

## **Influence of tempering parameters on the mechanical properties of a Ti alloyed supermartensitic stainless steel**

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***Abstract.** Supermartensitic are a new generation of martensitic stainless steel with promising application in petrochemical industry. In this work, a Ti-alloyed supermartensitic steel was quenched from 1000°C and tempered at different temperatures in the 300°C to 650°C range. Double tempered samples (600°C-2h + 670°C-2h or 670°C-8h) were also produced. The toughness and tensile properties were measured, and the results were correlated to the microstructural analysis. The toughness was evaluated by Charpy impact tests at room temperature and – 46°C. The material presents high highimpact energy in the as quenched condition, but a slight temper embrittlement is observed at room temperature tests. The temper embrittlement became more important in the low temperature tests, and was detectable in the 400°C – 600°C range. Nominal and true stress-strain curves were obtained for all heat treatment conditions in order to analyze the influence of tempering parameters on yield and ultimate strength, work hardening coefficient and ductility.*

***Keywords:** supermartensitic stainless steel, mechanical properties, heat treatments*

### **1. INTRODUCTION**

Supermartensitic stainless steels were developed with the objective of profit the high mechanical resistance of the tempered martensitic structure, and obtain higher toughness and corrosion resistance than the conventional martensitic stainless steels (Kondo et al., 2002).

According to Olden et al. (2002), supermartensitic alloys are divided into three groups: low alloy (11Cr-2Ni), medium alloy (12Cr-4.5Ni-1.5Mo) and high alloy (12Cr-6.5Ni-2Mo). These three classes have quite different corrosion resistances and  $M_s$  temperatures. The choice of one specific alloy depends strongly on the enviromental conditions (A. Dhooze, 1999).

The carbon content of SMSS must be lower than 0.03 wt.% and rigid control of impurities such as S and P must be achieved to obtain satisfactory corrosion resistance and toughness. Recently, some SMSS were modified by the addition of Ti or Nb, with the announced benefits of grain refinement and increase of corrosion resistance (Rodrigues et al., 2007).

The final properties of quenched and tempered steels are strongly dependent on the final tempering treatment. As an example, Figure 1 shows the variation of mechanical properties of a conventional AISI 431 stainless steel with tempering temperature.

In the present work, an experimental supermartensitic stainless steel was single and double tempered at different temperatures. The mechanical properties were determined and analyzed. The correlations with microstructure features were discussed.

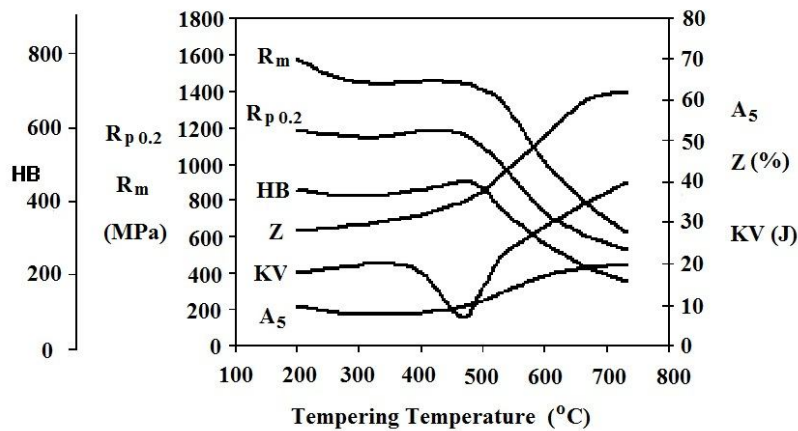


Figure 1. Variation of mechanical properties of AISI 431 with tempering temperature. ( $R_{p0.2}$  = Yield point at 0.2%,  $R_m$  = ultimate strength, Z = reduction of area,  $A_5$  = elongation, KV = toughness) (Béla Leffler, 1998).

## 2. EXPERIMENTAL METHODS

The chemical composition of the supermartensitic steel studied was carried out by Valourec Mannesman, and is shown in table 1. Elements C, N and S were analyzed by combustion method, while the contents of the other elements were determined by optical emission technique. The material was purchased as a 200 mm of diameter tube with 10 mm of thickness.

Table 1. Chemical composition of the supermartensitic stainless steel (wt.%).

%C	%Cr	%Ni	%Mo	%Mn	%Ti	%P	%S	%N
0.0278	12.21	5.8	1.95	0.519	0.28	0.0112	0.0019	0.013

Specimens for tensile and impact Charpy tests were roughly machined. The specimens were heat treated by water quenching and tempering. The quenching was carried out after soaking at 1000°C for 1 hour. After quenching the specimens were tempered according to the conditions detailed in table 2.

Table 2 – Heat treatment conditions and specimens identification

Identification	Heat treatment
T	Quenching from 1000°C
QT-300	Quenching from 1000°C, tempered at 300°C for 1h
QT-400	Quenching from 1000°C, tempered at 400°C for 1h
QT-500	Quenching from 1000°C, tempered at 500°C for 1h
QT-550	Quenching from 1000°C, tempered at 550°C for 1h
QT-575	Quenching from 1000°C, tempered at 575°C for 1h
QT-600	Quenching from 1000°C, tempered at 600°C for 1h
QT-625	Quenching from 1000°C, tempered at 625°C for 1h
QT-650	Quenching from 1000°C, tempered at 650°C for 1h
DT-1	Quenching from 1000°C, Double tempered (670°C / 2h + 600°C / 2h)
DT-2	Quenching from 1000°C, Double tempered (670°C / 2h + 600°C / 8h)

After the heat treatments, a finishing machining operation was performed to remove scale and achieve the final dimensions of the specimens (standard ASTM A-370). The tensile tests were performed with constant velocity of 5.8

mm/min at 22±2°C. Nominal and true stress *versus* strain curves were obtained. Yield and ultimate strengths, elongation, area reduction and work hardening exponent were the parameters obtained from the tensile tests analysis.

Vickers Hardness tests were performed with load of 30 kgf.

The microstructures of the specimens were characterized by magnetic measurements and scanning electron microscopy (SEM). The magnetic measurements were performed in a vibrating sample magnetometer (VSM), with the specimens cut and machined as fine discs with 3.5 mm of diameter. A maximum external field of 15000 Oe (1.5T) was applied. A typical magnetization curve obtained with the VSM is shown in figure 2. The main parameter extracted from the test is the magnetization saturation ( $m_s$ ). This is used to quantify the austenite content according to equations based on the method described by Cullity (1978):

$$C_M = \frac{m_s}{m_{S(i)}} \quad (1)$$

$$1 = C_M + C_\gamma \quad (2)$$

where:  $C_\gamma$  is the austenite volumetric fraction;  $m_s$  is the magnetization saturation; and  $m_{S(i)}$  is the magnetization saturation intrinsic of martensite.

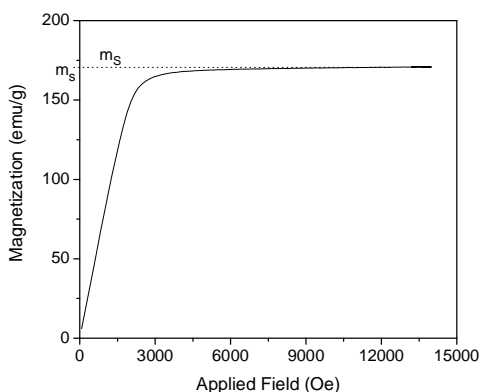


Figure 2. Magnetization curve of specimen QT-500 indicating  $m_s$  determination.

### 3. RESULTS AND DISCUSSION

Figure 3 shows a comparison of the tensile tests curves of specimens T, QT-300, QT-500, QT-625 and DT-1. This figure shows the strong influence of tempering on the tensile properties of the material. Figure 4 shows the variation of the yield limit and ultimate strength, and figure 5 shows the variations of total and uniform elongations with tempering parameters.

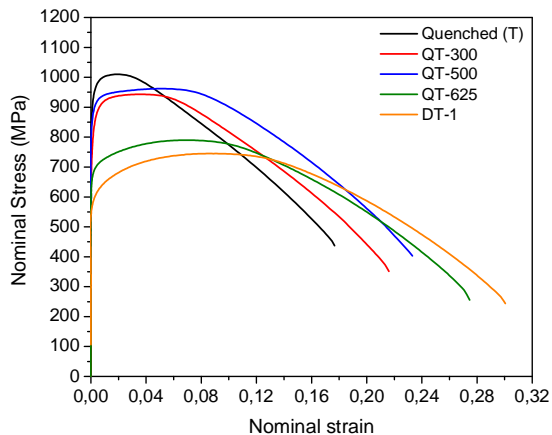


Figure 3. Tensile test curves of specimens T, QT-300, QT-500, QT-625 and DT-1.

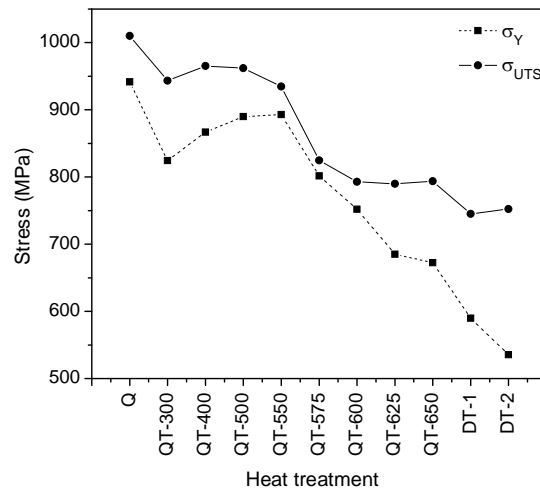


Figure 4. Variations of yield limit ( $\sigma_Y$ ) and ultimate tensile strength ( $\sigma_{UTS}$ ) with heat treatments.

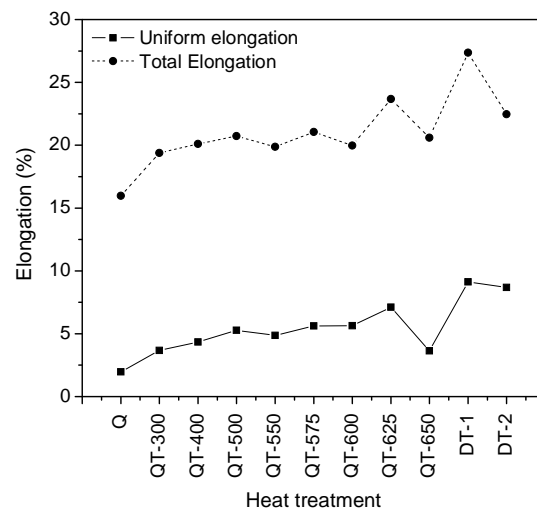


Figure 5. Variations of total and uniform elongation with heat treatments.

Figure 6 shows the behavior of the impact toughness at 22°C and hardness as function of the tempering treatment. The material shows a hardening effect during tempering in the 500 – 550°C range. Conventional martensitic stainless steels with Mo, V and/or W also present this increase of hardening, which is attributed to fine carbides precipitation (Pickering, 1978). Since the Mo content of the supermartensitic steel studied is 1.95% (table 1), probably the secondary hardening effect observed is due to Mo<sub>2</sub>C precipitation.

The as quenched steel (specimen Q) showed a high toughness (159J) with a typically ductile fracture (not shown). A decrease of toughness is observed in specimens tempered at 450°C and 500°C, although their fractures are also ductile, as shown in figure 7 from specimen QT-500.

The results of figure 5 shows that specimens tempered at 400°C (QT-400) and 500°C (QT-500) were more ductile than the as quenched material (Q), which means that the decrease of impact toughness observed in figure 6 was not accompanied by a decrease of ductility in the tensile tests. A correspondence between the impact toughness and the total energy per unit of volume from the tensile test wasn't observed either (figure 8).

It is well reported the temper embrittlement of conventional martensitic steels (Pickering, 1978; Folckhard, 1984) in the 400 – 600°C range. Figure 1 shows that the AISI 431 presents a toughness decay in the 400 – 550°C in room temperature impact tests. In the case of the supermartensitic steel studied in this work, the decrease of toughness observed in room temperature tests is very slight and all the fractures were ductile, although the coincidence of the minimum toughness with the maximum hardness (specimen QT-500) indicates a similarity with conventional

martensitic stainless steels (Pickering, 1978). The higher purity and the lower carbon of SMSS are the main reasons for the good toughness observed in room temperature tests.

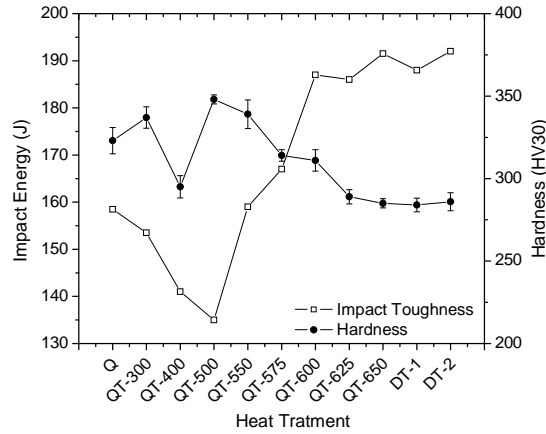


Figure 6. Variation of the impact toughness at 22°C and hardness as function of the tempering treatment.

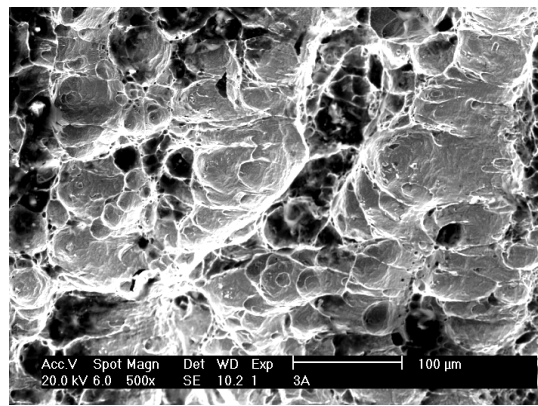


Figure 7. Fracture of specimen QT-500 tested at 22°C.

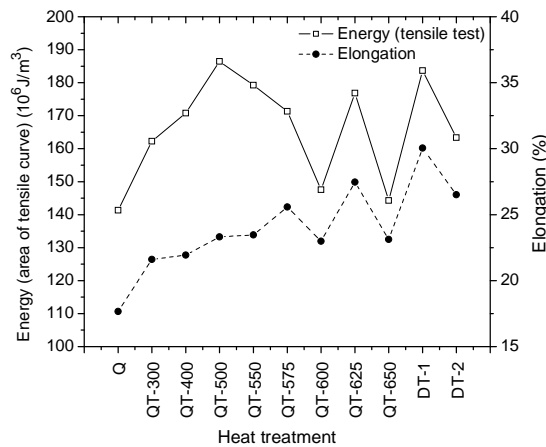


Figure 8. Comparison between the area of the tensile curve and the impact energy.

Figure 9 shows the impact toughness behavior in specimens tested at 22°C and -46°C. The comparison of the two curves clearly shows that the material has a slight decrease of toughness in room temperature tests, but a well

defined temper embrittlement in the 400 – 600°C in tests conducted at –46°C. Figure 10 shows the brittle fracture aspect of specimen QT-500 tested at –46°C.

Another interesting fact is that the specimen Q (as tempered) has shown excellent impact toughness at –46°C, with ductile fracture (not shown). A considerable decrease of impact energy is observed with tempering at 300°C, which is different from the behavior observed in conventional martensitic stainless steels (Pickering, 1978).

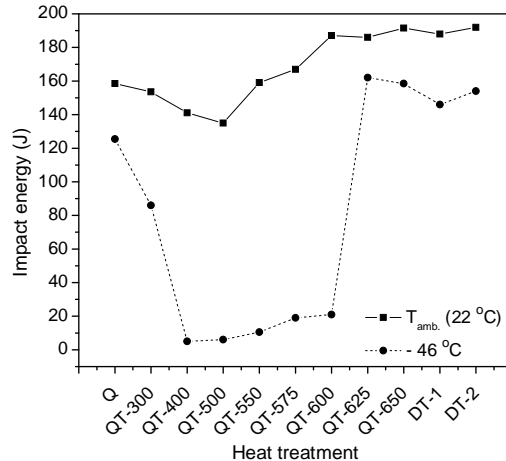


Figure 9. Variation of impact toughness with heat treatments: comparison between tests at 22°C and at –46°C.

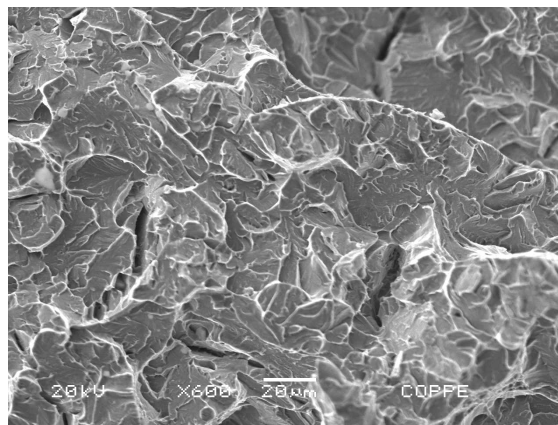


Figure 10. Fracture the specimens QT-500 tested at –46°C.

Figure 11 shows the austenite volume fraction as function of the heat treatment. Previous works have also shown that high alloyed martensitic stainless steels may undergo reverse austenite formation during high temperature tempering (Nakagawa, 1999; Folkhard, 1984; Tavares, 2010). A pronounced increase of austenite volume fraction was obtained with double tempering treatments.

The  $A_{c1}$  temperature for the steel composition calculated with MAP\_STEEL\_AC1TEMP software (Carrouge, 2001) was 607°C. This  $A_{c1}$  value is in agreement with the abrupt increase of austenite fraction with the increase of tempering temperature from 600°C to 625°C.

A decrease of austenite volume fraction with the increase of tempering temperature from 625°C to 650°C is observed. As explained by Folkhard [8], the behavior of the amount of reversed austenite at room temperature in soft martensitic steels as function of the tempering temperature passes through a maximum. The austenite formed always increase with tempering temperature above  $A_{c1}$ , but after a certain point this high temperature austenite becomes unstable, due to its chemical composition, and partially re-transforms on cooling. The decrease of total and uniform elongations observed with the increase of tempering temperature from 625°C to 650°C (figure 5) is probably due to the fresh martensite which is formed on cooling of specimen QT-650.

The first tempering of the double tempering treatment promotes the formation of a high amount of unstable austenite, which partially transforms into martensite on cooling. The  $A_{c1}$  temperature of this fresh martensite is lower than 600°C, due to its high nickel content, and, as a consequence, the second tempering causes the copious precipitation

of reversed austenite. Similar results with these treatments were obtained by Bilmes et al. (2001). Figure 12 shows the microstructure of specimen DT-1 with austenite phase as precipitated platelets between martensite laths.

Despite of the high austenite volume fraction of specimens double tempered (DT-1 and DT-2), the toughness of these samples were not superior to specimens QT-625 and QT-650, as shown in figure 9.

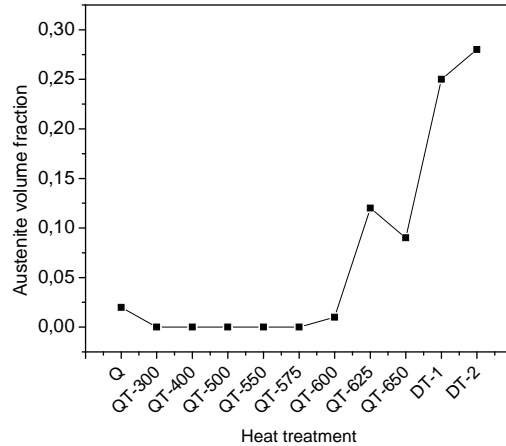


Figure 11. Austenite volume fraction as function of heat treatment.

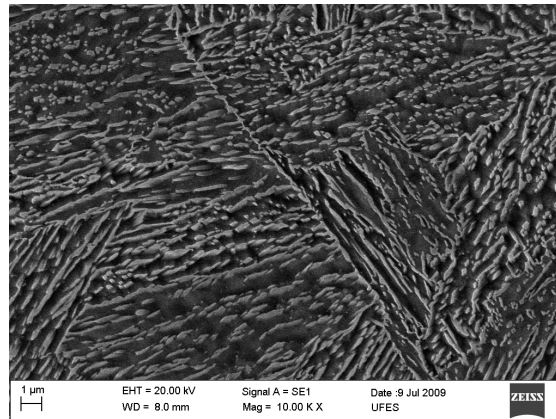


Figure 12. Microstructure of specimen DT-1.

The flow stress curves were analyzed in the region between the proportionality limit and the ultimate strength. The curves were modeled by Holloman's equations:

$$\sigma_T = K \varepsilon_T^n \quad (1)$$

$$\ln \sigma_T = \ln K + n \ln \varepsilon_T \quad (2)$$

where K and n are constants of the material. The parameter n is known as strain-hardening exponent, and K is the strength coefficient (Dieter, 1988).

Two types of modeling were experimented, as shown for the specimen QT-300 in figures 13(a) and 13(b). In figure 13(a) one equation was fitted for the interval. The correlation coefficient in this case was  $R = 0.9956$ . A better correlation can be obtained with two Holloman's equations, as shown in figure 6(b). In this case one curve was fitted for the first part ( $R=0.9995$ ), and another was fitted for the second part of the flow stress curve ( $R=0.9959$ ), suggesting that the material shows two work hardening stages. Specimens QT-550, QT-650 and DT-2 were not modeled with two equations because the one equation model has given satisfactory correlation coefficients.

Figure 14 shows the variation of the strain-hardening exponents with heat treatments. Note that n was obtained with one equation model, while  $n_1$  and  $n_2$  were obtained with the more precise two equations model. The strain-

hardening exponents of specimen Q are very low, typical of quenched steels. An increase of strain-hardening exponents was obtained with tempering at 300°C. After this, the strain hardening exponents passes through a minimum in the 500 – 600 °C range. Tempering above 625°C and double tempering caused the increase of strain-hardening exponents due to increase of austenite volume fraction. A comparison between Figures 14, 4 and 5 shows that conditions with higher n exponent are those with higher  $\sigma_{UTS}/\sigma_Y$  ratio, but there is no relation between the n value and the uniform elongation, as it could be expected from the application of the instability criterion of Considère (Dieter, 1988).

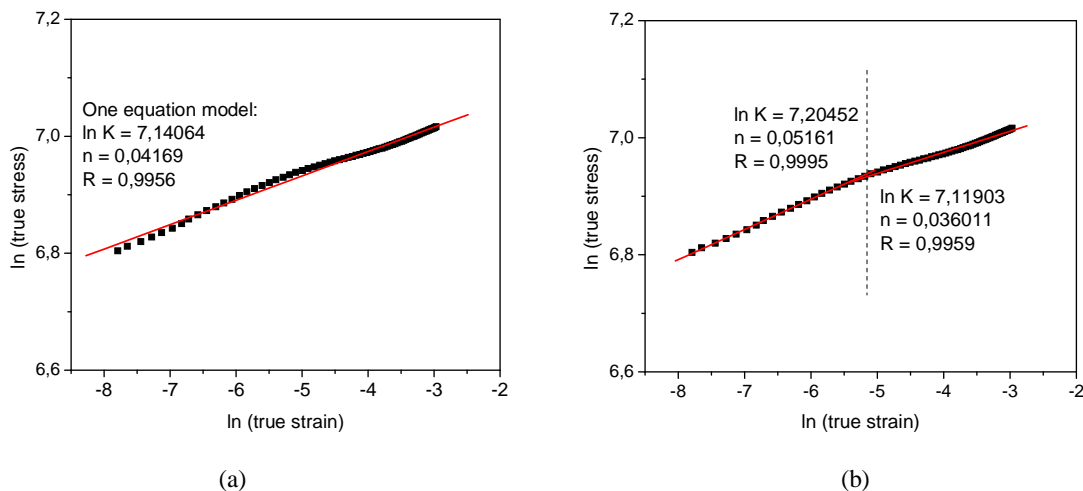


Figure 13. Plots  $\ln \sigma_T \times \ln \epsilon_T$  and fittings with Holloman's equations: (a) one equation model; (b) two equations model.

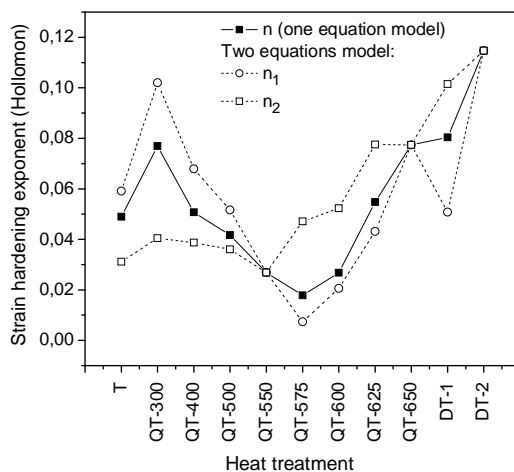


Figure 14: Variation of the strain-hardening exponents with heat treatments.

#### 4. CONCLUSIONS

The mechanical properties of the Ti-alloyed supermartensitic stainless steel studied in this work are strongly influenced by the final tempering treatment.

In the as quenched condition the material showed surprisingly high impact toughness in tests conducted at 22°C and – 46°C.

In room temperature tests, a small decrease of impact energy was detected in specimens tempered at 400°C and 500°C. The minimum of toughness at this temperature was coincident with a maximum hardness (specimen tempered at 500°C). Specimens double tempered and single tempered at temperatures equal or higher 550 °C presented excellent toughness at 22°C.

In impact tests temperature tests at – 46°C a pronounced temper embrittlement effect was observed in the 400 – 600°C, which is the same range of temperatures for temper embrittlement in conventional martensitic steels. The difference is that these steels presents this embrittlement effect in room temperature tests. The higher purity and the



lower carbon of supermartensitic steels are the main reasons for the high toughness observed in the room temperature tests of this material.

Single tempering treatments at 625°C and 650°C promoted the formation of 12% and 9% of reverse austenite. Double tempering treatments at 670°C (2h) and 600°C (2h and 8h) resulted in 25 and 28% of reverse austenite. Despite of the higher austenite content, double tempered specimens showed impact toughness at 22°C and -46°C similar to specimens tempered at 625°C and 650°C.

Yield and ultimate strengths decreased with the increase of tempering temperature, as expected. In general, the ductility increased with the increase of tempering temperature, except for specimen treated at 650°C which must contain a considerable amount of un-tempered martensite.

The decrease of impact toughness observed at 400 – 500°C range in room temperature tests, was not detected by tensile tests, i.e. the ductility and toughness measured by area of tensile curves did not follow the same trend of impact tests.

The tensile flow stress curves were modeled by Holloman's equations. It was observed that the strain hardening exponent (n), which was very low in the as quenched condition, increased with tempering at 300°C. The strain hardening exponent decreased to minimum values in the 500 – 600°C range, and increased with tempering above 600°C and double tempering. The formation of reversed austenite is responsible for the increase of strain hardening exponent to 0.11 in the specimen double tempered at 670°C (2h) and 600°C (8h).

## 5. ACKNOWLEDGEMENTS

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