Review of passivity and electrochemical properties of nanostructured stainless steels obtained by surface mechanical attrition treatment (SMAT): trend and progress

Abstract: Surface nanocrystallization provides the opportunity to produce gradient-structured metallic materials with improved properties. Several attempts have been made to produce nanostructured stainless steel (SS), along with the study of the resultant corrosion resistance. However, the current knowledge is insufficient to address the corrosion mechanism and the possible ways of enhancing the corrosion resistance after surface treatment. The present work reviews the past significant works on the effect of surface treatment by surface mechanical attrition treatment (SMAT) method as well as its processing parameters on the corrosion properties of SS. The corrosion resistance of nanostructured SS is influenced by the extent of grain refinement, compactness, and homogeneity of the passive film, Cr content, grain boundary structure, composition, and alloying elements. In addition, the resulting corrosion properties can be controlled by choosing the right processing parameters during treatment. Progress on the corrosion behavior of nanostructured steels was summarized and new avenues for further research and developments are proposed.

Keywords: corrosion resistance; electrochemical properties; passivation; stainless steel; surface nanocrystallization.

1 Introduction

Fabricating nanostructured materials with excellent mechanical properties is always the dream of material scientists. This is often achieved by subjecting them to surface treatment which results in some exceptional features such as high strength and hardness, thanks to the effect of surface nanocrystallization. Most of the material related failures such as corrosion and wear occur on the material surface with time. However, through surface treatment, a new layer (nanostructured layer) with improved overall properties can be successfully produced on the material surface thereby reducing the material failures to a minimum (Feng et al. 2013; Gatey et al. 2016; Kou et al. 2014; Li et al. 2017; Markushev 2011; Singh et al. 2018). The various surface treatment techniques include shot peening (Feng et al. 2013), equal-channel angular pressing (Figueiredo and Langdon 2009), cryogenic rolling (Markushev 2011), ball rolling (Koch 1992), severe plastic deformation (Valiev et al. 1993, 2000), surface mechanical attrition treatment (SMAT) (Arifvianto and Mahardika 2012; Cheung et al. 2012; Gatey et al. 2016; Olugbade et al. 2019; Olugbade and Lu 2019a, b; Olugbade 2019; Tao 2003; Tao et al. 2008), high pressure torsion (HPT) (Edalat and Horita 2016), friction stir processing, consolidation of ultrafine powders (Cheung et al. 2012; Koch 1997), ball-milling and consolidation (Koch 1997), crystallization of amorphous solids (Lu 1996), and electrodeposition (Dang et al. 2018a, b; Erb et al. 1993). The present paper reviews the electrochemical properties of nanostructured stainless steels, as produced by the SMAT technique, with the view of discussing the important factors that determines the aftermath electrochemical properties.

1.1 Surface treatment by SMAT – an overview

Compared to other surface nanocrystallization processes (Feng et al. 2013; Figueiredo and Langdon 2009; Koch 1992;
Markushev 2011; Valiev et al., 1993, 2000), surface nanocrystallization by SMAT is a unique method of generating a gradient-layered structure on the material surface with the sole aim of enhancing the properties without altering the inherent chemical compositions of the material (Gatey et al. 2016; Olugbade et al. 2019; Olugbade and Lu 2019a; Tao et al. 2008). The process entails the bombardment of the sample surface with very fast moving random spherical balls (Figure 1a) at room or predetermined temperature. As illustrated in Figure 1b, the balls continue hitting the sample and induce plastic deformation leading to the formation of nanostructured layers which are capable of improving the overall properties of sample materials without altering their original properties. The power energizing the balls normally originates from the generator which supplies a constant energy needed to move the balls. The balls can be made from tungsten carbide, ceramic, steel, or zirconium oxide (ZrO₂). Surface nanocrystallization occurs through grain refinement mechanism via mechanical deformation. A higher fraction of grain boundaries is often induced by SMAT at high temperature. As shown in Figure 2, the SMAT technique has been applied on different materials to produce nanocrystalline (NC) materials, which include pure iron (Tao 2003), titanium (Zhang and Han 2010; Zhu et al. 2004), copper (Wang et al. 2006), cobalt (Wu et al. 2005a,b), aluminum alloy (Chang et al. 2012; Wu et al. 2002, 2005a,b), Ni-alloy (Tao et al. 2004), Inconel 600 (Tao et al. 2003), intermetallic compound (Tao et al. 2003), Mg-alloy (Sun et al. 2007), carbon steel, and stainless steel (Mohammed et al. 2016; Olugbade and Lu 2018; Olugbade and Lu 2020a,b; Olugbade et al. 2021a,b; Olugbade 2020). Surface mechanically treated (SMATed) stainless steel with improved properties can find applications in aircraft, automobiles, reactors, biomedical devices, manufacturing, and production industries.

Stainless steels find applications in many engineering areas due to their remarkable passivation ability, high strength, and excellent corrosion resistance (Dai et al. 2004; Mordyuk et al. 2007; Todaka et al. 2006; Yan et al. 2007). It is however important to know that SMAT has a notable effect on the corrosion behaviour of steels in terms of surface roughness and martensite phase formation (Dai et al. 2004; Koch 1992; Markushev 2011; Valiev et al. 2000). However, only austenitic stainless steels are affected by austenite–martensite phase transformations during SMAT. The degree of austenite-martensite phase transformations during SMAT is a function of the treatment time, nature and size of the ball, nature of stainless steel, and frequency of vibration. In addition, the deformation induced martensite formation and the processing parameters (ball material and size, ball quantities, and treatment time) have a
remarkable influence on the corrosion behaviour of stainless steels (Guan et al. 2005; Li et al. 2006a,b; Nikitin et al. 2005; Olugbade 2021, 2022a,b; Olugbade et al. 2021a,b,c; Umemoto et al. 2004; Zu et al. 2020).

Some of the important operating parameters during SMAT operation, which were not fully covered in the literature are the chamber dimension (chamber height and diameter), residual stress, roughness, cell size evolution, and misorientation. The chamber dimensions influence the frequency of ball–ball and ball–boundary collisions during SMAT and consequently affect the corrosion resistance.

Several factors could impact the corrosion properties of stainless steels, including extent of grain refinement, process parameters, surface roughness, etc (Guo et al. 2007; Umemoto 2003). Despite the various studies on the influence of SMAT on the corrosion properties, the mechanism behind the corrosion resistance of SS subjected to SMAT still needs further attention and study.

2 Preparation of surface after SMAT

The inherent corrosion resistance of SS can be influenced by the introduction or presence of foreign materials such as iron particles on the material surface after surface treatment by SMAT. This can hinder the formation of the chromium oxide film which protects the steels surface from corrosion. Hence, there is a need for passivation and proper cleaning of sample surface after SMAT before subjecting them to service. During surface treatment by SMAT, it is important to note that the surface of stainless steels may be contaminated with the material of the balls that impacted on them. Hence, stainless steels require some cleaning and passivation after treatment before they are put in use. To remove debris, dirt, and unwanted deposits on the sample surface after surface treatment by SMAT, the treated surfaces are usually thoroughly cleaned in ethanol followed by ultrasonic bath. A slight polishing is therefore required to reduce the surface roughness and defects induced during SMAT. However, care should be taken while polishing so as not to remove all the nanostructured layers already formed.

The knowledge of the composition, topography, structure, and thickness of passive films is a key point to fully understand the corrosion resistance of nanostructured SS (Merello et al. 2003; Pistorius and Burstein 1994). A thick passive film – about 2 nm (Olugbade et al. 2019) with an improved structure and topography, with a good amount of Cr can significantly enhance the corrosion resistance. The properties of passive films may be described by different variables (film thickness, composition, crystal structure, etc.) which may be measured by different techniques. For example, the thickness of the passive film in acid and neutral solutions can be described in detail using ellipsometry (Merello et al. 2003). The passive film breakdown and the influence of alloying elements on passive film and its formation remain an interesting area for many material scientists. The passive film formed on stainless steel in acid aqueous solutions consists of two layers; the inner barrier layer of a Fe–Cr rich oxide and the outer layer with hydroxide (Wegrelius and Olefjord 1993, 1995). In addition, the topography and atomic arrangement of the passive films can be studied by scanning tunneling microscopy (STM) and atomic force microscopy (AFM).

Corrosion behavior of SS strongly depends on the characteristics of the passive film which is greatly influenced by Cr content. It is well known that the Cr rich passive layer is formed by selective dissolution of Fe and oxidation of Cr (Hamm et al. 2002; Rao and Singhal 2009; Wallinder et al. 2002; Wegrelius et al. 1999; Zimmer and Birringer 2008). The characteristics of the passive film and its connection with the alloy composition have been studied over time. A study of a series of Fe–Cr alloys indicated that the Cr content in the passive film formed in 0.5 M H2SO4 increased suddenly when Cr content in the alloy was more than 13% (Asami et al. 1978). This suggested the requirement of the critical Cr content in stainless steel to cause passivity, which was later explained based on percolation model (Qian et al. 1990; Ryan et al. 1995; Song et al. 1990; Williams et al. 1991).

3 Electrochemical properties of stainless steels

Generally, stainless steels are important and useful because of passive films. The resulting passive film on stainless steel is prone to breakdown due to temperature and pH changes as well as aggressive ions. Localized corrosion only occurs in the presence of an aggressive anion (mostly chloride), and passivity may be completely lost in very acidic solutions. However, localized breakdown of the passive film, known as pitting corrosion, results in quick dissolution of the underlying metal, which leads to the failure and degradation of stainless steels (Burstein 2010; Burstein and Moloney 2004; Frankel 1998). Pitting corrosion produces attack on stainless steel in the form of pits or spots. The corrosion attack most often occurs at points where the passive layer might be weakened due to imperfections, slag inclusions, or damaged
surface. It is important to note that the surface state greatly affects the susceptibility of stainless steel to pitting corrosion. Hence, there is a need to always protect the surface of the materials against pitting corrosion. Crevice corrosion is another form of localized corrosion of stainless steels.

In general, pitting can be grouped in three stages, (i) pit initiation, (ii) metastable pitting, and (iii) pit growth (Burstein et al. 1993; Burstein and Moloney 2004; Pan et al. 2013; Shibata and Zhu 1994; Zhang et al. 2009). The pit initiation is caused by passive film breakdown, the metastable pitting pinpoints where the pit growth stops, while the pit growth ensures the prevention of repassivation. In addition, metastable pitting is a good indicator for determining the pitting susceptibility (Laycock et al. 1998; Pistorius and Burstein 1992, 1994; Williams et al. 1994). In stainless steel, Cr content influences the pitting corrosion (Olsson and Landolt 2003). Increase in Cr content tends to an increase in the pitting potential. This indicates that the pitting potential is dependent on the content of Cr in the surface film and to a larger extent the percentage compositions of Mo and N.

Over the years, the study of metastable pitting behavior of different stainless steels in different corrosive media as well as the stable pits mechanism has received considerable attention (Abioye et al. 2017; Burstein et al. 2004a,b; Burstein and Liu 2007; Burstein and Mattin 1992; Burstein and Vines 2001; Tian et al. 2014). In addition, the pitting rate is largely dependent on how often metastable pitting events take place. This view was supported by many researchers for stainless steel (Frankel and Sridhar 2008; Olugbade 2021; Olugbade and Lu 2019a,b), as well as aluminum alloys (Gupta et al. 2012a,b, 2014; Pride et al. 1994). Consequently, the large number of metastable pitting events can provide reliable information on the stable pitting corrosion of stainless steel (Burstein and Souto 1995; Punckt et al. 2004).

4 Influence of alloying elements on pitting resistance

Alloying elements have a significant influence on pitting corrosion of stainless steel (Fernandez-Domene et al. 2014; Lu et al. 1993; Malik et al. 1995; Olugbade et al. 2021a,b,c). It was reported that Ni had a moderate enhancement in the pitting resistance (Oh et al. 2014). Meanwhile, there was a significant enhancement in pitting resistance of stainless steel by the addition of small amounts of V and Mo (Ilevbare and Burstein 2001; Kaneko and Isaacs 2002), Cu (Oguzie et al. 2010; Tomio et al. 2014), W, and N (Ha et al. 2012, 2014; Jargelius-Pettersson 1999). Meanwhile, the combined effect of these alloying elements on the corrosion properties can be determined by the pitting resistance equivalent number (PREN) (Betts and Hebdon 2000; Merello et al. 2003; Perren et al. 2001), which is often quantified (in wt%) as follows.

\[
\text{PREN} = [\text{Cr}] + 3.3[\text{Mo}] + 30[\text{N}] \quad \text{(1)}
\]

From the PREN equation, N, Mo, and Cr are the main elements which enhance pitting resistance. Further investigations and discussion on the electrochemical properties of stainless steel are available in (Ke and Alkire 1995; Malki et al. 2008). The major parameters or factors that influence the electrochemical properties of SMATed stainless steels in various conditions are the Cr content, microstructure, alloying elements, and impurities (Meng et al. 2003; Ryan et al. 2002, 2003; Salvago and Fumagali 1992; White 1992). These parameters are strongly dependent on surface nanocrystallization with time. In summary, the passivation and pitting corrosion mechanism must be properly investigated to fully understand the influence of surface treatment on the electrochemical properties of steels.

5 Passivity and corrosion properties after surface nanocrystallization by SMAT

Induced by plastic deformation, surface treatment by SMAT often leads to grain refinement with the formation of bulk gradient layer on the surface. The impact of the treatment decreases across the sample layers and the microstructure of the surface layer is refined up to nanoscale. As evident in Figure 3 (Waltz et al. 2009), where there is a change in grain size from the treated top layer (nanostructured layer), transition layer, up to the matrix layer. Finer grains promote passivation through the formation of dense protective passive films on the sample surface thereby resisting corrosion attack (Balusamy et al. 2010; Li and Wang 2018; Waltz et al. 2009).

The corrosion behaviour of nanostructured materials is mostly influenced by the material passivation ability and the nature of the corrosive medium (Balusamy et al. 2013; Jin et al. 2014; Kou et al. 2014; Liu et al. 2010; Wu et al. 2017). Evident in literature, surface nanocrystallization is a promising method for the formation of passive film and enhancement in the corrosion properties of materials depending on the nature of the materials and environment,
as well as the processing parameters during treatment (Balusamy et al. 2013; Chen et al. 2011). Experimental investigations also reported that the surface nanocrystallization enhanced the passivity and improved the corrosion property of 304 stainless steel in 3.5% NaCl solution with a lower generalized corrosion rate (Inturi and Szklarska-Smialowska 1992; Wang and Li 2002).

Surface treatment by SMAT can enhance the passivity and corrosion properties of materials. In 3.5% NaCl solution, the SMATed AISI 2205 sample reportedly exhibits a better corrosion resistance as compared with the untreated sample (Singh et al. 2018) in terms of reduced corrosion current density. The increase in the passivation behavior of nanostructured AISI 2205 can be attributed to the increase in the thickness of chromium oxide. It is important to note that post-SMAT process such as annealing at temperature of about 300–380 °C, plasma carburizing (Atul et al. 2016; Bell 2002; Sun et al. 1999; Thaiwatthana et al. 2002), and nitriding (Zhang and Bell 2013) can also yield a good corrosion resistance. The post-SMAT treatment has been used for various SS in the past including 316L SS (Olugbade and Lu 2020a,b) and 1Cr18Ni9Ti SS (Abioye et al. 2020; Assadian et al. 2014; Christiansen and Somers 2005; Majid et al. 2012; Wang et al. 2006), and AISI 2205.

The surface nanocrystallization by SMAT using 2 mm Ø balls increased the corrosion resistance of 409 SS in 0.6 M NaCl solution at room temperature after polarization at 315 mV (SCE). This may be attributed to the ability of surface treatment to form a passive film at the material surface at nanoscale level. In addition, using a small ball size tends to create a fine smooth layer on the sample surface hence reducing the surface roughness and improving the corrosion behavior in the process. It is well believed that the lower the surface roughness the better the corrosion resistance behavior (Balusamy et al. 2013; Olugbade et al. 2021a,b,c; Olugbade and Omiyale 2021; Olugbade et al. 2019). A similar improvement in corrosion properties of materials could be found in (Balusamy et al. 2010; Hao et al. 2009; Lalish and Kargar 2011; Li et al. 2017; Lu et al. 2006; Meng et al. 2006; Olugbade et al. 2022; Sun and Bailey 2014; Wang et al. 2006; Wang and Li 2003; Ye et al. 2006, 2009). As a result of the nanocrystalline layer produced on the material surface by SMAT with high amount of Cr, an improvement in the corrosion resistance of the nanostructured 316L SS was achieved compared to untreated samples in 0.05 M H$_2$SO$_4$ + 0.25 M Na$_2$SO$_4$ aqueous solution at room temperature, with a reduced corrosion current density and higher corrosion potential (Lu et al. 2006). In contrast, a reduction in the corrosion resistance was achieved during the nanocrystallization by SMAT of 316 SS in 0.1 M NaCl (Hao et al. 2009) and 409 SS using 5 and 8 mm Ø balls for 900 and 1800 s (Balusamy et al. 2010). Evidenced with an increased corrosion current density and reduced corrosion potential, the reduction in corrosion resistance of 316 SS is attributed to the introduction of surface defects and increased in surface roughness (Hao et al. 2009).

With an increased corrosion potential and reduced corrosion current density shown in Figure 4, surface

![Figure 3: Cross-section of a 316L stainless steel after subjected to surface nanocrystallization by SMAT revealing the extent of grain refinement across the material layers (reprinted from Waltz et al. 2009, copyright 2009 TransTech Publications, with kind permission of TransTech Publications).](image)

![Figure 4: Comparison between the corrosion behavior of untreated 301, 304, and 316 stainless steels (SS), and SMATed 301 SS in 0.6 M NaCl solution at room temperature. Figure modified from (Olugbade et al. 2019).](image)
treatment by SMAT tends to create more diffusion path on 301 SS through which Cr can easily move from the matrix to the top layer (Olugbade et al. 2019) at high temperature, as compared with its 304 and 316 counterparts.

The formation of passive film is necessary before discussing on whether there will be an improvement or reduction in the corrosion resistance of stainless steel. The Cr$_2$O$_3$ and Cr(OH)$_3$ components of the passive film play vital role in the corrosion resistance behaviour of stainless steels. An increase in the intensity of the signal of Cr$_2$O$_3$ and that of Cr(OH)$_3$ decreases with increasing SMAT time Li et al. (2017), showing the positive effect of SMAT on the corrosion resistance. The Cr$_2$O$_3$ in the passive film is the stable crystalline form of chromium oxide, which can passivate the surface of a metallic material in the steady state at high temperature while Cr(OH)$_3$ is the unstable form of chromium hydroxide. However, Cr$_2$O$_3$ may show different types of crystal structures in a passive film. Hence, an increase in Cr$_2$O$_3$ will enhance the passivation ability while increase in Cr(OH)$_3$ will make the passive film to be more unstable and hence decrease the passivation ability. It is interesting to know that the Cr content in the passive film significantly increases with nitriding process after the SMAT process (Figure 5), with an improvement in corrosion resistance of 316L in simulated steam generator environment at high pressure and temperature (Li and Wang 2018) i.e., the Cr value is higher in the SMATed 316L sample than its untreated counterpart. The higher corrosion properties result from the formation of a Cr-rich layer on the sample surface. Similar increase in corrosion resistance was measured when 304L SS was treated by SMAT (Gatey et al. 2016). Hence, surface treatment and grain size reduction could enhance the passivity behavior and enhance the electrochemical properties of materials.

5.1 Effects of SMAT processing parameters on the corrosion resistance of stainless steel

The SMAT processing parameters including treatment time, ball size or diameter, ball material, and ball quantities are the main factors influencing the corrosion resistance of stainless steels. An increase in ball size and treatment time increases the roughness, decreases the grain size, and increases the microstrain. That is, increasing the ball size during surface treatment results in an increase in the surface roughness and the extent at which surface nanocrystallization occur, leading to deterioration in the corrosion resistance since higher surface roughness increases the corrosion rates i.e., the larger ball has more detrimental effects on the corrosion resistance than the smaller ball. In addition, an increase in treatment time increases the accumulated hits on the material surface, generating more nanostructured layers in the process which strengthens the treated surface but at the expense of the corrosion properties. That is, the treatment time does not affect the rate of moving balls. There is an increase in the accumulated hits and not the hit rate. Apparently, increasing the ball size and treatment time during treatment increases the surface roughness hence reducing the corrosion resistance behavior.

Therefore, there is a need to properly select these parameters to obtain a good corrosion performance. It was reported that the SMAT operating factors have a great effect on the corrosion resistance of 409 SS, 304 SS and Fe (Balusamy et al. 2010, 2013; Laleh and Kargar 2011). There is also an increase in corrosion resistance of 409 SS when subjected to SMAT using 2 and 5 mm Ø 316L SS balls for 900 s. In contrast, the treated 409 SS experienced a decrease in the corrosion resistance using 8 mm balls for 900 s (Balusamy et al. 2010). It has been established that

Figure 5: Compositions of the oxide films formed on the surface of 316L stainless steel: (a) untreated, (b) SMATed (reprinted from Li and Wang 2018, copyright 2018, with permission from Nature).
factors including grain refinement, microstrain, and defects induced during the SMAT operation greatly affect the corrosion properties of steels (Balusamy et al. 2010; Laleh and Kargar 2011; Lu et al. 2006). Increasing SMAT time decreases the grain size and increases the surface defects such as cracks leading to reduction in corrosion resistance. The resulting corrosion properties can be controlled by choosing the right processing parameters. To reach a general conclusion, varieties of materials using different SMAT parameters must be investigated. Regarding ball size and SMAT time (among other parameters), it is important to note that there must be an optimal value for each parameter i.e., practical issues must bound the value of each parameter. Hence, increasing/decreasing these parameters may not always lead to the same results. However, the effect of SMAT on dislocation density, microcracks, and phase transformations needs to be characterized and their influence on corrosion resistance remains to be studied.

5.2 EIS study of nanostructured stainless steel induced by SMAT

The electrochemical impedance spectroscopy (EIS) technique is an effective method for studying the corrosion performance of stainless steel after being subjected to surface treatment. Through EIS studies (Nyquist, Bode impedance, and phase angle plots), polarization resistance of nanostructured stainless steels with different processing times can be adequately evaluated. Some of the findings on corrosion resistance of nanocrystalline SS speculated that the SMAT processing parameters have a strong effect of the polarization resistance. Balusamy et al. (2010) compared the polarization resistance of untreated AISI 409 SS and those subjected to SMAT at various processing parameters. Using 8 mm balls at all treatment times studied and those treated using 5 mm balls for 30 and 45 min, the SMATed samples were reported to exhibit a decrease in resistance and an increase in capacitance, compared to the untreated one. This is related to the dislocations induced during SMAT treatment, strain induced martensite, and introduction of surface defects on sample surface, as well as an increased surface roughness. The defects induced the treatment results in the generation of defective interfaces in corrosive environment, preventing the formation of protective passive film on the sample surface hence exposing it to corrosion attack. The reduced corrosion resistance can also be linked to the increased defect density and microstrain. While surface nanocrystallization leads to the formation of protective passive film in some metals leading to enhanced corrosion resistance, increased in surface roughness and defects may be the case in other metals deteriorating the corrosion properties. Hence, the corrosion properties of metallic materials after SMAT are multidirectional and mainly depends on the extent of deformation or nanocrystallization, surface roughness, processing parameters, nature of the environment and materials, and others (Olugbade and Lu 2019a, b; Sun and Bailey 2014).

The corrosion resistance of stainless steels can also be obtained from the EIS study, in terms of the diameter of the capacitance loop in Nyquist plot. As indicated in Figure 6, the Nyquist plot revealed a much larger diameter for the 301 SS samples subjected to SMAT at all processing times as compared with the as-received sample with a smaller diameter of the capacitive loop (Olugbade et al. 2019). A similar case was observed for 409 SS samples treated using 2 and 5 mm ø balls for 900 s (Figure 7) implying that more protective passive films had formed on these samples, hence an improved corrosion resistance. The Nyquist plot explains better the corrosion resistance of materials in terms of the real and imaginary impedance. It is generally believed that the higher the diameter of the capacitive loop, the higher the compactness and the film stability, hence the higher the corrosion resistance (Olugbade et al. 2019; Olugbade and Lu 2019a,b).

Phase angle maximum is another important factor for determining the corrosion resistance behavior of materials. Generally, an increase in the phase angle maximum means there is a formation of a compact passive film at the surface depicting an increase in the corrosion resistance (Olugbade and Lu 2019a,b; Olugbade et al. 2019). On the other hand, a
porous film is formed on the sample surface if there is a decrease in the phase angle maximum signifying a lower corrosion resistance. Hence, surface treated stainless steel samples with higher phase angle maximum are expected to possess improved corrosion resistance behavior (Balusamy et al. 2013).

6 Corrosion resistance mechanism after surface treatment

Based on potentiodynamic polarization and EIS studies, the recent studies have helped in understanding the mechanism behind the corrosion resistance of materials subjected to SMAT. The main mechanism of the formation of the passive film is nucleation and growth. Nucleation mostly occurs because of dislocations, grain boundaries, impurities, etc. The change in nucleation and growth mechanism due to nanocrystallization has been reported to enhance the passivation abilities of 304 SS (Olugbade et al. 2021a,b,c). Furthermore, density and diffusivity of the defects in the passive film are the major parameters in determining passivity and pitting resistance. Nanocrystallization leads to a faster repassivation rate therefore the probability of metastable to stable pit formation in nanostructured SS can be reduced (Liu et al. 2010). Oxygen adsorption is an important factor in the corrosion mechanism since it is a determinant to the formation of passive monolayer films on the sample surface (Taylor and Ke 2021).

Table 1 summarizes the reported corrosion parameters of nanocrystalline stainless steel prepared by SMAT. The reported effects of surface treatment by SMAT on the pitting corrosion and passivation of stainless steel are summarized in Table 2. Some of the investigations revealed that nanocrystalline SS produced by SMAT experienced lower pitting corrosion resistance, which was attributed to the defects during treatment (Balusamy et al. 2014, Olugbade et al. 2021a,b,c). It is interesting to note that SMAT may either enhance or reduce the corrosion resistance of passive films (Table 2). For instance, due to reduced grain size and increased microstrain energy, there is a reduction in the corrosion resistance behavior of 316L SS in 3.5 wt% NaCl after surface treatment using 3 mm Ø 316L balls for 60 min (Li et al. 2017). The prolonged treatment time may be responsible for the reduced grain size and increased microstrain energy which ultimately reduces the corrosion properties. Once the nanostructured layers are formed, it is advisable to stop the treatment because treating the sample beyond this point may deform the nanostructured already formed leading to an increase in surface roughness hence a decrease in resistance and an increase in capacitance. The surface treatment of 304 SS using 6 mm Ø SS balls 3 min (Sun and Bailey 2014) also results in the reduction of corrosion resistance when immersed in 0.9% NaCl, which is possibly attributed to an increase in surface roughness and microstrain as well as the formation of interfacial boundaries in austenitic–martensitic transformation.

In contrast, there is an improvement in the corrosion resistance behaviour of 409 SS (Balusamy et al. 2010) in 0.6 M NaCl after surface treatment by SMAT using 2 mm Ø 316L SS ball for 15 min. The lower critical corrosion current density and enhanced passivation behavior are the possible reasons behind the enhanced corrosion resistance. Treatment at a moderate time of 15 min is another contributing factor for the improvement.

Despite the beneficial effects of the mechanical surface modification by SMAT, the process is characterized with some limitations including dislocations, strain induced martensite, and introduction of surface defects and increased surface roughness (Balusamy et al. 2010). These can easily influence the corrosion resistance because the higher the surface roughness, defects, and dislocations introduced on the sample surface during treatment, the lower the resistance of the material to resist corrosion attack. Limitation in the sample size is another setback because large dimension of sample cannot be easily treated due to the diameter of the chamber diameter which is often pecked at 70 or 80 mm (Olugbade and Lu 2019a,b; Olugbade et al. 2019). This means that any sample above this diameter cannot be easily treated and will need to be cut into the required sizes first.
Table 1: Corrosion parameters of nanocrystalline stainless steel prepared by SMAT.

<table>
<thead>
<tr>
<th>Material</th>
<th>Corrosive medium</th>
<th>Average grain size (nm)</th>
<th>SMAT condition</th>
<th>Scan rate (mV/s)</th>
<th>Potential range (mV)</th>
<th>Current density (µA/cm²)</th>
<th>Corrosion potential (V/SCE)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L SS</td>
<td>0.05 M H₂SO₄ + 0.25 M Na₂SO₄</td>
<td>~ 60</td>
<td>8 mm Ø balls for 60 min</td>
<td>0.33</td>
<td>~ 900</td>
<td>0.004</td>
<td>~0.05</td>
<td>Lu et al. (2006)</td>
</tr>
<tr>
<td>316L</td>
<td>3.5 wt% NaCl</td>
<td>9</td>
<td>3 mm Ø 316L balls for 60 min</td>
<td>1.67</td>
<td>~100 to +120</td>
<td>~0.0065</td>
<td>~0.35</td>
<td>Li et al. (2017)</td>
</tr>
<tr>
<td>409 SS</td>
<td>0.6 M NaCl</td>
<td>~ 100</td>
<td>5 mm Ø 316L SS balls for 60 min</td>
<td>1.67</td>
<td>~500 to +2000</td>
<td>0.19</td>
<td>~311</td>
<td>Balusamy et al. (2010)</td>
</tr>
<tr>
<td>304 SS</td>
<td>0.6 M NaCl</td>
<td>11–25</td>
<td>2 mm Ø 316L SS ball for 30 min</td>
<td>1.67</td>
<td>~250 to +800</td>
<td>0.45</td>
<td>~185</td>
<td>Balusamy et al. (2013)</td>
</tr>
<tr>
<td>304 SS</td>
<td>0.9% NaCl</td>
<td>6</td>
<td>6 mm Ø SS balls for 3 min</td>
<td>1</td>
<td>~700 to +350</td>
<td>0.1–0.3 mA</td>
<td>~350</td>
<td>Sun and Bailey (2014)</td>
</tr>
<tr>
<td>316 SS</td>
<td>0.1 M NaCl</td>
<td>19</td>
<td></td>
<td>0.3</td>
<td>~1500</td>
<td>~0.0048</td>
<td>~550</td>
<td>Hao et al. (2009)</td>
</tr>
<tr>
<td>409 SS</td>
<td>0.6 M NaCl</td>
<td>~100</td>
<td>2 mm Ø 316L SS balls for 15 min</td>
<td>1.67</td>
<td>~500 to +2000</td>
<td>0.28</td>
<td>~259</td>
<td>Balusamy et al. (2010)</td>
</tr>
<tr>
<td>409 SS</td>
<td>0.6 M NaCl</td>
<td>&lt;60</td>
<td>8 mm Ø 316L SS ball for 15 min</td>
<td>1.67</td>
<td>~500 to +2000</td>
<td>3.05</td>
<td>~730</td>
<td>Balusamy et al. (2010)</td>
</tr>
</tbody>
</table>

The corrosion potential values are given with respect to a reference electrode, saturated calomel electrode (SCE).

Table 2: Influence of surface treatment by SMAT on the corrosion resistance of stainless steel.

<table>
<thead>
<tr>
<th>Material</th>
<th>Corrosive medium</th>
<th>SMAT condition</th>
<th>Corrosion resistance</th>
<th>Remarks/Reasons</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L SS</td>
<td>3.5 wt% NaCl</td>
<td>3 mm Ø 316L balls, 60 min</td>
<td>Reduced</td>
<td>(i) Reduced grain size and increased microstrain energy (ii) Increased Cr oxide in the passive film</td>
<td>Li et al. (2017)</td>
</tr>
<tr>
<td>409 SS</td>
<td>0.6 M NaCl</td>
<td>2 mm Ø 316L SS ball, 15 min</td>
<td>Enhanced</td>
<td>(i) Enhanced passivation behaviour (ii) Lower critical corrosion current density</td>
<td>Balusamy et al. (2010)</td>
</tr>
<tr>
<td>304 SS</td>
<td>0.6 M NaCl</td>
<td>2 mm Ø 316L SS ball, 30 min</td>
<td>Reduced</td>
<td>(i) Induced plastic deformation during treatment (ii) Less dislocations</td>
<td>Balusamy et al. (2013)</td>
</tr>
<tr>
<td>304 SS</td>
<td>1.9% NaCl</td>
<td>6 mm Ø SS balls, 3 min</td>
<td>Reduced</td>
<td>(i) Increase in surface roughness and microstrain (ii) Formation of interfacial boundaries in austenitic-martensitic transformation</td>
<td>Sun and Bailey (2014)</td>
</tr>
<tr>
<td>409 SS</td>
<td>0.6 M NaCl</td>
<td>8 mm Ø 316L SS ball, 15 min</td>
<td>Reduced</td>
<td>(i) Microstrain and defect density induced during treatment (ii) Higher microcracks induced during treatment (i) Presence of cracks on the surface (ii) Presence of some structured defects or preferential pit initiation sites</td>
<td>Balusamy et al. (2010)</td>
</tr>
<tr>
<td>316 SS</td>
<td>0.1 M NaCl</td>
<td></td>
<td>Reduced</td>
<td>(i) Attributed to twin boundaries with a special low energy (ii) Presence of nanocrystalline boundaries</td>
<td>Hao et al. (2009)</td>
</tr>
<tr>
<td>316L SS</td>
<td>0.05 M H₂SO₄ + 0.25 M Na₂SO₄</td>
<td>8 mm Ø balls, 60 min</td>
<td>Enhanced</td>
<td>(i) Enhanced passivation behaviour (ii) Lower critical corrosion current density</td>
<td>Balusamy et al. (2010)</td>
</tr>
</tbody>
</table>

before treatment. In addition, the SMAT process is very efficient in enhancing the overall properties of stainless steels provided the appropriate processing parameters are utilized. However, the process is very expensive in terms of the machine and accessories cost, operating conditions, and environmental factors. This limits its application and usefulness to everybody especially people who cannot afford the process cost.
7 Summary and future work

The present review covers the body of literature on the influence of surface nanocrystallization by SMAT on the corrosion resistance of stainless steels. Through the SMAT process, nanostructure layer can be produced on the surface of stainless steels, which can be attributed to the multidirectional repetitive loading and large strain and strain rate. This decreases the grain size and changes the surface roughness, which significantly influences the corrosion behavior of stainless steels in various electrolytes. By SMAT, the high density of grain boundaries produced on the surface nanocrystalline layer can help forming a thin passive film. This could restrict the movement of metal ions from metal surface to the solution, thus improving passivation behaviour of stainless steels and reducing corrosion. The greater Cr enrichment developed by nanocrystalline structure could be because of a higher fraction of grain boundaries induced by SMAT. The effect of SMAT processing parameters was also summarized; increase in ball size and treatment time can increase the roughness, decrease the grain size, and increase the microstrain.

Having discussed the progress on the corrosion resistance of nanocrystallized stainless steels, the following prospects are therefore identified for future research.

(1) The role of SMAT and the associated processing parameters which cause changes in the microstructures are not investigated in detail. The microstructure and electrochemical corrosion behavior of nanostructured stainless steels must be fully investigated to understand the corrosion mechanisms and properties.

(2) Furthermore, alloying elements such as Mn, S, Mo, Ni, etc. demonstrate a vital part in the pitting corrosion and passivation of nanostructured stainless steels. The role of the alloying elements, their combinations and influence on the corrosion behavior of nanostructured stainless steels has not been fully investigated and needs further research attention.

(3) The role of local heating in the SMAT process, which is an important factor in the process of grain refinement has not been studied, and the consequential effect on the corrosion resistance of stainless steel also needs further investigation.

Acknowledgments: T.O. Olugbade specially appreciates the efforts of the members of Centre for Advanced Structural Materials (CASM), City University of Hong Kong, Hong Kong SAR as regards the surface mechanical attrition treatment (SMAT) method.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: None declared.

Conflict of interest statement: The authors declare that they have no conflicts of interest regarding this article.

References


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