Tempering of 2.25 Pct Cr-1 Pct Mo Low Carbon Steels

JOHN PILLING and N. RIDLEY

The effect of carbon level on the tempering behavior at 700 °C of 2.25 pct Cr-1 pct Mo steels having typical weld metal compositions has been investigated using analytical electron microscopy and X-ray diffraction techniques. The morphology, crystallography and chemistry, of each of the various types of carbides observed, has been established. It has been shown that each carbide type can be readily identified in terms of the relative heights of the EPMA spectra peaks for iron, chromium, molybdenum, and silicon. A decrease in the carbon level of the steel increases the rate at which the carbide precipitation reactions proceed, and also influences the final product. Of the carbides detected, $M_{23}C_6$ and M_7C_3 were found to be chromium-based, and their compositions were independent of both the carbon level of the steel and the tempering time. The molybdenum-based carbides, M_2C and M_6C, however, showed an increase in their molybdenum contents as the tempering time was increased. The rate of this increase became greater as the carbon content of the steel was lowered.

I. INTRODUCTION

LOW carbon 2.25 Cr-1 Mo steels are used as filler materials for joining 0.5 Cr-Mo-V steam piping employed in modern power stations.[1,2] The joints are typically multipass butt welds and are laid down under conditions of severe structural restraint. The residual stresses thus developed may be of the same order of magnitude as the yield stress, and are relieved by applying a post welding heat treatment which involves heating for several hours in the temperature range 690 to 720 °C.

The carbon level of the weld is usually specified as 0.10 pct maximum, but in practice this has been found to vary between 0.02 and 0.12 pct. The present work examines the effect of a variation in the carbon level of wrought steels, made to weld metal compositions, on hardness and microstructure after tempering at 700 °C for times up to 12 hours. In particular, the morphology, distribution, crystal structure, and composition of the carbides which are precipitated in the initially coarse-grained bainitic/martensitic microstructure have been investigated.

II. EXPERIMENTAL

The steels used in the investigation were prepared by melting Japanese electrolytic iron in a vacuum induction unit, with the alloy additions being made immediately prior to vacuum casting. The ingots, each weighing 25 kg with a diameter of 85 mm, were hot worked to 14 mm square bars which, after air cooling, were machined to 12 mm diameter rods. The compositions of the three steels examined are given in Table I.

Specimens, 12 mm diameter and 10 mm long, of each steel were austenitized at 1250 °C for 30 minutes, furnace cooled, and then re-solution treated at 1100 °C for 30 minutes before oil quenching to give a coarse-grained bainitic/martensitic structure. The specimens were then tempered for up to 12 hours at 700 °C and water quenched. All the heat treatments were carried out under a vacuum of better than 10^{-3} torr.

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Table I. Compositions of the Steels (Wt Pct)

Steel	C	Cr	Mo	Mn	Si	P	S
A	.018	2.34	0.99	1.02	0.47	.005	.007
B	.06	2.25	1.00	1.00	0.42	.005	.007
C	.09	2.30	0.99	1.00	0.45	.005	.007

The variation in hardness of the three steels with tempering time was followed using a Vickers diamond indentation test with a load of 30 kg. The hardness values reported are the mean of five indentations per specimen.

For microstructural studies, carbon extraction replicas were prepared from specimens which had been polished and lightly etched in two pct Nital. About 80 carbide particles from each sample were quantitatively analyzed using electron probe microanalysis (EPMA), and either selected area (AEI EMMA-4) or convergent beam (Philips EM400T) diffraction patterns were recorded from the precipitates. To follow qualitatively the changes in proportions of carbide types during tempering, use was made of the characteristic EPMA spectra of the various carbides, determined as outlined above and as described by Titchmarsh.[3] Approximately 400 carbide particles from each specimen were identified during a systematic examination of the extraction replicas in the electron microscope.[4] The results of this analysis were supplemented by an X-ray diffraction study of carbides electrolytically extracted in 10 pct HCl in methanol, using the method described by Lietnaker et al.[5]

III. RESULTS AND DISCUSSION

3.1 Hardness

On tempering for 30 minutes at 700 °C, the quenched steels all showed a marked drop in hardness (Figure 1). Further tempering resulted in only slight additional falls in hardness levels, indicating that after only 30 minutes tempering, the carbides were already present in the overaged condition.

3.2 Carbide Morphology, Crystallography, and Chemistry

Examination of the carbide extraction replicas showed the presence of four distinct carbide morphologies. The grain
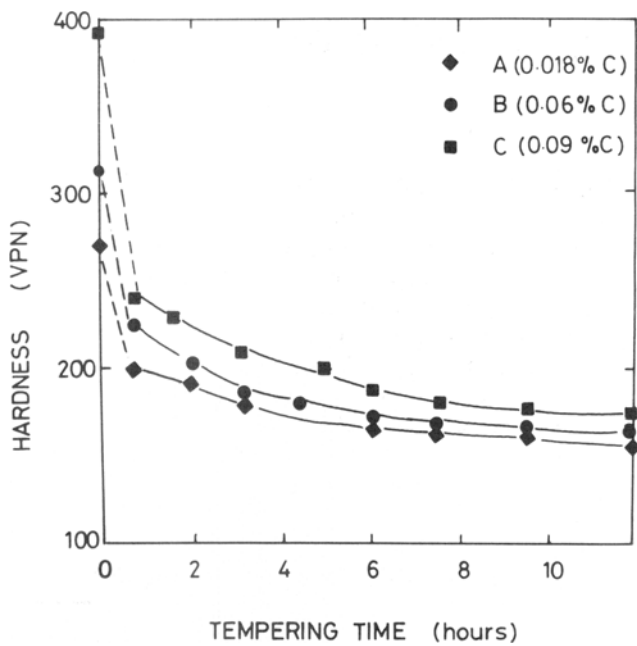
Fig. 1 — Hardness variation on tempering at 700 °C.

boundaries, both prior austenite and lath, were outlined by globular precipitates of between 900 and 5000 A diameter, with the smaller of these precipitates being located on the lath boundaries (Figure 2(a)). The matrix contained rod-like precipitates lying parallel to the longitudinal axis of the laths (Figure 2(b)), and clusters of small needle-shaped precipitates (Figure 2(c)). These carbides were interspersed with small parallelogram-shaped precipitates (Figure 2(d)).

Electron diffraction showed that the bulk of the grain boundary carbides and the majority of the rod-like precipitates had an fcc crystal structure with lattice parameters of between 10 A and 12 A. This would indicate that these particles were either $M_{23}C_6$ (a approximately 10.7 A) or M_6C (a approximately 11.0 A). The measured error in the lattice parameter was approximately five pct and therefore it was not possible, from diffraction evidence alone, to distinguish between the two carbide types. The remainder of the rod-shaped precipitates and the small parallelogram-shaped carbides showed streaks in their diffraction patterns (Figure 3). Dyson and Andrews[6] have shown that the carbide M_7C_3 can be easily recognized by its streaky electron diffraction patterns, a phenomenon which results from the presence of extensive stacking faults in planes perpendicular
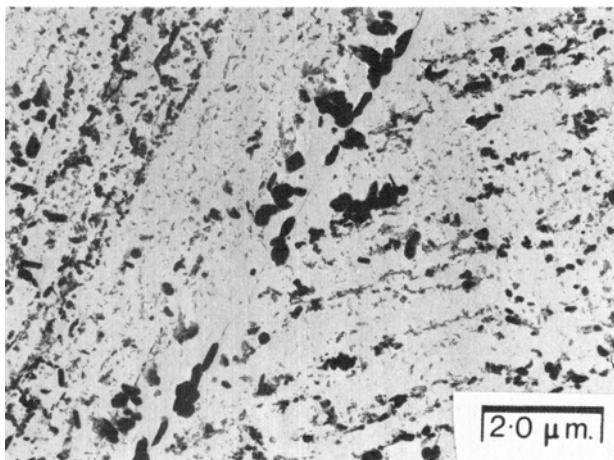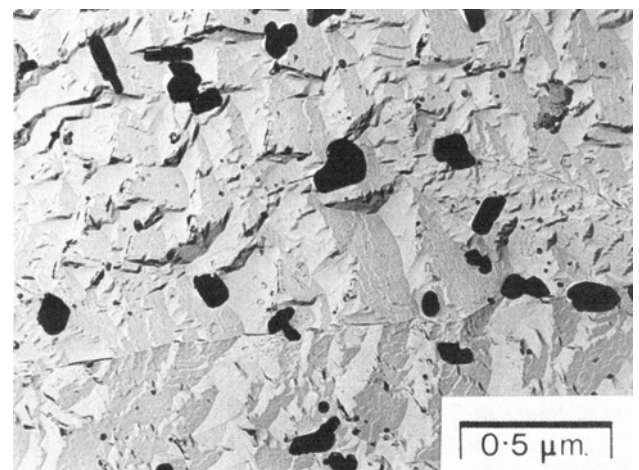

(a)
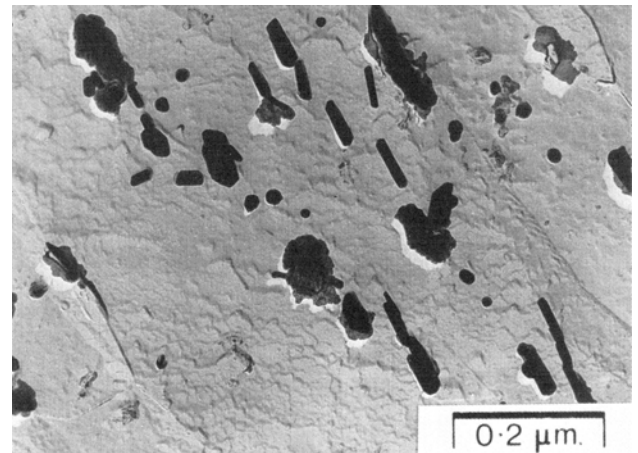
(b)
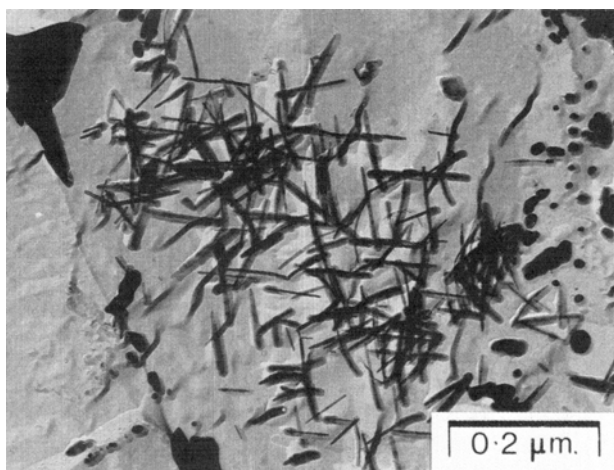
(c)

(d)

Fig. 2 — Carbide morphologies: (a) grain boundary carbides, (b) rod-shaped carbides, (c) clusters of needles, (d) parallelogram-shaped carbides.
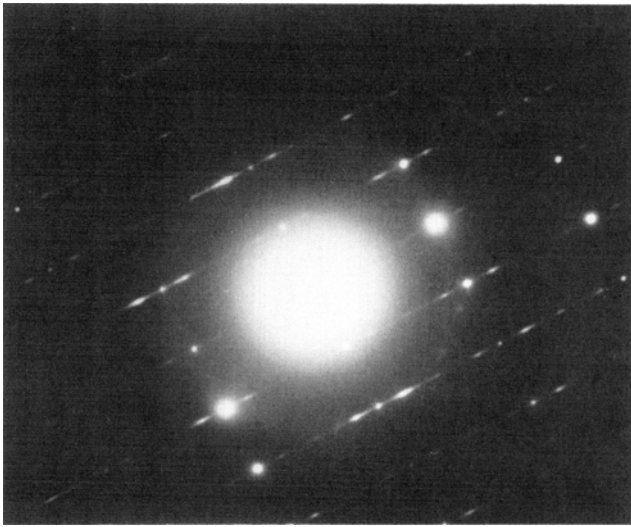
Fig. 3—Electron diffraction pattern from M_7C_3.

to the basal plane. The patterns were therefore indexed in terms of the hexagonal unit cell of M_7C_3 (a approximately $14.0\,A$, c approximately $4.5\,A$). The fine needles were too small to enable diffraction patterns to be obtained from individual precipitates, but the clusters of needles have ring patterns which were identical to those from Mo_2C.

EPMA showed that the carbides, when analyzed, gave one of four characteristic X-ray spectra (Figure 4). The spectra designated Types 1, 2a, and 2b, were associated only with the fcc carbides, while Type 3 arose from the

M_7C_3 particles. The clusters of M_2C gave the Type 4 spectrum. The Type 2 spectra were characterized by the presence of silicon, with the Mo:Cr ratio showing a continuous variation between the two extremes illustrated in Figure 4.

It was found that the proportion of Type 2 carbides present in the replicas from all the steels increased as tempering progressed, while the proportion of Type 1 carbides remained approximately constant (Table II). A similar trend was noted for the M_6C and $M_{23}C_6$ contents, respectively, of the extracted carbide residues. It can therefore be inferred that the Type 1 carbides are $M_{23}C_6$, while the Type 2 precipitates are M_6C. The proposition is supported by the work of Lietnaker et al,[5] who reported that M_6C was enriched in silicon. Further, the composition of $M_{23}C_6$ obtained in the present investigation agrees with that obtained by Titchmarsh[3] for a commercial wrought 2.25 Cr-1 Mo steel, as do the compositions of M_7C_3 and M_2C. However, the composition of M_6C reported by Titchmarsh corresponds only with the low chromium (Type 2b) spectra, although no value for the silicon content of this carbide was quoted. Titchmarsh[3] also reported a composition for M_3C carbide, but this carbide was not detected after any of the heat treatments given to the relatively low carbon steels examined in the present work.

IV. TEMPERING BEHAVIOR OF THE STEELS

Results of both the X-ray and EPMA analyses of the carbides (Table II) indicate that a reduction in the carbon
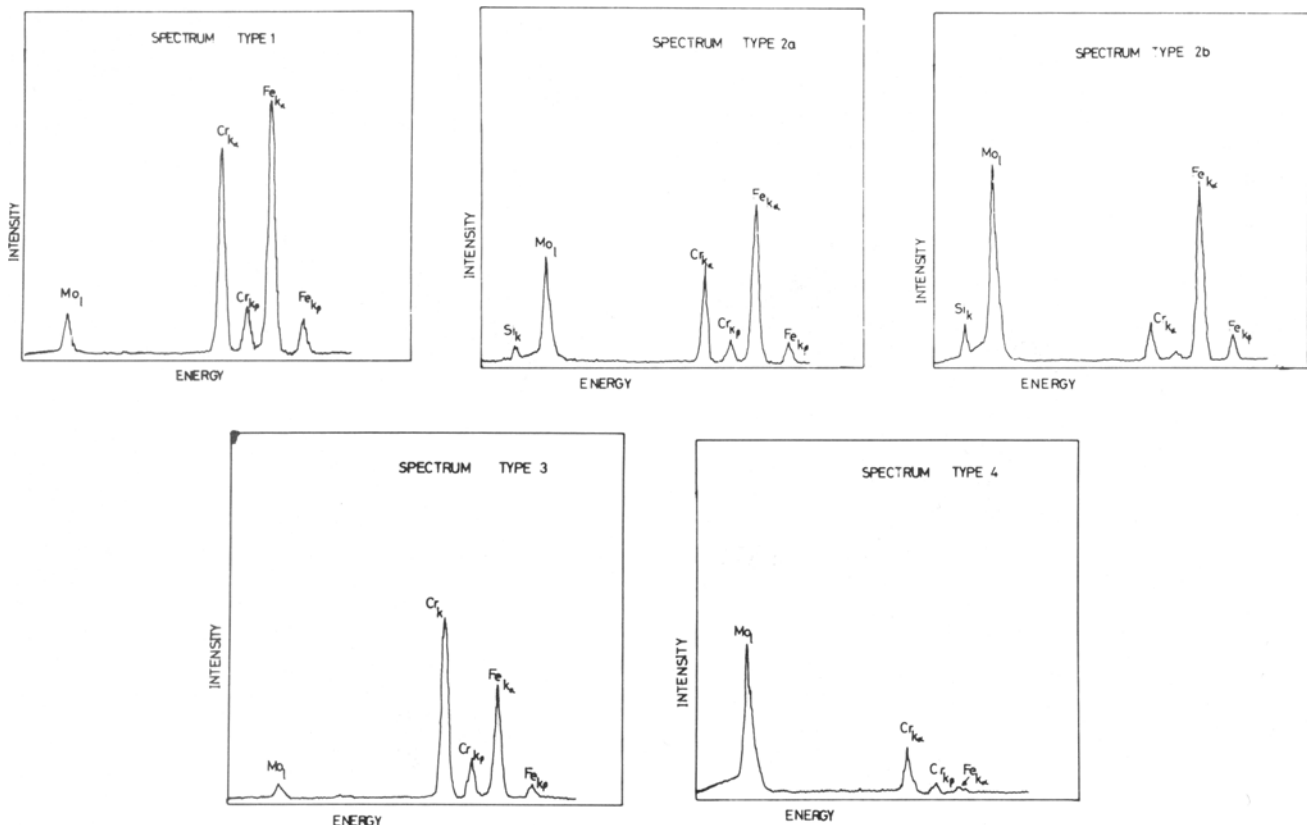

Fig. 4—Characteristic X-ray spectra of carbides. Type 1, $M_{23}C_6$; Types 2a and 2b, M_6C; Type 3, M_7C_3; and Type 4, M_2C.

| Steel | Tempering Time at 700 °C (Hours) | Carbide Type (EPMA Spectra) | | | | Carbides in Order of Decreasing Predominance (X-ray) |
		1 $M_{23}C_6$	2 M_6C	3 M_7C_3	4 M_2C	
A	3	0.27	0.01	0.51	0.21	$M_7C_3, M_{23}C_6, M_2C$
	6	0.25	0.32	0.25	0.18	$M_{23}C_6, M_7C_3, M_6C$
	9	0.24	0.59	0.10	0.07	$M_{23}C_6, M_6C, M_7C_3$
	12	0.14	0.85	0.01	—	$M_6C, M_{23}C_6$
B	3	0.25	0.01	0.50	0.24	$M_7C_3, M_{23}C_6, M_2C$
	6	0.26	0.16	0.34	0.24	$M_{23}C_6, M_7C_3, (M_2C)$
	12	0.39	0.48	0.12	0.01	$M_{23}C_6, M_6C$
C	3	0.28	—	0.37	0.35	$M_7C_3, M_{23}C_6, M_2C$
	6	0.27	—	0.42	0.31	$M_7C_3, M_{23}C_6, M_2C$
	12	0.23	0.03	0.47	0.27	$M_7C_3, M_{23}C_6, (M_2C) (M_6C)$

content of the steel alters the rates of the carbide precipitation reactions and the equilibrium products.

Oil quenching from 1100 °C resulted in bainitic/martensitic structures with pre-existing austenite grain sizes of 80 ±5 μm (mli) in all three steels (Figure 5). In steel A, with 0.018 pct C, the carbides M_2C and M_7C_3, which were present together with $M_{23}C_6$ after 30 minutes tempering, dissolved during further tempering, and were replaced by M_6C. After 12 hours tempering, the $M_{23}C_6$, the proportion of which had up to that time remained approximately constant, also began to dissolve. The structure therefore appeared to be tending to one of M_6C in ferrite (Figure 6).

The compositions of M_7C_3 and $M_{23}C_6$, which are chromium-based carbides, remained constant during tempering. The error involved in measuring the composition of any individual carbide particle was less than ±1 at. pct. However, there was a spread in composition between carbides of the same type in the same specimen but this was no greater than ±4 at. pct. The compositions shown in Figures 7 and 8 are the mean values of at least 30 measurements made on each carbide type in a given sample. The
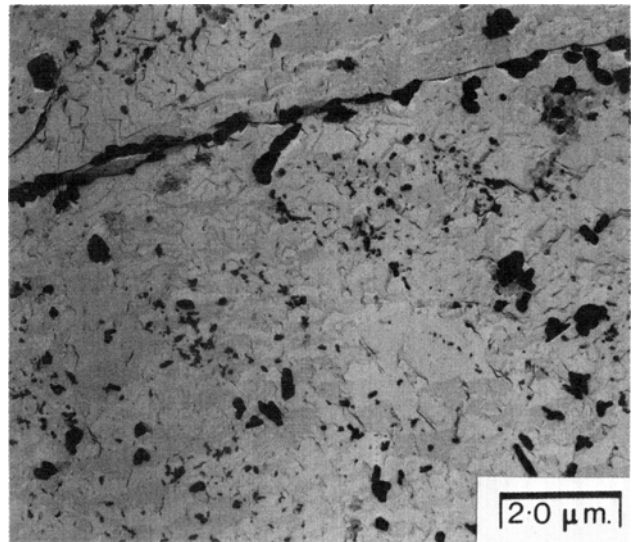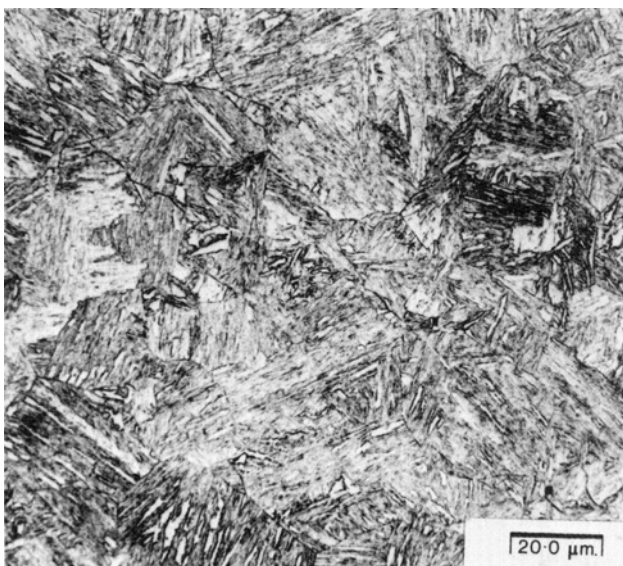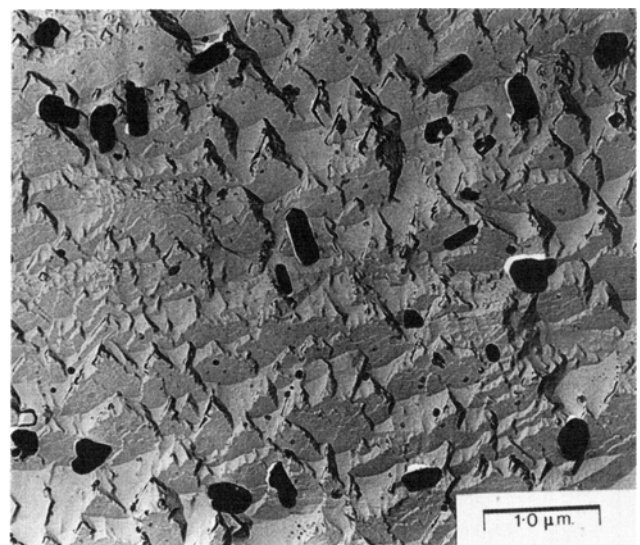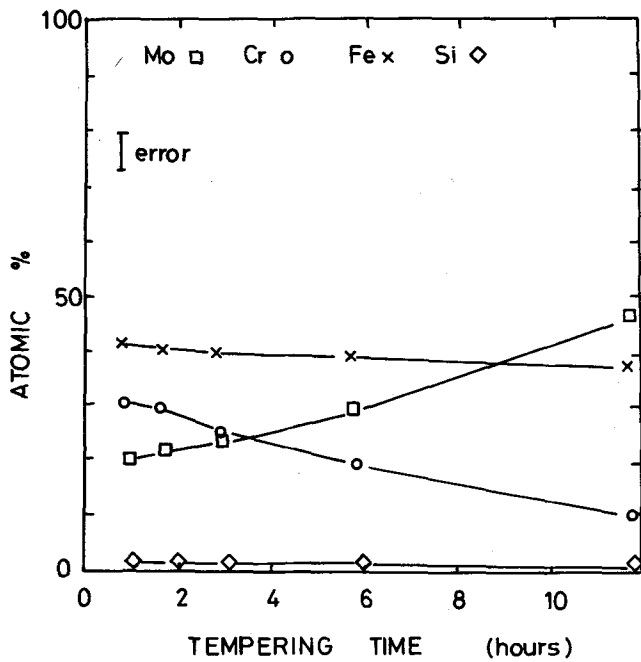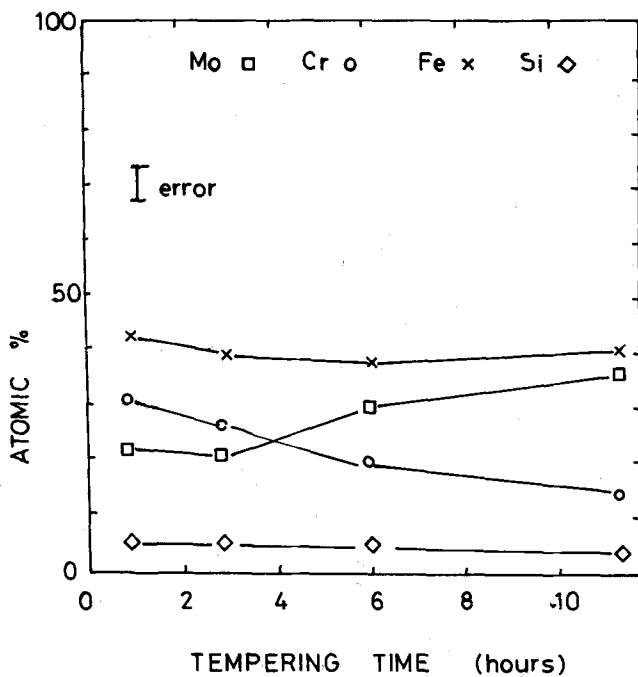

Fig. 5 — As-quenched structure of steel B (0.06 pct C).

(a)

(b)

Fig. 6 — Steel A (0.018 pct C) carbide distribution after (a) 3 h, (b) 12 h.

Fig. 7 — Variation in composition of M_6C on tempering at 700 °C. (a) Steel A (0.018 pct C), (b) steel B (0.06 pct C), after ZAF correction.
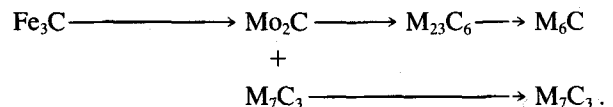
molybdenum-based carbides, M_2C and M_6C, however, showed a significant increase in their molybdenum contents (Figures 7 and 8). During tempering the M_2C decreased in volume fraction, thereby releasing molybdenum into solution to be absorbed by those particles of M_2C which were coarsening. It also provided a source of molybdenum for the M_6C which was being nucleated, as well as for that which preexisted.

The precipitation processes in steel B, 0.06 pct C, were similar to those of steel A (Figure 9). After tempering for 30 minutes, the structure consisted of grain boundary $M_{23}C_6$ with M_2C and M_7C_3 precipitates distributed throughout the matrix. The extent of the carbide transformation reactions and the compositional changes in the molybdenum-based carbides (Figures 7 and 8) were, however, much less than in steel A, after tempering for similar times. The structure after 12 hours at 700 °C consisted of massive grain boundary carbides of either $M_{23}C_6$ or M_6C, with the matrix containing rapidly dissolving M_7C_3 particles, and rod-shaped M_6C precipitates which were undergoing coarsening.

In steel C, 0.09 pct C, both M_2C and $M_{23}C_6$, which were present in large proportions after 30 minutes tempering, dissolved during the 12 hour tempering treatment, while the M_7C_3 distribution was unaffected (Figure 10). Again, the compositions of both $M_{23}C_6$ and M_7C_3 remained constant during tempering and were the same as determined for steels A and B. The M_2C particles absorbed molybdenum as they coarsened during tempering with the composition varying from 50 at. pct Mo after one hour to 60 at. pct Mo after 12 hours (Figure 8). The rise in molybdenum content was at the expense of both chromium and iron. This compares with an increase from 65 at. pct Mo to 82 at. pct Mo over the same period for the M_2C in steel A. M_6C was detected only after 12 hours tempering and was of the low molybdenum (spectrum 2a) type.

The structure of steel C, after 12 hours tempering, appeared to be moving toward the equilibrium structure predicted by the work of Andrews et al,[7] namely, M_7C_3 and M_6C in ferrite. The structure of steels A and B, however, appeared to be tending to either M_6C, or $M_{23}C_6$ and M_6C, in ferrite, which is similar to the equilibrium structure shown by 0.1 pct C steels containing higher chromium and molybdenum levels than were present in the alloys examined in the current work.[7]

The microstructural and compositional features discussed above are not fully consistent with the precipitation sequence which has been proposed by Baker and Nutting[8] and by other workers[5,9] for commercial 2.25 Cr-1 Mo steels. This sequence may be summarized as:

$$Fe_3C \longrightarrow Mo_2C \longrightarrow M_{23}C_6 \longrightarrow M_6C$$
$$+$$
$$M_7C_3 \longrightarrow M_7C_3 .$$

In the current work, cementite present in the low carbon bainites dissolves in the very early stages of tempering and is replaced by the molybdenum-based carbide, M_2C, and the chromium-based carbides, M_7C_3 and $M_{23}C_6$. The latter carbides probably nucleate simultaneously as in 9 pct Cr steels.[10] During tempering M_7C_3 (alloys A, B) or $M_{23}C_6$ (alloy A) dissolves, releasing carbon for the formation of the more stable M_6C carbide. The initially large volume fraction of M_2C particles would result in a low level of molybdenum in the matrix and hence the first M_6C particles to be nucleated would be of the low molybdenum (spectra 2a) type. However, as the M_2C particles dissolve during tempering, molybdenum is made available for both nucleating and coarsening M_6C precipitates, and as was described earlier, the composition changes to that of the high molybdenum (spectra 2b) type carbide.
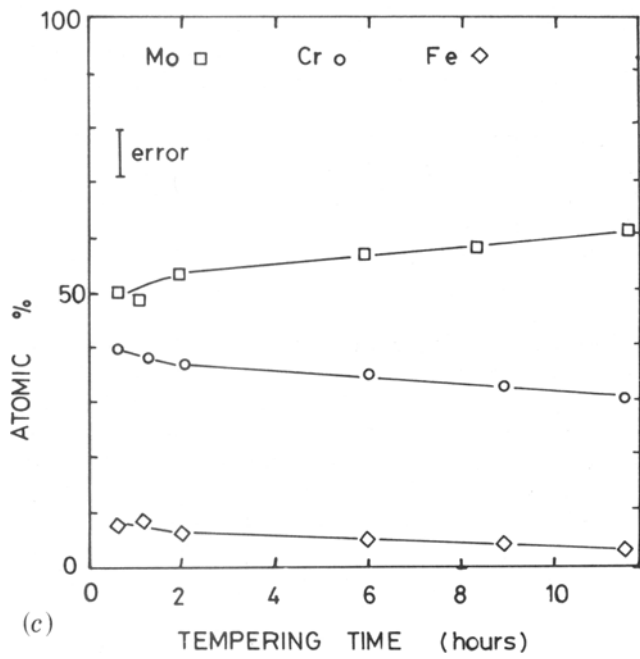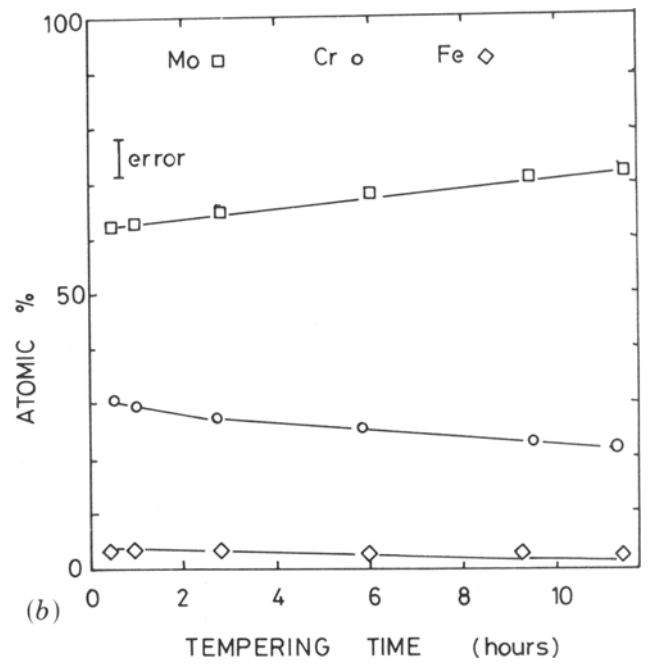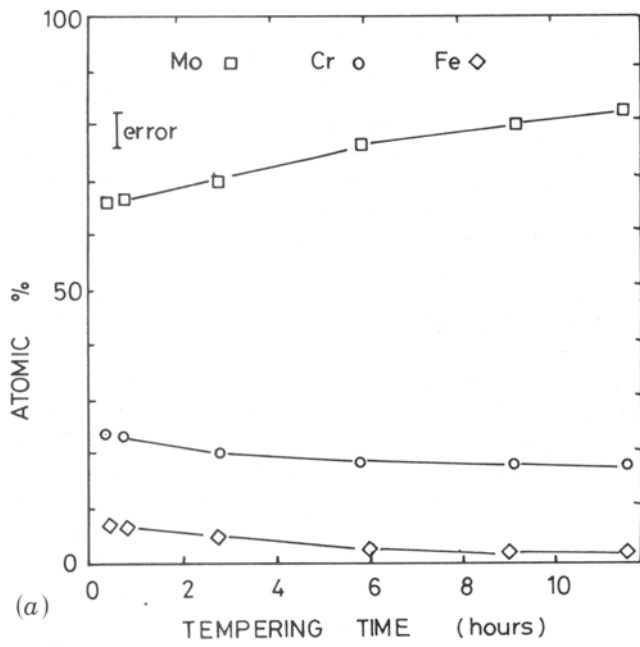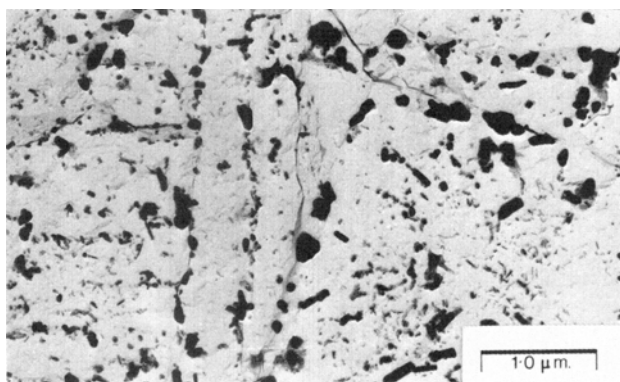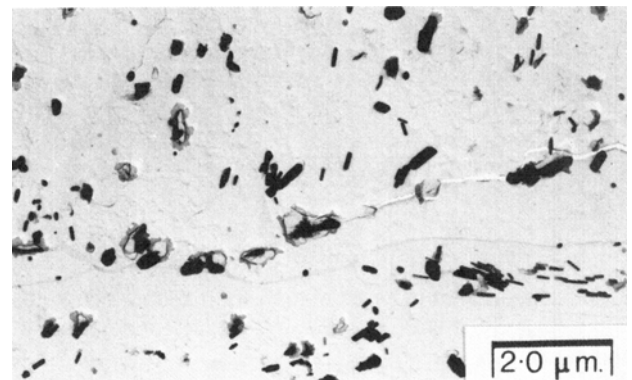
Fig. 8 — Variation in composition of M₂C on tempering at 700 °C. (a) Steel A (0.018 pct C), (b) steel B (0.06 pct C), (c) steel C (0.09 pct C), after ZAF correction.

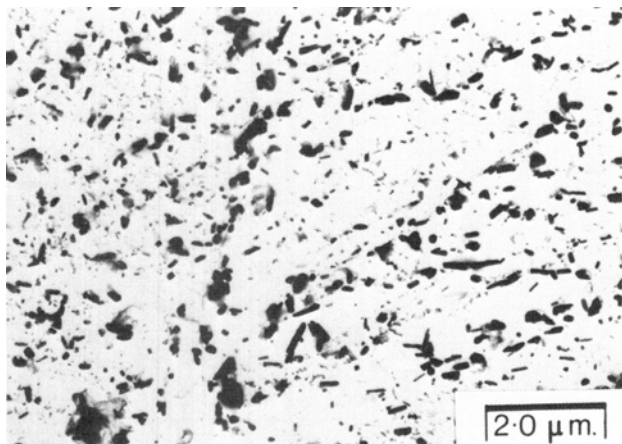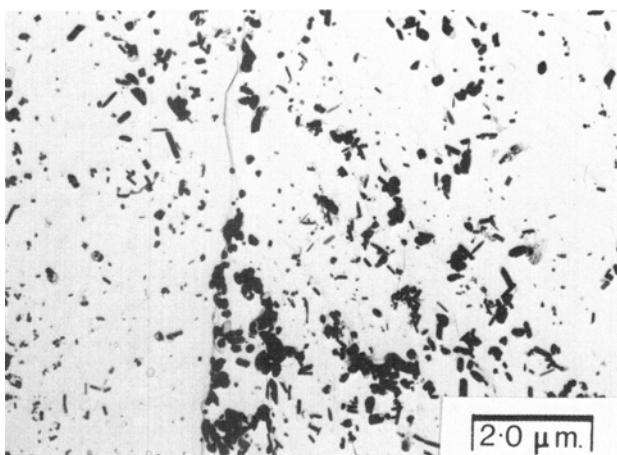Fig. 9—Steel B (0.06 pct C) carbide distribution after (a) 3 h, (b) 12 h at 700 °C.

(a)

(b)

Fig. 10—Steel C (0.09 pct C) carbide distribution after (a) 3 h, (b) 12 h at 700 °C.

The displacement in equilibrium structure with changing carbon level is not unexpected. In terms of the Cr + Mo:C atom ratio, a decrease in the carbon content of a particular alloy steel would have the same effect as increasing the Cr + Mo content while maintaining the carbon level constant. Further, an increase in the effective alloy content above that for stoichiometry would tend to increase the driving force for the precipitation reactions. This was particularly true for the case of molybdenum, where an increase in the Mo:C ratio increased the level of molybdenum in the molybdenum-based carbides as well as promoting the more rapid formation of a greater volume fraction of M_6C.

The Cr:C ratio would appear to be less important than the Mo:C ratio, as the composition of the chromium-based carbides was not affected by changes in the carbon level of the steel or by the duration of tempering. The compositions of $M_{23}C_6$ and M_7C_3 were

$$Cr_{8.4}Fe_{12.0}Mo_{2.6}C_6$$

$$Cr_{4.2}Fe_{2.4}Mo_{0.4}C_3 ,$$
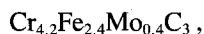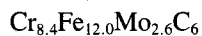
respectively. The composition of M_7C_3 was similar to that

reported by Tunney et al[11] for M_7C_3 in a tungsten modified En 40 C die steel, with tungsten and vanadium having substituted for molybdenum.

V. CONCLUSIONS

1. The microstructure of 2.25 Cr-1 Mo steels tempered at 700 °C is dependent on carbon level. A reduction in the carbon from 0.09 to 0.06 pct displaces the equilibrium structure from M_7C_3 and M_6C in ferrite to one of $M_{23}C_6$ and M_6C in ferrite. A further reduction to 0.02 pct produces only M_6C in ferrite.
2. The rate at which the carbide replacement reactions take place increases as the carbon content of the steel is reduced.
3. The carbides contained in tempered 2.25 Cr-1 Mo steels can be uniquely identified in terms of the relative heights of the EPMA spectra peaks for Fe, Cr, Mo, and Si.
4. The compositions of the chromium-based carbides, $M_{23}C_6$ and M_7C_3, are independent of both the carbon content of the steel and of the duration of tempering at 700 °C.
5. The compositions of the molybdenum-based carbides, M_2C and M_6C, show an increase in molybdenum level with increasing time of tempering at 700 °C, and the level of molybdenum content was found to be greater as the carbon content of the steel was reduced.

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