Tensile Properties of Duplex UNS S32205 and Lean Duplex UNS S32304 Steels and the Influence of Short Duration 475 °C Aging

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Duplex stainless steels are high strength and corrosion resistant steels extensively used in the petrochemical and chemical industries. The aging at 475 °C for long periods of time provokes embrittlement and deterioration of corrosion resistance. However, short duration aging at 475 °C may be used as heat treatment to improve mechanical resistance with small decrease in the other properties. In this work the flow stress curves of lean duplex UNS S32304 and duplex UNS S32205 steels were modeled with Hollomon’s equation and work hardening exponents (n) were determined. The analyses were conducted in specimens annealed and heat treated at 475 °C for short periods of time. The aging at 475 °C for 4 hours, 8 hours and 12 hours promoted significant hardening with small decrease of ductility. The work hardening exponents of both steels were compared, being higher in the duplex steel than in the lean duplex grade.

Keywords: duplex stainless steel, heat treatment, tensile properties, work hardening exponent

1. Introduction

The use of austenitic-ferritic stainless steels has been increasing inside industry environment, replacing traditional austenitic grades for a number of components. The success of this subclass of stainless steels is due to its excellent combination of corrosion resistance, mechanical resistance and toughness.

For many applications of austenitic-ferritic steels, where high corrosion resistance and low temperature toughness are necessary, the maximum service temperature allowed is 350 °C. The reason is because the long term aging in the 350-550 °C may provoke the precipitation of very fine Cr-rich particles formed by spinodal decomposition mechanism from the ferrite phase (δ). This reaction is commonly written as δ → α′ + α″, where α′ is the chromium rich precipitates and α″ is the Cr-depleted ferrite matrix. It is worth noting that in the literature α′ is also used to designate the bcc magnetic martensite which appears in many austenitic and duplex stainless steels subjected to cold deformation. These two different phases may occur in duplex and lean duplex stainless steels. In this work, α′ refers to the small Cr-rich precipitates formed through the spinodal decomposition of ferrite.

Several previous works have shown that the kinetics of α′ precipitation is higher at 475 °C. The deterioration of mechanical and corrosion resistance properties of duplex and superduplex aged at this temperature were also extensively reported. However, short duration treatments may be used to improve mechanical resistance with minimum decrease of other properties. For instance, in the work of Marques et al. the abrasion wear resistance of a superduplex steels was increased by aging at 475 °C for periods of time up to 12 hours without embrittlement and corrosion resistance decay.

The UNS S32205 steel is a wrought duplex stainless steel grade very similar to the more traditional grade UNS S31803. Both contain low carbon (<0.03 wt. %) and average contents 22%Cr, 5%Ni and 3%Mo, but the UNS S32205 has a more controlled and higher nitrogen content (0.14-0.20 wt. %) than the UNS S31803 (0.08-0.20%).

The UNS S32304 is a lean duplex grade with average composition 23%Cr, 4%Ni, 0.10%N and low carbon (<0.03%). Its corrosion resistance is lower than duplex grades due to the lower Mo addition (0.05-0.60%) (wt. %). In this work the effects of short duration heat treatments on the tensile mechanical properties of UNS S32304 and UNS S32205 steels were investigated.

2. Experimental

Two sheets of 1.8 mm of thickness of duplex UNS S32205 and UNS S32304 with chemical compositions shown in Table 1 were studied. In this work the nomenclatures duplex (or DP) and lean duplex (or LD) will be used to the two steels investigated.
The materials were received in the as solution treated (annealed) with austenitic ferritic microstructure. The ferrite and austenite contents of the materials were determined by quantitative metallography with specimens prepared with Behara’s etching (80 mL distilled water, 20 mL HCl, 0.3 g of potassium metabissulfite).

Specimens for tensile tests were machined according to ASTM A-370-09 standard\(^1\). Specimens for hardness tests were cut with 10 × 10 × 1.8 mm\(^3\) dimensions.

After cutting, the hardness specimens were aged at 475 °C for different periods of time up to 14 hours. Vickers Hardness tests were performed with load of 30 kgf. The hardness curves were used to select the conditions for tensile tests.

After machining the tensile specimens were heat treated at 475 °C for 4 hours, 8 hours and 12 hours. The tensile tests were performed with constant velocity of 12 mm/min at 22 ± 2 °C. Nominal and true stress-strain curves were obtained. Yield and ultimate strengths, elongation, absorbed energy and work hardening exponent were the parameters obtained from the tensile tests analysis.

Magnetization curves of unaged specimens of duplex and lean duplex steels were obtained in a Vibrating Sample Magnetometer (VSM). The maximum applied field was 1.4 T. The specimens for VSM were carefully cut from three regions of the fractured tensile test specimens: i) undeformed part (head); ii) uniform deformation region; and iii) localized deformation region (neck and fracture). The magnetic tests were conducted to evaluate the formation of bcc martensite induced by plastic deformation in both steels.

3. Results

Figures 1a, b show the microstructures of the materials in the as received condition. The ferrite contents measured by quantitative metallography in 10 fields were (59.3 ± 4.0)% in the lean duplex, and (58.5 ± 3.0)% in the duplex steel.

Figure 2 shows the hardness curves for both steels aged at 475 °C up to 14 hours. The hardening due to \(\alpha'\) formation is faster and more intense in duplex steel than in lean duplex. The age hardening at 475 °C is restricted to the ferrite phase, where Mo and Cr are concentrated. Observing that the Cr contents are similar in both steels, the more pronounced hardening of duplex steel may be attributed to the influence of Mo on the intensity and kinetics of \(\alpha'\) precipitation.

The hardness increase of duplex steel with aging for 4 hours, 8 hours and 12 hours were 48 (±7) HV, 58 (±8) HV and 60 (±8) HV, respectively. The hardness variation in lean duplex for the same periods of aging time were 43 (±7) HV, 50 (±8) HV and 51 (±9) HV. The heat treatments for 4 hours, 8 hours and 12 hours were selected for a more detailed analysis with tensile tests.

Figures 3a, b show the nominal stress-strain curves of duplex and lean duplex, respectively. The yield limit (\(\sigma_y\))

<table>
<thead>
<tr>
<th>Steel</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>N</th>
<th>C</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNS S32205</td>
<td>22.5</td>
<td>5.30</td>
<td>2.90</td>
<td>1.85</td>
<td>0.32</td>
<td>0.17</td>
<td>0.02</td>
<td>0.03</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>UNS S32304</td>
<td>22.4</td>
<td>3.59</td>
<td>0.22</td>
<td>0.93</td>
<td>0.41</td>
<td>0.13</td>
<td>0.02</td>
<td>0.02</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

Figure 1. Microstructures of a) duplex and b) lean duplex steels investigated.

Figure 2. Age hardening curves of DP UNS S32205 and LD UNS S32304 for aging at 475 °C.
and ultimate strength (σ_y), total elongation (Elong.) and uniform ductility (El-U) obtained from the curves and from the final dimensions of the fractured specimens are shown in Table 2. From these data, the short duration aging produces significant increase of σ_y and σ_UTS with some decrease of ductility parameters (Elong. and El-U). In duplex steel, the increase of aging time from 8 hours to 12 hours did increase significantly σ_y and σ_UTS.

True stress-strain curves, also known as flow stress curves, were obtained from the nominal stress and strain points. Figures 4a, b show the curves of unaged duplex and lean duplex specimens, respectively. The curves were modeled using the Hollomon’s equation (Equations 1, 2): 

\[ \sigma = K\varepsilon^n \]  
\[ \ln \sigma = \ln K + n \ln \varepsilon \]  

where \( \sigma \) is the true stress, \( \varepsilon \) is the true strain, \( K \) is a constant and \( n \) is the work hardening exponent.

Figure 5 shows the plot of \( \ln \sigma \) versus \( \ln \varepsilon \) for duplex steel as received (annealed). First, the whole curve was modeled by one Hollomon equation, finding \( \ln K = 6.874 \) and

<table>
<thead>
<tr>
<th>Steel</th>
<th>Aging</th>
<th>( \sigma_y ) (MPa)</th>
<th>( \sigma_{UTS} ) (MPa)</th>
<th>Elong. (%)</th>
<th>El-U (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duplex</td>
<td>unaged</td>
<td>535</td>
<td>717</td>
<td>27.7</td>
<td>19.9</td>
</tr>
<tr>
<td></td>
<td>475 °C/4 hours</td>
<td>651</td>
<td>807</td>
<td>25.0</td>
<td>17.0</td>
</tr>
<tr>
<td></td>
<td>475 °C/8 hours</td>
<td>695</td>
<td>865</td>
<td>24.1</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>475 °C/12 hours</td>
<td>708</td>
<td>870</td>
<td>23.2</td>
<td>16.2</td>
</tr>
<tr>
<td>Lean duplex</td>
<td>unaged</td>
<td>510</td>
<td>678</td>
<td>29.0</td>
<td>19.3</td>
</tr>
<tr>
<td></td>
<td>475 °C/4 hours</td>
<td>617</td>
<td>733</td>
<td>26.2</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td>475 °C/8 hours</td>
<td>707</td>
<td>796</td>
<td>24.1</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>475 °C/12 hours</td>
<td>754</td>
<td>840</td>
<td>21.4</td>
<td>13.6</td>
</tr>
</tbody>
</table>
n = 0.099, with correlation coefficient $R^2$ equal 0.975 (Figure 5a). A better correlation was obtained by dividing the curve in two parts and fitting the with two Hollomon’s equations, as shown in Figure 5b. Two work hardening exponents were measured by this way: $n_1 = 0.079$ for the first part of the curve, and $n_2 = 0.134$ for the second part. Figures 6a, b show the comparison of the models and the experimental points in the flow stress curve.

The same behavior was observed in specimens of duplex steel aged at 475 °C, i.e., the fitting with one equation could be performed, but a better correlation was obtained by dividing the curve and fitting with two Hollomon’s equations. Table 3 shows the values of constant K and work hardening exponents found with one and two equations models for the duplex steel. In all cases, the K value obtained with one equation model was placed between K1 and K2 from two equations model. The same was observed in the comparison of n with n1 and n2. It can be observed that n was between n1 and n2 because the curve that was firstly fitted with one line with slope n, was then divided in two lines, one with a lower slope (n1) and other with a higher slope (n2).

Figures 7a, b show the curves of lnσ versus lnε of lean duplex specimens unaged and treated at 475 °C for 4 hours. In these cases, the modeling with one equation resulted in bad correlation coefficients ($R^2 < 0.90$). Modeling with two equations was so performed in all lean duplex specimens, with results shown in Table 4.

![Figure 5](image-url)  
**Figure 5.** Plots of ln(true stress) versus ln(true strain) for unaged duplex steel: a) fitting with one Hollomon’s equation; b) fitting with two Hollomon’s equations.

![Figure 6](image-url)  
**Figure 6.** Comparison of the two models with experimental points for unaged duplex steel: a) one Hollomon’s equation; b) two Hollomon’s equations.

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>K (One equation model)</th>
<th>n</th>
<th>K1 (Two equations model)</th>
<th>n1</th>
<th>K2 (Two equations model)</th>
<th>n2</th>
</tr>
</thead>
<tbody>
<tr>
<td>unaged</td>
<td>966.8</td>
<td>0.099</td>
<td>870.5</td>
<td>0.079</td>
<td>1060.2</td>
<td>0.134</td>
</tr>
<tr>
<td>475 °C/4 hours</td>
<td>1035.9</td>
<td>0.080</td>
<td>893.3</td>
<td>0.049</td>
<td>1164.5</td>
<td>0.122</td>
</tr>
<tr>
<td>475 °C/8 hours</td>
<td>1121.9</td>
<td>0.081</td>
<td>987.6</td>
<td>0.053</td>
<td>1260.3</td>
<td>0.124</td>
</tr>
<tr>
<td>475 °C/12 hours</td>
<td>1112.0</td>
<td>0.076</td>
<td>976.8</td>
<td>0.048</td>
<td>1264.0</td>
<td>0.123</td>
</tr>
</tbody>
</table>

**Table 3.** Values of K, K1, K2, n, n1 and n2 obtained with one equation and two equations models for flow stress curves of duplex steel.
Magnetization curves of samples cut from different parts of the tensile specimens of unaged lean duplex are shown in Figure 8. Magnetization saturation ($m_s$) values extracted from the magnetization curves of undeformed duplex and lean duplex are shown in Table 5. Analyzing the results of lean duplex, the sample taken from the undeformed region presented $m_s$ equal 70.1 Am2.kg$^{-1}$. The $m_s$ of the sample from the uniform deformation region was 80.6 Am2.kg$^{-1}$, and in the localized deformation region the $m_s$ has increased to 95.6 Am2.kg$^{-1}$. This increase of magnetization saturation with plastic deformation indicates that part of the austenite phase was transformed into magnetic bcc martensite during the tensile test of lean duplex. On the other hand, the duplex steel did not show increase of $m_s$ with deformation, which indicates that martensitic transformation did not occur during the tensile test. A previous work on duplex steel has shown that significant martensitic transformation in UNS S31803 (similar to duplex UNS S32205) was only detected after true deformations higher than 1.0 by cold rolling. \[1\]

The division of the flow stress into two parts, each of them with one work hardening exponent indicates that the material has two work hardening stages. The two work hardening stages are much clearer and well defined in the lean duplex steel than in duplex steel. This difference may be related to the higher susceptibility of lean duplex to martensitic transformation, as observed by magnetic measurements.

Figure 9 shows the work hardening exponents of duplex and lean duplex steels as function of aging treatments. In lean duplex steel there is a clear trend of decrease of work hardening exponents with the increase of aging time. Duplex steel also shows this trend in the first 4 hours of aging. After this period of time the work hardening exponents remain unaltered by the increase of aging time.

In austenitic stainless steels the high work hardening exponent is somewhat related to deformation induced martensitic transformation during plastic deformation. However, a comparison between lean duplex and duplex steels shows that the higher work hardening exponents were found in the material less susceptible to martensitic transformation, i.e., duplex steel.

Table 4. Values of $K_1$, $K_2$, $n_1$, and $n_2$ obtained with two equations models for flow stress curves of lean duplex steel.

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>$K_1$</th>
<th>$n_1$</th>
<th>$K_2$</th>
<th>$n_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unaged</td>
<td>681.7</td>
<td>0.032</td>
<td>969.2</td>
<td>0.119</td>
</tr>
<tr>
<td>475 °C/4 hours</td>
<td>729.5</td>
<td>0.025</td>
<td>1022.5</td>
<td>0.109</td>
</tr>
<tr>
<td>475 °C/8 hours</td>
<td>800.0</td>
<td>0.020</td>
<td>1084.3</td>
<td>0.096</td>
</tr>
<tr>
<td>475 °C/12 hours</td>
<td>832.8</td>
<td>0.016</td>
<td>1108.9</td>
<td>0.083</td>
</tr>
</tbody>
</table>

Table 5. Magnetizations saturation ($m_s$) of samples collected from tensile tests specimens (after test).

<table>
<thead>
<tr>
<th>Region of tensile test specimen</th>
<th>Lean duplex $m_s$ (Am².kg⁻¹)</th>
<th>Duplex $m_s$ (Am².kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undeformed (head)</td>
<td>$78.1 \pm 1.3$</td>
<td>$70.2 \pm 1.5$</td>
</tr>
<tr>
<td>Uniform deformation</td>
<td>$80.6 \pm 1.0$</td>
<td>$69.0 \pm 2.0$</td>
</tr>
<tr>
<td>Localized deformation (neck and fracture)</td>
<td>$95.6 \pm 1.8$</td>
<td>$70.2 \pm 1.3$</td>
</tr>
</tbody>
</table>

Figure 7. Plots of ln(true stress) versus ln(true strain) for lean duplex steel: a) unaged; b) aged at 475 °C for 4 hours.

Figure 8. Magnetization curves from samples taken from three regions of the tensile tested specimen: undeformed region (head), uniform deformation region, and localized deformation region (neck and fracture).
dividing the flow curve in two parts and modeling with two Hollomon’s equations, which resulted in two work hardening exponents.

Lean duplex UNS S32304 could only be modeled by two Hollomon’s equation, each one corresponding to a work hardening stage.

Differently from duplex steel, lean duplex showed the transformation $\gamma \rightarrow$ bcc martensite during plastic deformation in tensile test, as concluded by magnetization saturation tests.

Lean duplex UNS S32304 and duplex UNS S32205 steels may be hardened by short duration heat treatments at 475 °C. Although a small decrease of ductility is also observed, heat treatments for 4 hours and 8 hours and 12 hours may be good options to increase the yield and strength limits.

The aging at 475 °C also promoted the decrease of work hardening exponents of Hollomon’s equations of lean duplex steel.

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4. Conclusions

The flow stress curves of duplex UNS S32205 steel could be reasonably modeled by simple Hollomon’s equations. However, better fittings were obtained by

References


