



Comparative analysis of corrosion behavior in compositionally modified hot-rolled AISI 430F: Assessing surface versus intrinsic substrate characteristics

Alessio Malandruccolo^{*}, Stefano Rossi, Cinzia Menapace

University of Trento Department of Industrial Engineering – DII, Via Sommarive, 9, Trento, 38123, Italy

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ABSTRACT

The experimental work described in this study was aimed at investigating the corrosion behavior and surface characteristics of a chemically modified AISI 430 F ferritic stainless steel. The modified composition was designed to improve machinability while optimizing the magnetic properties for specific application requirements. The samples were obtained from hot-rolled coils in the as-rolled condition, prior to any subsequent heat treatment or pickling process. The material's electrochemical response was assessed using potentiodynamic polarization curves and micrographic analysis across two distinct conditions: as-rolled and heat-treated. The characterization protocol involved a comparative evaluation of the oxide-free cross-sections (intrinsic bulk resistance) and the peripheral surface (material's response following high-temperature exposure) and for all tested conditions. This approach served a dual purpose: first, to quantify the differential electrochemical behavior between the bulk matrix and the surface oxide scale; and second, to compare the as-rolled and heat-treated states to determine the influence of thermal processing on both surface evolution and the corrosion behavior of the internal microstructure. The electrochemical results confirmed the non-protective nature of the external oxide scale and consistently indicate that the material fails to establish stable passivity across all investigated experimental conditions. Furthermore, the heat treatment modifies the microstructure and has influence on the localized corrosion morphology. This effect is mainly attributed to alterations in the electrochemical response of the MnS-based inclusions, which are deliberately engineered within this steel grade. The thermal cycle appears to modulate the galvanic coupling between the surrounding matrix and the inclusions, thereby influencing their electrochemical behavior.

1. Introduction

Stainless steels are alloys characterized by a minimum Cr content of 10.5 wt%, although in industrial practice this threshold is established at 13 wt% to ensure homogeneity and adequate corrosion resistance. Their corrosion resistance is mainly promoted by the formation of a thin, protective, Cr-rich oxide passive layer. The inherent versatility of the Fe-based system concerning alloying possibilities permits the presence of key elements such as Mo, Mn, N, and Ni in stainless steels. Given the different behavior of the alloying elements in stabilizing the various phases of the Fe system, stainless steels are conventionally categorized into five main groups: austenitic, ferritic, martensitic, duplex, and PH (precipitation-hardening) [1]. The different classes of stainless steels also exhibit non-negligible variations in processability deriving from

various factors such as strain hardening resulting from cold working operations, or phase transitions and precipitation hardening induced by heat treatment. Consequently, given their wide range of properties and inherent durability afforded by the countless possible combinations of alloying elements, stainless steels have achieved widespread application across virtually all industrial sectors. These applications span a wide range of fields, including: automotive and transportation, architecture and construction, aerospace and defense, chemical and process industries, consumer goods and equipment, marine engineering, oil & gas, and paper and pulp sectors [2–4].

Ferritic stainless steels are characterized by relatively low mechanical properties that cannot be enhanced through heat treatment, but only through work hardening induced by cold working. Ferritic grades are essentially Fe–Cr–C alloys, where the Cr content can reach up to 27 wt%

^{*} Corresponding author.

E-mail addresses: a.malandruccolo@unitn.it (A. Malandruccolo), stefano.rossi@unitn.it (S. Rossi), cinzia.menapace@unitn.it (C. Menapace).

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(30 wt% in case of some superferritic grades). Their corrosion resistance is generally intermediate to that of martensitic and austenitic steels; however, they demonstrate superior performance compared to austenitic grades in specific environments, such as those involving contact with alkalis and alkaline salts. Stainless steel long products are an interesting category, particularly concerning the sequence of operations involved in their production process and the peculiarities arising from their processing after hot-working. Generally speaking, regardless of the type of stainless steel, the primary hot-working process for producing long products is hot rolling, either with single-stands or in continuous rolling mills (tandem mills) [5]. After hot rolling, depending on the type of stainless steel, direct heat treatment or warehouse storage (indoor or outdoor) may be selected, postponing heat treatment to a later stage when the material is retrieved from the warehouse. In many cases, long products undergo subsequent cold working operations, for the production of fasteners, cold-drawn coils and bars, or other products. In this context, the surface of the material is unsuitable for such processes due to the presence of an oxide scale layer developed during the hot rolling process and successively evolved during thermal treatment. This layer comprises alloying element oxides migrated from the bulk due to diffusive phenomena activated thanks to the high temperature. Moreover, the oxide scale turns out to be different for the same material depending on a considerable number of parameters. In fact, as highlighted by Li and Celis [6], the properties and characteristics of the oxide scale are highly contingent upon the reheating furnace parameters prior to hot rolling, the contaminants on the surface before heat treatment, and the parameters of heat treatment themselves. In fact, in addition to the temperature at which reheating of thermal treatment processes are carried out, the effective soaking time and the air/fuel ratio also play a key role. This is because the oxide scale evolves differently depending on the specific parameters' values, and same happens to the resulting depleted substrate [2,6]. The removal of oxide scale from the material's surface can be achieved by several methods, with pickling being one of the most popular. Pickling has the dual task of removing the oxide scale from the surface along with the depleted layer in order to restore the corrosion resistance of the material thanks to the reformation of the Cr-rich passive layer [2]. The calibration of pickling solutions directly depends on the materials being processed and the composition of the corrosion products requiring removal. Therefore, characterizing the oxides and surface species on the material is of critical importance for both designing the optimal pickling mixture and accurately predicting its operational service life [6,7]. Optimal storage management is also crucial, particularly because semi-finished products are often stored outdoors, where they are exposed to varying degrees of corrosive environments. Consequently, it is necessary to quantify the differential in corrosion behavior between the material in the as-rolled or as-treated condition and its corresponding oxide-free state.

A commercially available modified version of the AISI 440 F ferritic grade with a chemical composition aimed at improving magnetic and machinability features produced in wire and wire rod form was selected for laboratory tests. While belonging to the stainless steel family, this grade does not exhibit exceptional corrosion resistance because its chemical composition is specifically optimized to prioritize enhanced machinability and superior magnetic properties [2,8]. In fact, this alloy belongs to the group of the so-called free-machining stainless steels. These grades contain sufficient S to induce the precipitation of MnS directly from the melt (S content up to 0.35%, which significantly exceeds the traditional stainless steel limit of 0.03%). At sufficiently high concentrations of Mn and S, MnS precipitates interdendritically during solidification. This mechanism is advantageous as it bypasses solid-state precipitation, thereby maintaining the Mn solute concentration within the solid matrix (i.e., avoiding depleted zones). Furthermore, Mn S inclusions frequently nucleate heterogeneously on preexisting inclusions, such as silicates originating from the deoxidation stage of the steel-making process [9]. During machining, the fine dispersion of MnS inclusions acts as a fracture initiator, thus enhancing chip fragmentation

by creating structural discontinuities within the metal matrix. This mechanism significantly improves the machinability of these alloys, enabling higher cutting speeds, superior surface finishes, and increased depth of cut [1,2]. Some research has previously addressed the influence of MnS inclusions on the corrosion behavior of free-machining stainless steels. However, the literature currently lacks comparative studies addressing the relationship between the alloy's intrinsic corrosion resistance and the surface condition of semi-finished products at different stages of industrial processing. While the standard AISI 430 F ferritic stainless steel has been extensively investigated, there seems to be no literature regarding a characterization, such as that performed in [10], for the specific modified variant evaluated in this study. Specifically, investigation is missing concerning its surface oxide scale characteristics, intrinsic corrosion behavior expressed by the bulk material, and the role of MnS inclusions, which may differ from that determined for standard compositions. This study seeks to provide information in this context by systematically comparing the electrochemical response of the bulk material with that of the surface generated during specific production stages, specifically, post-hot rolling and subsequent heat treatment. Furthermore, while the oxide scales formed during these thermal processes are generally recognized as non-passive, an electrochemical characterization and comparison between these surface layers and the underlying bulk substrate remains largely absent from the literature.

The core of this research is a comparative assessment of the surface characteristics and intrinsic corrosion behavior of the selected alloy in two distinct states, representing fundamental milestones in the manufacturing of long products: the as-rolled and the heat-treated conditions. To establish a baseline, the potentiodynamic response of the oxide-free bulk material was first evaluated. Afterwards, the electrochemical behavior of the lateral surfaces was characterized in both the as-hot-rolled and subsequent laboratory heat-treated states. Finally, the electrochemical responses across all conditions were systematically compared to isolate the effects of the respective processing states. The experimental methodology employed was adapted from the approach previously validated in [10] for a martensitic stainless steel and all electrochemical experiments were performed in duplicate for each evaluated condition. Furthermore, potentiodynamic polarization testing used in this work were employed with the primary objective of determining the dependency of the material's passive characteristics and corrosion susceptibility on its specific surface state and processing thermal history. In particular, attention was focused on the shape of the anodic branch of the obtained polarization curves, which shape is known to possibly indicate the onset and stability of passive behavior. Potentiodynamic polarization in 0.5 M H₂SO₄ solution was first employed to evaluate the corrosion behavior of the material in the as-rolled state. Although sulfuric acid is known to be a strong acid, it was selected as electrolyte to facilitate the study of the hypothesized passive film formation on the oxide-free transverse sections. This medium allows for a controlled investigation of the active-passive transition on freshly polished surfaces, providing insights into the material's ability to develop a protective layer in an aggressive environment. To ensure clarity, the oxide-free transverse section of the specimens is hereafter referred to as the bulk (or cross-section). This nomenclature identifies the internal volume of the material, which remains isolated from environmental exposure and is inherently free from processing-induced scales or corrosion products. Accordingly, the bulk is intended to correspond to the region of the material that demonstrates its inherent corrosion resistance. This distinction is established to differentiate it from the external surface, which refers to the peripheral areas of the specimens characterized by the presence of scales and corrosion products resulting from both thermomechanical processing and environmental interaction. Following the initial tests, the material was subjected to test in a 3.5 wt% NaCl solution. This electrolyte was intended to simulate an aggressive, chloride-rich environment specifically designed to destabilize the Cr-rich passive film characteristic of

stainless steels. The presence of Cl^- ions is well-documented to induce the localized breakdown of passivity, subsequently triggering phenomena such as pitting corrosion. This breakdown occurs when the integrity of the passive film is compromised, exposing the underlying metal substrate and facilitating accelerated corrosive attack. Of course, the severity of the breakdown is influenced by factors such as pH and temperature and, of course, Cl^- concentration [11,12]. To comprehensively evaluate the full spectrum of supply conditions, electrochemical polarization tests in NaCl-based solution were also conducted on the surface retaining the high-temperature scale generated during heat treatment (i.e., the material's most common supply condition). A final set of potentiodynamic polarization curves was then obtained from heat-treated samples to evaluate the intrinsic behavior of the thermally-processed state. Concurrently with the electrochemical characterization, micrographic analyses were performed across all conditions. These integrated datasets were utilized to elucidate the complex interplay between microstructure, surface state, and the detected corrosion behavior.

2. Experimental

2.1. Materials

The present work focuses on long products. To address the objectives outlined in the introductory section, samples of a modified AISI 430 F ferritic stainless steel were obtained from hot-rolled material.

The samples used are identified by AISI 430 F* and are characterized by a lower Cr content (13%, on average) with respect to standard AISI 430 F, employed on purpose by manufacturers to further improve machinability. Furthermore, AISI 430 F* has been designed for magnetic applications that require high permeability and low coercivity. The chemical composition of the sample material is given in Table 1 and was determined by inductive coupled plasma-optical emission spectroscopy (ICP-OES) technique using an Agilent 720/725 ICP-OES spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA).

The Cr content of AISI 430 F* is significantly lower than that of the standard AISI 430 F (16–18%), approaching the minimum threshold required for a steel to be included in the stainless steel group. This reduction in Cr concentration, coupled with the high S content, suggests a material with non-exceptional corrosion resistance attitude, as evidenced by established literature [13,14]. Furthermore, the MnS inclusions within this alloy are expected to influence both the corrosion behavior and the underlying degradation mechanisms. While these characteristics are documented for standard compositions, there is a lack of available data regarding custom variants such as the one analyzed in this study [13,14]. Determining whether these sulfides exhibit anodic or cathodic behavior relative to the surrounding matrix and evaluating how this relationship evolves across the tested conditions (i.e., as-rolled and heat-treated), could be of interest for the overall assessment of the corrosion behavior of the material. Furthermore, given the Mn/S ratio of 2.35 of the sample material, the thermodynamic conditions should permit the coexistence of MnS and Cr_5S_6 [13]. The latter exhibits a distinct electrochemical response compared to MnS, which may significantly influence the experimental observations. Moreover, literature suggests that MnS inclusions can undergo Cr enrichment at the expense of Mn, depending on the material's thermal history. Specifically, hot rolling typically promotes Cr depleted sulfides, whereas subsequent heat

treatment may facilitate Cr diffusion into the sulfide phase, potentially altering the overall electrochemical response [13].

As it can be inferred from the typical production sequence of this alloy shown in Fig. 1, after hot working the material can be stored prior to the annealing treatment since it is not subjected to phase transformation upon cooling, or at low temperature.

At this stage, however, storage must take into account the fact that typically the oxide produced during hot working operations could not have protective attitudes. Therefore, the material exposed to external environment in case of external storage could be subjected to the formation of additional corrosion products that would add to those subsequently formed during heat treatment. In this latter concern, the typical process to which the material is subjected is an annealing process designed to optimize magnetic properties. With regard to processability, as already stated, the high machinability of this steel is a consequence of the relatively low Cr for a ferritic grade together with high S content. The use of these steels is not recommended for marine environment. They are, instead, widely used in the automotive industry and for the production of soft magnetic components. Some examples are: antilock brake systems, fuel injection components, solenoids valves, electromagnetic pumps, screws, spindles and nuts [2,8,14].

2.2. Experimental setup

As previously introduced in Section 1, the adopted methodology demonstrates full consistency with the approach detailed in [10]. Specifically, the experimental framework adopted for the investigated alloy involved potentiodynamic polarization tests conducted in 0.5 M H_2SO_4 and 3.5 wt% NaCl solutions using samples whose geometry is schematically summarized in Fig. 2:

Furthermore, the microstructure corresponding to each condition (i.e., as-rolled or heat-treated) was characterized via optical microscopy. Complementarily, the resulting surface morphology following the potentiodynamic tests was analyzed using a combination of optical and scanning electron microscopy.

A Gamry Reference 600 + potentiostat (Gamry Instruments Inc., Warminster PA, USA) with a standard cell setup was employed for potentiodynamic testing. An Ag/AgCl reference electrode (RE, +0.197 vs SHE) was employed, with a Pt wire serving as the counter-electrode (CE) and the sample operating as the working electrode (WE). All potentiodynamic tests were conducted at $25 \pm 1^\circ\text{C}$ in 0.5 M H_2SO_4 and 3.5 wt% NaCl aerated solutions. A scan rate of 0.2 mV/s was set, with the initial potential at -50 mV vs open circuit potential (E_{oc}). This cathodic polarization was deliberately limited to a value that avoids irreversible alterations to the surface layer, thereby enabling the evaluation of the surface oxides characteristic of each processing state analyzed. With regard to heat treatment and, consequently, the heat-treated condition, a laboratory process was performed to simulate the corresponding supply condition. The position of the heat treatment within the production sequence can be derived from the data presented in Fig. 1. To obtain the best properties, the industrial annealing process for the material under investigation is executed at 810°C and, in many cases, it is carried out in furnaces without controlled atmosphere, i.e., in a high-temperature oxidizing atmosphere. Consequently, it was expected that this heat treatment resulted in a significant alteration of the material's surface characteristics. As a consequence of this, a thermal cycle was applied to the specimens to induce specific changes in both the

Table 1

Chemical composition of AISI 430 F*. AISI 430 F* is a custom variant of AISI 430, whose reference standard for chemical composition is EN 10088–1:2023. Element content expressed in wt%.

		C	Cr	Ni	Mo	Mn	Si	P	S	Fe
AISI 430 F*	min	-	12	-	0.2	-	-	-	0.15	Bal.
	max	0.025	14	-	0.6	1.5	1	0.04	0.35	Bal.
	sample	0.02	13.1	-	0.35	0.8	0.70	0.02	0.34	Bal.

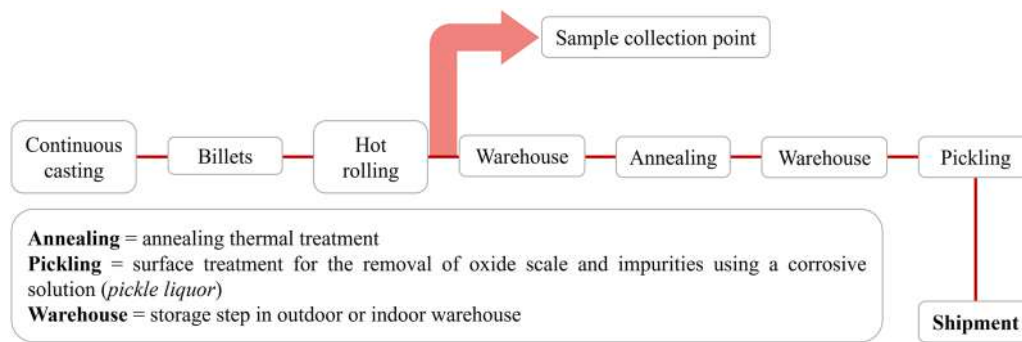


Fig. 1. Schematic of the most common production sequence of hot-rolled wires and wire-rods made of AISI 430 F and/or AISI 430 F*.

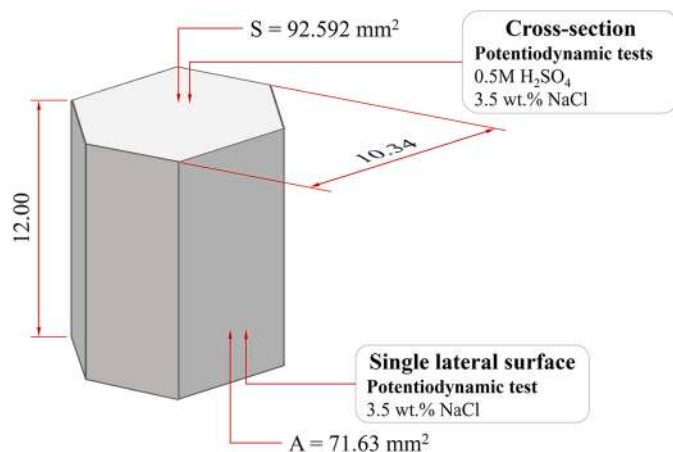


Fig. 2. Schematic representation of the tested sample geometry highlighting the cross-sectional area (S) and lateral surface area (A), alongside the respective testing conditions applied to each one.

material's microstructure and surface characteristics. To replicate industrial furnace conditions, the material was processed in an uncontrolled atmosphere using a TGA STA Netzsch 409 Lux (Netzsch, Selb, Germany). The thermal cycle involved heating the samples to 810 °C at a rate of 50 °C/h and a subsequent isothermal hold for 5 h. Cooling to 400 °C at the maximum available rate was employed and after this the samples were exposed to ambient laboratory air for free cooling.

Surface and microstructural characterization employed both optical and electron microscopy. The microstructure and surface features in the transverse direction with respect to the rolling direction (i.e., cross-sectional surface) were analyzed by means of optical microscope for both the material's conditions (i.e., as-rolled and heat-treated). Low-magnification surface inspection was performed with a Nikon SMZ 25 stereomicroscope (Nikon Instruments, Tokyo, Japan). For high-magnification analysis, an Olympus DSX 1000 (Olympus Corp., Tokyo, Japan) microscope was employed. In this context, Kalling No.2 reagent was used for etching the cross-section of the samples after polishing. This etchant is appropriate for ferritic steels due to its selective action: it is able to quickly attack ferrite without attacking carbides [15]. Scanning electron microscopy (SEM) analyses were conducted using both secondary electron (SED) and backscattered electron (BED) detection modes. EDXS elemental mapping was conducted on selected regions to provide crucial data for the interpretation of results, supporting results interpretation and allowing for a detailed characterization of the material's behavior under the specified experimental conditions. The SEM analyses utilized a JSM IT300LW microscope (JEOL, Tokyo, Japan) equipped with XFLASH 630 M detector (Bruker Corp., Billerica, MA, USA) and EDXS Quantax (Bruker Corp., Billerica, MA, USA).

In addition, the Thermo-Calc® 2025b software (Thermo Calc

Software AB, Råsundavägen, Sweden), utilizing the TCFE12 database, was employed to perform thermodynamic calculations based on the specific chemical composition of the alloy under investigation. The results provided crucial information allowing for prediction of the equilibrium phase types and fractions, supporting both the microstructural and experimental interpretation.

3. Results and discussion

The results of the experimental activity described in Section 2.2 are reported in the following. The discussion is organized by material condition, with an initial focus on the properties of the as-rolled specimens and a subsequent analysis of the heat-treated specimens.

3.1. As-rolled condition

3.1.1. Microstructure

As indicated in Fig. 3, thermodynamic modeling utilizing Thermo-Calc® software allowed for obtaining a pseudobinary phase diagram (Fig. 3a) and for the prediction of type and volume fraction of the phases at equilibrium (Fig. 3b and Fig. 3c), thereby complementing the microstructural analysis.

As illustrated in Fig. 3b and Fig. 3c, the formation of MnS (MS_B1 phase) is predicted to occur upon solidification, which is consistent with the discussion presented in the introduction of this work. Fig. 4 shows the microstructure of the as-rolled material revealed after etching, characterized by very fine grain structure. This feature, only discernable under high magnification, provides evidence of dynamic recrystallization occurring during the hot rolling process [16]. A significant volume fraction of sulfides was identified thanks to the microstructural analysis, with maximum dimensions exceeding 5 μm . The identification of the phases as MnS was established without requiring supplemental SEM-EDXS analysis. This classification is strongly supported by the existing microstructural data and is consistent with extensive literature regarding precipitation in the reference alloy system. The phases evidenced in Fig. 4 are visually consistent with MnS, which characteristically appears as grey inclusions easily differentiated from the ferritic matrix [14,15].

These considerations are further substantiated by the pseudobinary phase diagram in Fig. 3a and by thermodynamic equilibrium simulation results presented in Fig. 3b and Fig. 3c. Finally, the volume fraction of MnS observed in the micrographs in Fig. 4 is significantly greater than the prediction shown in the thermodynamic calculations displayed in Fig. 3b and Fig. 3c. This discrepancy is likely attributed to the non-equilibrium conditions inherent to the actual industrial production process of the studied material.

To confirm that the phases identified in Fig. 4 are indeed MnS, Fig. 5 shows the backscattered electrons SEM micrograph of sample's cross-section in the as-rolled condition after polishing. The surface was characterized prior to chemical etching to prevent the integrity of the

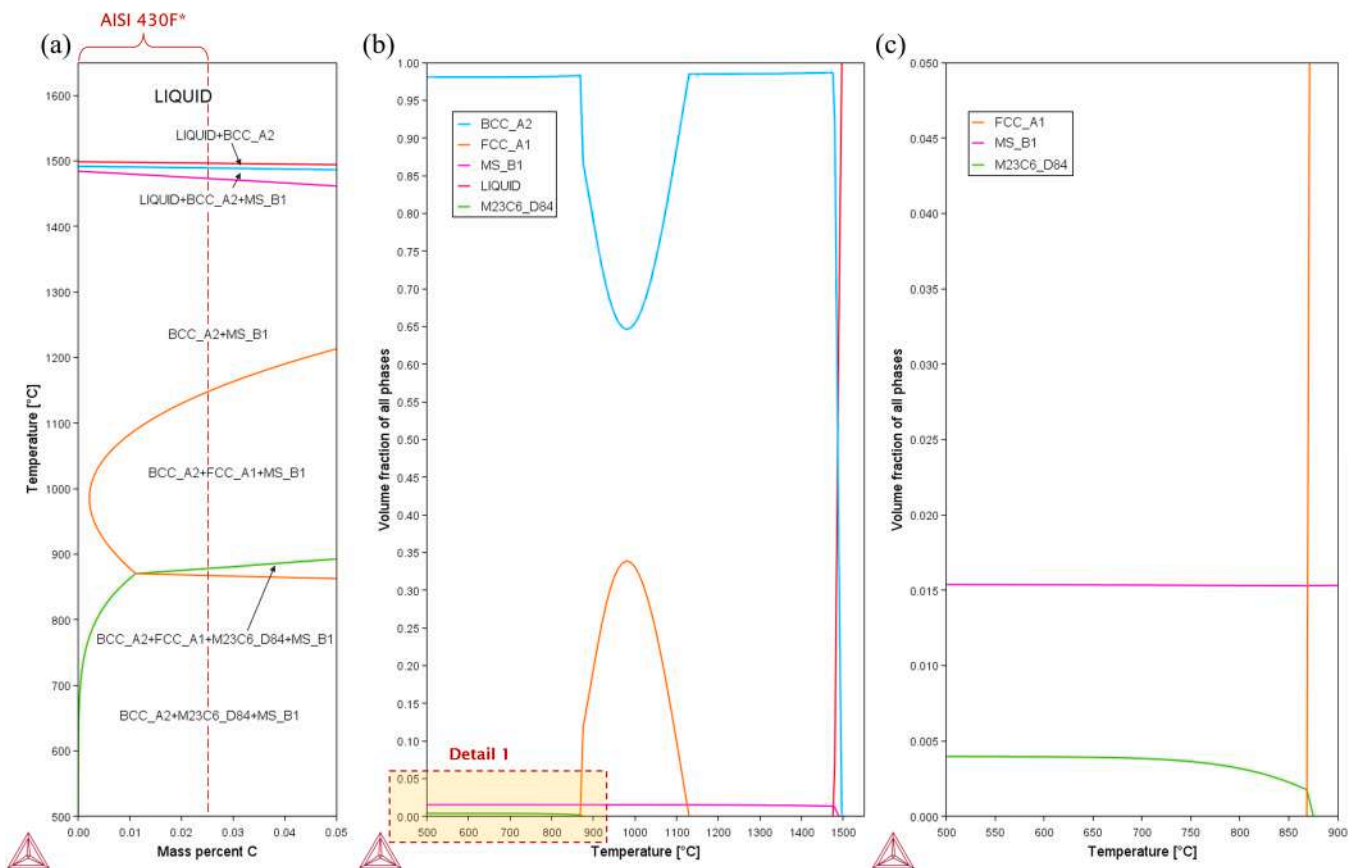


Fig. 3. a) Pseudobinary phase diagram with evidence of the composition range of AISI 430 F in terms of C content; b) Volume fraction of all phases vs temperature plot at equilibrium as a function of the chemistry of AISI 440 F* stainless steel as reported in Table 1; c) Detail 1 showing the diagram represented in b), but truncated at a volume fraction of 0.10 in the 500–900 °C temperature range. Please note the figures were obtained by simulating an AISI 430 F* composition corresponding to 0.02C-13Cr-0.4Mo-0.75Mn-0.5Si-0.03P-0.3S. BCC_A2 phase corresponds to the ferritic α matrix, FCC_A1 indicates austenite (γ), MS_B1 phase corresponds to the MnS sulfide, M23C6_D84 is the $M_{23}C_6$ carbide.

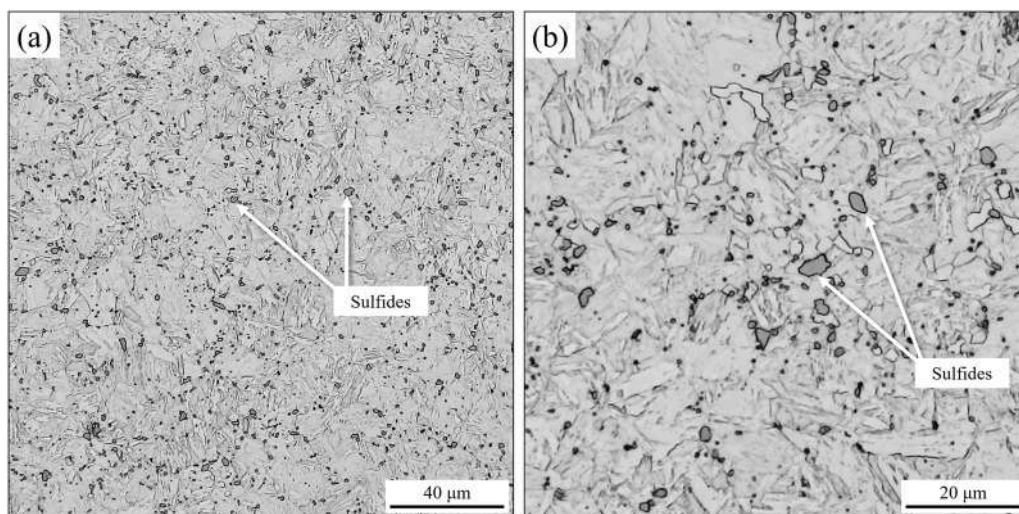


Fig. 4. a) Optical micrograph of AISI 430 F* sample's cross-section, etched with Kalling No.2 reagent in the as-rolled condition; b) Higher magnification optical micrograph of the same sample, etched with Kalling No.2 reagent.

secondary phases from being altered by etchant-induced localized corrosion process. The elemental signals for Mn and S in Fig. 5 confirm the initial microstructural identification performed via optical microscopy. The chemical compositions corresponding to points 1–3 in Fig. 5 are detailed in Table 2, along with a representative area analysis of the

matrix. The elemental data presented in Table 2 confirm the chemical identity of these secondary phases, i.e. MnS. Furthermore, the Cr concentration at measurement points is relatively low, falling below the nominal baseline of the surrounding alloy matrix. Additionally, the matrix composition is substantially depleted in S, which substantiates

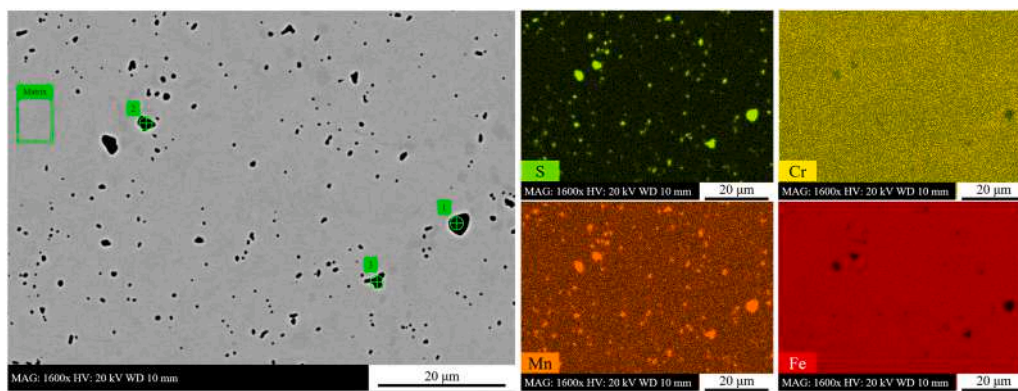


Fig. 5. Backscattered electrons SEM micrograph of AISI 430 F* sample's cross-section in the as-rolled condition after polishing and EDXS point and area analysis along with S, Cr, Mn, and Fe elemental mapping.

Table 2

Summary of the SEM – EDXS analysis results given Fig. XX.

Spectrum	Cr	Mn	S	Si	Fe
1	6.28	44.87	23.33	0.24	25.28
2	5.38	44.04	22.49	0.23	27.86
3	8.61	31.37	16.73	0.33	42.97
Matrix	12.66	0.59	0.07	0.64	86.04

the MnS precipitation mechanism outlined in the introduction featuring interdendritic precipitation directly from the liquid [9].

3.1.2. Potentiodynamic polarization in H_2SO_4 0.5 M solution

Fig. 6 shows the potentiodynamic curve of the material in H_2SO_4 0.5 M solution. The corrosion potential (E_{corr}) was -528 mV Ag/AgCl. The cathodic reaction taking place in this test configuration is the reduction of H^+ . Furthermore, the examination of the figure reveals that the current densities over the whole test can reach values up to tenths of A/cm^2 .

The corrosion potential clearly indicates a non-noble material behavior. Furthermore, the curve's shape of the anodic branch confirms the absence of any tendency toward stable or evident passivity, underscoring the material's active corrosion state. This active behavior was corroborated by post-test visual inspection, which revealed a surface

uniformly covered by dark corrosion products, the accumulation which confirms the absence of a stable passive film during the experimental procedure. In fact, in acidic electrolytes, stainless steels with relatively low Cr concentrations undergo rapid uniform or quasi-uniform corrosion, as Cr oxides are thermodynamically unstable at low pH values.

3.1.3. Potentiodynamic polarization in 3.5 wt% NaCl solution

Potentiodynamic test in 3.5% NaCl solution was performed on the bulk (i.e., the bare, oxide-free cross-section) of the as-rolled material, as described in Section 2.2. The resulting potentiodynamic curve is shown in Fig. 7 and the cathodic reaction taking place in this test configuration is the reduction of oxygen. The measured corrosion potential coupled with the current density values suggests an intermediate situation: it is neither low enough to indicate completely active behavior nor high enough to classify the material as stably passive. For instance, under identical solution and scan rate conditions, a material with known superior wet corrosion resistance, such as AISI 316 L stainless steel, typically exhibits an E_{corr} ranging between -100 and -200 mV Ag/AgCl [11]. In light of this evidence, the measured E_{corr} leads to hypothesize the presence of an unstable passive layer. This is supported by the immediate breakdown observed upon reaching anodic polarization, followed by a continuous current increase.

Furthermore, the relatively low current density values suggest an initial tendency toward passivity, but the observed electrochemical

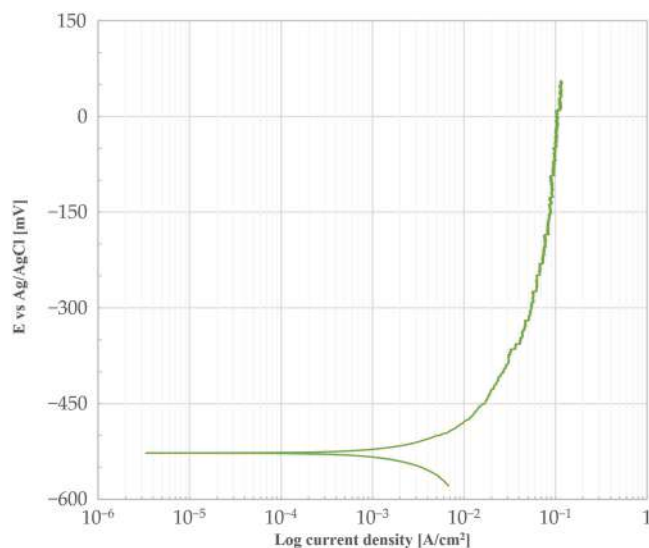


Fig. 6. Potentiodynamic polarization curve of the AISI 430 F* sample's bulk in 0.5 M H_2SO_4 (as-rolled condition).

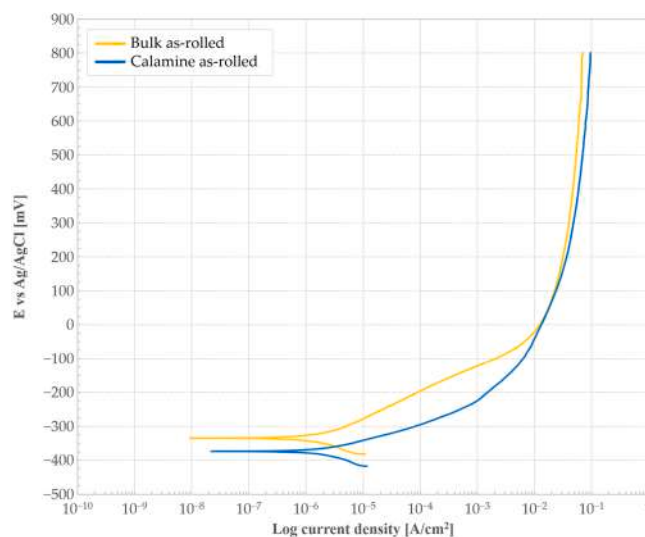


Fig. 7. Potentiodynamic polarization curve of the AISI 430 F* sample's bulk and external surface (i.e., calamine) in 3.5 wt% NaCl solution in the as-rolled condition.

response is indicative of a breakdown phenomenon. This seemingly contradictory behavior is characteristic of materials prone to localized corrosion attack. Examination of the cross-sectional surface after testing definitively confirmed the localized nature of the corrosion attack. Specifically, as shown in Fig. 8, obtained by optical microscopy, the cross-sectional surface (i.e., the bulk) is characterized by localized attack (i.e., pitting) displaying an apparently cavernous morphology. The pits are located at various points on the sample's surface, appearing both isolated (Fig. 8a and Fig. 8b) and in colonies (Fig. 8c). Furthermore, areas exhibiting orange corrosion products, most likely consisting of Fe oxides, are also present (Fig. 8a). The corrosion phenomenon observed on the surface following the potentiodynamic test (Fig. 8) was further investigated using scanning electron microscopy. Specifically, Fig. 9 presents the backscattered electron micrograph alongside the corresponding EDXS elemental maps for S and Mn.

As evidenced in Fig. 9, the corrosion phenomenon seems to exhibit a nucleation mechanism specifically localized at the MnS inclusions. The literature documents a dual behavior for MnS inclusions as a function of the inherent corrosion behavior of the alloy matrix [13,17,18]. In fact, in both C steels and steels exhibiting weak passivity, MnS acts as a pitting initiator because it is cathodic relative to the matrix, thus stimulating attack immediately in correspondence of the sulfide. Additionally, the presence of interfacial voids between the sulfide and the alloy matrix can further promote a crevice corrosion mechanism [13].

In contrast to its behavior in active alloys or those exhibiting weak passivity, MnS is documented to behave anodically in austenitic stainless steels (e.g., AISI 304). This phenomenon induces the preferential dissolution of the sulfide, which subsequently promotes the onset of pitting corrosion and leaves behind characteristic cavities at the inclusion sites [13,17,18].

In light of the evidence presented in Fig. 9 and in Fig. 10, it is reasonable to conclude that the MnS inclusions exhibit active electrochemical behavior relative to the alloy matrix, thus acting as local anodes. This process establishes a galvanic cell that initially localizes the anodic reaction effectively on the sulfide. Subsequently, following the partial dissolution of the inclusion, the anodic reaction transfers to the material beneath the sulfide, ultimately leading to the formation of a cavity, as evidenced in Fig. 10. Significantly, no evidence of a Cr-depleted zone was observed around the MnS. This finding effectively rules out a sensitization-like mechanism, confirming that the corrosion is not driven by Cr depletion from carbide formation (see Cr and Fe elemental maps in Fig. 10). The internal pit morphology is noteworthy, showing undissolved material that retains a characteristic filiform (thread-like) shape.

Consistent with the methodology detailed in Section 2.2, the electrochemical response of the as-rolled external surface was evaluated via potentiodynamic polarization tests. These measurements were performed on the lateral faces of the hexagonal specimens immersed in a 3.5 wt% NaCl solution. In this context, it is also essential to consider the oxide layer inherently present on hot-rolled products. This compact, high-temperature-formed layer is primarily composed of magnetite

(Fe_3O_4) and is industrially designated as mill scale (or *calamine*) [10]. This work also aims to assess the performance of this oxide layer in the context of corrosion, specifically to determine whether or not it possess protective capacity. The potentiodynamic test results are presented in Fig. 7. Alongside the bulk test results, to provide a direct comparison between the electrochemical behavior of the two different sample regions.

The shape of the potentiodynamic curve for the mill scale suggests active corrosion behavior with a clear absence of stable passivity. Compared to the bulk material, the anodic branch exhibits a different trend up to approximately -100 mV. The measured E_{corr} values suggest inferior corrosion resistance of the calamine relative to the bulk. The low current density values could mask a complex, localized corrosion mechanism. In fact, the presence of inherent discontinuities of the mill scale suggest that the current density could locally be much higher. The resulting attack is highly localized at defects within the mill scale, possibly leading to the spalling of oxide fragments. This degradation is likely compounded by the initiation of crevice corrosion at the interface between the bulk material (which behavior has been previously described) and the highly adherent mill scale. Based on the experimental results, the mill scale layer does not appear to offer any protective capabilities under the specified test conditions. This conclusion is visually confirmed by the images presented in Fig. 11. Fig. 11a displays the sample surface after the potentiodynamic test, characterized by corrosive attack, detached mill scale fragments and stains of Fe-based corrosion products. A distinct striped pattern, oriented longitudinally and resulting from the turned rolls, is evident. This pattern introduced surface irregularities that likely acted as preferential nucleation sites for the corrosive attack and the formation of corrosion products, and likely accelerated the spalling of the corrosion products themselves. The rolls pattern was inherited by the mill scale and subsequently reproduced on the corrosion products, illustrating the strong influence of the initial surface topography. SEM analysis of the surface (Fig. 11b) reveals a fibrous morphology in the corrosion products, which replicates the stripped pattern inherited from the hot rolling process. These products are primarily composed of Fe oxide, as evidenced by Fig. 11c and Fig. 11d. Furthermore, the irregularity of the underlying substrate influences the subsequent growth, resulting in irregular corrosion products that tend to fragment due to the associated increase in volume upon their formation.

3.2. Heat-treated condition

As described in Section 2.2, the chosen laboratory heat treatment was specifically designed to replicate the industrial procedure used to achieve optimal mechanical and magnetic properties in the tested material. A further objective of the thermal treatment was the intentional modification of the specimen's lateral surface state to study the evolution of the outer mill scale and evaluate its subsequent impact on corrosion resistance.

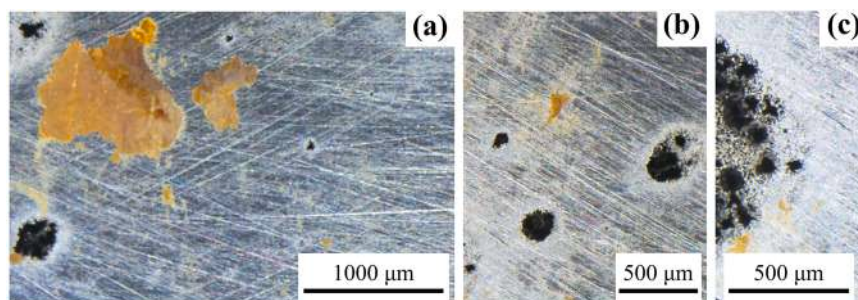


Fig. 8. AISI 430 F* sample's bulk in the as-rolled condition after potentiodynamic polarization in 3.5 wt% NaCl solution; a) isolated pitting corrosion and Fe-based oxides; b) isolated pitting corrosion; c) pits' colonies.



Fig. 9. Backscattered electrons SEM micrograph and EDXS S and Mn elemental mapping of the AISI 430 F* sample's bulk in the as-rolled condition after potentiodynamic polarization in 3.5 wt% NaCl solution.

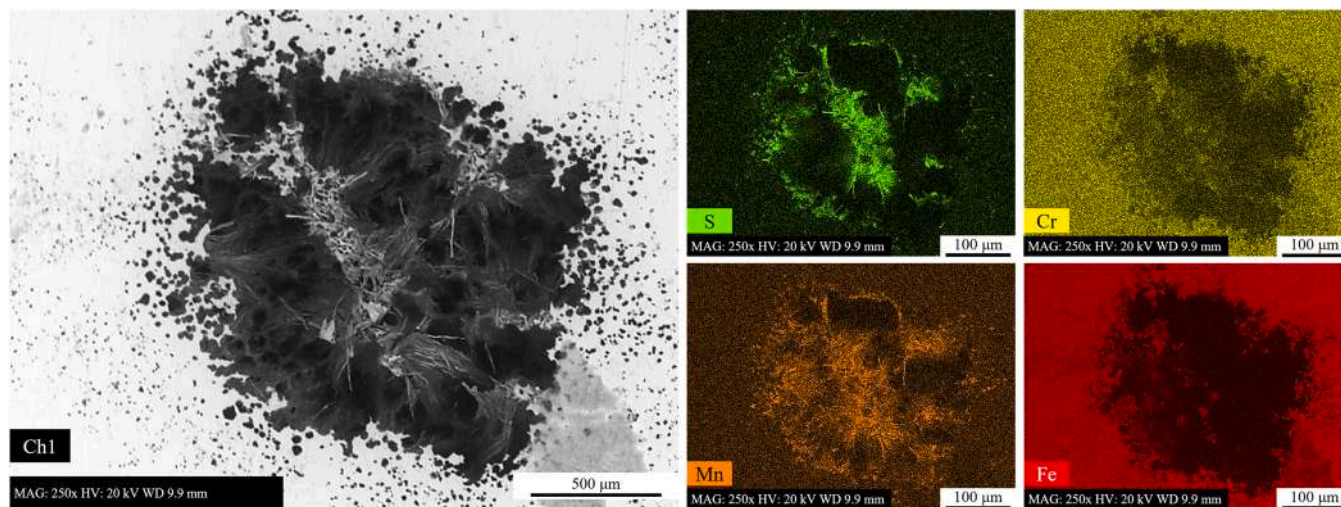


Fig. 10. Backscattered electrons SEM micrograph and EDXS S, Cr, Mn, and Fe elemental mapping of a single pit found on the AISI 430 F* sample's bulk in the as-rolled condition after potentiodynamic polarization in 3.5 wt% NaCl solution.

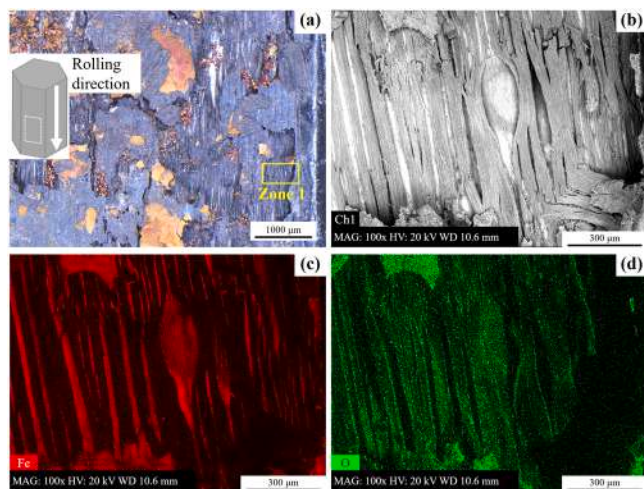


Fig. 11. Analysis of the sample's external surface (i.e., mill scale) after potentiodynamic polarization in 3.5 wt% NaCl solution; a) External surface of the sample observed through stereomicroscopy together with schematic representation of the analyzed area with respect to the rolling direction; b) Backscattered electrons SEM micrograph of zone 1; c) EDXS Fe elemental mapping of zone 1; d) EDXS O elemental mapping of zone 1.

3.2.1. Microstructure

The bulk region of the heat-treated samples (i.e., the bare, oxide-free cross-section) was polished and etched using Kalling No. 2 reagent. The

resulting ferritic microstructure, shown in Fig. 12, exhibits slightly coarser grains compared with the as-rolled condition presented in Fig. 4. The sulfides are characterized by a more rounded morphology, a condition consistent with spheroidization resulting from prolonged exposure to the high temperatures of the heat treatment stage. The maximum size of the sulfides was observed to be consistent with the pre-treatment condition, measuring approximately 10 μm in the heat-treated sample.

Consistent with the protocol used for the as-rolled condition, a backscattered electron SEM micrograph of the heat-treated sample's cross-section was acquired following polishing and prior to chemical etching (Fig. 13). The EDXS Cr map in Fig. 13 exhibits a slight increase in elemental heterogeneity compared to that of the as-rolled condition, which appeared more uniform in the signal distribution. Furthermore, the point analysis detailed in Table 3, performed on three distinct sulfide inclusions, reveals an elevated Cr concentration in these samples relative to the as-rolled state. This observation is consistent with a thermally induced enrichment of Cr within the sulfides resulting from the heat treatment. Furthermore, the experimental analyses did not reveal the presence of Cr carbides. Although predicted by the thermodynamic equilibrium modeling (Section 3.1.1), these phases remained below the detection limit. This observation aligns with the low C content of this steel, which is specifically designed to suppress carbide precipitation as a consequence of high-temperature thermal cycles.

Finally, the compositional data obtained from the matrix analysis are entirely consistent with those observed in the as-rolled condition.

3.2.2. Potentiodynamic polarization in H₂SO₄ 0.5 M solution

Consistently with the testing procedure for the as-rolled material (Section 2.2), the oxide-free cross-section of the heat-treated samples (i.

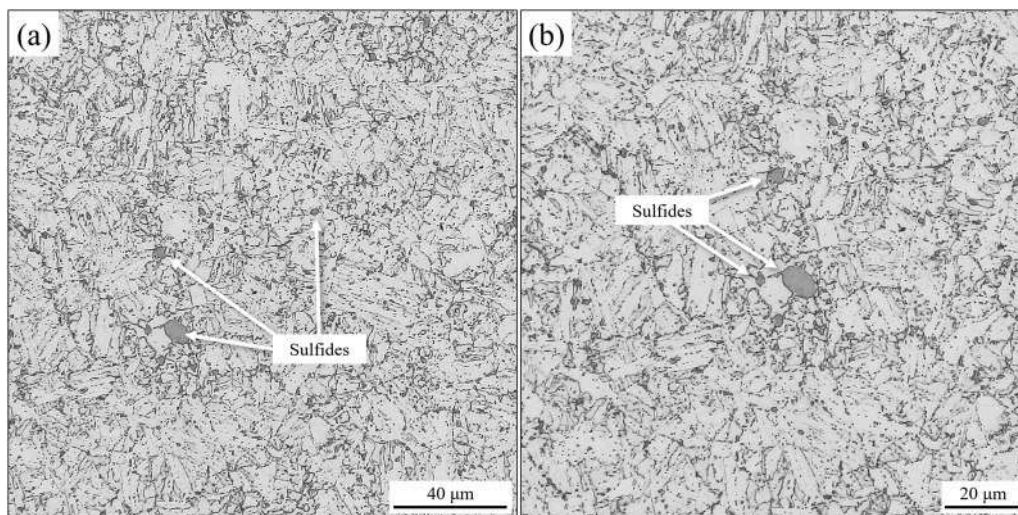


Fig. 12. a) Optical micrograph of the AISI 430 F* sample's cross-section, etched with Kalling No.2 reagent in the heat-treated condition; b) Higher magnification optical micrograph of the same sample, etched with Kalling No.2 reagent.

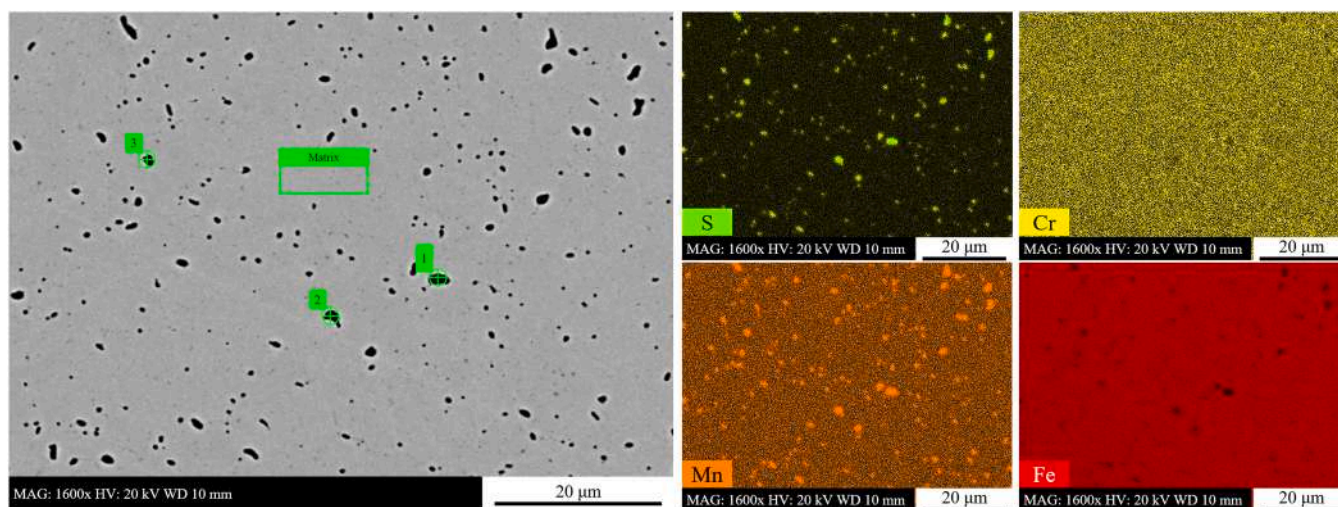


Fig. 13. Backscattered electrons SEM micrograph of AISI 430 F* sample's cross-section in the heat-treated condition after polishing and EDXS point and area analysis along with S, Cr, Mn, and Fe elemental mapping.

Table 3

Summary of the SEM – EDXS analysis results given Fig. 13.

Spectrum	Cr	Mn	S	Si	Fe
1	12.24	25.84	37.58	0.50	23.84
2	13.11	39.25	32.12	0.26	15.26
3	11.03	41.59	27.05	0.13	20.20
Matrix	12.27	0.75	0.06	0.51	86.41

e., the bulk was subjected to potentiodynamic test in 0.5 M H₂SO₄ solution. The resulting potentiodynamic curve is presented in Fig. 14. The measured corrosion potential E_{corr} was -523 mV Ag/AgCl. Examination of the curve reveals that the current densities over the whole test can reach values up to tenths of A/cm². The corrosion potential values indicate a non-noble material behavior. Additionally, the active behavior was visually confirmed by the sample's surface, which was found to be completely covered with dark corrosion products after testing, in agreement with the mechanism previously stated in Section 3.2.1.

The data from the plot in Fig. 12 confirm that the material's behavior can be defined as active, as no discernible transition to a passive regime

can be detected. However, a noticeable shift in current density toward higher values occurs at approximately -270 mV. This electrochemical response could be indicative of a mechanism likely attributable to the accumulation of generalized corrosion products across the specimen surface. This behavior is likely traced back to a two-stage process: in the initial phase of the anodic polarization, the generalized corrosion products may have hindered the corrosive phenomenon with a pseudo-protective behavior. The subsequent sharp current density increases at approximately -270 mV could be traced back to a potential-induced breakdown of this layer, thus resulting in the rapid and direct attack on the underlying metal substrate by the corrosive solution. This hypothesis seems to be supported by the direct comparison with the curve of the as-rolled material, as shown in Fig. 12. On one hand, in both conditions, the material shows an active behavior. On the other hand, the heat-treated microstructure is characterized by a lower anodic current density, demonstrating an improved capacity to resist corrosive process in a strongly oxidizing environment, despite the absence of evident passivity. In any case, the material's performance indicates it is not suitable for deployment in corrosive environments. Although classified as a stainless steel, the material remains unsuitable for use in corrosive environments. This deficiency is plausibly linked to its

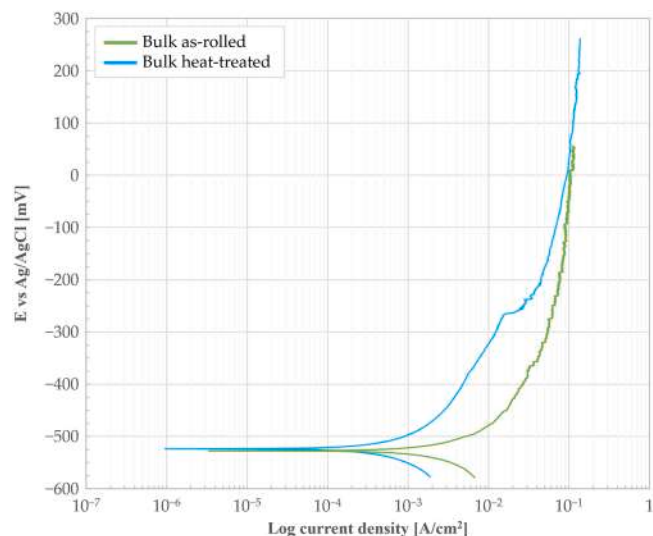


Fig. 14. Potentiodynamic polarization curve of the AISI 430 F* sample's bulk in both the as-rolled and heat-treated condition in 0.5 M H_2SO_4 .

unfavorable chemical composition, specifically the lower level of Cr and the higher S concentration with respect to standard AISI 430 F [14].

3.2.3. Potentiodynamic polarization in 3.5 wt%NaCl solution

Maintaining consistency with the testing of the as-rolled material, the heat-treated material was electrochemically evaluated using potentiodynamic testing in 3.5 wt% NaCl solution. Fig. 15 shows the test result related to both the bulk and the external surface of the sample (i. e., calamine).

The measured corrosion potential E_{corr} was -469 mV Ag/AgCl. The material's electrochemical response suggests an active behavior with no evidence of stable passivity being developed. The results, when compared to the as-rolled bulk data in Fig. 7, show that the heat treatment apparently adversely affected the material's performance. In particular, a shift to a more negative E_{corr} happened, suggesting a non-negligible reduction in the overall corrosion resistance. This result is not entirely unexpected. A comparison between the as-rolled (Fig. 4) and heat-treated (Fig. 12) microstructures suggests that the coarser and more jagged grains in the latter case may have adversely affected

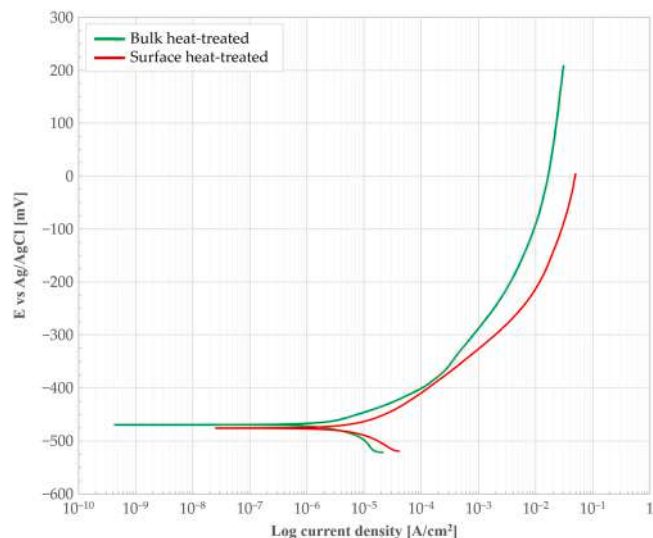


Fig. 15. Potentiodynamic polarization curve of AISI 430 F* sample's bulk and external surface (i.e., calamine) in the heat-treated condition in 3.5 wt% NaCl solution.

corrosion resistance. Furthermore, the change detected in the chemical composition of Mn sulfides may have also contributed. This last statement refers to the fact that Mn sulfides in resulfurized stainless steels may also contain a certain amount of Cr depending on the Mn/S ratio. Given that the Mn/S ratio for the material under investigation is 2.35, the MnS sulfides in this steel may contain Cr, potentially leading to the coexistence of Cr_5S_6 (as explained in [13]). This statement is supported by literature evidences indicating that, in ferritic stainless steels, increasing the annealing temperature results in a corresponding Cr enrichment in the MnS at the expense of Mn. Compositional variations in the MnS inclusions could also carry significant implications for the corrosion behavior. Specifically, Cr enrichment of the sulfide leads it to become more noble. This leads to the possibility for the sulfide to show cathodic behavior during electrochemical processes involving the inclusion and the steel matrix. Furthermore, it has been observed that increasing the annealing temperature leads to greater Cr enrichment and an increased tendency for the MnS to exhibit cathodic behavior [19].

The heat treatment may have thus promoted localized Cr migration from the metal matrix to the Cr-containing sulfides, as highlighted by the SEM EDXS results given in Table 3. This microstructural change likely acted synergistically with the grain evolution, resulting in the observed decrease in corrosion resistance. The just mentioned increased susceptibility to corrosion is substantiated by the appearance of the bulk surface after testing (Fig. 16a).

The surface appears attacked, featuring cavernous localized pitting that shows more numerous and widespread initiation points. Furthermore, a fair number of brown spots, likely Fe-based oxides, are observed across the surface. Examination of Fig. 16a reveals a heterogeneous pitting attack, contrasting with the surface in Fig. 8. At least three pit conditions are evident: zone 1, which shows pitting similar to the as-rolled condition and is devoid of significant Fe oxide traces; zone 2, characterized by circular cavities bordered by corrosion products; and a third type (zone 3), featuring irregular cavities encased by a heavy, cracked corrosion product.

The backscattered electron micrograph in Fig. 16b and the EDXS elemental mapping (Figs. 16c, 16d, and 16e) for zone 1 show features comparable to the as-rolled sample (Fig. 9). However, the special distribution of Mn and S signals suggests a difference: the MnS inclusions encircle the pit perimeter, as opposed to being situated inside the pit as observed in the as-rolled condition (Fig. 9 and Fig. 10). Given the preceding observation regarding sulfide composition in terms of Cr-Mn balance and increased Cr content in the sulfides detected in the bulk of the heat-treated samples, the spatial relationship (i.e., pit circumscribed by the MnS inclusions) seems to point toward an intensified cathodic role of the sulfide itself. This shift in the sulfide-matrix cell behavior could be traced back to the combination of altered microstructure and sulfide composition resulting from the heat treatment and is also sustained by the increased current density values associated to the heat-treated bulk with respect to the as-rolled condition. Fig. 17 shows a characteristic pit from zone 2 (Fig. 16a) exhibiting a circular morphology with preferential penetration localized at a single point. The pit is surrounded by corrosion products primarily based on Fe oxide, as evidenced by the Fe and O signals in the corresponding EDXS maps. A comparative analysis of the Fe and S signals suggests that the dissolution reaction occurred primarily surrounding the MnS inclusions, rather than being centered on the MnS inclusions themselves. This finding supports the interpretation of the MnS acting as a local cathode, driving anodic dissolution in the adjacent matrix. Finally, Fig. 18 illustrates the highly specific morphology detected in zone 3 (Fig. 16a). The backscattered electron image highlights a deeply penetrating and cavernous pit that is significantly more irregular in shape compared to those observed in zone 1 and zone 2. A particularly noteworthy feature is the residual material above the cavity, which appears porous in nature and suspended above the pit, likely anchored by the surrounding ring of corrosion products. This ring itself appears raised and cracked, a feature that is likely the result of a combination between growth-related volume increase during

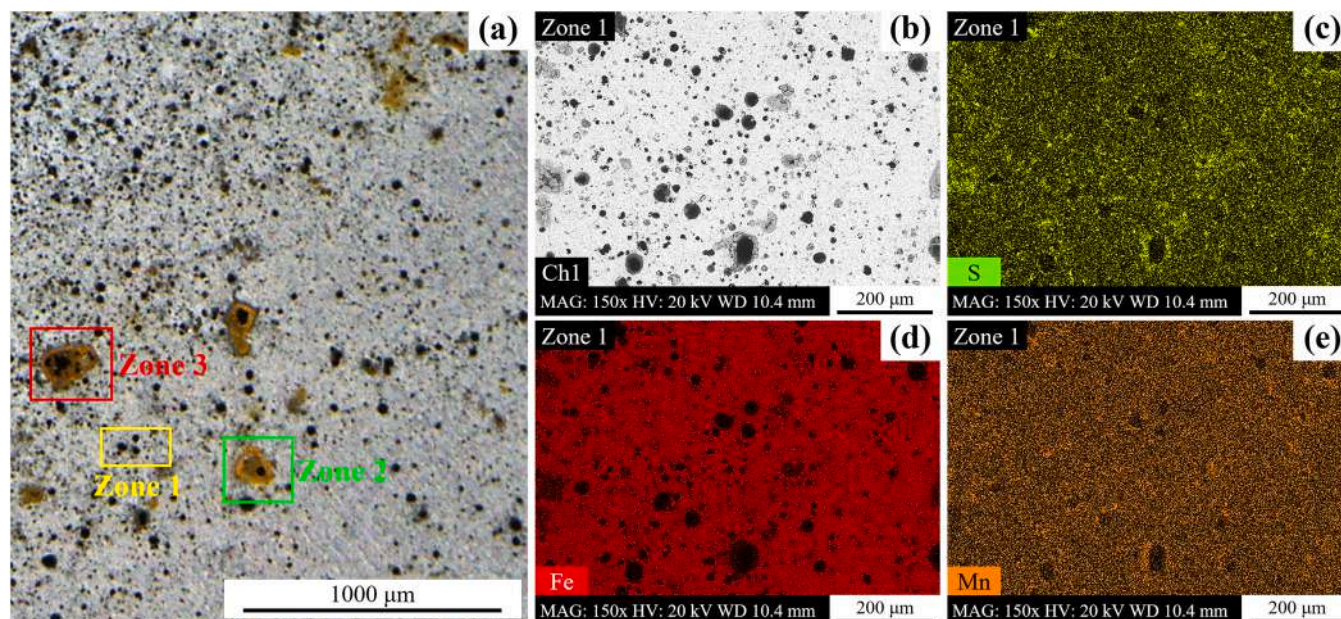


Fig. 16. Analysis of the heat-treated AISI 430 F* sample's bulk after potentiodynamic polarization in 3.5 wt% NaCl solution; a) Stereomicroscopy observation of the aspect of the cross-sectional surface of the sample; b) Backscattered electrons SEM micrograph of zone 1; c) EDXS S elemental mapping of zone 1; d) EDXS Fe elemental mapping of zone 1; e) EDXS Mn elemental mapping of zone 1.

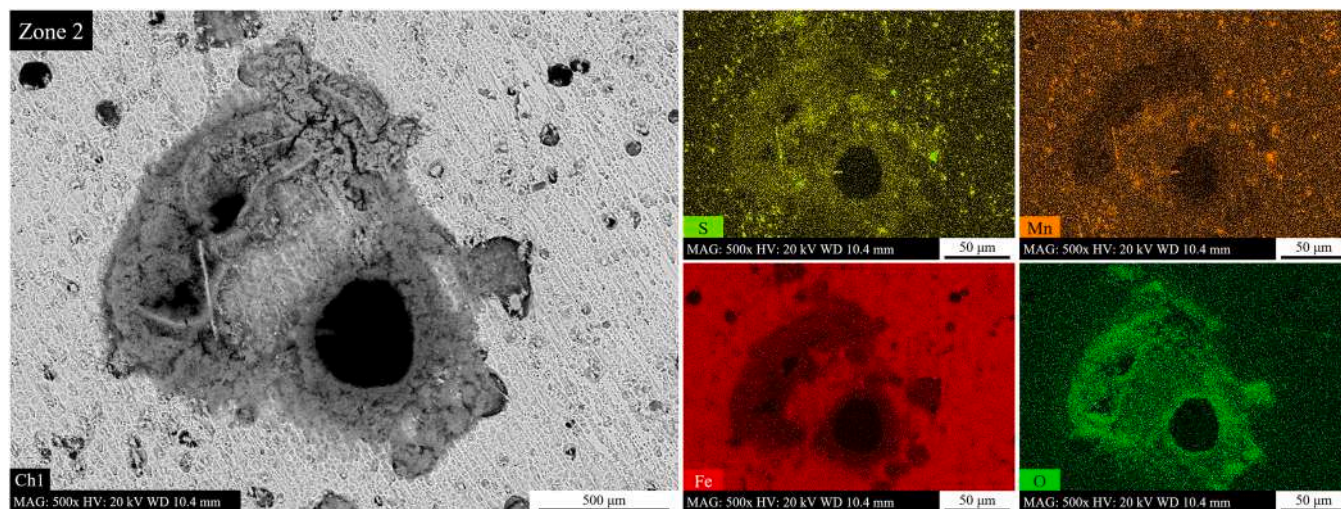


Fig. 17. Backscattered electrons SEM micrograph and EDXS S, Mn, Fe and O elemental mapping of a single pit (zone 2 in Fig. 16) found on the AISI 430 F* sample's bulk in the heat-treated condition after potentiodynamic polarization in 3.5 wt% NaCl solution.

oxide formation and dehydration shrinkage that occurred after the potentiodynamic test. The EDXS mapping of Fe, O, and S confirms that the corrosion products are predominantly Fe oxides. This analysis also highlighted the localization of the MnS, which is observed to circumscribe the pit perimeter instead of being centrally located within the cavity, contrasting the morphology displayed in Fig. 10.

The lateral surface of the sample showed in Fig. 19 (i.e., oxide layer formed during the thermal treatment stage) was characterized by regions with distinct color variations. The original mill scale layer featured a darker gray color, apparently better adhesion and a glossier appearance. After heat treating, the resulting surface oxide layer exhibited a different morphology, presenting as a light gray, opaque layer with apparently reduced adhesion. Visual evidence supporting this interpretation is provided by the secondary electron micrograph in Fig. 19c, which highlights the more granular and porous structure of the surface.

The predominant surface layer can be categorized as a thermally

induced modification of the original mill scale (calamine). However, the presence of brown regions (Fig. 19a) suggests the formation of oxides with different compositions, likely arising from varying oxidation states of Fe. These are deemed secondary oxides that have formed either in areas where the original mill scale layer was jeopardized, or directly on top of the existing, thermally-evolved layer. Furthermore, the surface topography still displays a horizontal, striped pattern, which is consistent with the rolling direction (Fig. 19a and Fig. 19b).

After heat treatment, the sample was tested in 3.5 wt% NaCl solution to evaluate the corrosion response of the lateral surface, specifically targeting the oxide layer formed during the heat treatment. As shown by the red curve in Fig. 15, the potentiodynamic test indicates an active behavior of the material. The corrosion potential E_{corr} value was -476 mV Ag/AgCl. The comparison between the curves obtained from the bulk and the external surface in Fig. 15 clearly shows the non-protective nature of the oxide evolved on the external surface of the

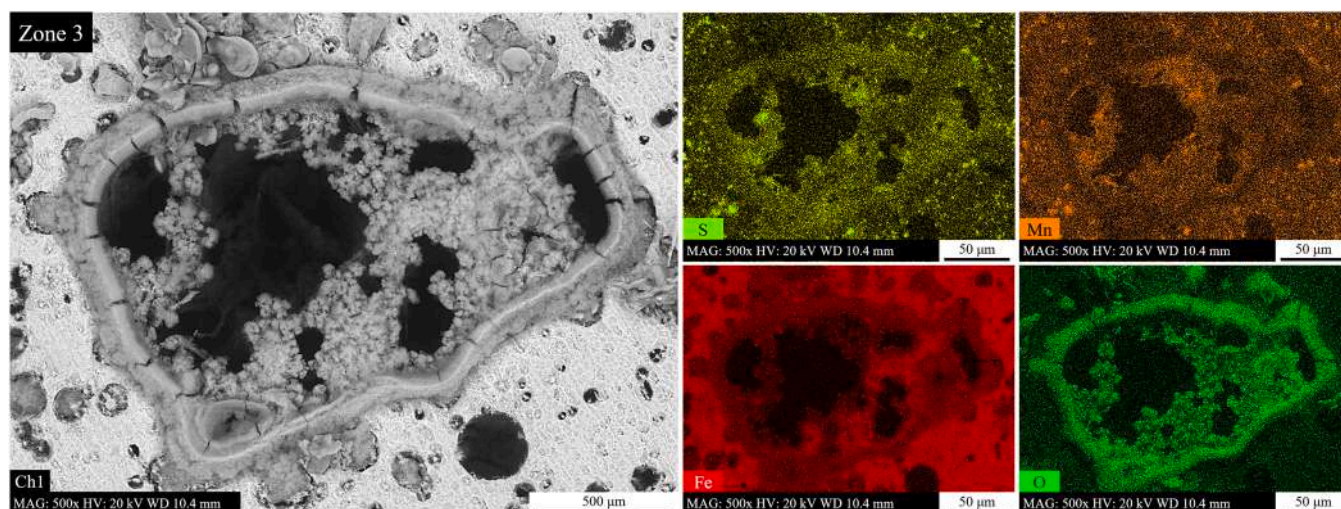


Fig. 18. Backscattered electrons SEM micrograph and EDXS S, Mn, Fe and O elemental mapping of a single pit (zone 3 in Fig. 16) found on the AISI 430 F* sample's bulk in the heat-treated condition after potentiodynamic polarization in 3.5 wt% NaCl solution.

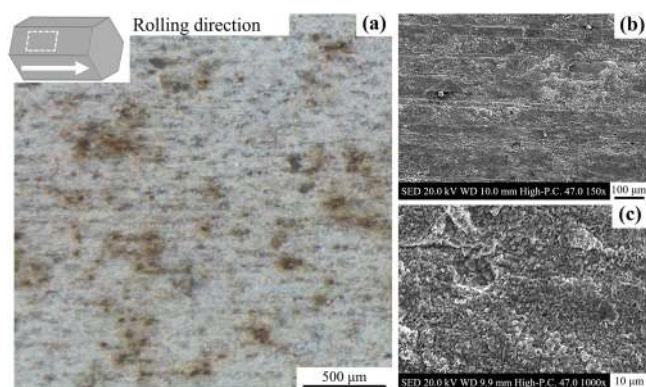


Fig. 19. Analysis of the AISI 430 F* sample's surface (i.e., mill scale) after heat treatment; a) Stereomicroscopy of sample's surface; b) Secondary electrons SEM micrograph of the surface; c) Secondary electrons SEM micrograph of the surface at higher magnification.

specimen. Taken together, the findings substantiate that the heat treatment process negatively impacted the material's performance, leading to reduced corrosion resistance when compared to the as-rolled condition. The comparison between the surface after heat treatment (Fig. 19) and the surface post-potentiodynamic test (Fig. 20) highlights a morphological evolution on the sample surface, indicating the effects of the electrochemical process. As illustrated in Fig. 20a, the surface exhibits localized damage, alternating between regions where the oxide formed during thermal treatment remained intact (zone 1) and areas where the oxide was damaged or spalled off (zone 2), resulting in the exposure of the substrate. Regarding the regions of intact oxide (zone 1), the potentiodynamic test appears to have had no significant effect on the surface characteristics. The comparison between the surface morphology before (Fig. 19c) and after (Fig. 20b) the test reveals no substantial differences. In areas where the oxide layer has been damaged, thereby exposing the substrate (Fig. 20, zone 2), thread-like corrosion products are clearly evident (Fig. 20c and Fig. 20d). EDXS elemental mapping of these raised products showed that they should be essentially Mn- and S-based, forming on top of an Fe oxide surface.

3.3. Results' summary and comparison

The experimental work carried out according to the procedure

described in Section 2 yielded a substantial amount of data relevant to the interpretation of the material's electrochemical behavior. A comprehensive summary of the quantitative results is provided in Table 4. Concerning the bulk material's response to potentiodynamic tests in H_2SO_4 0.5 M solution, Fig. 14 highlights non-negligible differences when comparing the as-rolled and heat-treated conditions. The material fails to achieve stable passivity in both conditions. Nevertheless, the thermal treatment appeared to have a positive influence, resulting in a reduction in the anodic current density value. This occurred in the absence of any obvious passivity. It would appear that the heat treatment changed the microstructure in such a way to allow the material to develop a layer of generalized corrosion products capable of mitigating the corrosive process up to a certain potential (approximately -270 mV), beyond which a potential-induced breakdown occurred.

The results of the potentiodynamic tests conducted on the bulk in 3.5 wt% NaCl solution clearly indicate that the material is unsuitable for use in environments containing chlorides. As reported in Fig. 7 and Fig. 15, the curves show no evidence of a stable passivity region. This finding is further corroborated by the superimposition of the potentiodynamic polarization curves for both experimental conditions, as illustrated in Fig. 21. Furthermore, the heat treatment does not appear to have conferred any positive effects on the material's behavior. Specifically, a comparative analysis of Fig. 21 and the data compiled in Table 4 shows that the corrosion potential shifts to more active values for the heat-treated condition, i.e. a decrease of more than 100 mV. This highlights that the thermal cycle typically employed is more geared toward improving magnetic properties than corrosion resistance, unlike what is observed in other stainless steels (e.g., austenitic). In fact, in addition to optimizing the microstructure and mechanical properties, heat treatment applied to austenitic stainless steels serves the crucial function of maximizing corrosion resistance [20].

The electrochemical behavior of MnS inclusions appears to change between the as-rolled and the thermal-treated condition. Consistent with observations in austenitic stainless steels, MnS exhibits anodic behavior in the as-rolled condition [13,17,18]. This promotes its dissolution and the onset of pitting corrosion as depicted by Fig. 10. After heat treatment, however, its behavior appears to shift to cathodic due to a compositional change within the inclusion itself, as indicated by the data in Table 2 and Table 3. Specifically, the heat treatment seems to promote the incorporation of Cr into the sulfide, which promotes a passive character. This change in nobility is considered to be responsible for the subsequent localization of the anodic process in the surrounding

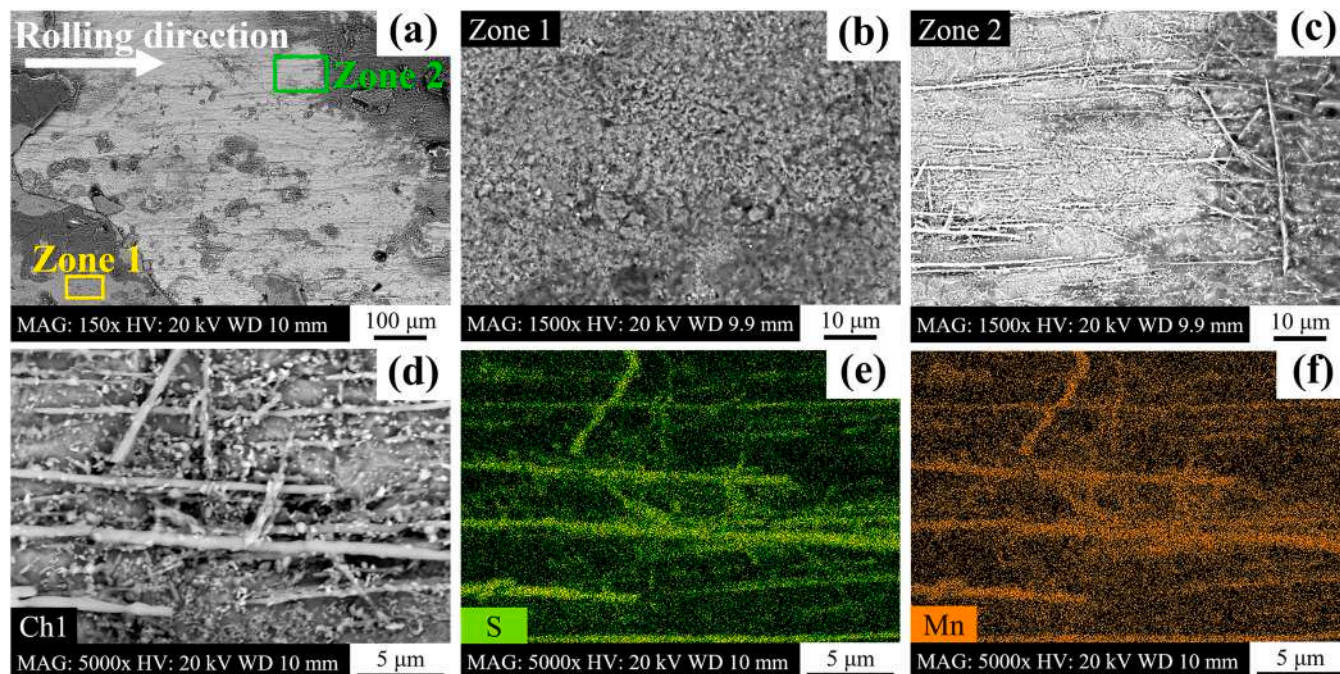


Fig. 20. Backscattered electrons SEM micrograph of the AISI 430 F* sample's surface (i.e., mill scale) in the heat-treated condition after potentiodynamic polarization in 3.5 wt% NaCl solution and EDXS elemental maps; a) Sample surface showing areas with intact oxide (zone 1) and areas with damaged and spalled oxide exposing the substrate (zone 2); b) Zone 1 where intact oxide was observed; c) Backscattered electrons SEM micrograph of zone 2; d) Backscattered electrons SEM micrograph of zone 2 at higher magnification; e) EDXS S elemental mapping; f) EDXS Mn elemental mapping.

Table 4

Summary of the results obtained from the potentiodynamic experimental activities.

Solution	Condition	Testing region	E_{corr} vs Ag/AgCl [mV]
H ₂ SO ₄ 0.5 M	As-rolled	Bulk	-528
	Heat-treated	Bulk	-523
3.5 wt% NaCl	As-rolled	Bulk	-335
	As-rolled	Surface	-374
	Heat-treated	Bulk	-469
	Heat-treated	Surface	-476

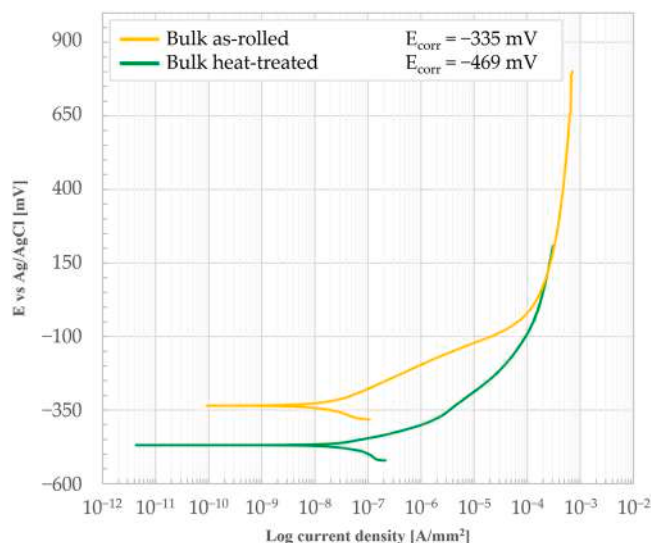


Fig. 21. Potentiodynamic polarization curve of AISI 430 F* sample's bulk in both the as-rolled and heat-treated condition in 3.5 wt% NaCl solution.

steel matrix (see Fig. 16, Fig. 17 and Fig. 18), rather than at the sulfide inclusion site [13,19].

Finally, the analysis of the sample's lateral surface response also yielded interesting results. Although mill scale (calamine) is sometimes regarded in industrial practice as an adherent oxide layer with potential barrier properties, it exhibited negligible protective efficacy under the specific experimental conditions investigated. In fact, calamine was ineffective in preventing corrosion, failing to offer a protective barrier comparable to a passive film. The thermal treatment, conducted within an uncontrolled oxidizing atmosphere, induced profound transformations in the surface layer, which were macroscopically evident through a distinct change in the specimen's optical appearance. The results shown in Fig. 15 and Fig. 20 unequivocally demonstrated that this new surface condition is not protective. Consequently, the oxide scale generated during thermal treatment offers negligible protection against corrosion in humid and, more critically, chloride-rich environments. Rather than serving as a barrier, the morphological and electrochemical characteristics of this thermally evolved layer suggest that it actively facilitates the corrosive degradation of the underlying substrate.

As a result of these findings, the industrial practice of storing the material indoors and minimizing its proximity to aggressive agents can certainly limit surface deterioration. However, preventing corrosion entirely is difficult unless the atmosphere is non-aggressive or environmentally controlled. For semifinished products, such as wire and wire-rod coils, optimizing the lead time between heat treatment and pickling is surely industrially advantageous. Minimizing this interval mitigates the accumulation of corrosion products, thereby reducing sludge formation and sediment buildup within the pickling baths. In the context of the pickling operation, the analyses carried out have demonstrated that the primary corrosion products requiring removal are Fe oxides. This finding is of significant interest for the management of the pickling baths and the resulting sludge disposal, particularly when designing the optimal pickling sequence for processes involving multiple material substrates.

4. Conclusion

The comprehensive experimental campaign, involving microstructural characterization, potentiodynamic polarization testing, and post-test surface analysis, provided critical insights into the corrosion behavior of modified AISI 430 F stainless steel in both the as-rolled and heat-treated conditions. Based on the experimental findings and the analytical framework established in this study, the following primary conclusions can be drawn:

- Testing the material in H₂SO₄ revealed that AISI 430 F* modified stainless steel is unable to develop stable passive behavior in both tested conditions. Slightly better behavior seems to characterize the heat-treated condition.
- Tests carried out in 3.5 wt% NaCl solutions showed that the bulk is characterized by active behavior with the development of pitting corrosion.
- The observed microstructural modifications resulting from the heat treatment appear to induce a detrimental effect on the inherent material's corrosion resistance.
- Calamine (i.e., the oxide scale or mill scale) lacks protective characteristics, either when immersed in the NaCl-based electrolyte or during exposure to the elevated temperatures applied in the laboratory-simulated thermal treatment cycle.
- The oxide layer formed post-heat treatment and developed atop the pre-existing calamine, exhibited the lowest corrosion resistance among all investigated test conditions.
- The electrochemical behavior of the MnS phase appears to shift from anodic in the as-rolled state to cathodic following the heat treatment. This transition can be directly correlated with the measured increase in Cr concentration within the sulfide inclusions of the heat-treated material.
- Regarding the steel grade under investigation, the corrosion products targeted for elimination during the pickling process are predominantly composed of Fe-based oxides.
- In future investigations targeting this material, quantification of inclusion size and distribution, area fraction, and pit density could be employed to increase the data available for AISI 430 F*. Furthermore, deploying complementary surface-sensitive and structural characterization techniques (e.g., XPS, Raman spectroscopy, or XRD) would provide deeper insights into the underlying mechanisms.

Abbreviations

BED	Backscattered electrons detection mode
CE	Couter-electrode
EDXS	Energy-dispersive X-ray Spectroscopy
PH	Precipitation hardening
PH	Precipitation hardening
RE	Reference electrode
SED	Secondary electrons detection mode
SEM	Scanning electron microscopy or microscope
TGA	Thermogravimetric analysis
WE	Working electrode
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

CRediT authorship contribution statement

Alessio Malandrucolo: Writing – review & editing, Writing – original draft, Validation, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Stefano Rossi:** Writing – original draft, Validation, Supervision, Project administration, Methodology, Formal analysis. **Cinzia Menapace:** Writing – original draft, Validation, Supervision, Project administration, Methodology, Formal analysis.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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Data availability

Data will be made available on request.

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