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# Low-temperature Thermochemical Treatments of Stainless Steels – An Introduction

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Additional information is available at the end of the chapter

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## Abstract

Plasma technology used to perform thermochemical treatments is well established for the majority of steels, but it is not the case for the different stainless steel classes. Thus, important scientific and technological achievements can be expected in the coming years regarding plasma-assisted thermochemical treatment of such steels. The metallurgical aspects as well as the application cost-efficiency of stainless steels impose specific requirements for the thermochemical treatment, such as easy native chromium-rich oxide layer removal and surface activation at low temperature, which do not appear for other steel classes (plain, low-alloy, and tool steels). Thus, due to the highly reactive physico-chemical environment created by the plasma, plasma-assisted technology presents advantages over other “conventional” technologies like those performed in gas or liquid environments. Low temperature is needed to avoid the reduction of corrosion resistance of stainless steels, by suppressing chromium carbide/nitride precipitation, and, in this case, good surface properties are achieved by the formation of treated layers containing metastable phases. Such attributes make the low-temperature plasma thermochemical treatments of stainless steels an important R&D field in the domain of plasma technology and surface treatments, and the goal of this chapter is to introduce the reader to this important topic.

**Keywords:** Nitriding, Carburizing, Low-temperature thermochemical treatments, Stainless steels, Surface treatments

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## 1. Introduction

Stainless steels are iron alloys mainly based on the Fe-Cr-Ni and Fe-Cr-C systems. The main characteristic of this class of alloys is its expressively high corrosion resistance when compared with other iron-based alloys. Thus, the main applications of these materials are related to parts exposed to corrosive operation environments, from cutlery to petroleum and nuclear indus-

tries. The corrosion resistance of these steels is related to the formation of a continuous and passive chromium-rich oxide layer on the steel surface, also termed native oxide layer. This layer is promptly formed when the part is exposed to atmospheres containing oxygen, for steels containing at least 10.5 wt.% Cr in solid solution (solved in the steel matrix), which result in the so-called stainless steels. Due to the raw materials and processing costs, stainless steels are usually more expensive than other steels and have their application restricted to cases where corrosion resistance is important. However, in most of these applications, it remains very competitive compared with other corrosion-resistant alloys.

Even for the case of high-strength stainless steels, like those of the martensitic class, the need for high-performance parts strongly justifies the use of surface-hardening treatments, aiming to enhance the wear/fatigue resistance and to extend the part service life. Keeping in mind that corrosion resistance is the dominant criterion for these steels, it is unacceptable for any applied surface treatment to cause significant corrosion resistance decrease of a treated part.

Thermochemical treatments like nitriding and carburizing are among the most known surface-hardening treatments. As an example, very good results have been achieved when (plasma) nitriding is applied to plain, low-alloy, and tool steel parts. In such cases, treatment temperatures in the order of 500°C–580°C, and for times not much longer than 36 h, are usually applied. Differently, inappropriate results are observed if similar treatment temperatures and times are used to nitride stainless steels, since their treated surfaces will present strong corrosion resistance reduction, due to chromium nitride ( $\text{CrN}/\text{Cr}_2\text{N}$ ) precipitation. Thus, for stainless steels, making it possible to produce very hard treated surfaces with the same, or even higher, corrosion resistance than the untreated stainless steel surface. Such achievements can be obtained if the treatment temperature is set to a value high enough to activate interstitial (N and C) atom diffusion, and low enough to avoid significant Cr (substitutional) diffusion, thus keeping unaltered the chromium content in solid solution.

Another important aspect to be considered when applying a thermochemical treatment in a stainless steel is that the native oxide layer, important for corrosion resistance, also acts as a diffusion barrier for atoms from the treatment atmosphere (N and C) diffusing into the steel surface. Thus, in such thermochemical treatments, it is necessary, first of all, to remove or reduce this oxide layer to allow the diffusion of N/C atoms, aiming to alter the composition of the surface under treatment. Therefore, in the case of plasma-assisted thermochemical treatments, plasma has two main tasks:

- i. To reduce and/or remove by sputtering the native oxide layer; and
- ii. To create an environment for which the N/C chemical potential is higher than its chemical potential in the original steel surface, enabling the N/C surface alloying, and thus the surface hardening.

Considering the aforementioned main points, to present the plasma-assisted low-temperature thermochemical treatments of stainless steels in a didactical way, the next two sections will discuss some fundamentals on stainless steels and plasma-assisted thermochemical treatments. After presenting the fundamentals, a section is devoted to present the typical results of low-temperature thermochemical treatments of stainless steels, and then, the chapter ends with some conclusions and final remarks.

## 2. Fundamentals of stainless steels and low-temperature thermochemical treatments

Depending on the alloy composition, mainly on the Cr, Ni, and C contents, stainless steels can present different microstructures at room temperature, being classified by this criterion. The three main stainless steel classes are the austenitic, martensitic, and ferritic, with duplex, and precipitation-hardening classes also present. Since Cr is the most important component regarding stainless steel corrosion resistance, it plays a major role in low-temperature thermochemical treatments, independently of the considered stainless steel class.

At low temperature, Cr has higher affinity to N/C than to Fe. Thus, under the thermodynamics basis, instead of an interstitial solid solution, chromium nitrides/carbides would be expected to be formed during the stainless steel surface alloying with such elements, leading to a consequent reduction of Cr content in solid solution. Nevertheless, the nucleation of a new phase presents some energetic barriers that need to be overcome, implying the existence of a critical nucleus size to start the precipitation of a new phase. Since the nucleation process is strongly related to atomic diffusion, and it is especially restrictive in solid state, the main parameters to be controlled to prevent nitrides/carbides nucleation process are temperature and time. If low enough temperature and time are used, no nucleation process is started and no chromium nitride/carbide is formed. In such conditions, metastable supersaturated solid solutions known as N/C-expanded phases tend to be formed. The above-mentioned aspects comprise the basis of the low-temperature thermochemical treatments used to stainless steels surface hardening.

The formation of these important metastable phases are possible since the atoms being introduced in the treated surface are interstitials (N and C), and Cr is a substitutional atom. As it is well-known from diffusion processes, interstitial atoms tend to present high diffusion coefficients and low diffusion activation energies when compared to substitutional atoms. Thus, it is possible to heat stainless steel components up to a temperature that is

- i. high enough to attain a significant diffusion of interstitial (N and C) atoms; and
- ii. low enough to avoid significant diffusion of substitutional (Cr) atoms.

At these conditions, the kinetics of the treated layer growth is acceptable and the energetic barrier for nucleation of chromium nitrides/carbides is not overcome. In stainless steels, the N/C surface alloying is accompanied by an expansion of the lattice parameters, which explains the use of the term “expanded” to the obtained phases. For austenitic stainless steels, the obtained phases can be termed as nitrogen- or carbon-expanded austenite, also known as S-phase, for the nitriding and carburizing treatment, respectively. The analog phases for martensitic stainless steels are nitrogen- or carbon-expanded martensite, respectively.

At this point, it is important to inform the reader that the precipitation of chromium nitrides/carbides will consume Cr atoms from the steel matrix. Therefore, in the surrounding of the precipitates, the original steel matrix Cr content in solid solution will be depleted and the corrosion resistance will be locally reduced. In several cases, the Cr content in such areas can

be reduced to values lower than 10.5 wt.%, which is the minimum acceptable value for stainless steels, leading the steel to be sensitized. This phenomenon is referred to as sensitization and must be strongly avoided since, as aforementioned, the high corrosion resistance of stainless steels is the main property justifying its use instead of other lower cost steels.

It is worth mentioning that the corrosion resistance in stainless steels is attributed to the formation of a passive and very stable native oxide layer that hinders the oxidation process continuity. The very negative Gibbs free energy variation for the Cr-rich native oxide layer formation is directly related to the high Cr-O atoms affinity, and to its strong stability. Thus, this native oxide layer is hard to reduce/remove at low temperatures by conventional (gas/liquid) processes, and if it is present in the treating surface, the thermochemical treatment cannot be successfully carried out since the oxide layer prevents the diffusion of O atoms as well as the diffusion of N/C atoms. At this point, it is possible to assert that the reduction/removal of the stable oxide layer is easily attained by plasma processes, but as the affinity of Cr with O is even higher than its affinity with N and C atoms, special attention must be spent for two technological aspects of the low-temperature thermochemical processes, to know

- i. the process gas mixture purity; and
- ii. the vacuum chamber leakage and/or degassing.

Even very low oxygen partial pressures can inhibit the reduction/removal of the native oxide layer of the stainless steel surface, practically stopping the diffusion of interstitial atoms (N and C) from the gas phase into the steel. On the other hand, if the oxygen content in the atmosphere is low enough, the action of the very reductive plasma species like atomic hydrogen (H), allied to sputtering process (usually using Ar atoms in the plasma gas mixture for this purpose), will make the native oxide layer reduction/removal easier, enabling N and C atoms to diffuse into the steel.

The last aspect that merits to be considered in this section is only important for martensitic stainless steels, which can present a metastable phase matrix (the martensite phase), for different metastability degrees, depending on the tempering stage for which the as-quenched martensite was subjected. Consequently, besides considering the possibility of chromium nitride/carbide formation instead of expanded phases during thermochemical treatment, it is also important to take into account the possibility of variations in the martensite properties. It will occur if the martensite tempering process takes place simultaneously with the thermochemical treatment, it can be undesirable or a strategy to reduce the treatment steps. The temperatures applied in low-temperature thermochemical treatments, usually in the 300°C–450°C range, is similar to the temperatures used for the tempering of steels. Thus, aiming to keep practically unaltered the treated material bulk properties, thermochemical treatments must be carried out at a temperature lower than that applied in the tempering treatment (as a reference, the reader can specify 50°C lower than the tempering temperature). However, if the thermochemical treatment is carried out at a higher temperature than the tempering was performed, the bulk material properties will be compatible to those obtained for a part tempered using the thermochemical treatment temperature and time.

After this brief presentation on the most important metallurgical aspects of stainless steels for understanding the main aspects related to its low-temperature thermochemical treatments, in

the next section, the reader will be introduced to the fundamentals of the plasma low-temperature thermochemical treatments technology. For readers who want to go deeper into the metallurgical aspects of this important class of steels, the authors suggest the following books or review papers [1–3].

### 3. Fundamentals of plasma for low-temperature thermochemical treatments

This section aims to present the fundamentals of low-temperature plasma thermochemical treatments in a comprehensive way, focusing on the most important physicochemical interaction between the plasma and the stainless steel surface. Most of the fundamentals presented are valid for all stainless steel classes and thermochemical treatments.

As indirectly mentioned in the previous section, the term low-temperature thermochemical treatment, when applied to stainless steels, refers to a treatment condition (temperature and time) where the Cr diffusion and new Cr-rich phase formation can be neglected. In such a condition, Cr is kept in solid solution, and no important reduction of the surface corrosion resistance is expected. At low-temperature treatment, even if the formation of the undesirable Cr-nitride/carbide phases is expected by thermodynamics, it does not occur since the transformation kinetics is limited by the atomic diffusion process, which is negligible in present case. Consequently, both the treatment and the formed phases are not in thermodynamic equilibrium.

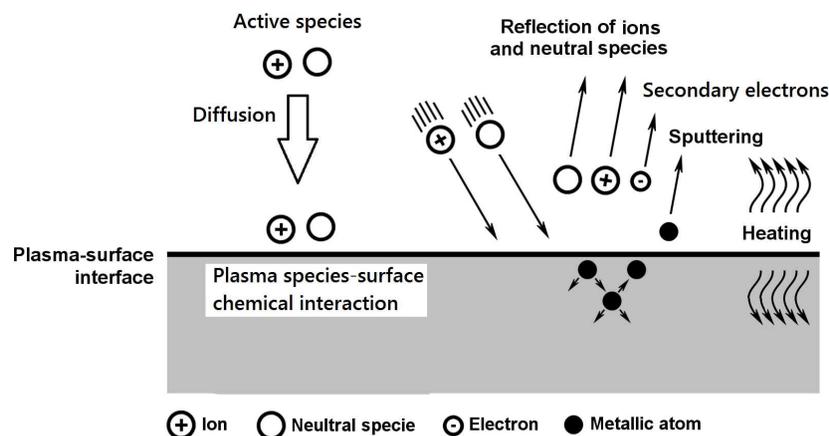
Therefore, in the treated surface, metastable phases will be formed, the so-called expanded phases, as previously seen. These phases are supersaturated solid solutions containing N/C interstitial atoms (N for nitriding, C for carburizing, and both N and C for nitrocarburizing) in a metastable condition. The temperature limit to produce expanded phases, in detriment of precipitates, will be dependent on the steel structure, which exerts important influence on the diffusion process, being typically lower than 450°C and 400°C for austenitic and martensitic stainless steels nitriding, respectively. As a diffusion-controlled process, time is also important, varying typically from 4 to 48 h depending on the steel class, treatment temperature, and desired treated layer thickness. In fact, these values are only guidelines since it can be dependent on several other parameters. Thus, other aspects influencing the diffusion rate will also influence the limit temperature as, for example, the steel composition and its previous heat treatment [4, 5]. Considering the different types of stainless steels, as a general rule, limit temperature and time are higher for austenitic than for martensitic stainless steels. Taking into account the different types of thermochemical treatments, as a general rule, limit temperature and time are higher for carburizing than for nitriding, which is related to the different N-Cr and C-Cr affinities.

For low-temperature treatments, the necessary heating effect to attain the treatment temperature can be easily reached using only plasma heating. However, the use of hot wall reactors (with auxiliary heating systems) can be desirable for some applications, which enable the control of plasma reactivity and treatment temperature independently. Nevertheless, plasma

also plays other important roles on low-temperature thermochemical treatments, which can be listed as follows:

- i. It creates a very reactive environment with high N and/or C chemical potential, enabling N/C atoms to be added to the surface under treatment;
- ii. It creates a very reductive environment helping the removal of the native oxide layer and preventing its re-formation (related to hydrogen species present on the gas mixture);
- iii. It promotes sputtering of the native oxide layer from the stainless steel surface (mainly related to heavy species on the gas mixture, like Ar); and
- iv. It heats the parts to the desired temperature by momentum transfer as energetic species bombard the part's surface (for hot wall plasma reactors, the treatment temperature is controlled by the auxiliary resistive heating system, and for other reactors, it is controlled by adjusting the plasma parameters).

All the above-mentioned “plasma roles” are related to the plasma physicochemical environment. Points iii and iv are related to plasma physical interactions with the part surface, and points i and ii are related to the nonequilibrium plasma state and so very reactive chemical environment. This very active physicochemical environment is created principally by inelastic collisions of energetic electrons with neutral atoms/molecules from the gas mixture, promoting, for example, ionization, excitation, and dissociation. These reactions occurring in the plasma environment are important for thermochemical treatments since, for example, by using typical plasma nitriding/carburizing parameters in a hot wall reactor, the atmospheres are not active if plasma is off. In other words, nitriding/carburizing will only take place if the plasma glows, promoting the formation of nitriding/carburizing species like atomic nitrogen from molecular nitrogen and/or atomic carbon from hydrocarbides ( $C_xH_y$ ) molecules present in the plasma gas mixtures. The most important physical and chemical plasma–surface interactions for these treatments are schematically presented in Fig. 1.



**Figure 1.** Main plasma–surface physicochemical interactions on low-temperature thermochemical treatments of stainless steels.

The aforementioned interactions are due to the high-energy plasma species (electrons, ions, and neutrals). The mechanism by which these species gain energy will depend on the applied plasma excitation technology, and virtually all of them could be applied for the purpose of thermochemical treatments. However, direct current (DC) plasma is the most applied in the industrial applications of low-temperature thermochemical treatments<sup>1</sup> due to its relative low cost and high versatility if compared to other plasma technologies. Thus, DC plasma and related physicochemical phenomena (Fig. 1) is briefly discussed, aiming to present more details on the important physicochemical aspects related to low-temperature plasma thermochemical treatments. It is worth mentioning that the plasma fundamental aspects, related to its very active physicochemical environment, are very similar for DC and other plasma technologies, being the main difference the relative importance of each phenomenon on each treatment.

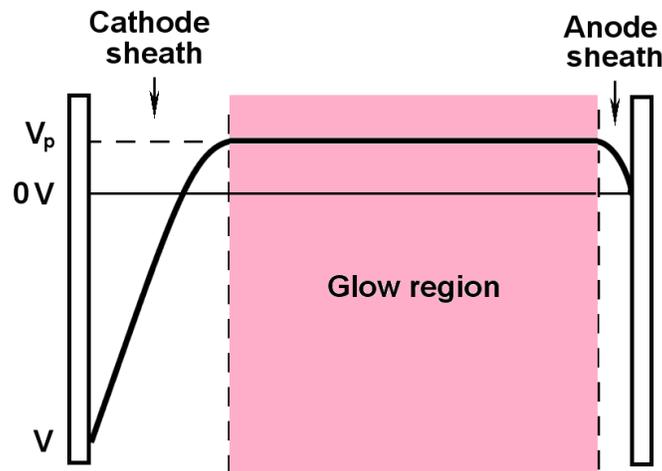
The simplest way to generate DC plasma is by applying a difference of potential between two electrodes placed into a low pressures chamber with the desired gas mixture. For thermochemical treatments, these parameters are in the range of 300–1000 V and 1–10 Torr, respectively. After applying a sufficient difference of potential between two electrodes, gas breakdown will occur. If the parameters were correctly set, after a short time (on the order of some microseconds), a steady-state abnormal glow discharge will be established, covering the whole cathode surface, which is essential for the homogeneity of the treatment. In this condition, the interaction of fast<sup>2</sup> electrons and neutrals will create charged species by ionizing collision/reaction, and the net charge distribution in the interelectrode gap will be modified, thus modifying the potential distribution in the interelectrode gap. In an abnormal glow discharge, it will be similar to that presented in Fig. 2.

Due to this potential distribution (Fig. 2), the electric field is restricted to the cathode and anode sheath, being that the cathode fall is considerably more intense than the anode fall. Thus, the most energetic species of DC plasma will be found close to the cathode sheath boundaries. In the cathode sheath region, high-energy ions and fast neutrals (created by charge exchange collisions) are found, being accelerated to the cathode surface by the referred potential fall. However, electrons, pulled away from the cathode (part) surface (also termed “secondary electrons”; for more details, the reader is invited to see Chapman [6]) due to the impinging species bombarding the surface (see Fig. 1), enter the glow region with very high energy. Positive ions are mainly created by electron-neutral collisions in the glow region and are accelerated in the cathode sheath toward the cathode surface. The charge exchange collision occurs just when an ion travelling along the sheath collides with a neutral species. In such a case, an electron from the neutral slow specie is transferred to the fast ion (presenting kinetic energy proportional to the work performed by the electrical field on the charged particle), neutralizing it. At this moment, the original ion becomes a fast neutral, and the slow neutral

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1 To be precise, the most industrially applied plasma excitation technology is the “pulsed-DC plasma excitation.” In this case, the plasma behavior is very similar to continuous DC excitation. Pulsed DC technology is used to reduce the arcing problems, which are more frequent in industrial reactors. This reduction is achieved by introducing a period of some tens of microseconds where plasma is switched off.

2 The terms “fast” and “slow” are related to species with high and low kinetic energy, respectively. As a reference, slow species have kinetic energy near to that related to thermal agitation level.



**Figure 2.** Typical potential distribution on a DC glow discharge, also known as DC plasma.  $V_p$  is the plasma potential, and  $V$  is the potential imposed to the cathode by the powder supply.

(presenting kinetic energy related to the environment thermal agitation level) becomes a slow ion. This new-formed ion will be also accelerated by the remainder potential fall towards the cathode. For a typical operating condition, this phenomenon is important, and as a consequence, the mean energy of ions striking the cathode is lowered and an important number of fast neutrals will also strike it. Such ions and fast neutrals are the origins of the most important physical interactions presented in Fig. 1. As previously commented, the plasma species bombardment will also promote the ejection of secondary electrons from the cathode surface, which are also represented in Fig. 1. Despite secondary electrons not being directly related to thermochemical treatments, in DC plasma, they have a fundamental role in the discharge maintenance. Since secondary electrons travel along the cathode sheath and due to their high mean free path achieve high energy, in a steady-state discharge, they are the origins of most ionization (ion creation), excitation, and dissociation collisions/reactions in the glow region. As a matter of fact, the electron collision processes are the origin of the very reactive plasma environment creation.

In most DC plasma thermochemical treatments, the part subjected to the treatment acts as the cathode of the discharge, where most of the energetic species bombardment tends to occur. In addition, since the species excitation close to the cathode is more intense (related to the high-energy electrons accelerated by the higher potential fall), generally, the cathode is subjected to a more reactive environment than that close to the anode. Thus, for parts acting as cathodes, this means that those parts are surrounded by the most active physicochemical environment of the discharge.

The aforementioned phenomena are valid for all thermochemical treatments. However, to perform different thermochemical treatments, different sources/precursors of interstitial atoms can be considered. The most common gases applied for this purpose are  $N_2$  and  $CH_4$ , for nitriding and carburizing, respectively, which are the most applied stainless steels low-

temperature thermochemical treatments. Besides the interstitial atoms precursor, other gases are also present in the discharge gas mixture to accomplish particular roles. To ensure a very reductive plasma environment,  $H_2$  has been strongly applied. In this case, the dissociation of  $H_2$  molecules will produce H atoms, and it will substantially increase the capability of the environment to reduce oxides. Eventually, Ar is also added to the gas mixture to enhance heating and/or sputtering effects without participating directly in the surface chemical reactions.<sup>3</sup> Thus, the most frequently used gas mixtures are  $N_2 + H_2$  (+ Ar eventually) and  $CH_4 + H_2$  (+ Ar eventually) for nitriding and carburizing, respectively. The volumetric content of each gas varies for each specific application. For example, for carburizing, the maximum  $CH_4$  content is limited by the undesired soot formation, which is potentially detrimental for the DC glow discharge stability, and also acts as a physical barrier for the diffusion of C atoms from the plasma environment onto the treating surface. In this case, the maximum reported  $CH_4$  content is on the order of 5 vol.%. It is important to keep in mind that the maximum value is also a function of the reactor design, operating parameters and the material to be treated. Thus, in some cases, 1 vol.%  $CH_4$  is enough to enable soot formation.

In short, the two main plasma tasks in low-temperature thermochemical treatments, as previously presented, are easily attained. The inelastic collisions/reactions in the glow region are responsible by creating active/reactive species in enough amounts to increase the N/C chemical potential on the stainless steel surface, with consequent diffusion into the material. Additionally, the reduction/sputtering of the stainless steel native oxide layer, necessary to effectively allow N/C surface alloying, is a direct consequence of the plasma–surface physicochemical interactions. To accomplish this task, plasma acts by two ways, as follows:

- i. by means of sputtering, which is a mechanical/physical interaction, being efficiently promoted by heavy species bombardment like argon; and
- ii. by means of oxide reduction, which is due to the high reductive environment created by hydrogen-containing gas mixtures that can considerably reduce the temperature for oxides reduction [7, 8]. By considering that the native oxide layer is composed by Cr-oxide only (without Fe atoms), thermodynamic data have shown that, for 1 atm pressure, a hydrogen gas purity of 99.999% is not enough to reduce Cr-oxide at temperatures up to 700°C (such statement is taken from the reading of Ellingham–Richardson diagrams for oxide formation). Thus, one can conclude that plasma is essential to remove/reduce the native oxide layer at low temperatures. It is worth noting that this point is not yet completely understood by researchers, but it is a consensus that plasma strongly contributes to remove the oxide layer by sputtering and/or to reduce it by means of reductive species, which is the case of atomic hydrogen. Despite the absence of any comments here about the role of C in oxidation–reduction reactions, C also tends to promote reduction of oxides. Thus, C atoms possibly would be important when aiming to reduce the stainless steel native oxide layer, at least for the case of low-temperature plasma carburizing treatments.

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<sup>3</sup> Other heavy noble gases could also be used, but Ar is the most abundant, and of lower cost, very important aspects to be considered for an industrial process.

Finally, from a technological point of view, gas purity and leakage in the plasma reactor used for low-temperature thermochemical treatments are to be also emphasized. If these “parameters” are adequate, no special attention must be paid to ensure the native oxide layer reduction, being one important advantage of plasma over other possible low-temperature gas/liquid environment thermochemical treatments of stainless steels.

On the other hand, it is important to mention that the two very probable main drawbacks of plasma process are

- i. its relatively high cost of installation (despite the low-temperature DC plasma technology and know-how that can be easily transferred to companies specialized in “conventional” plasma thermochemical treatments, with the possibility of using existing equipment); and
- ii. the existence of some important geometric restrictions, which can be related to the component as well as to the discharge design. In this case, hollow cathode formation, edge effects, and difficulties to treat internal surfaces of too low diameter holes or narrow gaps are examples of the related geometric restrictions.

For readers who want to go deeper into plasma physics for materials treatment, the authors suggest to consult some books such as Chapman [6] and Lieberman and Lichtenberg [9], or the other chapters of this book.

#### **4. Typical results obtained for low-temperature thermochemical treatments of stainless steels**

Ichii et al. 1986 cited by [10] is one of the oldest references found using low-temperature thermochemical treatments and obtaining the related expanded phases. Its title is “Structure of the ion-nitrided layer of 18–8 stainless steel.” Thus, apparently, one of the earliest successful low-temperature thermochemical treatments was plasma nitriding, which at first was known as ion nitriding.

Low-temperature thermochemical treatments of austenitic stainless steels are by far the most studied subject in the present area, with the majority of papers dealing with low-temperature nitriding, followed by low-temperature carburizing and then, in minor amounts, other treatments like nitrocarburizing or sequential (nitriding/carburizing) treatments. Probably this fact is related to the great number of industrial applications of this steel type. Regarding the other stainless steel classes, the application of low-temperature thermochemical treatments for martensitic stainless steel is the second more studied group. In this case, again, the majority of papers deal with the nitriding process, and only few papers have been devoted to carburizing and other thermochemical treatments. The other stainless steel classes are considerably less studied. To illustrate this point, the authors present the results of a recently performed bibliographic research on the subject in Table 1.

Studied thermochemical treatment	Low-temperature treated stainless steel class				
	Austenitic	Martensitic	Ferritic	Duplex	Precipitation Hardening
Nitriding	[10] [11] [12] [13]				
	[17] [18] [19] [20]				
	[21] [22] [23] [36]	[4] [5] [24] [28]			
	[40] [41] [42] [44]	[30] [31] [38] [39]	[55] [69]	[43] [53] [55] [67]	[31] [58]
	[46] [48] [49] [50]	[52] [54] [68] [81]		[70]	
	[51] [55] [60] [61]				
	[62] [66] [76] [77]				
	[79]				
Carburizing	[11] [14] [15] [18]				
	[35] [36] [37] [45]	[25] [26] [27] [29]			[58]
	[47] [48] [59] [72]	[71]			
	[73] [74] [75] [77]				
	[78]				
Nitrocarburizing	[32] [34] [48] [56]	[33] [63]			[64] [65] [80]
	[57]				
Sequential nitriding/ carburizing	[34] [35]				[58]

**Table 1.** List of works devoted to the study of low-temperature thermochemical treatments of stainless steels ranked by type of treatment and stainless steel class

As the main objective of thermochemical treatments is to promote surface hardening and the main required characteristic of stainless steels is its corrosion resistance, several works are devoted to determining both the wear and corrosion resistances of low-temperature treated surfaces. Another group of papers has been devoted to the study of more fundamental aspects, like the process kinetics, the metastable phase formation, the metastable phase structure, and the chromium nitrides/carbides precipitation phenomena.

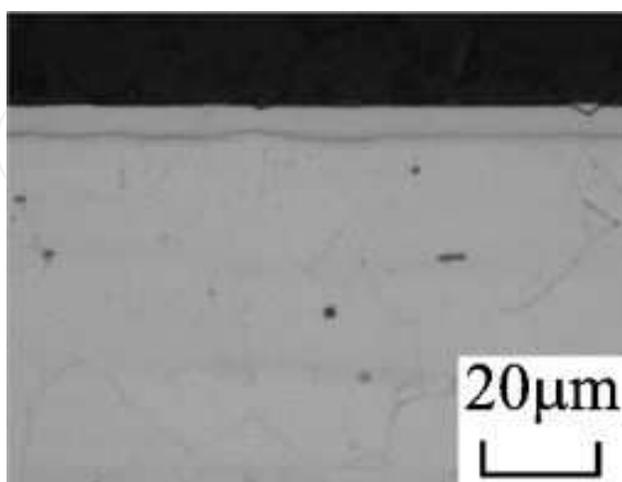
In the next subsections, based on works referred to in Table 1, the typical results obtained by plasma low-temperature thermochemical treatments for the different classes of stainless steels are presented concerning scientific as well as technological aspects. Considering that more information is available for austenitic and martensitic stainless steels nitriding and carburizing treatments, these topics are treated in more details. For other stainless steels and treatments, only some guidelines are presented.

#### 4.1. Austenitic stainless steels

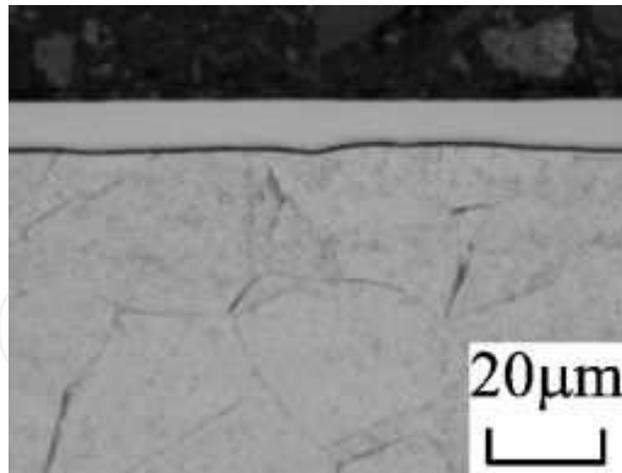
Despite the large number of works dedicated to low-temperature thermochemical treatments of austenitic stainless steels, the large majority of research is carried out for AISI 304, 304L, 316, and 316L steels. Since nitriding and carburizing processes are very similar, typical results for both treatments are discussed together.

For austenitic stainless steels, the low-temperature treated surface is constituted of N-expanded and C-expanded austenite for nitriding and carburizing, respectively. These phases consist of supersaturated interstitial solid solutions, for which the crystalline structure lattice parameters are expanded by the presence of the interstitial atoms solved in it, as previously commented. The enlargement of the austenite lattice parameter can be easily detected by the shift of the diffraction peaks to lower  $2\theta$  angles in X-ray diffraction (XRD) measurements. In the microstructural analysis performed by means of cross-sectional micrographs of treated samples, the expanded austenite tends to present a white aspect, when the polished cross-section for analysis is etched by using Vilella or Marble etchants. The white aspect of the expanded phase layer is directly related to its higher resistance to the etchant if compared with that of the bulk material (chemically unaltered). To illustrate the aspect referred to, Figs. 3 and 4 present typical cross-sectional micrographs of nitrided and carburized AISI 316 austenitic stainless steel, respectively. By confronting Figs. 3 and 4, it is possible to notice that the growth kinetics of the carburized layer is higher than that of the nitride layer. This fact is common for most steels treated at low-temperatures, and it is attributed to the different diffusivities of N and C in the steel solid solution matrix.

When the treatment temperature is too high or the treatment time is too long, precipitation of chromium nitrides/carbides can be observed along the original austenite grain boundaries, being strongly indicative that the corrosion resistance of the treated surface was decreased. According to Egawa et al. [11], the limit temperature for low-temperature nitriding and carburizing, related to chromium nitrides/carbides precipitation in the grain boundaries, is practically independent of the steel composition. For treatments of 4 h, Egawa et al. [11] reported a limit temperature in the range of 430°C–440°C and 540°C–560°C for the low-temperature nitriding and the low-temperature carburizing of austenitic stainless steels, respectively, this difference being attributed to the different N-Cr and C-Cr chemical affinities.



**Figure 3.** Cross-sectional micrograph of a low-temperature nitrided AISI 316 STEEL, treated at 400°C for 4 h (adapted from Egawa et al. [11]).



**Figure 4.** Cross-sectional micrograph of a low-temperature carburized AISI 316 STEEL, treated at 400°C for 4 h (adapted from Egawa et al. [11]).

For the nitriding process, the N-expanded austenite microstructure confers a surface hardness that usually attains 1200 HV, which is associated to a dissolved nitrogen content ranging between 20 and 45 at.% [10-13]. For carburizing, the typical surface hardness is around 1000 HV, which is associated to a dissolved carbon content of about 10 at.% [14-16].

Concerning the depth hardness profiles, in the low-temperature nitrided layers, a sharp hardness decrease is usually observed in the treated layer/substrate bulk interface, whereas for low-temperature carburized layers, a smooth transition tends to be observed. From a mechanical point of view, the referred smooth transition all over the treated layer leads to a smooth properties transition, being, in this case, preferable with respect to the sharp one.

The treated layers performance, regarding their potential industrial applications, is closely linked to the treated layer microstructure, and it has been the main subject of several works. The treated surface characteristics enable considerable gains to the surface wear resistance, with reported wear reductions by a factor of up to 20. Such gains are accomplished with the maintenance or even enhancement of the surface corrosion resistance. Additionally, due to the compressive stresses introduced in the treated layer, fatigue life is also increased, and compressive residual stresses between 2 and 3 GPa are commonly reported (information compiled from refs. [10, 11, 13, 17-23]).

For the treated surface, corrosion resistance results found in the literature are less conclusive, but generally, if the low-temperature treatment condition is respected, there is a tendency to obtain increased corrosion resistance for the treated surfaces. The most important gains in corrosion resistance are reported for low-temperature carburizing treatments.

#### **4.2. Martensitic stainless steels**

In martensitic stainless steels, due to the high crystalline defects density of the as-quenched martensite tetragonal structure, the diffusion of atoms tends to be faster (higher diffusion coefficients for both the interstitial and substitutional atoms) than those verified for the

austenite face-centered cubic structure. On the one hand, it enables higher growth kinetics to the treated layer, but, on the other hand, it also reduces the limit treatment temperature to avoid chromium nitrides/carbides precipitation. Thus, thermochemical treatments of martensitic stainless steels are usually performed at lower temperatures and for shorter times than those used for austenitic ones. Among the martensitic stainless steels, AISI 420 is the main studied steel of the present group, and it is taken as an example to illustrate this section.

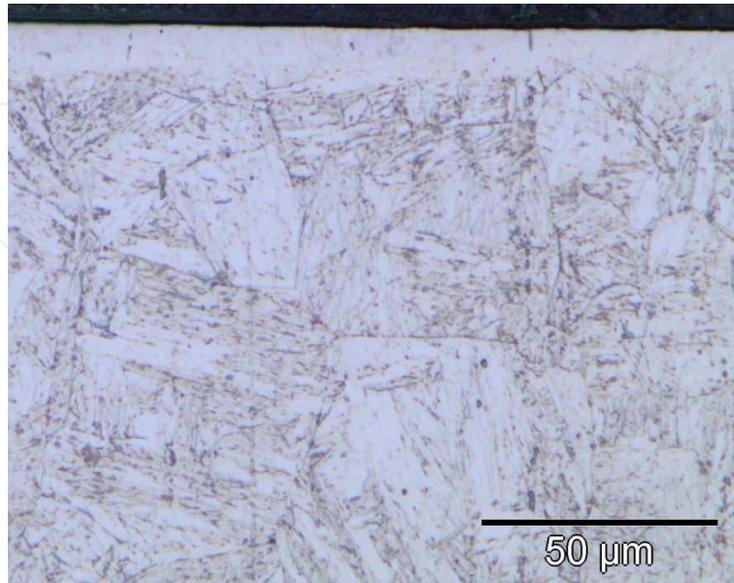
In contrast to austenitic stainless steels, the low-temperature treated surface of martensitic stainless steels is usually composed of expanded phases, such as the nitrogen-expanded martensite for nitriding and carbon-expanded martensite for carburizing, as well as nitrides and carbides ( $\epsilon$ - $M_{2-3}N$  and  $M_3C$  type, respectively).<sup>4</sup> Depending on the composition of the martensitic stainless steel, for which Ni is also present (it is the case of the ASTM CA-6NM grade martensitic stainless steel), and on the used plasma processing parameters, expanded austenite can be also formed together with the expanded martensite phase in the treated layer (referred to Allenstein et al. [24]).

The expanded martensite is also a supersaturated interstitial solid solution, and similar to the expanded austenite, it is detected by the shift of diffraction peaks to lower  $2\theta$  angles in XRD measurements. In the microstructural analysis of cross-sectional micrographs of the treated samples, distinct characteristics of the treated surface are observed for nitrided and carburized samples. Fig. 5 depicts the cross-sectional micrograph of a low-temperature nitrided AISI 420 martensitic stainless steel sample, showing the white aspect of a treated layer composed by N-expanded martensite and nitrides. Once again, the white aspect is related to the higher resistance of the treated layer to the etchant when compared with the substrate bulk (chemically unaltered). By confronting the results in Figs. 3 and 5, it is possible to notice that the growth kinetics of the nitrided layer is higher for the martensitic steel than that verified to the austenitic one, even at a lower treatment temperature. Such a fact is also related to the aforementioned difference of the diffusion coefficients for the different crystalline structures. Fig. 6 presents the cross-sectional micrograph of a low-temperature carburized martensitic stainless steel. In this case, a thin white-aspect layer containing cementite (termed as “outer layer”), probably in addition to C-expanded martensite phase, can be observed. The occurrence of a diffusion layer up to 40  $\mu\text{m}$  in depth [25], composed of C-expanded martensite only, is also present, but it is only detected by means of microhardness depth profile measurements, as presented in the right side of Fig. 6 (for more details, the reader can check ref. [26]).

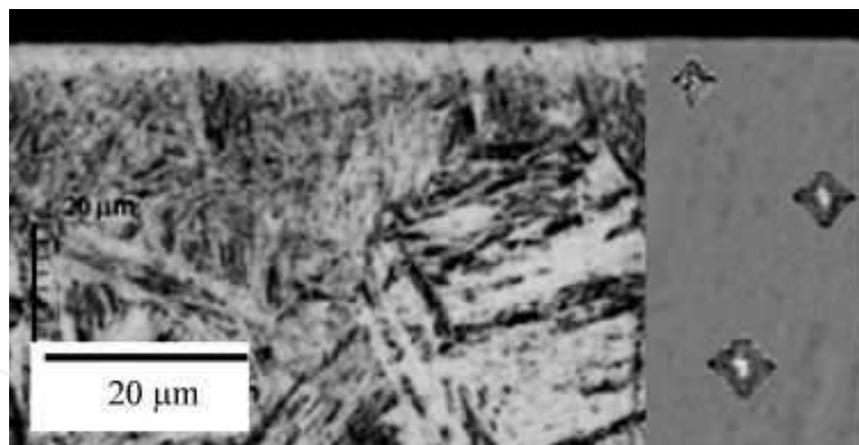
For martensitic stainless steels, the limit temperature for nitrides/carbides precipitation in the grain boundaries is around 350°C–400°C [4] and 450°C [27] for 4 h low-temperature nitriding and carburizing, respectively. As this class of steels tends to present a metastable matrix, the heat treatment performed prior to the surface treatment (in this case, the steel tempering treatment) has significant influence on low-temperature nitriding as presented by Cardoso et

<sup>4</sup>  $\epsilon$ - $M_{2-3}N$  and  $M_3C$  are closely related to  $\epsilon$ - $\text{Fe}_{2-3}N$  and  $\text{Fe}_3C$  (cementite) phases, but as the treatment is performed at low temperature, Cr is supposedly also solved in  $\epsilon$ -iron nitride and cementite. Hence, the most precise way to describe such phases would be by substituting Fe by M, where M would represent the main substitutional (metallic) alloying elements present on the steel. Thus, the possible more precise description for such compounds would be  $(\text{Fe}, \text{Cr})_{2-3}N$  and  $(\text{Fe}, \text{Cr})_3C$ , respectively.

al. [4]. Due to the similarities between nitriding and carburizing, it is expected that the same effect can be important on low-temperature carburizing.



**Figure 5.** Cross-sectional micrograph of a low-temperature nitrided AISI 420, treated at 350°C for 4 h.



**Figure 6.** Cross-sectional micrograph of a low-temperature carburized AISI 420, treated at 450°C for 4 h (adapted from Scheuer [25]).

For the nitriding process, the obtained treated layer microstructure confers a surface hardness that usually attains 1470 HV, associated to a dissolved nitrogen content of 11 at.% [28]. For carburizing, the typical surface hardness is around 900 HV [27]. Up to this moment, no information has been found on the carbon content of the C-expanded martensite. Unreported measurements from the authors of this chapter indicate carbon contents on average at the white-aspect layer (outer layer) in the order of 25 at.% and around 4 at.% in the diffusion layer, but additional efforts must be conducted to confirm such results.

Concerning the depth hardness profiles, similar to austenitic stainless steels, low-temperature nitriding presents a sharp hardness decrease in the treated layer/substrate bulk interface, whereas for low-temperature carburizing a smooth hardness decrease is present.

Similar to the case of austenitic stainless steels, the treated surface characteristics enable considerable gains in the material wear resistance (a wear reduction of 97% is reported in ref. [29]), accompanied by the maintenance or even an enhancement of the surface corrosion resistance. Again, due to compressive stress in the treated layer, the fatigue life is also increased (information compiled from refs. [28–31]).

For the treated surface corrosion resistance results, few papers have been found, but it seems that the general trend is similar to that of the austenitic steels.

### **4.3. Ferritic, duplex, and precipitation hardening stainless steels**

Works on low-temperature thermochemical treatments of ferritic stainless steels are rare in the literature and, apparently, it is more difficult to form expanded phases in such steels. The low-temperature treatments of Duplex stainless steels are roughly similar to those performed in austenitic as well as in ferritic stainless steels at the same time. However, the diffusion of interstitials from one phase to the other one, perpendicular to the surface under treatment, especially for substrates of small grain size, can be important making the treatment kinetics closer than expected for grains of different phases. However, unpublished results of the authors of this chapter, working on low-temperature Duplex steel plasma nitriding, have shown that the layer growth kinetics next to austenite grains is expressively higher than that verified next to ferrite grains. As in the other steels, the treatments promote a considerable hardening and as a consequence increase in the wear resistance.

Precipitation hardening steels tend to present similar behaviors verified for the martensitic steels. As it is the case for all stainless steels, after low-temperature thermochemical treatments, significant surface hardening is obtained, leading the wear resistance of the treated surface to become also improved. Concerning the corrosion resistance, the results presented in the literature are somehow in disagreement. Some papers present an enhancement of the surface corrosion resistance after treatment and others present a decrease of this important property.

Taking into account the results on low-temperature thermochemical treatments of stainless steels, it seems that the corrosion resistance is very sensitive to the treatment parameters, and generally, there is a set of parameters that makes it possible to enhance the corrosion resistance of the treated surface with respect to the chemically unaltered substrate bulk.

### **4.4. Nitrocarburizing and sequential treatments**

The main idea in applying low-temperature nitrocarburizing and sequential low-temperature carburizing and nitriding treatments is related to the possibility of obtaining a treated layer with a smoother hardness transition, when compared to the nitride layers, and higher surface hardness than that obtained in the carburized surfaces. Another motivation would be verifying if the C introduction into the surface would enable the obtainment of precipitation-free treated surfaces at higher treatment temperatures than that used for the nitriding process.

According to Cheng et al. [32], for AISI 316 (austenitic) steel, the plasma nitrocarburizing process has the advantages of both nitriding (high hardness) and carburizing (deep case depth and smooth hardness profile) treatments. However, it was observed that the addition of CH<sub>4</sub> to the gas mixture did not increase the limit temperature to obtain precipitation-free layers. Treating the AISI 420 (martensitic) steel, Anjos et al. [33] obtained a component that is closer to the nitriding process, so the advantages pointed out for austenitic stainless steels was not clearly found for the studied martensitic steel.

Studies on the sequential treatments, especially in austenitic stainless steels, also present the possibility of obtaining high hardness (typically attained from nitriding) and smooth hardness profiles (which is typically attained from carburizing) [34,35].

Considering the performance of both treatments in terms of wear, when the primary objective of high hardness and smooth hardness profiles are achieved, it tends to be better than nitriding and carburizing. Concerning corrosion resistance, the treated surface also tends to present higher corrosion resistance than the untreated surface.

## 5. Conclusion and final remarks

The studies on low-temperature plasma thermochemical treatments of stainless steels are relatively new, but they are already applied and accessible industrially. Most of the present knowledge on this subject comes from works developed for austenitic stainless steels, which occur in profusion in the literature. Considering the treatments of martensitic stainless steels, the number of works is considerably lower, and for the other stainless steels, the respective works are considerably rare. The application of such treatments has proved to be very efficient in producing surfaces with high hardness, wear, and corrosion resistances and compressive residual stresses. As a consequence, the treated parts tend to present longer life when subject to severe wear, corrosive environments, and also cyclic loadings. Thus, from a technological point of view, such plasma-assisted treatments can be broadly applied. On the other hand, from the scientific point of view, several opened questions remain to be answered. As these treatments are carried out at low temperatures, the thermodynamic equilibrium cannot be attained in the solid state, and metastable phases tend to be formed. Thus, the mechanisms of formation of such phases are not yet completely understood. Considering the application potentiality, the mechanism on the origin of the corrosion resistance of surfaces composed or containing such phases is not yet completely explained. These are some examples of very basic opened questions, so it is clear that low-temperature plasma thermochemical treatments nowadays comprise an important R&D field. The development of research will very probably extend the current known range of application potentialities, enabling new industrial applications, while also being expected to bring important growth to this plasma technology in the coming years.

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