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Additional Information

Degradation mechanisms in martensitic stainless steels: wear, corrosion and tribocorrosion appraisal

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Abstract

A deep understanding of degradation mechanisms of metals is crucial for developing new materials with high performance. Within the different families of stainless steels, martensitic stainless steels are widely used in a great variety of industrial applications where mechanical properties, such as strength, wear resistance and fatigue behavior, need to be high. In many of those applications, such as bearings or gears, martensitic stainless steels may be subject to tribological conditions leading to wear. Furthermore, when a contact operates in a corrosive environment its deterioration can be significantly affected by surface chemical phenomena, leading to a tribocorrosion degradation mechanism. Indeed, martensitic stainless steels degrade through a great variety of wear and corrosion mechanisms. This paper aims to review the published data from 2005 to present related to wear, corrosion and tribocorrosion of martensitic stainless steels. Individual studies of tribological and corrosion behavior of martensitic stainless steels have been widely published since 2005. From the wear point of view, ploughing or abrasive wear in dry contacts involving martensitic stainless steel has been reported, while pitting corrosion is the most common mechanism for those steels. However, only nine papers were found since 2005 related to tribocorrosion of martensitic stainless steels, although most authors concluded that this joint action is the most important material degradation in martensitic stainless steels.

Keywords: Martensitic stainless steels, wear, corrosion, tribocorrosion

1. Introduction

Stainless Steel can be defined as iron based alloys that contain a minimum of about 12 wt.% Cr, the amount needed to guarantee a high corrosion resistance by the formation of a passivating oxide film [1]. This amount of Cr needs to be dissolved within the metallic matrix in order to ensure passivation. While the Fe–Cr system forms the basis, modern stainless steels, besides Cr, also contain other alloying elements whose presence enhances specific properties (i.e. hardness, tensile strength, ductility, corrosion resistance etc...), such as nickel, manganese, molybdenum, copper, titanium, silicon, niobium, aluminum, sulfur, and selenium [2]. The hardness of the martensitic class is mainly determined by the carbon content, whereas hardenability is due to other alloying elements. Although the role of the alloying elements in stainless steels is complex, an overview is summarized below:

- Carbon (C): It increases the hardness and the strength of stainless steel by heat treatment. The content of this element is typically kept at low levels in stainless steels, except in the martensitic grades, in which the carbon level is deliberately increased to obtain higher specific properties (e.g. hardness) and to make these alloys heat treatable by quenching and tempering to develop the martensite phase. Carbon can have a detrimental effect on the corrosion resistance by combining with chromium to form chromium carbides and reducing the chromium availability in the metallic matrix to form the passive layer to ensure corrosion resistance [3]. In general, carbides have been widely studied by the research community, in which the $M_{23}C_6$ carbide (where M represents the metal) is the most common and extensively analyzed [4].

- Chromium (Cr): The passive film consists essentially of chromium in its trivalent state, forming a stable oxide Cr_2O_3 which shows a very low corrosion rate. In acidic solutions, the cationic fraction of Cr in the passive film has been reported to be around 50-70% [3]. For basic solutions, the solubility of Cr increases, resulting in a higher fraction of iron. Cr content in stainless steels thus increases the corrosion resistance and limits the propagation of stable pitting. Chromium oxide is the main component of the inner part of the passive film [5] while chromium hydroxide $Cr(OH)_3$ has been also found in the outer part of the passive film [6].

- Nickel (Ni): The presence of Ni stabilizes the austenitic structure and Ni acts on the deformation behavior of the material, improving the toughness at low temperature, promoting cross dislocation glide and/or causing solid solution softening [7]. Nickel is less oxidized than iron and chromium. Consequently, there is an enrichment of Ni in its metallic state in the metal closest to the oxide/metal interface [8] and it is, therefore, rarely detected in the passive film. Ni could also decrease the overall dissolution rates of Fe and Cr.

- Molybdenum (Mo): Molybdenum is an alloying element with a strong beneficial influence on the passive film stabilization and pitting resistance of stainless steels, especially in the presence of chloride ions. Mo can accelerate the passive film formation and can improve depassivation resistance [9]. It is incorporated into the passive film showing complex oxide chemistry with different oxidation states: Mo^{+4} in the inner part and M^{6+} in the outer part [8]. Different mechanisms have been proposed to explain the role of Mo in the

passivity of stainless steel (e.g. in neutral solution with Cl⁻ ions, Mo diminishes the adsorption of these ions on the passive film due to the formation of oxides of Mo^{+6} in the passive film which reduces Cl⁻ ion penetration [10,11]).

- Nitrogen (Ni): Nitrogen is an alloying element that stabilizes the austenite and has an important influence on passive film properties [12]. Nitrogen was reported to have the strongest influence on localized corrosion in the Pitting Resistance Equivalent Number formula (PREN) [8]. Different types of synergism with Mo have also been proposed. Nitrogen shows strong concentration gradients in the passive film. Ammonia or ammonium ions react with free chlorine to form combined species that are less effective oxidants, inhibiting chlorination enhanced localized corrosion [11]. Another possibility is the formation of a nitride at the metal/film interface that decreases the dissolution rates for the individual elements of the alloy [13,14]. Nickel, carbon, silicon and copper diminish the solubility of nitrogen, while chromium, manganese and molybdenum increase solubility.

- Other alloying elements: Recently, addition of manganese to stainless steels has been used to increase the solubility of nitrogen and molybdenum, both of which have a strong beneficial influence on pitting resistance [8]. Copper is added to highly corrosion resistant austenite to further boost the corrosion resistance and it is also used to give anti-bacterial properties to the surface [8]. Tungsten has only fairly recently been used as a major alloying element in commercial stainless steels. Tungsten has similar properties to those of molybdenum, but the stability of oxides in acidic solution is different [8]. Vanadium forms carbides and nitrides at lower temperatures, which increases hardness, and promotes ferrite in the microstructure.

Three main types of microstructures exist in stainless steels, i.e., ferritic, austenitic, and martensitic [2]. These microstructures can be obtained by properly adjusting the steel chemistry. Out of these three main microstructures, stainless steels may be categorized into several main classes [4]: (1) ferritic stainless steels, (2) austenitic stainless steels, (3) martensitic stainless steels, (4) and duplex stainless steels. The different types of stainless steels possess different properties that have been extensively studied and documented in the literature [2,15–19]. A useful summary of some of the compositional and property linkages in the stainless steel family is performed by Davis JR [1].

Martensitic Stainless Steels typically contain 12~17 wt.% Cr, 0~4 wt.% Ni and 0.1~1.0 wt.% C (C < 0.015 wt.% for the supermartensitic grades) [4]. Alloying elements like Mo, V, Nb, Al and Cu are added for the enhancement of specific properties. Mo improves pitting corrosion resistance and Cu machinability [20]. The high-nitrogen grades are being more popular as they possess higher strength, toughness [21] and pitting corrosion resistance [22]. The hardness of the martensitic class is mainly conferred by the carbon content, whereas hardenability is imparted by other alloying elements.

Martensitic stainless steels are commonly used for applications where high mechanical performance is required [23–25]. They are used as bulk material in a variety of industrial applications, such as hot working dies and tools, propellers, pump impellers, ball bearings and races, bushings, valve seats, industrial knives, etc...,

where high strength or wear resistance and moderate corrosion resistance are needed [26]. It is well known that the properties of these steels are strongly influenced by heat treatments. The amount of carbides in the quenched microstructures exerts an important influence on the properties of these materials: hardness and resistance to corrosion and wear [27].

New martensitic stainless steels with properties that suit specific applications have been developed with the aim to provide high mechanical properties by surface treatments and to improve corrosion resistance. Two of such martensitic stainless steels have, therefore, been developed: (1) precipitation hardening martensitic stainless steels; and (2) martensitic stainless steels with 12 wt.% Cr.

1.1. Precipitation hardening martensitic stainless steels

"Martensitic Age Hardening" (aka Maraging) are martensitic stainless steels with a very low carbon and high alloy steel. These steels were first developed in the 1960s for applications requiring ultra-high strength (greater than 1400 MPa) reached by the formation of high-density intermetallic precipitates uniformly dispersed in a martensitic Ni-rich matrix and combined with good fracture toughness [28]. The alloy gains strength from the precipitation of intermetallic phases in the martensite matrix [29]. The morphology and crystal structure of precipitates depends on the composition of the alloy, aging temperature, and time. Typically, these steels are solution-treated in the fully austenitic (γ) region in a temperature range of 815–900°C and quenched to produce a complete bcc martensite (α') matrix, after which they are aged at a temperature range of 400–600°C. The main use of xxx is in the aerospace, tooling, machinery and structural engineering industry [18]. In this range, 17-4 PH, 15-5 PH, 16-4 Mo, PH 13-8 Mo and Maraging stainless steels are now amongst the steels with greatest production [19]. The MLX17 is also part of the category of martensitic stainless steels hardened by precipitation. Based on their properties, such as high ductility, fracture toughness and stress corrosion resistance, they can be used as materials for structural parts in the aerospace industry (landing gears, actuators, flaps, rod ends ...).

Increasing carbon content to increase the strength of the martensite favors the formation of chromium carbides, which leads to fragility damage by impact and poor corrosion behavior. To combine corrosion resistance, high strength and ductility is necessary to reduce the carbon content. However, carbon also has the role of promoting high temperature austenite formation (in order to obtain a predominantly martensitic structure during cooling). To compensate for the carbon reduction, it is necessary to add alternative elements, such as nickel. This element has the advantage of limiting the amount of delta ferrite δ (which decreases the mechanical strength) during heat treatment at high temperature. By varying the concentration, it is possible to change the martensitic transformation temperature, and therefore the amount of existing residual austenite at room temperature. The carbon depletion also promotes the formation of softer martensite. Thus, other elements, such as aluminum and/or titanium, which will cause precipitation hardening, are added in addition. However, aluminum and titanium also cause new intermetallic precipitates as β'-NiAl and η-Ni_3(Ti, Al) [30–32], as in the case of MLX17 steel.

1.2. 12 wt.% Cr martensitic stainless steels

Martensitic stainless steels with a minimum of 12 wt.% of Cr have a good combination of mechanical properties, including good ductility and high mechanical

strength, as well as corrosion resistance due to the Cr content. These steels are austenitic in a temperature range of 1000 to 1050 °C, and the martensite transformation can occur even with air-cooling, because of very good hardenability. In terms of corrosion resistance, however, which can be decreased by precipitation of chromium-rich carbides, air-cooling should be avoided. In order to produce a good combination of strength, ductility and toughness, these steels are generally tempered at temperatures between 100 and 150 °C. These steels are extensively used for high-temperature and/or creep resistant applications [33].

To optimize the 12wt.% Cr martensitic stainless steels, other alloying elements, such as molybdenum, vanadium, and niobium are added [33]. The major role of alloying elements is to strengthen the secondary precipitation and to stabilize the formation of carbides. The addition of molybdenum and vanadium, which are ferrite stabilizers, improves the strength and resilience after tempering [19]. Niobium, in contrast to the molybdenum and vanadium, combines with carbon to form niobium carbides that are stable at a conventional austenitization temperature (1050 °C). In addition to a stabilizer of the δ ferrite, this element thus decreases the amount of available carbon in solid solution.

The steel type AISI 410 (12 wt.% Cr, 0.1 wt.% C) is one of the most popular materials within this grade of steels and is used in a wide variety of applications in general engineering. New martensitic stainless steels, such as the XD15NW™ steel have, however, been developed with the aim to replace AISI 440C for cryogenic aerospace bearings because of its improved tribological and fatigue properties [34]. The CX13VD steel is a carburizing stainless steel that is also part of the stainless steels with 12 wt.% Cr and steels with the addition of nickel, molybdenum and vanadium. It is used in the aerospace industry and industrial applications, such ball screws, blade propellers and gears.

2. Wear of martensitic stainless steels

In order to develop suitable martensitic stainless steels with better resistance to wear in a certain environment, it is important to know which factors are primarily influencing the wear rate and wear mechanisms. Published papers dealing with wear behavior of martensitic stainless steels from 2005 to present are presented below and summarized in Table 1. Only papers providing results obtained under well-defined conditions (i.e. motion contact geometry, load…) in martensitic stainless steels, essentially on tribometers at low temperature, were considered. For comparison purposes the average Hertzian contact pressure, sliding velocity, coefficient of friction, and wear coefficient were extracted from the reported data (when enough data was available). Most papers studied commercially available martensitic stainless steels, such as AISI 410, 420 and 430, as well as precipitation hardening 17-4PH steel.

Wear studies were carried out under different mechanical conditions due to the flexibility of experimental set-ups and tribometers. In all cases a ball-on-disc configuration was used, however, with the exception of one case where a plate-on disc configuration was used [35]. Counterparts differed in many cases, depending on the considered application. The average speeds used lied between 0.5 and 1000 mm/s, while the average loads were between 1 and 800 N. The wear coefficient varied from 10^{-6} to 10^{-5} mm^3/Nm, with the exception of one case that reported a wear

coefficient around 10^{-9} mm^3/Nm due to the different contact geometry (plate-on-disc) [35]. With respect to the coefficient of friction, most reported values lied between 0.4 and 0.98, and only one low value was observed [36], which corresponded to the effect of the DLC films [36] on the bulk alloy that significantly reduce the coefficient of friction; and two very high values [37,38]. The most typical wear phenomena identified from cited papers in treated and/or untreated martensitic stainless steels are ploughing (abrasive wear) and adhesive wear. In many cases, delamination and surface and subsurface cracks were also observed. Martensitic stainless steels exhibit high surface hardness and the presence of carbides promotes the generation of hard wear debris particles and abrasive wear. However, heat treatments in martensitic stainless steels (quenching, tempering…) generate residual stress in the bulk material, which promotes the formation of cracks. Figure 1 shows a schematic illustration of the main wear mechanisms of martensitic stainless steels while rubbing in a dry contact.
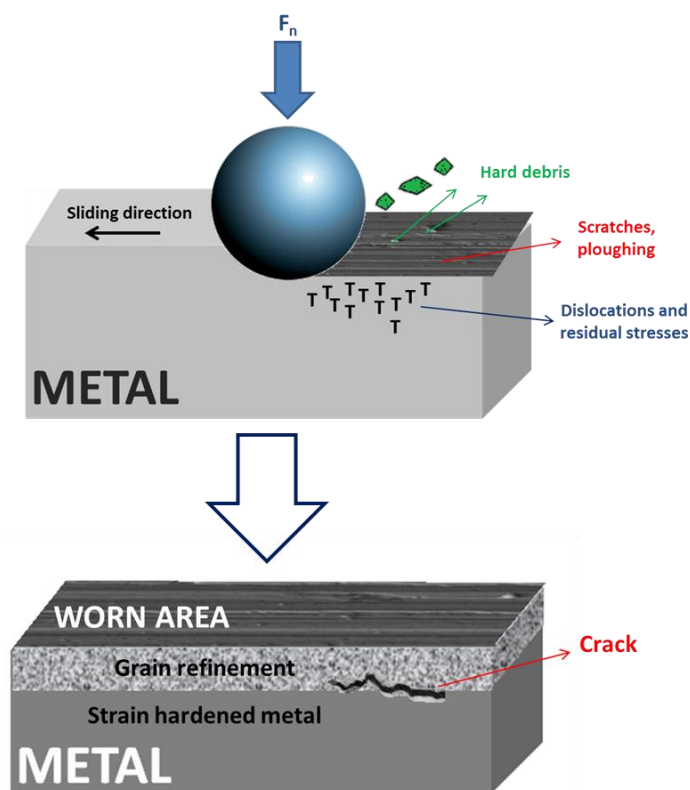

Figure 1. Schematic illustration of the main wear mechanisms of martensitic stainless steels while rubbing in a dry contact.

Microstructure plays an important role in the wear behavior of martensitic stainless steels. The amount of retained austenite, as well as the amount of carbides, modifies wear behavior. The schematic representation of the formation of the abrasive groove in a tool steel with retained austenite with a microstructure formed of carbide particles dispersed in a martensitic matrix is shown in Figure 2. It has been concluded by Colaço et al. [39] that the stress-induced transformation of the retained austenite of the studied samples (up to 15 %) into martensite and the consequent work hardening decreased the wear coefficient when increasing the applied load in the studied conditions (Figure 2a and b). When carbides were present in the microstruture of the studied material, however, the extraction of these carbide

particles, which increases with increasing load, was responsible for increasing the wear coefficient.
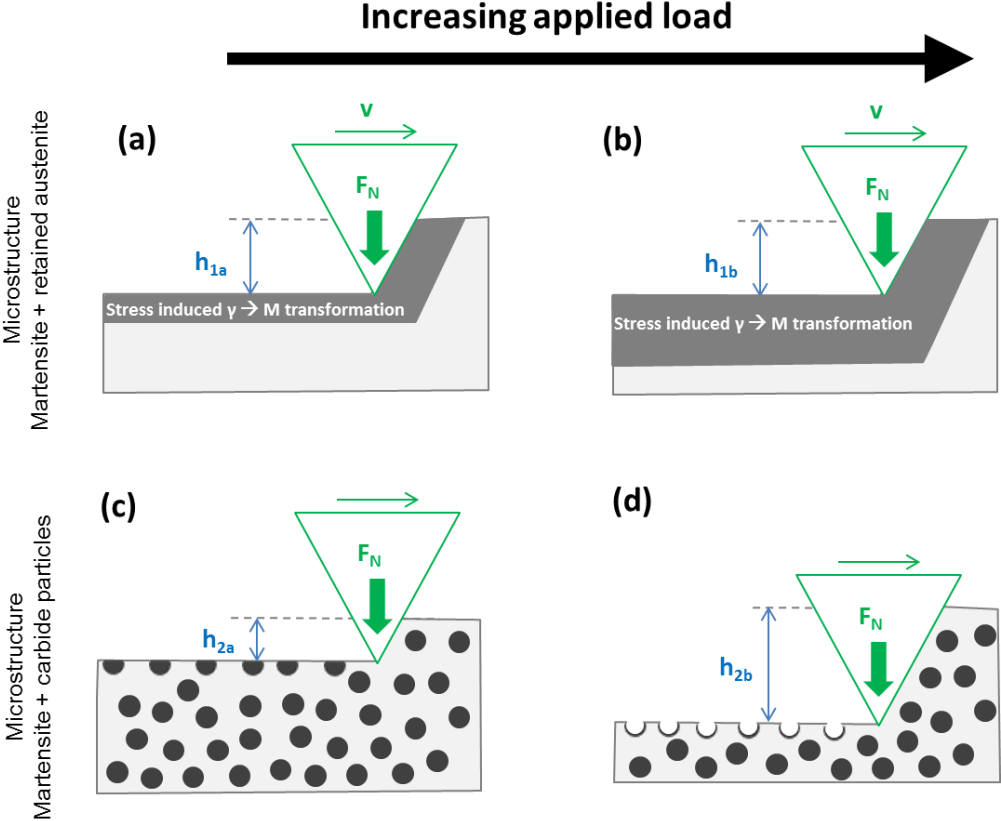
Increasing applied load

Figure 2. Schematic representation of the formation of the abrasive groove in a tool steel with retained austenite in its microstructure (a and b) with a microstructure formed of carbide particles dispersed in a martensitic matrix (c and d) – adapted from [39].

A great effort has been made in research on martensitic stainless steels to minimize wear. For that purpose, most studies have focused on the evaluation of surface treatments and/or coatings carried out on martensitic stainless steel to improve the wear resistance of bulk materials. Results showed that plasma nitride is an excellent candidate to improve the wear resistance of stainless steels for dry contacts.

Table 1. Wear studies of martensitic stainless steels.

Ref.	Martensitic stainless steel (Surface Treatment)	Counterpart (Diameter) [mm]	Motion Contact geometry	Load [N] (Avg Press) [MPa]	Avg speed [mm/s] (Duration) [s]	Friction range	Wear coefficient [mm^3/Nm]	Wear mechanism
Manova et al. 2005 [40]	AISI 420 X46Cr13 AISI 431 AISI 430F 17-4PH	Al$_2$O$_3$ ball (4.76) WC ball (3)	Reciprocating ball-on-disc	3 (1000)	17 – 68	0.45 – 0.56	$0.5 \cdot 10^{-5}$ – $2.5 \cdot 10^{-5}$	
Colaço and Vilar 2006 [39]	AISI 420 (laser surface melted)	AISI 440C ball (10)	Sphere-on-plate	1, 0.15, 2	300 (333)			Abrasive wear and plastic deformation
Corengia et al. 2006 [41]	AISI 410 (plasma nitrided)	Al$_2$O$_3$ ball (6.33)	Sliding pin-on-disc	8	700	0.4 – 0.8		Abrasive-oxidative wear (surface delamination and microcracks)
Gülsoy 2007 [35]	17-4PH	D2 tool steel plate	Reciprocating plate-on-disc	30	2750 (363 – 2181)		$2.3 \cdot 10^{-9}$ – $11 \cdot 10^{-9}$	Plastic deformation and delamination (subsurface cracks)
Xi et al. 2008 [42]	AISI 420 (plasma nitrided)	Si$_3$N$_4$ ball (4.75)	Sliding ball-on-disc	4.98	110.17 (1800)	0.6 – 0.8		Abrasive wear (microcracks)
Esfandiari and Dong 2008 [43]	17-4PH (plasma nitrided)	WC ball (8)	Sliding pin-on-disc	10	0.5			Adhesive and abrasive wear
Bressan et al. 2008 [44]	17-4PH	17-4 PH pin (50)	Sliding pin-on-disc	30	600 (4000)		$8 \cdot 10^{-5}$ - $17 \cdot 10^{-5}$	Micro-grooving, adhesion and micro-delamination
Kikuchi et al. 2009 [45]	AISI 440C (high-frequency induction heating)	Al$_2$O$_3$ ball (3.17)	Reciprocating ball-on-disc	4.9	5 (9600)			Adhesive wear
Liu and Yan 2009 [46] Liu et al.	17-4PH (plasma nitrocarburized)	WC ball (5)	Sliding pin-on-disc	10	100 (3600)	0.44 – 0.64		Severe surface plastic deformation, adhesive and oxidative wear

2010 [47]

Reference	Material	Counterbody (diameter, mm)	Test type	Load (N)	Speed (sliding distance)	Friction coefficient	Wear rate	Wear mechanism
Liu and Yan 2010 [48]	17-4PH (plasma nitrocarburized)	WC ball (5)	Reciprocating pin-on-disc	10	100 (3600)	0.42 – 0.67		Severe surface plastic deformation, adhesive and oxidative wear
Puli et al. 2012 [49]	AISI 410 (friction surfacing and metal arc coatings)	Tool steel discs (56)	Sliding pin-on-disc	50	1000 (1000)	0.6 – 0.75		Mild oxidation wear and delamination
Dalibon et al. 2014 [36]	Corrax (nitrided and DLC coated)	Al_2O_3 ball (6) 52100 steel ball (4.76)	Sliding pin-on-disc	5 (854 – 861)	100 (10000)	0.03 – 0.8		Abrasive wear
Dalmau et al. 2015 [50]	M1 12Cr11Ni2Mo M2 12Cr2.5Ni1.6Mo M3 14Cr2Ni4.7Mo	Al_2O_3 ball (6)	Sliding pin-on-disc	5 (1236)	19 (1800)	0.77 – 0.84	$1.4 \cdot 10^{-12}$	
Goyal et al. 2015 [51]	13Cr4Ni	EN-31 steel balls (10)	Sliding pin-on-disc	5, 10, 20 (1120, 1400, 1770)	157 (900)	0.92 – 0.98	$1.2 \cdot 10^{-12}$	Adhesion, abrasion and delamination of oxide layer
Angelini et al. 2016 [52]	AISI 420 (low temperature plasma carburizing)	EN100Cr6 steel	Sliding block-on-ring	5, 10 (40, 60)	300 (3333)	0.8 – 1.5		Mild tribo-oxidative wear
Li et al. 2017 [38]	AISI 420 (active screen plasma treatment)	AISI 52100 ball (4)	Reciprocating pin-on-disc	10	150 (900)	0.93 – 1.02		Oxidative wear
Prieto and Tuckart 2017 [53]	AISI 420 (deep cryogenic treatment)	Tungsten carbide ball (5)	Sliding pin-on-disc	5, 10, 15, 20, 25 (1100 – 1900)	60 (8333)	0.45 – 0.60	$3.2 \cdot 10^{-12} - 5.5 \cdot 10^{-15}$	Adhesive, oxidative and delamination wear

3. Corrosion and passive behavior of martensitic stainless steels

The outstanding corrosion resistance of stainless steels results from the presence of a thin oxide film on the metal surface. This oxide film is more enriched in chromium than the substrate, and typically 1-3 nm thick [3]. The alloy composition, the environment and conditions of formation are some of the factors affecting the passivation phenomenon, which results to be very complex. Although their good mechanical properties, their corrosion resistance is still an issue. Thus, with the aim of investigate the corrosion and passive behavior of the martensitic stainless steels, a review of the published articles has been carried out. Table 2 summarizes the published papers related to corrosion studies of martensitic stainless steels from 2005 to present. For this, only papers providing results obtained under well-defined conditions (i.e. solution, electrochemical parameters…) in martensitic stainless steels at low temperature were considered.

Different grades of martensitic stainless steels have been studied with different chemical composition and heat treatments. Most scientific studies are focused on the improvement of the properties of the martensitic stainless steels by surface treatments such as ion implantation [54], laser surface melting [8,55,56] or plasma nitriding [42,57]. These surface treatments not only increased their surface hardness but also improved the corrosion resistance of the martensitic stainless steels, when compared to the bulk alloys.

Test solution ranges from saline NaCl and/or H_2SO_4 solutions to complex electrolytes (i.e. 10 wt.% HCl + 1.5 wt.% HF + 3 wt.% HAc + 5.1 wt.% corrosion inhibitor [58]). The choice of the corrosion environments depends on the further application of the stainless steel.

Different electrochemical measurements (direct current, DC and alternative current, AC) were carried out in order to analyze the corrosion behavior of the martensitic stainless steels. Immersion tests, potentiodynamic polarization curves and external applied potential allowed obtaining useful information about the corrosion resistance. Indeed, all papers reported potentiodymanic results to analyze the general corrosion behavior of the studied alloys. Electrochemical Impedance Spectroscopy (EIS) allowed characterizing the interface metal/electrolyte which commonly complements the results obtained by DC measurements. EIS experimental data were commonly interpreted using Electrical Equivalent Circuits (EEC). The typical EEC employed to fit the electrochemical results from martensitic stainless steels consisted in a simple resistance–capacitance (RC) circuit [6,59–62] or a parallel configuration of two RC circuits [6,52,63,64]. The reported polarization resistance (R_p) from these EEC varied from 10 to 1800 kΩ·cm^2.

Surface analysis techniques were employed to carry out the metallographic studies before and/or after the electrochemical tests, and to analyze the different corrosion mechanisms. The most used techniques were optical microscopy and Scanning Electron Microscopy (SEM), which provides general information about the miscrostructure and/or the surface morphology after the corrosion tests [6,52,38,56,58,60,63–72]. Some studies were focused on the study of microstructural properties and/or the surface treatments and coatings of martensitic stainless steels. For that purpose, surface analysis such as X-Ray Diffraction (XDR), Transmission Electron microscopy (TEM) and Electron Backscattered Diffraction (EBSD) were

used in the reviewed studies [42,48,49,57,61,64,66,67,71–78]. The X-Ray Photoelectron Spectroscopy (XPS) is a useful tool to characterize the surface chemistry, i.e. coating and passive film composition and thickness and 8 above 36 authors used it [6,38,56,58,60,63,65,66]. Martensitic stainless steels spontaneously passivate by forming an oxide layer mainly composed of Fe and Cr and around 3-5 nm in thickness. The Fe/Cr ratio reported from the literature varies from 1.5 to 7.2, depending on the studied conditions [6] (Figure 3). Thickness and structure of the passive film of martensitic stainless steels are markedly influenced by the heat treatments applied to the alloys. It has been found that the Cr-rich carbides precipitation reduces the passive film and pitting corrosion resistances [63]. Microstructures with high content of retained austenite prevent the formation of Cr precipitates and preserve higher Cr content in solid solution (leading to thicker anodic films) [8,59,67,73], and the pitting potential linearly increases with the volume of retained austenite [55].
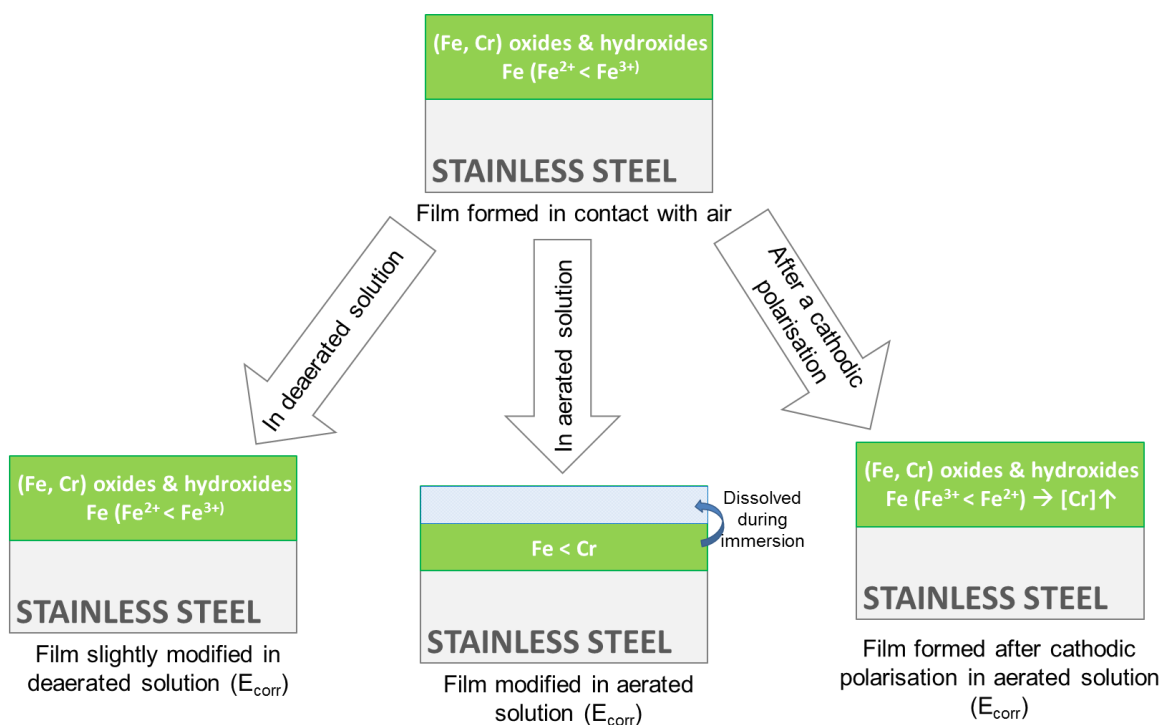

Figure 3. Schematic illustration of the passive films formed under different conditions based on impedance results and XPS analyses (films composition) – adapted from [6].

In presence of certain anions, in particular chloride, metals lose their passivity above a critical potential, called the pitting potential, and metal dissolution takes place from local sites where the passive film breaks. The localized dissolution leads to the formation of deep pits on a passive surface [79]. Pitting corrosion requires the presence of aggressive anions, most often chloride ions, and of an oxidizing agent such as oxygen or ferric ions. A corrosion cell forms between the growing pit which is the anode and the passive surface surrounding the pit which serves as the cathode (Figure 4). Because the anode/cathode surface ratio is small, the dissolution rate inside the pit can be quite fast. The pitting potential as a property of the metal-environment system, depends on a number of factors as the chemical composition and microstructure of the metal, the surface state and the presence of inclusions, the chemical composition of the electrolyte, in particular the concentrations of the

aggressive and non-aggressive anions, the temperature and the prevailing convection conditions.
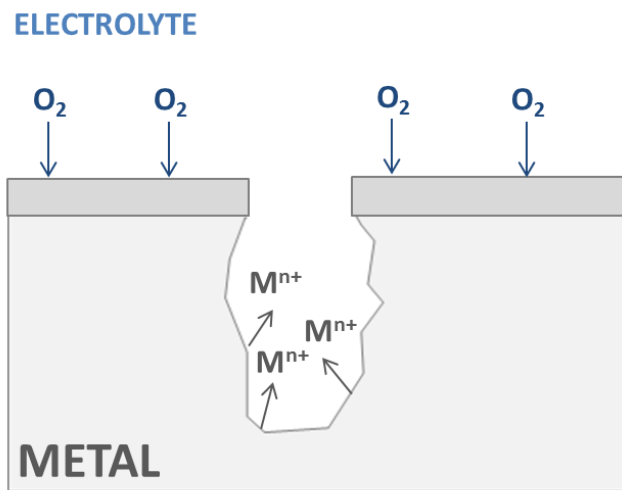

Figure 4. Partial reactions in pitting corrosion – adapted from [79].

Pitting corrosion has been extensively studied among the reviewed papers. Some of them show that is a phenomenon showing a statistical and probabilistic nature [77,78,80]. The methodology of the studied papers involves two independent experimental techniques to calculate pitting potentials (i.e. potentiodynamic polarization curves and potential steps) using micro electrodes and large-scale electrodes. On the other hand, pitting susceptibility was estimated in two main different ways (based on pitting potentials and on susceptibility to localized attack values following empirical expressions) using statistical data analysis. A correlation between sensitization and pitting potential was established in the supermartensitic stainless steels weldments by Aquino et al. [74], indicating that the probability of pitting corrosion enhanced as the sensitization increased. Marcelin et al. [62] founded the critical conditions for the depassivation of the martensitic stainless steel: $[Cl^-] > 0.4$ M or pH < 1.5. When these conditions are reached, the stainless steel cannot repassivate and the corrosion rate in the crevice increases. On the other hand, Vignal et al. [66] studied the influence of the microstructure on the corrosion behavior of low-carbon martensitic stainless, concluding that pits generally initiate at subgrain boundaries in martensite grains and at grain boundaries between martensite grains. Pits were found to grow first isotropically, and then they propagate along preferential paths corresponding to subgrains and grains with spread grain orientation values. This was also confirmed by Taji et al. [60].

From Table 2, 31 of 36 cited papers have identified pitting as the main corrosion mechanisms of their studied martensitic stainless steels under their test conditions. Intergranular and crevice corrosion have been also identified as secondary corrosion mechanisms in the published papers. Corogenia et al. [81] stated that intergranular corrosion is a consequence of tempering associated to surface treatments.

Table 2. Corrosion studies of martensitic stainless steels.

Ref.	Martensitic stainless steel (Surface Treatment)	Environment[1]	Electrochemical technique[2]	Surface analysis[3]	Investigated parameters	Corrosion mechanisms
Zhang et al. 2005 [63]	13Cr-type	Different solutions with Cl- and CO_2 T = 90, 120, 150°C DC	PD, EIS	OM, SEM, XPS	E_{corr}, i_{corr} Electrical Equivalent Circuit (EEC) Morphology Surface chemistry	Pitting
Li and Bell 2006 [25]	AISI 410 (plasma nitrided)	3.5 wt.% NaCl 1 wt.% HCl RT, AC	PD, IT	OM, XRD, SEM, GDS	E_{corr}, i_{corr}, E_b Corrosion rate Morphology Cr depth profiles	Crevice Pitting
Choi et al. 2007 [59]	0.3C–14Cr–3Mo–1.5Mn–0.5Si–0.2V–1.5Ni–0.12N (austenized)	0.6 M NaCl 30°C	PD, PS, EIS	OM, XRD	Microstructure E_b, i_p Rp	Pitting
Van Ingelgem et al. 2007 [56]	X30CrMoN15 (laser surface hardened)	0.5 M NaCl	PD	OM, SEM, XPS	Microstructure Surface chemistry Morphology OCP, E_b, i_p	Pitting
López et al. 2007 [82]	AISI 410 (gas nitrided)	3.5 wt.% NaCl RT, AC	PD	SEM	Microstructure E_{corr}, R_p, E_b Surface analysis	Pitting
Fu et al. 2007 [65]	AISI 420 (nitrogen/silicon ion implanted)	0.1 M NaCl	PD	SEM, XPS	Morphology	Pitting
Park and Park 2007 [73]	14Cr–3Mo (austenized)	0.6 M NaCl	PD	TEM, XRD	Microstructure E_b	Pitting
Xi et al. 2008 [42]	AISI 420 (plasma nitride)	5 wt.% NaCl + H_2SO_3 pH = 2 RT	PD, SSF	OM, XRD	Microstructure Wear rate Morphology E_{corr}, E_b	Pitting
Satish Kumar et al. 2008 [83]	AISI 410 (tungsten arc welded)	Different solutions Neutral: 0.01, 0.1,	PD	OM	Microstructure E_{corr}, i_{corr}	Pitting

		0.5 and 1 M NaCl Acid: 1 M H_2SO_4 + 0.1 , 0.5 and 1 M NaCl			Corrosion rate	
Aquino et al. 2009 [74]	12.6Cr-1.8Mo 11.4Cr-2.6Mo (welded)	5 wt.% NaCl	DL-EPR, PD	SEM, XRD	Microstructure Morphology E_{corr}, E_b Degree of sensitization (DOS)	Pitting Intergranular
Brühl et al. 2010 [57]	M340, N695 and Corrax (plasma nitride)	3.5 wt.% NaCl RT, AC	CST, SSF, PD	SEM, EDS, XDR, OM	Microstructure Morphology E_{corr}, E_b, E_{rp}	Crevice Pitting
Liu and Yan 2010 [48]	17-4PH (plasma nitrocarburized)	3.5 wt.% NaCl RT	PD	XRD,	Microstructure Wear Morphology E_{corr}, E_b, i_p	Pitting
Gervasi et al. 2011 [75]	13CrNiMo (annealed/tempered)	0.5 M Na_2HPO_4 RT, DC pH = 9.2	PD, GS, PS	XRD, SEM	Microstructure E_{corr}, i_p E vs time Film thickness	Pitting
Pereda et al. 2011 [80]	13CrNiMo (arc welded)	1 M NaCl + 1 M $NaSO_4$ RT, AC	PD, IT,	SEM	Microstructure OCP, E_b, E_{rp} Pitting probability Susceptibility to localized attack Morphology	Pitting
Puli et al. 2012 [49]	AISI 410 (friction surfacing and manual metal arc welding)	1 M H_2SO_4 3.5 wt.% NaCl RT, AC	PD	TEM, SEM, EDS, XRD	Microstructure Wear rate E_{corr}, i_{corr}, E_b	Pitting
Marcelin et al. 2013 [6]	X12CrNiMoV12-3	0.1 M NaCl + 0.04 M Na_2SO_4 AC, DC	PD, IT, EIS	XPS	E_{corr}, E_b EEC Surface chemistry	-
Lü et al. 2014 [58]	15Cr-type (tempered)	Different solutions 10 wt.% HCl + 1. 5 wt.% HF + 3 wt.% HAc + 5.1 wt.% corrosion inhibitor	IT, PD	XPS	E_{corr}, i_{corr} Corrosion rate Pitting rate Morphology	Pitting

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Reference	Material	Solution	Electrochemical techniques	Analysis techniques	Parameters	Corrosion type
Samih et al. 2014 [76]	AISI 420 (High Current Pulsed Electron Beam – HCPEB - treatment)	0.5 M H_2SO_4	PD	SEM, EBSD, GDS, FEG	Microstructure E_{corr}, i_{corr} Morphology Surface chemistry	Pitting Galvanic
Vignal et al. 2014 [66]	X4CrNiMo16.5.1 (tempered)	-	EMT, PD, PS	SEM, EDS, EBSD, AES, XPS	Microstructure Surface chemistry Passive film thickness Morphology	Pitting
Nakhaie and Moayed 2014 [77]	17-4PH (cold rolled)	3.5 wt.% NaCl RT	PD, PS	SEM, EDS	Microstructure E_b Pitting probability i vs time	Pitting
Taji et al. 2015 [78]	AISI 403 (annealed/tempered)	Different solutions 0.01 – 0.5 M H_2SO_4 (+Na_2SO_4 / KSCN) 3.5 wt.% NaCl RT	DL-EPR, PD, PS	OM, SEM, EDS	Microstructure Morphology Degree of sensitization (DOS) E_p, Pitting probability i vs time	Intergranular Pitting
Lu et al. 2015 [61]	13Cr-type (tempered)	3.5 wt.% NaCl pH = 5.6 – 5.8	PD, EIS	XRD, SEM, EDS, TEM	Microstructure OCP vs time E_{corr}, E_b Morphology Electrical Equivalent Circuit (EEC)	Pitting
Marcelin et al. 2015 [62]	X12CrNiMoV12-3	Different solutions 0.1 – 3 M NaCl + HCl/H_2SO_4	PD, IT, EIS	OM	E_{corr} i vs [Cl-], i vs pH R_p vs pH Morphology	Crevice
Guo et al. 2015 [60]	15-5PH	3.5 wt.% NaCl	IT, PD, EIS	XPS, AFM, SEM	OCP, E_{corr}, i_{corr}, E_b, i_p EEC Morphology Surface chemistry	Pitting

Abel et al. 2015 [84]	DIN 1.4035	Fuel + ethanol/ acetic acid/ water RT	IT	OM	Pit density and morphology	Pitting
Calabrese et al. (2016) [85]	X12Cr13	NACE TM0177 standard solution RT, DA	IT	OM	OCP Evolution of pittings during time Acoustic emission technique	Ptiing
Pahlavan et al. 2016 [86]	AISI 403	Halide bearing solution	PD, PS	OM	OCP, E_{corr}, i_{corr}, E_b, i_p Morphology Cumulative distribution of metastable pits	Pitting
Lei et al. 2016 [67]	Super 13Cr (water quenched + tempered)	3.5 wt.% NaCl 25ºC, AC	PD, PPT	XDR, TEM, SEM, EDS	Microstructure OCP E vs i i vs time Pitting morphology Surface chemistry	Pitting
Li et al. 2016 [52]	Cr12Ni3Co12Mo4W	0.1 mol/L Na2SO4 + 0, 0.1 wt.%, 0.5 wt.%, 1 wt.%, 3.5 wt.% NaCl	PD-EIS	SEM	E vs i E_p vs [Cl$^-$]	Pitting
Anantha et al. 2017 [64]	AISI 420	0.1 M NaCl	OCP, PD	SEM, EDX, AFM, XRD, SKPFM	Microstructure In-situ corrosion	Pitting
Qi et al. 2017 [68]	N0 – N4 samples (different meltings) (annealed, austenitized, quenching and tempered)	3.5 wt.% NaCl RT	IT, PD, EIS	SEM, EDS, XDR	OCP i vs E EEC Pit morphology Surface chemistry	Pitting
Loto 2017 [69]	AISI 410	1 - 6 M HCl	IT, PD	SEM, EDS	Corrosion rate vs time E vs i Corrosion morphology	Pitting

Zepon et al. 2017 [70]	Supermartensitic stainless steel modified with boron additions	3.5 wt.% NaCl (pH 4)	OCP, PD, EIS	OM, SEM	Microstructure i vs E Corrosion morphology	Pitting
Al-Sayed et al. 2017 [72]	AISI 416 (laser surface treatment)	3.5 wt.% NaCl 23 °C, AC	PD	SEM, EDX, XDR	Microstructure i vs E E_{corr}	
Liu et al. 2017 [71]	300M steel (AerMet100 steel coating)	3.5 wt.% NaCl RT, AC	PD	OM, SEM, TEM, XDR	i vs E E_{corr} vs Cr, Ni and Mo content	
Li et al. 2017 [38]	AISI 420 (active screen plasma treatment)	3.5 wt.% NaCl RT, AC	PD	SEM, EDX, AFM, XPS	i vs E	Pitting

[1]Envirnoment: RT, room temperature; AC, aerated conditions; DA, deaerated conditions.

[2]Electrochemical technique: SSF, Salt spray fog; IT, immersion tests; CST, $CuSO_4$ spot test; PD, potentiodynamic curves; PS, potentiostatic tests; GS, galvanostatic tests; EIS, Electrochemical Impedance Spectroscopy; DL-EPR, double loop electrochemical potentiodynamic; EMT, electrochemical microcell technique; PPT, potentiostatic pulse test.

[3]Surface analysis: OM, Optical microscopy; XRD, X-Ray Difraction; SEM, Scanning Electron Microscopy; GDS, Glow Discharge Spectrometry; TEM, Transmission Electron Microscopy; EDS, Energy Dispersive Spectroscopy; EBSD, Electron BackScattered Diffraction; FEF, Field Emission Gun; AES, Auger Electron Spectroscopy; AFM, Atomic Force Microscopy; XPS, X-Ray Photoelectron Spectroscopy; SKPFM, scanning Kelvin probe force microscopy.

4. Tribocorrosion in martensitic stainless steels

Knowledge about the mechanisms of the simultaneous action of wear and corrosion leads to the development of new tools and components, which enable forecasting wear in sliding pairs of machines under regular operating conditions [87]. Tribocorrosion is defined as a solid surface alteration that involves the joint action of relatively moving mechanical contact with chemical reaction in which the result may be different in effect than either process acting separately [88]. Tribocorrosion may occur under a variety of conditions (i.e. sliding, fretting, rolling, impingement) in a corrosive medium [89]. It involves different degradation phenomena depending on duty cycle location [90]: corrosion, that occurs on the whole metal surface exposed to the corrosive fluids, wear accelerated corrosion that occurs in the wear track which has been depassivated and mechanical wear that occurs only in the contact area (Figure 5). In practice, it is important to be able to identify the contribution of corrosion and wear to material removal by tribocorrosion in order to minimize material degradation and to prevent their early failure.
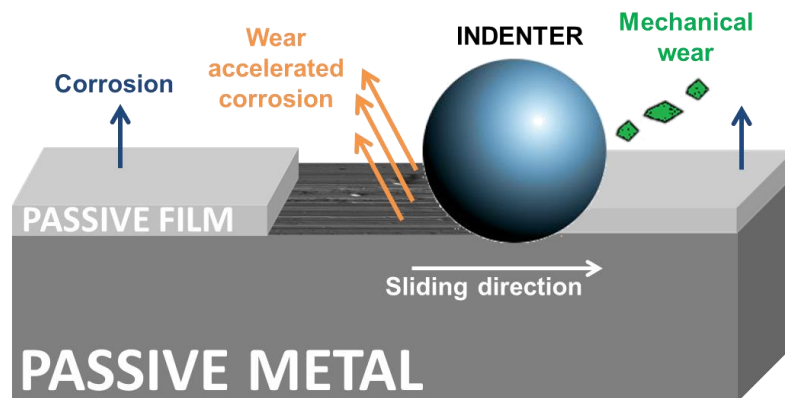

Figure 5. Schematic illustration of the degradation mechanisms of passive metals subject to tribocorrosion [91], adapted from [90].

A review of tribocorrosion behavior of martensitic stainless steels is presented below and related papers from 2005 to present are summarized in Table 3. Only papers providing results obtained under well-defined conditions (i.e. motion contact geometry, load, solution and electrochemical conditions) in martensitic stainless steels, essentially on tribometers at low temperature, were considered. For comparison purposes the average Hertzian contact pressure, sliding velocity, coefficient of friction and wear coefficient were extracted from the reported data when enough data was available.

The tribocorrosion behavior of martensitic stainless steels has been scarcely explored, just nine articles were found with these criteria studying different martensitic stainless steels. Testing conditions and solutions are very different among the studied papers. Different solutions were employed for the tests, depending on the further applications of the materials. Seven papers carried out an electrochemical control (OCP or applied potential) in the tribocorrosion tests [87,91–96]. Similar loads were found among the considered studies, which varied from 1 to 20 N. However, the coefficient of friction varied from 0.18 to 0.37, which is found to be lower than the

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average values of the coefficient of friction in dry conditions. Only two studies report the wear volume, which lies around 10^{-6} mm^3/N·m and it is in the same order of magnitude than those reported in the dry wear tests.

Among these articles, two of them deal with the study of surface treatments: plasma nitriding [43] and chromizing coating [97], which enhanced surface hardness and wear resistance to the bulk material. Esfandiari and Dong [43] studied the effect of the plasma nitriding temperature on the 17-4PH stainless steel under sliding conditions in a 3.5 wt.% NaCl solution. They found that plasma nitriding can effectively improve the surface hardness and the sliding wear resistance, as well as increase the corrosion–wear resistance due to the formation a thick surface layer. Lin et al. [[97] investigated the effect of the chromizing coating on the P110 oil casing tube steel under dry and wet sliding conditions against two different counterparts. Their results showed that the chromizing coating on the P110 steel had higher surface hardness and lower mass losses than that the bulk steel under tribocorrosion conditions. When sliding against a GCr15 ball, chromizing coating showed no obvious friction–reduction effect, but indicated an anti-friction property when sliding against Si$_3$N$_4$. Under the same testing conditions, chromizing coating always showed lower mass loss in comparison with P110 steel substrate. Abrasive wear was considered the main wear mechanism in this study.

From the reviewed studies, abrasive [43,92,93,95–97], adhesive [43,93,97] and delamination [91][96] wear have been observed in the worn areas. Those wear morphologies differed from the observations carried out under dry conditions. The chemical contribution to the overall degradation mechanisms modifies the worn patterns.

In a tribocorrosion situation, in which the cyclic mechanical detachment of the passive film by the mechanical action is followed by a constant rebuilding of it, repassivation taking place during rubbing creates a dynamic evolution of the material in the wear track [92]. Indeed, Huttunen-Saarivirta et al. [93] concluded that "fast repassivation kinetics" is a more important material behavior than high hardness. Those authors observed that, if the friction coefficient is systematically lower, the anodic dissolution rate is slower and the overall material behavior more stable at different potentials [93]. This observation was latter supported by other authors who stated that synergistic interactions between wear and corrosion contribute in a larger extent to the material damage of the studied martensitic stainless steels [87,93]. It was then highlighted that the combined action of wear and corrosion has to be specifically studied as a joint phenomenon.

Therefore, not only mechanical but also electrochemical, chemical or material properties have to be considered to approach a tribocorrosion situation. From this point of view, recent available literature is not sufficient to describe the tribocorrosion mechanisms in martensitic stainless steel and further tribocorrosion studies are needed to understand their tribo-electrochemical behavior. First of all, a much more detailed result report should be provided in the studies dealing with tribocorrosion systems (i.e. quantification of wear loss, hardness of the tested surfaces and electrode potential). Future research should be focused on the elucidation of the mechanisms that produce wear under tribocorrosion conditions taking into account the involved phenomena which also should include lubrication aspects. To do that, theoretical models are available nowadays [98] and could be used and/or improved

to understand tribocorrosion of martensitic stainless steels. From this point of view, numerical tools to describe the dynamic evolution of wear and corrosion in a tribocorrosion situation would be very helpful to simulate different operating conditions and to get a deeper insight into those involved mechanisms. This understanding would then establish the basis for material and surface engineering which will allow design metallic components for the specific tribocorrosion situations.

Table 3. Tribocorrosion studies of martensitic stainless steels.

Ref.	Martensitic stainless steel (Surface Treatment)	Counterpart (Diameter) [mm]	Motion Contact geometry (Frequency, amplitude) [Hz, µm]	Solution	Load [N] (Avg Press) [MPa]	Avg speed [mm/s] (Duration) [s]	Electroch. control	Friction range	Wear coefficient [mm³/Nm]	Main wear mechanism
Berradja et al. 2006 [92]	SS 3M®	Corundum ball (10)	Reciprocating Ball on flat (1-10, 20)	Ringer's	1, 2, 5 (493, 621, 842)	$(2 \cdot 10^4, 2 \cdot 10^5)$	OCP, applied potential, potential sweep			Abrasive and fatigue wear
Esfandiari and Dong 2007 [43]	17-4PH (plasma nitrided)	WC ball (12)	Reciprocating Pin on disc (1.15, 35)	3.5 wt.% NaCl	5, 10	30 $(3.6 \cdot 10^4, 7.2 \cdot 10^4)$	-		$52.9 \cdot 10^{-6}$ – $0.1 \cdot 10^{-6}$	Adhesive and abrasive wear (untreated) Mild oxidation wear (treated)
Stachowiak and Zwierzycki 2011 [87]	AISI 420	WC ball (0.5)	Reciprocating Pin on plate (5, 6)	0.5 M H_2SO_4	(12, 45)	60 (1800)	Applied potential	0.18 – 0.28		Surface micro-cutting
Lin et al. 2012 [97]	P110 steel (chromized)	GCr15 steel ball (5) Si₃N₄ ball (5)	Ball on disc	Simulated oilfield solution	20	140.7 (7200)	-	0.20 – 0.37		Abrasive and adhesive wear
Huttunen-Saarivirta et al. 2016 [93]	AISI 440B (vacuum hardening, quenched)	Alumina ball (10)	Ball on disc	0,01 M NaCl	1, 2, 5 N (200)	30, 100 and 210 (7500)	OCP, potentiodynamic measurements	0.5 -0.8		Abrasive and adhesive wear
Dalmau et al. 2016 [91]	X1CrNiMoAlTi12-11-2 X12CrNiMoV12-3	Alumina ball (6)	Ball on disc	3 wt.% NaCl	5 (1236)	18,8 (3600)	OCP Applied potential	0.35 -0.47	$23 \cdot 10^{-6}$ – $14 \cdot 10^{-5}$	Delamination and low-cycle fatigue wear
Zhang et al. 2016 [95]	AISI 410	Alumina cylinder (Φ4 x 3)	Pin on disc	Seawater ASTM D1141-98	40, 60, 80	- (1000)	OCP, potentiodynamic measurements	0.36 – 0.44		Abrasive wear
Ramos et al. 2017 [94]	DIN 1.4110 (as-received and cryogenic quenching)	Alumina ball (4.76)	Reciprocating ball on flat (1, 2)	0,05mol.L⁻¹ NaCl	2	- (12000)	OCP	0,37-0,4		Plowing (untreated) Cutting wear (treated)
Zhang et al. 2017 [96]	AISI 410	Alumina cylinder (Φ4 x 3)	Pin on disc	Seawater ASTM D1141-98	80	- (3600)	OCP, potentiodynamic measurements	0.36-0.48		Abrasive and delamination wear

5. Concluding remarks

Tribological and corrosion damage in martensitic stainless steels has been widely studied from 2005 to present. Martensitic stainless steels degrade though ploughing or abrasive wear due to their mechanical properties and microstructure. Surface treatments and coatings are proposed to improve both wear and corrosion behavior of martensitic stainless steels. The most promising surface treatment seems to be plasma nitride as an excellent candidate to improve the wear resistance of the stainless steels in dry contacts.

Pitting has been identified as the main corrosion mechanism of the martensitic stainless steels. The microstructure of these stainless steels, the amount of precipitated carbides, the sensitization and the Cr depleted regions, plays an important role in the corrosion resistance of the stainless steels, increasing their susceptibility to localized corrosion. The published results pointed as a key way to minimize the corrosion degradation on bulk martensitic stainless steels the reduction of the carbon content as well as the optimization of the heat and/or surface treatment processes, depending on the final application of the steels. The improved corrosion resistance is related to the combined effect of the solid solution of Cr and the high chemical stable phases on the matrix of the martensitic stainless steels.

Most of the research studies have been focused on the analysis of wear and/or corrosion of martensitic stainless steels separately. However, the synergistic action between wear and corrosion has been scarcely explored. Just nine papers were found from 2005 to present related to tribocorrosion of martensitic stainless steels. All authors highlighted that tribocorrosion contribute the most to the material damage/degradation in the studied martensitic stainless steels. Six of the nine reviewed papers reported that abrasion is the main wear mechanism in the studied stainless steels, and two papers reported that a reduction in friction is possible by surface treatments (e.g. plasma nitriding and chromizing coating). Localized corrosion was also found to be enhanced in the wear track of the martensitic stainless steels due to the combine action of sliding and oxidizing conditions. This phenomenon was also linked to the microstructure of these stainless steels. In order to minimize the corrosion degradation, the microstructure of the steels can be homogenizing by modifying the alloying elements and/or by using heat treatments. Surface modifications were also pointed as key point to reduce friction and corrosion.

Tribocorrosion is an important phenomenon often neglected or still poorly understood in industrial environments. Further work is required to understand the tribocorrosion mechanisms of martensitic stainless steels and to develop guidance for the conception of new materials with high performance. Research and developing activities are required to take these ideas forward.

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