Effect of Multiple Tempering on Mechanical Properties and Microstructure of Ledeburitic Tool Steel AISI D3

Víctor Alcántara Alza

Abstract: The effects of multiple tempering on the mechanical properties and microstructure of ledeburitic tool steel AISI D3 were investigated. Austenized samples at: 940 °C and 970 °C were used. The subsequent tempering was carried out in three stages with the same temperatures: 250-350-450-550 °C; for 1 hr. The microstructure was revealed at optical (OM) and electronic (SEM) levels and then X-ray diffraction analysis (DRX) was made along with an X-ray scatter spectrometry (EDS) test. It was found that the yield stress (σy), the maximum tensile strength (σr) and ductility (ε) decrease with the number of tempering treatments. The microstructures, in the three stages, show primary, massive and small carbides of type M6C, M7C3, and Cr7C3 accompanied by precipitated fine carbides of the same type, with the presence of the phases: Fe3C, Cr63Fe6,97 and residual austenite (γ), the latter phase is minimized with the third temper. These precipitates occur at each stage of tempering simultaneouly or as the temperature increases. The variation of these properties is closely related to the microstructure obtained.

Keywords: Austenitizing, carbides precipitation, ledeburitic steel, multiple tempering

I. INTRODUCTION

Cold work tool steels are used for forming processes below 200 °C. Within this group we have, AISI D series, where chromium with 12%, is the main alloy element [1]. Among them, AISI D3 steel with 12% Cr - 2% C stands out, which in some cases is alloyed with W and V, to increase its wear and toughness resistance, combined with a high compression resistance, as specified in [2].

Group D steels are generally used in quenching and tempered state, where carbides precipitation and evolution of matrix during tempering, determine their mechanical properties [3]. Quenching it is common do it on air throughout D series that contains molybdenum, with exception of AISI D3, which is recommended do it in oil; because, having no molybdenum, the transformation of austenite into perlite is accelerated, and martensitic microstructures are formed without perlitic or soft bainitic constituents [1]. Another characteristic of these steels is presence of large amounts of undissolved carbides during austenitizing; Although they provide high hardness and wear resistance, at the same time, they reduce their toughness to bear cracking mechanism in the tool fracture [4]. Only the refinement of highly concentrated carbides can improve the hardness and toughness of these steels [5]; being also, the size of the grain and the state of the carbides, critical aspects in the fracture process [6].

Important aspect during quenching is the decomposition of retained austenite (RA), which is an incomplete quenching product, due to the low Ms temperatures. RA can be beneficial in some cases and harmful in others. Its decomposition can lead a transformation into martensite, bainite or of ferrite and cementene combinations. RA behavior during tempering varies for different steel types, and leads to the assumption that microstructures formed from that transformation could improve material properties [7]. Nevertheless; It is known that in cold work tool steels applications, presence of RA damages the tool useful life, despite the high hardness and relative good toughness achieved with heat treatments [8].

High carbon content and / or alloy elements, increses RA content; so, it is necessary to cause the subsequent transformation, total or partial, of RA [9]. For this purpose, there are several treatments; the most commonly used: quenching with multiple tempering (MT) and cryogenic treatment decrease RA content. However, this last process, while minimizing the amount of RA, also increases the probability that the piece will fracture during the cooling cycle [10].

Nykiel et al. [11]; studied the effect of tempering on the mechanical properties of AISI D3 steel. Samples were austenitized in the range: 1000-1150 °C, then, on tempering, an increase in hardness was observed in the range, 350-600 °C, arguing this effect is related to the bainitic transformation of RA, in some cases partially in martensite. In a subsequent study, the same authors [12] reported carbide transformations during tempering of AISI D3 steel, austenitized at 1050 °C for 30 min, and tempering in range: 200–700 °C, for 2h. Using X-ray diffraction (DRX) and electron microscopy It was found, carbides and precipitates: (Fe3C) type in (200 °C - 350 °C), and (M6C; M7C3) in range: (500°C - 700°C) . Primary massive and fine carbides of the M6C3 type were also observed, which did not dissolve during austenitizing. Ghazi et al., [13] reported studies on the influence of conventional and cryogenic treatments on wear resistance and mechanical tensile properties of AISI D3 steel. It was found that the modulus of elasticity (E) is affected by both treatments. Moreover the highest mechanical strength (2900 MPa) was obtained by cryogenic treatment at -198 °C for 36 h and tempering at 200 °C for 30 min. Tariq et al., [14] studied the mechanical properties in tempering samples of high-strength alloy steels with low carbon (0.3% C).
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They used two austenized temperatures: 930 °C and 1000 °C, and the tempering temperature: 200-500 °C. For TA = 930 °C, the (σf) increased to 300 °C, then decreased to 500 °C; while (σr) showed oscillating values. For samples austenized at 1000 °C the (σf) remained almost constant, with a slight decrease from 450 °C to 500 °C, while σr decreased to 270°C, then stabilized to 400 °C and finally decreased up to 500 °C. Elongation (ε), for the two austenitized temperatures and over the entire tempering interval, the values were oscillating. These variations were also observed in the works of Li et al., [15] studying the effect of tempering on the mechanical properties of AISI 6150 alloy steel (0.5% C).

Not many studies are reported on the tensile mechanical properties on this steels, which is why the present study aims to describe and explain how the mechanical tensile properties of the AISI D3 ledeburitic steel are affected, when submitted to treatment (MT), in three stages, seeking relationships between mechanical properties and their correlation with the microstructure.

II. MATERIALS AND METHODS

A. Material

Steel chosen for this study was AISI D3 (DIN: X 210 Cr 12), of high carbon content, being at the limit of the classification of steels and foundries.

Table 1 shows the chemical composition in percentage

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>2.05</td>
<td>0.25</td>
<td>0.3</td>
<td>11.5</td>
<td>0.02</td>
<td>0.025</td>
</tr>
</tbody>
</table>

B. Experimental methodology

For tensile tests, specimens according to ASTM E8 standard, of circular type, with a diameter of 6mm, 50 mm in length in the test area and 125 mm in total length were made. The Instron Universal 8801 10 Tn machine was used.

Austenizating, at the temperatures (TA = 940°C - 970 °C), was carried out, using two lots of samples for each temperature. Three samples groups were formed from each lot, to apply: 1° tempering (1°R) 2° tempering (2°R) and 3° tempering (3°R). The samples were austenizating on Thermolyne digital electric oven for 30min, and then cooled in oil, then tempering was done in the same oven. TA were selected, following the manufacturer specifications given in [16], and the CCT diagram for this material shown in [17] was taken as a reference. For (MT), on each stage, the same tempering temperatures (Tt, 250-350-450-550 °C) were used, with the same holding time: 2h. The selection of these Tt was made following the specifications given in [17].

Microstructure at the optical level (MO) was revealed, using the ZEISS 1000X microscope, and at the electronic level (SEM) using the SEM PHILIPS S-505 microscope. Tests were complemented with a spectrometric analysis of X-ray scattering (EDS), and X-ray diffraction (DRX), which allowed determining the matrix composition, and precipitated phases during tempering at each stage. Different zones were chosen to observe the microstructure. The samples were encapsulated, polished and attacked with Nital 3% for 30 s.

III. RESULTS AND DISCUSSION

A. Tensile tests.

Table 2 shows the results of tensile tests for samples with different TA and Tt, Temperatures, with MT in 3 stages. In Figure 1, we have the respective trend curves extracted from Table 2. The curves of (σf); (σr) and (ε) are observed from Figure 1a) to 1f), for different values of TA and Tt with three-stage tempering.

As can be seen, module (E) shows slight increases with tempering. In the austenitized at 940°C values fluctuate between: (208.2 - 212.0) GPa, representing a variation of 1.8%. For austenitized at 970 °C the variation is 2.0%. These variations are in accordance with [18,19] where point out that the elastic modulus of metal alloys varies between 1 and 10% with cold mechanical work and with heat treatments.

For TA = 940 °C (Fig. 1a), σf decreases with the number of temperings, but not with the tempering temperature. In the 1°R σf increased to a maximum of 1500 MPa (Tt = 450 °C). In 2°R and 3°R of values are oscillating, and have maximum of 1401MPa and 1250MPa respectively on the same temperature (Tt = 450°C). In both cases: for Tt > 450°C σr decreases.

For TA = 970 °C (Fig. 1b), σr decreases with the number of temperings from 370 °C onward; but, while in 1°R of values varies slightly. In 2°R and 3°R, a drastic fall from Tt > 370 °C is observed.

In Figures 1c) and 1d), for the two taustenizing temperature, variation of σr with Tt is shown. Curves show similar trends to the (σf) curves. The values maximum are: 1749 MPa and 1658 MPa, corresponding to 1°R with Tt = 250 °C. It is also observed that for TA = 970 °C, σr falls drastically, from Tt. En las Figuras 1c) y 1d), se muestra la variación de σr con Tt, > 350°C.

In Figures 1e) and 1f) the elongation curves “ε” that measure ductility are presented. It is observed that by increasing the number of temperings, the ductility decreases. This phenomenon will then be explained based on the precipitation of carbides with the number of temperings. For samples with TA = 940 °C, the temperature Tt almost does not affect “ε”; taking values ≈ 7% (1° R), and ≈ 4% for (2°R and 3°R). On the other hand, for TA = 970 °C the ε values are oscillating as Tt increases. These are of the order of ≈ 5% (1° R); ≈ 3-5% (2° R) and ≈ 2-4.5% (3° R). These values indicate an increase in fragility with the number of temperings (the index “ε”falls).

In general, tensile results show that, the increase in temperature Tt does not always decrease “σf” or “σr”, nor does it cause an increase in “ε” in ledeburitic steels, as is the case with simple carbon steels.
Table 2. Tensile mechanical properties in standardized samples of AISI D3 steel with multiple tempering treatment

<table>
<thead>
<tr>
<th>Tempering</th>
<th>$T_A$ (°C)</th>
<th>$E$ (GPa)</th>
<th>$\sigma_f$ (MPa)</th>
<th>$\sigma_r$ (MPa)</th>
<th>$\varepsilon$ (%)</th>
<th>$E$ (GPa)</th>
<th>$\sigma_f$ (MPa)</th>
<th>$\sigma_r$ (MPa)</th>
<th>$\varepsilon$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1° R.</td>
<td>250</td>
<td>208.2</td>
<td>1375</td>
<td>1749</td>
<td>7.14</td>
<td>207.2</td>
<td>1500</td>
<td>1658</td>
<td>5.07</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>209.0</td>
<td>1400</td>
<td>1417</td>
<td>7.1</td>
<td>207.8</td>
<td>1400</td>
<td>1488</td>
<td>5.46</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>210.5</td>
<td>1500</td>
<td>1672</td>
<td>7.02</td>
<td>209.3</td>
<td>1500</td>
<td>1550</td>
<td>5.24</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>211.4</td>
<td>1475</td>
<td>1670</td>
<td>7.11</td>
<td>210.5</td>
<td>1380</td>
<td>1627</td>
<td>5.7</td>
</tr>
<tr>
<td>2° R.</td>
<td>250</td>
<td>208.4</td>
<td>1354</td>
<td>1354</td>
<td>4.18</td>
<td>207.6</td>
<td>1595</td>
<td>1595</td>
<td>2.29</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>209.3</td>
<td>1120</td>
<td>1170</td>
<td>4.22</td>
<td>208.3</td>
<td>1500</td>
<td>1615</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>210.7</td>
<td>1401</td>
<td>1522</td>
<td>4.22</td>
<td>209.1</td>
<td>1022</td>
<td>1022</td>
<td>2.85</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>211.6</td>
<td>1148</td>
<td>1148</td>
<td>4.09</td>
<td>210.2</td>
<td>1048</td>
<td>1048</td>
<td>3.77</td>
</tr>
<tr>
<td>3° R.</td>
<td>250</td>
<td>208.7</td>
<td>1200</td>
<td>1200</td>
<td>4</td>
<td>208.5</td>
<td>1350</td>
<td>1350</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>209.4</td>
<td>1000</td>
<td>1050</td>
<td>3.95</td>
<td>209.8</td>
<td>1300</td>
<td>1450</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>211.6</td>
<td>1250</td>
<td>1325</td>
<td>4.05</td>
<td>210.8</td>
<td>950</td>
<td>950</td>
<td>2.8</td>
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<tr>
<td></td>
<td>550</td>
<td>212.0</td>
<td>1100</td>
<td>1150</td>
<td>4.2</td>
<td>211.5</td>
<td>1000</td>
<td>1000</td>
<td>3.7</td>
</tr>
</tbody>
</table>

E = Elasticity modulus; $\sigma_f$ = Yield stress; $\sigma_r$ = maximum tensile stress; $\varepsilon$ = Elongation
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Fig. 1. Trend curves of the mechanical tensile properties of AISI D3 steel due to the effect of austenized temperature and multiple tempering (MT): a) b) \( \sigma_f \); c) d) \( \sigma_r \); e) f) \( \varepsilon \).

Variations of mechanical properties with tempering, can be explained as follows: At tempering temperatures below 300 °C, internal stresses generated are not completely released; then, with the complete recovery of tensions at 300 °C, a rearrangement of the dislocations structure occurs, which restricts its movement and leads to an increase in yield stress (\( \sigma_f \)). With the increase in Tt, the concentration of martensite decreases, and the presence of ferrite and carbides increases; mainly, due to the diffusion of carbon atoms in the cementite and the movement of dislocations by thermal assistance [20]; Therefore, in this period of increase in Tt, the maximum resistance (or) and yield stress (of) decrease. However, elongation (\( \varepsilon \)) may increase or decrease due to hardening of the matrix or precipitation of carbides as Tt increases.

B. Microstructure

Fig. 2. Microstructures (OM) before tempering: a) Supply status (annealing) b) TA = 940 °C, quenching in oil c) TA = 970 °C, quenching in oil.

Fig. 2a) shows the microstructures of the material in a state of supply (annealing). A perlite matrix with defined grain boundaries surrounded by massive and fine primary carbides is observed.

Fig. 2b) and Fig. 2c), show microstructures after quenching without tempering. These have a martensite matrix white residual austenite, also massive and fine carbides which did not dissolve in the austeniziting. The massive carbides of polygonal shape has up to ~ 50 µm long, and the small ones are of the order ~ 3µm. The austeniziting at TA= 970°C presents a greater carbides distribution and dispersion.

In Fig. 3, it has a sample of the microstructural evolution of the austenized specimens at TA = 940 °C and tempered at Tt = 350 °C \& 550 °C. In all them, a matrix of tempered martensite is seen, surrounded by massive and fine primary carbides of the type M7C3 and Cr7C3 not dissolved during austeniziting, and also secondary carbides precipitated during tempering.

For TA = 940 °C \& Tt = 350 °C (Figures 3a; 3b and 3c) it is observed that the carbides evolve between coarse and fine at each stage of tempering, explaining the variation of the mechanical properties in this range shown in the Figures (1a, 1c; 1d).

For TA = 940 °C \& Tt = 550 °C (Figures 3d; 3e and 3f) the same phases are observed with slight changes in size and carbide dispersion. It is noted in this case, the microstructures obtained for the 2°R and 3°R are almost identical, which would explain the same results obtained for the three mechanical properties at this point.
In Figure 4, four samples observed with SEM microscopy together with their respective EDS analysis are presented. Figure 5 shows the DRX diffraction pattern for each case. The phases identified were: martensite matrix surrounded by carbides of types (Fe Cr)₂C₃ or M₇C₃, Cr₇C₃ and cementite Fe₃C. Also the intermetallic phase Cr₀.₀₃Fe₀.₉₇ was identified. Moreover, a small remnant of residual austenite γᵣ is observed. These phases are found in all samples at different concentrations, as indicated in DRX analysis.

Precipitated carbides can be compared with those obtained in the experiments done by T. Nykiel and T. Hryniewicz [12], who studied the transformations that carbides follow during tempering of AISI D3 steel. Parameters used were: Tₐ = 1050°C, 30 min and then tempered for 2h in the range: 200-700°C. Carbide precipitates that followed the sequence indicated in equations (1) - (5) were found. These transformations show the transition of unstable carbides to stable ones, depending on the temperature. They precipitate according to sequence:

\[
\begin{align*}
200°C & \rightarrow χ + Fe₃C & (1) \\
350°C & \rightarrow ε + χ + Fe₃C & (2) \\
500°C & \rightarrow M₇C₃ + M₇C₃ & (3) \\
600°C & \rightarrow χ + M₇C₃ + C & (4) \\
700°C & \rightarrow M₇C₃ + N₇C₃ & (5)
\end{align*}
\]

Figures 4a) and 4b) show SEM microstructures (Tₐ = 940 °C a Tt = 350 °C for 1°R and 3°R respectively), together with their EDS analysis for each case.

According to EDS and DRX analysis (Fig.4; Fig.5) the carbides present in the matrix were identified as: M₇C₃; Cr₇C₃; and Fe₃C. The Cr₀.₀₃Fe₀.₉₇ phase is little observable and not well defined. It can be a transition carbide or an intermetallic compound. Microphotographs show that carbides are nucleated intergranularly and transgranularly, within a matrix of martensite. In addition, a higher precipitation of carbides for 3°R is observed. These results are not very consistent with the results of equation (2); but it should be borne in mind that equations (1) - (5) shown in [12] correspond to a temperature higher than those used in the present study. Therefore these equations are only referential.

Microstructures for Tₐ = 970 °C a Tt = 550 °C (1°R and 3°R respectively), shown in Figures 4c) and 4d). The same primary carbides and precipitates are observed; with the difference, that in this case, the carbides M₇C₃ and Cr₇C₃ are the predominant precipitates. It is also observed that Fe₃C carbide is almost dissolved together with the Cr₀.₀₃Fe₀.₉₇ phase. This sequence of precipitates is in good agreement with the sequence shown in equations (3) and (4), if it is assumed that phase χ is the equivalent of phase Cr₀.₀₃Fe₀.₉₇.
Fig. 4. SEM microphotographs of selected samples, austenized and tempered, together with their respective EDS analysis: a) $T_A = 940 \, ^\circ C$, $T_t = 350 \, ^\circ C$, 1°R; b) $T_A = 940 \, ^\circ C$, $T_t = 350 \, ^\circ C$, 3°R; c) $T_A = 970 \, ^\circ C$, $T_t = 550 \, ^\circ C$, 1°R; d) $T_A = 970 \, ^\circ C$, $T_t = 550 \, ^\circ C$, 3°R.
Phase $\text{Cr}_{0.03}\text{Fe}_{0.97}$ is found in almost all temperings, in the same way as $\chi$ phase is presented in the sequence of tempering shown in equations: (1) - (5). But if takes into account that for two austenitizing temperatures: $T_A = 940 \degree C, 970 \degree C$, carbides dissolution is not total (see Figures 2b and 2c); therefore, carbides precipitation sequence in the tempering cannot be the same as shown in equations (1) - (5), which correspond an austeniziing temperature $T_A = 1050 \degree C$, where all carbides are almost completely dissolved [12]; Therefore, to say that $\text{Cr}_{0.03}\text{Fe}_{0.97}$ phase is the equivalent of the $\chi$ phase does not mean that they have the same stoichiometric composition.

For both austenized temperatures; If the samples tempered at 350 °C and 550 °C are compared, the latter show a greater amount of precipitated carbides, observing furthermore that retained austenite is almost insignificant in (3°R) in all cases. Iron carbides formed during the martensite tempering, adopt several structures, which are classified according to the interstices occupied by the carbon atoms: tetrahedral interstices (TP) and octahedral interstices (O). The type (TP) carbides are more stable than those type (O) [21]; which explains the greater or lesser stability of carbide precipitation shown in the evolution of the tempered samples.

Carbides percentage after quenching of AISI D3 steel can be estimated according to experimental equation (6), valid in the austenitizing range: 900 to 1150 °C, for 30 minutes; equation proposed by Nykiel et al., [22].

$$cb\% = 28.60 - 0.4e^{0.067T}$$ (6)

Where:

$cb\%$: percentage of carbides (by weight)

$T$: austenitising temperature (°C)

Applying (6):

For 940 °C $cb\% = 21.89\%$

For 970 °C $cb\% = 21.26\%$

For both austenitizing temperatures, equation (6) provides almost similar results with respect to the percentage of carbides precipitated during tempering. But these values can be estimated in a more direct and approximate way, using another study by Nykiel et al., [23], where they reported that AISI D3 steel, after an austenized at 950 °C; 30 min, contains 20% total weight of carbides. Then in tempering happens: Upon reaching 250 °C the total percentage rises to 21.9% and when it reaches 550 °C it is 23.8%. It follows, that in the entire interval there was a precipitation of 3.8% of the total weight of carbides.

In summary: in tempering temperature range studied (350-550 °C), when reaching the temperature of 550 °C, 96% of the total carbides weight corresponds to the primary carbides not dissolved during austenitizing, and 4% remaining are carbides precipitated during tempering. This great difference indicates; that the carbides precipitated in the tempering (Fig3; Fig4) must be fine and ultrafine carbides, which are nucleated mainly at grain boundaries.
Finally, according to the DRX analysis, multiple tempering (MT) does not eliminate retained austenite (RA) totally. The important thing is that RA remained has significantly been stabilized. It is known that the most relevant factor in the stability of (AR) is the carbon content [24], which for the study material corresponds to the maximum of steels.

**IV. CONCLUSION**

From the study of the effect of MT on the mechanical tensile and microstructure properties of the AISI D3 ledeburitic steel, it is concluded:

- Module (E) is affected by the MT. The overall variation is 1.8%, considering all treatments.
- For Both austenitizing temperatures: values of ($\sigma_f$, $\sigma_r$, $\epsilon$) generally decrease with the number of temperings.
- The loss of ductility is assumed to be due to the presence of embrittlement phases; such as $C_\text{t,03}$ Fe$_{0,97}$.
- The microstructures in the three tempering stages, show primary, massive and fine carbides of type $M_C$, and $Cr_3C_2$; cementite Fe$_3C$; the $C_{t,03}$ Fe$_{0,97}$ phase and very little $\gamma_r$. These precipitates appear according to $T_t$ and dissolve accordingly to their stability.

**REFERENCES**


**AUTHOR PROFILE**

**Dr. Víctor Alcántara A.**, working as a professor in Mechanical Engineer Department of the National University of Trujillo- Peru. Mechanical engineer, Master in Materials Engineering (1996) and Doctor in Materials Science (2006) Lima-Peru. Member of the Materials Research Institute of the Post Graduate School at the National University of Trujillo. Specialization in characterization of ferrous and non-ferrous materials, carried out at the University of Cartagena of Spain. Author of multiple manuals and texts on materials and manufacturing processes. International speaker at multiple conferences in the Latin American region. Author of several articles in indexed journals.

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