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The mechanism of thermal oxide film formation on low Cr martensitic stainless steel and its behavior in fluoride-based pickling solution in conversion treatment

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Abstract:
(Attention: for corrosion science, the abstract must not exceed more than 100 words)

In this research, first a multi-analytical approach was carried out to propose a mechanistic model for the formation of the thermal oxide film on low Cr stainless steel. It describes the effects of kinetically and thermodynamically driven phenomena on the growth of a Fe-Cr complex oxide film at 950°C. Second, the behavior of the thermal oxide film in the presence of fluoride ions, as a relevant pickling agent in conversion treatment, was investigated. It was shown that fluoride ions enter the oxide film and form a complex with Fe and preferentially dissolve hematite islands through a complexation mechanism.

Keywords: thermal oxide film, stainless steel, conversion coating, XPS, Raman spectroscopy, ICP-MS, fluoride-induced dissolution
1 Introduction

According to new environmental regulations regarding reductions of greenhouse gas and fine particles emission, car manufacturers are designing lighter vehicles to achieve this goal. One strategy is to use very high strength materials which can be implemented in automotive structural parts and chassis parts in reduced thicknesses compared to conventional materials, such as Press Hardening Stainless Steels [1][2]. In addition, it has been reported that the chromium content has an optimal threshold around 10 wt% to have a compromise between good hardness and efficient wear and corrosion resistance [3][4][5][6][7]. The stainless steels containing 11 wt% chromium which show a ferritic microstructure can be thermally treated in order to achieve a higher strength and mechanical performance and to obtain a martensitic microstructure. This heat treatment is often applied during one of the main forming processes of this stainless steel, being the hot stamping. During this thermal treatment, an oxide film (1-3 μm) will be formed on the surface exhibiting a complex structure [8].

The oxide film on the surface of stainless steel can be formed during air exposure (native oxide film) or thermal treatment (thermal oxide film). There are quite a few publications regarding the characterization of the native oxide film on the surface of conventional grades of stainless steel during air exposure [9][10][11][12][13]. This literature reports that the native oxide film on the stainless steel surface has a bilayer structure consisting of Cr oxide in the inner part and Fe oxide at the outer surface with a thickness of several nanometers [14][15][16]. They also reported that these two layers have a distinct boundary. On the other hand, the formation of thermal oxide films at elevated temperature can be remarkably complex due to the difference in kinetics and thermodynamics of oxidation. Therefore, the oxide growth can be a function of several parameters from thermal treatment conditions and/or substrate. The dependence of the thermal oxide formation on heat treatment conditions such as temperature, oxygen partial pressure and duration of thermal treatment has been extensively studied [17][18][19][20][21]. These results showed that an increase in oxidation temperature and decrease in oxygen partial pressure will lead to the formation of a protective Cr oxide layer. However, there is always a compromise between oxidation conditions and mechanical properties.

Moreover, the microstructure and the composition of the alloy has a key role in the composition and structure of the oxide film [22][23][24][25][26][27]. It has been reported that the thermal oxide film on stainless steel has a uniform multilayer structure with a distinct boundary like the native oxide film [28][29][20]. During the native oxide film formation, the only driving force for the oxidation is the difference in diffusion coefficient of various elements in the oxide film and their affinity to oxygen. However, at higher temperatures, the changes in crystal structure and substitution of some elements into other oxide crystal structure can play an important role in addition to aforementioned parameters. The role of these parameters in the formation of the thermal oxide film has been investigated on conventional stainless steel in various conditions [22][30][31][32]. L.Q.Guo et al. [33] elucidated that the formed oxide film on different crystal microstructures present at the surface (austenite or ferrite) exhibits different compositions and thickness. They demonstrated that the oxide film covering the ferrite structure contains a Cr-enriched layer extending to the top surface, while the austenitic part shows the typical bilayer structure. E. Huttunen-Saarivirta et al. [30] characterized the microstructure of a thermally grown oxide film on five different ferritic stainless steels with various chemical compositions. It was indicated that at higher temperature (600°C), alloying elements play an important role in the formation of the oxide film. They can be observed in the inner or outer layer of the oxide film.
film, depending on their diffusion coefficients. G. Zijlstra [3] studied the effect of crystal orientation on the oxide formation of polycrystalline stainless steel. It was revealed that various crystal orientations show a different oxidation rate at different oxidation temperatures. In addition, a uniform multilayered structure was considered for the thermal oxide film structure including a stack of hematite, magnetite and Cr oxide from surface to bulk, respectively. It has been also reported that the increase in Cr content of the alloy results in the formation of protective Cr oxide film on the surface which can hinder further oxidation [34][35]. For the compositions with less than 10 wt% Cr concentration, the formation of a uniform Cr oxide layer is not possible anymore and the oxide film will contain a non-protective Fe-rich oxide [36]. Although the increase in the Cr content leads to formation of a more protective layer, it also results in the loss of mechanical properties [37]. The stainless steel (MaX1.2HY) used in this study contains 11 wt% chromium showing the optimal characteristics.

One of the applications of this low Cr stainless steel is in automotive industries, in which the material will undergo a chemical pretreatment process by the application of a conversion coating. During this process, the surface will obtain a better corrosion resistance and adhesion properties for subsequently applied organic coatings [38]. Automotive conversion coatings have been developed in 1911 by Coslett [39], and the technology has been evolving during the past century to more environmentally friendly and more efficient coatings [28][29][41][42]. In both conventional and advanced forms of automotive conversion treatments, one of the most important steps is the activation or pickling step in a F-containing solution [43][44][45][46]. During this step, the surface of the metal or metal oxide is dissolved to form a more protective component and deposits on the surface as a coating [38][40][47][48][49]. Therefore, the formation of enough dissolved species during this step is crucial to have a robust coating in the next steps.

The behavior of the oxide film on stainless steel in F-containing pickling solutions has not been reported to the best of our knowledge, but there are some scientific works about the behavior of stainless steel in acidic solution. N. Mazinanian et al. [50] investigated the metal release mechanism from the surface of the native oxide film of stainless steel grade AISI 304 into citric acid solution at weakly acidic conditions. They demonstrated that the citric-acid-induced metal release is governed by a surface complexation mechanism. Z. Wang et al. [51] studied the Cl\(^-\) induced alteration of the native oxide film on 316 austenitic stainless steel. They indicated that Cl\(^-\) enters through the bilayer structure of the native oxide film, mostly in the outer part and preferentially dissolves the iron oxide. Nonetheless, the accurate structure of the thermal oxide film was not considered in the dissolution mechanism and the fact of “preferential dissolution” is not fully perceived.

The first aim of this study is to propose an accurate mechanism for the formation of the thermal oxide film on this special type of stainless steel as a potential substrate in automotive industries. Due to the different chemical composition and crystal structure of this material, the oxide structure and formation mechanism in elevated temperature is not unraveled yet. Therefore, the characterization of this oxide film is substantial to understand the behavior of the material in further industrial processes like the application of conversion coatings. This model will consider the composition, topography and morphology of the oxide film laterally and/or axially.

The second goal is to investigate the dissolution mechanism of the thermal oxide film in a F-containing pickling solution as a relevant initiator in the conversion process. Due to the formation of a thermal oxide film on the surface of this stainless steel during thermal treatment, it is essential to study the
reactivity of the surface during immersion in pickling solution to predict the behavior of the material in the conversion treatment. To achieve this goal, the characteristics of the surface oxide after immersion in the pickling solution will be correlated to the initial state of the oxide film. To this purpose, a multi-analytical approach will be deployed to have a complete understanding of the surface behavior during the pickling step.

2 Experimental

2.1 Materials and solution

This study was carried out using Fe-11Cr stainless steel sheets from Aperam with dimensions of 10*10*1.5 mm. The thermal oxide film was obtained during a heat treatment process at 950° C during 5 minutes at room atmosphere.

The sample was then cleaned respectively in an ultrasonicated bath of acetone, ethanol (Merck, purity 99.99%) and milli-Q water, each for 3 minutes and then dried using filtered compressed air. The surface of the samples was covered by PVC tape to have a reproducible exposure area of 0.8 cm² during the pickling step.

To investigate the effect of fluorides, HF (Merck, purity 99.99%) was added to milli-Q water (resistivity < 18 MΩ) to obtain a total F⁻ concentration of 100 mg/L. The activity of F⁻ was measured using a fluoride ion selective electrode in conjunction with Ag/AgCl reference electrode from Xylem analytics at room temperature.

The pickling process was carried out by dipping the samples in a fluoride-containing solution for 60 s and 180 s, followed by rinsing with distilled water and drying with filtered compressed air.

2.2 Analysis method

2.2.1 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

The microstructure and morphology of the surface before and after immersion in the fluoride-containing solution was observed by scanning electron microscopy (SEM) using a JEOL JSM-IT300 system. Both Lower Electron Detector (LED) and Back Scattered Electron Detector (BSD) were employed with an acceleration voltage of 15 kV and a working distance of 10 mm.

The coupled Energy Dispersive X-ray spectrocope (EDX) was exploited to collect the elemental maps of Fe and Cr from a cross section, embedded in the epoxy resin. Prior to embedding, the surface of the oxide film was covered with a copper layer to protect the oxide film during high temperature embedding. Beam energy of 15 kV was utilized to perform a mapping of 250 frames and 50 μs dwell time.

2.2.2 Wavelength Dispersive X-ray Fluorescence spectrometer (WDXRF) and elemental analyzer

The mass composition of the stainless steel was verified using a Wavelength Dispersive X-ray Fluorescence spectrometer (WDXRF) model Zetium from Malvern Panalytical except for N and C. An elemental analyzer from LECO analysis was used to measure the N and C content of the alloy using infrared absorption and thermal conductivity detection. This was performed after converting the elements from the sample into their oxidized form by utilizing the gas fusion method (for N) and the combustion method (for C).
2.2.3 White-light interferometry
The 3D topography measurements of the oxide film were performed using a vertical scanning white-light interferometer from Bruker (ContourGT-I 3D Optical Microscope). The magnification of the lenses was set to ×50 times and an internal magnification of ×0.5 (final magnification of ×26.8) has been utilized in order to achieve the best lateral resolution for acquiring the largest field-of-view image.

2.2.4 X-ray Photoelectron Spectroscopy (XPS)
The chemical top surface composition of the oxide film before and after immersion was collected by X-ray Photoelectron Spectroscopy (XPS) using a PHI-5600ci Multitechnique system (Physical electronics). An Al Kα X-ray monochromated source (hv= 1486 eV) was used. The pressure in the analysis chamber was maintained at 10⁻⁹ Torr during the analysis. For all the measurements, a circular analysis area of 400 µm diameter with a maximum depth of 10 nm was probed. The kinetic energy of the photoelectrons was recorded with a take-off angle of 45°. A high pass energy (187.85 eV) with an energy step size of 0.1 eV was used to record a wide scan spectrum. High resolution spectra of O 1s, C 1s, Fe 2p and Cr 2p were obtained with a pass energy of 23.5 eV and 0.05 eV step size. The energy scale of the XPS spectra was calibrated relative to the binding energy of aliphatic carbons in the C 1s peak at 284.8 eV. CasaXPS software was used to fit the high-resolution spectra with a Shirley type background and a Gaussian-Lorentzian peak shape. The values of the relative sensitivity factors were extracted from the PHI Multipak software database for quantification. XPS depth profiles were carried out using argon ions with an acceleration voltage of 2 kV and an ion beam current of 20 mA. The reproducibility of the XPS measurements was verified by three repetitions.

2.2.5 Raman spectroscopy
The samples were analyzed with a LabRAM HR Evolution confocal Raman spectroscope from Horiba Scientific to accurately identify the chemical composition of the oxide film. The green laser (532 nm) was employed with 10 % filter and 100× objective for optical images and Raman measurements. The data was analyzed with the standard LabSpec 6.2 software, including spike removal and background correction.

2.2.6 Inductively coupled plasma-mass spectroscopy (ICP-MS)
The concentration of the dissolved Fe and Cr in solution was measured using a Thermo Scientific Element 2 sector field ICP-mass spectrometer. A representative volume of solution (10 mL) was first evaporated in precleaned teflon (Savillex) beakers. The resulting gel-like substance was then re-dissolved using sub-boiled 7 M HNO₃ and re-dissolved in this acid at 110°C for 24h. Following a dilution with 3% HNO₃ (by a factor of 5), the concentrations of Cr and Fe in the solutions were determined. Indium was used as an internal standard, quantification took place versus an external calibration curve, and the results for multiple isotopes measured in medium resolution (i.e. m/Δm = 4000) were averaged. The results were validated through the addition of a known amount of single standard element solutions to a blank medium sample. Based on three measurements, the analytical precision of the procedure outlined above is estimated to be in the range of 5-10% relative standard deviation (RSD).
3 Results and discussion

Table 1 shows the chemical composition (wt. %) of substrates that was measured by WDXRF and elemental analyzer.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Si</th>
<th>N</th>
<th>C</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal.</td>
<td>11</td>
<td>0.5</td>
<td>0.4</td>
<td>0.4</td>
<td>0.01</td>
<td>0.06</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

In the first section, the thermal oxide film will be characterized to give a better understanding of the original state of the oxide film. In the second section, the primary state of the oxide film will be correlated to the surface properties after immersion, to investigate the effect of the fluoride pickling process on the surface.

3.1 Thermal oxide characterization

In this section, a multi-analytical approach has been used to characterize the thermal oxide film on top of the low chromium stainless steel substrate. In this regard, a set of techniques were used to have an understanding of chemical composition, morphology and topography of the oxide film. In addition, cross sectional analysis was carried out to investigate the compositional structure of the oxide film in depth. By considering all the obtained results, a mechanistic model for the formation of the thermal oxide film will be proposed.

3.1.1 Analysis of the chemical composition

Raman spectroscopy measurements have been utilized in the first step, in order to have a macroscopic understanding of the chemical composition of the surface. Fig. 1 shows an optical image of the surface of the oxide film. Dark islands (zone B), surrounding areas with gray color (zone A1) or brown color (zone A2) and grain boundaries can be observed.

In order to characterize these distinct zones, Raman spectra of different zones on the surface of the oxide film were obtained (Fig. 2) and compared to literature Raman shifts. Table 2 indicates the reported Raman shift for Fe$_{2x}$Cr$_x$O$_3$ oxides structure with different x values. Table 3 shows the same for Fe$_{3x}$Cr$_x$O$_4$ oxides structure [52].

The blue curve in Fig. 2 shows the Raman spectra corresponding to dark particles (zone B) in Fig. 1. According to Table 2, a series of hematite (α-Fe$_2$O$_3$) peaks can be clearly distinguished [52]. Additionally, the characteristic peak around 660 cm$^{-1}$ shows the formation of Fe$_{2x}$Cr$_x$O$_3$ in a corundum structure. According to the reference spectra for this structure [53], the higher the Cr content in this formula (higher x value), the stronger the characteristic peak around 660 cm$^{-1}$ will be. Therefore, in this zone the formation of hematite and Fe$_{2x}$Cr$_x$O$_3$ structure with a small contribution of Cr can be observed.

The Raman spectrum related to the zone A1 in the optical image exhibits the formation of Fe$_{3x}$Cr$_x$O$_4$ (x<2) with the main peak around 670 cm$^{-1}$. Based on Table 3, during the formation of Fe$_{3x}$Cr$_x$O$_4$ (x<2) from magnetite, with increasing Cr content, the peak at 542 cm$^{-1}$ becomes stronger and shifts towards 550 cm$^{-1}$. Also, a shoulder at 636 cm$^{-1}$ can be observed for this complex besides the main peak at 670 cm$^{-1}$.
Therefore, the most important oxide structure in this zone is magnetite and Fe$_{3-x}$Cr$_x$O$_4$ in a spinel structure. In addition, a small participation of hematite and Fe$_{2-x}$Cr$_x$O$_3$ structure can be observed here according to Table 2.

Eventually, the spectrum that was recorded at the Zone A2 (red curve in Fig. 2) depicts a stronger peak at 550 cm$^{-1}$, proving an increase in Cr content in the solid solution structure of Fe oxide with respect to the same peak in zone A1. Fig. 3 illustrates the heterogeneous composition of the oxide surface from a top view. Most of the surface area is covered by a Fe$_{3-x}$Cr$_x$O$_4$ spinel structure, with a variable amount of Cr depending on the surface position. This is in contrast with some literature [32][54], that only reports on pure magnetite. Moreover, we observe that hematite and a Fe$_{2-x}$Cr$_x$O$_3$ corundum structure appear as discrete islands on the surface.
Fig. 1. The optical image (×100 magnification) from the surface of the oxide film on top of the martensitic stainless steel

Fig. 2. The Raman spectra corresponding to the defined areas in Fig. 1
Table 2. The values of Raman shift for the Fe$_{2-x}$Cr$_x$O$_3$ structure in cm$^{-1}$

<table>
<thead>
<tr>
<th>Complex</th>
<th>Peak(I)</th>
<th>Peak(II)</th>
<th>Peak(III)</th>
<th>Peak(IV)</th>
<th>Peak(V)</th>
<th>Peak(VI)</th>
<th>Peak(VII)</th>
<th>Peak(VIII)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe$_2$O$_3$</td>
<td>236</td>
<td>253</td>
<td>298</td>
<td>413</td>
<td>502</td>
<td>616</td>
<td>-</td>
<td>1319</td>
</tr>
<tr>
<td>Fe$<em>{1.73}$Cr$</em>{0.27}$O$_3$</td>
<td>-</td>
<td>-</td>
<td>298</td>
<td>417</td>
<td>508</td>
<td>616</td>
<td>664</td>
<td>1328</td>
</tr>
<tr>
<td>Fe$<em>{1.20}$Cr$</em>{0.80}$O$_3$</td>
<td>-</td>
<td>-</td>
<td>303</td>
<td>424</td>
<td>521</td>
<td>620</td>
<td>673</td>
<td>1343</td>
</tr>
<tr>
<td>Fe$<em>{0.93}$Cr$</em>{1.07}$O$_3$</td>
<td>-</td>
<td>-</td>
<td>310</td>
<td>382</td>
<td>527</td>
<td>639</td>
<td>682</td>
<td>1359</td>
</tr>
<tr>
<td>Fe$<em>{0.40}$Cr$</em>{1.60}$O$_3$</td>
<td>-</td>
<td>-</td>
<td>310</td>
<td>385</td>
<td>547</td>
<td>648</td>
<td>685</td>
<td>1381</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>-</td>
<td>304</td>
<td>353</td>
<td>529</td>
<td>553</td>
<td>616</td>
<td>-</td>
<td>1398</td>
</tr>
</tbody>
</table>

Table 3. The values of Raman shift for the Fe$_{3-x}$Cr$_x$O$_4$ structure in cm$^{-1}$

<table>
<thead>
<tr>
<th>Complex</th>
<th>Peak(I)</th>
<th>Peak(II)</th>
<th>Peak(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$</td>
<td>542</td>
<td>-</td>
<td>671</td>
</tr>
<tr>
<td>Fe$<em>{2.6}$Cr$</em>{0.4}$O$_4$</td>
<td>562</td>
<td>-</td>
<td>682</td>
</tr>
<tr>
<td>Fe$<em>{2.2}$Cr$</em>{0.8}$O$_4$</td>
<td>-</td>
<td>-</td>
<td>681</td>
</tr>
<tr>
<td>Fe$<em>{1.8}$Cr$</em>{1.2}$O$_4$</td>
<td>548</td>
<td>636 (S)</td>
<td>674</td>
</tr>
<tr>
<td>Fe$<em>{1.4}$Cr$</em>{1.6}$O$_4$</td>
<td>550</td>
<td>636 (S)</td>
<td>679</td>
</tr>
<tr>
<td>FeCr$_2$O$_4$</td>
<td>531</td>
<td>636 (S)</td>
<td>686</td>
</tr>
</tbody>
</table>

Fig. 3. Illustration of the surface composition of the oxide film from top view

Fe$_{3-x}$Cr$_x$O$_4$ * 0 < x < 2

Fe$_{3-x}$Cr$_x$O$_4$ structure with more Cr content
3.2 Morphological and topographical characterization

SEM and white-light interferometry were used to investigate the morphology and topography of the thermal oxide film from top. Fig. 4(a-c) present SEM images from the surface of the thermal oxide film at two different magnifications. From these images, two different microstructures can be observed on the surface: a porous nodule-like island (zone B) and an area with a more compact microstructure (zone A). In addition, the backscattered electron image of the same area of the oxide (Fig. 5) shows that the surface has two different compositions in two separate zones (A and B). Zone B appears as a darker area, indicating a lower atomic weight than zone A which appears as brighter area. According to the Raman measurements, zone B in Fig. 1, consisting mainly of Fe$_2$O$_3$, has a lower atomic weight than zone A with a Fe$_{3-x}$Cr$_x$O$_4$ composition. Therefore, the dark zones in the backscattered electron image with porous microstructure correlate to the dark particles in Fig. 1 (zone b) with the hematite structure. This shows that hematite appears as discrete areas all over the surface.

Fig. 6 shows the topography of the oxide surface in an area of 167×223 µm$^2$, as measured by white-light interferometry. Some cracks with lower roughness (navy blue and orange colors show the most negative and most positive height values in the image, respectively) and some islands with higher roughness can be observed on the surface. By looking at the distribution and geometry of these islands, it can be concluded that these islands correspond to zone B in Fig. 1, 4 and 5. Therefore, the surface of the oxide film is covered by two different zones with different composition, microstructure and roughness. Zone A, consisting mainly of the Fe$_{3-x}$Cr$_x$O$_4$ structure, with a non-porous microstructure and low roughness, is covering most of the surface. Zone B, with a lower atomic weight consisting of hematite and the Fe$_{2-x}$Cr$_x$O$_3$ structure, having a more porous microstructure and higher roughness, appears as repetitive islands on the surface.

![Fig. 4. Secondary electron image of the surface of the oxide film at a) 500 and b) 2000 c) 10000 times magnification](image-url)
3.2.1 Cross sectional SEM/EDX analysis

Cross sectional SEM/EDX analysis was exploited to investigate the change of the composition in depth. Fig. 7 shows the cross section of a selected area of the oxide film. Two distinct features can be observed: the flat area of the surface (zone A) and the islands (zone B). The outer layer shows the copper layer that was deposited in order to protect the oxide film during resin embedding. Fig. 8(a-c) illustrate the cross-sectional SEM image and EDX quantitative maps for Cr and Fe corresponding to zone A (uniform area in Fig. 7) in the oxide film. According to Fig. 8(b,c) a homogenous distribution of Fe along the oxide film and at the outer side can be observed. An enrichment of Cr at the interface between the substrate and the oxide film is observed (indicated by the red rectangle). Fig. 9a shows the cross sectional image of zone B and the EDX maps of Cr and Fe are depicted in Fig. 9(b,c). In this zone, two distinct areas with different elemental distribution can be observed. Zone B1 at the outer part shows an iron-rich nodule-like structure, depleted of Cr. Zone B2 appears as an underlying layer in which the elemental distribution is similar to zone A. However, in addition to the Cr-enriched layer at the oxide/metal interface, another Cr enrichment at the boundary between sub-zone B1 and sub-zone B2 can be distinguished (indicated by the red rectangle).

Fig. 6. Back scattered image of the oxide film with 500 times magnification

Fig. 5. 3D topographic image showing the roughness of the oxide film using white-light interferometer

Fig. 7. Cross sectional view of the oxide film
3.2.2 Chemical characterization by XPS

X-ray photoelectron spectroscopy (XPS) has been carried out to characterize chemically and quantify the composition of the 8-10 nm top layer of the oxide film.

Fig. 10 presents the XPS wide-scan spectrum of the surface of the thermal oxide film. This spectrum has been recorded after 5 s of Ar⁺ sputtering, removing ambient contamination (hence the Ar contribution in the spectrum). O, Fe, Cr, Mn, Si, Nb and C are identified, with following relative composition (at. %): O: 63.2; Fe: 8.1; C:18.2; Cr: 7.5; Mn: 2.2; Si: 0.6 and Nb: 0.2.
Fig. 10. XPS survey spectrum for the thermal oxide film

Fig. 11(a-c) show XPS Fe2p3/2, Cr2p3/2 and O1s core level spectra recorded for the thermal oxide film. The values of BE (binding energy), FWHM (full width at half maximum) and relative intensity of each component are listed in Table 4 [12][51][55][56][57]. A multiplet splitting approach was carried out to fit the Fe and Cr spectra to analyze the Fe and Cr oxidation states on the surface [58][59].

The Fe2p3/2 core level spectrum (Fig. 11a) is deconvoluted into three main series of peaks. A series of 5 peaks (red peaks) relates to the hematite structure (α-Fe₂O₃) in the oxide structure. The green and blue series of peaks correspond to magnetite (Fe₃O₄) and Fe-Cr solid solution, respectively. By considering the surface area of these peaks, the contribution of each Fe complex is as follows: 58.0(±1) % for magnetite, 22.3(±0.5) % for hematite and 19.7(±0.5) % for Fe-Cr solid solution. It is obvious that Cr tends to form a solid solution with Fe rather than a pure oxide on this substrate.

The Cr2p3/2 core level spectrum (Fig. 11b) is decomposed into three components including Cr₂O₃ (red series of peaks), Fe-Cr solid solution (blue series of peaks) and metallic chromium. Again, by calculating the surface area of these peaks, the contribution of each Cr complex is as follows: 1.1(±0.3) % for metallic Cr, 19.5(±0.5) % for Cr₂O₃ and 79.4 (±1.5) % for Fe-Cr solid solution. It is obvious that Cr tends to form oxide complexes with Fe rather than a pure oxide on this substrate.

The O1s spectrum includes the main peak of the oxide and smaller peaks of the hydroxide and water [19][52].

By quantification of these peaks and by taking into account relative concentration of Cr and Fe in the oxide film, using relative sensitivity factors of Fe and Cr [60][61][62], the total contribution of each complex on the oxide film is as follows: magnetite (28.5%), hematite (12%), Cr₂O₃ (10%) and Fe-Cr solid solution (49.5%). These data show that the formation of Fe-Cr solid solution in the outer layer of the oxide film is more favorable than the formation of a pure Cr oxide layer and that Cr tends to form oxide complexes with
Fe oxide. Additionally, this quantification shows that the hematite nodule-like islands has the contribution of 12% in the oxide composition.
Fig. 11. XPS core level spectra of (a) Fe_{2p3/2}, (b) Cr_{2p3/2} and (c) O_{1s} for the thermal oxide film
Table 4. The values of binding energy (BE), FWHM (BE) and relative intensity of the components measured by XPS

<table>
<thead>
<tr>
<th>Complex</th>
<th>Peak no</th>
<th>BE (±0.1 eV)</th>
<th>FWHM (±0.1 eV)</th>
<th>Relative intensity* (%)</th>
<th>Complex</th>
<th>Peak no</th>
<th>BE (±0.1 eV)</th>
<th>FWHM (±0.1 eV)</th>
<th>Relative intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>1</td>
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<td>1.1</td>
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*Area of each split relative to total area of the relevant peak

3.2.3 Oxide growth mechanism

Fig. 12 represents the schematic process of the oxidation as a combination of thermodynamically and kinetically driven phenomena. From thermodynamic point of view, the difference in the oxygen partial pressure at the surface and in the deeper region results in the oxidation under a chemical potential gradient [62]. From kinetic point of view, the oxidation also depends on the diffusion property of the metal elements present in the alloy [24][58]. Consequently, the total oxide growth is a sum of an inward oxidation (with diffusion of O²⁻) and an outward oxidation (with diffusion of metal ions).

According to the results obtained from Raman spectroscopy, SEM, EDX mappings of the cross section and XPS, the oxide composition can be illustrated as shown in Fig. 13.

The oxide structure in zone A is consist of a mixture of Fe₂O₃/ Fe₃₋ₓCrₓO₄ that covers a layer with enrichment of Cr oxide. The oxide formation in the zone A can be explained through following steps:

1. **Formation of Cr₂O₃/ Fe₃₋ₓCrₓO₄**: it has been extensively reported that the surface of an alloy will be enriched by the component that forms the strongest chemisorption bond with oxygen [62]. The formation of Cr oxide at a temperature of 950 °C is thermodynamically more favorable than Fe oxide [9][63][64]. Therefore, Cr oxide can be formed on the surface at the first stage of the oxidation as a thermodynamically driven phenomenon. However, the concentration of Cr in the alloy is not high enough (11 wt%) to form a fully covering Cr₂O₃ layer as it is possible for stainless steels with higher Cr content [34]. Consequently, a mixture of Fe oxide and Cr oxide will be formed on the surface. According to the chemical potential diagram of Fe-Cr-O [62], at higher oxygen activity, the formation of hematite
is thermodynamically more favorable. Therefore, at the early stage of oxidation, when the surface of the alloy is in contact with the air, the formation of Fe$_{2x}$Cr$_x$O$_3$ will occur with presence of more Cr.

2. **Diffusion of Fe through the Cr oxide layer:** according to the fact that Fe has a higher diffusion coefficient in the oxide compared to Cr, there will be more Fe available to move outward to be oxidized [65]. Therefore, from kinetic point of view, Fe$^{2+}$ from the metal phase will diffuse through the inner oxide sublayer and Fe$_3$O$_4$ will be formed on top of the Cr oxide [66].

3. **Formation of the Fe$_{3-x}$Cr$_x$O$_4$ spinel structure:** During the diffusion of Fe through Cr oxide, it will react with the inner oxide and will be enriched in the Cr oxide layer to form a spinel structure of Fe$_{3-x}$Cr$_x$O$_4$ (0≤x<2) with a uniform distribution [67][17].

4. **Formation of a Cr-enriched layer:** due to the fact that outward diffusion of Fe and oxide growth happen faster than the spinel formation and also due to the low diffusion rate of Cr in the solid solution oxide, an enrichment of Cr in the substrate/oxide interface will be observed. As a result of these 4 steps, a mixture of Fe$_3$O$_4$/ Fe$_{3-x}$Cr$_x$O$_4$ will cover an enriched layer of Cr oxide.

The structure of the oxide film in zone B is divided into two sub-zones: sub-zone B1 including some nodule-like islands with hematite structure and sub-zone B2 with the same structure as zone A. The formation of the oxide in the sub-zone B2 follows the same mechanism as zone A, but the formation of hematite islands in sub-zone B1 shows a different mechanism in two main aspects as follows:

1. The first difference is the formation of some nodule-like islands with hematite structure, which do not fully cover the surface. The dependence of second-stage oxidation on the grain boundaries and porosity of the oxide film that was formed in the first stage of the oxidation, can explain this phenomenon [68]. From thermodynamic point of view, during the oxidation, the species with higher affinity to oxygen can travel and diffuse from porosities and grain boundaries of the oxide film to reach the top surface. Therefore, these complexes cannot fully cover the surface of the oxide film due to the limited number of porosities and grain boundaries. According to the chemical potential diagram of Fe-Cr-O and the fact that hematite formation consumes more oxygen, hematite islands will be formed in the outer surface of the oxide film. Due to the selective diffusion of Fe ions through porosities, this type of Fe oxide can be observed in the form of nodule-like islands, in contrast with numerous publications considering it as a uniform layer [54][9][69].

2. The second difference in oxidation mechanism of sub-zone B1 is the depletion of Cr in the nodule-like structure of these islands and the presence of another enriched layer of Cr at the boundary of sub-zone B1 and B2. The Cr depletion in sub-zone B1 can originate from different lattice orientations of the hematite and magnetite structure of Fe oxide. The diffusion of metal ions through the metal oxide crystal structure with different lattice orientations can result in a change of the diffusion rate. The diffusion of trivalent Cr through the rhombohedral lattice system of hematite happens slower than in the FCC (face cubic centered) lattice system of magnetite [70] and as a result, Cr depletion can be observed in the sub-zone B1. Due to this decrease in diffusion of Cr in the hematite islands another enrichment can be observed at the boundary of sub-zone B1 and sub-zone B2.
3.3 F-induced alteration of the oxide film

In this section, the impact of F ions on the surface of the previously described thermal oxide film will be investigated. In this regard, a multi analytical approach will be used to examine the impact of F ions present in the pretreatment pickling solution on the morphological and chemical state of the oxide film.

3.3.1 Morphological and compositional study
The influence of F ions on the oxide film was first examined by means of scanning electron microscope in LED and BSD mode, in order to track the general change of morphology and composition of the surface, respectively. Fig. 14 shows the backscattered images of the oxide surface with low magnification before and after immersion in fluoride-containing pickling solutions for 60 s and 180 s. The dark particles that were characterized as the hematite islands in the previous part (zone B) are clearly dissolving in the solution after
60 s (Fig. 14b). The surface of the oxide film after 180 s immersion in the F-containing solution (Fig. 14c) shows no extra change in the BSD mode imaging.

Fig. 15 depicts the surface morphology of the oxide film before and after immersion in the F-containing solution for 60 s and 180 s. As shown in this figure, dissolution of porous nodule-like particles (zone B) can be clearly observed after 60 s of immersion which is in agreement with Fig. 14. The surface of the oxide film after 180 s immersion in F-containing solution shows no significant change in morphology compared to the previous sample, only some attacks in the uniform part of oxide film could be observed (zone A).

Fig. 14. The backscattered electron images of the oxide film before (a) and after immersion for 60 s (b) and 180 s (c) in the F-containing solution.
3.3.2 Solubility measurements

In order to describe the dissolution process mechanistically, ICP-MS was used to measure the concentration of dissolved elements in the solution.

Table 5 shows the concentration of Cr and Fe in a representative volume of F-containing solution (10 mL) in which the sample was immersed for 60 s and 180 s. Elements were monitored using multiple isotopes when possible (e.g., $^{52}\text{Cr}$ and $^{53}\text{Cr}$, $^{56}\text{Fe}$ and $^{57}\text{Fe}$) and the presented result is the average for the monitored isotopes. Additionally, the concentration of dissolved Fe and Cr in the third column relates to the sample that was immersed in a 0.02 M NaCl solution for 180 s. This was performed to provide an estimation for the dissolution of the oxide film in a non-acidic and non-corrosive environment.

Based on the values in Table 5, a higher amount of dissolved Fe can be monitored in the first step of immersion while the amount of Cr dissolution is almost negligible. After 180 s of immersion, the dissolution of Fe into the solution rises but at a slower rate while Cr dissolved at a higher rate compared to the first 60 s. In addition, the amount of dissolved Fe and Cr in the NaCl solution provides an indication for the amount of oxide residues on the surface of the oxide. The comparison between the amount of dissolved...
Fe and Cr during the pickling process and that during immersion in NaCl solution indicates that these dissolved oxides result from fluoride pickling and not from the dissolution of oxide residues on the surface.

According to the concentration of dissolved Fe and Cr, it can be observed that Cr oxide is less soluble in the pickling solution than Fe oxide. In addition, it was concluded from the previous section (Fig. 13) that Fe-Cr solid solution covers the surface of the substrate except for some islands consisting of mainly Fe oxide (zone B). Based on these observations, the preferential dissolution of these islands in zone B (Fig. 4) can directly be linked to the presence of less Cr oxide in this zone, and thus they are less resistive against dissolution.

According to the proposed model of the oxide film (Fig. 13), further dissolution of the oxide film until 180 s immersion time means the dissolution of the Fe-Cr solid solution containing a higher amount of Cr. Due to the lower solubility of Cr oxide in the pickling solution, the dissolution occurs with a lower rate than for Fe oxide. Therefore, Cr enriches the surface of the oxide and prevents significant alterations of the surface during longer immersion times. For this reason, the concentration of Fe in the solution between 60 s and 180 s increases with a lower rate. Furthermore, one can observe a higher amount of Cr in solution due to an increased surface concentration of Cr after the first minute of pickling.

Table 5. The values of dissolved Fe and Cr into the solution

| Dissolved element | Concentration of dissolved element (ppb) |  |
|-------------------|----------------------------------------|--|---|
|                   | After 60 s immersion | After 180 s immersion | After immersion in NaCl for 180 s |
| Fe                | 373.8                  | 472.4                  | 53.4                      |
| Cr                | 2.4                    | 16.3                   | <LOD                      |

Based on repeated measurements, the analytical precision of the procedure is estimated to be in the range of 5-10% RSD. LOD – limit of detection (0.01 ppb for Cr and 0.33 ppb for Fe)

### 3.3.3 The change of chemical composition

XPS was utilized to follow the change of the chemical composition of the top surface of the oxide film before and after immersion.

Fig. 16 presents the contribution of Fe and Cr (in atomic percentage) at the top surface of the oxide film before and after immersion in F-containing solution for 60 s and 180 s. After immersion for the first 60 s, the contribution of the Fe oxide decreases at the surface of the oxide film compared to the blank sample. Consequently, the contribution of Cr oxide shows a higher value. However, the composition of the oxide film after 180 s immersion shows no changes compared to the immersion for 60 s.

According to the ICP-MS data, Fe oxide dissolves easier in the pickling solution compared to Cr oxide. Therefore, the decrease in the Fe oxide contribution on the oxide surface can be attributed to the higher solubility of this oxide (in zone B) in the F-containing solution. Consequently, the contribution of Cr oxide at the top of the oxide film increases and after 60 s immersion in pickling solution, the enrichment of Cr oxide turns the surface of the oxide film to a more passive surface. Due to the fact that the Fe-Cr solid solution on the surface does not tend to dissolve (based on 3.2.1), therefore, the surface is less prone to the release of Fe into the solution with increasing immersion time and the composition of the oxide film will be less altered.

The results so far showed that when a Fe-Cr alloy with a complex oxide film is immersed in the relevant pickling solution during conversion treatment, there is a preferential dissolution of the surface. However, it is of great importance to study the change of the oxide film through depth, to have a better understanding
of this preferential dissolution. In this regard, XPS depth profiling was utilized. Fig. 17 presents the variation of the contribution of Fe and Cr (in atomic percentage) versus time of sputtering with Ar⁺. In Fig. 17a, it can be observed that for the non-immersed sample, Cr and Fe have the same atomic concentrations until 30 min sputtering time before immersion in the fluoride solution. Thereafter, the concentration of Fe increases and the Cr concentration decreases by passing the oxide film and reaching to the substrate. However, the depth profile of the oxide film after 60 s and 180 s immersion in F-containing solution (Fig. 17b,c) shows a different behavior. After immersion in the F-containing solution, the concentration of Fe decreases compared to Cr until a certain depth for both samples. For the oxide film immersed for 60 s, the intersection of the Cr and Fe atomic concentration can be observed after 26 min sputtering. In the case of the sample immersed for 180 s, this intersection is observed after 40 min sputtering.

The depth profile of the oxide of the blank sample confirms the hypothesis of the solid solution oxide film on top of the substrate. However, after immersion in the F-containing solution, the change of the composition cannot only be observed on the surface, but also in depth. The lower concentration of Fe oxide compared to Cr oxide indicates the entry of F⁻ through the oxide film and dissolution of Fe oxide. This leads to the presence of more Cr on the surface as it can be observed in the depth profile (Fig. 17) and Fig. 16. The intersection of equal atomic concentrations of Fe and Cr (like the oxide of the blank sample) can be observed more in depth with increasing immersion time.

These results, together with the previous data, confirm that fluoride ions enter through the oxide film and preferentially dissolve the less resistant Fe oxide during immersion in the F-containing solution. From section 3.2.1, it was observed that the preferential dissolution of hematite particles is directly attributed to the presence of lower amounts of Cr in this oxide structure.

To investigate the governing mechanism of the dissolution, the XPS core level spectrum of F1s was recorded for the surface after immersion in the F-containing solution (Fig. 18). The F1s contribution located at a binding energy of 684.6 eV (FWHM=1.7) corresponds to Fe-F formation on the surface of the oxide [71].

As reported by Hedberg et al.[72], the dissolution of the metal oxide into the acidic solution can be divided into three categories. Depending on the immersing solution, metal dissolution can occur by complexation-induced, protonation-induced or reduction-induced mechanisms. Due to the weak acidic nature of HF, the protonation-induced dissolution is negligible. Instead, the formation of Fe-F complexes on the surface indicate the complexation driven mechanism of the oxide dissolution. This shows that during the immersion in the F-containing pickling solution, the chemical bonds of Fe-O can be broken easier than Cr-O. Therefore, F ions will react with the Fe ions to form a Fe-F complex on the surface and this leads to dissolution of Fe oxide in the solution. Fig. 19 illustrates the dissolution mechanism of this substrate in a F-containing solution. The dissolution of Fe oxide activates the surface for further chemical reaction during conversion treatment to form the conversion coating. This paper is a part of ongoing research regarding the study of the behavior of conversion coatings on this new stainless steel material. The results showed the surface is active and the modification by conversion coating can be foreseen.
Fig. 16. The contribution of Fe and Cr in the oxide film before and after immersion in the F-containing solution measured by XPS

Fig. 17. The depth profile of the oxide film before (a) and after immersion in F-containing solution for 60 s (b) and 180 s (c)
Fig. 18. XPS core level spectra of F1s from the surface of the oxide after immersion in the F-containing solution for 180 s.

Fig. 19. The schematic presentation of dissolution mechanism of the thermal oxide film in a F-containing solution.
4 Conclusion

In this research, the effect of fluoride ions, as the relevant pickling agent in conversion treatment, on the surface of the thermal oxide film on top of MaX1.2HY (low Cr martensitic stainless steel) was investigated. In this study, we were able to make a correlation between the primary state of the oxide film and the alteration of the surface after immersion. In this regard, the surface of the thermal oxide film on top of the stainless steel was characterized first. A multi-analytical procedure, focusing on morphological, topographical and compositional aspects, has been used to fully characterize the complex composition of the oxide film on the surface of this low Cr stainless steel. The complementary results from the first section elucidated below items:

1. The low Cr content in the alloy composition results in the formation of an inhomogeneous Cr oxide layer. Unlike the oxide layer on top of the classical stainless steel with higher Cr content, this oxide layer does not stop the oxidation and allows Fe ions to diffuse from substrate for further oxidation.
2. The oxide growth on the surface of the low Cr stainless steel has a complex mechanism which is a function of thermodynamically and kinetically driven phenomena. The different diffusion coefficients of the metal oxides lead to a depth distribution of the components in the oxide film.
3. The proposed model for the oxide composition illustrates the oxide film from oxide/substrate interface as follow: Cr-enriched layer, Fe-Cr oxide solid solution with Fe$_{3-x}$Cr$_x$O$_4$ structure and Hematite islands.

The study of fluoride impact on the thermal oxide film was conducted by considering the primary chemical composition and morphology of the oxide film and by comparing the surface before and after immersion in F-containing solution. The results from the second section clarified the mechanism of pickling as below:

1. Fluoride ions enter the complex oxide film and penetrate and/or dissolve the oxide component. The effect of fluoride penetration was more pronounced after 180 s immersion than after 60 s immersion.
2. During this immersion, fluoride ions will break the less strong chemical bonds to form a complex with the oxide components. This results in the formation of Fe-F bands on the surface rather than Cr-F bands.
3. Hematite particles will preferentially dissolve in the pickling solution through a surface complexation mechanism due to the presence of less Cr in these nodules. This shows the activity of the surface during the pickling action, being an important part of the conversion treatment, and therefore modifications by conversion coatings on the surface are expected.

5 Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.
6 References


[41] E. Alibakhshi, M. Akbarian, M. Ramezanzadeh, B. Ramezanzadeh, M. Mahdavian, Evaluation of the corrosion protection performance of mild steel coated with hybrid sol-gel silane coating in


