite forms. The carbon extraction replica taken from a specimen tempered for 47 h at 565°C shown in Fig. 3a illustrates this point. The contrast between the dense cementite precipitation in



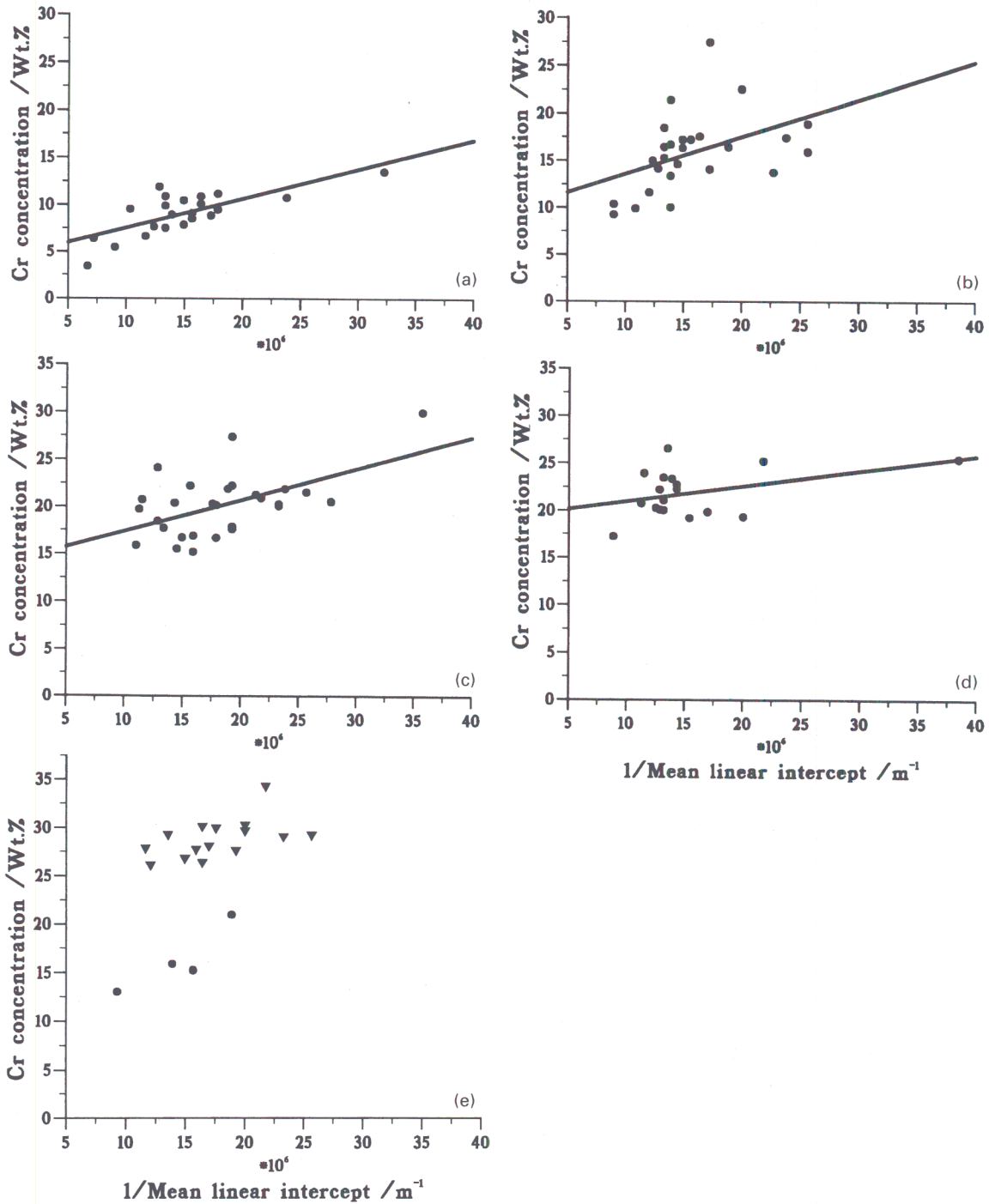
3 Carbon extraction replica from mixed microstructure specimen tempered for 47 h at 565°C showing a dense cementite precipitation and *b* contrast between dense cementite precipitation in bainitic regions and empty allotriomorphic ferrite regions

the bainitic regions and the relatively empty ferritic regions is illustrated in Fig. 3b. Large  $M_6C$  particles are also visible on the ferrite grain boundaries.

It is significant that the bainitic and martensitic regions contain extensive cementite precipitation, whereas the ferritic regions contain  $M_2C$  (which is gradually replaced by  $M_6C$  on prolonged tempering). This difference must be related to the mechanism of transformation. The allotriomorphic ferrite forms by reconstructive transformation, a process which requires the diffusion of all elements. The atomic mobility inherent in this process provides the opportunity for the simultaneous precipitation of alloy carbides. The growth of bainite and martensite is on the other hand displacive, precluding the formation of alloy carbides during transformation.

Table 1 Summary of experimental measurements of chromium concentration in cementite and particle size for mixed microstructure specimens tempered at 565°C

Tempering time, h	Correlation coefficient	Average chromium concentration, wt-%	Average particle size, nm
1	0.74	9.1	76
47	0.44	15.9	68
80	0.55	20.2	59
128	0.41	21.9	71
180 (martensitic)	...	26.2	63
180 (bainitic)	...	16.2	74



a 1 h; b 47 h; c 80 h; d 128 h; e 180 h

**4 Chromium concentration in cementite plotted as function of reciprocal particle size for various tempering times at 565°C for mixed microstructure specimens**

**CHROMIUM CONTENT OF CEMENTITE**

Plots of chromium concentration versus the reciprocal of particle size are shown in Fig. 4 for the mixed microstructure specimens tempered at 565°C for 1, 47, 80, 128, and 180 h respectively. The results for the 180 h specimen again begin to show a division of the cementite into those particles associated with the bainitic and martensitic regions. The results of these analyses are summarised in Table 1.

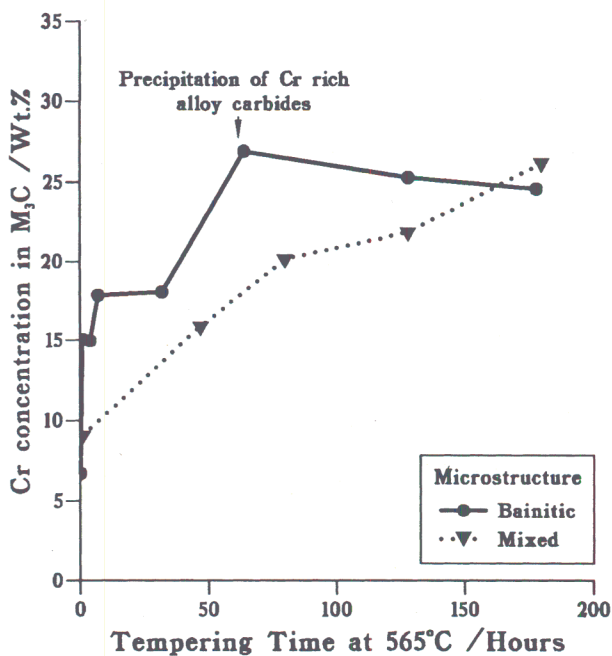
**COMPARISON WITH THEORY**

The experimental measurements of chromium concentration in cementite as a function of tempering time at 565°C in the fully bainitic and mixed microstructure

specimens are plotted in Fig. 5 (see Part 1 also). It is clear that the cementite in the fully bainitic specimens enriches more rapidly than in the specimens containing only 50% bainite. This is to be expected because the formation of allotriomorphic ferrite in the mixed microstructure specimens causes an increase in the carbon concentration of the bainitic regions. The carbon concentration in the two different regions can be determined from a simple mass balance equation

$$\bar{x} = V_x x_x + (1 - V_x) x_y \dots \dots \dots (1)$$

where  $\bar{x}$  is the average carbon concentration in the alloy,  $V_x$  is the volume fraction of allotriomorphic ferrite,  $x_x$  and  $x_y$  are the carbon concentrations in the ferrite and austenite

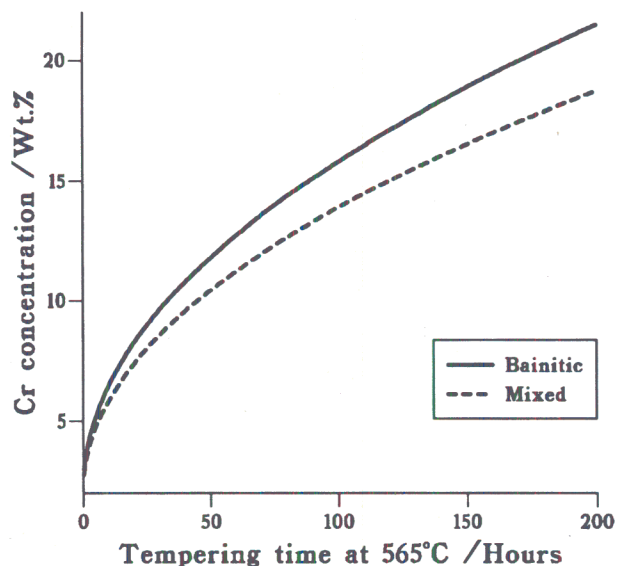


5 Comparison of average chromium content in cementite in fully bainitic and mixed microstructure specimens as function of tempering time at temperature of 565°C

respectively,  $\bar{x}$  is 0.15%,  $V_x$  is  $\sim 0.5$  in the specimens used,  $x_z = 0.0228\%$ ,<sup>4</sup> and hence  $x_y$  is calculated to be 0.277%. This is by definition the carbon concentration in the bainite which forms from the carbon enriched austenite. There is therefore approximately twice as much carbon available for carbide precipitation initially in the mixed microstructure specimens than in the fully bainitic specimens.

The model<sup>1</sup> used in Part 1 was modified to allow for mixed microstructures.<sup>5</sup> The mixed microstructure was treated as an asymmetric diffusion couple, in which a cementite particle was 'sandwiched' between different amounts of ferrite. The method of solution of the diffusion equations was essentially the same as in the original symmetric model,<sup>1</sup> although four boundary conditions are now needed; two at the two ferrite/cementite interfaces and two at the extremities of the diffusion couple. Solution by numerical finite difference methods can take into account the differences in enrichment rate due to the different proportions of ferrite and cementite in mixed microstructures.

The modified model was used to predict the enrichment rate of cementite in the fully bainitic and mixed microstructures respectively. The calculations were carried out for 565°C, and for average particle sizes of 60 nm in the bainitic and 70 nm in the mixed microstructures. These are consistent with the measured particle sizes. The two curves are shown in Fig. 6, plotted as a function of time. It is observed experimentally (Fig. 5) that the bainite in the mixed microstructure specimens, which has formed from enriched austenite, contains cementite which enriches more slowly than that in the fully bainitic specimens. This is consistent with the predictions of the model.



6 Predicted rate of enrichment in cementite in bainitic and mixed microstructure specimens using asymmetric finite difference model

## Conclusions

Detailed experimental studies of cementite composition changes in bainitic and mixed ferritic-bainitic microstructures have revealed significant differences in the way in which cementite composition changes during tempering. The enrichment rate was found to be slower in the bainitic regions of the mixed microstructures, when compared with the fully bainitic specimens. These observations can be interpreted using a model which allows for the modified cementite distribution in a mixed microstructure.

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