

Carbide compositions in 12Cr1MoV power plant steels
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Carbide precipitation studies in 12Cr1MoV steel are discussed in this chapter. As a result of the very high chromium concentration of 12Cr1MoV steel, the reaction kinetics are rapid compared to those in low alloy steels. It is found that the equilibrium alloy carbide precipitates during the commercial stress-relief heat treatment and does not change in composition during further tempering. This is an important result; indications are that once the cementite transforms to alloy carbides, any changes in their composition are not large enough for this method to be used as a quantitative estimation of remanent life. (Low alloy steels, however, contain cementite for a considerable fraction of their useful service life.)

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7.1 Introduction

The vast majority of creep-resisting steels used in power plant or in the petrochemical industry are based on low-carbon, low-alloy steels containing carbide forming elements such as chromium, molybdenum and vanadium as deliberate additions. In addition to creep resistance, prolonged service at elevated temperatures also requires good oxidation and hot-corrosion resistance, possibly in environments containing hydrogen and sulphur. In the United Kingdom, the steels are often used within the temperature range 480–565°C, the service stresses being of the order of 15–30 MPa over time periods of some thirty years. There is currently considerable research in progress to implement higher alloy steels with the aim of improving the creep strength so that the service temperature can be increased (Alberry and Gooch, 1983; Middleton, 1986). Alternatively, the higher strength can be exploited by reducing section size, which can be beneficial from the viewpoint of welding, thermal fatigue and the reduced cost of support structures. A lot of the effort to date has focussed on 12Cr1MoV steel. The purpose of this work was to examine the effect of representative heat-treatments on the chemistry and some other characteristics of the carbides to be found in 12Cr1MoV type steels.

7.2 Materials and heat treatment

The material used in this work was a 12Cr1MoV steel supplied by National Power Technology and Environment Centre, Leatherhead, from heat 60348. The steel was supplied in the form of a rod of diameter 4 cm×1 m long. Thinner rods of 3 mm diameter and bars 1×1×4 cm were machined from the original sample. Experimental results were compared with ‘ex-service’ material (i.e. steel which has been in service in a power station), courtesy of Laborelec, Belgium. The service history of this latter pipe was 68,646 hours at 592°C followed by 146,000 hours at 587°C, both at a pressure of 175 bar. The compositions of both steels, which are both within British Standard, BS3604, and the German standard X20 for 12Cr1MoV steels, are given in Table 7.1. In spite of this, it is worth noting that the chromium concentration of the ex-service steel is significantly higher.

Heat treatments were carried out in order to recreate the microstructures used in the commercial condition when the steels are first implemented for service. The material is metallurgically complex and requires careful control of the heat treatment to ensure that the starting

Table 7.1: Chemical compositions of the 12Cr1MoV steels in wt. %

	C	Si	Mn	P	S	Cr	Mo	V	Ni	Cu	Al	Co	Nb+Ta
12Cr1MoV	0.21	0.25	0.46	0.009	0.012	10.9	1.03	0.30	0.52	0.02	<0.005	0.02	0.06
Ex-service X20CrMoV12 1	0.18	0.22	0.58	0.01	0.007	12.4	1.07	0.28	0.64	0.13	0.01	0.03	<0.01

microstructure is 100% martensitic. The specimens were sealed in silica tubes containing a partial pressure of argon of 150 mm Hg. Austenitisation was carried out at 1060°C for 15 minutes. It has been shown by Barraclough and Gooch (1985) that the austenitising temperature for 12Cr1MoV steels is crucial in determining the microstructure and mechanical properties. Too low a temperature will cause heavily spheroidised microstructures with dramatically reduced creep resistance, and too high a temperature can result in the formation of δ ferrite and a large austenite grain size, which is undesirable. Yet the temperature must be high enough to ensure the complete dissolution of carbides. After austenitisation the specimens were air-cooled, and re-sealed in silica tubes and tempered for up to 2 hours at 700°C, in order to simulate the commercial stress-relief heat treatment, and then further tempered at 565°C to simulate service conditions.

7.3 Results

7.3.1 Microstructural changes

A typical optical micrograph is shown in Figure 7.1. It can be seen that the microstructure is 100% martensite and does not contain any δ ferrite. TEM micrographs of the as-quenched microstructure are presented in Figure 7.2. Figure 7.2a) shows martensite platelets containing some internal twins, confirmed by selected area electron diffraction. Figure 7.2b) demonstrates the fact that there are no carbides in the as-quenched microstructure, i.e. that no autotempering has occurred. Gooch (1982) reported that the microstructure obtained by cooling from 1100°C contained a fine dispersion of cementite particles. This difference is attributed to the relatively slower speed of the quench.

Figure 7.3a) and b) illustrate the carbides beginning to form at prior austenite grain and lath boundaries, and also intra-lath, in a specimen which has been tempered at 700°C for 15 minutes. The carbides were identified by selected area electron diffraction as both M_7C_3 and $M_{23}C_6$.

The carbide M_7C_3 was also found in specimens aged for up to 30 minutes at 700°C, but these had all dissolved at the end of the stress-relief heat treatment. Figure 7.4 shows that

M_7C_3 was mainly found within the martensite laths and distant from the clustered $M_{23}C_6$ precipitates. This is in agreement with Beech and Warrington (1966) who found that $M_{23}C_6$ and M_7C_3 were both present from an early stage of tempering, and that on spheroidisation the particles within the martensite laths disappeared. The diffraction pattern in Figure 7.4 illustrates the characteristic streaks of M_7C_3 resulting from its faulted structure compared with that of pure Cr_7C_3 (Westgren *et al*, 1928). No difference in morphology was found between M_7C_3 and $M_{23}C_6$, apart from a tendency for the former carbides to be much finer.

A typical carbon extraction replica from a sample which had been given the commercial stress-relief heat treatment, i.e. tempering at 700°C for 2 hours, is shown in Figure 7.5. The distribution of the carbides in relation to the martensite boundaries is clearly illustrated. The carbides at the end of the stress-relief heat treatment were found to consist chiefly of a dispersion of $M_{23}C_6$ particles concentrated on the austenite grain and lath boundaries.

A comparison between the distribution of coarse $M_{23}C_6$ carbides in the ex-service material and in a specimen isothermally heat treated at 700°C for 1173 hours is presented in Figure 7.6. The empirical Larson-Miller (Larson and Miller, 1952) parameter, defined as $T(20 + \log t)$, where T is the temperature in Kelvin and t is the time in hours, indicates that these two different heat treatment conditions are comparable. The carbide size and distribution is similar in the two materials, although for reasons which are not clear there appears to be a tendency for increased clustering of the carbides in the ex-service material.

Macrohardness measurements were made on all the specimens using a 30 kg load. These results are presented in Table 7.2. Each data point is the average of three measurements on each sample, with the total scatter being no more than 10 HV. The macrohardness data confirms that the microstructure of the ex-service material and the 12Cr1MoV steel are similar, and that little change in carbide precipitation occurs on tempering.

Table 7.2: Macrohardness measurements

Specimen	Macrohardness /HV
Pre-tempering	622
700 °C-15 mins	315
700 °C-30 mins	309
700 °C-60 mins	296
700 °C-120 mins	315
700 °C-1173 hours	293
Ex-service material	302

The appearance of additional phases, such as Laves phase, on tempering a 12Cr1MoV steel depends critically upon the base composition of the steel. In the steels used in this work no additional phases were found during tempering which is consistent with the work of Briggs and Parker (1965).

7.3.2 Thermodynamic calculations

Thermodynamic calculations were performed using MTDATA in order to calculate the equilibrium phases in the 12Cr1MoV steel. The carbide $M_{23}C_6$ was found to be the stable carbide, coexisting with ferrite, at all temperatures in the range of interest, 400–800°C. The equilibrium solution temperature of the carbides was found to be 950°C. Barraclough and Gooch (1985) found that 30 minutes at 950°C was not an adequate solution heat treatment, although 30 minutes at 1000°C was satisfactory. The temperature at which delta ferrite became stable on heating was calculated as 1220°C in the 12Cr1MoV steel, and as 1110°C in the ex-service material, which contained an additional 1.5 wt.% chromium. This difference is consistent with the work of Irvine *et al.* (1960) who found that an increase in chromium content of 1 wt.% led to an increase in δ -ferrite content of $\simeq 14\%$. This confirms that the commercial austenisation temperature range of 1020–1070°C is adequate to completely dissolve carbides and will not produce large amounts of δ -ferrite.

$M_{23}C_6$ was found to be the most stable carbide, then M_7C_3 , followed by cementite. A precipitation sequence of $M_3C \rightarrow M_7C_3 \rightarrow M_{23}C_6$ is therefore possible.

The results of the thermodynamic calculations for 700°C (the stress-relief heat treatment) and for 565°C (the service temperature) are presented in Table 7.3. The alloying element content of the two carbides of interest, M_7C_3 and $M_{23}C_6$, is presented as a function of temperature in Figure 7.7a) and b).

Table 7.3: Chemical compositions of the carbides in both the 12Cr1MoV steels used in wt.%. The calculations were performed using MTDATA at 700°C and 565°C respectively.

	12Cr1MoV Steel					'Ex-service' 12Cr1MoV steel				
	Fe	Cr	Mo	Mn	C	Fe	Cr	Mo	Mn	C
700°C										
M_7C_3	5.2	82.2	3.1	0.6	8.9	4.6	83.2	2.7	0.7	8.8
$M_{23}C_6$	10.7	65.1	19.1	–	5.1	9.0	66.4	19.5	–	5.1
565°C										
M_7C_3	1.6	84.4	4.5	0.7	8.8	1.4	85.1	4.0	0.7	8.8
$M_{23}C_6$	4.2	70.3	20.4	–	5.1	3.6	70.9	20.4	–	5.1

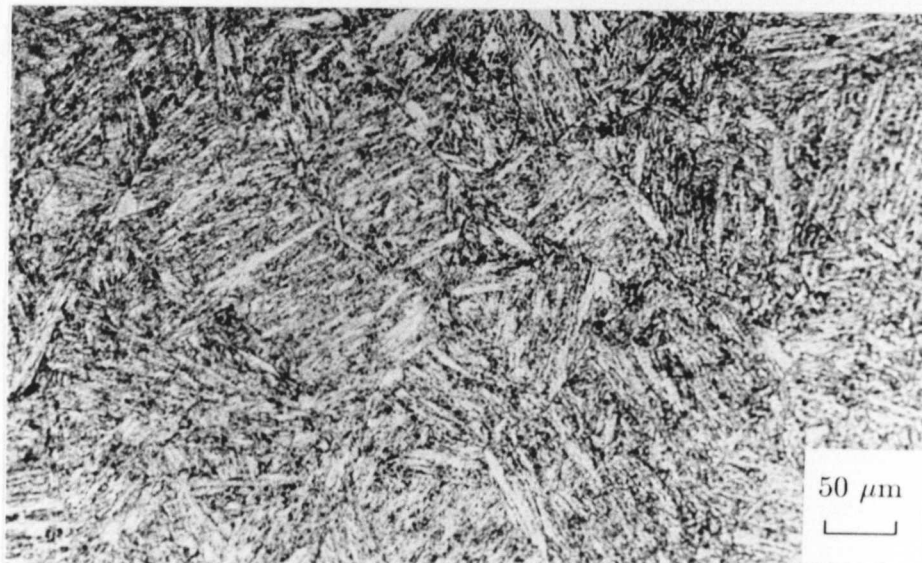
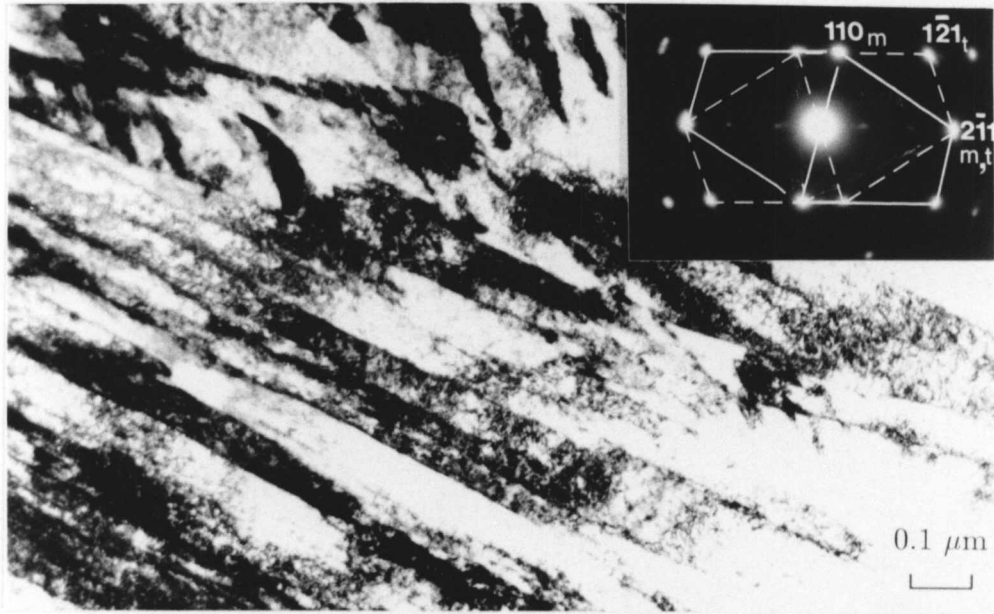


Figure 7.1: Optical micrograph for specimen austenitised at 1060°C 15 mins, air cooled, and tempered for 2 hours at 700°C.

a)



b)

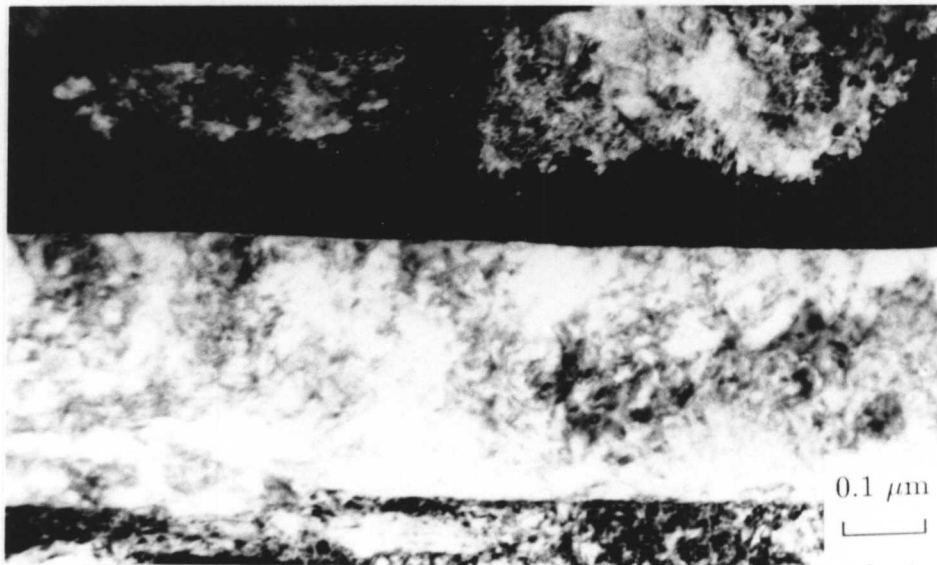
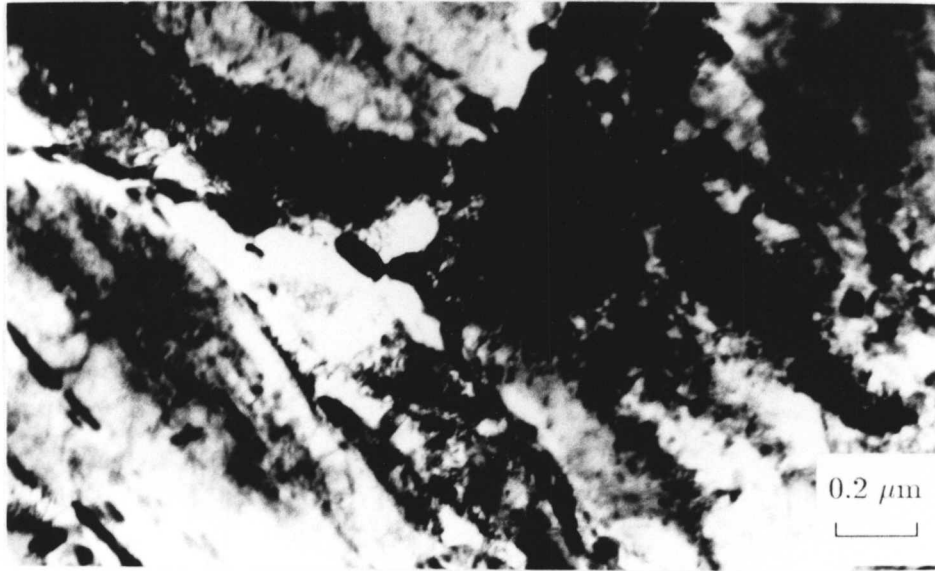


Figure 7.2: Transmission electron micrographs from the as-quenched microstructure. a) illustrates the twinned martensite microstructure; the inset is a selected area diffraction pattern showing the twin (t) and matrix (m) reflections. The twin plane is $2\bar{1}1$. b) is a higher magnification image showing that no auto-tempering has occurred.

a)



b)

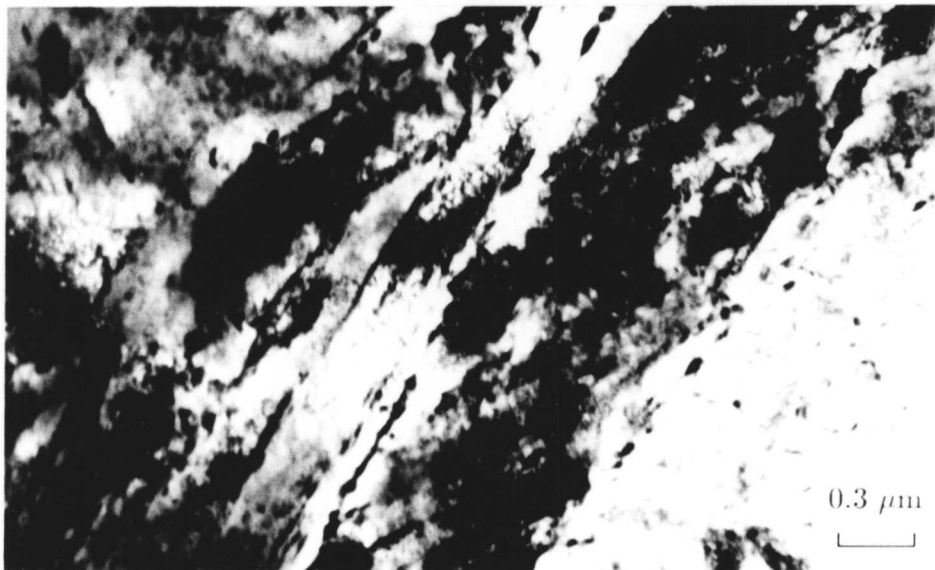


Figure 7.3: Transmission electron micrographs illustrating carbide formation at both the grain a) and lath b) boundaries in a specimen tempered for 15 minutes at 700°C.

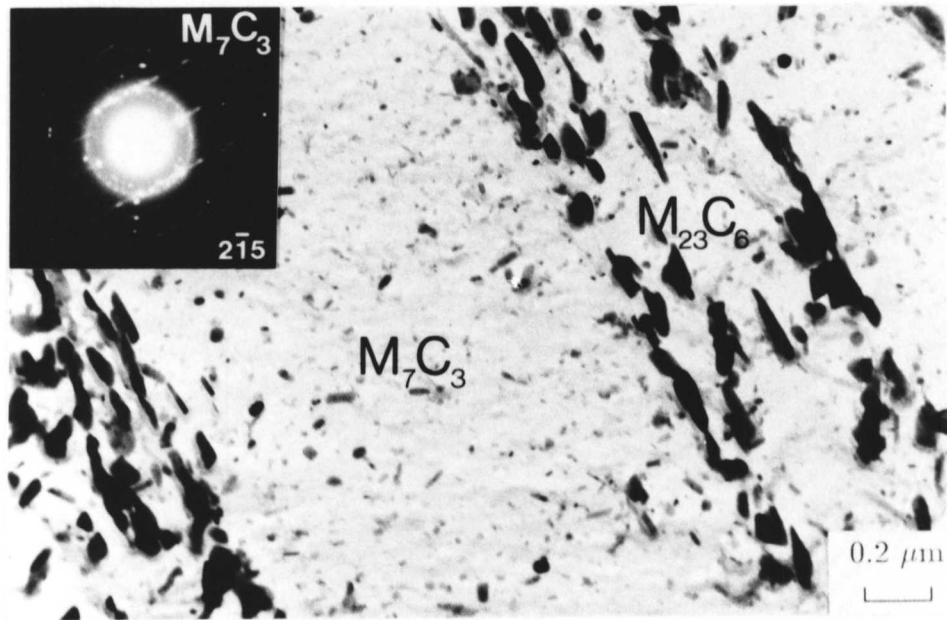


Figure 7.4: Carbon extraction replica showing small M_7C_3 particles distributed within the martensite laths and distant from the larger $M_{23}C_6$ particles clustered on the lath boundaries. The inset is a selected area diffraction pattern of M_7C_3 , the zone axis being $[2\bar{1}5]$ and showing characteristic streaks.

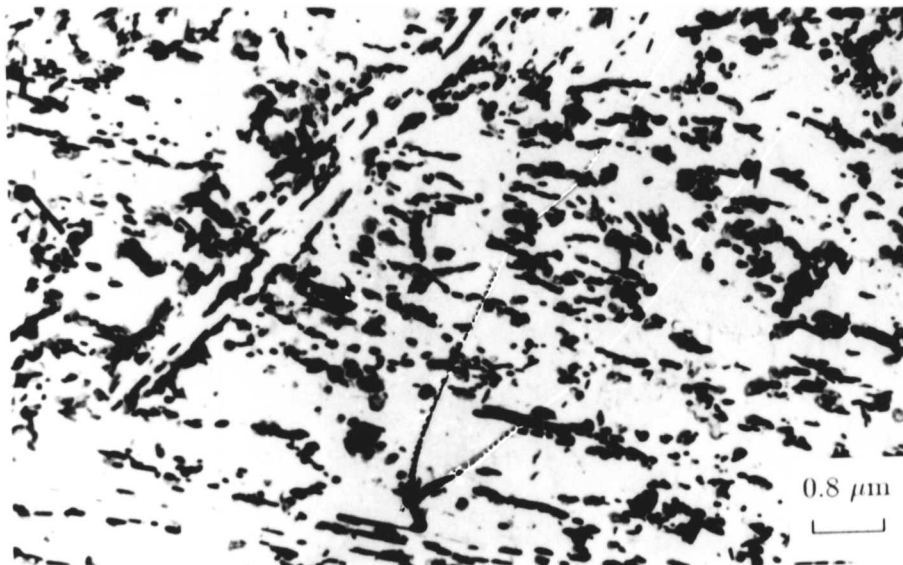


Figure 7.5: Carbon extraction replica from a specimen tempered for 2 hours at 700°C illustrating the distribution of $M_{23}C_6$ carbides with respect to martensite lath boundaries.

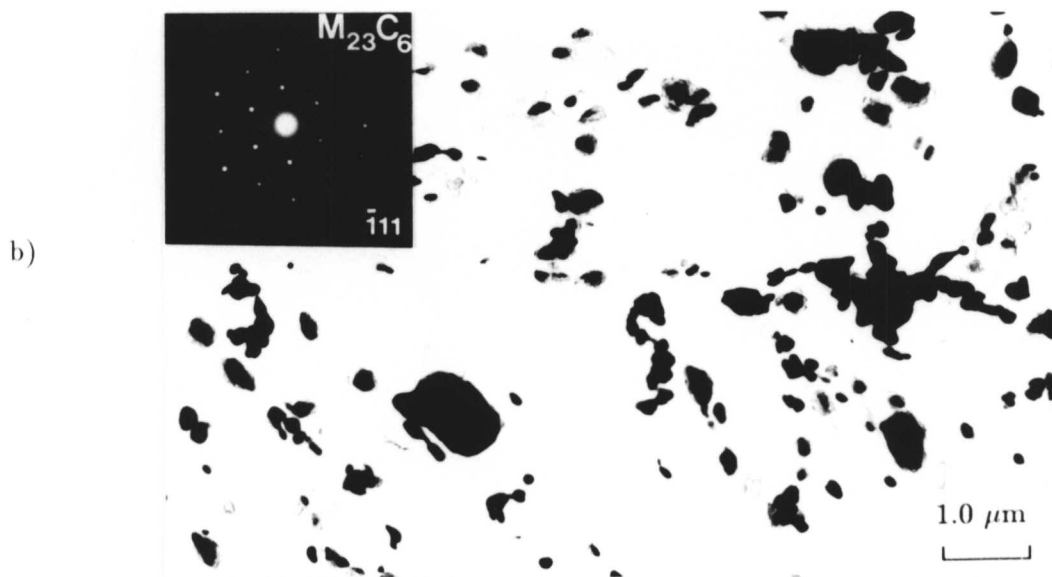
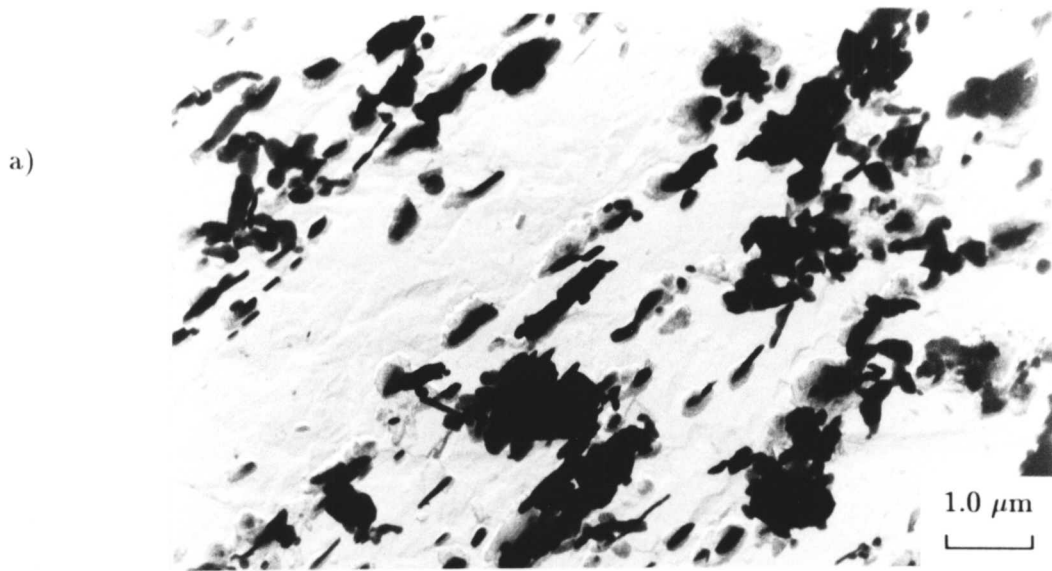


Figure 7.6: A comparison between the distribution of $M_{23}C_6$ carbides in the ex-service material a) and in the specimen isothermally heat treated for 1173 hours at 700°C b) which represent comparable heat treatments according to the empirical Larson–Miller parameter. The inset in figure b) is a selected area electron diffraction pattern of $M_{23}C_6$ in the $[\bar{1}11]$ orientation.

The carbides found in the microstructural investigation were M_7C_3 and $M_{23}C_6$, in good agreement with the sequence predicted by thermodynamic calculations. The EDXS results show that the equilibrium chromium content of the carbide M_7C_3 is higher than that in $M_{23}C_6$. The absolute levels of Cr and Mo predicted to be in the carbides are slightly higher than those observed experimentally (e.g. 65 wt.% Cr and 20 wt.% Mo are predicted in $M_{23}C_6$, whereas 60 wt.% Cr and 10 wt.% Mo, allowing for 5 wt.% C, are measured experimentally), however, there is good general agreement. The chromium content of both carbides in the ex-service material is larger due to the increased bulk chromium content of the alloy. The carbides can support a greater substitutional alloying content as the temperature is lowered. It is possible, therefore, that when the steel is in service at the lower temperature of 565°C, after the stress-relief heat treatment, the chromium content of the $M_{23}C_6$ may increase by approximately 4–5 wt.%. It is likely, however, that this approach to equilibrium will be extremely slow and difficult to detect within the experimental error of energy-dispersive X-ray spectroscopy.

7.3.3 Cementite precipitation

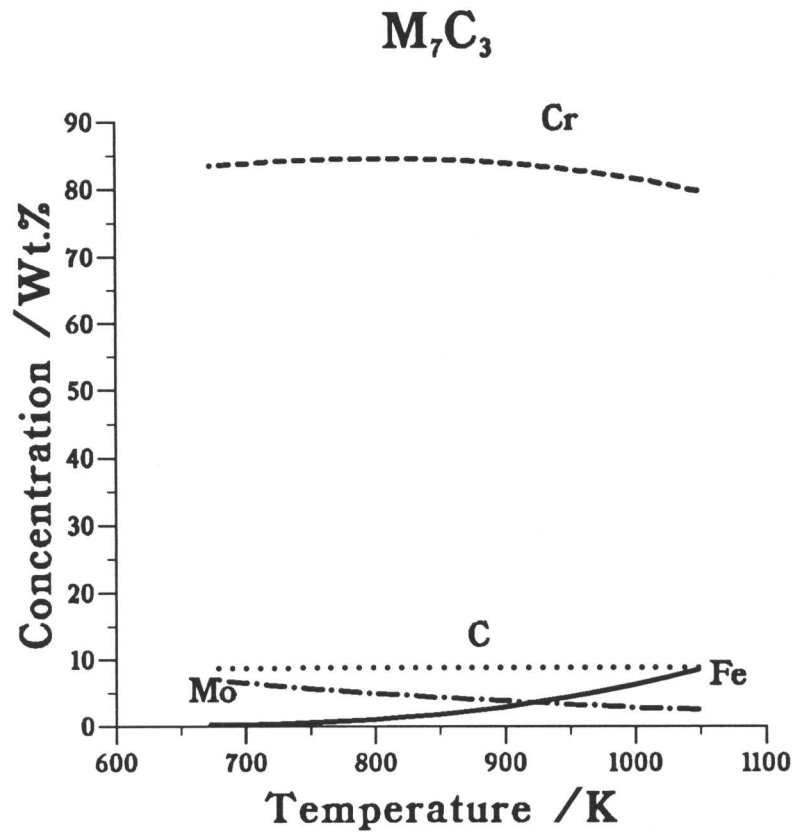
It is interesting to note that no cementite was found in any of the specimens, even during the earliest stages of tempering, because cementite is usually expected to be the first carbide to form on tempering martensite. Therefore the computer model described in Chapter 3 was used to investigate the time for cementite, with an initial composition determined by assuming a paraequilibrium transformation mechanism, to reach its predicted equilibrium composition. The results of these calculations are presented in Figure 7.8. The chromium concentration in the cementite is plotted against the time allowed for diffusion at 700°C for a range of particle sizes between 10 and 30 nm. It can be seen that cementite in fact saturates in an extremely short time, of the order of a few minutes. It is concluded that with the large amount of chromium in the base composition of the steel, the driving force for alloy carbide precipitation is large, and that cementite will only be seen in this steel if tempering takes place at a much lower temperature, or possibly immediately after tempering has begun.

7.3.4 X-ray microanalysis

Extensive measurements of carbide composition and particle size were performed on carbon extraction replicas using EDX. The results of the analyses on the carbides contained in specimens tempered at 700°C for 15, 30, 60 and 120 minutes respectively are presented in Figure 7.9a)–d) as plots of the chromium concentration against particle size, measured in terms of a mean linear intercept.

It can be seen in the 15 minute specimen that M_7C_3 (with a composition of approximately

a)



b)

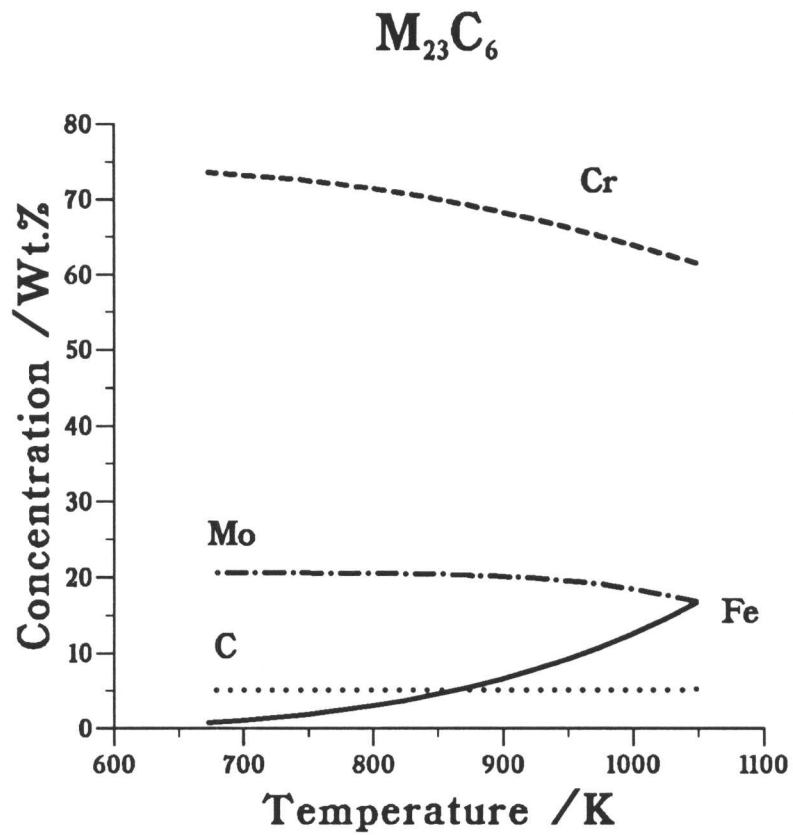


Figure 7.7: Alloying element content of M_7C_3 a) and $M_{23}C_6$ b) carbides as a function of temperature in the 12Cr1MoV steel.

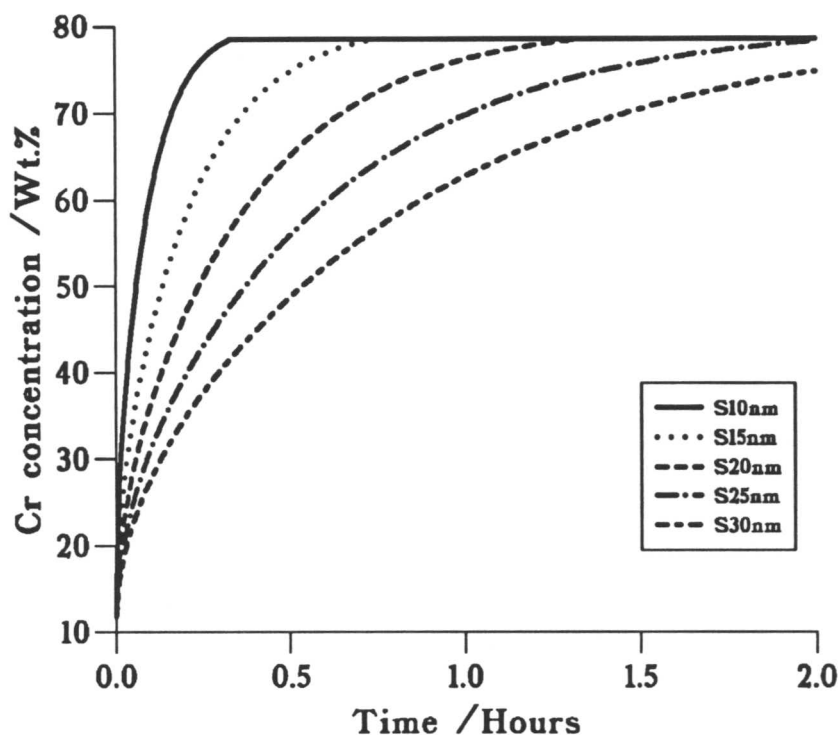


Figure 7.8: Calculated rate of cementite enrichment with respect to chromium concentration for particles of sizes 10–30 nm using a finite difference model.

75 wt.% Cr, 20 wt.% Fe and small amounts of molybdenum and manganese) is found to co-exist with $M_{23}C_6$ (with a composition of approximately 60 wt.% Cr, 30 wt.% Fe and 10 wt.% Mo). These compositions are in general agreement with those of Beech and Warrington (1966), the absolute values being dependent on the base composition of the steel. The average chromium concentration in $M_{23}C_6$ in all the specimens ranged from 60–63 wt.%. The transition from M_7C_3 to $M_{23}C_6$ is picked up in the 30 minute specimen. After 1 hour there is very little evidence of any M_7C_3 being present in the microstructure, and after the completion of the stress-relief heat treatment all the M_7C_3 has redissolved. Figure 7.9e) compares data from the ‘ex-service’ material and the specimen tempered for 1173 hours at 700°C. The chromium content in the carbides in the ‘ex-service’ material is larger than that in the isothermally tempered specimen, but this difference can be attributed to the the higher chromium content in the base composition of the steel and the longer tempering time. In both cases, however, the chromium content is constant.

7.3.5 X-ray diffraction analyses

X-ray diffraction analyses on particles extracted from the steel matrix using the method described in Chapter 4 for specimens tempered at 700°C for 10 minutes and 2 hours respectively

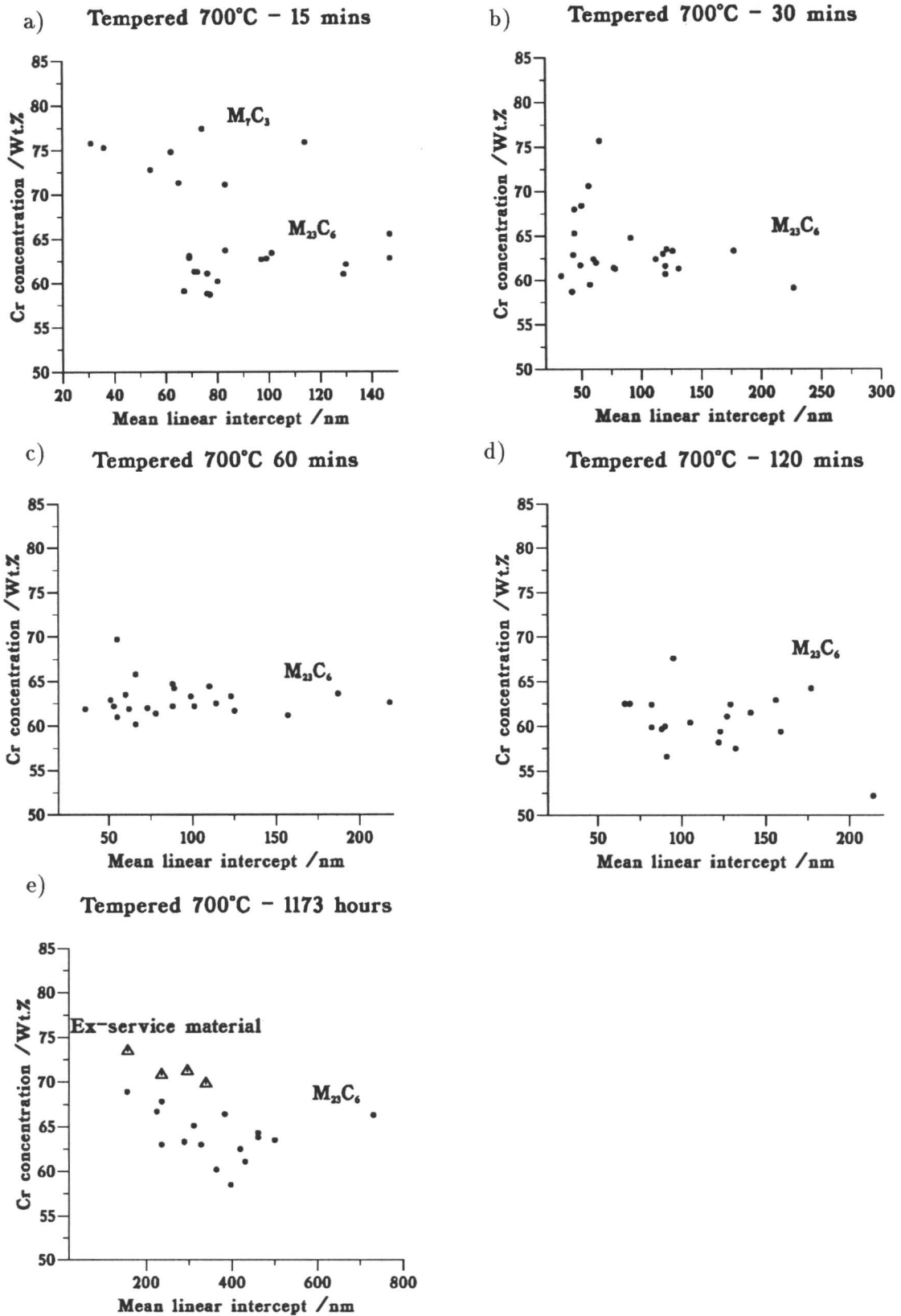


Figure 7.9: a)–e) Cr concentration versus particle size for specimens tempered at 700°C for varying times. In e) the results are compared with the composition of $M_{23}C_6$ in the ex-service material.

are presented in Figure 7.10a) and b). In the spectra for the specimen tempered for 10 minutes, the 420 and 202 peaks from M_7C_3 are clearly visible, whereas these have disappeared after tempering for 2 hours. The 420 and 202 peaks are the strongest visible peaks for M_7C_3 because the strong 421 peak overlaps with the strong 511 peak of $M_{23}C_6$. There was no further change in the diffraction pattern for specimens tempered up to 1200 hours at 700°C. The lattice parameters for $M_{23}C_6$ extracted from all the heat-treated specimens of the 12Cr1MoV steel were calculated using the measured values of d-spacings. Errors can arise in the measured values of the d-spacings factors such as the geometry of the diffractometer and absorption in the specimen. These were corrected for by fitting a polynomial function to the d-spacings of the internal standard, which are known to a high degree of accuracy. $M_{23}C_6$ is cubic and therefore the d-spacings and plane indices are related by the equation

$$d_{hkl}^2 = \frac{a^2}{h^2 + k^2 + l^2}.$$

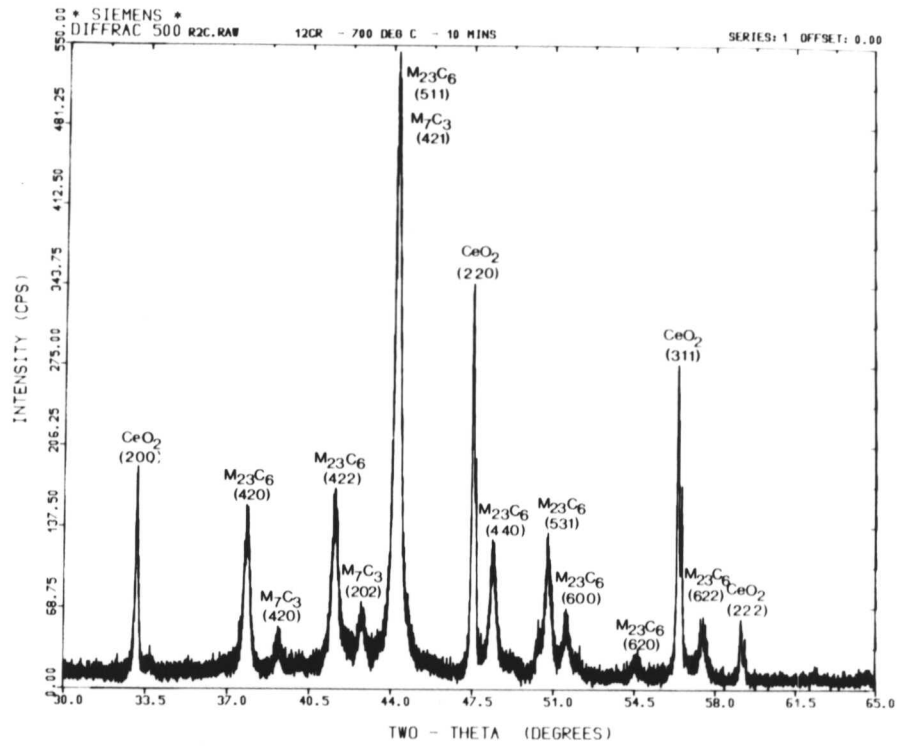
The adjusted d-spacings were fitted to this equation using a non-linear least-squares procedure. The calculated lattice parameters are presented in Table 7.4.

Table 7.4: Lattice parameters of $M_{23}C_6$ determined by X-ray diffraction.

Time at 700°C	Lattice parameter / Å
10 mins	10.64 ± 0.01
15 mins	10.65 ± 0.01
30 mins	10.66 ± 0.01
1 hour	10.65 ± 0.01
2 hours	10.65 ± 0.01
1173 hours	10.66 ± 0.01
2 hours + 16 hrs at 565°C	10.65 ± 0.01

The lattice parameter of $(Fe, Cr)_{23}C_6$ containing 60 wt.% Cr extracted from a commercial steel containing 14 wt.% Cr has previously been measured as 10.595 Å (Gullberg, 1971). In order to estimate the change in lattice parameter due to the molybdenum content in the $M_{23}C_6$ in this work the relative sizes of the atoms are considered. Molybdenum atoms are 10% larger than chromium and may replace up to 8 out of 92 of the metal atoms in the unit cell (Franck *et al*, 1982). The 10 wt.% Mo measured in the carbide corresponds to $Cr_{16}Fe_6Mo_1C_6$, and therefore an increase in lattice parameter to $10.59(1+0.1 \times \frac{1}{23}) = 10.64 \text{ Å}$ is predicted. This is

a)



b)

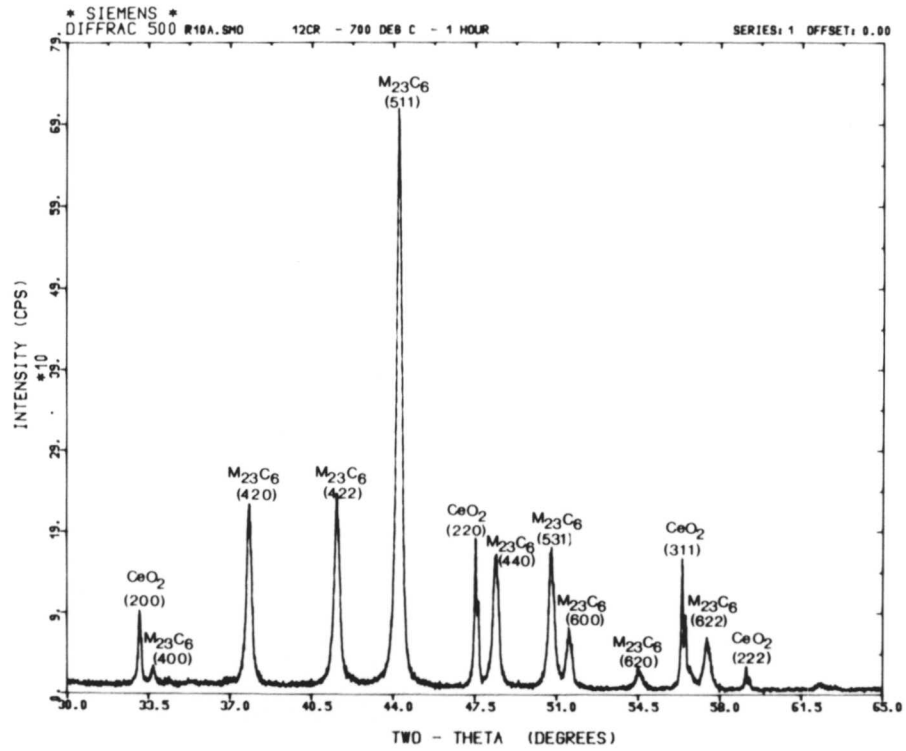


Figure 7.10: X-ray diffraction patterns for specimens tempered at 700°C for 10 mins a) and 1 hour b) respectively illustrating that M_7C_3 initially present along with $M_{23}C_6$ has dissolved after tempering for 1 hour.

in good agreement with the calculated value. The calculated lattice parameters differed by no more than 0.02Å, indicating again no significant differences in the composition of the $M_{23}C_6$ after tempering.

7.4 Discussion

The carbides precipitating during the stress-relief heat treatment in 12Cr1MoV steel have been identified by X-ray diffraction and selected area electron diffraction as M_7C_3 and $M_{23}C_6$. Therefore, before entering service at approximately 565°C, the steel contains a distribution of $M_{23}C_6$ particles. The initial composition of the carbides is close to that predicted using equilibrium thermodynamics, and it has been established by EDX that there is no further change in the composition of the carbides with tempering. No significant dependence of chromium concentration on particle size was found. Lattice parameter measurements and comparison with ex-service material confirm that there is no change in composition of the $M_{23}C_6$ on tempering, especially with respect to molybdenum, which might have been expected from the thermodynamic calculations. The fact that there is no enrichment occurring on tempering in 12Cr1MoV steel is in contrast to the low alloy steels reported in the previous chapter. Du (1986) found that the chromium content in $M_{23}C_6$ precipitating in a $\frac{1}{2}Cr\frac{1}{2}Mo\frac{1}{4}V$ steel increased with time. Whether or not alloy carbides precipitate at their equilibrium composition is therefore dependent on the concentration of alloying elements available in the base composition of a steel. Recent work by Bjärbo (1991) (for an alloy with a higher chromium content than that used in this work) has shown that $M_{23}C_6$ which precipitates during the stress-relief heat treatment is enriched in chromium by less than 5 wt.% during a creep test for 20,000 hours at 600°C.

7.5 Conclusions

The kinetics of carbide precipitation in 12Cr1MoV steels are rapid when compared with other low-alloy steels of the type commonly used in power plant. This is attributed to the fact that the steel studied has relatively large concentrations of carbide-forming substitutional solutes. Thus, unlike the low-alloy steels, relatively stable alloy carbides have been found to dominate in the microstructure immediately after the stress-relief heat treatment. Since this heat treatment is always necessary before implementing the alloy in service, there seems little prospect of estimating the thermal history of a component from the chemical composition of its carbides. In fact, both the thermodynamic analysis and the experimental data show that the chromium concentration of the $M_{23}C_6$ carbide is very sensitive to the average chromium concentration of the steel. It is found that variations in the chromium concentration within

the accepted industrial specifications, can lead to larger corresponding variations in carbide compositions, than would be caused during service.

It has been established that there is no significant change in the carbide identity or composition during service after the stress-relief heat treatment. Therefore, the question arises as to which other microstructural changes could be fruitfully investigated. It seems from a comparison of figures 7.9d) and e), which show an increase in particle size from about 125–300 nm, that carbide coarsening could potentially be used as a microstructural parameter.

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