RELATIONSHIP BETWEEN MICROSTRUCTURE
AND MECHANICAL PROPERTIES OF A 5% CR
HOT WORK TOOL STEEL

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Abstract Usual mechanical properties of martensitic steels are strongly linked to their complex microstructure obtained after heat treatment. Heat treatments are generally performed in order to achieve a good hardness and/or tensile strength with a sufficiently acceptable ductility. Nevertheless, microstructural parameters (connected with carbides and dislocations) giving suitable mechanical properties at the initial state are never totally investigated. Our reference grade is the well-known X38CrMoV5 (AISI H11) steel.

The main goal of this work deals with a quantitative identification of relevant microstructural parameters ensuring a good mechanical strength of these steels at working temperatures. Particularly, influences of the tempering temperature and of the fatigue strain amplitude are discussed.

Keywords: 5% Cr martensitic steel, TEM observations, X-Ray Diffraction, X-Ray profile analysis, microstructure, dislocations, carbides, fatigue, second tempering
INTRODUCTION

Mechanical properties and particularly yield stress of tempered martensitic steels for high temperature forming operations (such as pressure die casting for light alloy injection, forging dies, mandrels, etc.) are strongly influenced by heat treatments and cyclic plasticity [1, 2]. For example, Fig. 1 shows that hardness level may decrease from 52 HRC to 40 HRC for a tempering temperature increasing from 580 °C to 640 °C (typical second tempering temperature range). Figure 2 shows the strong softening effect occurring during an isothermal fatigue test [1].

![Figure 1. Hardness versus tempering temperature for Mod. AISI H11 steel.](image)

The most relevant microstructural elements in martensitic structure are the thin laths (their width can be less than 0.1 µm, the dislocation density generated during quenching, the fine carbide precipitation occurring during tempering, prior austenitic grains and of course, the chemical composition and the crystal structure of the martensitic matrix. Though some investigations of martensitic steel cyclic softening were carried out [3, 4, 5, 6], quantitative evaluations of relevant microstructural elements responsible for the good mechanical strength and fatigue resistance at high temperatures
are not so often performed and published. However, it would be essential to estimate evolutions of these parameters with time, temperature and strain amplitude in order to take into account the fatigue resistance and behaviour in the definition of heat treatment conditions. The ultimate intention of such a study, which consists in understanding the interactions between microstructure and properties, is to ensure a good prediction of the cyclic behaviour [7] in order to optimise tool conceptions and to derive a new life model based on microstructural considerations.

A first step would be to constitute a clear correlation between the yield stress and the microstructure. Several mechanisms contribute to the yield stress of tempered martensitic steels. Even if we can discuss a long time on the validity of the simple additive decomposition of the yield stress, several successful attempts have been performed on steels [8, 9], and the general equation of the following form is often quoted [8].

$$\sigma_y = \sigma_0 + \sigma_{ss} + \sigma_p + \sigma_d + \sigma_{sg} + \sigma_t + \sigma_{hp}$$  \hspace{1cm} (1)

where $\sigma_0$ is the friction stress, $\sigma_{ss}$ is the solid solution strengthening, $\sigma_p$ is the precipitation strengthening, $\sigma_d$ is the dislocation strengthening, $\sigma_{sg}$ is the strengthening due to subgrains, $\sigma_t$ is the crystallographic texture strengthening and $\sigma_{hp}$ is the contribution of the grain (prior Austenitic grain and lath).
boundary strengthening. Nevertheless, probably due to the complex microstructure of tempered martensitic steels, clear quantitative contributions of each mechanism are infrequently determined.

In a previous study [1], we have noticed that prior austenitic grain size and martensitic lath size are not influenced by second tempering temperatures (between 580 °C and 640 °C) and a fatigue total strain amplitude (Δεt < 1% and 200 °C < T < 550 °C). Conversely, TEM observations show a clear evolution in both cases of carbide sizes and dislocation densities. The present investigation deals with the evolution of individual contribution to strengthening of dislocations and precipitates with tempering temperatures and fatigue loading.

The steel investigated and the experimental programme are presented in the next part. Results are presented and discussed in the third part. The final discussion is devoted to the first determinations of the contribution of carbides and dislocations to mechanical strength for the tempering temperatures investigated and to the microstructural interpretation of cyclic softening.

**STEEL INVESTIGATED AND EXPERIMENTAL PROCEDURE**

The composition of the modified AISI H11 grade investigated is shown in Table 1. Heat treatment consists in austenitizing for one hour followed by air cooling, first tempering at 550 °C for two hours, second tempering for two hours between 550 °C and 640 °C depending on desired hardness. A nital etch reveals a tempered martensitic structure with heterogeneous lath sizes. An electrolytic chromic acid etch reveals prior austenitic grain. The average diameter is 14 µm for 50 grains measured.

<table>
<thead>
<tr>
<th>Mod. AISI H11 chemical composition (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
</tr>
<tr>
<td>0.361</td>
</tr>
</tbody>
</table>

Microstructures were investigated by TEM. Observations were performed on a JEOL 2010 and a Philips CM12 microscopes, the last one is equipped with an Energy Dispersive X-ray analysis (EDX). Carbides were extracted from the martensitic matrix using the replica technique (see Fig. 3).
tion in the selected area mode (SAD) and EDX have been performed in order to determine their chemical composition and crystal structure. Statistics on carbide size were performed directly on TEM photos on nearly 300 carbides for each sample. Next, dislocations structure were studied on thin foils prepared by classical electropolishing.

In order to evaluate carbides weight fraction, a technique of dissolution of the martensitic matrix was used. Carbides were extracted by an electrolytic method described in [10, 11]. Their crystal structure and chemical composition analyses (for each heat treatments) are performed using a Brucker D5000 diffractometer equipped with a Cu-Kα radiation and a graphite crystal monochromator and scintillation counter.

X Ray diffraction experiments on the bulky material were also performed with peak profiles measurements in order to evaluate dislocation densities by using the modified Williamson-Hall plot and the modified Warren-Averbach analysis [12, 13]. The diffraction peak profiles were measured in the Eötvös University of Budapest by a special high resolution double-crystal diffractometer with negligible instrumental peak broadening [14].
The Table 2 shows references and heat treatments of analysed samples. Fatigue experiments conditions are described elsewhere [2].

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Heat treatments conditions and fatigue test</th>
<th>Thin foil TEM</th>
<th>Carbides extraction / TEM</th>
<th>Dissolution carbide weight fraction</th>
<th>XRD on carbide powder</th>
<th>X Ray profiles analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Annealed</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>A2</td>
<td>As quenched</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>A3</td>
<td>Tempered 550 °C</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>A4</td>
<td>Tempered 550 °C+ 580 °C</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>A5</td>
<td>Tempered 550 °C+ 600 °C</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>A6</td>
<td>Tempered 550 °C+ 620 °C</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>A7</td>
<td>Tempered 550 °C+ 640 °C</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>A8</td>
<td>A6 + $\Delta \varepsilon_t = 1.5%$ at 550 °C</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>A9</td>
<td>A6 + $\Delta \varepsilon_t = 2%$ at 550 °C</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION
THIN FOILS TEM OBSERVATIONS

Bright field transmission electron photographs of samples A4, A6 and A7 are shown in Figs. 4 to 6. In Fig. 4 at low magnification, laths are generally separated by elongated iron carbides. In addition, the observations of thin foils show a high density of intralath entangled dislocations even for high tempering temperatures (see Fig. 6). Consequently, the identification of the individual dislocations (Burgers vector and slip plane) and density evaluation becomes very difficult using the classical TEM method. Prior to fatigue testing, dislocation distribution is quite homogeneous on the whole even if, at a nanometric scale, a high density of dislocations was observed near lath boundaries and around carbides (see Fig. 7). To compare dislo-
cation structures obtained at different tempering temperatures qualitatively, the observations were performed in the same crystallographic orientation conditions $\vec{g} = [1\bar{1}0]$. Lath lightening is observed when second tempering temperature increases. Therefore, recovery of the microstructure is stated by a clear decrease of the dislocation density. This effect is strongly increased by the application of a cyclic strain (see Fig. 8) and a strong reduction of the intralath dislocation density is observed after a fatigue test. As the dislocation tangle is crushed during the fatigue test, such a configuration promotes a free dislocation movement between lath boundaries or carbides. The free slip distances are therefore probably increased by dislocation annihilation stated by lath lightening. This decrease of dislocation density seems to be one of the main mechanisms for cyclic softening. Nevertheless, dislocation annihilation is strongly heterogeneous and seems to take place in the bigger laths (breadth nearly $> 0.3 \mu m$). In addition, dislocation cell development generally observed in tempered martensitic stainless steels after fatigue [5] does not seem to take place in the 5% Cr steel even for the highest total strain amplitude investigated.

![Figure 4.](image)

**Figure 4.** Bright field TEM micrographs of dislocation structure in tempered steel at $550^\circ C$ (2 hours) and $580^\circ C$ (2 hours) (sample A4). (a) Low magnification, (b) high magnification: intralath dislocation structure $\vec{g} = [1\bar{1}0]$.

**CARBIDES TEM OBSERVATIONS**

Carbides extracted from the martensitic matrix were observed at TEM (see Fig. 9). Crystal structure and chemical composition were analysed by electronic diffraction and EDX. For all tempering conditions (samples A3
Figure 5. Bright field TEM micrographs of dislocation structure in tempered steel at 550 °C (2 hours) and 620 °C (2 hours) (sample A6). (a) Low magnification, (b) high magnification: intralath dislocation structure \( \mathbf{g} = [\overline{1}10] \).

Figure 6. Bright field TEM micrographs of dislocation structure in tempered steel at 550 °C (2 hours) and 640 °C (2 hours) (sample A7). (a) Low magnification, (b) high magnification: intralath dislocation structure.

to A7), four types of carbides were found depending on their morphology (see figures 10(a) – 10(d)):

1) Angular and elongated intralath carbide: \( M_7C_3 \) Chromium iron carbide, Hexagonal structure
Figure 7. Bright field TEM micrographs of dislocation structure in tempered steel at 550 °C (2 hours) and 640 °C (2 hours) (sample A7), pinning of dislocations on a large carbide.

2) Globular intralath carbide: MC vanadium carbide, Face Centred Cubic (FCC) structure. Small size = secondary carbides, large size (100 nm – 300 nm) = carbides not dissolved during the austenitization

3) Globular intralath carbide: $M_23C_6$ Chromium iron carbide, FCC structure, only important size (100 nm – 300 nm) = carbides not dissolve during the austenitization

4) Elongated carbides situated at lath boundaries: $M_3C$ Iron chromium carbide, Orthorhombic structure (determined by XRD)

Statistics on carbide size are shown in tables 3 and 4. Three different populations were identified after tempering:

1) Small sized carbides MC and $M_7C_3$ types with an average size near 6 nm. This population is always found for all tempering conditions.

2) Middle sized carbides, mainly $M_7C_3$ type, with an average size near 30–40 nm. This population is found for tempering temperatures between 600 °C and 640 °C.
Figure 8. Bright field TEM micrographs of the dislocation structure after a fatigue test at 550 °C(Δεt = 2%) (sample A9). (a) Low magnification, (b) high magnification: intralath dislocation structure $\vec{g} = [1\bar{1}0]$.

Figure 9. TEM micrograph of the extracted carbides from a tempered steel at 550 °C(2 hours) and 620 °C(2 hours) (sample A6).
3) Scarce large M₂₃C₆ and MC type carbides with an average size > 100 nm. This population is found for all tempering conditions and also in the as quenched sample (A2). These carbides are probably not dissolved during the austenitization. As these carbides were so scarcely encountered (less than 6/300), we did not take this population into account in the statistics.

Table 3. Statistics on carbide size

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of carbides</th>
<th>Average size (nm)</th>
<th>Standard deviation</th>
<th>Student law: 99% confidence interval on the average size</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3</td>
<td>293</td>
<td>6.42</td>
<td>2.97</td>
<td>5.97 &lt; m &lt; 6.87</td>
</tr>
<tr>
<td>A4</td>
<td>291</td>
<td>6.14</td>
<td>4.10</td>
<td>5.52 &lt; m &lt; 6.76</td>
</tr>
<tr>
<td>A5</td>
<td>259</td>
<td>6.97</td>
<td>2.32</td>
<td>6.60 &lt; m &lt; 7.34</td>
</tr>
<tr>
<td>A6</td>
<td>224</td>
<td>6.61</td>
<td>4.13</td>
<td>5.90 &lt; m &lt; 7.32</td>
</tr>
<tr>
<td>A7</td>
<td>188</td>
<td>5.81</td>
<td>2.95</td>
<td>5.26 &lt; m &lt; 6.36</td>
</tr>
<tr>
<td>A8</td>
<td>121</td>
<td>13.56</td>
<td>3.66</td>
<td>12.69 &lt; m &lt; 14.43</td>
</tr>
<tr>
<td>A9</td>
<td>78</td>
<td>15.19</td>
<td>3.20</td>
<td>14.23 &lt; m &lt; 16.15</td>
</tr>
<tr>
<td>A9</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>A4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>A5</td>
<td>35</td>
<td>32.84</td>
<td>9.03</td>
<td>28.67 &lt; m &lt; 37.01</td>
</tr>
<tr>
<td>A6</td>
<td>76</td>
<td>34.38</td>
<td>11.8</td>
<td>30.79 &lt; m &lt; 37.96</td>
</tr>
<tr>
<td>A7</td>
<td>111</td>
<td>42.07</td>
<td>14.58</td>
<td>38.45 &lt; m &lt; 45.69</td>
</tr>
<tr>
<td>A8</td>
<td>179</td>
<td>33.03</td>
<td>10.14</td>
<td>31.08 &lt; m &lt; 34.98</td>
</tr>
<tr>
<td>A9</td>
<td>222</td>
<td>33.07</td>
<td>10.17</td>
<td>31.31 &lt; m &lt; 34.83</td>
</tr>
</tbody>
</table>

Evolution of average carbide size is shown in Fig. 11. Increase of the average size is stated above 600 °C with the formation of the second population. It is important to note that both populations have nearly a constant average size for all the tempering conditions. The carbide growth is mainly due to the increase of the amount of the second population carbides. After a fatigue test at 550 °C, an increase of the average carbide size is observed (see Fig. 11). As no coalescence of carbides was observed during a second tempering at 580 °C for 2h (A3) compared to a single tempering at 550 °C (A2), we can obviously conclude that this coalescence is induced by cyclic strain.
Mechanisms of carbide growth during fatigue are still unclear and are now investigated.

**CARBIDES WEIGHT FRACTION**

In order to get an estimation of the volume fraction of carbides; XRD experiments on the bulk can be performed. Nevertheless, as major peaks coming from carbides are generally situated near peaks coming from the martensitic matrix, accurate calculations are difficult and time consuming. Therefore, a technique of dissolution of the martensitic matrix was used in order to assess carbide weight fractions and then carbide volume fractions (see Tables 5 and 6). (* In each case, we assumed that all the carbon (C) or all the alloying element (Cr, V) precipitates).

**Table 5. Theoretical maximal volume fraction of carbides**

<table>
<thead>
<tr>
<th>Carbides</th>
<th>( M_3C )</th>
<th>( M_7C_3 )</th>
<th>( M_{23}C_6 )</th>
<th>MC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical maximal volume fraction*</td>
<td>5.7% (C)</td>
<td>4.8% (C)</td>
<td>6.0% (Cr)</td>
<td>8.1% (V)</td>
</tr>
<tr>
<td>Carbides density</td>
<td>7.7</td>
<td>6.9</td>
<td>7.0</td>
<td>5.7</td>
</tr>
</tbody>
</table>

An increase of the weight fraction of carbides is observed for tempering temperatures above the secondary hardening peak situated near 550 °C. So, these results clearly show that formation of precipitates still occurs during
Table 6. Estimation of the volume fraction of carbides

<table>
<thead>
<tr>
<th>Sample</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A5</th>
<th>A6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight fraction</td>
<td>0.7%</td>
<td>3.4%</td>
<td>4.0%</td>
<td>5.5%</td>
<td>5.7%</td>
</tr>
<tr>
<td>Volume fraction range</td>
<td>0.7%&lt;f&lt;1.0%</td>
<td>3.5%&lt;f&lt;4.7%</td>
<td>4.1%&lt;f&lt;5.5%</td>
<td>5.6%&lt;f&lt;7.6%</td>
<td>5.9%&lt;f&lt;7.9%</td>
</tr>
<tr>
<td>Average:</td>
<td>0.85%</td>
<td>4.1%</td>
<td>4.8%</td>
<td>6.6%</td>
<td>6.9%</td>
</tr>
</tbody>
</table>

the second tempering. The formation seems to saturate for second tempering temperatures above 600 °C (results at 640 °C are not available at that time).

**X RAY DIFFRACTION**

**CARBIDES X-RAY ANALYSIS**

Analysis of the X-Ray diffraction of carbides extracted from the martensitic matrix, confirm and complete the TEM results. Figure 12 shows the evolution of the carbide composition according to the heat treatment. So, the annealed steel contains Mo₂C, Fe₃C, M₂₃C₆ (M = Fe and Cr) and a small ratio of VC. After quenching, only the vanadium carbide (VC) and a small quantity of M₂₃C₆ which are probably not dissolved during the austenitisation were found.

After the first and the second tempering, the X-ray analysis confirm the presence of Fe₃C, Cr₇C₃, M₂₃C₆ (M = Fe and Cr) and trace of VC. Only the annealed steel contains molybdenum carbides.

**PEAK PROFILE ANALYSIS**

Two different methods of diffraction profile analysis (modified Williamson-Hall and modified Warren-Averbach) are tested. The classical Williamson-Hall plot of the Full Widths at Half Maximum (FWHM) values of the first six reflections shows a strong strain anisotropy, as can be seen in Fig. 13. The same values of the FWHM are plotted according to the modified Williamson-Hall procedure [15] and the intersection at $K = 0$ gives the coherently scattering domain size (see Fig. 14).

Table 7 shows the evolution of the coherently scattering domain size with the heat treatment. The increase of the second tempering temperature logically enlarges the coherently scattering domain size and the same ef-
fect is observed after fatigue test. These conclusions are still in agreement with TEM observations. However, quantitative results can be obtained with this technique. Moreover, diffraction profile analysis allows getting more information on the microstructure of the steel like dislocation structure ([12, 13, 14, 15, 16]). For example, the comparison between samples after quenching (A2) and after tempering (A7) shows quantitatively the decrease of dislocations density from $95 \cdot 10^{14} \text{m}^{-2}$ (A2) to $10 \cdot 10^{14} \text{m}^{-2}$ (A7).

Therefore, diffraction profile analysis seems to be the most interesting way to obtain coherently scattering domain size and dislocation structure in such complex microstructures.

Table 7. Average size of coherently scattering domains versus heat treatment and fatigue loading

<table>
<thead>
<tr>
<th></th>
<th>A4</th>
<th>A6</th>
<th>A6 + $\Delta \varepsilon_f = 1.8%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDD (nm)</td>
<td>560</td>
<td>1070</td>
<td>1990</td>
</tr>
</tbody>
</table>

CONCLUSION

Transmission electron microscopy and X Ray diffraction are two complementary ways of investigation giving considerable information on these complex martensitic structures. Quantitative data on carbides and only qualitative knowledge on deformation mechanisms and structures of dislocations are available by TEM. Conversely, relevant quantitative indirect information can be obtained by XRD on both carbides and dislocation structures.

Results have shown that decrease of dislocations density and growth of carbides are two mechanisms involved in the decrease of the yield stress during a fatigue test and a second tempering. Nevertheless, possible modification of the contribution of the solid solution strengthening or potential subgrains formation in highly deformed material has not been investigated. These evaluations can constitute an interesting outlook to this work.

ACKNOWLEDGMENTS

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REFERENCES

(a) TEM micrograph of $M_7C_3$ carbide (1), corresponding EDS spectra analysis (2), and electron diffraction pattern (3).

(b) TEM micrograph of $MC$ carbide (1), corresponding EDS spectra analysis (2), and electron diffraction pattern (3).

(c) TEM micrograph of $M_{23}C_6$ carbide (1), corresponding EDS spectra analysis (2), and electron diffraction pattern (3).

(d) TEM micrograph of $M_3C$ carbide (1), corresponding EDS spectra analysis (2).

*Figure 10.*
Figure 11. Evolution of the average size of carbides with second tempering temperatures and influence of cyclic plasticity.

Figure 12. Precipitation sequence in a Mod. AISI11 steel.
Figure 13. The FWHM in the classical Williamson-Hall plot applied on the A4 sample.

Figure 14. The FWHM according to the modified Williamson-Hall plot applied on the A4 sample.