Duplex and Superduplex Stainless Steels: microstructure and properties evolution by surface modificaction processes

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Abstract: The paper presents an overview of diffusion surface treatments, especially nitriding processes, applied to duplex and superduplex stainless steels in the last five years. Research has been done mainly to investigate different nitriding processes in order to optimize parameters for the most appropriate procedure with the scope of improving mechanical and wear resistance without prejudice to the corrosion properties of the duplex and superduplex stainless steels. Our investigation pointed also on trying to understand the effect of the nitriding layer on the precipitation of secondary phases after any heating step.

1.   Duplex and Superduplex Stainless steels

Duplex stainless steels (referred to DSS) are stainless steels classified according to their composition and thermomechanical treatment. DSSs are characterized by their microstructure which contains both delta ferrite and austenite phases with approximately equal volume fractions and an unusual combination of mechanical strength, toughness and corrosion resistance [1]. Because of their content of Cr, Mo and N, these steels are particularly resistant to pitting corrosion and can be differentiated in terms of pitting resistance equivalent number (PREN) which is often defined as:

$$PREN = \% \, Cr + 3.3 \, (\%Mo) + 16 \, (\%N) \qquad (1)$$

Typically, DSSs contain 17-30 wt% Cr and 3-13 wt% Ni [2] and according to eq(1) the addition of chromium, molybdenum and nitrogen rises the pitting corrosion resistance. PREN is useful for comparing and ranking the grades of duplex stainless steels but rarely can be useful as a prediction for a suitable application. Duplex stainless steels with a PREN higher than 40 are extremely resistant to pitting corrosion and are designated as super DSS (SDSS) [3].

Due to the promising corrosion properties, the high mechanical strength combined with a good enough toughness, these steels are widely used in chemical tankers, petrochemical

industry as well as marine and nuclear power industries [4]–[6]. However, studies for new alloys with even higher strength than that of the DSSs and SDSSs have increased in the past few years with new demanding applications, especially in the oil-gas industry [7]. For these challenges, new high alloyed duplex stainless steels have been developed, characterized by a PREN close to 50, termed as hyper duplex stainless steels (HDSS) [8], [9].

Regarding applications, one of the main restrictions of duplex stainless steels has been the exposure to elevated temperatures. The unstable ferrite phase at higher temperatures leads to its decomposition and degradation of both mechanical and corrosion properties [3]. In the temperature range 250-500ºC decomposition of ferrite and embrittlement may occur after long term exposure, inducing the decrease in toughness. At higher temperatures various types of precipitates may form at temperature range of 600-900ºC leading also to a reduction in corrosion resistance and/or reduction of toughness as well [5]. A variety of secondary phases, mostly undesirable, may form during isothermal aging or inappropriate heat treatments, essentially due to the instability mentioned before [5]. The following phases have been observed and have been under investigation for long time: σ phase, Cr_2N, CrN, secondary austenite, χ phase, R phase, π phase, M_7C_3, $M_{23}C_6$ and τ phase. A lot of literature can be found about their formation, conditions and properties influencing mostly the mechanical and corrosion resistance of duplex and super duplex stainless steels [5], [10]–[13].

Despite the excellent mechanical strength and corrosion resistance of DSS and SDSS, they have limited applications in industries where high wear resistance together with corrosion resistance are required. Thus, another restriction can be found in the tribological applications. Fortunately, in the past years exponential development in surface engineering has been done and consequently an important improvement in surface hardness and tribological properties is possible even to unusual alloys.

2. Surface modification technologies

Diffusion surface treatments including nitriding, carburizing or nitrocarburizing can be performed under controlled gas atmosphere as well as under plasma conditions [14]–[16]. Nitriding can be applied to unalloyed steels and irons to produce a corrosion and wear-resistant nitride layer. In alloyed steels containing nitride-forming elements (Cr, Mn, Mo, V, W, Al, Ti) a deeper diffusion layer develops. Nitriding techniques are suitable for the enhancement of wear resistance, improving hardness up to 1400 HV. However, due to the high content of chromium, nitride layers tend to be formed as a result of the strong bonding energy between chromium and nitrogen. Thus, chromium nitrides precipitation occurs which decreases the corrosion resistance. The precipitation of the other phases already mentioned is also critical for the corrosion and/or mechanical properties. Nevertheless, a moderate formation of the sigma phase is tolerable and can imply an improvement in the wear resistance. Among the possible solutions to this problem the development of an appropriate coating is critical. The goal is to produce layers of high hardness on the steel to improve tribological performance without degrading the corrosion resistance. Such coating can be achieved by accurate nitriding. Nitriding techniques can differ among others in the nitriding media and process parameters such as temperature, time, composition of the nitriding atmosphere and pressure [17]–[19].

Nitriding processes of austenitic stainless steels (- fcc phase) are the most studied for the enhancement of hardness and wear properties. Thermochemical surface engineering has been investigated as an effective path by alloying the surface with interstitial elements as C and N at elevated temperatures via diffusion. The nitrogen inlet produces a supersaturated austenite phase, which enhances the surface tribology and corrosion resistances. [20],[21]. This phase has been object of extensive investigation. In the 80s and 90s research demonstrated that the surface hardness was improved without loss of corrosion resistance by low temperature nitriding or carburizing [22]–[26], mainly due to the lack of Cr nitrides or carbides precipitation

at temperatures below 500ºC [16]. Ichii et al. [27] studied the evolution of phase transformation that takes place during the process. The XRD pattern of low temperature plasma nitride austenitic stainless steel contained five extra peaks shifted to the lower diffraction angles relative to the corresponding γ peaks. As they were not listed in the ASTM index, Ichii et al. denoted the term S-phase to describe the new phase. The term "expanded austenite" (γ_N) associated to this S-phase was used for the first time by Leyland et al. in 1993 [28]. S-phase or expanded austenite has received wide scientific interest and is considered as one of the most important issues in surface engineering research. During the last decade, several techniques to form S-phase in austenitic stainless steels have been developed. It has been also demonstrated that such phase can be generated in Ni-Cr, Co-Cr and Co-Cr-Mo alloys [29]–[32].
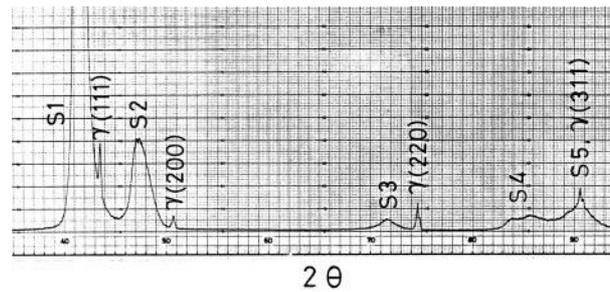

Figure 1. Ichii's original XRD pattern for S-phase [27]

Expanded austenite phase (γ_N) evolved with the understanding of its crystallographic structure. It was described as a duplex layer consisting of a microstructure of fcc γ' [(Fe, Cr, N)$_4$ N][16] and austenite or a compound layer with a structure of the type M_4N [M=(Fe, Cr, Ni,…][27]. It distinguishes from the γ by the high N-content, its concentration in solid solution reaches up to 25-38% in γ_N in comparison to equilibrium solubility of <0.65 at% in austenitic AISI316 [16], [22], [33], [34]. γ_N is also characterized by lattice rotation processes in the expanded fcc structure which cause anisotropic distortions in the normal surface direction [35], [36]. A very interesting microstructural analysis concerning N content and the properties associated to S-phase was carried out by Dahm and Dearnley [37].

On the other hand, the nitrogen diffusion to ferritic α stainless steel (bcc crystal structure) leads to the formation of iron nitrides (ε-Fe$_{2-3}$N, γ'-Fe$_4$N) and nitrides such as CrN [38], [39]. The nitrogen solubility in ferrite structure increases with chromium content but decreases its diffusivity and it is mostly found along the grain boundaries instead of being homogenously distributed interstitially [40], [41]. Hence, the main differences observed between austenite and ferrite structures regarding nitriding process are the result of the thermodynamic conditions during nitrogen diffusion.
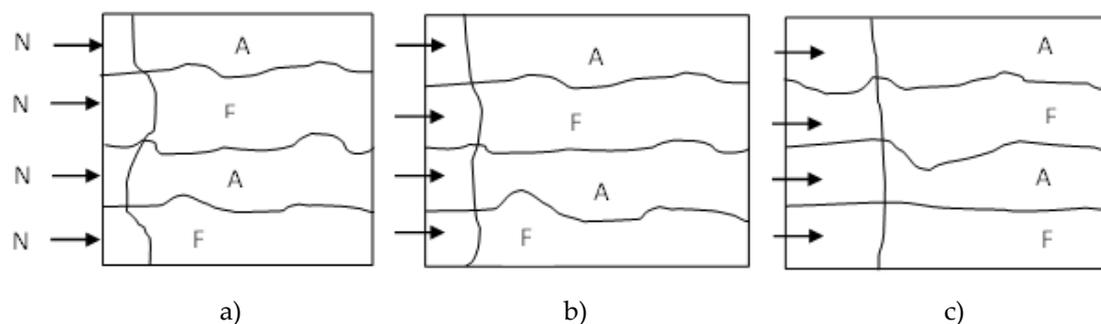
Duplex stainless steel and Super duplex stainless steels contain both austenite and ferrite phases, and eventually it is expected the appearance of, preferentially, expanded phases in austenite grains and nitride precipitates in ferrite grain boundaries [42]. However, it cannot be a general rule as it depends on the processing conditions as well as on the varied compositions in different alloys [21].

In the last five years, some scientific publications have been done with the objective of understanding the morphology, structure and composition of nitride layers in nitrided duplex stainless steels. It has been mainly examined the corrosion response by varying process parameters or trying to combine different methods of nitriding and/or nitrocarburizing with a view of studying the nature of the nitrogen-rich layer. One of the most important variables during the process is the temperature. Thus, low and high nitriding temperature processes can be differentiated among the works. For instance, several authors have demonstrated the formation of expanded austenite in DSS by nitriding at low temperature, assuring good corrosion resistance and improvement in hardness. This is due to the fact that chromium

nitrides formation is avoided at lower temperatures. Paijan et. al. [19] revealed this fact by analyzing DSS samples after nitriding in tubular furnace in the temperature range of 400 to 500ºC holding for 6 hours. Several researchers [19], [43], [44] found that above 500ºC chromium nitride precipitates are formed in the nitrogen enriched layer reducing significantly the corrosion resistance. It was also observed by Blawert et al. [45], and Larisch et al. [46] that after low temperature plasma nitriding of duplex stainless steel, transformation of ferrite into expanded austenite phase after the nitrogen incorporation took place. Bielawski et al. [17] and Chiu et al. [47] reported the generation of expanded ferrite (α_N) and expanded austenite (γ_N) in both ferrite and austenite phases, respectively. Pinedo et al. [42] also have explained the low-temperature plasma nitriding of duplex stainless steels carried out at 400ºC which led to the formation of expanded austenite on the austenite stringers and expanded ferrite on the ferrite stringers of the microstructure. Moreover, some deformation bands were detected inside the expanded ferrite, which were assigned to compressive residual stresses, without chromium or iron nitrides precipitation. On the contrary, in a more recent paper by Tschiptschin et al. [48] it is found that iron nitride (ε-Fe_3N) needles with a particular orientation relationship precipitate coherently inside the expanded ferrite regions of the nitride layer, increasing the hardness considerably. Similar ε-Fe_3N needles were precipitated from nitrogen saturated ferrite grains in a lean duplex stainless steel as determined by Li et. al. [49]. Both reports revealed by TEM that S-phase could not be formed on lean duplex stainless steel by low-temperature plasma nitriding. Tschiptschin et. al. [48] also revealed a duplex thermochemical diffusion treatment consisting of two steps, one gas nitriding conducted at high temperature and a final plasma nitriding at low temperature (HTGN + LTPN). UNS S31803 duplex stainless steel was the alloy selected by these researchers and they found an almost 4 µm thick nitrogen rich expanded austenite layer 1227±78 HV 00.1 formed on top of a high nitrogen austenitic layer of 330 HV hardness. Such experiment ensured a more homogenous microstructure and gentler hardness gradients, with suitable properties for wear bearing applications. Similar duplex thermochemical treatments were previously experimented by Mesa et. al in order to improve the cavitation resistance of the same duplex stainless steel [50].

Plasma nitrocarburizing influences the corrosion behavior in a similar way as plasma nitriding. The formation of larger amount of CrN in the alloy leads to a poor corrosion resistance at temperatures between 450ºC and 500ºC. It was found by Alphonsa et al. [43] that treatments at 350 ºC and 400ºC are beneficial, but 450 ºC and 500ºC treatments are better suited to duplex stainless steels for applications requiring a combination of both high hardness (1010 HV0.01) and corrosion resistance, for which it is observed better corrosion resistance maintaining high hardness values compared to the bare duplex stainless steel.

Concerning the morphology of the layer formed after nitriding some authors reported that the thickness of the layer is a function of the temperature. It was observed that the thickness over the two phases (austenite and ferrite) is different in the case of plasma nitride specimens whereas such a difference was not found in the plasma nitrocarburized samples. However, it was also described that treatments above 500ºC lead to similar thickness over both phases [51]. A schematic representation from Alphonsa et al. work is shown in Fig.2 [43].

a)   b)   c)
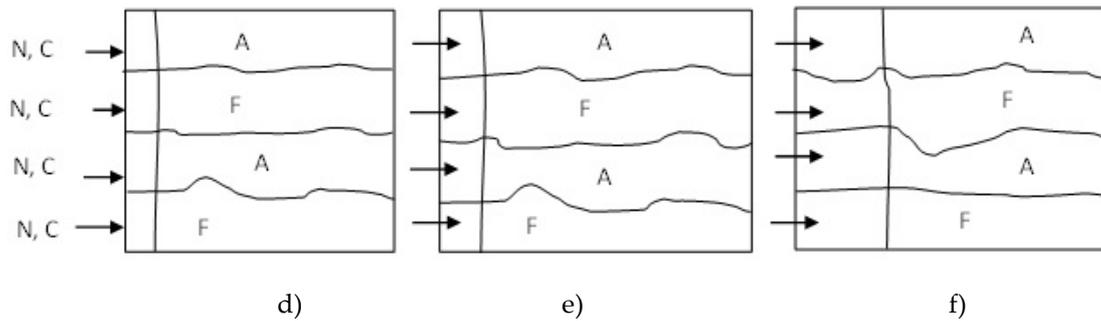
Figure 2. Schematic representation of nitrogen diffusion in austenite and ferrite phases of duplex stainless steel during plasma nitriding at a) 400 °C b) 450 °C and c) 500 °C and nitrogen and carbon during plasma nitrocarburizing at d) 400 °C e) 450 °C and f) 500 °C (Note: A=austenite phase, F= ferrite phase) [43]. The reason for the difference in nitrogen diffusion into the austenite and ferrite phases was discussed by Pinedo et. al. [42] and Bobadilla and Tschiptschin [51]. Diffusion of nitrogen not only occurs in the volume of the substrate but also through the grain boundaries. The lateral flow of nitrogen tends to move from ferrite to the austenite in order to reach the equilibrium.
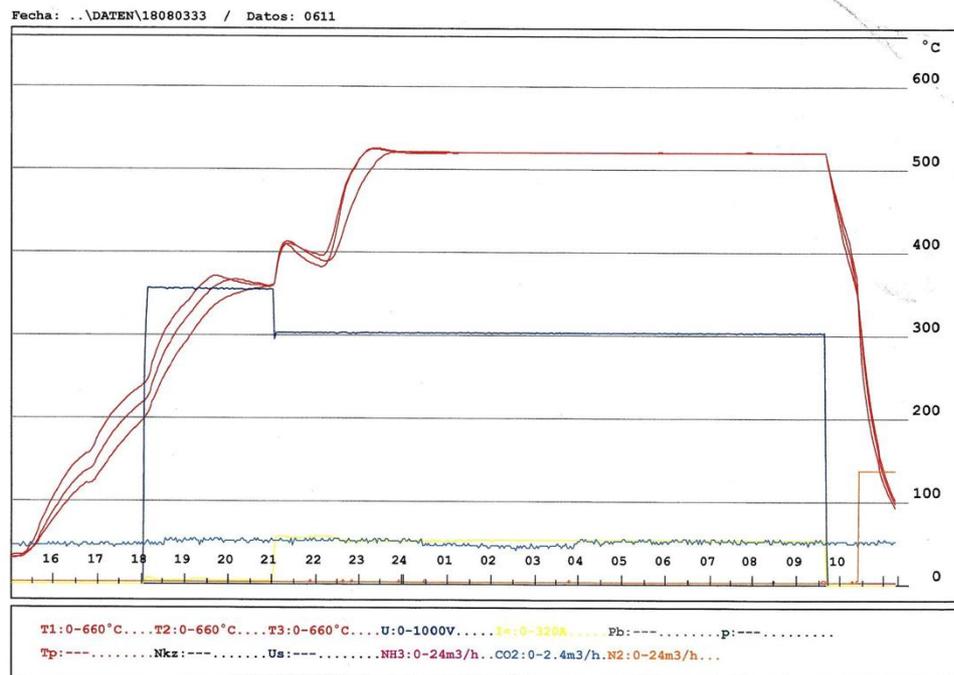
Some authors studied the plasma variables (such as frequency, pulse width and voltage) with the surface modification in order to understand the nitriding plasma based ion implantation [21]. Li et. al. [49] suggested an optimized plasma nitriding process as the best treatment for lean duplex stainless steel for only 10h at 450ºC and at 420ºC for dry-wear and corrosion-wear applications, respectively.

Most of the reported research mainly investigated the surface layer structure, morphology, hardness, corrosion and mechanical resistance as well as tribological and tribocorrosion properties as a function of the type of nitriding processes and mostly under low temperature procedures. Hence, our research aimed to study the plasma nitriding process applied to duplex stainless steel (S32205) and super Duplex stainless steel (S32750) at high temperature, 520ºC, during short time nitriding, (10 hours).

All samples were previously annealed to 1080ºC for 30 minutes and immediately water quenched in order to homogenize the structure before performing the nitriding process. Characterization of the microstructure of the formed layers and their potential to precipitate phases when heat treatment is carried out after nitriding is presented. Table 1 summarises the chemical composition of both DSS and SDSS used and in Fig. 3 is shown the graphic representation of the nitriding process.

Chemical composition wt%										
UNS	C	Si	Mn	P	S	Cr	Ni	Mo	N	Cu
S32205	0.015	0.4	1.5	0.018	0.001	22.49	5.77	3.21	0.184	0.18
S32750	0.018	0.26	0.84	0.019	0.001	25.08	6.880	3.82	0.294	0.17

Table 1. Chemical composition of Duplex and Super Duplex Stainless Steels.

Fecha: ..\DATEN\18080333 / Datos: 0611

T1:0-660°C....T2:0-660°C....T3:0-660°C....U:0-1000V.....I=:0-320A.....Pb:---.........P:---.........

Tp:---.........Nkz:---.......Us:---........NH3:0-24m3/h. .CO2:0-2.4m3/h.N2:0-24m3/h...

Figure 3. Graphic representation of the plasma nitriding process (x-axis is time in h*)*.

Layer morphology of treated samples under the same conditions is shown in fig. 4. The layer structure appears with the outer zone enriched in nitrogen (fig. 4a, c, e). A line scan of some elements diffusion confirmed the nitride layer formation and the excellent continuous interphase within the substrate.

Backscattered electron (BSE) micrographs at higher magnification (fig. 4b, d, f) show the microstructure of samples extracted from a SDSS tube, SDSS plate and DSS plate, respectively. Presence of a brighter phase among the grain boundaries of the expanded austenite and expanded ferrite is detected. Such phase is associated to the sigma precipitate characteristic of duplex stainless steels after thermal treatments in the range of 600 ºC and 850 ºC. This phase was identified through the EDS microanalyses showing a higher content of Mo than that of the ferrite phase. Precipitates of chromium nitrides (black dots) are also present and can be seen in fig 4b as expected after nitriding at a temperature of 520ºC. These chromium nitride precipitates are apparently distributed only in the expanded austenite. Fig. 4c and d show the microstructure of SDSS samples extracted from SDSS plate. Fig. 4d shows the sigma precipitation linking expanded austenite phase within expanded ferrite phase. Chromium nitrides are also noticed inside both phases.

In discordance with the literature, at the temperature of our experimental procedure, nitride layer showed an irregular thickness. The nitriding-substrate interface on austenite and ferrite phases, shown in fig. 4b, is very irregular. It was predicted that for duplex stainless steel a homogenous interphase and almost equal thickness of nitride layer on austenite and ferrite phases of the substrate should be found above 500 ºC [42], however, SDSS does not follow this trend.

On the other hand, any Mo enriched phase was not detected in samples extracted from DSS plate. This is probably due to the chemical composition of the alloy, as DSS has
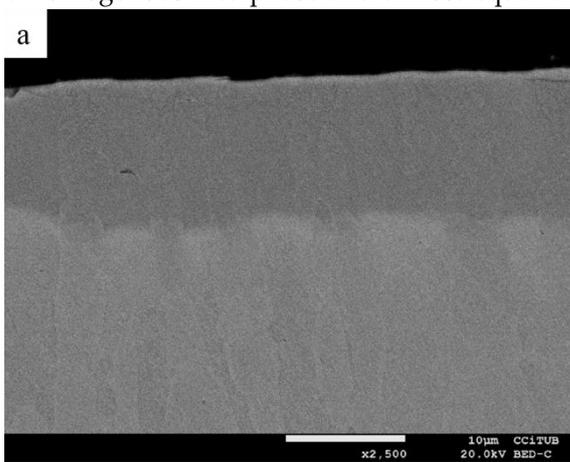
almost 0,5%wt less Mo than SDSS. Instead, DSS nitride layer has more black spots, identified as nitrides. These nitrides are mainly found in the outer part of the nitrided steel layer and help rising the hardness of the nitrided steels (Fig. 4f).

Figure 4. BSE micrographs of SDSS and DSS specimens after 10 h plasma nitriding at 520ºC (a) Cross-section nitride layer on SDSS tube, (b) detail of the nitride layer indicating the austenite (γ) and ferrite (δ) phases as well as sigma phase and chromium nitrides, (c) cross-section of the nitride layer of SDSS plate, (d) higher magnification of the nitride layer in (c) showing expanded austenite γ_N and expanded ferrite δ_N phases, as well as sigma phase in the boundaries, (e) longitudinal section of the nitride layer of DSS plate and (f) higher magnification of the nitride layer
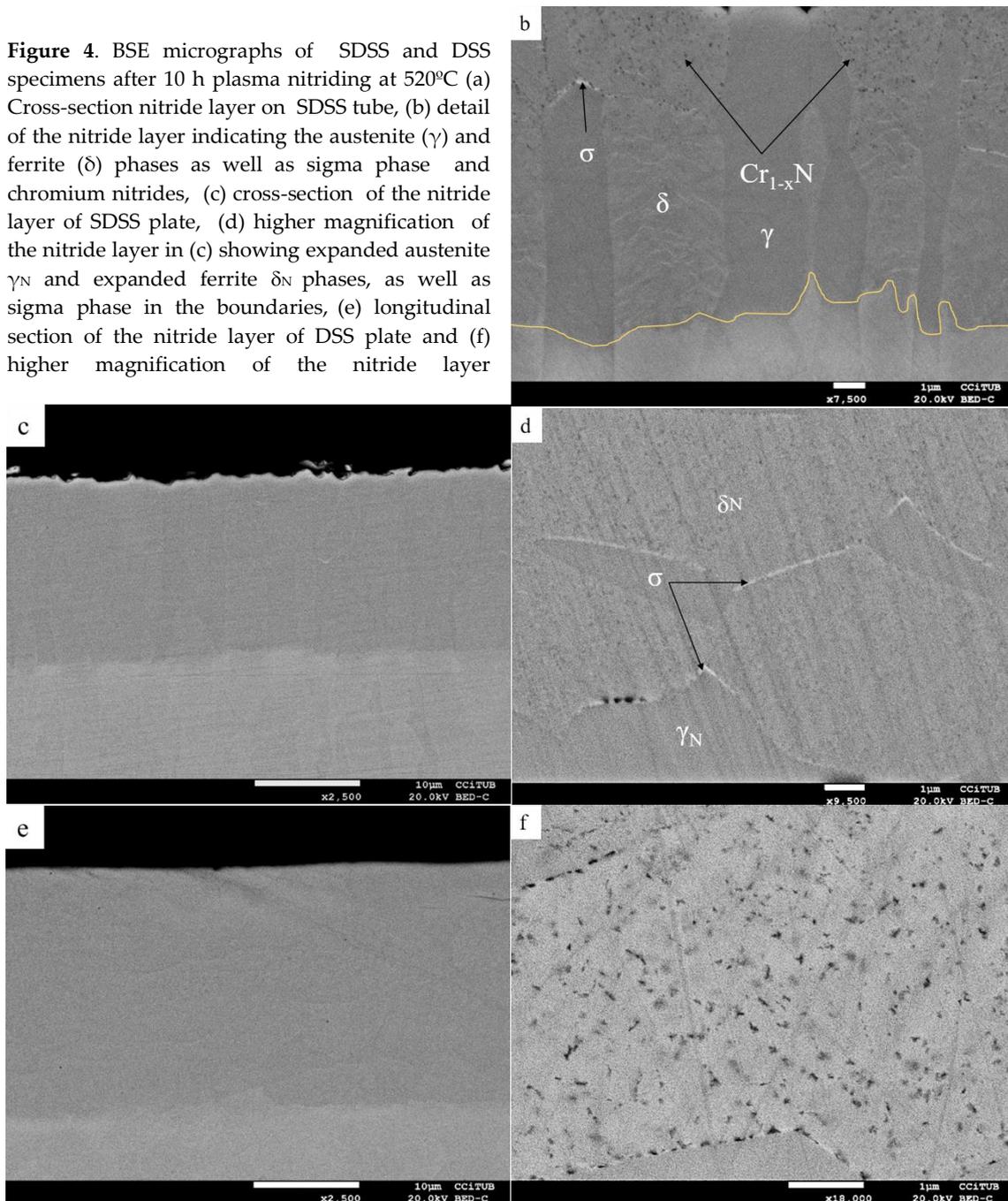
(expanded ferrite δ_N) on DSS plate showing the distribution of chromium nitrides inside.

Hardness of the nitride layer was measured in order to analyze the resistance obtained at higher temperature of plasma nitriding process. Minimum and maximum values of $HV_{0.3}$ and medium thickness with a standard deviation of the nitride layers are summarized in Table 2.

Material	$HV_{0,3}$	Thickness layer
Super Duplex S32750 tube	1263÷1393	13,7 ± 0,0006 µm
Super Duplex S32750 plate	1379÷1402	16,5 ± 0,0004 µm
Duplex S32205 plate	1263÷1329	23,5 ± 0,0003 µm

Table 2. Sample identification, $HV_{0.3}$ hardness (maximum and minimum range values) and medium thickness of the nitride layers.

After the plasma nitriding process, thermal treatment at 830ºC for up to 3 minutes was carried out to the superduplex stainless steels. Such treatment was selected in order to compare the precipitation of secondary phases before and after nitriding and the influence of a large concentration of nitrogen in that precipitation [52], [53] . As observed in the images from backscattered electron microscopy (BSE) cross-section of SDSS plate in Fig. 5a and 5b, precipitates of chromium nitride are identified inside expanded ferrite phase. Sigma phase is also seen in the grain boundaries of ferrite and austenite phases and also inside the ferrite.

SDSS tube sample shows the presence of sigma phase precipitate as well and less detectable the presence of chromium nitrides as can be observed in Fig. 5c and d.
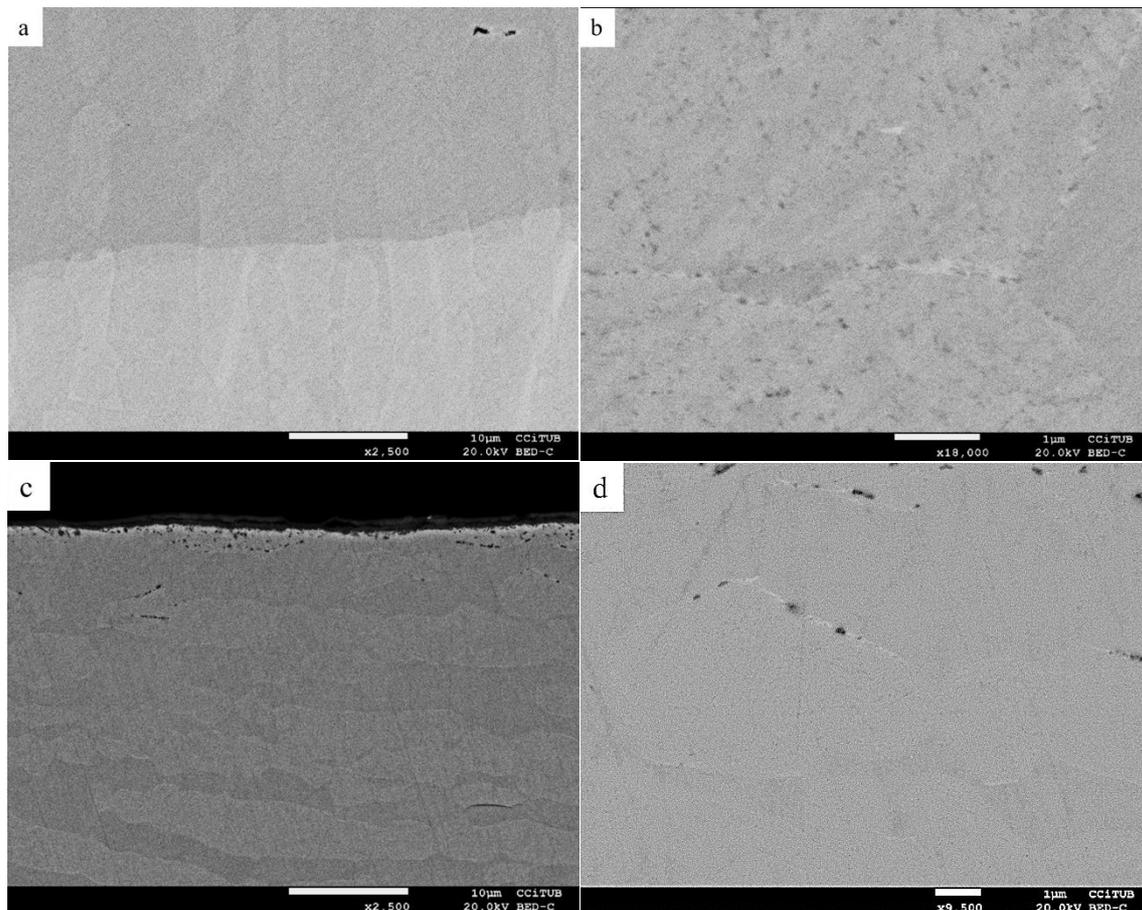
Figure 5. BSE micrographs of SDSS plate and SDSS tube samples after 10 h plasma nitriding at 520ºC and post heat treatment at 830ºC for up to 3 minutes (a) cross-section of SDSS plate sample b) Higher magnification of a), c) longitudinal section of SDSS tube after 10 h d) higher magnification of c).

In light of the results, it can be observed that the thickness of the nitride layer formed at the same processing conditions is mainly influenced by the composition of the stainless steel. For instance, DSS sample showed almost double thickness than SDSS samples. Nevertheless, both SDSS samples present higher hardness values eventually because of the higher amount of chromium nitrides, enhancing the hardness of the outer surface. Due to the higher amount of nitrogen and chromium in SDSS, chromium nitrides are consequently formed in higher amount. Another fact observed is that the microstructure resulting from the forming process is somehow influencing the diffusion through the steel. In this sense, rolled samples were previously annealed at 1080ºC for 30 minutes in order to homogenize them before performing the nitriding process, hence only forming microstructure remained before nitriding. Plate layer thickness is around 20% thicker than tube layer thickness at the same processing conditions.

Secondary phases, mostly sigma phase, were already formed within the nitriding process before any heat treatment applied to the SDSS samples. Such behaviour could not only be due to the temperature, but it can be regarded as high nitrogen ferrite and austenite help to induce its formation even at temperature as low as 520ºC. However, heating the sample after nitriding sigma phase formation is clearly enhanced, the latter occurs mostly in the SDSS tube, as it is detected not only at the phase boundaries (figs. 4b, 4d), but also inside the austenite phase (fig. 5b). Surprisingly, the SDSS plate prepared longitudinally (figs. 5c, 5d) did not showed sigma phase inside the austenite phase. This again confirms the importance of the microstructure facing the nitrogen diffusion: diffusion path involving grain boundaries (favoured by cross-section facing the outer surface) will enhance nitrogen diffusion and consequently the induced formation of secondary phases. On the contrary, longitudinal microstructure will difficult the amount of nitrogen able to diffuse through austenite or ferrite phases.

Conclusions

Surface properties enhancement on duplex stainless steels has been overviewed and supports the idea of an increasing demand on nitriding in order to enhance wear resistance. Plasma nitriding at 520ºC on duplex and superduplex stainless steels (UNS S32205 and S32750, respectively) has been carried out and the characterization of the nitride layer formed has been studied. This layer is dense and well-formed following the microstructure of the steel. One of the main conclusions found is that layer thickness is dependent on the composition of the steel, hence duplex and superduplex stainless steels show different thickness (20% aprox.). Furthermore, nitrogen diffuses more intensively in ferrite enhancing the formation of secondary phase precipitation (mainly sigma-phase) and its distribution along grain boundaries. Another interesting conclusion is that the oriented microstructure of ferrite and austenite from previous forming processes would influence the diffusion path of the nitrogen, plate samples showed thicker nitriding layer than tube ones.

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