

Effects of low temperature heat treatments on the mechanical properties and corrosion resistance of a duplex stainless steel UNS S32205

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Abstract. Duplex stainless steels are high strength and corrosion resistant stainless steels extensively used in the petrochemical and chemical industries. The purpose of this work was to evaluate the effects of low temperature aging heat treatments at 400°C and 475°C on the mechanical behaviour and corrosion resistance of duplex stainless steel UNS S32205. Vickers hardness and microhardness tests were performed to evaluate the hardening effect produced by the aging process. The hardness and microhardness curves were modeled for the temperatures investigated. Selected conditions were produced for tension tests and electrochemical pitting corrosion tests. The results show that short duration treatments at 475°C and 400°C may be performed to improve mechanical strength and hardness without decrease the corrosion properties. The decrease of ductility and toughness can be minimized by the proper selection of the heat treatment parameters.

Keywords: Duplex, hardness, tension test, pitting

1. INTRODUCTION

The use of austenitic-ferritic drastically increased in the last years due to the excellent combination of corrosion resistance, mechanical resistance and toughness. These properties can be attributed to alloying additions, microstructural features like grain equal amounts of austenite and ferrite and grain refinement (Muthupandi, 2003).

Previous studies have shown that by adding or removing some element from the steel's composition it's possible to increase or decrease the steels corrosion resistance (Charles, 2007). Steels with austenitic-ferritic microstructure may be divided into *lean duplex*, *duplex*, *superduplex* and *hyperduplex* (Tavares et al., 2010). With the exception of the *lean duplex* this classification is made based only on the steel's corrosion resistance, even if there may also be very significant changes on its mechanical properties, for the stainless steels it's not the priority. In order to better distinguish the classes of austenitic-ferritic stainless steel a parameter known as the pitting resistance equivalent (PRE) is used:

$$[PRE_N] = \%Cr + 3.3\%Mo + 16\%N \quad (1)$$

$$[PRE_w] = \%Cr + 3.3(\%Mo + \%W) + 16\%N \quad (2)$$

PRE formulae include the elements most important to pitting corrosion resistance, i.e., Cr, Mo, N and W. This parameter is commonly used to rank stainless steels and other corrosion resistant alloys, but it can be observed the influence of the microstructure is not taken into account. Steels with PRE higher than 40 are *superduplex* (SDSS), while the new hyperduplex steels have PRE higher than 50. *Duplex steels* (DSS) have PRE lower than 40, and *lean duplex* (LDSS) usually contain PRE < 30 due to their low Mo content.

It's also important to point out that the PRE number does not indicate the material's actual corrosion resistance, once it only accounts for the chemical composition of the steels and depending on the manufacturing process by which the material passes through may occur a number of undesirable phase transformations on the steels microstructure (Gunn, 2003; Linton et al., 2004; Hitchcock et al., 2001).

Figure 1 shows a schematic TTT diagram for the phase precipitation in duplex steels. The influences of alloying elements such as Cr, Si, W and Mo, are also shown. A group of reactions, such as $\delta \rightarrow \gamma_2$, $\delta \rightarrow \gamma_2 + \sigma$, $\delta \rightarrow \gamma_2 + M_{23}C_6$, $\gamma \rightarrow M_{23}C_6$ and $\delta \rightarrow \chi \rightarrow \sigma$ are predicted for high temperatures (600 – 1000 °C). In general, all these reactions cause embrittlement and corrosion resistance decay, but the formation of sigma phase (σ) is considered the most deleterious (Gunn, 2003; Linton et al., 2004; Hitchcock et al., 2001, Voronenko, 1997).

At lower temperatures (350 – 550 °C) the most important reaction is the spinodal decomposition of the ferrite phase into Cr rich α' coherent particles and a Cr-depleted matrix (α) (Sahu et al., 2009). The precipitates are very fine, and their observation was only achieved by transmission electron microscopy (Park et al., 2005, Weng et. al 2004). However, the effects of α' precipitation are easily observed, such as hardening, embrittlement and corrosion resistance decay (Tavares, 2005). It is consensual that the faster kinetics of α' precipitation occurs during aging at 475 °C, although prolonged aging at 400 °C or lower also produce hardening and embrittlement.

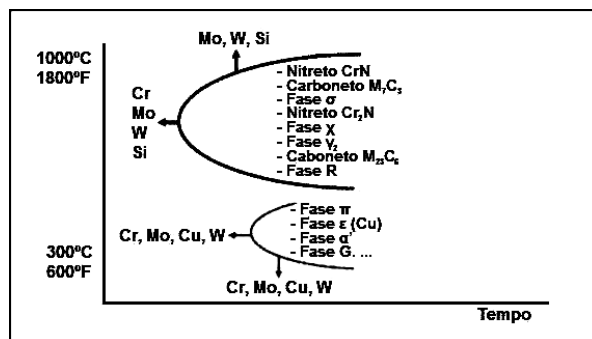


Figure 1. Diagram TTT schematics of precipitated phases in DSS (Charles, 2007).

It is known that prolonged aging in the range 350 – 550°C can decrease toughness and corrosion resistance, but short duration treatments may be used as a method of strengthening with minimal decrease of other properties. In this work the possibility of increase the mechanical resistance of a duplex stainless steel with low temperature and short duration heat treatments was investigated. A sheet of 1.8 mm of UNS S32205 duplex stainless steel was investigated. Hardness and tensile tests were performed to evaluate the increase of mechanical resistance and the decrease of ductility and toughness. The effects on corrosion resistance were also evaluated.

2. MATERIALS AND METHODS

A sheet of 1.8 mm of thickness of duplex UNS S32205 with chemical composition shown in Table 1 was studied. The material was received in the as solution treated (annealed) condition with tensile properties shown in Table 2.

Table 1. Chemical composition of the duplex steel studied (wt.%)

Grade	Cr	Ni	Mo	Mn	Si	N	Cu	C	P	S
UNS S32205	22.5	5.30	2.90	1.85	0.32	0.166	0.03	0.023	0.03	0.001

Table 2. Mechanical properties of the studied duplex sheet in the annealed condition.

Grade	σ_{LE} (MPa)	σ_{LR} (MPa)	Elongation (%)
UNS S32205	527	717	25.75

Specimens for tensile tests were machined according to ASTM A-370-09 standard (ASTM, 2004). Specimens for hardness tests were also cut with 10 x 10 x 1.8 mm³ dimensions.

After cutting, the hardness specimen were aged at 400 °C and 475 °C for different periods of time up to 24 h. The hardness curves were used to select the conditions for tensile tests.

After machining the tensile specimens were heat treated at 475 °C for 4h, 8h and 12h.

The tensile tests were performed with constant velocity of 12 mm/min at 22±2 °C. Nominal and true stress versus strain curves were obtained. Yield and ultimate strengths, elongation, absorbed energy and work hardening exponent were the parameters obtained from the tensile tests analysis.

Vickers Hardness tests were performed with load of 30 kgf. Curves of hardness versus aging time were constructed and modeled.

The effects of aging on the corrosion resistance were evaluated by electrochemical corrosion tests for determination of the critical pitting temperature (CPT). The CPT measurement was performed by the potentiostatic method. The potential was fixed in 0.700 V_{SCE} and the temperature was raised in a constant rate of 3°C/min. The CPT was the temperature correspondent to a current density of 100µA/cm². The method was similar to the ASTM G150 standard (ASTM, 2004).

3. RESULTS AND DISCUSSION

Figure 6 shows the hardness curves for specimens aged at 475 °C and 400 °C. As expected the hardening of DSS occurs at a faster rate when aged at 475 °C than at 400 °C.

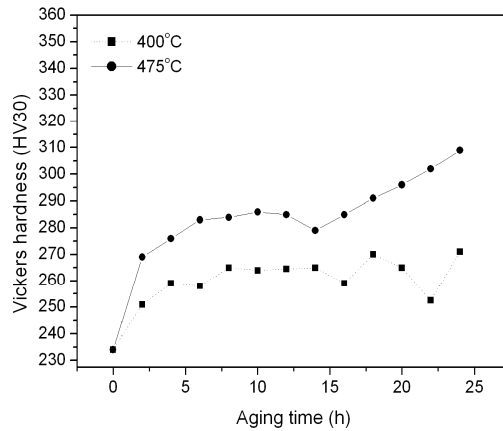


Figure 2: Hardness curves for duplex stainless steel UNS S32205 aged at 400 °C and 475 °C up to 24 hours.

The age hardening curves may be roughly divided into two parts. The initial stage is that of aging time up to 14 hours. At this initial stage the increase of hardening can be described by the equation (3):

$$HV_{(t)} = \frac{HV_i}{1 - a \cdot t^b} \quad (3)$$

where:

- $HV_{(t)}$ – Hardness as function of time (HV)
- HV_i – Initial value of hardness (HV)
- a – constant
- b – aging exponent
- t – aging time (h)

Figure 3 shows the experimental points and curve adjusted for 475 °C. Table 3 shows the values of a and b constants and correlation coefficients obtained.

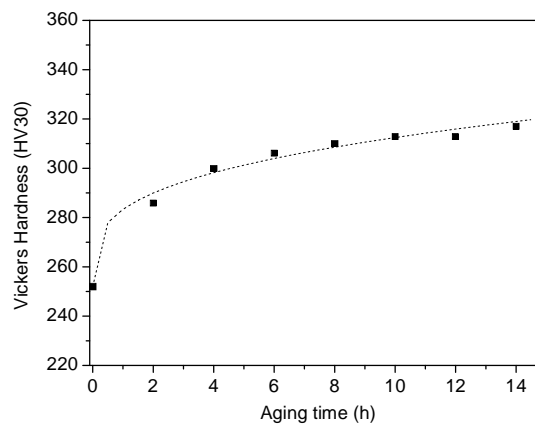


Figure 3: Experimental points and model equation for aging at 475 °C.

Table 3. Constants of equation (3) adjusted for duplex UNS S32205 aged at 400 °C and 475 °C.

Aging temperature	HV_i	a	b	R^2
475	252	0.10970	0.2476	0.9868
400	252	0.07694	0.1440	0.9713

The interest in the initial stage of age hardening is due to the possibility to perform heat treatments able to harden the material, with minimum prejudicial effects on corrosion resistance, ductility and toughness. In order to evaluate this possibility, three short duration heat treatments were chosen for a deeper analysis by tensile and corrosion tests. The heat treatment chosen were 475 °C/4 h, 475 °C/8 h and 475 °C/12 h. These heat treatments promote significant variation of hardness (ΔHV), as shown by the hardening curves.

Figure 4 compares the nominal stress *versus* nominal strain curves. Table 4 shows the yield limit ($\sigma_{Y.L}$), ultimate strength ($\sigma_{U.T.S}$) total elongation (El.), uniform elongation (U.E.) and hardness increase (ΔHV) obtained from tensile and hardness tests. As expected, the strengthening achieved by the heat treatments caused a slight decrease of ductility. Other important feature is that specimens treated at 8h and 12h have similar hardness, yield and ultimate strength, but the longer treatment causes a higher decrease of total and uniform elongation. From these results, can be inferred that the heat treatment for 12 h is not an interesting option.

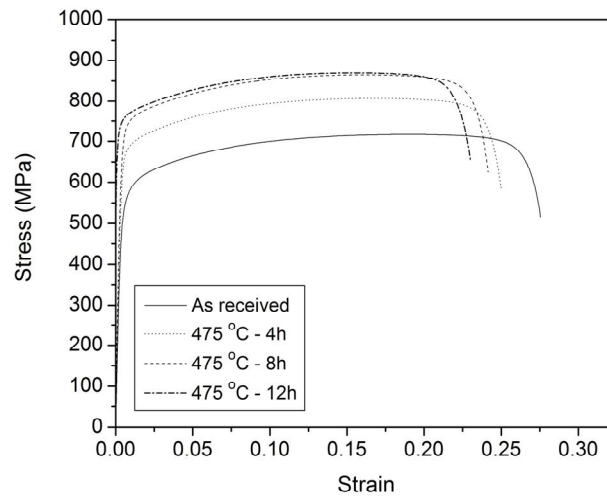


Figure 4. Nominal Stress – strain curves.

Table 4. Tensile properties ($0.2\% \sigma_{Y.L}$, $\sigma_{U.T.S}$, El. and U.E.) obtained from curves of figure 4.

Heat treatment condition	$(0.2\%) \sigma_{Y.L}$	$\sigma_{U.T.S}$	El.	U.E.	ΔHV
As received	535	717	0.277	0.199	-
475 °C – 4h	651	807	0.250	0.170	48
475 °C – 8h	695	865	0.241	0.167	58
475 °C – 12h	708	870	0.232	0.162	60

The tensile curves were converted into true (or real) stress (σ_T) *versus* true strain (ϵ_T) curves (figure 5), which were modeled by Hollomon's equation (Dieter, 1988):

$$\sigma_T = K \epsilon_T^n \quad (4)$$

$$\ln \sigma_T = \ln K + n \ln \epsilon_T \quad (5)$$

The flow curves were analyzed in the region between the $0.2\% \sigma_{Y.L}$ and the $\sigma_{L.R}$. Two types of modeling were experimented, as shown for the as received specimen in figures 6(a) and 6(b). In figure 6(a) one equation was fitted for the interval of study. The correlation coefficient in this case was $R^2 = 0.97$. A better correlation can be obtained with two Hollomon's equations, as shown in figure 6(b). In this case one curve is fitted for the first part, and another is fitted for the second part of the flow stress curve, suggesting that the material shows two work hardening stages. All specimens tested showed these two stages, and in all cases the work hardening exponent (n) of the second stage was higher than the first one. Figures 7(a) compares the experimental points in the flow stress curve of the as received material with the models with one equation. Figure 7(b) compares the model with two equations with experimental points.

Figure 8 shows the variation of the work hardening coefficients n , n_1 and n_2 with aging at 475 °C. A slightly decrease of work hardening coefficients is observed with the aging at 475 °C for 4h in a comparison to the as received material. However, the increase of aging time to 8h and 12h did not change these coefficients.

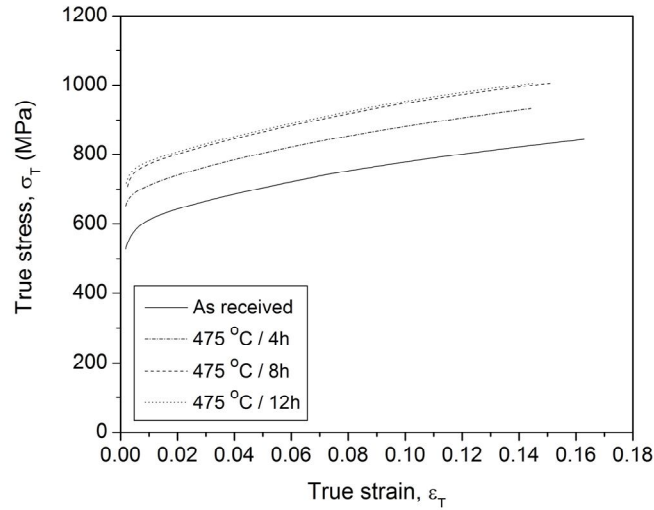


Figure 5. True – strain curves (flow stress curves).

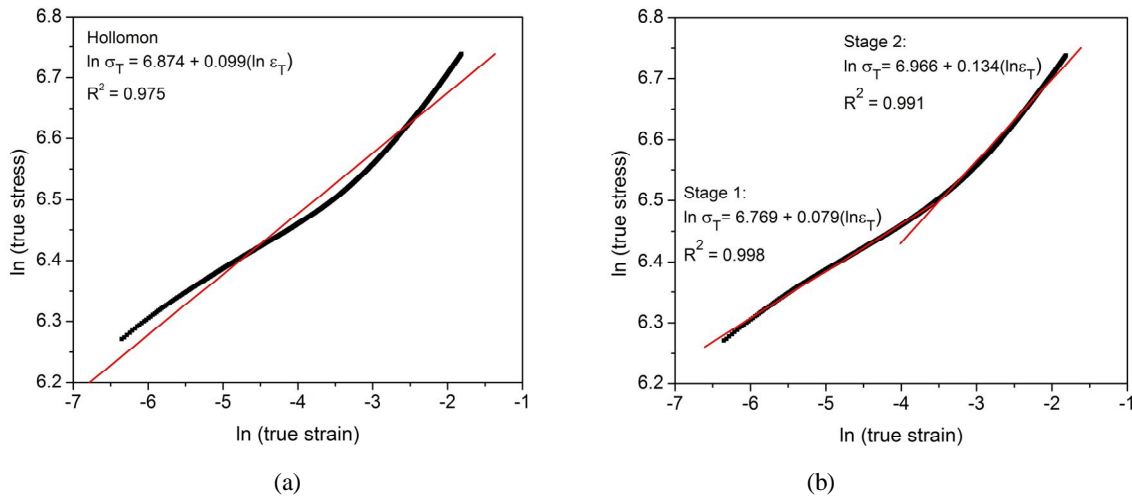


Figure 6. Curves of $\ln \sigma_T$ versus $\ln \epsilon_T$ to obtain parameters K and n of Hollomon's equation.

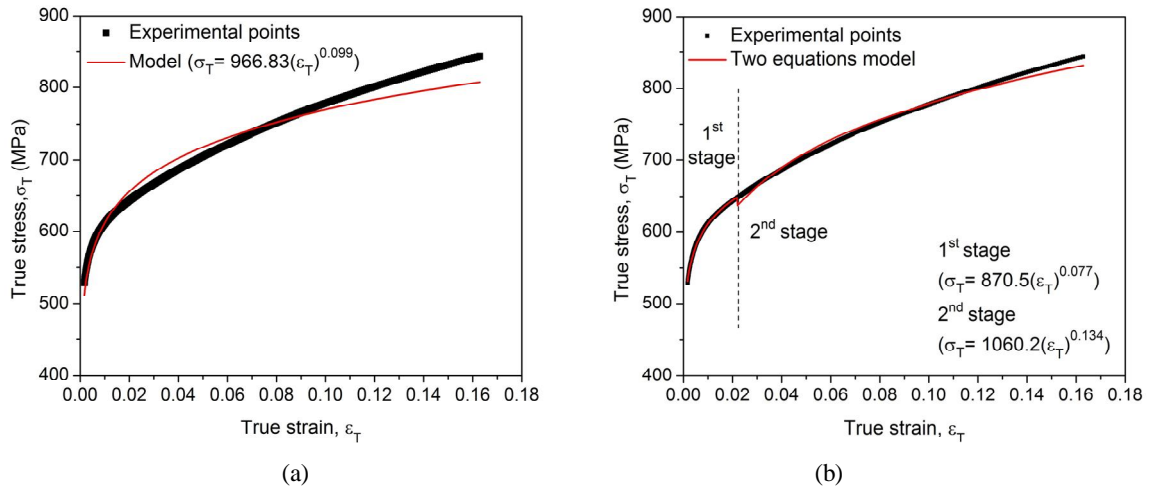


Figure 7. Comparison of experimental points and models obtained with Hollomon's equation: (a) one equation; (b) two equations (two work hardening stages).

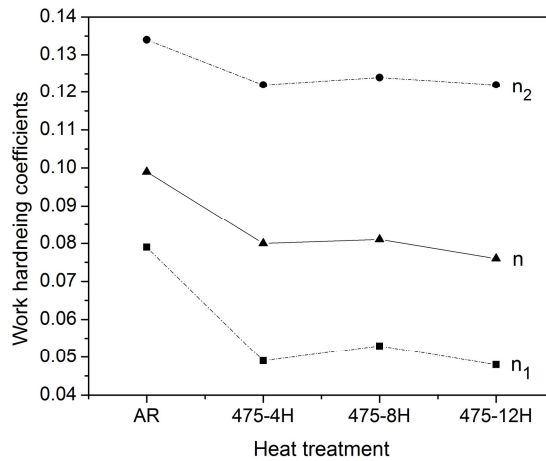


Figure 8. Variation of work hardening coefficients (n , n_1 and n_2) with heat treatments.

Figures 9(a-d) show the current density *versus* temperature curves used to obtain the critical pitting temperatures (CPT). This is an important parameter used to evaluate the pitting resistance of corrosion resistant alloys (Gunn, 2003). The CPT values of specimens which were heat treated at 475 °C for 4h and 8h were similar to the as received material, all above 50 °C. However, the increase of aging time from 8h to 12h promoted the decrease of CPT from 53 °C to 45 °C indicating a significant decrease of corrosion resistance.

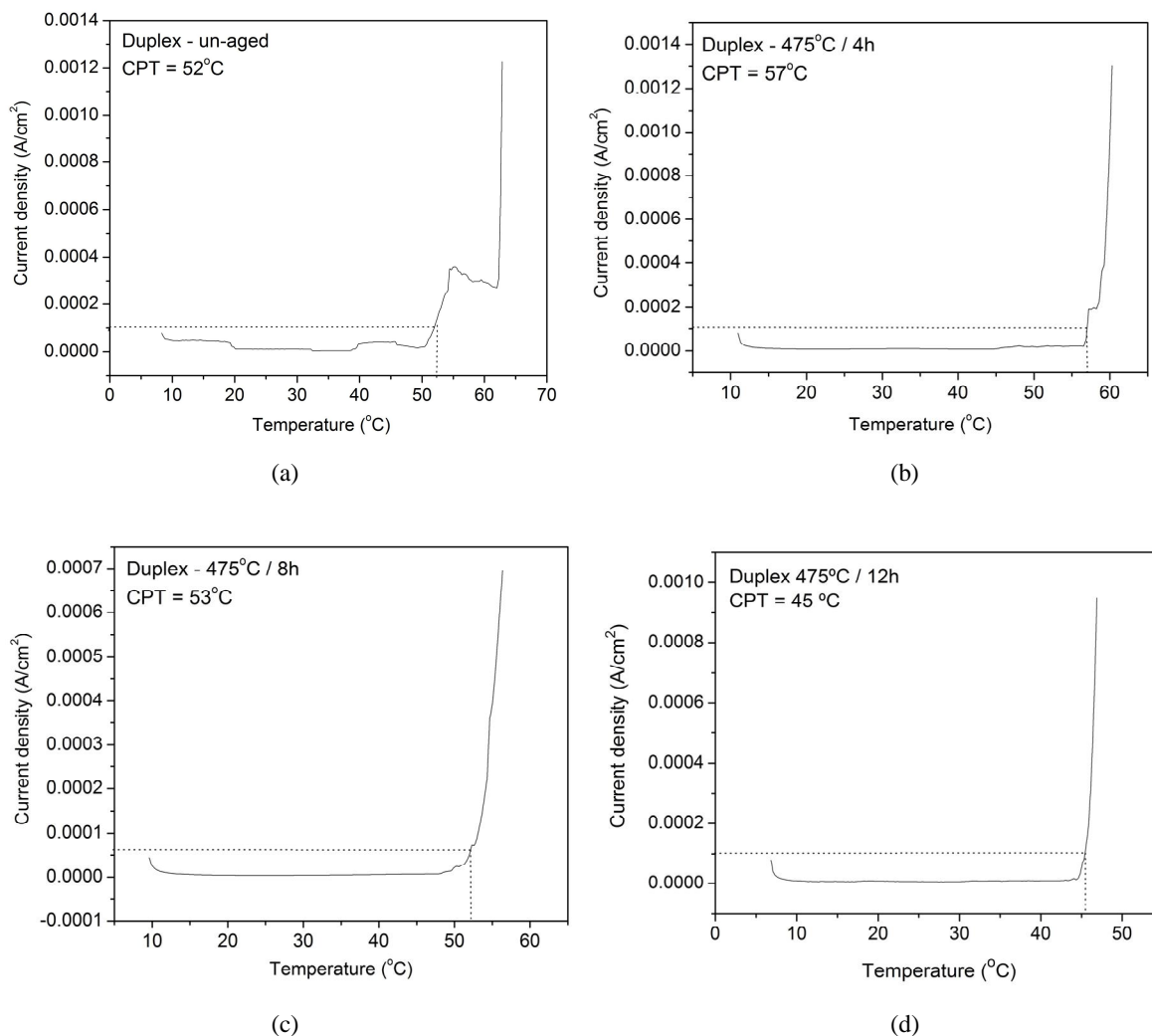


Figure 9. Current density *versus* temperature curves for CPT determination.

4. CONCLUSION

The main conclusions of the investigation about the influence of short duration low temperature treatments on the mechanical properties and corrosion resistance of UNS S32205 steel are:

- Heat treatments at 475 °C for 4h, 8h increased the hardness, yield and ultimate strength with small decrease of total and uniform elongation. The increase of aging time from 8h to 12h caused a further decrease of ductility without promoting significant hardening.

- The flow stress curves of as received and specimens heat treated at 475 °C for 4h, 8h and 12h could be modeled by Hollomon's equations ($\sigma_T = K\varepsilon^n$). The modeling using two Hollomon's equations, considering two work hardening stages, was more precise than the model using an unique equation.

- The pitting corrosion resistance was not affected by heat treatments at 475 °C for 4h and 8h. The increase of aging time from 8h to 12h caused an important decrease of the critical pitting temperature.

5. ACKNOWLEDGEMENTS

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