Enhanced Pitting Corrosion Resistance of 304 SS in 3.5 wt% NaCl by Ultrasonic Nanocrystal Surface Modification

Shengxi Li,a Zhencheng Ren,b Yalin Dong,b Chang Ye,b Gang Cheng,c and Hongbo Conga,*

Corrosion Engineering Program, Department of Chemical and Biomolecular Engineering, The University of Akron, Akron, Ohio 44325, USA
bDepartment of Mechanical Engineering, The University of Akron, Akron, Ohio 44325, USA
cDepartment of Chemical Engineering, The University of Illinois at Chicago, Chicago, Illinois 60607, USA

Surface nanocrystallization has been shown to increase corrosion resistance of metallic materials. Ultrasonic nanocrystal surface modification (UNSM) is a recently developed method, which utilizes low amplitude ultrasonic frequency vibrations superimposed on a static load to induce high strain rate plastic deformation on a material surface for grain refinement. The present work investigates the effective depth of the severe plastic deformation layer by UNSM treatment, identifies the microstructure change and phase transformation within this layer, and correlates them with the enhanced pitting corrosion resistance of 304 SS in 3.5 wt% NaCl solution. © The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.1781712jes] All rights reserved.

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Corrosion is generally regarded as an electrochemical process that occurs at the interface of a metal and the contacting aqueous environment. Therefore, the surface condition is of vital importance to the corrosion performance of a metallic material. It has been generally believed that nanocrystalline metallic surfaces have different corrosion performance than bulk materials with micron-sized grains, despite the absence of a unified theory.1 Nanocrystalline surfaces can be achieved using a number of processing routes such as rolling, working, extrusion, electrodeposition, sputtering, and various milling methods, but each might have different corrosion performance. For example, while studies showed that magnetron sputtered nanocrystalline surfaces, compared to that caused by the large amount of steel balls used in SMAT, induced surface nanocrystallization on the corrosion performance of 304L SS had inconsistent corrosion performance.2 In terms of the mechanism, the studies claiming that nanocrystalline metals have improved corrosion resistance attributed it to improved passive films. Because nanocrystalline materials have drastically increased volume fraction of grain boundaries, which have higher energies (i.e. they are more active) than the bulk material, nanocrystalline surfaces have higher reactivity, which facilitates the formation of protective oxide layer.1

The mechanical techniques for obtaining nanocrystalline surfaces include hydrostatic extrusion (HE),3 laser shock peening (LSP),4,5 surface mechanical attrition treatment (SMAT)6–8 and ultrasonic nanocrystal surface modification (UNSM).9,10 The SMAT technique involves mechanically inducing surface modifications through severe plastic deformation (SPD) using high-velocity (1–20 m/s) steel balls.11 These balls are accelerated by collision between the balls and a vibrating chamber. The vibrating chamber can be driven by either an electric motor (Type I SMAT) or an ultrasonic generator (Type II SMAT). The SMAT process achieved by an ultrasonic generator is named as ultrasonic shot peening (USP or USSP).11 In USP, the high intense ultrasonic vibration is usually larger than 20 kHz. The SMAT processing (including USP) has been successfully applied to fabricate nanocrystalline surfaces on carbon steel and stainless steels,12–14 titanium,15 aluminum alloys,16,17 and magnesium alloys.18,19 The grain refinement mechanisms include deformation via dislocation slip and mechanical twinning.11 The combination of surface nanostructure and residual compressive stress results in increased surface hardness, tensile strength, fatigue resistance, wear resistance, and friction properties.11

Besides mechanical properties of SMAT-treated metallic materials, their corrosion behavior has also been investigated.3,20–27 However, it is still controversial whether SMAT treatment enhances or diminishes the corrosion performance of the treated materials. Hao et al.23 discovered that SMAT induced a large number of cracks on 316 SS surface and therefore reduced its corrosion resistance in 0.1 M NaCl. Furthermore, they found that annealing of the SMAT-treated 316 SS could greatly improve the corrosion resistance of this material. Balusamy et al.22,24,25 found that SMAT had different effects on the corrosion resistance of 304 SS and 409 SS in 0.6 M NaCl and/or Ringer’s solutions depending on the size of steel balls (D = 2, 5, and 8 mm). In general, the smaller balls (D = 2 mm) resulted in enhanced corrosion resistance. They attributed the deterioration of corrosion performance by larger balls to the increase in roughness, martensite content and dislocation density via SMAT treatment. Gatey et al.20 found that only an appropriate extent of SMAT processing improved the corrosion resistance of 304L SS in 3.5 wt% NaCl and further increase in peening intensity adversely affected the corrosion resistance of SMAT-treated 304L SS. Li et al.27 also proved that an increment in SMAT duration increased the active dissolution rate of 316L SS at room temperature. However, the SMAT-treated materials had better corrosion performance at 300 °C (steam generator environment) due to the formation of a dense protective oxide layer on nanocrystalline surface.27 In addition to the defects and cracks caused by SMAT processing, contamination from the steel balls was also found to affect the corrosion performance of SMAT-treated materials, especially for aluminum and magnesium alloys.28,29

UNSM is a relatively new technique that involves mechanically striking the material surface using a stylus with a tungsten carbide (WC) ball, which has higher hardness and better wear resistance than the steel balls used in SMAT. In this technique, a static load is applied to the stylus and is superimposed with cyclic low amplitude, high frequency (10–30 kHz) ultrasonic striking (dynamic load).30,31 The interaction of both static and dynamic load with material surface during UNSM processing is a major advantage over other SPD technologies. Similar to the SMAT treatment, the UNSM process induces high-intensity SPD which leads to nanocrystallization of the sample surface.9 Moreover, UNSM is a better-controlled process compared to SMAT, in terms of intensity and density of the strikes and therefore it results in more homogeneously-modified surface layers. This well-controlled feature also renders the UNSM processing highly repeatable and thus more reliable for industrial applications. In addition, the use of a single WC ball induces less/no contamination on the treated surfaces, compared to that caused by the large amount of steel balls used in SMAT.

Despite increasing efforts on surface nanocrystallization of metallic materials using UNSM, most of the research activities mainly focused on the mechanical properties of the treated materials. Limited research has been performed to investigate the effect of UNSM-induced surface nanocrystallization on the corrosion performance of...
The phase information of 304 SS samples before and after UNSM treatment was obtained using a Rigaku Ultima IV X-ray diffraction (XRD) system. A Cu Kα radiation (40 kV, 35 mA) was used. The scan range was 40°–100° (2θ) and the scan speed was 1°/min. Both control and UNSM-treated 304 SS samples were lightly polished (<30 s) using 1 μm diamond slurry prior to XRD experiments.

**Experimental**

**Sample preparation, processing, and characterization.**—A 304 SS sheet material (McMaster Carr) with chemical composition shown in Table I was used for the majority of experiments, including UNSM treatment, surface and cross-sectional characterization, and electrochemical tests. Samples with a dimension of $25 \times 25 \times 3$ mm were cut from this 304 SS sheet. The supplied sheet had been polished (by the supplier) on one side to a reflective, mirror-like finish ($S_a = 106.26$ μm, by Alicona InfiniteFocus microscope) and was used for UNSM treatment after ultrasonic cleaning in acetone and isopropanol.

Another certified 304 SS material (chemical composition in Table I), which is a rod with a diameter of 25.4 mm (McMaster Carr), was also utilized to study the impact of UNSM on MnS inclusions. Disks with a thickness of 3 mm were cut from this 304 SS rod, abraded using 600 and 1200-grit sand papers, and polished using 3 μm and 1 μm diamond slurries (Buehler). The polished disks were then used for UNSM treatment. Note that in this manuscript, “304 SS” refers to the sheet material if not specified otherwise.

The UNSM treatment was conducted in a UNSM system equipped with a WC ball with a diameter of 4 mm. The WC ball was attached to an ultrasonic device using a stylus. The ultrasonic vibration frequency was 20 kHz and the vibration amplitude was 8 μm. A 2 kg static load was applied to the stylus and transferred to the samples. The movement of the stylus was controlled with a step size of 0.01 mm and a scan speed of 1000 mm/min. A 10% overlap was used between each line of scan.

The control and UNSM-treated 304 SS samples were polished using 1 μm diamond slurry for surface characterization and inclusion quantification analysis by scanning electron microscopy (SEM). Only light polishing (~30 s) was performed on the UNSM-treated samples to avoid removing excessive material from the surface layers. A TESCAN LYRA 3 field emission SEM (FE-SEM) equipped with energy dispersive X-ray spectroscopy (EDS) was used to characterize the inclusions on the 304 SS surfaces. All SEM/EDS analyses were conducted with an accelerating voltage of 20 kV. Backscattered electron (BSE) SEM images (×8) were obtained for quantitative analysis of the inclusions using the ImageJ software.

For cross-sectional characterization, the UNSM-treated sample was sectioned, mounted in epoxy resin (Buehler), successively abraded using 400, 600, 1200-grit sand papers, and polished using 3 μm and 1 μm diamond slurries. Next, the freshly polished sample was electrochemically etched in 60% HNO₃ at +1.5 V (vs. saturated calomel electrode (SCE)) for 1 min to reveal the cross-sectional microstructure, which was observed using the same SEM. Cross-sectional microstructure was also examined using scanning transmission electron microscopy (STEM) and TEM. STEM observation and TEM lamella preparation were conducted in the same TESCAN system while TEM observation and selected area electron diffraction (SAED) acquisition were carried out using a FEI Tecnai F30 system operated at 300 kV.

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**Table I. Chemical compositions (wt%) of the 304 SS sheet and rod materials.** Elements with contents less than 0.01% are not listed.

| Material | C   | Cr  | Ni  | Mn  | Si  | P   | S   | Cu  | N   | W   | Co  | Mo  | Nb  | V   | Fe  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Sheet    | <0.08 | 18–20 | 8–11 | <2 | <1 | <0.045 | <0.03 | -   | -   | -   | -   | -   | -   | Balance |
| Rod      | 0.023 | 18.23 | 8.18 | 1.83 | 0.28 | 0.035 | 0.024 | 0.67 | 0.062 | 0.032 | 0.132 | 0.3 | 0.024 | 0.06 |

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Results and Discussion

**Sample characterization.—** SEM/EDS characterization of the untreated 304 SS showed that most of the inclusion particles in the sheet material are composed of various oxides, i.e., Ti, Al, Mn, Ca, and Mg oxides (Figure S1), instead of sulfides such as MnS. MnS was only detected at the edge of some oxide inclusions, as an example shown in Figure 1.

SEM characterization of the inclusion particles in UNSM-treated 304 SS indicated that the amount of inclusions decreased after UNSM treatment, as an example shown in Figure S2. Quantitative analysis of inclusions was conducted on eight SEM images (BSE mode, each of $554 \times 415$ μm) from each group using the ImageJ software. Inclusion particles with area larger than 0.785 μm² (or diameter $D > 1$ μm) were counted and smaller inclusions were not counted due to the resolution limit of the images. Although similar counts of total inclusion particles

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were found from the eight regions on control 304 SS (388 particles) vs. UNSM-treated 304 SS (374 particles), the area fraction of inclusion particles on 304 SS surface significantly decreased after UNSM treatment (Figure 2). The UNSM-induced decrease in the total area of inclusion particles can also be seen from the size distribution of the inclusion particles shown in Figure 3. This result indicates that some inclusion particles were chipped off from the steel surface during the UNSM treatment, possibly due to the brittle nature of the non-metallic inclusions. While some inclusions were removed from the surface, others were crushed into smaller pieces, which distributed relatively evenly over the entire surface (Figure S2d). This phenomenon can be better seen from the high-magnification SEM images in Figure S3. EDS mapping (Figure S4) confirms that these small particles are inclusion particles, containing mostly Al-oxide and Ti-oxide. Similarly, mechanically-induced size reduction of intermetallic particles in SS have been previously achieved using hydrostatic extrusion.39

The SEM images in Figure 4 present the cross-sectional microstructure of UNSM-treated 304 SS after etching. Interestingly, the etching process only revealed grain boundaries in the 304 SS substrate but not in the 2 μm thick surface layer. This 2 μm thick surface layer is the nanocrystalline layer produced by UNSM. The contrast in brightness and absence of etched grain boundaries (Figure 4b) suggest better corrosion resistance of the nanocrystalline layer compared to the substrate in the etching solution. However, the deformation layer may be thicker than 2 μm, for example, ∼5–10 μm, as suggested by the distortion of grain boundaries underneath the apparent 2 μm-thick surface layer (arrow in Figure 4b).

A bright-field STEM image in Figure 5a confirms the ∼2 μm thick surface layer with refined grains (dashed line) and a bright-field TEM image in Figure 5b suggests these grains are typically less than 100 nm in size. An SAED pattern (Figure 5c) from this UNSM layer...
exhibits a series of rings that can be indexed to $\alpha'$-martensite, indicating grain refinement and phase transformation caused by UNSM treatment. In contrast, an SAED pattern (Figure 5d) obtained at $\sim 3 \, \mu m$ below the top surface shows no diffraction rings, and therefore indicates the absence of nano-grains. It is also evident in Figure 5a that the grain size gradually increases from the top surface into the underneath substrate, which indicates the weakening influence of plastic deformation with increasing depth. The deformation-induced formation of nanoscale crystallites has been achieved through SPD induced by several techniques. This grain refinement on the surface can be attributed to dislocation activities, deformation twining, and/or martensitic phase transformation.

Figure 6 presents the XRD patterns from the surfaces of a control 304 SS sample and a UNSM-treated 304 SS sheet material sample. While the control sample surface has both austenite and martensite phases, the UNSM-treated surface shows only martensite suggesting that the effective UNSM depth is larger than the XRD penetration depth. This transformation of austenite to martensite on 304 SS surface caused by UNSM is similar to that observed on 304 SS processed by ball milling and SMAT.

**Corrosion behavior.**—Figure 7a compares the CPP results of control and UNSM-treated 304 SS samples in deaerated 3.5 wt% NaCl. The UNSM-treated 304 SS has more noble pitting potential ($E_{np}$) and lower passive current density than the control sample, indicating enhanced pitting corrosion resistance of 304 SS after UNSM treatment.

Furthermore, the UNSM-treated 304 SS surface repassivates through localized corrosion repassivation mechanism with significantly higher repassivation potential ($E_{rp}$, $0.17 \, V_{SCE}$). In contrast, the control 304 SS repassivates only through the deactivation mechanism with lower $E_{rp}$ ($< -0.3 \, V_{SCE}$). This enhanced repassivation behavior is possibly related to the grain refinement to the nanoscale. The surfaces of the CPP samples (control and UNSM) were analyzed using XPS afterwards. The results revealed that the surface film on the UNSM-treated 304 SS has a higher content of Cr ($\text{Cr}/(\text{Cr} + \text{Fe})$ is $\sim 1.5$ times higher for UNSM-treated sample as compared to the control sample) indicating greater Cr enrichment in the passive film on UNSM-treated 304 SS surface than the control, which may explain the better passivation behavior and enhanced pitting resistance. Figures 7e and 7f compare the XPS analysis of Cl in the passive films. A statistically lower percentage of Cl was found to be incorporated in the passive film on UNSM-treated 304 SS compared to the control surface. This difference in Cl content also demonstrates the enhanced passive film properties via UNSM treatment.

The enhanced pitting resistance of UNSM-treated 304 SS was further verified by studying metastable pitting, which is considered as a critical step in the overall pitting process. Three potential levels, i.e., 250, 350, and 450 $mV_{SCE}$ were selected for potentiostatic tests based on CPP results (Figure 7a). At 450 $mV_{SCE}$, stable pitting corrosion occurred on the control sample (Figure 8a) with high current ($> 10 \, nA$). The stable pitting phenomenon was confirmed using optical microscopic examination which showed the formation of large corrosion pits on the sample surface. The current transients in $\sim 60$–95 s (inset in Figure 8a) were likely caused by the instability of the salt films formed inside the pits in the early stage or micro-crevices, instead of typical metastable pitting (inset in Figure 8c). In contrast, the UNSM-treated sample polarized at 450 $mV_{SCE}$ exhibited only five current transients ($> 10 \, nA$) typical of metastable pitting with a maximum current of $\sim 38 \, \mu A$ (Figure 8b). The control sample showed 36 current transients when polarized at 350 $mV_{SCE}$ (Figure 8c) and one at 250 $mV_{SCE}$ (Figure 8d). In comparison, the UNSM sample showed no metastable pitting events at these two potentials (Figures 8d and 8f). As a result, no statistical analysis (i.e., cumulative distribution) was conducted on the metastable transient curves for comparison purposes.

The comparison in Figure 8 clearly demonstrates that the UNSM-treated 304 SS samples had improved metastable pitting resistance than the untreated samples. In addition, Figure 8 reaffirms that the frequency and magnitude of metastable pitting events increases with increasing applied potential. Furthermore, majority of the metastable pitting activities was observed in the beginning of the experiments and decreased with time, which can be attributed to the decrease of the number of susceptible sites available for metastable pitting.

*The presence of martensite in the control sample may have been caused by the polishing process the manufacture used to achieve a reflective and mirror-like finish.*
Figure 7. (a) Representative CPP curves of control and UNSM-treated 304 SS sheet material samples in deaerated 3.5 wt% NaCl. The inset compares the mean $E_{\text{corr}}$ values of control and UNSM-treated 304 SS; (b and c) high-resolution XPS spectra of Cr and Fe from the passive films on control and UNSM-treated 304 SS samples after CPP tests; (d) quantitative comparison of the Cr/(Cr + Fe) ratio of the passive films on control and UNSM-treated 304 SS sheet material; (e and f) XPS spectra and quantitative comparison of Cl content on control and UNSM-treated 304 SS samples after CPP tests. All error bars represent one standard deviation.

The samples after metastable pitting tests were examined using SEM/EDS. On the control 304 SS sample polarized at 350 mV SCE, pits were found at the Ti oxide-containing inclusion particles (1 in Figure 9a and Table II). Because pitting usually initiates from the sulfide-containing inclusion particles,\textsuperscript{53,54} it is believed that the inclusion particle marked by ‘1’ in Figure 9a was a dual-phase (oxide and sulfide) particle (refer to Figure 1) and the MnS component preferentially dissolved and pitting occurred. EDS analysis conducted inside the pit indicated the complete dissolution of S (2 in Table II). Figure 9a also shows that the single-phase oxide inclusion particle (3 in Figure 9a and Table II, Ti oxide) did not initiate pitting. Figure 9b shows another type of pits without the presence of residual inclusion particle. This type of pits might have initiated from small inclusion particles and the inclusion particles totally dissolved, or were caused by defects in the passive film on 304 SS. Less metastable pits were observed on the UNSM-treated 304 SS tested at 450 mV SCE, as compared to the control sample tested at 350 mV SCE, which agrees with the electrochemical results shown in Figure 8. Pits similar to that shown in Figure 9a (marked by 2) were not found on the tested UNSM samples, possibly due to the significant decrease in the number of large MnS-containing dual-phase inclusion particles (Figure 3). Figure 9c shows a typical metastable pit found on the UNSM-treated 304 SS. EDS analysis revealed the presence of S inside the pit (4 in Table II). Therefore, this pit might have initiated from a small MnS-containing inclusion particle. Notice that the single-phase oxide inclusion particles such as the one shown in Figure 9d (5 in Table II, Al oxide) did not cause metastable pitting on 304 SS in 3.5 wt% NaCl, similar to the Ti oxide inclusion particle in control 304 SS (3 in Figure 9a). This is in agreement with the findings of Frankel et al. who demonstrated that only MnS-containing phases (MnS and MnS/oxide) dissolved but not the oxide phases in their pit initiation sites experiments.\textsuperscript{38}

In order to verify the effect of UNSM treatment on the MnS inclusion particles, another 304 SS rod material with MnS as the dominant inclusion (Figure 10a) was treated using UNSM. It was found that
Figure 8. Potentiostatic transient curves of control 304 SS sheet material samples (a, c, and e) and UNSM-treated 304 SS sheet material samples (b, d, and f) at 250, 350, and 450 mV <sub>SCE</sub> for 600 s in deaerated 3.5 wt% NaCl solutions.

Figure 9. SEM images showing the pits and inclusion particles on the control 304 SS sheet material samples after potentiostatic polarization at 350 mV <sub>SCE</sub> (a and b) and UNSM-treated samples at 450 mV <sub>SCE</sub> (c and d) for 600 s in deaerated 3.5 wt% NaCl solutions.

UNSM treatment completely removed MnS inclusions from the surface of the 304 SS rod material (Figure 10b). The results from two different 304 SS materials indicate that the UNSM treatment is able to break down and decrease oxide inclusions but remove Mn inclusion completely. However, it is not clear why the UNSM treatment has different effects on different types of inclusions, which may depend on the nature of the inclusions and the UNSM processing parameters. This warrants further research on surface treatment by UNSM.

The mechanisms for the UNSM-enhanced pitting corrosion performance of 304 SS can be hypothesized as follows. First, it is believed that nanocrystalline surfaces favor the formation of a more stable and compact passive film with low defect density. In previously published research, the higher density of grain boundaries and larger fraction of surface area in fine-grained stainless steel facilitate Cr diffusion into the passive film and therefore result in greater Cr enrichment in the passive film. The greater Cr enrichment in the passive film on nanocrystalline stainless steel is also proved in the present work (Figures 7b–7d). It was also suggested that the nanocrystalline structure could inhibit the incorporation of chloride anions in the passive films. Similarly, the XPS results in the present work showed that the passive film on the UNSM-treated 304 SS had less Cl than the control sample (Figures 7e and 7f). Second, the inclusion particle analysis showed that the mechanical strikes during the UNSM treatment

| Table II. EDS elemental compositions (at%) of pits and inclusion particles on the surfaces of control and UNSM-treated 304 SS after potentiostatic tests (Figure 9). |
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| Region | O | Al | S | Ti | Cr | Mn | Fe | Ni |
| 1  | 46.90 | 0.39 | - | - | 23.25 | 8.06 | 3.78 | 17.09 | 0.53 |
| 2  | 2.92 | - | - | - | 3.15 | 21.15 | 5.17 | 61.96 | 5.66 |
| 3  | 52.58 | 1.24 | - | - | 34.45 | 4.80 | 5.15 | 1.78 | - |
| 4  | 9.05 | 1.75 | 0.96 | 1.74 | 17.59 | 3.71 | 59.38 | 5.80 |
| 5  | 48.78 | 35.17 | - | - | 3.94 | - | 9.76 | 2.34 |
result in a cleaner surface by removing more than half of the inclusion particles (area fraction) on 304 SS surface (Figure 2). It is commonly accepted that pitting corrosion of stainless steels usually initiates from non-metallic inclusions. Although different mechanisms have been proposed for pit initiation at MnS inclusions, it is certain that sulfur plays an important role in pit initiation. The comparison between two different 304 SS materials (sheet vs. rod) suggests that the UNSM process can remove MnS inclusions completely. The removal of MnS inclusion particles from 304 SS surface by UNSM treatment diminished pitting susceptible sites and therefore enhanced the pitting resistance of 304 SS. The UNSM treatment might have also decreased the inclusion/matrix interfacial micro-cracks if any and thus reduces the occurrence of pitting. Third, it was found that UNSM processing generates compressive residual stress on 304 SS. The presence of compressive residual stress on the surface of UNSM-treated 304 SS may also increase the pitting corrosion resistance of this material, similar to what has been previously reported. Lastly, it is worth-while mentioning that the UNSM-induced transformation of austenite to martensite likely did not contribute to the corrosion performance enhancement of 304 SS, according to previous studies.

Conclusions

Surface nanocrystallization of 304 SS was achieved using a novel method called ultrasonic nanocrystal surface modification (UNSM). It was found that the UNSM-induced mechanical striking not only resulted in a nanocrystalline surface on 304 SS surface but also a cleaner surface (i.e., less area fraction of inclusion particles) as compared to the control sample. The nanoscale grain refinement led to greater Cr enrichment in the surface passive films on 304 SS, while the breakdown and removal of inclusion particles, especially MnS from 304 SS surface rendered less susceptible sites for pitting corrosion. Both factors contributed greatly to the improved pitting corrosion resistance of 304 SS in 3.5 wt% NaCl.

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