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Study of corrosion behavior of a 22% Cr duplex stainless steel: influence of nano-sized chromium nitrides and exposure temperature

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Abstract

Chromium nitrides may precipitate in duplex stainless steels during processing and their influence on the corrosion behavior is of great importance for the steel performance. In this study, the influence of nano-sized quenched-in chromium nitrides on the corrosion behavior of a heat treated 2205 duplex stainless steel was investigated at room temperature and 50 °C (just above critical pitting temperature). The microstructure was characterized by SEM/EDS and AFM analyses, and quenched-in nitrides precipitated in the ferrite phase were identified by TEM-analysis. Volta potential mapping at room temperature suggests lower relative nobility of the ferrite matrix. Electrochemical polarization and *in-situ* AFM measurements in 1 M NaCl solution at room temperature show a passive behavior of the steel despite the presence of the quenched-in nitrides in the ferrite phase, and preferential dissolution of ferrite phase occurred only at transpassive conditions. At 50 °C, selective dissolution of the austenite phase was observed, while the ferrite phase with the quenched-in nitrides remained to be stable. It can be concluded that the finely dispersed quenched-in nitrides do not cause localized corrosion, whereas the exposure temperature has a strong influence on the corrosion behavior of the duplex stainless steel.

Keywords: Duplex stainless steel, quenched-in nitrides, exposure temperature, localized corrosion, AFM

1 Introduction

Duplex stainless steels (DSSs), with austenite (γ) and ferrite (α) phases in almost equal amount, are widely used in marine environment, petrochemical, oil and gas, chemical and desalination industries, because of their greater corrosion and mechanical properties when compared to most of the austenitic stainless steels [1,2]. Products made of DSSs may require welding of different parts and/or exposure to high temperature during the processing of the material. Upon heating the material to high temperature for a sufficient time, undesirable secondary phases will precipitate in different areas and different amounts, with the risk of being detrimental for the mechanical and corrosion properties of the material. In order to minimize their nucleation and growth, particular procedures must be followed, i.e. by selecting the optimal welding temperature and by ensuring a fast cooling process after the heat treatment. However, even in this case the precipitation of secondary phases may occur [2]. The most common secondary phases in duplex stainless steels are the intermetallic sigma phase (σ), chromium nitrides (Cr_2N), chi phase (χ), carbides (M_{23}C_6) and secondary austenite (γ_2). Thermodynamic calculations by using Thermo-Calc software [3] are commonly used to predict the fraction of equilibrium phases obtained during heat treatment, e.g., annealing. However, short annealing times don't allow the steels to reach the thermodynamic equilibrium, and in this case secondary phases may precipitate in different ways and at different locations [4]. This should be kept in mind when comparing the thermodynamic calculation and the experimental results.

The chromium nitrides formed in DSSs are mostly present in the form of Cr_2N . Two types of Cr_2N have been observed after welding procedures and heat treatments: quenched-in Cr_2N particles that are finely dispersed in the ferrite phase, and isothermal Cr_2N particles that precipitate along phase and/or grain boundaries [5-9]. Quenched-in Cr_2N particles are formed during the cooling process from high annealing temperature. At properly chosen annealing temperature ferrite and austenite are the only stable phases, so the material should be free from chromium nitrides. However, during the water quench process the temperature drops at a very high rate, passing through the equilibrium temperature for the formation of chromium nitrides. Due to the fast cooling process the solubility of N in

ferrite decreases greatly. At this point the N present in the ferrite phase doesn't have enough time to diffuse towards the austenite phase, which has higher solubility of N, and consequently small quenched-in Cr_2N particles are formed and finely dispersed in the ferrite phase. On the other hand, at lower annealing temperatures, chromium nitrides become thermodynamically stable and N diffusion from the ferrite towards the austenite phase leads to the formation of isothermal Cr_2N particles, which precipitate along phase and/or grain boundaries. In this case the time at the annealing temperature has a crucial influence on the amount and the size of the precipitated isothermal Cr_2N particles.

The presence of chromium nitrides in DSSs is often observed in practice [5,10-12], especially for highly alloyed DSSs because of higher N and Cr contents. In some cases, nitrides may be detrimental for the corrosion resistance of the material when exposed to aggressive environments. However, the risk for the nitride particles to cause initiation of localized corrosion depends on their amount, size and distribution, as well as their location and their surrounding region. The corrosion behavior of the material also depends on the exposure environment and temperature, and the research focus on chloride containing solution is natural due to its presence in many of the media (e.g., sea water) in which duplex stainless steels are used [13]. The achievement of a deep understanding of the influence of chromium nitrides on the corrosion behavior of the material is of great importance, not only from a fundamental prospective but also for industrial applications of the DSSs. In an attempt to reach such understanding, we have prepared the DSS samples with chromium nitride particles through heat treatments, characterized the nitrides in detail, and then performed in-situ local probing studies of the dissolution behavior of the samples in a NaCl solution under electrochemical potential control. To investigate the effect of exposure temperature, the corrosion experiments were also performed at 50 °C, temperature just above the critical pitting temperature (CPT), and the corrosion attack was examined by post-analysis. In this communication, we report the study of the corrosion behavior of a heat treated 2205 grade of DSS in a NaCl solution at different exposure temperatures, aiming at clarifying the effect of nano-sized quenched-in chromium nitride particles. The phases and the precipitated chromium

nitrides were characterized by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) combined with selected area electron diffraction (SAED). An evaluation of corrosion tendency of the phases and precipitated particles in the tested material was done at room temperature by using atomic force microscopy-based Kelvin force microscopy (AFM/KFM), to examine the relative nobility difference between the ferrite, austenite and precipitated nitrides. In order to study the corrosion behavior of the heat treated 2205 DSS, potentiodynamic polarization measurements of the samples were carried out in 1 M NaCl at room temperature (T_{room}) and 50 °C. *In-situ* electrochemical atomic force microscopy (EC-AFM) measurements of the samples were performed in 1 M NaCl solution at T_{room} to examine whether or not the chromium nitride particles lead to localized corrosion initiation for the heat treated 2205 DSS. Furthermore, in order to verify the selectively dissolved phase at temperature just above the CPT, magnetic force microscopy (MFM) was used in combination with SEM/EDS for post-polarization analysis.

2 Experimental

2.1 Material and sample preparation

Samples of a Sandvik SAF 2205 duplex stainless steel (UNS S32205) in dimension of 20×20×2 mm were supplied by AB Sandvik Materials Technology, Sweden. The main elemental composition of this DSS is shown in Table I.

Table I. Chemical composition of the tested material (wt %).								
C	Si	Mn	Cu	Cr	Ni	Mo	N	Fe
<0.030	0.61	0.76	0.17	22.2	5.22	3.13	0.19	Bal.

The samples were subjected to an experimental heat treatment where the material was first annealed at 1250 °C (1 minute), followed by air cooling down to 950 °C at which it was water quenched. This heat treated material will, from now on, be called 2205 HT. The quenching temperature of 950 °C

was selected after the thermodynamic calculation (Figure 1) by means of Thermo-Calc [3] and TCFE6 database. The diagram in Figure 1 was obtained by the calculation using the exact composition of this batch of the material. At this temperature the expected equilibrium phases are shown to be ferrite, austenite and a small fraction of chromium nitrides.

Figure 1. Thermodynamic calculation of equilibrium phase fractions for the tested SAF 2205 as a function of temperature.

For general microstructure characterization by SEM, the 2205 HT sample was first embedded in bakelite, wet ground with SiC paper up to 1200 grit, polished with diamond paste successively up to 0.25 μm , and followed by final polishing with 0.04 μm silica suspension. The sample was then gently etched in diluted aqua regia (15 mL HCl, 5 mL HNO₃, 100 mL H₂O) at 40 °C. Note that this gentle etching was done only for the sample used for this preliminary SEM characterization.

Prior to the potentiodynamic polarization, the 2205 HT samples were wet ground with SiC paper up to 1200 grit, and then polished using diamond paste successively up to 0.25 μm . The samples used for the KFM measurements were also polished up to 0.25 μm in order to have a smooth surface and minimize the influence of roughness on the Volta potential signal. For the in-situ EC-AFM measurements, the small 2205 HT sample was cut from a received material and mounted on a brass disc by conductive

glue. It was then fixed in a plastic mold by epoxy, leaving an exposed area of 0.2 cm². Also in this case the sample was polished up to 0.25 µm with diamond paste. All the samples, including those used for post-polarization analysis, were ultrasonically cleaned in ethanol and dried in a N₂ gas stream prior to the experiments.

2.2 Solution

The solution containing 1 M NaCl was prepared from analytical grade NaCl and ultrapure water (Milli-Q, 18 MΩ cm).

2.3 SEM analysis

The SEM instrument used was a ZEISS Ultra 55 FE-SEM (FE-SEM). The secondary electron SEM mode imaging was performed on the gently etched 2205 HT sample to find areas with precipitated Cr₂N. The back scattering SEM mode was used for post-polarization analysis of the corroded surfaces.

2.4 TEM/EDS analysis and SAED phase identification

Thin foils for the TEM analysis were prepared by using focus ion beam/scanning electron microscopy (FIB-SEM, FEI Quanta 3D FEG). The area of interest, containing ferrite and austenite, was selected from a 2205 HT sample. The selected area was coated with a thin platinum layer in order to protect the surface from damage due to the ion beam cutting. Gallium ions were bombarded onto the edge of the selected area to cut and then lift the foil out. A JEOL JEM-2100F analytical TEM equipped with an EDS detector and electron diffraction operating at 200 kV was used for the identification of nano-sized quenched-in chromium nitrides in the 2205 HT sample.

2.5 KFM measurements

The Volta potential mapping of the polished sample surface was performed by using an Agilent 5500 scanning probe microscope equipped with a MAC III unit, having three lock-in amplifiers enabling multi frequency measurements. The topography and the Volta potential signals were recorded simultaneously using a single-pass mode to achieve a high lateral resolution. The topography signal was measured at the resonance frequency

of the cantilever (ca. 75 kHz), while the Volta potential signal at a much lower frequency (ca. 10 kHz) in order to avoid cross-talking disturbances between the two signals. The instrumental details have been described elsewhere [14,15]. The probes used for the KFM were Nanoprobes SPM probes of SCM-PIT type purchased from Bruker, with the length of 200-250 μm , a resonance frequency of 60-100 kHz, a spring constant of 1-5 N/m and with a conducting coating (Pt-Ir) necessary for the electrical measurement.

2.6 Electrochemical instrument and experiments

Potentiodynamic polarization measurements were performed to investigate passivity and eventual breakdown of the 2205 HT samples, in 1 M NaCl solution at room temperature (T_{room} , ca. 20 °C) and 50 °C. The temperature of 50 °C is slightly above the critical pitting temperature (CPT = 46 °C, value obtained for this special 2205 DSS) of this type of material, and it was selected in order to investigate the details of the corrosion behavior of the material at temperatures above CPT.

A Solartron 1287 electrochemical interface was used for the potentiodynamic polarization measurements. An Avesta Cell purchased from Bank Elektronik was used for the measurements, with the sample as working electrode, a saturated Ag/AgCl as reference electrode (197 mV vs. SHE) and a Pt mesh as counter electrode. The Avesta cell is designed to avoid crevice corrosion at the edge of the exposed area due to the sample mounting onto the cell, through an extremely low rate flow of distilled water around the border of the exposed area. The Avesta cell is equipped with a heating jacket connected to an external thermostat that can control the temperature of the solution in the cell. The solution was added in the amount of ca. 300 mL and the exposed sample area was 1 cm^2 . N_2 gas was continuously blown in the solution in order to reduce the oxygen content. The potentiodynamic measurements were initiated when the temperature had reached the set value. The potential was swept upwards from -0.2 V vs. open circuit potential (OCP), with a scan rate of 10 mV/min, up to 1.2 $V_{\text{Ag/AgCl}}$ for the measurements at T_{room} , whereas the measurements performed at 50 °C were stopped when the potential had reached 0 $V_{\text{Ag/AgCl}}$, due to a great increase of the recorded current.

2.7 In situ EC-AFM measurements

The measurements were performed at T_{room} by using an Agilent 5500 scanning probe microscope equipped with a MAC III unit and a built-in potentiostat, and an exclusively designed three-electrode cell. The working electrode (the sample) was fixed onto the bottom of the cell; a platinum sheet was used as counter electrode and a saturated Ag/AgCl electrode as reference electrode. The solution was added in a volume of 5 mL in order to cover the sample surface by a solution layer of ca. 3 mm in thickness. The probes used for the contact mode AFM operation were ContAl-G silicon probes, purchased from Budget Sensors, with a resonance frequency of 13 kHz and a spring constant of 0.2 N/m. The topographic changes of the sample immersed in 1 M NaCl solution were monitored at increased applied potentials. High resolution images were recorded by using 1054 points/line with a scan rate of 0.8 Hz, where the acquisition time of each image was ca. 40 min. The potential of the sample was controlled by the potentiostat and all the values referred to the reference electrode. The topography images of the sample were acquired at preselected potential values, starting from the OCP, stepwise increased through the passive range and at several potentials in the transpassive region. At the high anodic potentials, the AFM imaging was repeated at least two times at each applied potential in order to monitor the topography changes caused by the electrochemical polarization. Since it was not possible to control the temperature of the solution in the AFM system, the in-situ AFM measurements were only performed at T_{room} .

2.8 MFM post-polarization analysis

MFM measurements were performed for post-polarization analysis of the 2205 HT samples in order to record the magnetic domain images, which enable unambiguous verification of the phase suffering selective corrosion at temperature above the CPT. A Dimension 3100 AFM from Veeco was used for the MFM imaging, and the probes of MESP type used were purchased from Bruker, with a CoCr coating necessary for the magnetic imaging, a resonance frequency between 60-100 kHz and a spring constant between 1-5 N/m. The images were recorded by using 512 points/line with a scan rate of 0.5 Hz. A dual-scan lift mode was used to obtain concurrent topography and the magnetic images of the scanned area. The topography data was recorded

during the first line scan, while the magnetic signal was recorded in the second pass where the tip was lift up 50 nm from the surface in order to avoid signal cross-talking disturbances. The magnetic properties of the material were mapped in the phase image with a scale unit expressed in degree (deg).

3 Results

3.1 Characterization of the phases and precipitated chromium nitrides

3.1.1 FE-SEM characterization

The 2205 HT sample was characterized by secondary electron FE-SEM after gentle etching of the surface. The ferrite and austenite phases could be distinguished from the contrast in the backscattering mode SEM images. However, because of limitation of the lateral resolution of the technique, it was not possible to detect finely dispersed small quenched-in nitrides by the SEM/EDS analysis. Even after the gentle etching, only some isothermal nitrides (a few hundreds of nm in size or smaller) could be detected either along the ferrite/austenite boundaries or at the ferrite/ferrite boundaries, as shown in Figure 2.

Figure 2. Secondary electron SEM micrograph of isothermal nitrides along the α/α boundary of the 2205 HT sample after gentle etching with diluted aqua regia.

To detect and unambiguously identify the very small quenched-in nitrides precipitated in the 2205HT sample, further efforts were made to perform TEM and electron diffraction analyses as described in the experimental part.

3.1.2 TEM/EDS analysis and SAED phase identification

Phase identification by TEM and SAED was performed on the selected parts of the 2205 HT sample. Examples of the TEM micrographs of the ferrite with very small chromium nitride particles, and austenite phases are shown in Figures 3a and 3b, respectively, while the SAED patterns shown in Figures 3c and 3d unambiguously identify the ferrite and the austenite phases (diffraction patterns taken from the areas shown in Figure 3a and 3b).

Figure 3. (a) TEM micrograph (bright field) of an area in the ferrite phase, with large number very fine (tens of nm in size) $\beta\text{-Cr}_2\text{N}$ precipitated with dense dislocation nets along $\{110\}$ atomic planes. (b) TEM micrograph (bright field) of an austenite phase area. No secondary phases were found in the austenite, whereas typical twin boundaries were observed. (c) Composed SAED pattern from the zone axis of $\langle 001 \rangle_\alpha$ which reveals the crystalline nature of the ferrite phase, where the quenched-in nitrides were found. (d) Composed SAED pattern from the area shown in Fig. 3b which reveals the crystalline nature of the austenite phase with twin boundaries free from secondary phase precipitates.

The “cloud” in Figure 3a consists of dislocation nets and a large number of very fine β -Cr₂N particles, several tens of nm in size. The SAED analysis of the β -Cr₂N nature of the precipitated chromium nitrides was performed in a previous study and reported elsewhere [16]. The electron diffraction pattern in Figure 3c proves that the grain with the Cr₂N particles is the ferrite phase. These results show clearly that large number nano-sized quenched-in Cr₂N particles were finely dispersed in the ferrite phase (Figure 3a), whereas no secondary phase precipitation was observed in the austenite phase. Instead, twin boundaries, typical of the austenitic phase, could be observed (Figure 3b). The SAED patterns reveal the crystalline nature of the analyzed ferrite and austenite phases (Figures 3c and 3d), and confirm the precipitation of quenched-in Cr₂N particles exclusively in the ferrite phase due to the heat treatment of this DSS.

Moreover, in order to obtain a more precise elemental composition and evaluate the partitioning between the ferrite and austenite, TEM/EDS point analysis was carried out at different randomly chosen locations of the 2205 HT sample. Cr and Mo are ferrite formers, having higher solubility in the ferrite phase, while Ni and N are austenite formers and enriched in the austenitic phase. Table II shows the average composition of at least 4 points for each phase. In this case, the N content was not analyzed by TEM/EDS due to limitations in the quantitative analysis. In Table II, the N content is given as 0 wt.% in the ferrite matrix, assuming that all the N in the ferrite phase has precipitated as Cr₂N particles. Whereas the N content in the austenite phase is assumed to be higher than 0.19 wt.% (nominal composition of the duplex steel) but lower than 0.38 wt.% (situation when all N is present in austenite).

Table II. Chemical composition (wt%) of γ and α , by TEM/EDS point analysis.

	Fe	Cr	Ni	Mo	Mn	Si	N
γ	68.3±0.9	21.5±0.2	5.8±0.3	2.8±0.4	0.8±0.1	0.7±0.2	0.19-0.38
α	65.4±0.5	24.6±0.6	3.6±0.1	4.9±0.4	0.7±0.2	0.8±0.1	0

Note: N content is given based on considerations on the heat treatment history of the material (section 3.1.2)

3.1.3 KFM characterization

Since the Volta potential is regarded as a measure of relative nobility, the Volta potential mapping has been increasingly used in corrosion research to evaluate variations in the Volta potential related to microstructure features in multi-element alloys, and provides useful information regarding preferential sites for corrosion, although the physical interpretation of the data is not straightforward. Figures 4a and 4b give examples of Volta potential maps for the 2205 HT sample obtained in air at T_{room} .

Figure 4. Volta potential maps of the 2205 HT sample with (a) ferrite and austenite, and (b) ferrite matrix with finely dispersed and clusters of quenched-in Cr_2N .

In general, Figure 4a shows the different tendency to corrosion of the ferrite and austenite, with ferrite expected to be more prone to corrosion (darker in Figure 4a) compared to austenite (brighter in Figure 4a). This is in agreement with previous studies where a higher susceptibility to dissolution of ferrite has been observed [8,17,18]. Moreover, a high resolution image in Figure 4b shows the Volta potential variation within a ferrite grain, with finely dispersed quenched-in Cr_2N exhibiting higher Volta potential (nobler) than the ferrite matrix. The higher Volta potential sites appear to have the size in the range from a few hundreds of nm to a few μm . Most likely they are related to single particles (nm size) or aggregated clusters (μm size) of the quenched-in nitrides, as revealed by the TEM/SAED analysis. Because of

the measure of a potential, the Volta potential mapping has the limitation to distinguish very small nano-sized particles as reported previously [9], so clusters of quenched-in nitrides may appear as μm -sized particles in the Volta potential map. This should be kept in mind when considering the size of very small nitrides. A higher Volta potential of the nitrides suggest that they are nobler than the ferrite matrix. As can be seen from the z-scale of the images, the Volta potential difference between the ferrite and austenite phases is relatively large, while the variations within the ferrite phase (with quenched-in nitrides) are relatively small.

3.2 *Electrochemical polarization and AFM measurements*

3.2.1 *Potentiodynamic polarization measurements*

Figure 5 shows typical polarization curves obtained for the 2205 HT sample in 1 M NaCl at T_{room} and 50 °C. At T_{room} , the sample exhibits high corrosion resistance, with a wide passive range and a passive current density below or around the order of 10^{-6} A/cm², in which a protective passive film is formed on the sample surface reducing the dissolution rate and protecting the material from corrosion attack. At anodic potentials higher than 1.2 V_{Ag/AgCl}, the current starts to increase due to transpassive dissolution of the steel, and probably water oxidation reaction [19]. This result indicates a passive behavior and high corrosion resistance of the 2205HT in 1 M NaCl solution despite the presence of finely dispersed quenched-in Cr₂N particles in the ferrite phase. The quenched-in nitrides in this DSS do not cause localized corrosion initiation in this solution at room temperature. Usually, precipitation of large chromium nitrides consumes Cr and N, key alloying elements for the corrosion resistance, which may lead to Cr and N depleted zones in the surrounding areas with the risk of becoming potential sites for localized corrosion initiation. In this case, however, the quenched-in Cr₂N particles are very small and formed without sufficient time for elemental diffusion, so these finely dispersed nitride particles may not cause significant local elemental depletion that might lead to breakdown of passivity and onset of local corrosion.

In contrast, at 50 °C, temperature slightly above the CPT, the current density increases sharply upon anodic polarization to a high level, i.e., the 2205 HT sample does not exhibit any passive range. In this case, no crevice

corrosion attack was observed on the surface after polarization at 50 °C, while selective dissolution was observed in the centre of the exposed area. The results indicate a strong influence of exposure temperature on the corrosion behavior of the DSS.

In order to gain a detailed knowledge on the initiation sites of the corrosion process and the influence of the microstructure, especially the quenched-in nitrides, *in-situ* EC-AFM measurements have been performed for the 2205 HT sample in 1 M NaCl at T_{room} , at different anodic potentials. Since it is not possible to perform such measurements at 50 °C with the AFM instrument, the surface of the sample polarized at this temperature was analyzed by SEM and MFM after the potentiodynamic polarization measurements.

Figure 5. Typical potentiodynamic polarization curves of the 2205 HT sample in 1 M NaCl solution, obtained at T_{room} and 50 °C.

3.2.2 *In-situ* EC-AFM

Figure 6 shows an example of the topography changes due to the increasing of the anodic potential applied to the sample. As seen in the polarization curve, the 2205 HT sample exhibits high corrosion resistance in 1 M NaCl

solution up to $1.2 V_{\text{Ag/AgCl}}$, above which a sharp increase in the current was observed. During the in-situ EC-AFM measurements, in order to detect topography changes and identify the starting site for transpassive dissolution, a surface area of $70 \mu\text{m}$ in size was repeatedly scanned at constant potential, while the potential was successively increased from the OCP, through the passive range, up to the transpassive region ($1.2 V_{\text{Ag/AgCl}}$). The scanned area was randomly chosen from the mirror-like freshly polished surface (note that the surface was not etched), and this large scan area was chosen to ensure the presence of both ferrite and austenite phases. At the OCP, the AFM topography image of the 2205 HT (Figure 6a) immersed in 1M NaCl solution shows a very stable surface. No change of the surface was detected after 1 hour exposure, and the fine polishing lines are visible in the topography image. In fact, during repeated scans upon anodic polarization at stepwise increased potential in the whole passive range and up to the potential of $1.1 V_{\text{Ag/AgCl}}$ (Figure 6b), no visible changes could be seen in the topography images. The polishing lines remained the same as in the starting conditions, and the surface remained very smooth as judged from the z-scale of the images. Even at a high resolution (smaller scan area), no sign of localized corrosion related to the quenched-in nitrides could be detected in the in-situ AFM experiments. These observations are consistent with the potentiodynamic polarization curves, which show a stable passive behavior for the 2205 HT sample in 1 M NaCl at T_{room} up to very high anodic potential.

At potential of $1.2 V_{\text{Ag/AgCl}}$, transpassive dissolution occurred and selective dissolution enabled the appearance of the duplex structure (Figure 6c), allowing the identification of the two major phases in the scanned area. It was easily verified by SEM and MFM that, at this high potential, the ferrite phase started to dissolve due to transpassive dissolution. Figure 6d shows the depth line profile from the image obtained after the polarization at $1.2 V_{\text{Ag/AgCl}}$, presenting a depth of ca. 200 nm between dissolved ferrite phase and the remaining austenite phase. Notable is the appearance of small particle-like features remained in the dissolved ferrite phase (Figures 6c and 6d). These small particles finely dispersed in the ferrite phase are most likely the quenched-in nitride particles or clusters found by the TEM analysis. The chromium nitrides, exhibiting higher relative nobility than the ferrite

matrix, are very resistant to dissolution and tend to remain in the matrix even under severe conditions.

Figure 6. In situ EC-AFM images of the same area of the 2205 HT in 1 M NaCl at T_{room} under electrochemical control at different applied potentials: (a) OCP, (b) 1.1 V_{Ag/AgCl}, (c) 1.2 V_{Ag/AgCl}, (d) depth line profile from the arrow in image (c) showing particles or particle clusters remained in the dissolved ferrite area.

3.3 Post-polarization SEM and MFM analyses

3.3.1 SEM post-polarization analysis

The corroded surfaces of the 2205 HT samples after the polarization up to 0 V_{Ag/AgCl} in 1 M NaCl solution at 50 °C were analyzed using backscattering

SEM/EDS and MFM imaging. Figures 7a and 7b display examples of the SEM micrographs of the corroded area, showing typical duplex structure of the elongated austenite and ferrite phases. It can be seen that, at temperature above the CPT, the corrosion attack exclusively occurred at one phase (black areas) with sharp edges. It is interesting to note that, for the corroding phase, different grains seem to have different susceptibilities to dissolution. In fact, sharp edges between corroded (dark areas) and uncorroded areas (bright areas) are found along the same phase. This could be due to different crystallographic orientations of adjacent grains of the same phase, which was reported to have a large influence on the susceptibility to corrosion attack in other studies [20,21]. Another reason could be a slightly different composition of the grains, which might have lead to preferential corrosion of the grain with lower amount of alloying elements.

Figure 7. (a, b) Backscattering SEM micrograph of the corroded area of the 2205 HT sample after potentiodynamic polarization up to $0 V_{Ag/AgCl}$ in 1 M NaCl solution at 50 °C. The EDS point analysis was performed in the marked phases (A, B) in (b).

In order to identify the phase that suffered preferential dissolution, SEM/EDS point analysis was carried out for the sample after polarization in 1 M NaCl at 50 °C up to $0 V_{Ag/AgCl}$. For the EDS point analysis, at least three points were taken in the two phases marked A and B in Figure 7b. The results obtained by the EDS point analysis (Table III) suggest phase A as austenite, with higher content of Ni and lower contents of Cr and Mo, and phase B as ferrite, with higher contents of Cr and Mo and lower content of

Ni. Based on the SEM images (Figure 7b), it appears that part of the austenite phase had been selectively dissolved (the dark corroded area is the continuation of phase A, identified as austenite by SEM/EDS), leaving the ferrite phase un-corroded. Thus, the SEM/EDS analysis suggests that some grains of the austenite phase preferentially dissolve during exposure in 1 M NaCl at temperature above CPT.

Table III. SEM/EDS point analysis (wt%)

	Fe	Cr	Ni	Mo
A	67.8	22.7	6.4	3.0
B	66.5	24.3	4.5	4.8

However, caution must be taken when considering the elemental composition obtained by SEM/EDS point analysis. The emission of the characteristic x-rays occurs in a “pear” shaped volume with a size of a few μm , which implies that the spatial resolution of the analysis is of the order of the μm , insufficient for the analysis of small particles or thin films [22]. Even for large grains, a different phase may lie underneath the surface and contribute to the quantitative data, leading to uncertainties and even misinterpretation of the results. Therefore, MFM was also used to unambiguously identify the phase suffering preferential dissolution at temperature above the CPT for the 2205 HT sample.

3.3.2 MFM post-polarization analysis

Figure 8a shows a light optical micrograph of a selectively corroded area after polarization of the 2205 HT sample up to 0 V_{Ag/AgCl} in 1 M NaCl at 50 °C. Note that the black areas on the left side of the image are parts of the corroded phase, whereas the black area down in the right corner of the image is the shadow of the AFM cantilever. The MFM imaging was performed on an uncorroded area of 35 × 35 μm in the vicinity of the selectively dissolved phases, due to the limitation of the AFM technique of scanning relatively rough areas. In fact, Figure 8b shows the topography

mapping of the selected area still presenting polishing lines from the sample preparation prior polarization.

Figure 8. (a) Light optical micrograph showing the selected area for post-polarization MFM investigation. The black areas on the left of the image are corroded areas, whereas the black area down in the right corner is the shadow of AFM cantilever. (b) AFM topography image of the scanned area (uncorroded) of the 2205 HT sample after polarization up to 0 $V_{Ag/AgCl}$ in 1 M NaCl solution at 50 °C; (c) MFM image of the same scanned area as the topography image, showing preferential corrosion of the austenite, as extended part of the corroded phases.

The MFM image in Figure 8c, taken in the exact position shown in the underlying optical micrograph, shows a clear picture of the magnetic domain distribution, which can be correlated to the microstructure of the duplex stainless steel. The ferrite phase, being ferromagnetic, exhibits a worm-like strip magnetic pattern, whereas the austenite, being paramagnetic, presents uniform contrast in the image. The differences in the contrast within the ferrite phase are most likely due to different

crystallographic and domain orientations [23]. It can be observed from Fig. 8c that the uncorroded phase between the two corroded areas in the left part of the optical image is the ferrite phase being the extension of the ferrite area shown in the MFM image. Instead, the extensions of the two corroded areas on the left side of the optical image are the austenite phase, exhibiting the typical uniform contrast in the MFM image. The MFM measurements were performed on at least three different areas of the corroded sample surface, and the results always confirmed the preferential dissolution of austenite at temperature above the CPT when exposed to 1 M NaCl solution.

4 Discussion

4.1 Influence of quenched-in chromium nitrides on the corrosion behavior of 2205 DSS

In practice, chromium nitride precipitates are quite often found in DSSs, especially in highly alloyed DSS grades, and sometimes cause corrosion problem but not in all the cases. It is known that different types of chromium nitrides can be formed in different amounts and at different locations in the DSSs, depending on the DSS grade, processing procedures and especially the heat treatment conditions. For industrial applications, it is of great importance to clarify the influence of the precipitated nitrides, not only their presence, but also their type, amount and size, as well as their distribution in the microstructure, on the corrosion behavior of the DSSs. This is a challenging task because the identification and quantification of the small nitrides are often difficult, requiring the usage of advanced techniques such as TEM and SAED. Simple post-corrosion analysis by SEM/EDS may get useful information, but often with some uncertainties in the interpretation and missing detailed information regarding the corrosion behavior under specific conditions.

In this study, by using available state-of-the-art techniques, we have combined detailed microstructure characterization, electrochemical measurements, *in-situ* microscopic experiments and post-polarization analyses, to investigate the effect of small quenched-in nitrides on the corrosion behavior on the 2205 DSS through a special heat treatment to

generate the nitride precipitates. The small nitrides could hardly be found by SEM examination, whereas the TEM and SEAD analyses clearly showed the presence of nano-sized quenched-in Cr_2N particles dispersed in the ferrite phase of the 2205 HT sample. At room temperature, the polarization curve obtained in 1 M NaCl solution showed a wide passive potential range with a low passive current density, and the presence of the finely dispersed quenched-in nitrides didn't show any noticeable influence on the corrosion behavior. This was verified by in-situ electrochemical AFM measurements at different anodic potentials, which showed a very stable surface in the potential range up to $1.1 V_{\text{Ag}/\text{AgCl}}$, and no pitting initiation was observed even at high lateral resolution. During transpassive dissolution at $1.2 V_{\text{Ag}/\text{AgCl}}$, the ferrite matrix started to dissolve, while the quenched-in nitrides remained to be stable, which is in accordance with the Volta potential mapping that shows higher relative nobility for the nitrides than the ferrite matrix. Even at temperature above the CPT (50°C), where selective dissolution readily occurred upon slight anodic polarization, it was the austenite phase that suffered selective dissolution whereas the ferrite phase with the quenched-in nitrides remained to be stable. All these results indicate that the small quenched-in Cr_2N finely dispersed in the ferrite phase do not cause localized corrosion of the 2205 DSS in 1 M NaCl solution.

It has been reported for different alloys such as austenitic alloys [24-26] and CoCrMo alloys [27] that the precipitation of secondary phases, e.g. nitrides or carbides, leads to weaker corrosion resistant areas in their surrounding regions, due to local Cr and N depletion. In this case, nano-sized quenched-in nitride particles are finely dispersed in the ferrite phase of the DSS. The precipitation of the quenched-in nitrides may also cause some Cr and N depletion in the ferrite matrix. However, in this case, the large number of very small nitride particles dispersed in the matrix formed during the fast cooling without sufficient time for elemental diffusion unlikely lead to a considerable compositional gradient in the boundary region around them. Furthermore, chromium nitrides (higher relative nobility) themselves are not susceptible to corrosion. These could explain why the small quenched-in nitrides finely dispersed in the ferrite phase do not cause localized corrosion. These observations indicate that the size and distribution of the

precipitated nitrides also have an influence on the local depletion and thus susceptibility to localized corrosion.

Transpassive dissolution of the sample occurred in this solution at very high anodic potential, $1.2 V_{\text{Ag/AgCl}}$ or above, which is a kind of selective dissolution under extreme anodic polarization. Under normal corrosion conditions, it is not likely that some cathodic reaction can support such a corrosion process.

4.2 Influence of temperature on the corrosion behavior of 2205 DSS

The results from this study about the selective dissolution of a 2205 HT sample at different temperatures show the importance of exposure temperature on the corrosion behavior of the DSS. At T_{room} the 2205 HT sample exhibited a wide passive range and a low passive current density despite the presence of quenched-in nitrides dispersed in the ferrite phase. At $1.2 V_{\text{Ag/AgCl}}$, the ferrite was preferentially dissolved at transpassive condition, while the austenite phase remained to be un-attacked, in accordance with the Volta potential mapping results. The higher tendency of ferrite to undergo transpassive dissolution at T_{room} was already observed on commercial grade 2205 DSSs (without nitride precipitates) in previous studies [28,29].

In contrary, at $50\text{ }^{\circ}\text{C}$, slightly above the CPT, a completely different corrosion process took place at the metal surface. In this case, selective dissolution of the austenite phase was the main reason for the sharp current increase upon anodic polarization. The observation indicates that at temperature above the CPT, the austenite phase becomes the weaker phase, less stable and more susceptible to corrosion in the NaCl solution. It would be interesting to perform the Volta potential mapping of the sample as function of the temperature, a subject for a future study.

In practice, the pitting resistance equivalent (PRE) number is often used for comparing the pitting corrosion resistance of stainless steels. Considering the following PRE formula (Eq. 1) [30,31] and using the elemental composition obtained by the TEM/EDS point analysis (Table II) except the N contents which are based on the considerations mentioned in section 3.1.2, it was found that the PRE number is between 34 and 35 for the austenite phase and around 41 for the ferrite matrix (excluding the nitride particles). This calculation would suggest a higher susceptibility of

austenite, having lower PRE number, to initiate pitting corrosion than the ferrite phase at temperature above the CPT.

$$\text{PRE}_{16} = (\% \text{Cr}) + 3.3 (\% \text{Mo}) + 16 (\% \text{N}) \quad (\text{Eq. 1})$$

The preferential pitting corrosion attack of the austenite phase at temperatures above the CPT has already been observed in other studies [32-36]. The lower amount of Cr and Mo in the austenite phase could be a reason of its higher susceptibility to pitting corrosion compared to the ferrite phase. The alloy composition thus seems to be of critical importance [13].

In the present study, at temperature above the CPT, the presence of finely dispersed quenched-in Cr_2N and some isothermal Cr_2N particles rarely found at phase and grain boundaries did not appear to have a negative influence on the corrosion behavior of the material. In fact, in this case the austenite was the phase suffering selective dissolution. This temperature increase (from T_{room} to 50 °C) is quite small and unlikely causes a significant change in the material properties. On the other hand, this temperature increase implies a considerably enhanced aggressiveness of the solution (especially Cl^- activity), which may reach a condition where the passive film on the austenite phase becomes unstable while the passive film on the ferrite phase is still stable.

However, to achieve a detailed understanding of the mechanisms for selective dissolution at temperatures above the CPT and for transpassive dissolution of such multi-elements and multi-phases DSS, further in-situ analyses with high lateral resolution of the surface layer at different temperatures, and at different anodic potentials, are needed to elucidate the chemical and structural changes in the passive film due to the increased temperature, and due to the increased anodic potential.

5 Conclusions

The influence of finely dispersed nano-sized quenched-in chromium nitrides, and the effect of exposure temperature, on the corrosion behavior of a heat treated SAF 2205, have been investigated by SEM/EDS, TEM/EDS,

SAED and KFM characterization, potentiodynamic polarization, EC-AFM and MFM measurements. The following conclusions can be drawn:

- In the heat treated SAF 2205, a large amount of nano-sized quenched-in Cr_2N particles dispersed in the ferrite phase, and a small number of isothermal Cr_2N particles in the α/γ and α/α boundaries were found. Whereas no nitrides were observed in the austenite phase.
- The Volta potential mapping performed at room temperature suggested lower relative nobility of the ferrite phase compared to the austenite phase, and higher relative nobility of the quenched-in Cr_2N particles compared to surrounding ferrite matrix.
- At room temperature in 1 M NaCl solution, the heat treated sample exhibited a wide passive range and very stable surface up to 1.2 $V_{\text{Ag}/\text{AgCl}}$, at which transpassive dissolution of the ferrite phase took place. The quenched-in Cr_2N particles remained stable in the material.
- At 50 °C (just above the CPT) in 1 M NaCl solution, fast selective dissolution of the austenite phase occurred upon anodic polarization. The lower contents of Cr and Mo in the austenite phase may be the reason for its higher susceptibility to dissolution at higher temperature.
- Finely dispersed nano-sized quenched-in Cr_2N particles and a small number of isothermal Cr_2N particles in this DSS do not cause localized corrosion in 1M NaCl solution. Whereas the exposure temperature has a strong influence on the corrosion resistance, changing the selective dissolution behavior of the DSS.

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References

- [1] K.N. Adhe, V. Kain, K. Madangopal, H.S. Gadiyar, Influence of Sigma-Phase formation on the localized corrosion behavior of a duplex stainless steel, *J. Mater. Eng. Perform.* 5 (1996) 500.
- [2] T.H. Chen, J.R. Yang, Effects of solution treatment and continuous cooling on σ -phase precipitation in a 2205 duplex stainless steel, *Mater. Sci. Eng. A* 311 (2001) 28.
- [3] J.O. Andersson, T. Helander, L. Höglund, P.F. Shi, B. Sundman, THERMO-CALC & DICTRA, Computational tools for material science, *Calphad.* 26 (2002) 273.
- [4] R.A. Perren, T. Suter, C. Solenthaler, G. Gullo, P.J. Uggowitzer, H. Böhni, M.O. Speidel, Corrosion resistance of super duplex stainless steels in chloride ion containing environments: investigations by means of a new microelectrochemical method: II. Influence of precipitates, *Corros. Sci.* 43 (2001) 727.
- [5] J.-O. Nilsson, G. Chai, The physical metallurgy of duplex stainless steel, Maastricht, The Netherlands: s.n., 21-23 October, 1997. Paper No. 206, vol. 1.
- [6] J.-O. Nilsson, Superduplex stainless steels, *Mater. Sci. Technol.* 8 (1992) 685.
- [7] J.W. Simmons, Influence of nitride (Cr_2N) precipitation on the plastic flow behaviour of high-nitrogen austenitic stainless steel, *Scr. Metall. Mater.* 32 (1995) 265.
- [8] N. Sathirachinda, R. Pettersson, S. Wessman, J. Pan, Study of nobility of chromium nitrides in isothermally aged duplex stainless steels by using SKPFM and SEM/EDS, *Corros. Sci.* 52 (2010) 179.
- [9] N. Sathirachinda, R. Pettersson, S. Wessman, U. Kivisäkk, J. Pan, Scanning Kelvin probe force microscopy study of chromium nitrides in 2507 super duplex stainless steel - Implications and limitations, *Electrochim. Acta* 56 (2011) 1792.
- [10] J. Liao, Nitride precipitation in weld HAZs of a duplex stainless steel, *ISIJ Int.* 41 (2001) 460.
- [11] K. Tamaki, K. Yasuda, M. Kimura, Corrosion performance of girth-weld joints of duplex stainless steels, *Corrosion* 45 (1989) 764.

- [12] T.H. Iversen, Intragranular chromium nitride precipitates in duplex and superduplex stainless steel, Norwegian University of Science and Technology, Trondheim (2012)
- [13] R.F.A. Pettersson, J. Flyg. Electrochemical evaluation of pitting and crevice corrosion resistance of stainless steels in NaCl and NaBr, *Acom.* 3 (2004) 2.
- [14] S. Magonov, J. Alexander, S. Wu, Advancing characterization of materials with atomic force microscopy-based electric techniques scanning probe microscopy of functional materials, in: A. Gruverman, S.V. Kalinin (Eds.), *Scanning Probe Microscopy of Functional Materials*, Ch. 9, Springer, New York, 2011, p. 233.
- [15] M. Sababi, S. Ejnermark, J. Andersson, P.M. Claesson, J. Pan, Microstructure influence on corrosion behavior of a Fe-Cr-V-N tool alloy studied by SEM/EDS, scanning Kelvin force microscopy and electrochemical measurement, *Corros. Sci.* 66 (2013) 153.
- [16] P. Liu, Phase analysis in steel using analytical transmission electron microscopy, Sandvik, Sandviken (2004) p. 64
- [17] N. Sathirachinda, R. Gubner, J. Pan, U. Kivisäkk, Characterization of phases in duplex stainless steel by magnetic force microscopy/scanning Kelvin probe force microscopy, *Electrochem. Solid-State Lett.* 11 (2008) C41.
- [18] M. Femenia, C. Canalias, J. Pan, C. Leygraf, Scanning Kelvin probe force microscopy and magnetic force microscopy for characterization of duplex stainless steels, *J. Electrochem. Soc.* 150 (2003) B274.
- [19] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous solutions*, Chapter IV, Section 1.1, Pergamon Press, 1996
- [20] J. Kruger, Influence of crystallographic orientation on the pitting of iron in distilled water, *J. Electrochem. Soc.* 106 (1959) 736.
- [21] R.S. Lilliard, Relationship between pitting corrosion and crystallographic orientation, an historical perspective, in: H.S. Isaacs, J.R. Scully, J.D. Sinclair, G.S. Frankel (Eds.) *Corrosion Science. A retrospective and current status in honor of Robert P. Frankenthal*, Pennington, New Jersey, USA, 2002, p. 334-343.
- [22] M. Rabiller-Baudry, F. Gouttefangeas, J. Le Lannic, P. Rabiller, Coupling of SEM-EDX and FTIR-ATR to (quantitatively) investigate

- organic fouling on porous organic composite membranes, in: A. Méndez-Vilas (Ed.) Current microscopy contributions to advances in science and technology, Formatex Research Center, Badajoz, Spain, 2012, p. 1066.
- [23] N. Sathirachinda, R. Pettersson, J. Pan, Depletion effects at phase boundaries in 2205 duplex stainless steel characterized with SKPFM and TEM/EDS, *Corros. Sci.* 51 (2009) 1850.
 - [24] Z. Ahmad, Principles of Corrosion Engineering and Corrosion Control, Butterworth-Heinemann, Oxford, 2006, p. 171.
 - [25] H. Sahlaoui, K. Makhlof, H. Sidhom, J. Philibert, Effects of ageing conditions on the precipitates evolution, chromium depletion and intergranular corrosion susceptibility of AISI 316L: experimental and modeling results, *Mater. Sci. Eng. A* 372 (2004) 98.
 - [26] T. Thorvaldsson, G.L. Dunlop, Grain boundary Cr-depleted zones in Ti and Nb stabilized austenitic stainless steels, *J. Mater. Sci.* 18 (1983) 793.
 - [27] E. Bettini, C. Leygraf, C. Lin, P. Liu, J. Pan, Influence of grain boundaries on dissolution behavior of a biomedical CoCrMo alloy: in-situ electrochemical-optical, AFM and SEM/TEM studies, *J. Electrochem. Soc.* 159 (2012) C422.
 - [28] M. Femenia, J. Pan, C. Leygraf, P. Luukkonen, In situ study of selective dissolution of duplex stainless steel 2205 by electrochemical scanning tunnelling microscopy, *Corros. Sci.* 43 (2001) 1939.
 - [29] M. Femenia, J. Pan, C. Leygraf, In situ local dissolution of duplex stainless steels in 1 M H₂SO₄ + 1 M NaCl by electrochemical scanning tunneling microscopy, *J. Electrochem. Soc.* 149 (2002) B187.
 - [30] J.-O. Nilsson, P. Kangas, T. Karlsson, A. Wilson, Microstructural stability and mechanical properties of a high nitrogen super duplex stainless steel, *Mater. Sci. Forum* 318-320 (1999) 751.
 - [31] J.E. Truman, *Proc. U.K. Corrosion '87*, Brighton, 1987, p. 111-129.
 - [32] R.F.A. Jargelius-Pettersson, J. Flyg, S. Wessman, The influence of nitrogen alloying on the pitting and crevice corrosion of austenitic and duplex stainless steel, *Mater. Sci. Forum* 318-320 (1999) 489.

- [33] B. Deng, Y. Jiang, J. Gong, C. Zhong, J. Gao, Jin Li, Critical pitting and repassivation temperatures for duplex stainless steel in chloride solutions, *Electrochim. Acta* 53 (2008) 5220.
- [34] F. Eghabali, M.H. Moayed, A. Davoodi, N. Ebrahimi, Critical pitting temperature (CPT) assessment of 2205 duplex stainless steel in 0.1 M NaCl at various molybdate concentrations, *Corros. Sci.* 53 (2011) 513.
- [35] N. Ebrahimi, M.H. Moayed, A. Davoodi, Critical pitting temperature dependence of 2205 duplex stainless steel on dichromate ion concentration in chloride medium, *Corros. Sci.* 53 (2011) 1278.
- [36] M. Adeli, M.A. Golozar, K. Raeissi, Pitting corrosion of SAF2205 duplex stainless steel in acetic acid containing bromide and chloride, *Chem. Eng. Commun.* 197 (2010) 1404.