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Review

Overview of Surface Modification Strategies for Improving the Properties of Metastable Austenitic Stainless Steels

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Abstract: Metastable austenitic stainless steels (MASS) are widely used in various industrial applications due to their exceptional compromise between mechanical properties and corrosion resistance. However, the mechanical properties of these materials can be further enhanced by surface treatments. This paper reviews various surface treatment methodologies used to improve the mechanical properties of MASS, with particular attention to laser treatments. The effects of these surface treatments on the microstructure and chemical composition in the thermal affected zone of the MASS are discussed, and their impact on the material's mechanical properties, such as hardness, tensile strength, and fatigue life, are investigated in detail. Additionally, the paper highlights the limitations of these surface treatments and points out some areas where further research is needed. The findings presented can be used to guide the selection of appropriate surface treatment techniques for specific applications, ultimately improving the performance and lifespan of MASS in various industrial settings.

Keywords: metastable austenitic stainless steels (MASS); transformation induce plasticity (TRIP) steels; surface modification treatments; microstructure; mechanical properties

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1. Introduction

Due to regulatory pressures and customer expectations, the automotive industry designs its components to promote vehicle weight reduction, which is known to decrease energy consumption and also greenhouse gas emissions in the case of combustion engines [1]. It has been estimated that for every kilogram of weight saved in a combustion vehicle, there is about 20 kg of carbon dioxide reduction [2]. Besides lightweight, formability, high mechanical strength, and energy absorption are the main requirements of the automotive industry, which require applicability at high production rates and low cost [3]. All these factors have put pressure on car manufacturers to find the most suitable material that can offer the lowest weight and price under service-like conditions [4]. This situation has stimulated competition between manufacturers of different materials, not only metallic alloys but also polymers and composites, to develop new grades and enhance the final quality. In particular, steel companies are continuously trying to improve the mechanical properties of conventional steels by combining different strengthening methods such as grain size reduction, solid-solution strengthening, precipitation hardening, and texture optimization [5]. Recently developed advanced high-strength steels (AHSS) present an optimal relationship between strength and formability thanks to their multiphasic microstructure, like for example, in the metastable austenitic stainless steels (MASS). In this regard, MASS includes some families where the materials under service-like working conditions induce either phase transformation (transformation-induced plasticity, TRIP) and/or twin formation (twinning-induced plasticity, TWIP) [6]. The present review paper focuses to observe the surface modification on TRIP steels; in particular to the austenite (γ-) to martensite (ε- and/or α'-) phase transformation and their effect in terms of mechanical properties.

Within the aforementioned information, the material failures usually start on the surface, due to the presence of superficial defects producing a reduction in the fatigue, wear, and/or corrosion resistance [7,8]. In this sense, superficial treatments promoting surface grain refinement at different length scales (also known as the nanostructuring process) lead to effectively enhanced global behavior and particularly service lifetime of materials under service-like working conditions [9]. A wide variety of surface nano-structuring techniques commercially exist, such as mechanical, chemical, physical, thermal, electrochemical, and most recently, the use of laser modification of metal surfaces. Focusing on MASS, this article aims to review and explain the different surface modification techniques and subsequently highlight the microstructural and mechanical effects induced by each technique at different length scales. The main methods studied by scientists in this field during the last 23 years (from 2000 up to 2023) have been summarized in Figure 1 as a function of the surface treatment employed. As it is shown in this representation, all the different surface modification methods started to gain interest during the last decades due to the number of manuscripts published in international journals increasing. However, laser treatment has not been extensively used in this sector, and the interest is growing slowly compared with the most commonly implemented techniques.

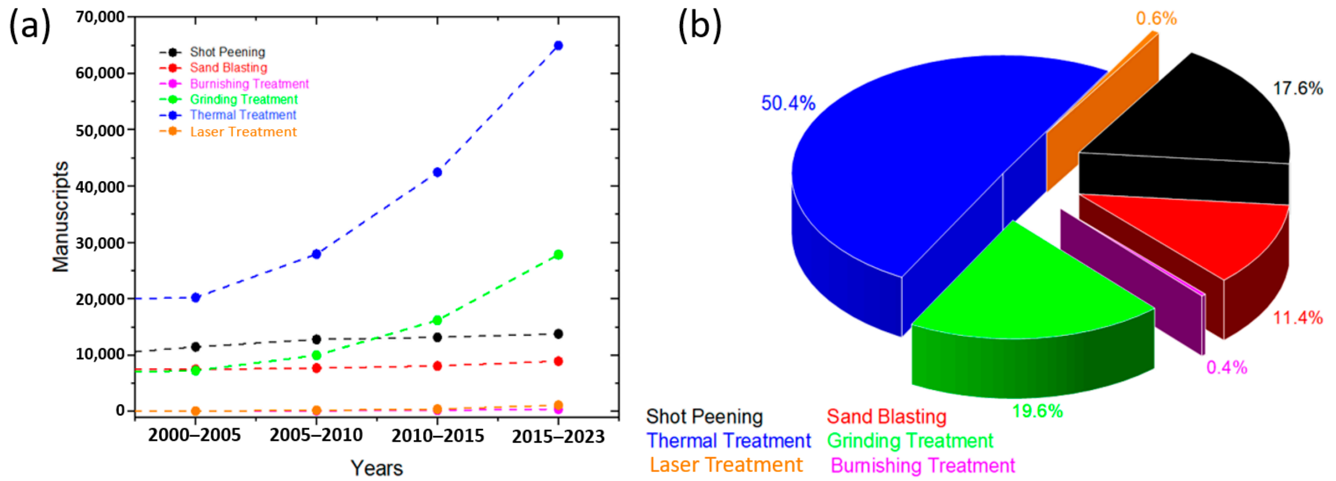


Figure 1. (**a**) Evolution of the research papers published over the last 23 years and (**b**) summary of the main published papers for the different surface modification techniques available in the literature and employed in the industrial sector.

Numerous factors (for example: costs, surface modification speed, among others) are the key parameters for correctly choosing the best surface treatment method for each specific material and final application. Nowadays, the main techniques used at industrial level are the thermal surface treatments and the grinding process (Figure 1a). Both techniques have a growing interest due to inducing microstructural changes that consequently enhance the mechanical properties of the investigated material [10]. On the other hand, mechanical surface treatment techniques (i.e., shot-peening and sand-blasting, labelled as SP and SB, respectively) are widely used in the industrial market, but the interest during the period of interest remains constant, which highlights that both technologies are stable [11]. Currently, the laser surface treatment (LST) technique is starting to receive more interest in this field [12]. Although the use of the laser method is faster compared with other surface modification techniques, the laser interaction with MASS presents unique challenges due to its inherent material properties [13]. However, the preliminary results reported on this method with the investigated material highlight a tremendous effect on the surface structure, enhancing the fatigue and corrosion resistance thanks to the phase transformation, from γ- to α'- and/or ε-martensite, induced near the affected zone [14].

Within the aforementioned information, this review has been divided into two different sections: the initial section, where the theoretical background for the different surface modification techniques is presented in detail, and subsequently, the second section, where the main effects on the surface of MASS are presented; the microstructure and the mechanical properties are the key parameters taken into consideration in this study.

2. Surface Treatment Methods: Theoretical Background

The different surface modification techniques can be classified into three main groups: mechanical, chemical and electrochemical, and thermal methods, as summarized in Figure 2. Furthermore, combinations of two or more treatments of each of the main groups are known as mixed treatments. These combined treatments combine the main advantages of each treatment to prove a final material with excellent mechanical and microstructural superficial properties, which considerably enhance the lifetime of the treated tool and/or workpiece under service-like working conditions.

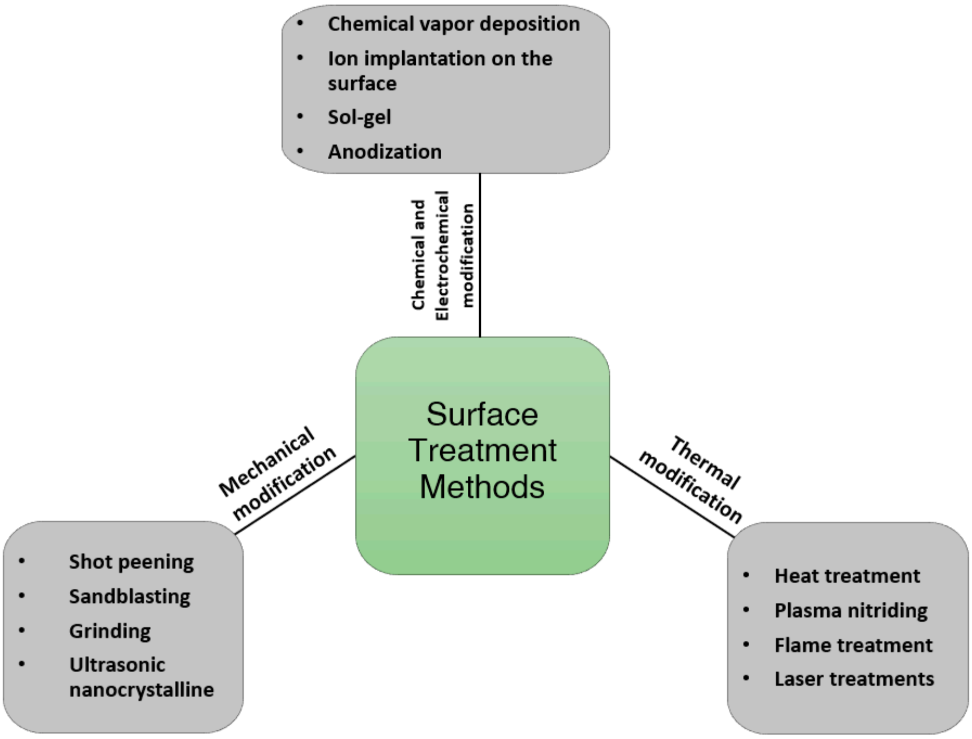


Figure 2. Schematic representation of the most used surface modification methods.

Table 1 compares the features of the three main categories related to the surface modification methods, as described below:

(a) Mechanical methods result in increased surface hardness and then improve the wear resistance of the treated materials. They are commonly used in manufacturing, tooling, and automotive industries because they are simple, cost-effective, and can be performed on a wide range of materials. Nevertheless, there is limited control over surface morphology and composition, which can result in surface damage.

(b) Thermal methods are commonly used in aerospace, automotive, and biomedical industries, for improving wear resistance. They offer precise control over surface morphology, composition, and microstructure; however, their application is limited by the requirement for specialized equipment.

(c) Chemical and electrochemical methods are mainly used for corrosion protection and improving biocompatibility. They provide a smooth surface finish but are limited to certain types of implant materials [15] and require careful control of reaction conditions.

Table 1. Comparison of the three most used surface modification methods.

Surface Modification Method	Surface Quality	Application	Advantages	Disadvantages
Mechanical	Increased surface hardness, improved wear resistance [16]	Manufacturing, tooling, automotive	Simple and cost-effective, can be performed on a wide range of materials [17–19]	Can result in surface damage, limited control over surface morphology and composition [20]
Thermal	Controlled microstructure, improved wear resistance	Aerospace, automotive, biomedical [21]	Precise control over surface morphology, composition, and structure	Limited to certain material types, requires specialized equipment [22,23]
Chemical and electrochemical	Smooth surface finish	Corrosion protection, improved biocompatibility [24]	Good adhesion to substrate, can selectively modify surface chemistry [25]	Limited to certain material types, requires careful control of reaction conditions [26]

2.1. Mechanical Methods

Mechanical surface modification methods have been developed in order to improve the mechanical properties of big workpieces with different dimensions and geometries. The surface of each workpiece can be reinforced by changing the microstructure (i.e., refining the grain size, inducing phase transformation, etc.) and the surface stress state (mainly inducing compressive residual stresses), which will increase the fatigue, corrosion, and wear resistance of the whole part [27]. These methods mainly reinforce the surface layer of the workpiece by inducing plastic deformation (increasing the dislocation density in the region near the surface that has been mechanically deformed) and as a direct consequence increase the residual compressive stresses and, therefore, the mechanical properties of the deformed region. Furthermore, due to these induced compressive residual stresses, the initiation and growth of fatigue cracks can be delayed, improving the fatigue properties of the workpiece [28]. The mechanical treatments that exist in the literature can be separated into the following groups: shot peening, sand blasting, grinding, and ultrasonic nanocrystalline surface modifications.

2.1.1. Shot Peening

The shot peening (SP) technique is the most common and used in the industry due to its simplicity, cost-effectiveness, and reliability. However, the induced roughness of around hundreds of micrometers [29] is not suitable for certain applications, such as engines for the aerospace industry [30]. The SP technique is based on the collision between spherical particles (also known as bullets), mainly glass, metal, or ceramic material (like alumina "Al_2O_3"), and the surface of the part that is to be treated. The particles are shot at a relatively high speed (values ranging between 40 and 90 m/s [31]) against the workpiece's surface and plastically deform the region of interest. Due to this process, the microstructure of the material changes, and the deformed layer increases its hardness by strain hardening, as well as the compressive residual stresses. This enhances the wear and corrosion resistance, and delays crack propagation improving considerably the fatigue behavior under service-like working conditions [7].

In the literature, several alternative techniques based on the same working principle can be found, such as air-blast shot peening (ABSP), rotationally accelerated shot peening (RASP), surface mechanical attrition treatment (SMAT), and ultrasonic shot peening (USP). In the ABSP methodology, particles with sizes between 0.25 and 1 mm are accelerated by compressed air against the workpiece's surface [32] while for the RASP treatment, the particles are propelled by centrifugal wheel paddles. SMAT and USP are emerging technologies, which are capable of inducing a nanostructured layer on the surface of the metallic components and are commonly used in order to improve the fatigue resistance [33]. Both techniques induce multi-directional impacts because the collisions happen inside a closed chamber. The achieved surface properties are mainly dependent on the vibration frequency of the chamber, the processing time, and the size of the shot particles [29]. SMAT has been recognized as a technique for upgrading the microstructures and properties of materials by generating a gradient-structured layer on the material surface without tampering with the local chemical compositions and near-surface compressive residual stresses. In the case of USP, an ultrasonic generator with high power and frequency (around 0.6 kW and 20 kHz, respectively [34]) is used to move the particles, whose size ranges between 1 and 5 mm in diameter. Figure 3 schematically displays the main differences between SP and other mechanical methods presented along this region.

The SP process has been applied to MASS to analyze the expected strain-induced martensite (α'- and/or ε-) after this mechanical treatment. In this context, Fargas et al. [35] carried out an SP treatment on MASSs (particularly AISI 301LN) to evaluate the α'- and/or ε-phase transformation and how it influenced the fatigue limit of the material. The effect of SP was analyzed for the same steel grade but considering two pre-existing martensite α'-phase contents: less than 3% for the annealed (A) condition and 38% for the cold rolled (CR) material. Extensive γ- to α'-martensite phase transformation was measured for the A condition after SP, reaching a rise up to 30%, whereas for CR specimens, the presence of pre-existing α'-martensite strongly slowed down the proportion of α'-martensite induced by SP. For the A specimens, similar fatigue behavior was observed after SP, in contrast to significant improvements in the fatigue limit for the CR specimens [36].

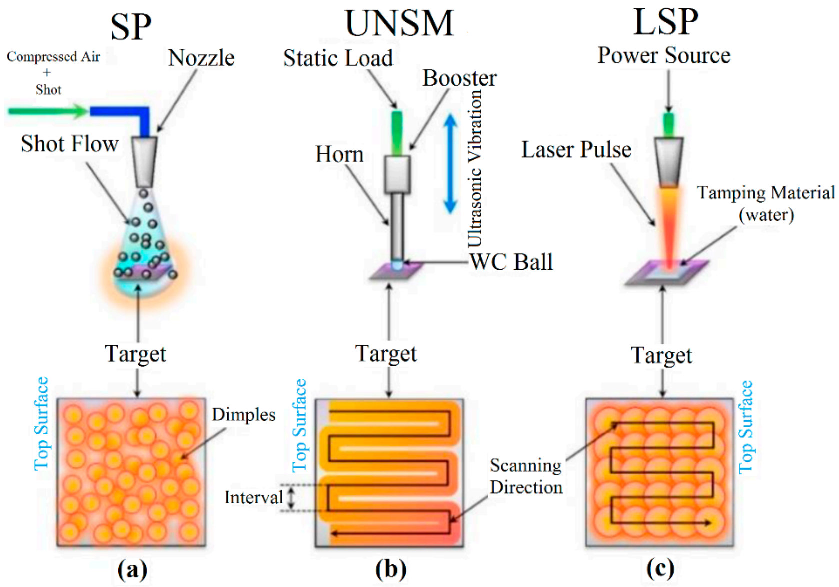


Figure 3. Schematic illustration of different surface severe plastic deformation (SPD) treatments and the corresponding plastically deformed top surface of the target material: (**a**) shoot peening (SP), (**b**) ultrasonic nanocrystalline surface modification (UNSM), and (**c**) laser shock peening (LSP) processes (reproduced from Ref. [37], with permission from MDPI, 2022).

2.1.2. Sand Blasting

Abrasive blasting, also known as sand blasting (SB), is a term used to describe the process of smoothing, shaping, and cleaning hard surfaces by applying high-pressure solid particles to the surface of interest (Figure 4). SB equipment is usually housed in a chamber and mixed with air pressure, and then directed to the surface of the workpiece at a very high speed through a movable nozzle. This nozzle comes in a variety of shapes, sizes, and materials. Boron carbide is the most applied nozzle because it is highly resistant to abrasive wear [38]. Tilgham invented this process in 1871, and it is used in today's SP [39–41]. The relationship between mechanical surface operation and increased fatigue strength was established by Foppl et al. [42,43]. So much research was carried out by Thum in the early 1930s on the SB benefits on front of rolling fatigue, corrosion fatigue, and fatigue of welded joints [42–45].

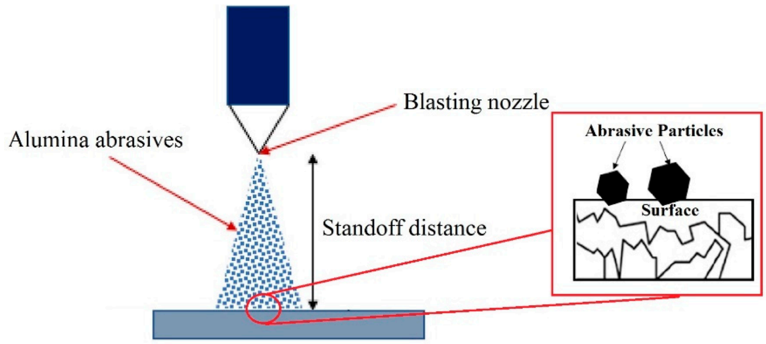


Figure 4. Surface roughening effect of the abrasive particles on the substrate (reproduced from Ref. [46], with permission from Elsevier, 2019).

2.1.3. Grinding Treatment

Grinding (G-) is one of the finishing processes that gives high accuracy and a good surface finish. In this process, an abrasive product is used, and the material removal rate is very low [47,48]. Usually, a rotating wheel that comes in to contact with a work surface is responsible for the operation [49,50]. This rotating wheel is made of abrasive grains that are bonded together. These abrasive grains act as cutting tools and remove tiny particles on the surface of the workpiece. Compared to other surface methods, this process is more expensive and should be used in conditions where is possible to control all parameters [51].

2.1.4. Ultrasonic Nanocrystalline

Among the many useful technologies for surface reinforcement, ultrasonic nanocrystalline surface modification (UNSM) technology is one of the most widely used nowadays to improve mechanical and tribological properties [52,53]. Conventional UNSM technology employs a tungsten carbide (WC) ball that is affixed to a supersonic transducer (see Figure 5). The transducer imparts impacts on the sample surface at a frequency of 20,000 times or more per second, with 1000 to 100,000 strikes per square millimeter. Further elaboration on the technical aspects of the UNSM technology is available in [54]. Strikes, which can also be described as micro-cold forging, cause severe plastic and elastic deformation at the near surface layer, thus creating a nanocrystalline structure with a compression residual stress of around 10 μm in depth [55]. Strikes also create controllable micro-narrows at the surface of the sample, which improves the tribological characteristics of the interlocking surfaces in relative motion [56]. Each of the micro-dimples produced by laser surface texturing can function as a micro-hydrodynamic bearing that mitigates the detrimental effects of poor lubrication in sliding or rolling contact conditions, thereby enhancing the performance and durability of the lubricated system [57]. Correction of surface layer nanostructures can occur simultaneously with increasing the resulting strength and flexibility of the sample according to the Hall and Petch relationship [58]. In other words, by doing this treatment, the surface integrity of the treated workpiece increases their surface integrity in terms of hardness and fracture toughness.

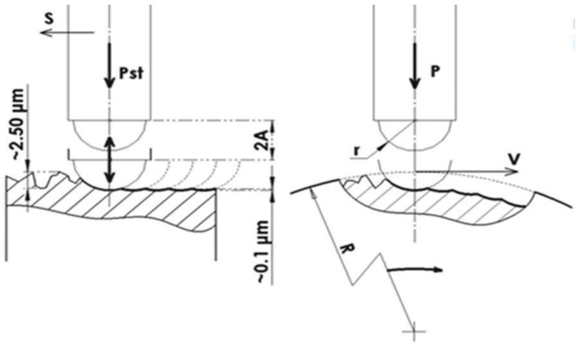


Figure 5. Schematic representation of the ultrasonic nanocrystalline surface modification (UNSM) method (reproduced from Ref. [29], with permission from MDPI, 2019).

2.2. Thermal Methods

Thermal surface modification methods offer a wide range of techniques to enhance the properties of materials and most of them have been applied to MASS. These methods involve thermal processes that directly alter the properties (even microstructurally and mechanically) of the near surface of the workpiece treated. Laser surface texturing, one of the prominent thermal methods, involves using high-energy laser beams to modify the microstructure on the surface of MASS. This technique allows precise control over the shape, size, and distribution of microstructures, such as micro-dimples or micro-grooves, which can significantly influence the tribological, mechanical, and corrosion resistance properties of the material. Additionally, cold working techniques, such as rolling, bending, and hammering, can induce plastic deformation on the surface of MASS, resulting in work-hardening and improved mechanical properties. Thermal surface modification methods offer versatile approaches to tailor the surface characteristics of MASS components, enabling improved performance and extended service life in various applications.

2.2.1. Surface Heat Treatments

This group of thermal processes refers to treatments where the surface layer has the requirement of a higher hardness to be more wear resistant than the core. Surface heat treatments are conventional and effective surface modification techniques employed to enhance the properties of metallic alloys. By subjecting the surface of MASS to controlled heating and cooling processes, their microstructure and composition can be precisely altered. One commonly used surface heat treatment method is carburizing, where the MASS surface is exposed to a carbon-rich atmosphere at elevated temperatures [59]. This process promotes the solid diffusion of carbon atoms into the surface layer, resulting in the formation of a hardened, wear-resistant outer layer known as a carburized case [60]. Another heat treatment technique is nitriding, which involves introducing nitrogen into the MASS surface. Nitrogen atoms diffuse into the material, forming a hard and corrosion-resistant nitride layer [61]. Heat treatment can also be employed to modify the residual stresses within the MASS surface. Controlled heating and subsequent cooling can induce thermal stress relief and promote the relaxation of residual stresses, thereby improving the dimensional stability and fatigue resistance of the material.

2.2.2. Plasma Nitriding

The temperatures usually employed for nitriding treatments of low alloy and tool steels cannot be used for stainless steels because they would promote the precipitation of hard chromium (Cr) compounds (nitrides, carbides). As a consequence, the Cr-depleted matrix will not be able to form a protective passive film, and corrosion easily occurs [62]. However, at lower temperatures, i.e., temperatures at which Cr diffusion is very low while interstitial atoms are able to diffuse (≤450 °C for nitriding [63]), the formation of nitrides is inhibited and modified surface layers can be obtained. These layers consist mainly of a metastable supersaturated phase, named the expanded austenite or S phase, with a high hardness and good corrosion resistance. The nitriding of austenitic stainless steels (ASS) at temperatures ranging between 495 and 565 °C has been well established since 1970s [64,65]. This nitriding is often conducted using plasma techniques, which allow for the removal of the surface oxide layers, and is known as plasma nitriding (PN). PN processes use discharging plasma in a combination of nitrogen and hydrogen gases. The most important advantages of PN over conventional nitriding processes are reduced cycle times, controlled growth of the nitriding surface layer, elimination of the white layer, reduced distortion, there is no need to finish operations, there are no pores, and mechanical masks instead plating are pointed out. Nitride layers include scattered layers of $Fe_{2-3}N$, FeN, Fe_4N, and Fe_2N_3. The layer's spread is from tens to hundreds of microns, and they are ideal for improving wear resistance by optimizing the nitrogen to hydrogen ratio. Some of the extra layers can be removed and corrosion properties improved (Figure 6) [66].

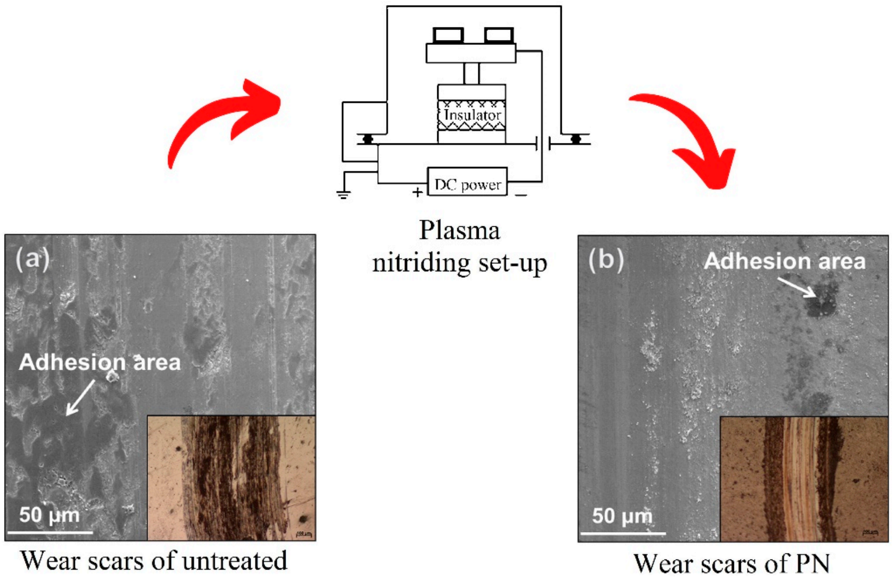


Figure 6. Wear scars of (**a**) untreated and (**b**) PN treated (reproduced from Ref. [67] with permission from Elsevier, 2006; and reproduced from Ref. [68], with permission from Elsevier, 2021).

2.2.3. Flame Treatment

Hardening of the surface by the flame heat treatment process is one of the methods in which a thin surface shell of a steel part is heated rapidly at a temperature higher than the critical temperature of the steel. Flame hardening is often carried out in various ways, including by using gas burners. Equipment and the range of flame range are important parameters in this process. The flame method has modes such as fixed, progressive, rotary, or a combination of rotary and progressive [69].

2.2.4. Laser Treatment

Laser treatment is a highly effective and versatile surface modification technique used to enhance the properties of MASS [70]. By utilizing high-energy laser beams, precise surface modifications can be made, resulting in improved surface characteristics and performance. Laser surface texturing (LST) is a prominent application of laser treatment, where controlled laser ablation is used to create microstructures such as micro-dimples, micro-grooves, or laser-induced periodic surface structures (LIPSS). These microstructures can significantly impact the tribological properties, such as friction, wear, and lubrication behavior of the material. Laser surface melting (LSM) is another laser treatment method (LTM) that involves selectively melting the surface layer of MASS to refine the grain structure, eliminate defects, and improve the surface finish. Additionally, laser heat treatment can be employed to modify the phase composition and microstructure of MASS by inducing localized heating and subsequent controlled cooling. This can result in the formation of desired phases, such as martensite, or the refinement of existing phases, leading to enhanced mechanical properties. LTM provides precise control over the treated area, depth, and intensity, making it a valuable technique for tailoring the surface properties of MASS for specific applications such as automotive, aerospace, and medical industries. The femtosecond (*fs*-) laser pulses are generated by an amplified solid-state Ti: sapphire laser chain. Low energy pulses are extracted from a mode-locked oscillator ~1.6 nJ/pulse, 80 MHz, 800 nm, and 120 fs. The pulses are then injected in an amplifier including an optical pulse stretcher, a regenerative amplifier associated with an amused pumping source, a 20 W Nd:YLF laser, and a pulse compressor. P-polarized pulses with a wavelength centered on 80 µm of 1.5 mJ and a 1 kHz repetition rate with a typical duration of 150 fs are obtained. Nanosecond (*ns*-) pulses are extracted from the same regenerative amplifier without any *fs*-pulse injection from the oscillator. The pulse duration obtained is then within the range of 7–8 ns. To allow a low energy regime ~typically 0.01–0.5 mJ/pulse, laser pulses are obtained without using the two-pass amplifier. Additional attenuation is then provided by a half-wave plate coupled with a polarizer. An external electronic clock device, which controls the voltage applied to the Pockels cell, also allows the use of this system in a single-shot mode [71,72].

Table 2 provides a comparison of various laser surface modification methods based on surface quality, applications, advantages, and disadvantages. Laser surface modification methods are used in a variety of industries such as aerospace, automotive, medical, and nuclear. Laser shock peening and submerged laser peening are effective methods to improve fatigue resistance and reduce stress corrosion cracking in materials. However, these methods are limited to small areas and can be expensive due to the specialized equipment required. Surfi-Sculpt processing is a high-precision method that can create complex shapes and patterns with improved surface texture and roughness, making it suitable for medical implants, aerospace components, and other high-performance materials. It is limited to small areas and can be expensive. Laser surface hardening is used in manufacturing, automotive, and aerospace industries to increase surface hardness, wear resistance, and corrosion resistance. The method provides precise control over the hardened area and depth, improving part longevity. Nevertheless, it is limited to ferrous materials and may result in distortion or cracking. Laser decontamination is a fast and efficient non-contact process used to remove surface contaminants such as paint, rust, and biological agents. The laser surface-structuring process improves surface texture, enhances adhesion, and increases hydrophobicity, making it suitable for medical devices, electronics, and other high-performance materials. The method provides high precision and accuracy, but it is limited to small areas and may result in material damage or surface roughening. Overall, laser surface modification methods offer unique advantages and disadvantages, making them suitable for specific applications. The choice of method depends on the desired surface quality, application, and available resources.

Table 2. Comparison of Laser surface modification methods together.

Laser Surface Modification Methods	Surface Quality	Applications	Advantages	Disadvantages
Laser shock peening	Improved fatigue resistance, reduced stress corrosion cracking [73–75]	Aerospace, automotive, medical, and nuclear industries [76]	Improved surface properties, deeper layer of compressive residual stress [77]	Limited to small areas, expensive [78]
Submerged laser peening	Improved fatigue resistance, reduced stress corrosion cracking [79,80]	Aerospace, automotive, medical, and nuclear industries	Reduced thermal damage to surface, deeper layer of compressive residual stress [81]	Limited to submerged surfaces, requires specialized equipment [82]

Table 2. *Cont.*

Laser Surface Modification Methods	Surface Quality	Applications	Advantages	Disadvantages
Surfi-Sculpt processing (three-dimensional laser surface modification)	Improved surface texture and roughness, increased hydrophobicity, enhanced biocompatibility [83]	Medical implants, aerospace components, and other high-performance materials [84]	High precision and accuracy, can create complex shapes and patterns [85]	Limited to small areas, expensive [86]
Laser surface hardening (LSH)	Increased surface hardness, wear resistance, and corrosion resistance [87,88]	Manufacturing, automotive, and aerospace industries	Precise control of hardened area and depth, improved part longevity Popoola	Limited to ferrous materials, potential for distortion or cracking
Laser surface-structuring process	Improved surface texture, enhanced adhesion, increased hydrophobicity [89]	Medical devices, electronics, and other high-performance materials [90]	High precision and accuracy, can create complex patterns and textures [91]	Limited to small areas, potential for material damage or surface roughening [92]

Laser Shock Peening

Laser shock peening (LSP) (Figure 7) is one of the common methods for improving the mechanical and surface properties of metals in industries. In this method, a laser is applied to the surface, and then residual stresses occur in the underlying layers, which improves mechanical properties such as fatigue, and some articles have even reported improvements in corrosion properties [93,94]. The depth of laser penetration is around 10 times higher than in the case of the same shot with the SP method. The depth of the effect is about 0.5 to 1.5 mm [93]. LSP involves exposing a metallic sample surface to high-intensity laser irradiation (up to 1–10 GW/Cm^2) for a very short time (less than 50 ns) [94]. The interaction between laser and metal induces a high-pressure plasma that produces high amplitude shock waves, inducing plastic deformation and creating compressive residual stresses. This type of interaction is called "direct ablation" as shown in Figure 7. Irradiating water-immersed surfaces (1–10 mm water thickness) enables a factor 5–10 intensification of the shock amplitude by a trapping-like effect on the plasma.

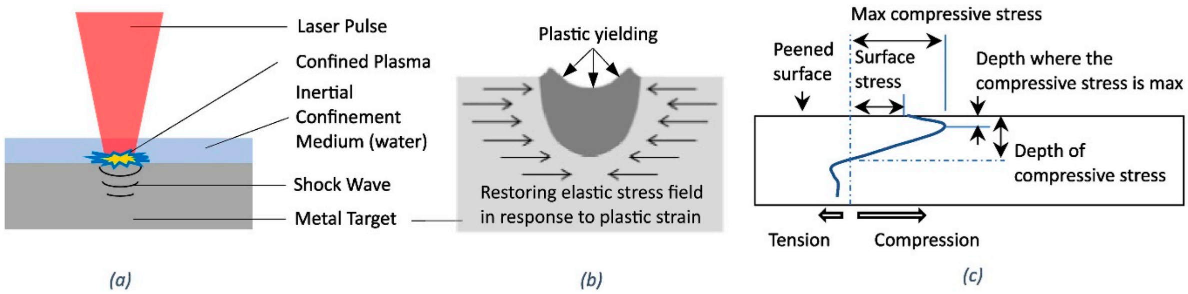


Figure 7. (**a**) A schematic of the LSP process, (**b**) peening induced plastic yielding with associated restoring stress reaction, and (**c**) a typical residual stress depth field introduced into the surface region by a peening action applied to the top surface (reproduced from Ref. [95], with permission from Elsevier, 2022).

Submerged Laser Peening

When a laser pulse with a *ns*-power of the beam is focused on a metal material, such as steel underwater, the surface of the material absorbs the laser energy and the metal plasma is created through a reducing interaction. The immobility of water acts to enclose the metal plasma and prevent its rapid expansion, and as a result, the plasma is formed by pressure on the metal surface. Plasma pressure, which affects the surface of the metal, reaches several GPa and exceeds the yield strength of the material. The metal around it limits a compressive stress state on the surface layer, as shown in Figure 8. The residual compressive stress can be applied by scanning the laser pulses to the entire surface used in the metal surface layer [96]. However, the conventional LPM uses a protective coating, or so-called victim, on the surface of the material to strengthen the laser absorption and prevent melting and damage to the surface. Before laser irradiation, surface control is usually performed using a black coating. Toshiba [97] has recently developed a process that does not require coverage, but instead has less laser power and uses controlled conditions to mechanically achieve the desired result.

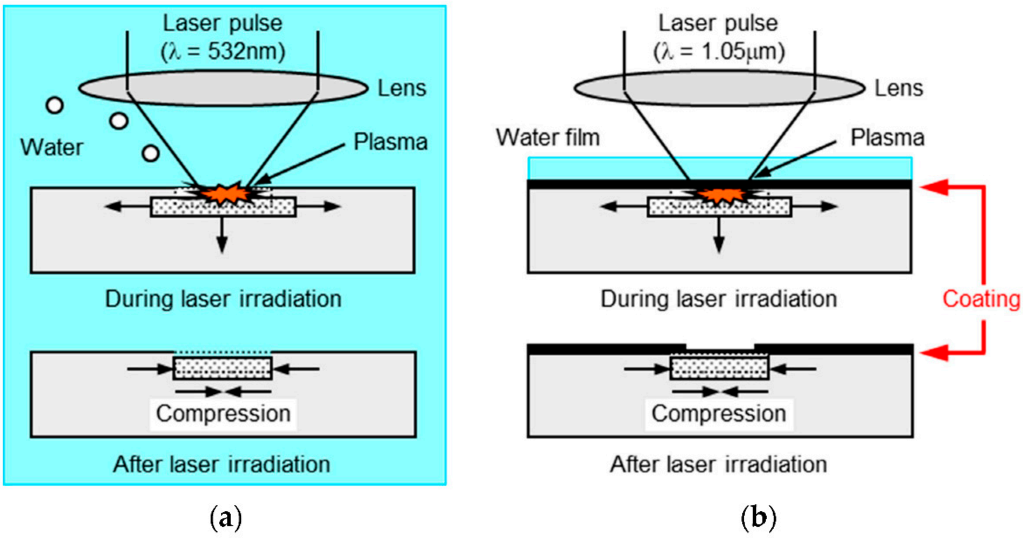


Figure 8. Fundamental process of underwater LP: (**a**) LP without coating (LPwC), and (**b**) LP with coating (reproduced from Ref. [46], with permission from Elsevier, 2019).

Surfi-Sculpt Processing (Three-Dimensional Laser Surface Modification)

Surfi-Sculpt®, a three-dimensional (3D) laser surface modification technique, is thought to be driven by a melt pool instability that is dependent on a quasi-steady-state temperature field. Attempting to control melt pool instability requires a better understanding of the heat input and the selection of optimized laser processing parameters. This allows for the optimal production of a variety of feature shapes, allowing this new manufacturing technique to be used in applications requiring increased substrate surface area or functional surface textures. Figure 9 depicts the steps of the Surfi-Sculpt process. As shown in Figure 9 (Step 1), the structuring process involves impinging an electron or laser beam (LB) against the metallic workpiece surface. First, the beam melts a volume of metallic material on the workpiece surface, creating a molten pool at a predetermined start point. Second, the beam is rapidly deflected sideways (swiping) over the workpiece surface using computer controlled electromagnetic coils (in the case of electron beam (EB)). As a result, the molten material is displaced in the direction opposite the EB deflection (Figure 9, Step 2). The combined effects of vapor pressure and surface tension allow the molten material to pile up and form a small protrusion at this point [98,99] (Figure 9, Step 3).

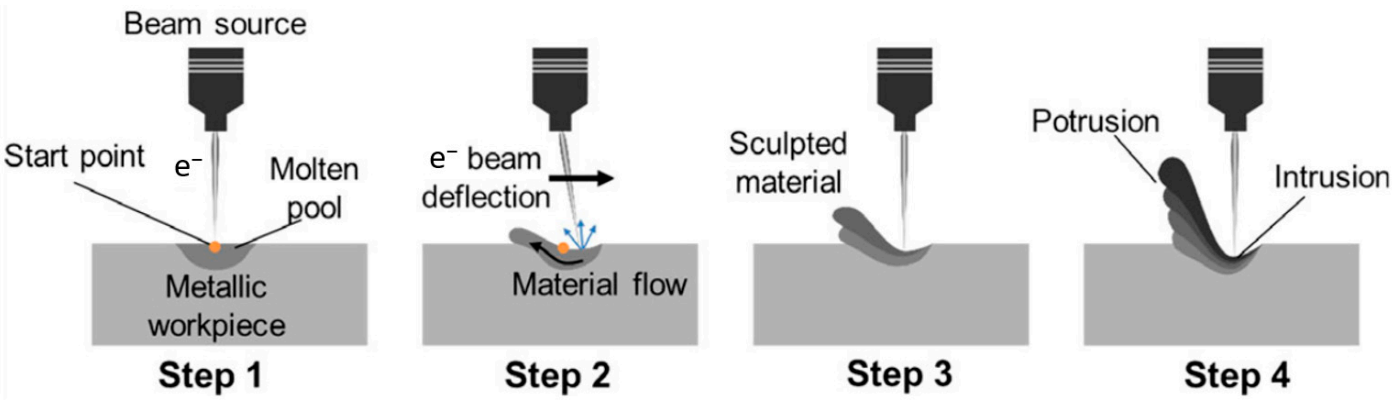


Figure 9. Schematic representation of the Surf-Sculpt process (reproduced from Ref. [100], with permission from Wiley, 2018).

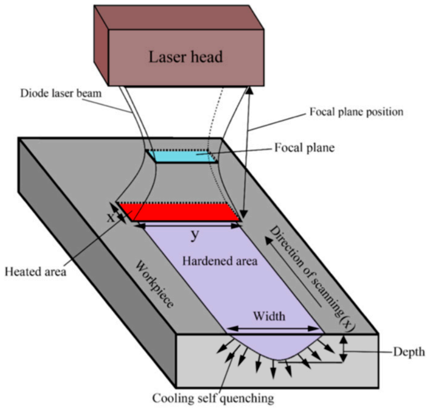
A structured protrusion and corresponding intrusion are created by repeating the beam deflection process multiple times in the same location over the workpiece surface, as shown in Figure 9 (Step 4). Instead of only one pair of protrusions/intrusions as shown in Figure 9, the Surfi-Sculpt process can be used to create a series of protrusions across a metallic workpiece at the same time. As a result, the process can generate a high aspect ratio of protrusions in a matter of seconds per square centimeter [101]. Furthermore, by adjusting the beam parameters, which include beam acceleration, current, focus, scanning frequency, and process duration, a wide range of different protrusion patterns and shapes across the metal surface can be produced [101,102]. When using EB, the size of the surface-modified workpiece is limited to the dimensions of the vacuum chamber in which the structuring process is carried out. By contrast, this limitation does not exist when LB is used.

Laser Surface Hardening

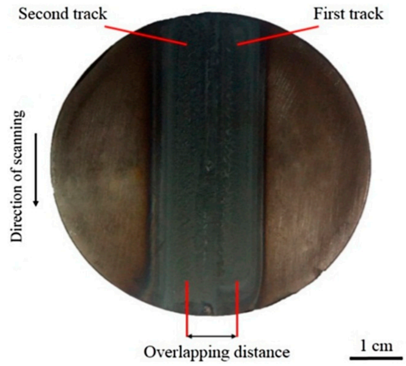
A high accuracy of the hardening process has been achieved by the laser surface hardening (LSH) process [103]. In this technique, the laser beam produces a high temperature on the top of the steel sample (Figure 10a), which transforms to γ-phase. After passing the laser from the heat affected zone (HAZ), the surface is quenched by environment air conditions (Figure 10b) and γ-changes to α'-and/or ε-phases, which is hard, and then the surface will have a better wear resistance. During the laser hardening, some defects may generate on the surface because the laser beam has been concentrated on a unique area. For instance, if the generated heat from the laser beam is too high, the surface can be melted. Also, sometimes micro-cracks generate after quenching [104].

Laser Surface-Structuring Process

Laser surface structuring is a promising surface treatment technique with potential applications in various fields, including the automotive, biomedical, and electronics industries. It is a laser-based surface treatment process that can modify the surface of materials in a controlled manner [105] to create micro- and nanometric scale surface features, such as channels, pillars, and cavities, which can be used to improve the surface properties of materials, such as friction, wear, and adhesion. Various laser sources, such as picosecond (*ps*-), *fs*-, and *ns*-lasers, have been used for surface structuring [106]. The choice of laser source depends on the desired surface structure, the material properties, and the processing parameters. Laser surface structuring has been applied to a wide range of materials, including metals, polymers, ceramics, and composites. It has been used for a variety of applications, such as surface texturing for friction reduction in engine components [107], surface functionalization for biomedical implants [108], and surface patterning for optical and electronic devices [109]. Recent studies [110] have focused on developing new techniques and methods for laser surface structuring, such as combining it with other surface treatments, such as plasma treatment or electrochemical deposition. Additionally, machine learning and artificial intelligence techniques have been used to optimize laser surface structuring parameters and to predict the surface structure of laser-treated materials [111].



(**a**)



(**b**)

Figure 10. (**a**) Schematic representation of the laser surface hardening, and (**b**) representation of the laser hardening tracks induced by means of this technique (reproduced from Ref. [104], with permission from Elsevier, 2019).

2.3. Chemical and Electrochemical Methods

Chemical surface modification methods can remove oxides and reveal the final microstructure without damaging the surface of interest. However, the main drawback of these methods is that the final geometry is strong. In some cases, acid washing may, in addition to cleaning, improve corrosion resistance by removing parts of the surface. Electro-polishing, pickling, and passivation are the most important methods included in this classification [112–115]. In this regard, the electro-polishing process typically produces a surface that has an optimal corrosion resistance. On the other hand, pickling is the most common chemical procedure used to remove oxides and iron contamination [116,117]. Pickling typically uses a mixture of nitric acid (HNO_3) and hydrofluoric acid (HF). Chloride-containing agents, such as hydrochloric acid (HCl), should be avoided since there is an obvious risk to induce pitting [118]. Table 3 summarizes the chemical composition, as well as the pickle ability, for the most common stainless steels available in the market.

Table 3. SS grades and their pickle ability. Pickle ability classification: 1 to 4 (from very easy to very difficult) [119].

Grade	International Steel Number	Steel Name	ASTM	Chemical Composition, Average %					DIN	SS	Pickle Ability	Reference
				C	Cr	Ni	Mo	Others				
1	1.4301	304	4301	0.04	18.1	8.3	–	–	1.4301	2333	1	[120]
	1.4401	316	4401	0.02	17.2	10.2	2.1	–	1.4401	2347	2	[121]
	1.4404	316L	4404	0.02	17.2	10.2	2.1	–	1.4404	2348	2	[122]
	1.4571	316Ti	4571	0.04	16.8	10.9	2.1	Ti	1.4571	2350	2	[123]
	1.4436	316	4436	0.02	16.9	10.7	2.6	–	1.4436	2343	2	[124]
2	1.4362	S32304	SAF2304™	0.02	23	4.8	0.3	–	1.4362	2327	3	[125]
	1.4462	S32205	2205	0.02	22	5.7	3.1	–	1.4462	2377	3	[126]
	1.4439	S31726	4439	0.02	17.8	12.7	4.1	–	1.4439	–	3	[127]
	1.4539	N08904	904L	0.01	20	25	4.3	1.5 Cu	1.4539	2562	3	[128]

Table 3. *Cont.*

Grade	International Steel Number	Steel Name	ASTM	Chemical Composition, Average %					DIN	SS	Pickle Ability	Reference
				C	Cr	Ni	Mo	Others				
3	1.4410	S32750	SAF2507™	0.02	25	7	4	–	–	2328	4	[125]
	1.4547	S31254	254 SMO®	0.01	20	18	6.1	Cu	–	2378	4	[129]
	1.4652	S32654	654 SMO®	0.01	24	22	7.3 Cu	3.5 Mn	–	–	4	[130]

Surface modification chemical methods, such as chemical vapor deposition (CVD), sol-gel and anodization, offer effective ways to alter the surface properties of materials, including MASS.

2.3.1. Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a technique that involves the deposition of thin films onto the surface of MASS using chemical reactions in a gaseous phase [131]. Precursor gases containing the desired elements are introduced into a reactor, where they react and form a solid coating on the material's surface. This method enables precise control over the film composition, thickness, and uniformity [131,132]. CVD can be used to deposit various functional coatings, such as protective, wear-resistant, or catalytic films, which can enhance the surface properties and performance of MASS.

2.3.2. Sol-Gel

Sol-gel is a versatile chemical method that involves the synthesis of thin films or coatings from a colloidal suspension, known as a sol [133]. The sol contains metal alkoxides or metal salts that undergo hydrolysis and condensation reactions, forming a gel-like network. The gel is then treated to remove the solvent and undergo drying and curing processes, resulting in the formation of a solid thin film. Sol-gel coatings can be tailored to provide functionalities such as corrosion resistance, anti-reflective properties, or biocompatibility, thereby improving the surface characteristics and applications of MASS [134].

2.3.3. Anodization

Anodization is a surface modification technique that involves the controlled electrochemical oxidation of a metal to form a protective oxide layer on its surface [135]. The material is immersed in an electrolytic solution and acts as the anode in an electrochemical cell. An electric current is applied, leading to the formation of a thick and dense oxide layer, known as an anodic film, on the MASS surface. This anodic film can enhance corrosion resistance, improve wear resistance, and provide decorative or functional properties to the material.

2.4. Electrochemical Methods

Electrochemical methods are based on the principle that deposits in their elemental form on solid electrodes are removed and recovered when potential or electricity is applied to the electrode. The basic reaction that occurs is the reduction of metals in various oxidation states to the zero-oxidation state (elemental state of the metal) at the cathode when electrons pass through the anode in the circuit [136,137].

Ion Implantation

Ion implantation is a process of surface modification of metals, which is frequently applied to stainless steels. Implanting ions on austenitic stainless steel causes changes in microstructure, including defects, phases, and staining [138,139]. Several works have been conducted on structural austenitic stainless steels using intermediate carbon and nitrogen atoms to induce microstructural changes and, consequently, enhance their mechanical properties [140,141].

3. Effects of Surface Modifications on MASS Mechanical Properties

In this section, the effect of surface modification on MASS will be presented in detail. In this sense, the mechanical properties (hardness, wear resistance, etc.) as well as the main microstructural (residual compressive stresses, corrosion resistance, etc.) effects will be presented.

3.1. Hardness

Surface modifications can significantly improve the hardness (*H*) of MASS. After SP, *H* increases by introducing dislocations and strengthening at the grain boundaries [142,143]. LSP is another technique that has been shown to significantly improve the *H* of MASS. This technique, by inducing compressive residual stresses, can improve the mechanical properties near the surface in terms of *H* [144,145]. Submerged laser peening also has the same trend on MASS [145]. Laser surface hardening (LSH) is another technique that has been used to improve the *H* of MASS [146]. LSH can significantly increase the *H* by introducing α'- and/or ε-martensitic transformation and compressive residual stresses [147]. Table 4 compares different surface modification techniques for MASS.

Table 4. Comparison of the increase in hardness obtained with different surface modification techniques.

Surface Modification Technique	Increase in Hardness (%)	References
Shot peening	5–15	[148,149]
Ultrasonic shot peening	10–30	[150]
Laser shock peening	20–40	[151,152]
Submerged laser peening	20–40	[81,153]
Surfi-Sculpt processing	50–100	[154]
Laser surface hardening	20–30	[155]
Laser surface-structuring	10–20	[89,105]

3.2. Wear Resistance

MASSs are widely used in a variety of applications due to their excellent combination of corrosion resistance, strength, and toughness [156–159]. However, these materials can still experience wear failures under certain conditions, such as when they are exposed to abrasive particles or subjected to high contact pressures. To improve their wear resistance, various surface modification techniques have been developed [160]. Table 5 compares typical ranges of wear rate reduction achieved with different surface modification techniques. Various surface modification techniques can be employed to enhance the properties of 301LN. SP has a positive impact by inducing a compressive stress layer that improves its fatigue strength, wear resistance, and resistance to stress corrosion cracking [161,162]. These effects make SP a valuable surface modification technique for enhancing the mechanical performance and durability of 301LN components [163]. LSP, on the other hand, utilizes laser pulses to generate compressive stresses in the material's surface. Submerged laser peening employs a high-energy laser beam in a liquid medium to produce shock waves and generate compressive residual stresses [164]. Surfi-Sculpt processing is a three-dimensional (3D) laser surface modification technique that creates complex surface structures, reducing contact area and enhancing wear resistance. Laser surface hardening involves melting and rapidly solidifying the surface layer using a high-energy laser beam to improve wear resistance [165]. Laser surface structuring creates precise patterns and textures, reducing contact area and increasing surface hardness, thereby improving wear resistance. By utilizing these techniques, the performance and durability of 301LN can be significantly enhanced [166,167].

Table 5. Wear rate reduction of different surface modification techniques.

Surface Modification Technique	Wear Rate Reduction (%)
Shot peening	10–40
Ultrasonic shot peening	10–50
Laser shock peening	30–70
Submerged laser peening	40–80
Surface hardening	20–40
Plasma nitriding	30–70
Ion implantation	20–50
Electropolishing	10–20

3.3. Fatigue Strength

MASSs are commonly used in a wide range of applications that require high strength and resistance to fatigue failure. However, they can experience fatigue failure over time due to cyclic loading [143,168,169]. To improve the fatigue strength of MASS, surface modifications can be applied to introduce compressive residual stresses, which help to prevent crack initiation and propagation.

Ultrasonic impact treatment (UIT) introduces compressive residual stresses into the material through high-frequency mechanical vibrations.

Compressive stresses induced by ultrasonic impact treatment (UIT) were investigated to counteract high tensile weld residual stress, a critical factor in stress corrosion cracking (SCC). X-ray diffraction (XED) analysis revealed a significant surface compressive residual stress of up to 325.9 MPa. Finite element analysis predicted the residual stress distribution in AISI 304 SS after UIT. SCC tests in a boiling 42% magnesium chloride solution demonstrated enhanced resistance in treated specimens compared to untreated ones, with no visible stress corrosion cracks observed even after 1000 h [170]. Microstructural observations confirmed the formation of a hardened layer and refinement of the surface's coarse-grained structure. These findings underscore the effectiveness of UIT in protecting weldments against SCC [171]. LSP, known for its favorable effects on fatigue behavior at room temperature, induces high dislocation densities, strain-induced martensite, and nanocrystalline regions that inhibit fatigue crack initiation. Moreover, the formation of deep compressive residual stresses reduces fatigue crack growth. However, the stability of these near-surface properties under elevated temperature conditions, such as those found in power plants or gas turbines, is influenced by the microstructures induced by surface treatments and the thermomechanical loading. The distinct near-surface microstructures with different thermal stability are investigated [172]. The findings highlight the importance of micro-stresses in enhancing fatigue life and shed light on the challenges associated with predicting fatigue life solely based on macro-stress data [173].

The fatigue crack growth behavior of AISI 316 austenitic SS annealed using a CO_2 laser was evaluated under different environments, including lab air, gaseous hydrogen, and saturated hydrogen sulfide solution [174]. The laser-annealed specimen exhibited consistent microstructures in all regions. Fatigue crack growth tests demonstrated improved resistance to crack propagation in the region preceding the laser-annealed zone (LAZ), regardless of the test environment. AISI 316 SS showed low sensitivity to hydrogen-accelerated crack growth. XRD analysis revealed partial γ- to α'- and/or ε-martensite transformation near the surface, with residual γ-effectively trapping hydrogen and reducing hydrogen embrittlement susceptibility. Fatigue fractography in air displayed transgranular fatigue fractures with flat facets, while specimens tested in H_2S solution or gaseous hydrogen exhibited quasi-cleavage fractures associated with hydrogen-enhanced crack growth. The presence of distinct striations on the fracture surface of embrittled specimens indicated hydrogen-activated slip processes ahead of the crack front [86,175,176]. Table 6 summarizes the effect of different surface modification techniques on the improvement of fatigue life.

Table 6. Improvement of failure cycles for austenitic stainless steels after different surface modification techniques.

Surface Modification Technique	Cycles to Failure Improvement (%)
Shot peening	10–30
Ultrasonic shot peening	20–50
Laser shock peening	50–100
Submerged laser peening	70–150
Ultrasonic impact treatment	50–100
Surface hardening (LSH)	10–30

3.4. Corrosion Resistance

Table 7 indicates the corrosion resistance effects on MASS that are produced by surface modification techniques. MASS can be susceptible to localized corrosion or stress corrosion cracking in some extreme environments. To enhance their corrosion resistance, surface modifications can be applied to alter the surface chemistry. One surface modification technique that has demonstrated its capacity for improving the corrosion resistance of MASS is ion implantation [20,177]. For example, nitrogen ions can be implanted into the surface layer of the material to form a nitrogen-enriched layer that is highly resistant to corrosion [178]. Another surface modification technique that can enhance the corrosion resistance of MASS is electropolishing. Other surface modification techniques such as plasma nitriding and laser surface modification can also be used to modify the material's surface chemistry and improve its corrosion resistance [179]. Plasma nitriding involves exposing the material to a nitrogen plasma, which can form a nitrogen-enriched layer on the surface that is highly resistant to corrosion. Laser surface modification techniques such as laser surface cladding and laser surface melting can also be used to form a protective layer on the material's surface that can improve its corrosion resistance.

Table 7. Corrosion resistance effects on the austenitic stainless steel in different surface modification techniques.

Surface Modification Technique	Corrosion Resistance Effect	References
Ion implantation (Nitrogen)	Highly resistant to corrosion	[180]
Plasma nitriding	Forms a nitrogen-enriched layer on the surface that is highly resistant to corrosion	[181]
Laser surface cladding	Forms a protective layer on the material's surface that can improve its corrosion resistance	[72]
Laser surface melting	Forms a protective layer on the material's surface that can improve its corrosion resistance	[182,183]

3.5. Microstructure

Surface modifications can significantly impact the microstructure of MASS, which can ultimately affect their mechanical properties. LSP waves create compressive residual stresses in the material, which can induce dislocations and cause grain refinement [183]. The dislocations generated by LP can lead to the formation of nanocrystalline grains in the material, which have a higher density of grain boundaries and can exhibit improved mechanical properties, such as higher strength and fatigue resistance [184,185]. Another surface modification technique that can alter the microstructure of MASS is SP, which can induce plastic deformation [37]. This process can cause strain hardening and dislocation formation, which can lead to improved mechanical properties. Surface modification techniques such as plasma nitriding and ion implantation can also modify the microstructure of the material. Plasma nitriding involves exposing the material to a nitrogen plasma, which can form a nitrogen-enriched layer on the surface [186]. This layer can alter the microstructure of the material, leading to improvements in its mechanical properties. Similarly, ion implantation involves implanting ions of a different element into the material's surface layer, which can modify the microstructure and improve its mechanical properties. Table 8 displays the effect on the microstructure and final microstructure of MASS in different surface modification techniques.

Table 8. Changes in microstructure of austenitic stainless steel after different surface modification techniques.

Surface Modification Technique	Effect on Microstructure	Final Microstructure	References
Laser peening	Induces dislocations and grain refinement	Nanocrystalline grains with higher density of grain boundaries	[183]
Shot peening	Induces plastic deformation and dislocation formation	Strain hardened material with increased dislocation density	[184]
Plasma nitriding	Forms nitrogen-enriched layer on surface	Alters microstructure leading to improved mechanical properties	[186]
Ion implantation	Modifies surface layer with implanted ions	Alters microstructure leading to improved mechanical properties	[180]

3.6. Residual Stresses

The generation of residual stresses in austenitic steels is attributed to various factors, including the evolution of austenite flexibility at different temperatures and under varying conditions such as chemical composition and magnitude of deformation. Talonen [187] showed that phase-transformation from γ- to α'- and/or ε-martensite occurs in the form of ε-martensite steel at the stacking faults (SFs) intersection and α'-martensite at µ-martensite and the intersections between the shear bands [188,189]. Hedayati [190] has shown that the chemical composition of the alloy affects important intrinsic properties related to the phase transformation mechanisms, such as stacking fault energy (SFE) and the starting temperature of martensitic transformation (Ms). Antunes [191] clearly states that the lower the number of alloying contents in austenitic steel and the lower the temperature during the deformation process, the more intense the martensitic evolution. Moreover, the residual stress fields near dislocations influence the nucleation of α'- and/or ε-martensite and then the γ- to α'- and/or ε-martensitic phase transformation may occur heterogeneously [192]. Residual stresses induced due to the phase transformation are mainly caused by increased volume, elastic incompatibility, and a lack of plastic compatibility between both constitutive phases. In standard steel, residual stresses are the consequences of the interaction between deformation, temperature, and microstructure [193,194]. Investigating the residual stresses in austenitic steel is one of the most important parts of any plastic deformation, and by examining these stresses, the effect of operations on steel can be achieved to some extent. Alvez [195] has achieved valuable results by conducting numerous experiments on AISI 304L SS, a grade which is prone to martensitic deformation caused by deformation. This phase change depends on the temperature as well. The residual stresses on 304L SS, in which martensitic phase transformations were induced by CR, were investigated for different sample thicknesses. The results show that the amount of phase transformation and the level of residual stresses depend on the thickness of the AISI 304L samples; despite all samples showing a compressive residual stress, the thickness of this AISI 304L sample was about 6.37 mm. Studies conducted on AISI 316L steel by Bohm [196] have discussed the residual stresses and the energy density [197]. Pal [198] examines the distribution of residual stresses in AISI 904L steel in both the surface and subsurface areas, which are the locations of the highest strain after SP [199]. Changes in the residual stress distribution in the underlying layers have been calculated, and the comparison is given in Table 9. The highest subsurface showed a depth of about 55 µm and was reported to be 560 MPa [197]. In Figure 11, residual stresses of AISI 301L, AISI 316L, and AISI 904L after SP treatment were compared, and as it shows, suitable steel is AISI 304L. In general, compressive residual stresses at the surface of a component is beneficial, and it is the unstable cause of more transformation phase during the treatment.

Table 9. Comparison of residual stress in AISI 304L, AISI 316L, and AISI 904L [65–67].

Steels Type	Sample Thickness (mm)	The Energy Density (J/mm^3)	Depth of Stresses (µm)	Residual Stresses (MPa)
AISI 304L			20	220
AISI 316L	6.37	71	20	190
AISI 904L			55	110

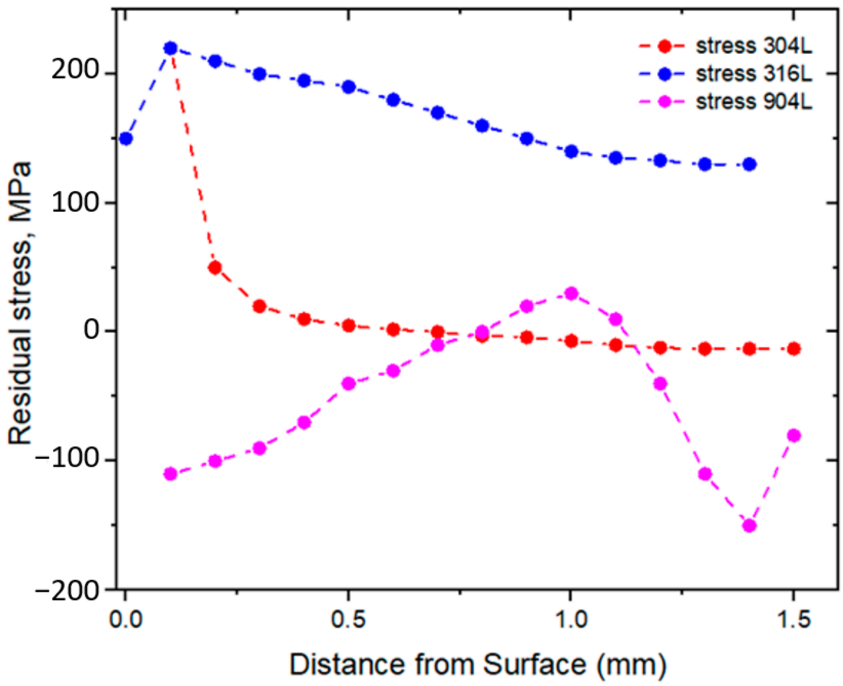


Figure 11. Comparison of residual stress in AISI 304L, AISI 316L, and AISI 904L after SP. Adapted from Refs. [65–67].

3.7. Correlation between Microstructure and Mechanical Properties

The combined effects of different surface modifications on the mechanical properties of MASS can be significant. Therefore, it is essential to understand how these techniques interact to achieve optimal results. Combining different surface modification techniques can achieve synergistic effects that can lead to even greater improvements in the material's mechanical properties. For example, SP and physical vapor deposition (PVD) coating are two common surface modification techniques used to improve the mechanical properties of MASS [200,201]. SP can induce compressive residual stresses and plastic deformation, while PVD coating can modify the surface chemistry and alter the microstructure. When combined, these two techniques can create a surface layer with improved corrosion resistance, wear resistance, and fatigue strength [35,202]. SP followed by PVD coating led to a significant increase in the material's hardness, wear resistance, and fatigue strength compared to SP alone. Another study demonstrated that the combination of SP and PVD coating led to improved corrosion resistance in high-speed steel [203]. Other studies have investigated the combined effects of different surface modification techniques, such as laser peening and plasma nitriding, on the mechanical properties of MASS [185,204]. These studies have shown that combining these techniques can improve the material's mechanical properties, such as higher strength, wear resistance, and corrosion resistance. Combined techniques for improving mechanical properties via surface modification are shown in Table 10.

Table 10. Combined techniques for improving mechanical properties via surface modification.

Surface Modification Techniques	Effects on Mechanical Properties
Shot peening and PVD coating	Increased hardness-improved wear resistance-improved fatigue strength-improved corrosion resistance
Laser peening and plasma nitriding	Increased strength-improved wear resistance-improved corrosion resistance-improved fatigue strength

4. Conclusions

Surface modification techniques have been widely used to improve the mechanical properties of MASS. However, the selection of a suitable method is dependent on the desired application and specific material properties that need to be modified. Traditional methods, such as shot peening, sandblasting, grinding treatment, heat treatment, and plasma nitriding have certain limitations, while alternative methods, such as ultrasonic nanocrystalline, and ion implantation on the surface offer precise control over surface morphology, composition, and structure. Laser surface modification methods have gained increasing attention due to their unique advantages, including precise control over surface morphology, reduced thermal damage, and deeper layers of compressive residual stress. These methods have shown significant improvements in surface quality, such as enhanced adhesion, increased hydrophobicity, improved wear and corrosion resistance, and reduced stress corrosion cracking. The effects of hardness, wear resistance, residual stresses, and fatigue resistance vary depending on the specific surface modification method used. Therefore, the choice of surface modification method should be based on a comprehensive analysis of the specific material properties that need to be improved and the desired application. The advancement of surface modification techniques will continue to play an important role in improving the performance and longevity of materials in various industries.

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