

**Influence of thermomechanical processing on mechanical properties and corrosion resistance
of super duplex stainless steel UNS S32750.**

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ABSTRACT

Super duplex stainless steels (SDSS) are characterized by a two-phase microstructure of approximately 50% ferrite (α) and 50% austenite (γ). SDSS are highly alloyed stainless steels with at least 25 % Cr, 3 % Mo, 6 % Ni and 0.2 % N and offer an excellent combination of good mechanical properties and resistance to general as well as localized corrosion. Despite their good combination of properties in typically solution annealed condition, there is a certain need to increase the strength of these materials. The tensile strength of SDSS can be increased by a thermomechanical process (TMP). The aim of this paper is to study the effect of a TMP on the mechanical properties, mainly tensile strength, and corrosion properties of UNS S32750 (1.4410). The material was submitted to a TMP at temperatures where detrimental phases should not precipitate according to thermodynamic calculations. After TMP, UNS S32750 still displays a ferritic-austenitic microstructure free of secondary phases and exhibits yield strength and ultimate tensile strength higher than 800 MPa (116 ksi) and 950 MPa (138 ksi), respectively. The pitting corrosion resistance UNS S32750 at room temperature is not affected by TMP. At 50 °C, there is a slight reduction of pitting corrosion resistance. The tensile strength of UNS S32750 can be increased without losing its corrosion properties by TMP, enabling the use of this SDSS for applications at high strength and in very aggressive environments.

Key words: Super duplex stainless steel, thermomechanical process, mechanical properties, pitting corrosion.

INTRODUCTION

Duplex stainless steels (DSSs) are based on the Fe-Cr-Ni system and are constituted of 30 to 70 % ferrite and austenite. They combine high tensile strength, good toughness, weldability, and excellent corrosion resistance including stress-corrosion cracking and resistance to localized corrosion.¹⁻³ DSSs can be classified according to the Pitting Resistance Equivalent Number ($PREN = Cr + 3.3 Mo + 16 N$) in lean duplex ($PREN = 22-27$), standard ($PREN = 28-38$), super duplex ($PREN = 38-45$) and hyperduplex ($PREN > 45$).

Super duplex stainless steels (SDSSs) are alloys containing 24 – 28 % Cr, 6 – 8 % Ni, 3 – 5 % Mo, 0.2 – 0.3 % N and other elements like Cu and W.⁴ They are prone to precipitation of nitrides, carbides ($M_{23}C_6$), intermetallic phases like sigma- or chi-phase, or even alpha prime at low temperatures due to the high content of alloying elements such as chromium (Cr), molybdenum (Mo), nitrogen (N) and tungsten (W). These phases have a negative effect not only on mechanical properties such as strength and toughness but also on the corrosion resistance.⁵⁻⁷ Due to the presence of these phases the production of SDSSs is very challenging. Consequently, hot deformation and heat treatment should avoid temperatures between 300 to 500 °C (149 – 260 °F) because of alpha prime formation as well as 600 to 1000 °C (315 - 538 °F) due to intermetallic phases, sigma phase, nitrides and carbides.⁵⁻¹⁰

In solution annealed condition, SDSSs have high mechanical strength with yield and ultimate tensile strength higher than 500 MPa (52 ksi) and 700 MPa (101 ksi), respectively. Their yield strength is twice that of austenitic stainless steels. They show outstanding pitting corrosion resistance in chloride environments and good stress corrosion cracking behaviour. Their corrosion properties are similar to super austenitic stainless steels (5-6 % Mo).⁵ Super duplex stainless steels are used in aggressive environments where high strength is required. Some common applications are umbilicals in oil and gas, chemical and petrochemical industries, desalination plants and urea production.¹¹⁻¹³

The global demand for energy is increasing continuously. Despite the use of renewable energy sources is growing, the use of hydrocarbons will continue for quite some time. The depletion of reservoirs leads to exploration in deep geological formation and harsher environments. Consequently, materials with excellent mechanical and corrosion properties are required. Super duplex stainless steels are well known for these challenging applications. Despite their good combination of properties in typically solution annealed condition, there is a certain need to increase the strength without sacrificing ductility and corrosion resistance of these materials. A thermomechanical process (TMP) can increase the tensile strength of duplex stainless steels. The TMP has been studied especially in flat products where a high cold rolling deformation (> 50 %) is one of the steps necessary to obtain high strength.¹⁴⁻¹⁶ However, there are no reports in the literature regarding TMP of duplex stainless steel bars and its effect on the corrosion properties. The aim of this paper is to study the effect of a thermomechanical processing on the mechanical properties, mainly tensile strength, and pitting corrosion in bars of the UNS S32750 (1.4410). Even though Norsok M 630 does not specify this high strength condition, mechanical and corrosion properties will be compared with it as base line.¹⁷

EXPERIMENTAL PROCEDURE

The material used in this study is UNS S32750 super duplex stainless steel. Its chemical composition is presented in Table 1.

Production / Thermomechanical processing

Figure 1 shows the production route of UNS S32750. Melting was carried in an electric arc furnace followed by continuous casting. The billet was heated to forging temperature and forged, and subsequently cooled in air. After forging, the material was solution annealed at 1080 °C (1976 °F) and water quenched. The solution-annealed material was submitted to thermomechanical process.

Table 1

Nominal chemical composition of the materials in wt. %

C Max.	Si	Mn	Cr	Mo	Ni	N	PREN*
0.03	0.35	0.55	25	3.8	7	0.27	42

* PREN = % Cr + 3.3 % Mo + 16 % N (% by weight)

The optimal TMP-parameters like deformation temperature, holding and quenching time were determined using thermodynamic simulation, i.e. Thermocalc ® * (Version 2021a, Database TCFE11), Forge[†], and laboratory tests. Cold-working should take place at temperatures where no detrimental phases are present. According to the phase diagram in equilibrium state (Figure 2), sigma phase precipitates between 450 (842 °F) and 1030 °C (1922 °F), while alpha prime (α') forms at temperatures lower than 500 °C (932 °F). The Time-Temperature- Transformation diagram (TTT diagram) of UNS S32750 shows the precipitation temperature ranges and precipitation kinetics of sigma phase, chi phase, nitride, alpha prime and other phases.⁸ The precipitation kinetics of these phases is affected by temperature and holding time. The maximum precipitation kinetics for sigma phase is found between 850 (1562 °F) and 900 °C (1652 °F), for alpha prime around 475 °C (887 °F).^{8,18} At temperatures below 700 °C (1292 °F), precipitation kinetics of sigma phase is slow, and the required holding time can be longer than 1 hour to form more than 5 % of sigma phase (Figure 3). In the case of α' , precipitation kinetics is slow at temperature above 475 °C. Thus, TMP was carried out in the temperature range between 500 and 650 °C (1202 °F) using two different degrees of cold-work (denominated “high” (H-CW) and “low” (L-CW), and fast quenching to avoid precipitation of α' . Cooling rate and time necessary to reach temperatures lower than 300 °C (572 °F) were simulated with Forge. Figure 4 shows an example of these simulations for two different quenching media.

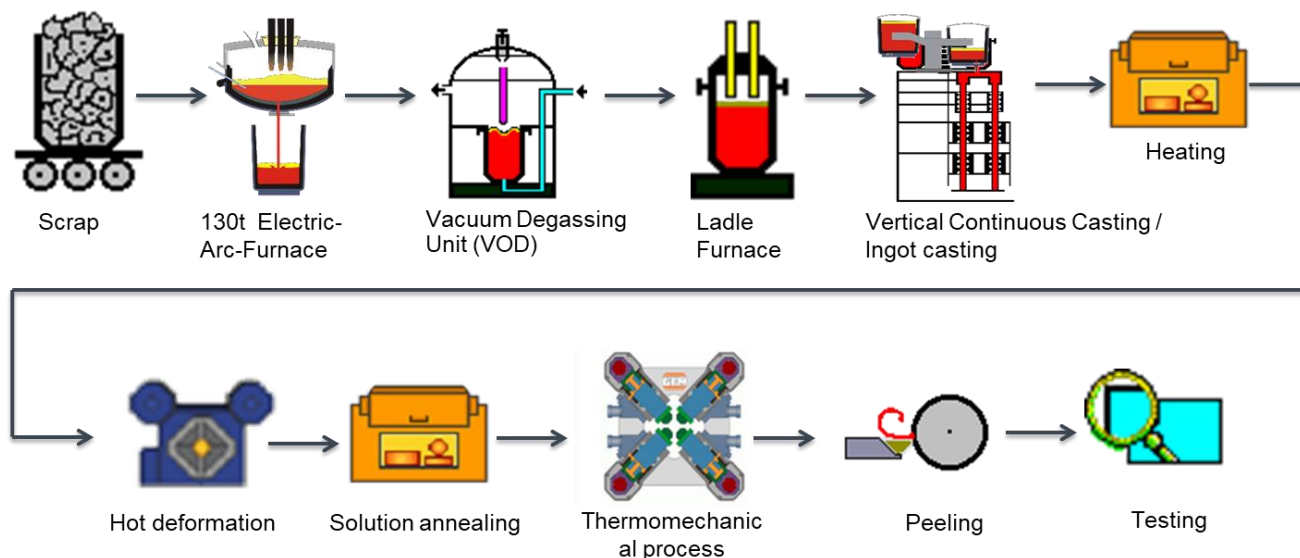


Figure 1: Schematic production of the super duplex stainless steel UNS S32750.

* Trade name

† Trade name

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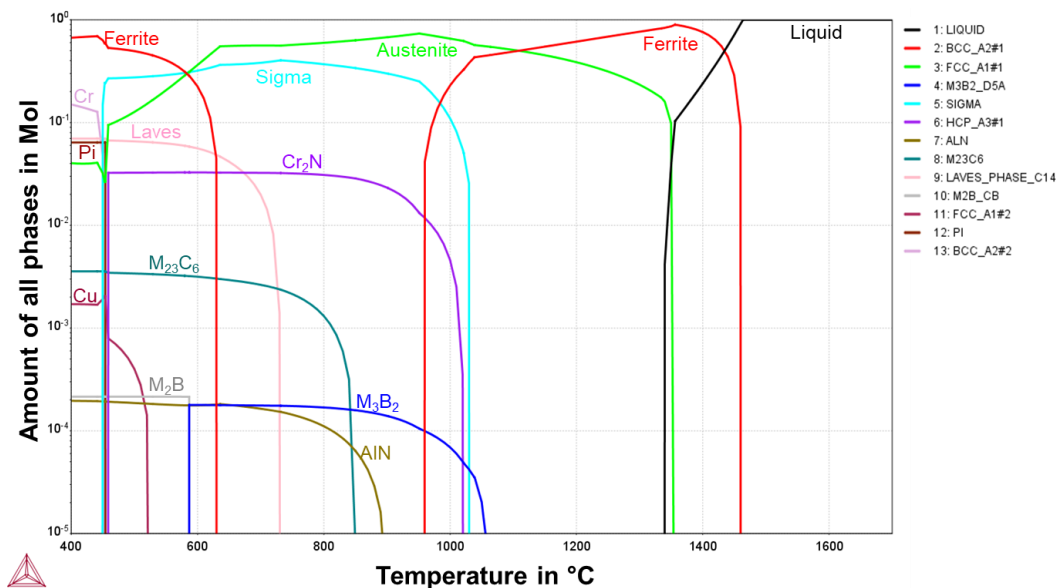
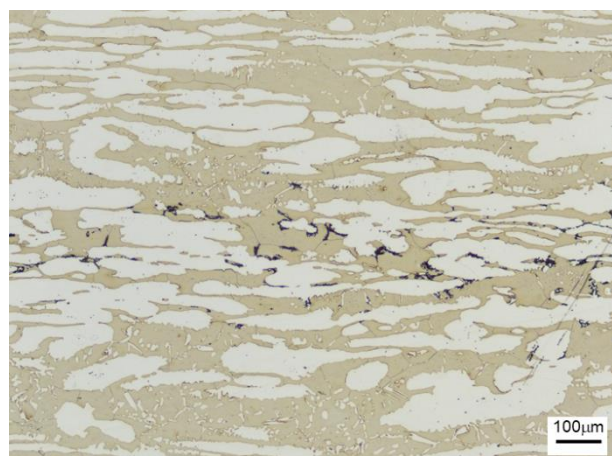
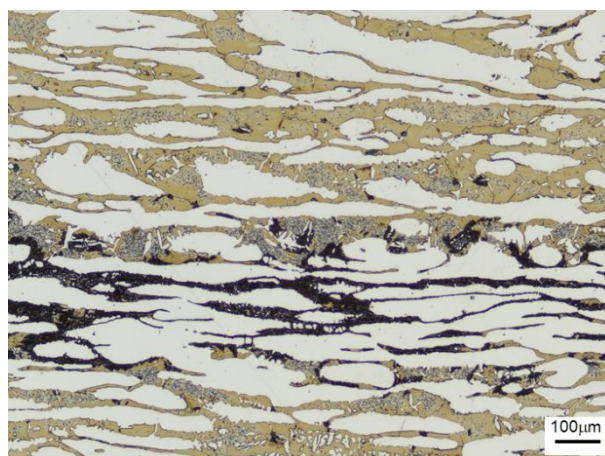


Figure 2: Phase diagram of UNS S32750



(a)



(b)

Figure 3: Microstructure of UNS S32750 after annealing treatment at 700°C for (a) one hour (0.5 % σ -phase) and (b) three hours (5 % σ -phase). (White = Austenite, brown = Ferrite. Etching: Murakami)

Test methods

Mechanical properties were evaluated according to ASTM A370,¹⁹ i.e. tensile and Charpy-V tests as well as hardness. The microstructure was characterized by optical microscopy. All specimens were taken in the center, mid-radius and surface of the rod in longitudinal and transversal direction.

The corrosion behavior of UNS S32750 was studied in annealed condition and after TMP. Samples were cut from the bars at 25.4 mm (1") below the surface. Pitting resistance testing was conducted per ASTM G48 in ferric chloride solution at room temperature (RT) and 50 °C for 24 and 72 hours.²⁰ Critical pitting temperature (CPT) was evaluated according to ASTM G48 Method E.²⁰ Specimens were kept in acidified ferric chloride solution at different temperatures for 24 hours. The starting temperature was estimated by Equation 1 minus 10 °C. It is equal to 55 °C (131 °F). The bath temperature was varied until pitting attack was observed.

$$\text{CPT (}^{\circ}\text{C)} = 2.5\%\text{Cr} + 7.6\%\text{Mo} + 31.9\%\text{N} - 41 \quad (1)$$