# Mechanical properties evolution on heat treated severe cold rolled UNS S32760 Super Duplex Stainless Steel

**C.M. Tromellini, A.F. Ciuffini, A. Gruttadauria, S. Barella, C. Di Cecca, C. Mapelli**

Super Duplex Stainless Steels (SDSSs) are characterized by the compresence of austenitic and ferritic grains. They display very high corrosion resistance, especially in chloride-rich environments. They also have better mechanical properties than single-phase counterparts. In the recent years, many studies have been performed to enhance the mechanical properties of SDSS without detrimental effects on corrosion resistance. In this work, Super Duplex Stainless Steel AISI F55 – UNS S32760 is cold rolled and heat treated at different temperatures and holding times to obtain a serious enhancement of the mechanical properties of the material. Much attention is devoted to the optimization of the heat treatment performed on the plastically deformed material, in order to obtain a suitable compromise between tensile strength and ductility, without the formation of undesired embrittling phases. The heat treatment at 620° C was considered the best compromise, combining 1539 MPa of tensile strength with 8,25 % of fracture elongation after 12,5 minutes of holding time.
A detailed microstructural analysis has been carried out to understand the strengthening mechanisms acting on the material and to explain the evolution of the microstructure that leads to superior mechanical properties of the treated steel. The corrosion resistance of the heat treated material has been checked for the most promising thermo-mechanical treatments.

**KEYWORDS:** SUPER-DUPLEX STAINLESS STEELS (SDSS), ANNEALING THERMAL TREATMENT, COLD ROLLING

## INTRODUCTION

Super Duplex Stainless Steels (SDSSs) are characterized by the compresence of austenitic and ferritic grains. They display very high corrosion resistance, especially in chloride-rich environments and have better mechanical properties than single-phase counterparts. Their unique combination of properties makes them the material of choice for many industries and the ever growing demand of better performing components for industrial and consumer applications ensure that the market for Super Duplex Stainless Steels will grow in the next future. Many studies have been performed to enhance the mechanical properties of SDSSs without detrimental effects on corrosion resistance. [01-03]
Cold plastic deformation with high reduction ratio followed by heat treatment is a well-known processing route to obtain a material with superior mechanical performances. [04]
The main purpose of this work is to document the effects of different heat treatments on the mechanical properties of a cold rolled UNS S32760 steel. The solution annealed material was cold rolled up to 88% of reduction. The rolled material was heat treated at five different temperatures, 550° C, 620° C, 700° C, 800° C and 1080° C with different holding times, ranging from 1,5 minutes to 60 minutes. Much attention was devoted to the optimization of the heat treatment performed on the plastically deformed material, in order to obtain a suitable compromise between yield strength and ductility, and avoid the formation of embrittling phases, deleterious both for mechanical and corrosion resistance. Tensile tests were performed to assess the mechanical resistance of the material.
A detailed microstructural analysis has been carried out to understand the strengthening mechanisms acting on the material and to explain the evolution of the microstructure that leads to the superior mechanical properties of the treated steel. Beside the enhanced mechanical properties, the corrosion resistance of the material has to be carefully checked to ensure a very limited loss of performance, if any. For that reason, the corrosion resistance of the heat-treated material has been checked for the most promising thermo-mechanical treatments.

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**EXPERIMENTAL PROCEDURE**

The material used in this work is a F55 – S32760 super duplex stainless steel with chemical composition accordant to the ASTM A240/A240M – 04 standard. Samples were cut from the ingot in the transversal direction, in order to obtain 10 mm thick slices. Then, the specimens were cold rolled using a lab-scale rolling mill to a final thickness of 1,2 mm, through many rolling steps. The samples were cooled during rolling, in order to keep the temperature of the material well below 250° C, which can be considered the limit working temperature for this material, preventing the precipitation of embrittling phases. [05]

The samples were loaded in a preheated muffle furnace and water quenched after the required holding time. Because of the reduced thickness of the specimens, the heating and cooling rates are very fast. This is important to isolate the effect of temperature and holding time on the material. The thermal treatments temperatures were: 550° C, 620° C, 700° C, 800° C, 1080° C. The soaking times of the thermal treatments vary from a minimum holding time of 2 minutes up to 60 minutes. (Table 1)

**Tab.1** - Compositions (wt%) of the samples and, determined with SEM-EDS for the major alloying elements, and with EPMA for nitrogen.

| THERMAL TREATMENTS SUMMARY | | | | | |
|---|---|---|---|---|---|
| | Temperature [° C] | | | | |
| Holding time [min] | 550 | 620 | 700 | 800 | 1080 |
| 1,5 | | | 7_1,5 | 7_1,5 | 10_1,5 |
| 2 | 5_2 | 6_2 | 7_2 | 7_2 | 10_2 |
| 3 | | 6_3 | 7_3 | 7_3 | 10_3 |
| 5 | 5_5 | 6_5 | 7_5 | 7_5 | 10_5 |
| 7,5 | 5_7,5 | 6_7,5 | 7_7,5 | 7_7,5 | 10_7,5 |
| 10 | 5_10 | 6_10 | 7_10 | | |
| 12,5 | 5_12,5 | 6_12,5 | 7_12,5 | | |
| 15 | 5_15 | 6_15 | 7_15 | | |
| 20 | 5_20 | 6_20 | | | |
| 25 | 5_25 | 6_25 | | | |
| 30 | 5_30 | 6_30 | | | |
| 40 | 5_40 | | | | |
| 60 | 5_60 | | | | |

In order to assess the mechanical resistance of the investigated material, tensile tests have been executed following the ASTM E8/E8M – 16 standard.

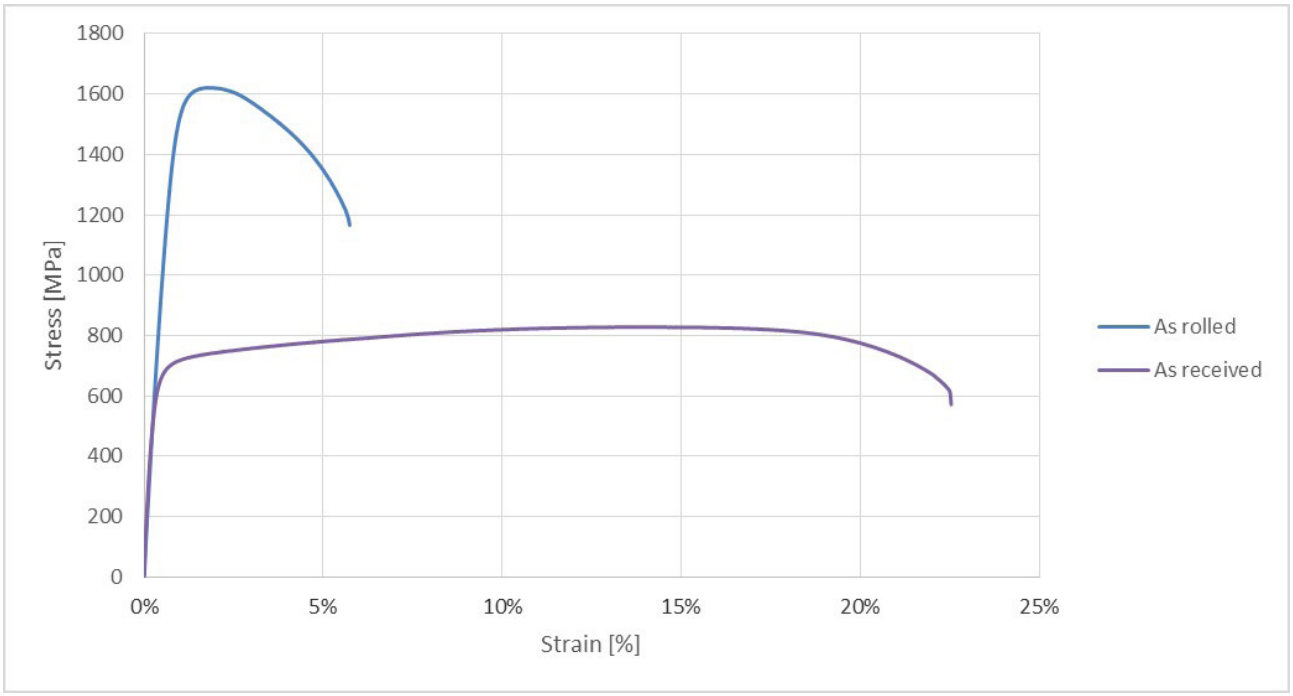
Potentiodynamic polarization testing is an electrochemical technique used to study the corrosion process of a metal alloy. In this work it has been performed following the ISO 17475 reference norm. A "three-electrode" Amel 2553 potentiostat was used. The working electrode was a sample of the material under examination. Two counter electrodes made of platinum were used to close the circuit, and a "saturated calomel electrode (S.C.E.)" was adopted as reference electrode. The electrode is included in a "Luggin capillary". All the above-mentioned components were submerged in an electrically conductive solution, the electrolyte, which properly simulates the aggressive environment where the steel has to work (marine environment). The solution was made by 35 g/L (0.6 M) of pure NaCl in distilled water. The voltage range was bounded between -600 and 1400 mV and the scan rate was set to 0,04 mV/s. All the tests were performed at room temperature. The surface of the samples was prepared according to the norm, in order to have an average roughness smaller than 1 micrometer. They were grinded by means of an abrasive paper up to 800 grit.

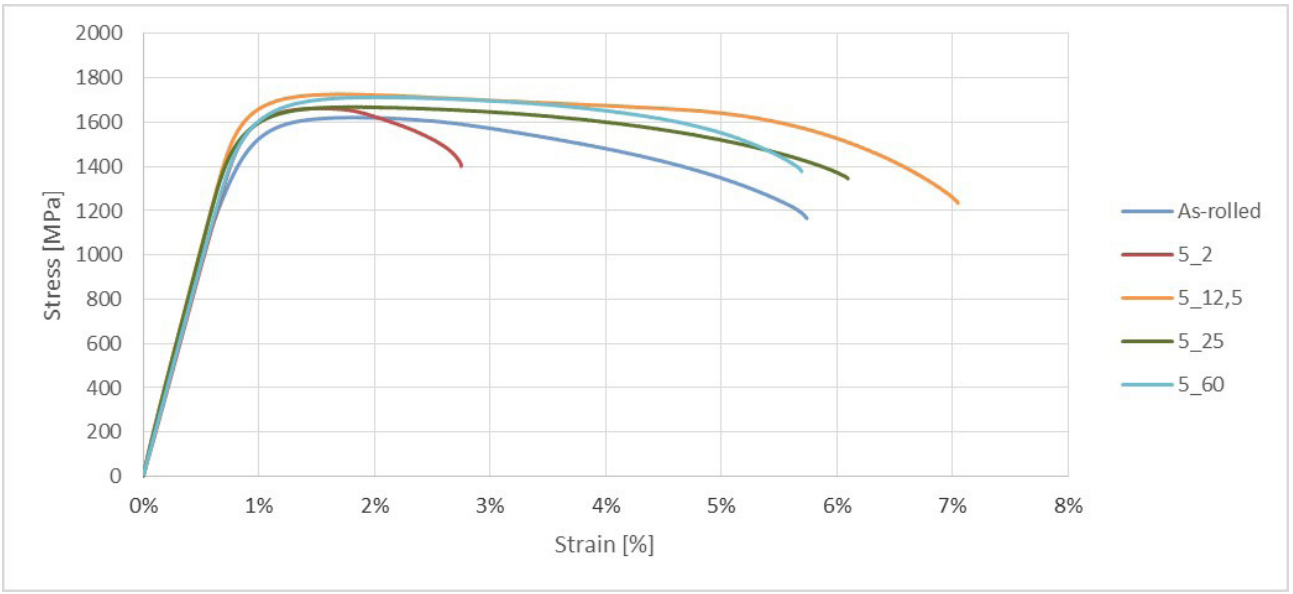
The X-ray diffraction method was used to assess the amount of the austenite volume fraction in the cold rolled and heat treated samples. A Stresstech Xstresses 3000 G3R X-ray diffractometer was used. The samples were mechanically grinded and polished up to a 1 micron diamond paste, to have a clear surface and to avoid the plastic deformation of the surface, which can generate strain-induced martensite and produce misleading results. The Kα radiation of Chromium was used as X-ray source, and the calculation of the phase fraction of austenite were carried out according to the ASTM E975-03 Standard Practice for X-ray Determination of Retained Austenite in Steel with Near Random Crystallographic Orientation. In this work, the evaluation of the diffraction peaks of the austenite at 130° and 80° degrees was carried out by using the "parabolic" function to reduce the background noise and

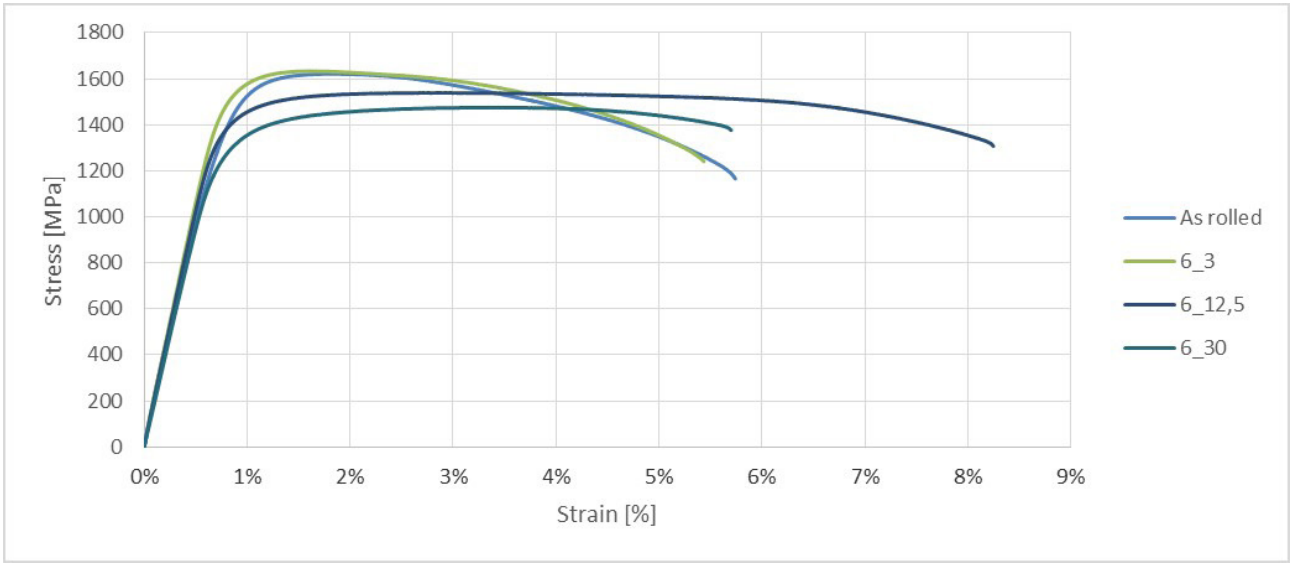
the "Gauss" function to fit the curve. For the diffraction peaks of the ferrite at 156,4° and 106,1° the Pearson VII function was used to fit the peaks and a linear function for noise reduction. The measure of the austenite content is based on the calculation of the areas under the diffraction peaks of the ferritic and austenitic phases, as these areas are proportional to the content of each phase.

## RESULTS

Tensile tests results are reported in the following, grouped on the basis of the temperature of the heat treatment. The as-rolled material was tested to assess the strain-hardening of the alloy subjected to cold rolling, up to a high reduction of the cross section. Heat treated samples show a further increase in yield stress, tensile strength and also fracture elongation with respect to the as-rolled condition. This leads to impressive results for the mechanical resistance.

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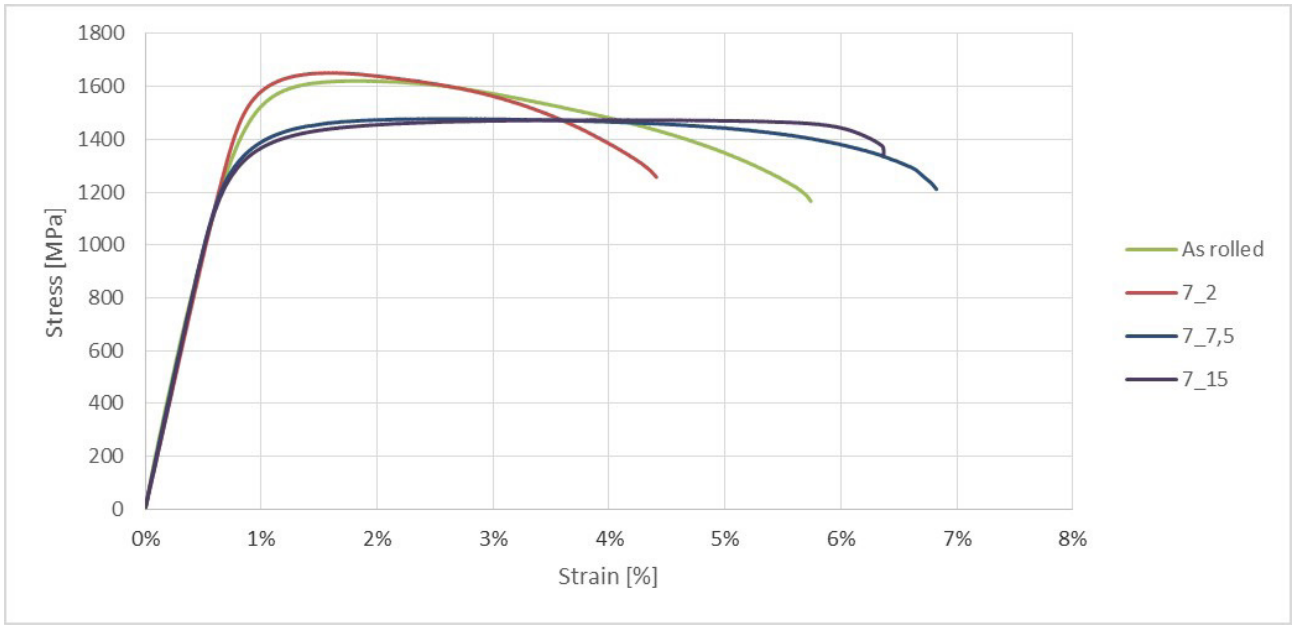
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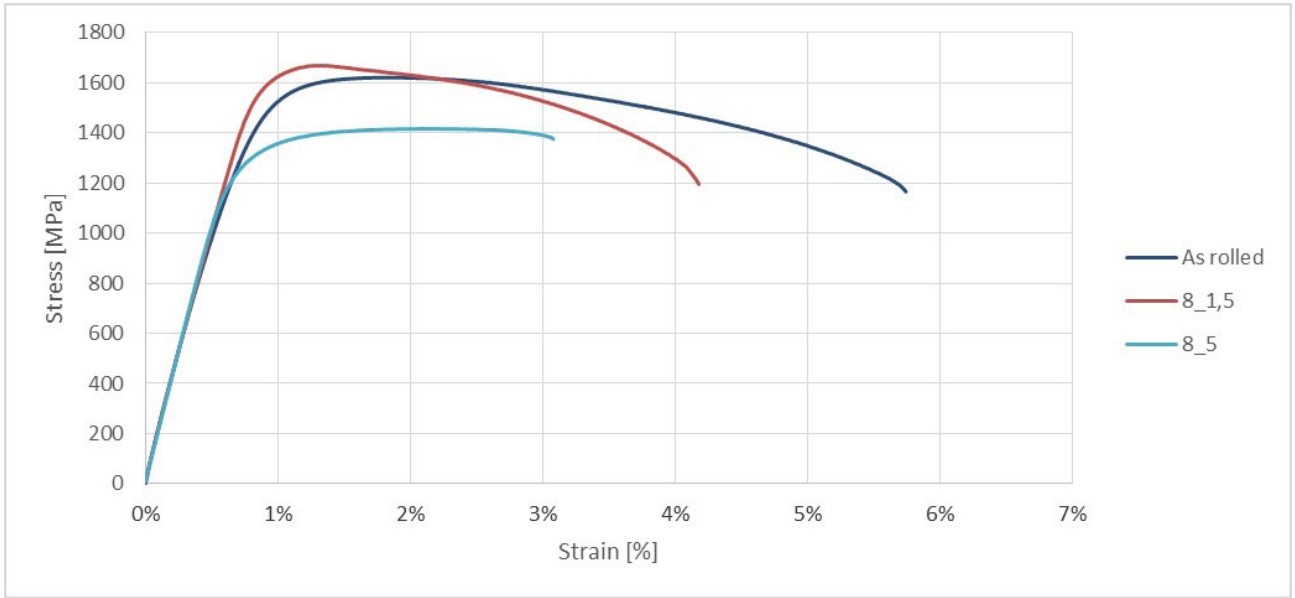
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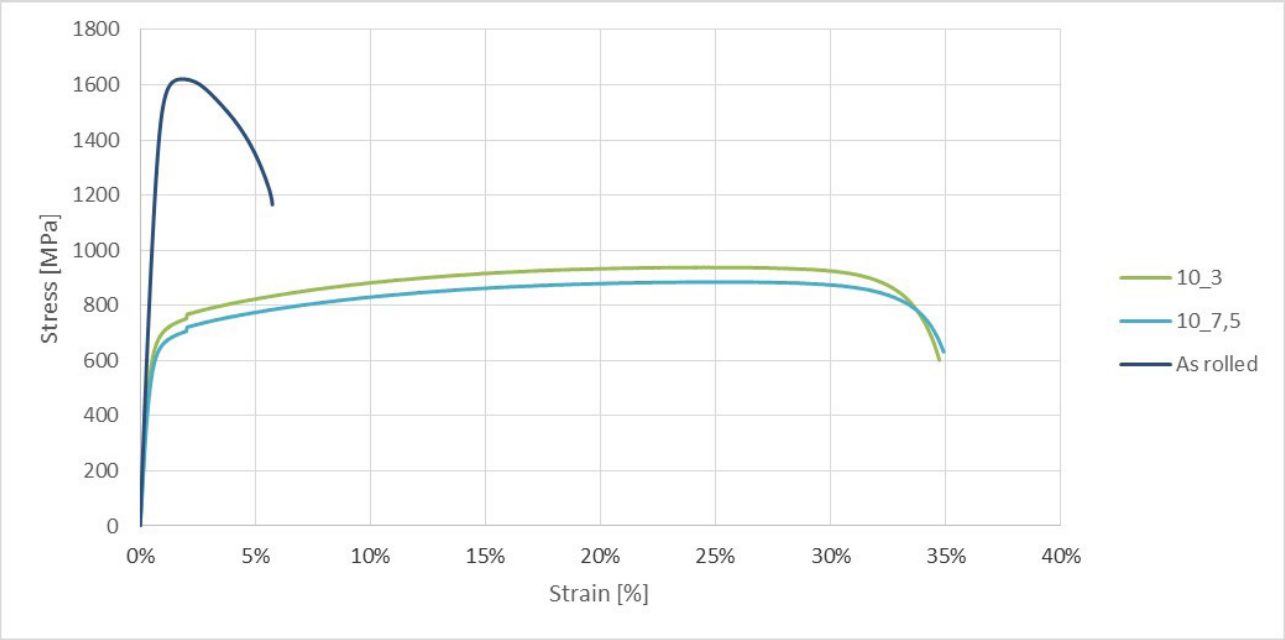


**Fig. 1** - Tensile tests results

The corrosion resistance results, extrapolated from the potentiodynamic polarization tests, have been reviewed in Table 2. It can be observed the slight loss in corrosion resistance related to the thermal treatments. The data related to the samples 7_12,5 and 10_7,5 are not detailed since a passive behavior has not been detected.

**Tab. 2** - Potentiodynamic polarization results

| CORROSION RESISTANCE | | |
|---|---|---|
| **Sample** | **Current density [A/m2]** | **Pitting potential [V vs SCE]** |
| As-received | 1,3 * 10^-2 | 0,95 |
| As-rolled | 4,6 * 10^-2 | 0,94 |
| 5_5 | 1,62 * 10^-1 | 0,93 |
| 5_7,5 | 1,81 * 10^-1 | 0,89 |
| 5_12,5 | 2,01 * 10^-1 | 0,92 |
| 6_5 | 3,41 * 10^-1 | 0,9 |
| 6_7,5 | 3,75 * 10^-1 | 0,92 |
| 6_12,5 | 2,72 * 10^-1 | 0,92 |
| 7_5 | 1,18 | 0,91 |
| 7_7,5 | 2,86 | 0,38 |
| 7_12,5 | -- | -- |
| 10_7,5 | -- | -- |

The X-ray analysis results, revealing the austenite content of the specimens after the thermos-mechanical treatments, have been reported in Table 3.

**Tab. 2** - Potentiodynamic polarization results

| AUSTENITE CONTENT | | |
|---|---|---|
| **Sample** | **λ phase [%]** | **Error [%]** |
| As-received | 35,7 | 0,2 |
| As-rolled | 22,6 | 0,4 |
| 5_5 | 20,2 | 0,2 |
| 5_7,5 | 18,7 | 0,1 |
| 5_12,5 | 18,6 | 0,3 |
| 6_5 | 19,7 | 0,3 |
| 6_7,5 | 26 | 0,5 |
| 6_12,5 | 21,5 | 0,2 |
| 7_5 | 26,8 | 0,2 |
| 7_7,5 | 27 | 0,3 |
| 7_12,5 | 30,6 | 0,5 |
| 10_7,5 | 37,9 | 0,3 |

**DISCUSSION**

When subjected to severe plastic deformation the material undergoes serious changes in the mechanical properties. Two main processes occur in the duplex structure under these conditions:

- strong grain fragmentation, that leads to a strong microstructure refinement.
- nucleation of strain-induced martensite, by the $\gamma \rightarrow \alpha'$ reaction.

Both these processes are responsible for a high work-hardening and loss of fracture elongation, but, as no diffusion of chemical species takes place during cold deformation, corrosion resistance should not be greatly influenced. This is perfectly adherent to the results obtained on as-rolled sample.

To assess the amount of austenite transformed into strain-induced martensite was used the direct comparison method described by Cullity et al. [06]. The result is around 13 % of strain-induced martensite, that is coherent with other results in literature.

During a heat treatment at around 550° C many changes in the microstructure of the material takes place:

- precipitation of α'Cr phase either by nucleation and growth or by spinodal decomposition.
- precipitation of G-phase.
- precipitation of Cr2N.

Precipitation of α'Cr phase is known to occur up to 550° C and plastic deformation can change the nature of the reaction $\delta \rightarrow \alpha + \alpha'$Cr from nucleation and growth to spinodal decomposition. The decomposition of ferrite is also responsible for enhancing the precipitation of Cr2N, which is frequently reported in case of spinodal decomposition of ferrite. [07]

G-phase does normally precipitates after ferrite decomposition, because is rich in alloying elements that segregates during the decomposition process. Preferential sites for G-phase nucleation are dislocations, probably due to the enhanced diffusion through the dislocation length.

The X-ray analysis reveal that the amount of austenite after 5 minutes of holding time is already lower with respect to the as-rolled material, and keeps lowering up to 7,5 minutes. After 7,5 minutes of holding time the amount of retained austenite stays constant up to 12,5 minutes (Tab. 3).

These results, combined with the results of the tensile tests, suggest that most of the precipitation processes take place in the first 10 minutes of heat treatment or less.

The changes in corrosion resistance are not dramatic, and the material still displays a satisfying stability against Cl-rich environments. This is in agreement with the hypothesis that the main microstructural change occurring in the material is the precipitation of α'Cr phase, which is known to have a weak effect on corrosion resistance. This also may discourage the hypothesis of Cr2N precipitation, as they are known to have small impact on mechanical properties but can seriously decrease the corrosion resistance. [08]

During heat treatment at 620° C there are four main reactions which can take place in super duplex stainless steels, especially if they are plastically deformed:

- strain-induced martensite reversion to austenite.
- static recovery.

• precipitation of secondary austenite through martensitic-shear process.
• precipitation of R-phase.
• precipitation of δ phase.

The first and the second processes may explain the softening of the material by the nucleation of austenite. The X-ray analysis of the austenite content may confirm the trend. Especially between 5 and 7,5 minutes, the amount of austenite in the material has a noticeable increase, weather after 12,5 minutes of holding time is almost the same amount as in the as-rolled material. This oscillation in the amount of retained austenite can be explained by the local phase transformations and the diffusive processes controlling the kinetics of the process (Tab. 3). [09]

Static recovery is thought to take place in the ferritic phase, but has a very marginal effect on fracture elongation and tensile stress. This fits the experimental results that show a very high tensile stress and only moderate increase in fracture elongation, with respect to the "as-received" condition.

The precipitation of R phase is known to occur at maximum rate around 600° C, and cold working significantly favors the precipitation of this intermetallic phase. R phase has a limited impact on tensile strength, whether is known to reduce the fracture elongation. [08,10]

Analyzing the corrosion resistance results, they may suggest that a microstructural transformation happens already at 5 minutes of T. T. holding time, as there is a change in both passive current and shape of the overall potentiodynamic curve. This change may be also related to the R phase precipitation, as shown by Kim et al. [08]. Combining the two results it may be assumed that the variation of tensile properties is due to the combined effect of γ2 and R phase nucleation, which lead to a best combination around 12,5 minutes of holding times. For longer holding time the coarsening of R phase leads to an overall decrease of the mechanical properties of the material.

During heat treatment at 700° C the corrosion resistance sharply decreases, where the mechanical properties do not change so drastically, even though a certain decreasing trend in Rm and Rp0,2 may be present. This behavior is explained with the precipitation of Chromium carbides and nitrides, because they have a small impact on mechanical properties but can seriously compromise the corrosion resistance of the alloy. They are known to precipitate around 700° C, but because of the very low amount of Carbon present in the analyzed alloy, the reduction of corrosion properties may be related to nitrides precipitation only. The shape of the stress strain curve on the other hand shows quite a change as the heat treatment goes on, and for longer holding times the strain hardening is much more evident. This behavior may be coupled with the results from the X-ray evaluation of the austenite content, which shows a continuous increase in austenite content with holding time.

It may be assumed that the main reaction responsible for the increasing amount of austenitic phase should be $\sigma \rightarrow \gamma 2 + \sigma$, as the eutectoid reaction is known to be favored by cold working. The precipitation of σ phase can be also responsible for losses in corrosion resistance, but cannot be claimed to be the only one, as the mechanical properties of the material do not follow such a fast degradation, which is expected since both properties are strongly affected by this precipitation process. [08]

During aging at 800° C there are many precipitation processes that may occur. The first is the precipitation of Chromium nitrides, at phase boundary between austenite and ferrite. After that, the precipitation of χ phase and σ phase, which will form through the eutectoid reaction $\delta \rightarrow \gamma 2 + \sigma$, takes place, and seriously affect the mechanical properties of the material. It is also known that cold working shortens the incubation time for σ phase precipitation and increases the precipitation kinetics. In effect, it has been reported dislocation can act as nucleation site for σ phase. [11]

The results of the mechanical testing show a fast and serious degradation of the material, especially the fracture elongation, which may be related to the ductility of the material. This implies that the precipitation inside the material must be relevant, and the only reaction able to compromise the properties of the material to such an extent is the eutectoid reaction $\delta \rightarrow \gamma 2 + \sigma$.

At 1080° C, the only stable phases are ferrite and austenite, which implies that the precipitation of any other phase may not takes place during the heat treatment. Moreover, at this temperature recovery, recrystallization and coarsening of ferritic and austenitic phase occur. This would bring back the material to the solution annealed condition. A sufficiently intense plastic deformation can induce grain refinement, which is known to enhance the mechanical properties of the material. [12]

This is in agreement with the results of the tensile test, that show a sudden decrease in yield stress and tensile strength, together with a noticeable increase in fracture elongation, typical of recrystallization phenomena. Around two minutes of holding time there is also a small peak in the mechanical resistance, that can be related to grain refinement.

After 7,5 minutes of holding time, the amount of austenite inside the microstructure of the material is almost the same as in the as-received case, that suggests no other phases are left after annealing at this temperature, and the material is approaching the equilibrium microstructure (Tab. 3).

The results for corrosion resistance show a serious deterioration with respect to the as-received material. This can happen due to the high cooling rate imposed to the material when water-quenched. At temperatures above 1000° C, if the cooling rate is too high, nitrogen cannot diffuse towards γ phase, and a supersaturated ferritic phase give rise to precipitation of very fine Chromium nitrides inside the ferritic grains. These nitrides have almost no influence on the mechanical properties, but do affect the corrosion resistance because they create a small zone around them depleted both in Cr and N, and for this reason susceptible to localized corrosion attack. [13] This can explain the loss of corrosion resistance in the samples heat treated at 1080° C.

## CONCLUSION

In this work, the mechanical properties of super duplex stainless steels have been enhanced, preventing losses in corrosion resistance. The material was cold rolled and heat treated at different temperatures and for different holding times.

The most important results can be summarized as follows:

• The as-rolled material shows a great enhancement of tensile strength, as result of the formation of strain-induced martensite during the rolling process. The corrosion resistance is almost the same as the solution annealed material.

• The heat treatment at 550° C gives the best results for yield strength (Rp0,2=1645 MPa) and tensile strength (Rm=1726 MPa) at around 12,5 minutes of holding times, but the material shows very limited strain-hardening. The corrosion resistance of the alloy is still very good, even though there is a limited loss with respect to the as-rolled condition. The decomposition of the ferritic matrix along with the precipitation of G phase are the responsibles for this change in material's behavior.

• The heat treatment at 620° C leads to the best compromise in terms of mechanical properties and corrosion resistance. Around 12,5 minutes of holding time the material shows excellent yield stress (Rp0,2=1407 MPa) and tensile stress (Rp=1539 MPa), a reasonable fracture elongation (Ax=8,25 %) and a certain strain-hardening behavior. The corrosion resistance is lower with respect to the as-rolled material but still shows a clear passive behavior. The reversion of strain-induced martensite and a certain recovery, alongside with precipitation of R phase and secondary austenite are thought to be the main processes acting during treatments at this temperature.

• At 700° C and 800° C the corrosion resistance is negatively affected by the precipitation of Chromium nitrides and/or $\sigma$ phase. Further, the mechanical properties obtained do not compensate such losses, precluding any possible application.

• The 1080° C treatment restores the mechanical behavior of the solution annealed material by promoting recrystallization. There is an increase of the fracture elongation (Ax=35,58 %) and a certain increase in tensile stress (Rm=954 MPa). However, the material shows poor corrosion resistance due to the precipitation of Chromium nitrides, generated by an excessive cooling rate.

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