Chapter 6

Sample Preparation and Characterisation

6.1 Sample preparation

$2\frac{1}{4}$Cr1Mo steel

A section of a $2\frac{1}{4}$Cr1Mo power plant steel from Drax Power Station was supplied by National Power plc. The composition is given in Table 6.1.

A piece of this steel of approximate dimensions 100 × 100 × 12 mm was placed in a furnace at 500°C. The temperature was increased to 1000°C and held for 30 minutes to transform the steel to austenite. The sample was then quenched directly into water. During quenching, it was agitated to prevent the buildup of a layer of bubbles which would provide insulation and reduce the cooling rate.

Using a spark-cutter, square plates of the material of side 10 mm and approximate depth 1 mm were cut from the large piece, taking care to discard

C	Si	Mn	P	S	Cr	Mo	Ni	Al	As
0.12	0.29	0.51	0.021	0.021	2.22	0.97	0.21	0.008	0.030
Co	Cu	Nb	Pb	Sn	Ti	V	W	Sb	
0.027	0.23	<0.005	0.009	0.022	<0.005	0.017	0.019	0.015	

Table 6.1: Composition of $2\frac{1}{4}$Cr1Mo steel; all quantities in wt. %. Data supplied by Bodycote Materials Testing Ltd., Bridgwater, Somerset.

the decarburised layer on the outside. The thickness of this layer was estimated at 0.05 mm using the constant-concentration solution to Fick's second law, but 2 mm was cut from each edge to be sure of excluding decarburised material.

In order to prevent decarburisation and oxidation during tempering, the square plates were sealed into silica tubes which were evacuated and backfilled with a small partial pressure of argon to provide an inert atmosphere. Two plates were placed into each tube so that the samples for Barkhausen analysis and for electron microscopy would receive exactly the same heat treatment.

The samples were subjected to tempering heat treatments of between 1 hour and 512 hours at 500°C and at 600°C, and between 1 hour and 8 hours at 700°C. This last series was intended to replicate the microstructural changes during the pre-service tempering treatment of power-plant steels (Morris, personal communication). As-quenched (AQ) samples were retained for comparison with the tempered steels.

After tempering, the samples were allowed to air-cool while remaining within the silica tubes. The tubes were then broken, and the samples were hot-mounted in Bakelite, ground using 2500 grit silicon carbide paper and polished to 1 μm using diamond paste. Finally, the surfaces were etched using 2% nital to remove the strained layer and reveal the microstructure for observation using an optical microscope and a Hitachi S-4200 Field Emission Gun SEM.

Long-term specimens

Specimens of 11Cr1Mo wt. % steel which had been heated for several thousands of hours at 550°C were supplied by Corus RD&T. These were from creep tests, and comprised a screw-thread, which was used to hold the specimen in place, and a gauge length tapering to a fracture surface (Figure 6.1). In order to study only the effects of prolonged exposure to high temperature, samples for BN testing and microscopy were cut from the threaded area, which was not subjected to stress, using a Struers Accutom lubricated rotary cutter.

C	Si	Mn	P	S	Cr
0.205	0.36	0.49	0.011	0.009	11.15
Mo	Ni	Nb	V	W	
0.85	0.34	0.01	0.28	0.02	

Table 6.2: Composition of creep-tested steel; all quantities in wt. %. Data supplied by Corus RD&T.

The steel composition is given in Table 6.2 and details of the heat treatment in Table 6.3. The surfaces were prepared in the same way as those of the power plant steels, except that Kalling's No. 2 reagent (2 g $CuCl_2$, 40 ml HCl, and 40-80 ml ethanol; Vander Voort, 1984) was used as an etchant since 2% nital would not etch this steel.

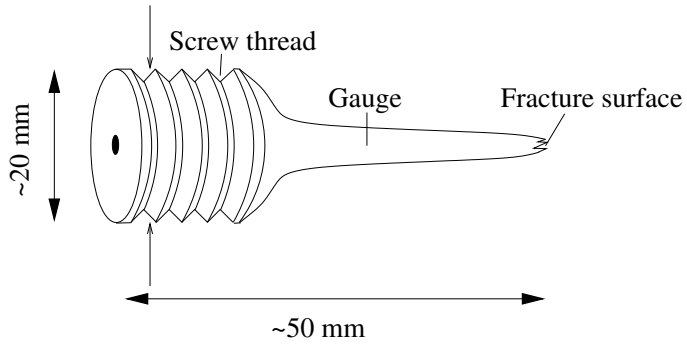

Figure 6.1: Failed creep test specimen. The arrows show the position at which the Barkhausen test specimen was cut.

6.2 Optical microscopy

6.2.1 As-quenched sample

In Figure 6.2, the prior austenite grains and their substructure of packets can clearly be seen. Packets occupy almost the entire grain in some cases, but are much smaller in others. A larger-scale micrograph of the same area allows the packets to be resolved more easily (Figure 6.3).

Temperature / °C	Applied stress / MPa	Time / h
550	278	2347
550	247	5849
550	216	16530
550	185	36191

Table 6.3: Testing conditions of creep specimens provided by Corus (Clarke, personal communication).

6.2.2 Tempering at 500°C

Figure 6.4–Figure 6.7 show specimens tempered at 500°C for a variety of times. Microstructural changes at this temperature are very gradual. The features present in the as-quenched microstructure can still be seen after tempering for 256 h, but their edges have become less distinct.

6.2.3 Tempering at 600°C

Samples tempered at 600°C are shown in Figure 6.8–Figure 6.11. The former martensitic structure is still in evidence, especially at shorter tempering times, but gradual coalescence of the narrow features into larger units can be seen as tempering progresses. The coalescence is more obviously visible in the SEM images presented below.

6.2.4 Tempering at 700°C

Microstructural changes occur much more rapidly on tempering at 700°C, as is evident from Figure 6.12–Figure 6.15, which show the microstructure corresponding to times between 1 and 8 hours. Even after 1 hour, much of the fine structure in the AQ sample has coalesced into larger units, which coarsen with increasing tempering time. Tempering for 8 hours causes most of the original martensitic structure to be lost, and lines of carbides delineate former block boundaries.

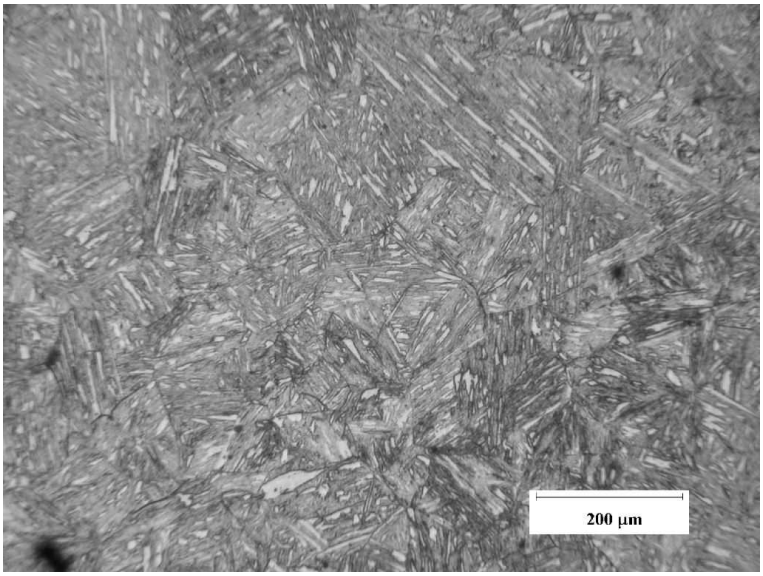

Figure 6.2: As-quenched microstructure of $2\frac{1}{4}$Cr1Mo steel.

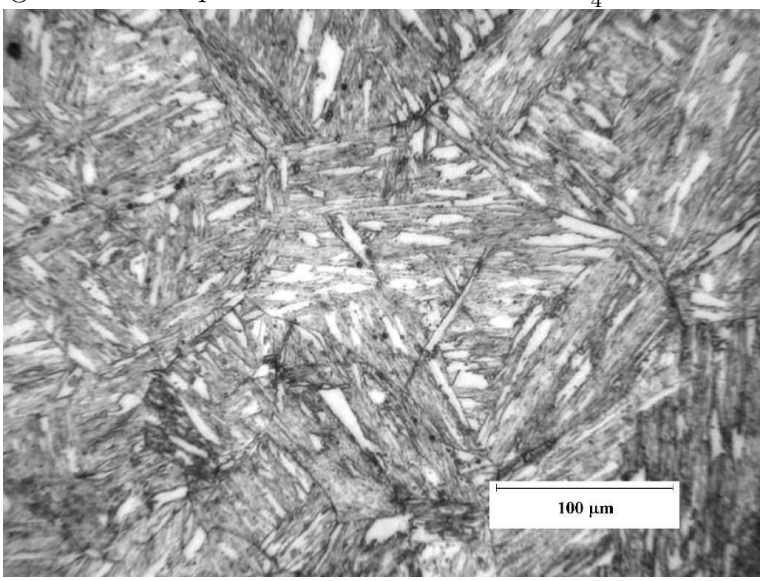

Figure 6.3: As-quenched microstructure of $2\frac{1}{4}$Cr1Mo steel.

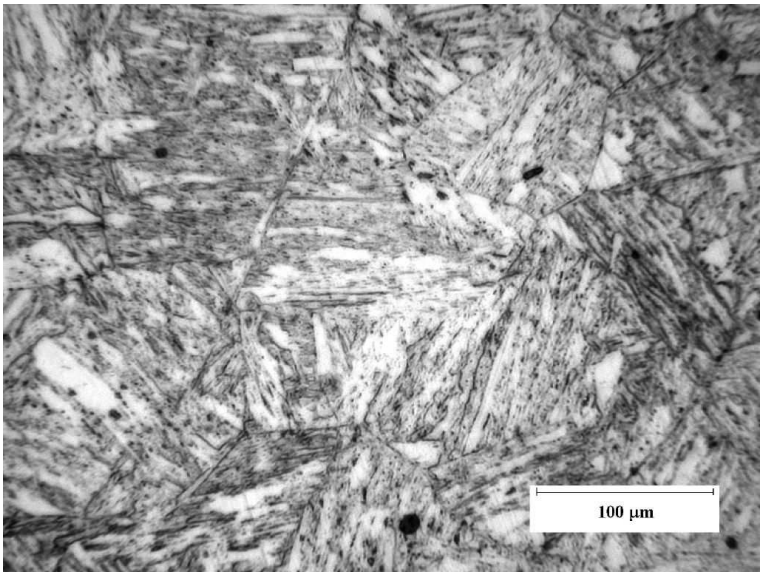

Figure 6.4: $2\frac{1}{4}$Cr1Mo steel tempered for 1 hour at 500°C.

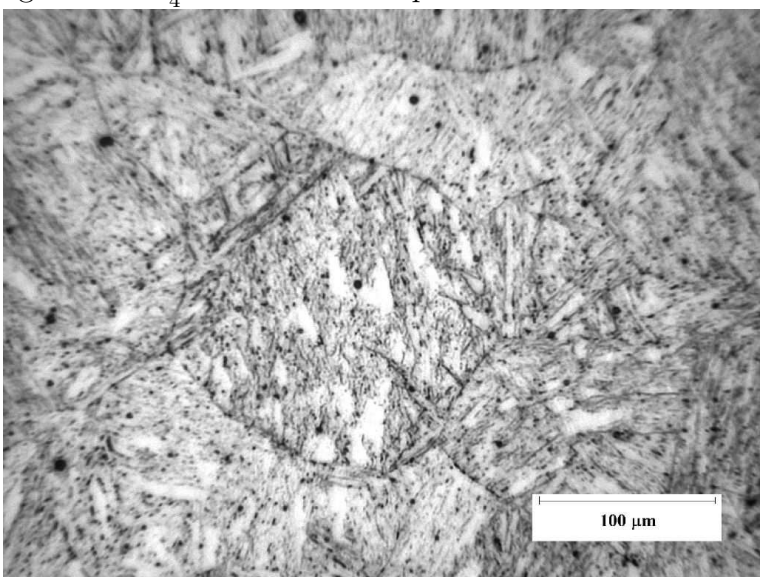

Figure 6.5: $2\frac{1}{4}$Cr1Mo steel tempered for 4 hours at 500°C.

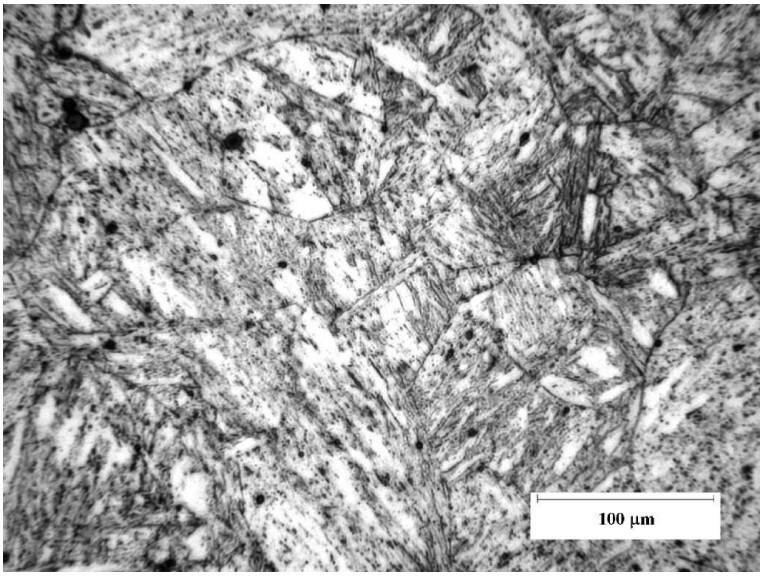

Figure 6.6: $2\frac{1}{4}$Cr1Mo steel tempered for 32 hours at 500°C.

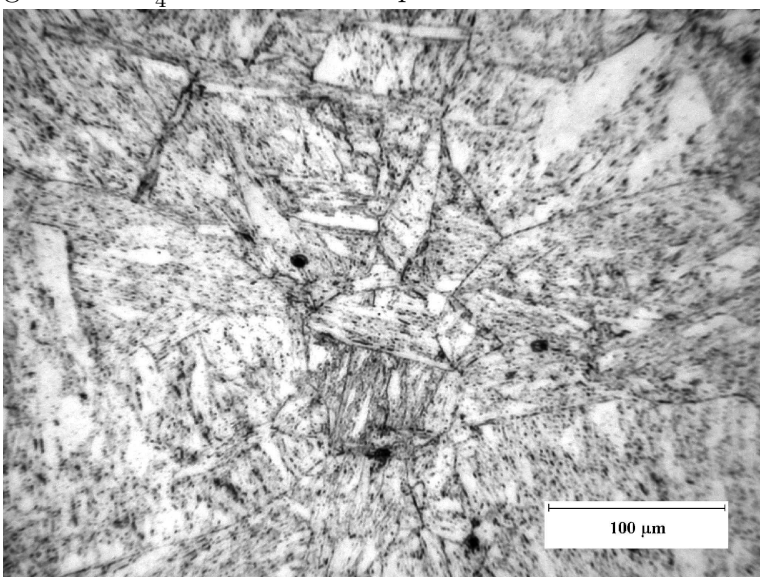

Figure 6.7: $2\frac{1}{4}$Cr1Mo steel tempered for 256 hours at 500°C.

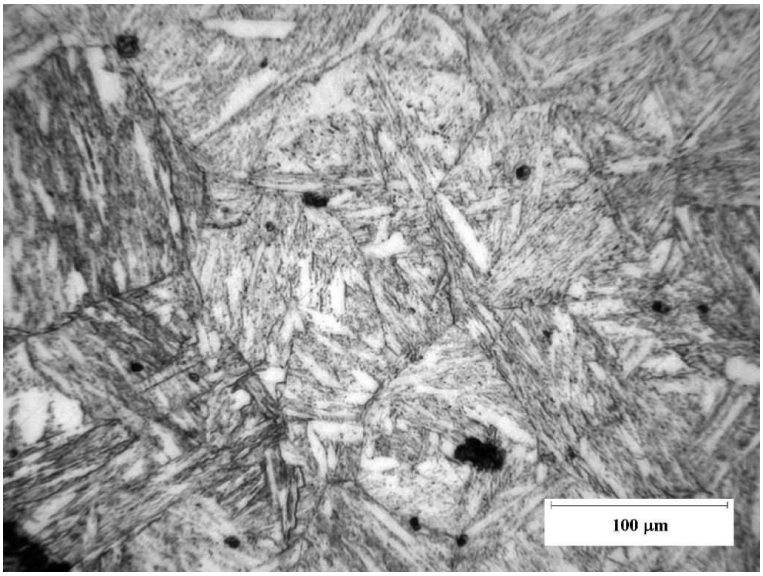

Figure 6.8: $2\frac{1}{4}$Cr1Mo steel tempered for 4 hours at 600°C.

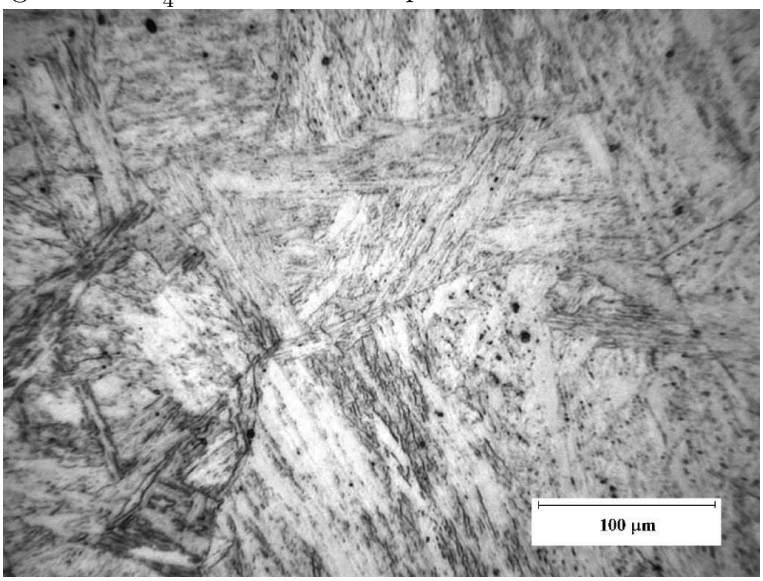

Figure 6.9: $2\frac{1}{4}$Cr1Mo steel tempered for 16 hours at 600°C.

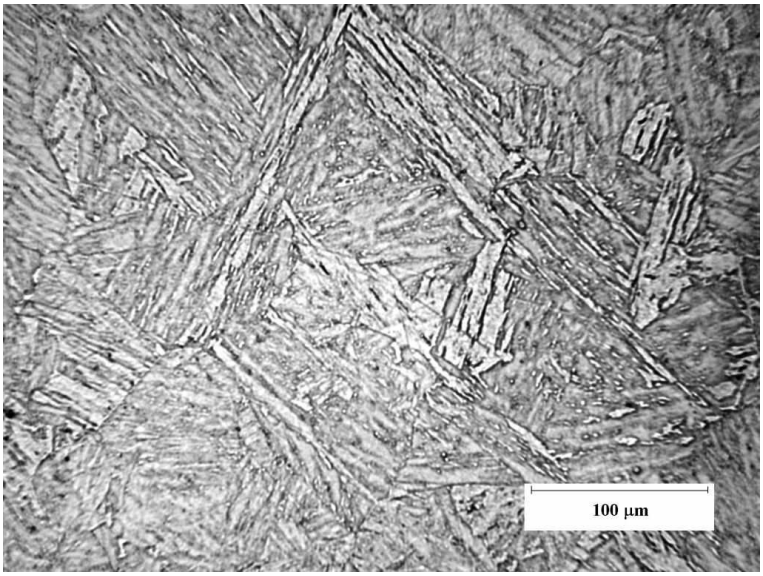

Figure 6.10: $2\frac{1}{4}$Cr1Mo steel tempered for 256 hours at 600°C.

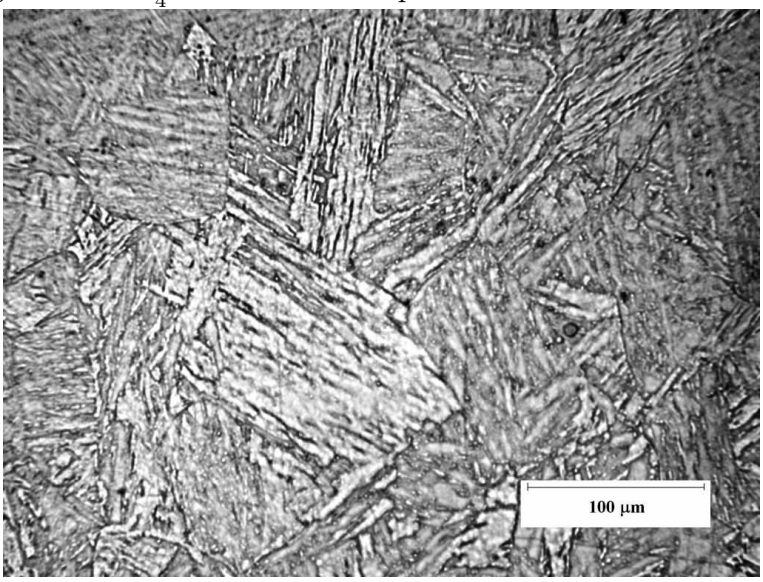

Figure 6.11: $2\frac{1}{4}$Cr1Mo steel tempered for 512 hours at 600°C.

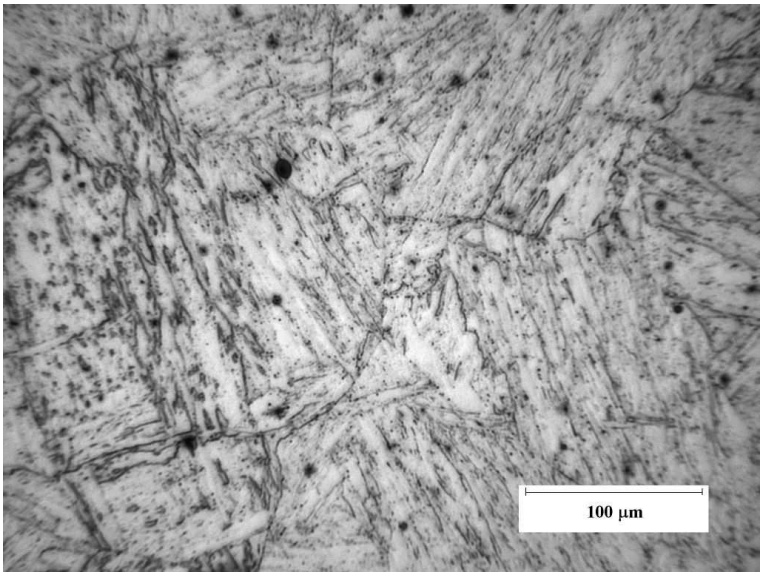

Figure 6.12: $2\frac{1}{4}$Cr1Mo steel tempered for 1 hour at 700°C.

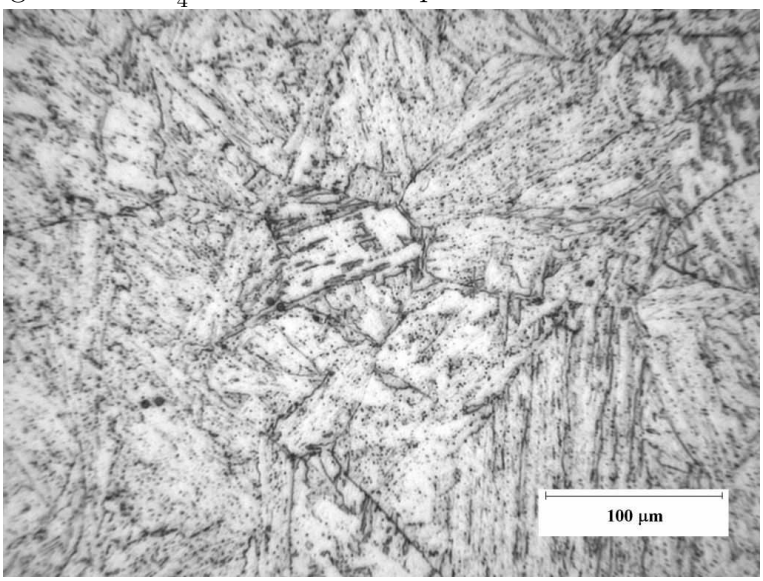

Figure 6.13: $2\frac{1}{4}$Cr1Mo steel tempered for 2 hours at 700°C.

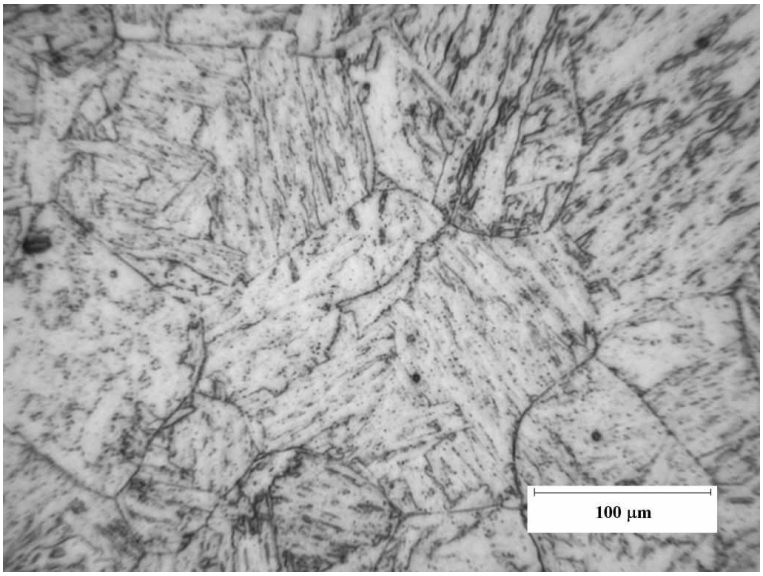

Figure 6.14: $2\frac{1}{4}$Cr1Mo steel tempered for 4 hours at 700°C.

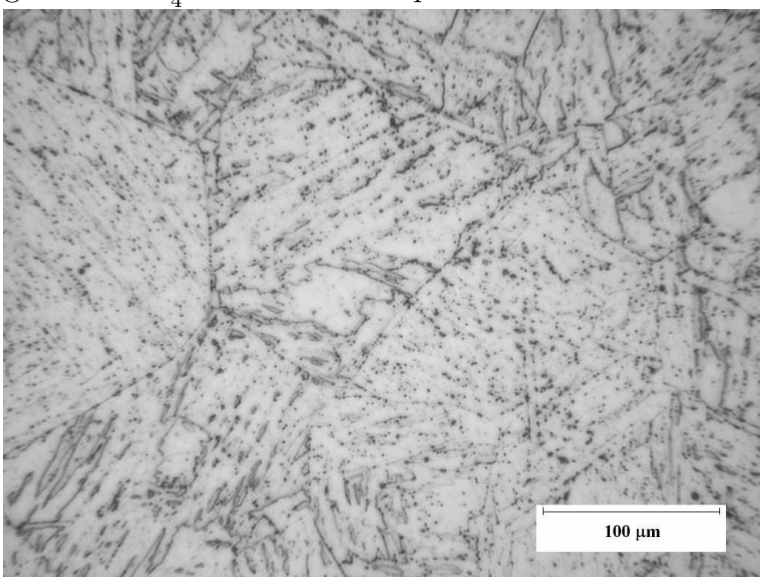

Figure 6.15: $2\frac{1}{4}$Cr1Mo steel tempered for 8 hours at 700°C.

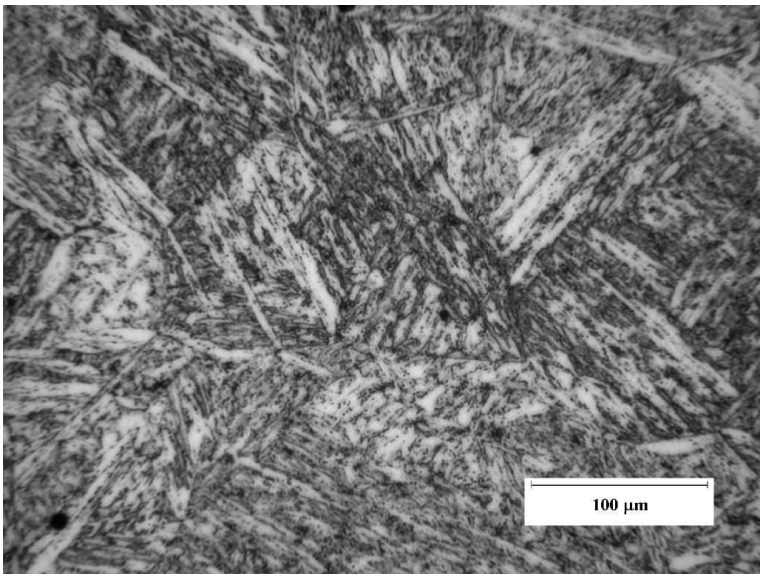

Figure 6.16: 11 wt. % Cr steel heated for 2347 hours at 550°C during creep test.

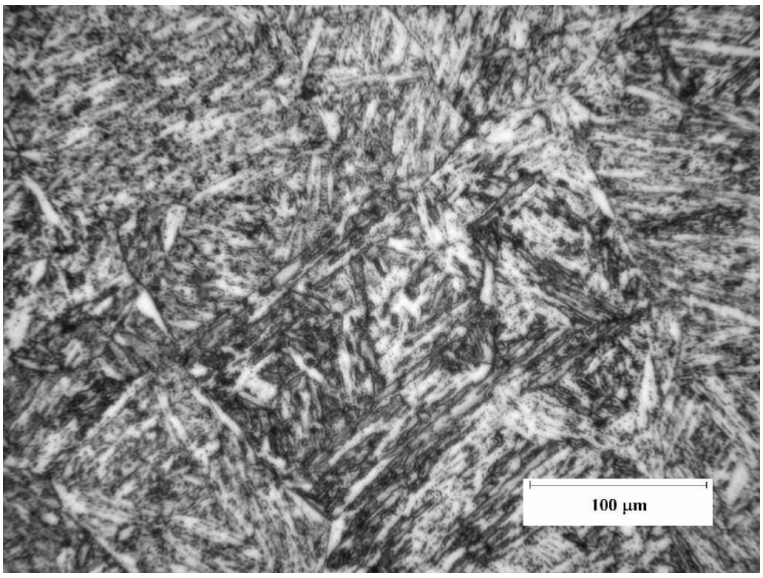

Figure 6.17: 11 wt. % Cr steel heated for 5849 hours at 550°C during creep test.

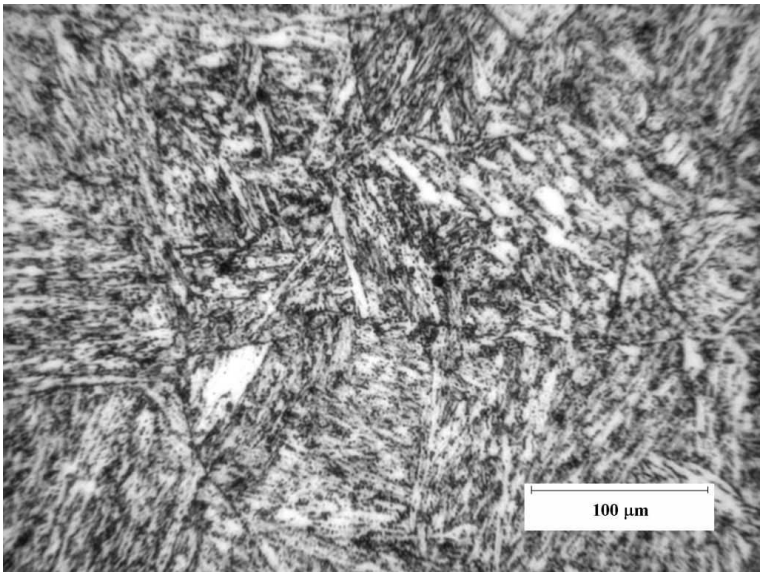

Figure 6.18: 11 wt. % Cr steel heated for 16530 hours at 550°C during creep test.

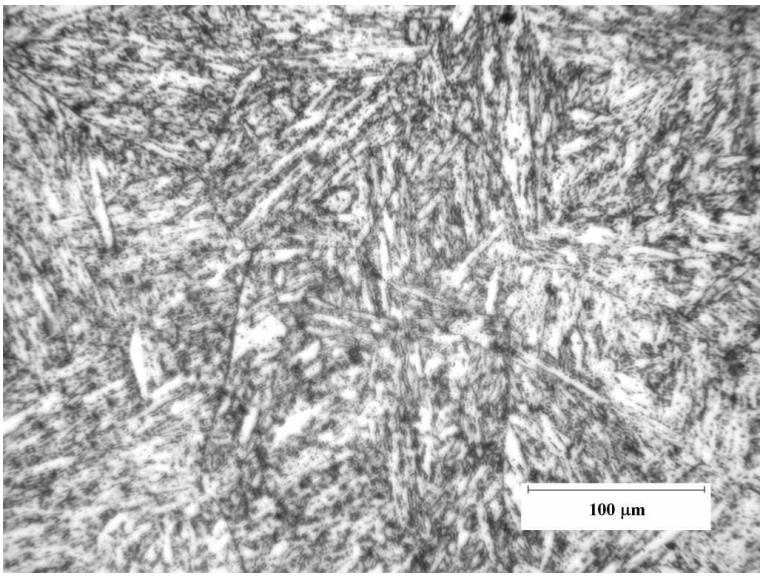

Figure 6.19: 11 wt. % Cr steel heated for 36191 hours at 550°C during creep test.

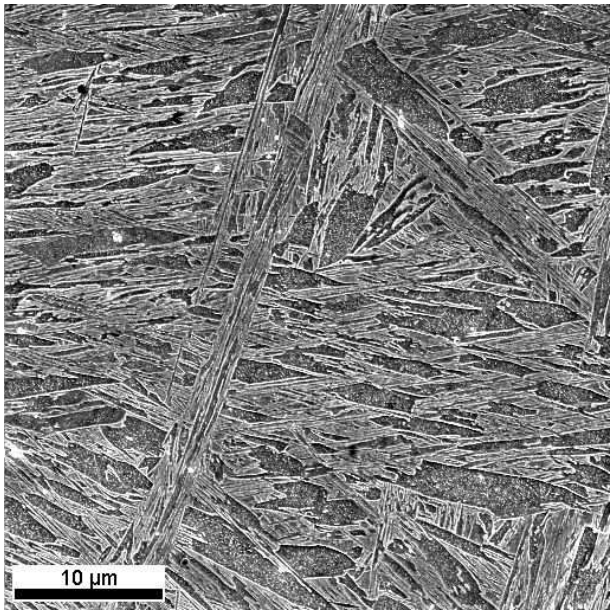

Figure 6.20: SEM micrograph of as-quenched $2\frac{1}{4}$Cr1Mo steel.

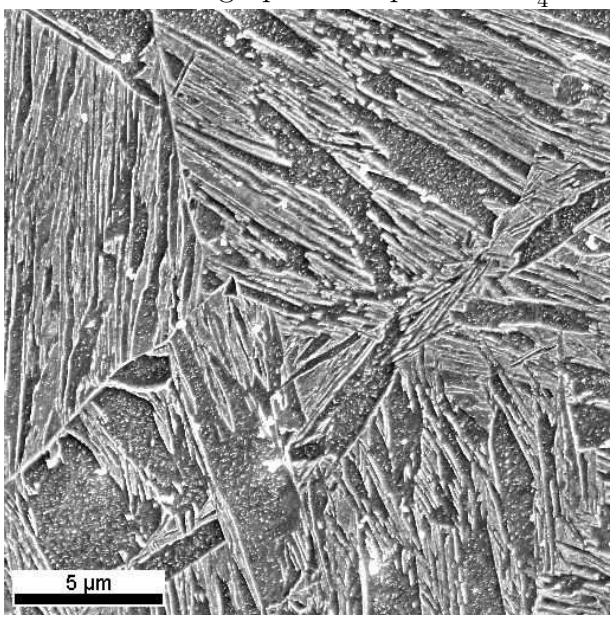

Figure 6.21: SEM micrograph of as-quenched $2\frac{1}{4}$Cr1Mo steel.

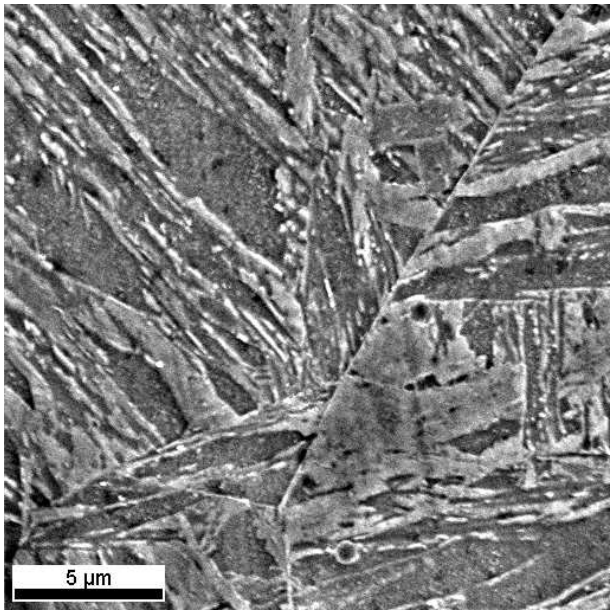

Figure 6.22: SEM micrograph of $2\frac{1}{4}$Cr1Mo steel tempered at 500°C for 1 hour.

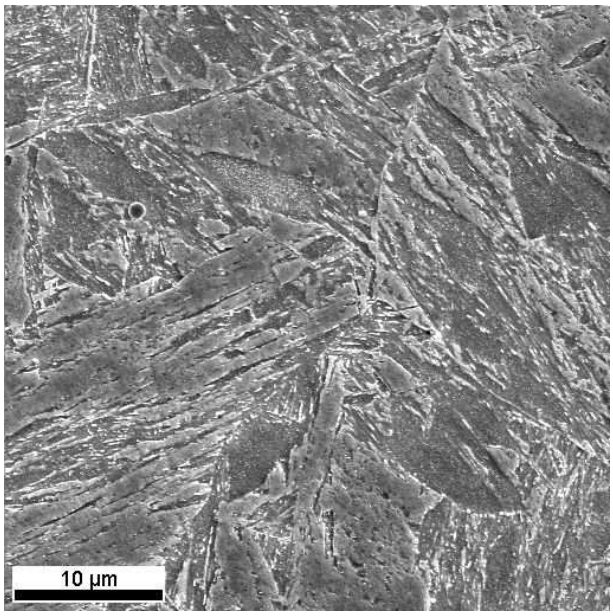

Figure 6.23: SEM micrograph of $2\frac{1}{4}$Cr1Mo steel tempered at 500°C for 256 hours.

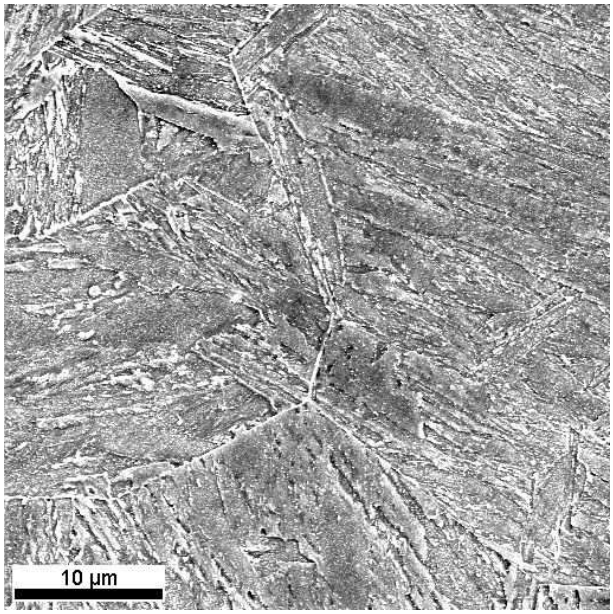

Figure 6.24: SEM micrograph of $2\frac{1}{4}$Cr1Mo steel tempered at 600°C for 16 hours.

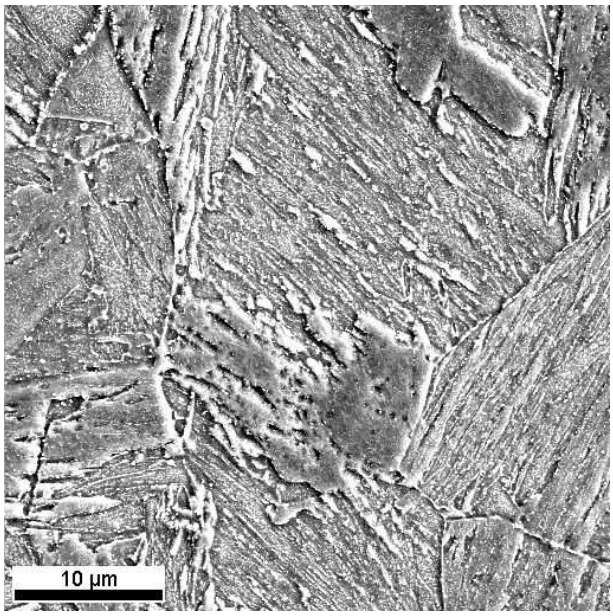

Figure 6.25: SEM micrograph of $2\frac{1}{4}$Cr1Mo steel tempered at 600°C for 256 hours.

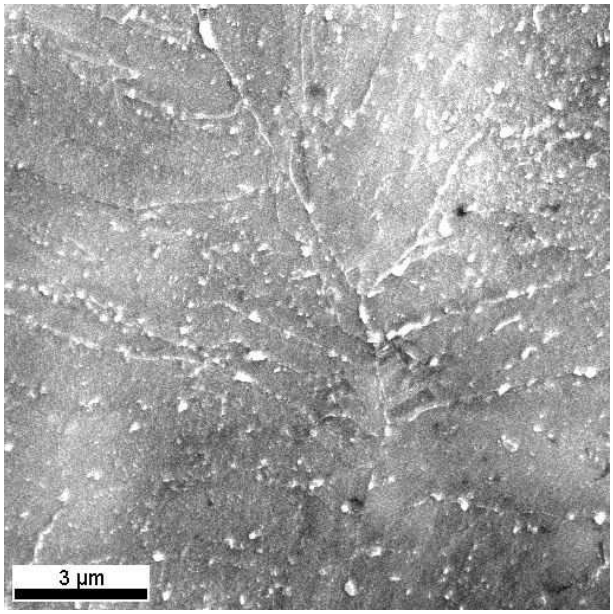

Figure 6.26: SEM micrograph of $2\frac{1}{4}$Cr1Mo steel tempered at 700°C for 1 hour.

6.2.5 Long-term specimens

Figure 6.16–Figure 6.19 are optical micrographs of the 11Cr1Mo wt. % steel specimens. In all of these, the structure is very similar to that of the $2\frac{1}{4}$Cr1Mo steel in its early stages of tempering at 500°C, but finer. There is no obvious microstructural change visible on this scale, even after prolonged tempering (36000 hours). This is as expected since this steel has been deliberately designed to resist microstructural changes in service over much longer periods than this (30 years or more, *i.e.* around 300000 hours).

6.3 Scanning electron microscopy

Figure 6.20 illustrates some of the different lath lengths and orientations within a region of the AQ structure, and Figure 6.21, at a higher magnification, demonstrates how the laths stop at a prior austenite grain boundary.

After even a short tempering treatment of 1 hour at 500°C, some of the laths have coalesced to form wider regions (Figure 6.22). Tempering for a

longer time, 256 hours, at 500°C produces more coalescence (Figure 6.23). The process is accelerated by tempering at 600°C (Figure 6.24, Figure 6.25). After 1 hour at 700°C, only traces of the original structure can be seen (Figure 6.26).

6.4 Feature size measurements

As discussed in previous chapters, the sizes and spacings of microstructural features is believed to affect magnetic domain wall behaviour. In equiaxed, single-phase materials, the grain size is the most important microstructural dimension, but in martensitic steels, there are various levels of structure – laths, blocks, packets and prior austenite grains – any or all of which may affect the magnetic behaviour. Tempering introduces carbides, whose sizes and spacings must be considered, and at high temperatures causes recovery and recrystallisation.

The Heyn linear intercept method described by Vander Voort (1984) was used to determine prior austenite grain sizes. An acetate overlay was placed on an optical micrograph, and the grain boundaries identified and marked. A transparent grid was placed on the overlay, and the intercepts of the horizontal grid lines with grain boundaries were counted. A simple intercept scored 1, a triple junction intercepted by the grid line, $1\frac{1}{2}$, and a tangent hit to a grain boundary, $\frac{1}{2}$. The number of intercepts per unit length N_L was calculated from the total number of grains intercepted N, the total line length L_T and the magnification M as follows:

$$N_L = \frac{N}{L_T/M} \tag{6.1}$$

The mean lineal intercept (mean intercept length) $\bar{L}_3$ was then obtained from:

$$\bar{L}_3 = \frac{1}{N_L} \tag{6.2}$$

The intercept measurements were repeated using the vertical grid lines. Prior austenite grain size measurements were obtained from three samples -

AQ, 600°C-8 h and 700°C-8 h - to check that the grain size was the same in each, as expected, and to increase the data set size. Packet size measurements were obtained on the AQ sample using the same Heyn method.

Block size measurements were made using the Heyn method on SEM micrographs of the AQ material. Lath widths were determined by measuring the width of a group of laths parallel to the lath length, then dividing this by the number of laths. The average sizes of the microstructural features are given in Table 6.4.

Feature	Average size / μm
Prior austenite grain	433
Packet (AQ)	97.5
Block (AQ)	1.68
Martensite lath (AQ)	0.25

Table 6.4: Sizes of microstructural features as estimated from micrographs.

6.4.1 Coarsening in 700°C tempered steel

A quantitative measure of microstructural coarsening in the 700°C samples was made using the Heyn method. Prior austenite grain boundaries and former lath, block or packet boundaries were delineated on an acetate overlay and the number of intercepts counted as above. In some cases, it was difficult to determine whether a linear feature was a block boundary or simply a row of carbides, so the method is rather imprecise. Nonetheless, a clear trend towards larger spacings with increasing tempering time is visible in Table 6.5 and Figure 6.27.

Tempering time / hours	1	2	4	8
Spacing (dir. 1) / μm	3.48	3.29	3.70	4.57
Spacing (dir. 2) / μm	4.10	4.36	4.27	5.47
Mean spacing / μm	3.79	3.83	3.99	5.02

Table 6.5: Feature spacings in samples tempered at 700°C: measurements in two perpendicular directions (1 and 2) and mean.

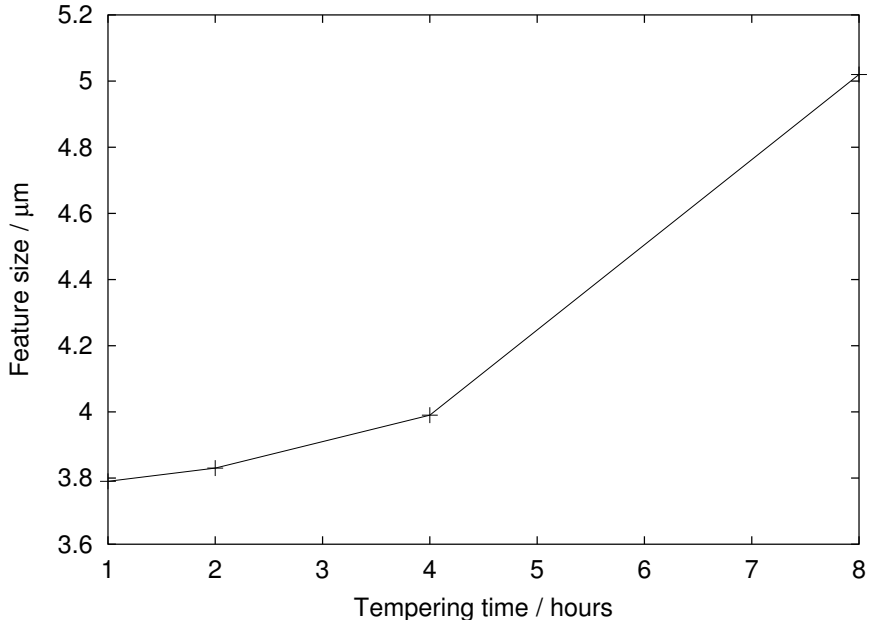

Figure 6.27: Changes in average feature spacing with tempering time at 700°C.

6.4.2 Carbide phases

The carbide phases expected in the tempered samples can be obtained from the carbide stability diagram for $2\frac{1}{4}$Cr1Mo steel (Nutting, 1998; Figure 2.6). The phases present after tempering at 600 and 700°C are shown in Figure 6.28 and 6.29 respectively. The Nutting diagram does not extend down to 500°C, but by extrapolation, M_3C is likely to be the most stable phase until at least 100 hours.

Fujita (2000) characterised the carbides occurring in $2\frac{1}{4}$Cr1Mo steels after tempering at 600°C using TEM. His results are summarised in Table 6.6. These suggest a later onset of M_7C_3 than Figure 6.28 and Figure 6.29.

6.5 Hardness

The hardness of each sample was measured using a Vickers indenter with a mass of 30 kg and an objective of 2/3 ", taking the mean of three indents.

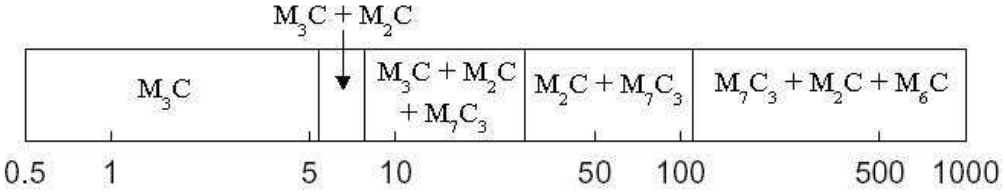

Figure 6.28: Carbide phase stability at 600°C in $2\frac{1}{4}$Cr1Mo steel, after Nutting (1998).

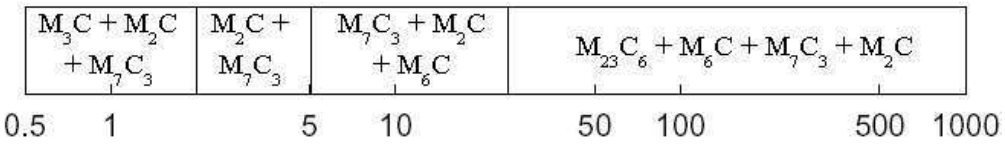

Figure 6.29: Carbide phase stability at 700°C in $2\frac{1}{4}$Cr1Mo steel, after Nutting (1998).

Time / hours	Observations
1	Most precipitates were needle- or plate-like M_3C
10	Most precipitates were needle- or plate-like M_3C
200	M_3C + needle array of M_2C
1000	M_3C + M_2C + blocky M_7C_3

Table 6.6: Carbide phases present in $2\frac{1}{4}$Cr1Mo steel after tempering at 600°C (Data from Fujita, 2000).

Results for the $2\frac{1}{4}$Cr1Mo steel are shown in Figure 6.30. At 500°C, after an initial decrease in the first hour, the change in hardness is very small on further tempering. The hardness is much lower at 600°C, and decreases with increasing tempering time. At 700°C, the rate of hardness decrease is more rapid.

Figure 6.31 shows the hardness of the 11Cr1Mo samples held at 550°C. A clear decrease in hardness with time is visible, but the rate of change is much lower than in the $2\frac{1}{4}$Cr1Mo steel.

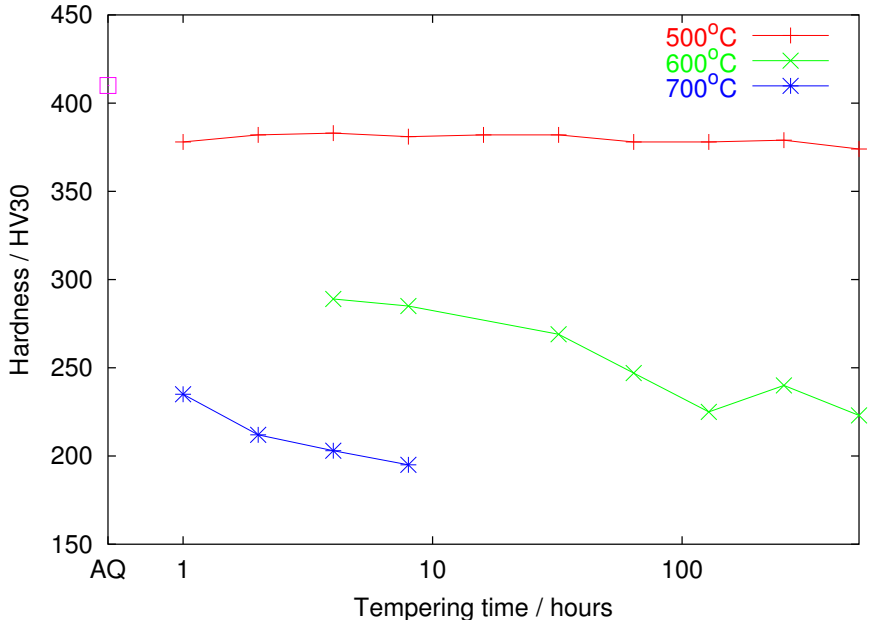

Figure 6.30: Hardness of tempered $2\frac{1}{4}$Cr1Mo steel samples.

6.6 Magnetic hysteresis measurements

The coercive fields of $2\frac{1}{4}$Cr1Mo steel samples tempered at 600°C for various times were obtained by measuring hysteresis loops using a vibrating sample magnetometer (VSM)[1]. Figure 6.32 shows a rapid decrease in H_C after a short tempering time, followed by a more gradual decrease at longer times. A small peak, probably due to carbide precipitation, is visible at 2 hours.

[1]The design and operation of the VSM are described by Foner, 1996.

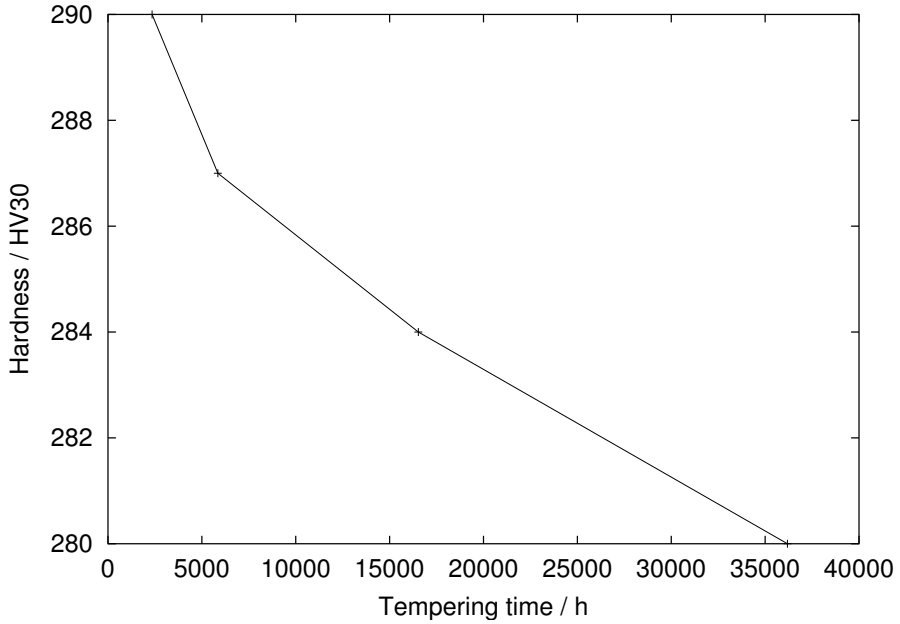

Figure 6.31: Hardness of creep-tested 11Cr1Mo wt. % steel samples.

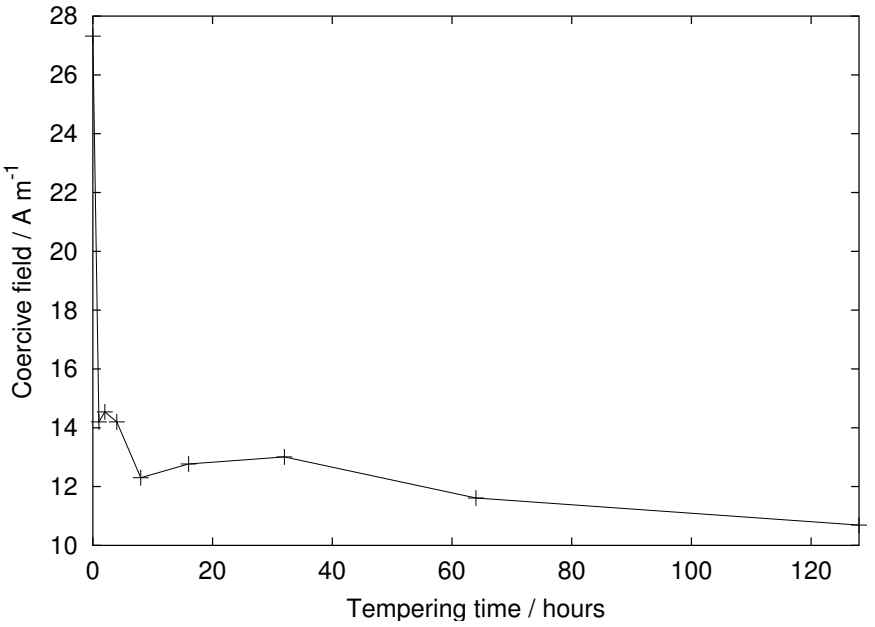

Figure 6.32: Coercive field of $2\frac{1}{4}$Cr1Mo steel tempered at 600°C. Data from M.Sci. dissertation of present author, 1999.

6.7 Conclusion

Changes in microstructure and hardness were very small for $2\frac{1}{4}$Cr1Mo samples tempered at 500°C, although martensite lath coalescence could be seen using SEM. At 600°C, the change in hardness was more pronounced, lath coalescence was observed, but the changes visible in the optical microscope were subtle and gradual. The coercive field decreased rapidly at short tempering times, and more gradually at longer times. Tempering at 700°C caused a rapid reduction in hardness and microstructural coarsening. On tempering at 600°C, needlelike M_2C is expected to form after a few hours of tempering, and spheroidal carbides to appear later. The samples tempered at 700°C should have both M_2C and M_7C_3 in the microstructure, as well as M_3C, at the tempering times used in this study.

In the 11Cr1Mo wt. % samples held at 550°C, there were no visible microstructural changes and a very gradual decrease in hardness with time.