Influence of nitrogen uptake and heat treatment on the microstructural characteristics and corrosion performance of X190CrVMo20-4-1 steel produced by supersolidus liquid-phase sintering

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Abstract
Martensitic stainless steel powder exhibits a high nitrogen uptake when densified by supersolidus liquid-phase sintering in a nitrogen atmosphere, but the optimum uptake, which is beneficial to its resistance to corrosion, is unknown. In this study, the resistance of high-carbon martensitic stainless steel X190CrVMo20-4-1 densified in a nitrogen atmosphere against pitting corrosion was explored. This was to clarify the impact of nitrogen uptake in the steel matrix in the quenched and tempered condition on its corrosion resistance in an aqueous solution. Samples were subjected to potentiodynamic polarisation tests in a de-aerated, 1 wt% NaCl solution. Results revealed that the X190 steel densified in a nitrogen atmosphere at 40-kPa pressure, subjected to deep cryogenic treatment in liquid nitrogen at an austenitising temperature of 1150°C and tempered at 200°C, had the best pitting corrosion resistance with a breakdown potential of 142 ± 11 mV/SCE and a hardness of 738 ± 4 HV10. The matrix around the M7C3 carbides and MX carbonitrides suffered high pitting susceptibility. The implications of this study serve as a basis for the improvement of the functional properties of steels.

KEYWORDS
heat treatment, martensitic stainless steel, nitrogen atmosphere, pitting corrosion, supersolidus liquid-phase sintering

1 INTRODUCTION

Industrial applications with severe wear and corrosion exposure necessitate the development of resilient materials to combat the degradation over a long service period. For this purpose, martensitic stainless steels are developed for the manufacture of cutting utensils, moulds and dies for food, plastic, chemical, mining and mineral processing industries. These industrial parts are made of cast and wrought steels and are also produced via powder metallurgical routes such as hot isostatic pressing (HIP) and supersolidus liquid-phase sintering (SLPS), among others. However, SLPS offers flexibility in terms of the densification atmosphere employed for the production of cold work tool
The densification atmosphere is an important factor, as a significant microstructural modification is possible through it to augment the steel properties. Employing a nitrogen atmosphere during the SLPS promotes nitrogen uptake of the steel, which modifies its alloy chemistry. Farayibi et al.\cite{5} observed that the nitrogen uptake achieved through the SLPS of a pre-alloyed powder of steel in a nitrogen-pressurised environment is dependent on the applied partial pressure. Gimenez et al.\cite{4} reported that the chemical composition of the steel influences its nitrogen uptake, as pre-alloyed steels with high vanadium and carbon content possess a higher ability to have nitrogen dissolved in them. Thus, the equilibrium concentration of nitrogen in the densified steel during SLPS is dependent on the applied partial pressure and the steel elemental content. In a previous study, Farayibi et al.\cite{5} noted that the dissolved nitrogen results in an in situ synthesis of vanadium-rich carbonitride, MX-type precipitates, homogeneously dispersed in the hard martensitic matrix. The synthesised carbonitrides with other carbide-type precipitates in a quench-hardened steel matrix improve the hardness and wear resistance.

Moreover, it is known that dissolved nitrogen in the steel matrix enhances the corrosion resistance of the steel, besides promoting the formation of carbonitrides. Speidel\cite{6} reported that nitrogen dissolved in the matrix of stainless steel improves its resistance against pitting corrosion. The solubility of nitrogen is always higher in the austenite phase of iron and nitrogen has a similar effect as carbon on stabilising the steel as an austenitic phase.\cite{7} In addition, the nitrogen solubility in the austenite iron (γ-Fe) is reported to be dependent on temperature, pressure and alloy composition. As for tool steel, it is desired that the matrix becomes martensitic upon rapid quenching from a suitable austenitising temperature. The martensitic matrix enriched with nitrogen is expected to have enhanced resistance to pitting corrosion. However, modification of the steel matrix chemistry by the dissolved nitrogen makes its martensite finish temperature to drop below the room temperature, as observed from a previous study.\cite{8} This can result in a high volume of austenite retained in the matrix enriched by nitrogen if not optimally heat treated. With increased retained austenite in the tool steel matrix, hardness and surface contact deformation resistance are greatly reduced. Hence, a sufficient amount of nitrogen soluted in the martensitic steel matrix and a little amount of retained austenite is necessary to achieve an optimum combination of wear and corrosion resistance.

An early study by Leda\cite{9} has shown that an increasing nitrogen content of the γ-Fe phase enhances the resistance of the martensitic steel against corrosion by pitting, and the chromium content in the carbide precipitates (M23C6 and M7C3) and the grain size of the γ-Fe phase decrease. In another study, Li et al.\cite{10} found that the electric potential required for pitting to occur on a super martensitic stainless steel at a current density of 100 µA/cm² decreased with increasing NaCl concentration and temperature in the presence of CO₂. Closed and open pits were observed on the corroded steel samples with pitting potentials measured as 150 mV/SCE in 1 wt% NaCl solution and 49.5 mV/SCE in 3 wt% NaCl solution at a temperature of 50°C. Seifert et al.\cite{11} explored the corrosion performance of HIP-produced, multiphase martensitic X190CrVMo20-4-1 stainless steel specimens heat-treated at different conditions in NaCl electrolytes. The steel exhibited the best corrosion resistance when tempered at low temperatures between 100°C and 200°C. In a similar study, Taji et al.\cite{12} investigated the influence of tempering at different temperatures on the corrosion performance of AISI 403 martensitic stainless steel, and they reported that samples tempered at 550°C had the lowest pitting potential and highest degree of sensitisation. Moreover, Yoon et al.\cite{13} reported that carbon- and nitrogen-enriched stainless steel possesses better pitting corrosion resistance when compared with those with nitrogen only, as carbon substitution lowers the pit growth rate, which improves the nobility of the steel matrix. In a recent study, Bignozzi et al.\cite{14} noted that high austenitisation temperature and tempering at low-temperature heat treatment are advantageous for the resistance of X190CrVMo20-4-1 stainless steel against corrosion, as more Cr is soluted in the matrix at higher austenitisation temperature to enhance corrosion resistance.

Previous studies have shown that martensitic stainless cold work tool steels with high vanadium content have a high nitrogen uptake ability when pre-alloyed powder is densified in a nitrogen atmosphere at increasing applied partial pressures.\cite{4,5} This results in the in situ synthesis of carbonitrides serving as reinforcements in the steel matrix to promote enhanced surface contact deformation resistance. The volume fraction of the in situ synthesised carbonitrides is dependent on the applied partial pressure of nitrogen during densification. However, the influence of the amount of in situ synthesised carbonitrides on hardness is outweighed when the matrix is optimally quench-hardened. This implies that irrespective of the applied partial pressure during densification of the steel powder, its matrix can be optimally heat-treated to achieve similar hardness and wear resistance characteristics. Moreover, nitrogen soluted in the matrix of stainless steel performs a significant role in increasing the resistance against corrosion by pitting.\cite{6,9} However, previous studies did not establish the suitable amount of nitrogen that can be soluted in the martensitic matrix of a Cr- and V-rich stainless tool steel and suitable heat treatment. As the aim is to produce wear- and corrosion-resistant steel, it is necessary to investigate the effect of the nitrogen...
uptake on the corrosion performance of the quench-hardened steel, which is yet to be elucidated.

Hence, this study examines the influence of nitrogen uptake of martensitic X190CrVMo20-4-1 stainless steel during SLPS process on its pitting corrosion resistance. This needs to be done to clarify whether increasing nitrogen uptake implies increasing nitrogen soluted in the steel matrix. In addition, the influence of tempering heat treatment after quench hardening of the samples on its corrosion performance is examined to establish the beneficial tempering temperature regime.

2 | EXPERIMENTAL

2.1 | Materials

In this study, a pre-alloyed steel powder (X190CrVMo20-4-1), 'X190', commercially sourced, was employed for the densification experiments. The powder particles have a size ranging between 45 and 62 µm and exhibit a spherical morphology. The global chemical composition of the steel powder densified in a vacuum, assessed using an optical emission spectrometer machine (model QSG750; OBLF), is presented in Table 1.

2.2 | Densification process

A horizontal tubular furnace with 40-mm internal diameter (model 7/75; Heraeus) was employed for the SLPS of the pre-alloyed steel powder. The furnace can be operated in a vacuum condition or using nitrogen gas at a maximum operating temperature of 1300°C. As this study examines the impact of nitrogen uptake on the corrosion behaviour of the steel, densification experiments were performed in vacuum and under an atmosphere partially pressurised by nitrogen, as reported in Farayibi et al.[3] The pre-alloyed steel powder was filled into an alumina crucible (15 mm deep, 90 mm long) at a densely tapped condition before placing the crucible in the furnace. The alumina crucible has a trapezoidal cross-section for easy removal of the densified sample with an internal base width of 10 mm and a top width of 15 mm. For the densification in a vacuum to prevent oxidation (5-Pa pressure maintained), the temperature of the furnace was elevated to the densification temperature of 1280°C at 10 K/min rate of heating. To achieve nitrogen uptake, the steel powder in the alumina crucible was densified by raising the furnace temperature to 1100°C under a vacuum condition to avoid oxidation, and then nitrogen was backfilled into the furnace. Samples were prepared using nitrogen pressures of 10, 40, 50 and 80 kPa. Soaking time of 30 min was allowed with the furnace temperature maintained at 1100°C, and thereafter the temperature was increased to 1280°C. The nitrogen at the preset pressure in the furnace was held constant throughout the densification period. All samples were held at the densification temperature under vacuum for a duration of an hour with furnace cooling in the furnace to ambient temperature afterwards. All samples, upon cooling, have their sizes similar to the internal dimension of the alumina crucible having 15-mm height, 90-mm length, top width of 15 mm and base width of 10 mm with minimal shrinkage.

2.3 | Heat treatment

To explore the influence of heat treatment on corrosion performance, densified samples were subjected to different austenitisation, quenching and tempering procedures. The target is to determine the processing condition and the necessary heat treatment procedure to produce a sample with the best corrosion performance as well as a high hardness. Specimens with 10-mm length were cut from the middle section of each densified sample. Specimens were held for 30 min at the selected austenitising temperatures, followed by quenching to induce austenite-martensite transformation of the matrix. Some of the selected austenitising temperatures have been identified to help achieve a high hardness for the specimens, based on a previous study.[3] The vacuum-sintered sample was austenitised at 1150°C, the nitrogen-sintered samples densified under a partial pressure of 10 kPa were austenitised at 1100°C and the nitrogen-sintered samples produced under partial pressures of 50 and 80 kPa were subjected to 1000°C austenitising temperature. Two specimens were prepared from the 40-kPa nitrogen-sintered sample, one was subjected to quenching in oil and the other to deep cryogenic treatment (DCT) using liquid nitrogen after austenitising at 1150°C. Subsequently, all quench-hardened specimens, except one, were tempered at a low temperature of 200°C and only

| Steel       | C (wt%) | N (wt%) | Cr (wt%) | V (wt%) | Mo (wt%) | Si (wt%) | W (wt%) | Mn (wt%) | Ni (wt%) | Fe (wt%) |
|-------------|---------|---------|----------|---------|----------|----------|--------|----------|----------|----------|
| X190 vacuum | 1.82 ± 0.01 | 0.05 ± 0.01 | 19.02 ± 0.07 | 3.64 ± 0.09 | 0.88 ± 0.01 | 0.65 ± 0.02 | 0.46 ± 0.01 | 0.35 ± 0.01 | 0.25 ± 0.01 | Bal.     |
one specimen from a 10-kPa nitrogen-sintered sample was subjected to tempering at 540°C. The tempering was carried out for 2 h in a single cycle to relieve internal stresses and promote secondary hardening. Table 2 gives the summary of the heat treatment carried out on each specimen before testing their corrosion performance.

### 2.4 Characterisation

After heat treatment, specimens were prepared for microstructural characterisation. Samples, embedded in a conductive carbon polymer, were ground and polished using a suspension solution containing diamond grits of 1-µm size to achieve a surface-mirror finish. Before optical and scanning electron microscopy, a V2A solution, comprising hydrochloric acid (HCl, 100 ml), nitric acid (HNO₃, 100 ml), 0.3 ml Vogel’s inhibitor and distilled water (H₂O, 100 ml), was used to etch the samples to reveal the microstructure.[15] An optical microscope (Leica DM2700) and a scanning electron microscope (Tescan Vega3 SBH SEM) were employed for the examination of the sample microstructure. An accelerating electron voltage of 20 kV with a working distance of 15 mm and a beam spot size of 83 nm was used during the examination. The volume fraction of phases formed in the sintered steel after heat treatment was assessed through an image binarisation of five SE-SEM images of each sample. This was done by subjecting the sample micrographs to image processing using an open-source ImageJ application package. To identify phase constituents, the experimental patterns of the samples were recorded using an X-ray diffractometer (Bruker D2 Phaser). A voltage and a current of 30 kV and 20 mA, respectively, were employed in operating the diffractometer to produce X-ray radiation, Cu K(α), with wavelengths λ_{CuKα1} = 1.54059 Å and λ_{CuKα2} = 1.54449 Å. The diffractograms were recorded over a 2θ range of 35°-55° at 3-s counting time per data point with a step size of 0.02°. Phase constituents were identified by comparing the reflections in the experimental diffractograms with standard reflections in the PDF-2 2016 database provided by the International Centre for Diffraction Data. Heat-treated specimens were subjected to a hardness test by applying a weight of 98.1 N for 10 s using a Vickers indenter mounted on a hardness testing machine (ATM Carat 930).

### 2.5 Computational thermodynamics

In this study, thermodynamic computation was made to supplement experimental observations. These evaluations were done using commercially available Thermo-Calc 2020a software with the Fe database, TCFE10 licensed by Thermo-Calc AB, Stockholm. The compositions of the steel sintered in a vacuum (Table 1) served as the component inputs for the thermodynamic evaluations. Computational simulations were made to determine the amount of nitrogen uptake by the steel powder and the evolution of the phases in the steel from a calculated steel phase diagram with respect to its nitrogen content under an equilibrium condition. The pitting resistance equivalent number (PREN) and martensite start (Ms) temperature were evaluated in the Thermo-Calc software for the quenched austenitic phase of the sintered steel using the empirical formula in Equations (1)[16] and (2).[17] The empirical formula for the martensite start temperature was adjusted by considering the nitrogen to exhibit similar influence on the matrix austenite stabilisation and hardenability as carbon.[7]

\[
P_{RE}=Cr+3.3Mo+20N\text{ (all in wt%)},
\]

\[
M_{s}(°C, \text{wt%})=545-330(C+N)-14Cr-23Mn-5Mo-13Ni-7Si+4V.
\]

### 2.6 Electrochemical tests

The performance of the heat-treated samples in a corrosive environment was evaluated by subjecting them to potentiodynamic polarisation tests. The embedded samples in a nonconductive polymer were ground with final mechanical grinding on a 1500-SiC grit paper for 240 s. The surface area of the samples (0.6–1.0 cm²) exposed to the electrolyte was isolated from the resin using a hydrophobic lacquer and measured using an image processing technique. At the rear side of the polished surface, a weldable, conductive, nickel–chrome (NiCr6015) alloy wire was joined to the sample by spot welding. To mimic the exposure of these...
materials to the food processing environment, a saline medium (1 wt% sodium chloride, NaCl) was used as the electrolyte. A PGSTAT204 Metrohm Autolab potentiostat controlled by Nova 2.0 software connected to a three-electrode cell was employed for the electrochemical tests. The samples serve as the working electrode, saturated Hg/HgCl₂ calomel electrode (SCE + 244 mV vs. standard hydrogen electrode) as a reference electrode and a 10 × 10 mm² platinum plate as the auxiliary/counter electrode. Before the sample immersion, the electrolyte was de-aerated by purging with N₂ gas for 30 min and the pH value of the electrolyte was measured to be 6.72 at a temperature of 25°C. Thereafter, the surface of the sample was cleaned by subjecting it to a cathodic prepolarisation at −1244 mV for 60 s, and the open circuit potential (OCP) of the sample was measured for 600 s to ensure that a similar preliminary state of the sample surface-electrolyte interface is maintained in all experiments. All potentiodynamic polarisation scans were made over a range of −100 mV/SCE below the OCP to 1500 mV/SCE above OCP at a standard sweep rate of 1.67 mV/s. Subsequently, the current flowing from the sample to the counter electrode was recorded. To ensure the reproducibility of results, the tests were repeated at least three times. According to ASTM G150-99,[18] a breakdown potential, \( E_b \), as current density rises and remains above 100 µA/cm² is taken as the pitting potential to serve as a basis of comparison among samples tested, as a clear and sharp increase in the current per unit area could not be observed in the polarisation scan of stainless steel tested in NaCl solution.

3 | RESULTS

3.1 | Thermodynamic calculations

Figure 1a depicts the thermodynamically computed equilibrium nitrogen content of the steel powder pre-alloyed at a soaking temperature of 1100°C under an atmosphere with different nitrogen partial pressures applied. The nitrogen content of the steel increases as the nitrogen partial pressure applied during sintering increases. The nitrogen content of the powder, when sintered under a vacuum condition, is 0.05 wt%. However, the calculated N contents of the steel under nitrogen partial pressures 10, 40, 50 and 80 kPa are 0.83, 1.23, 1.54 and 2.31 wt%, respectively, at 1100°C. Figure 1b shows the equilibrium phase diagram of the X190 steel with respect to variation in nitrogen content from 0 to 2.5 wt%, as calculated by Thermo-Calc. The largest phase field consists of austenite (\( \gamma \)-Fe), M₇C₃ carbide and MX carbonitride on the phase diagram, where M means substitutional elements and X means a combination of carbon and nitrogen (C + N). The appearance of the liquid phase occurs first in the steel at a solidus temperature (\( T_{sol} \)) of 1249°C with zero nitrogen content. However, the solidus temperature of the steel increases slightly as the nitrogen content of the steel increases. To achieve the densification of the steel powder with low porosity, sufficient liquid phase is required with 40 vol% liquid targeted; hence, the sintering phase field at 1280°C consists of liquid, L, MX carbonitride and austenite.

The dotted vertical lines represent the calculated equilibrium nitrogen content of the steel samples produced in this study. It can be noted that the steel matrix of the samples is expected to be predominantly austenitic at the austenitising temperature of each sample (Table 2) before quenching. Under an equilibrium condition, the vacuum-sintered sample at an austenitising temperature of 1150°C is expected to possess ferrite (\( \delta \)-Fe), \( \gamma \)-Fe, MX and M₇C₃ phase constituents. Moreover, the nitrogen-sintered samples are all expected to possess \( \gamma \)-Fe, MX and M₇C₃ phase constituents at their selected austenitising temperatures.

![Figure 1](wileyonlinelibrary.com)
3.2 Microstructural examination

The SE-SEM micrographs of the etched samples vacuum-sintered and in nitrogen-containing atmosphere, quenched at a temperature of 1150°C and tempered at a low temperature of 200°C are presented in Figure 2. Owing to the quenching of the samples, the steel matrix in all samples exhibits a primarily martensitic microstructure. In the vacuum-sintered sample, the carbides of type MC and/or $M_xC_{1-x}$ are identified as tiny, light grey, near-spherical particles dispersed in the matrix. However, coarser, near-spherical, dark MX carbonitrides are observed in the samples processed in a nitrogen atmosphere. In all samples, the $M_7C_3$ carbides are clearly identified as light-grey precipitates with eutectic morphology. Besides the apparent MX carbonitrides and the $M_7C_3$ carbides, fine precipitates were also observed to be dispersed in the matrix with a brighter contrast, especially in the nitrogen-sintered samples. Table 3 presents the measured composition of the steel samples densified in a nitrogen-pressurised atmosphere. The global nitrogen content in the samples rises as the partial pressure of nitrogen applied during the densification process increases. These values are slightly lower than those computed at a soaking temperature of 1100°C (Figure 1a) under an equilibrium condition due to degassing and a decrease in nitrogen solubility at the densification temperature of 1280°C. As previously reported, the nitrogen soaking temperature of 1100°C is effective and degassing is minimal at sintering temperature, as the global nitrogen content of these samples was slightly lower than the calculated nitrogen content. Table 4 presents the measured volume percent of the MX carbonitrides and the

![Figure 2: Scanning electron micrograph of the sintered X190 pre-alloyed steel quenched and tempered at 200°C (a) vacuum; (b) N$_2$, 10 kPa; (c) N$_2$, 40 kPa—deep cryogenic treatment; (d) image of the red box in (c); (e) N$_2$, 50 kPa; (f) N$_2$, 80 kPa. [Color figure can be viewed at wileyonlinelibrary.com]]
M7C3 carbides in the densified and heat-treated steel samples over a micrograph area of $2.2 \times 10^5 \, \mu m^2$. Over this micrograph area, the MX precipitates in the vacuum-sintered samples cannot be measured owing to their small sizes, predominantly <1 µm, and by thermodynamic computation, the quantity of the carbonitrides is evaluated to be 0.73 vol%.\(^{19}\) The fraction of the MX carbonitrides increases with increasing nitrogen partial pressure applied during densification process, whereas the volume of the M7C3 carbides remains fairly similar for the nitrogen-processed samples. However, the sample processed in vacuum has the volume fraction of the M7C3 carbides (16.4 ± 1.1 vol%), which is the highest among other samples. Figure 3 depicts the distribution of the MX precipitates size in the nitrogen-processed samples. Besides having different volume percentages of the MX precipitates with an increasing partial pressure, a significant difference in the size distribution is observed.

| Sample          | C     | Cr    | V     | Si    | W     | Mn    | Mo    | Ni    | N    |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|------|
| 10 kPa, N\(^2\) | 1.80  | 18.92 | 4.26  | 0.63  | 0.44  | 0.35  | 0.89  | 0.25  | 0.67 |
| 50 kPa, N\(^2\) | 1.72  | 18.90 | 4.66  | 0.62  | 0.43  | 0.35  | 0.89  | 0.24  | 1.55 |
| 80 kPa, N\(^2\) | 1.73  | 18.54 | 5.14  | 0.62  | 0.42  | 0.34  | 0.88  | 0.23  | 1.92 |

Note: SE ≤ 0.34.

| Phase | Vacuum | 10 kPa, N\(^2\) | 40 kPa, N\(^2\) | 50 kPa, N\(^2\) | 80 kPa, N\(^2\) |
|-------|--------|-----------------|-----------------|-----------------|-----------------|
| M7C3  | 16.4 ± 1.1 | 13.9 ± 0.3      | 13.1 ± 0.3      | 14.1 ± 1.1      | 14.5 ± 0.3      |
| MX    | 3.1 ± 0.2   | 4.6 ± 0.2       | 5.4 ± 0.1       | 6.7 ± 0.1       |

*Not measured.

**FIGURE 3** Size distribution of MX precipitates in the nitrogen-sintered X190 steel (a) 10 kPa, N\(^2\); (b) 40 kPa, N\(^2\); (c) 50 kPa, N\(^2\); (d) 80 kPa, N\(^2\) [Color figure can be viewed at wileyonlinelibrary.com]
pressure of nitrogen gas applied during processing, the frequency of the MX precipitates increases as applied partial pressure of nitrogen employed increases. However, for all the samples, the size distribution of the MX precipitates is right-skewed and precipitates with size $\leq 2.5 \mu m$ are prevalent in all. Moreover, precipitates as large as $15 \mu m$ in size are present in all samples.

The optical micrographs of the X190 steel samples in the heat-treated conditions are depicted in Figure 4. Retained $\gamma$-Fe is predominantly observed in the regions around the M$_7$C$_3$ carbides in the microstructure. This is indicated by the bright contrast regions in the microstructure around the carbides which have not suffered significant attack during etching. The retained austenite is considered to have a blocky morphology as evident in the micrographs. However, the nitrogen-sintered (10 kPa) samples subjected to a high-temperature tempering at 540°C after quenching showed a reduced bright field and hence reduced the presence of retained austenite around the eutectic M$_7$C$_3$ carbides. Fine carbides/carbonitrides are observed in the regions around the M$_7$C$_3$ carbides, as evident in Figure 4d.

### 3.3 | Phase constituents

The XRD patterns of some of the sintered X190 steel samples after heat treatment over a 2$\theta$ range of $35^\circ$–$55^\circ$ are presented in Figure 5. The most prevalent phase is the martensite $\alpha'$-Fe phase with a strong reflection of the

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**Figure 4** Microstructure of the steel samples determined by optical microscopy shows retained austenite (RA) in the region around the carbides in the sample (a) vacuum-sintered, tempered at 200°C; (b) nitrogen-sintered 40 kPa, deep cryogenic treatment (DCT), tempered at 200°C; nitrogen-sintered 10 kPa, tempered at (c) 200°C; (d) 540°C; (e) nitrogen-sintered 50 kPa, tempered at 200°C; (f) nitrogen-sintered 80 kPa, tempered at 200°C [Color figure can be viewed at wileyonlinelibrary.com]
(110) plane observed at 44.5°. A standalone, low-intensity reflection of retained austenite, $\gamma$-Fe(111), is observed at 2$\theta$ position of 43.5°. This reflection, $\gamma$-Fe(111), is distinctly seen in the vacuum-sintered and nitrogen-sintered (10-kPa pressure, tempered at 200°C) samples but becomes part of the broad base of the $\alpha'$-Fe(110) reflection for other samples. For the nitrogen-sintered (10 kPa) sample, tempered at 540°C, the austenite reflection cannot be distinctly observed, as it is obvious for the samples tempered at low temperature (200°C). This indicates that the majority of the retained austenite has been transformed owing to a high-temperature tempering, which corroborates the observations in its optical micrograph in Figure 4d. For all the sintered steel samples, a significant volume of the matrix experienced martensitic transformation and a little amount of $\gamma$-Fe is retained upon quenching from the austenitising temperature. With exception to the vacuum-sintered sample, the presence of vanadium-rich carbonitride, MX, is identified by the (111) reflection observed at 2$\theta$ position of 38° in all the nitrogen-sintered samples. The intensity of this MX reflection increases with increasing nitrogen partial pressure applied during the steel powder densification. This agrees with the increase in the volume of this MX phase, as nitrogen partial pressure increases, in the samples (Table 3). Moreover, the reflections of $M_2C_3$ phase are present and are identified in the diffractograms of all sintered steel samples, as observed in Figure 2. Some weak reflections were also observed for $M_23C_6$ and $M_6C$ carbides in the diffractograms. These reflections are attributed to the fine precipitates observed in the SEM micrographs in Figure 2.

As for the influence of the DCT on the steel matrix transformation, Figure 6 presents the diffractograms of the nitrogen-sintered (40 kPa) sample when quenched in oil and when subjected to DCT. It is observed that after oil quenching from an austenitising temperature of 1150°C, the steel matrix predominantly remains as austenite ($\gamma$-Fe). However, when the same sample was subjected to quenching in liquid nitrogen at $-196^\circ$C, a significant proportion of the matrix is transformed to martensite ($\alpha'$-Fe).

### 3.4 | Hardness

As the quench-hardened steel matrix achieved by the $\gamma$-$\alpha'$ transformation is beneficial for enhanced resistance against surface contact deformation, the measured hardness of the sintered steel is presented in Table 5. For all samples, hardness ranges between 700 and 800 HV10, with exception of the nitrogen-sintered (10 kPa) sample, tempered at 200°C, which has a hardness of 769 ± 4 HV10.
689 ± 2 HV10. However, the nitrogen-sintered (10 kPa) sample, tempered at a higher temperature of 540°C, has the highest hardness of 769 ± 4 HV10. For all samples tempered at a low temperature of 200°C, the higher hardness of the nitrogen-sintered 50 and 80-kPa samples is attributed to reduced retained austenite and increasing MX precipitates, which is substantiated by their XRD patterns (Figure 5) and measured carbonitride volume percent (Table 4). As for the nitrogen-sintered (40 kPa) sample subjected to DCT, it possesses a hardness of 738 ± 4 HV10, which is indicative of a significant transformation of the steel matrix to martensite. However, the hardness of the oil-quenched, nitrogen-sintered (40 kPa) sample was not measured as it is expected to be low, owing to the large portion of the untransformed austenite matrix, as evident in its X-ray diffractogram (Figure 6i).

3.5 Corrosion performance

Table 6 presents the OCP of the sintered specimens subjected to the potentiodynamic polarisation test. The OCPs of the specimens are near zero and indicate that all specimens exhibit a similar surface/electrolyte state after 600 s before the polarisation scan. Figure 7 depicts the current density–potential curves with focus on the breakdown potential for the heat-treated sintered samples densified in different sintering atmospheres. The polarisation curves are representative examples out of three to five measurements for each sample. In the anodic polarisation scan, the oxidation of the samples indicating current flow rises to a steady state. In the steady-state condition, current density remains relatively constant with an increase in applied potential. During the steady state, the samples exhibit passivity against corrosion as a passive film is formed. A pitting potential is reached when the current density begins to rise due to the breakdown of the passive film as the applied potential increases after the steady state. However, there is an exception to the nitrogen-sintered sample (10 kPa), quenched and tempered at 540°C, which does not have a glaring passive region like the other samples. In the passive region of the anodic scan, there are no signs of current density fluctuations, indicative of a stable passive film formed during the test. For comparison sake, the red dotted line indicates a current density of 100 µA/cm² at which the threshold breakdown potential, Eₜₘ, is noted. A higher breakdown potential indicates a better pitting corrosion resistance. Sample F (N₂, 40 Pa) subjected to DCT at 1500°C and tempered at 200°C displayed the best resistance against corrosion by pitting among other samples, followed by the Sample B (N₂, 10 kPa) subjected to quenching at 1100°C and tempered at 200°C. However, Sample C, which is similar to Sample B, except that it was tempered at a higher temperature of 540°C, had the poorest corrosion performance. For samples tempered at a low temperature of 200°C, Sample F sintered under the nitrogen partial pressure (40 kPa) is nobler than the vacuum-processed Sample A and nitrogen-processed Samples B (10 kPa), D (50 kPa) and E (80 kPa).

Table 7 shows the mean threshold breakdown potential for each of the samples measured at 100-µA/cm² current density. The higher the value of the threshold potential, the better is the resistance of the sample to pitting corrosion. For the samples oil-quenched and tempered at a temperature of 200°C, the nitrogen-sintered (10 kPa) sample has the highest breakdown potential of 127 ± 7 mV, whereas the nitrogen-sintered (80 kPa) sample exhibited the lowest breakdown potential of 31 ± 3 mV. It is noteworthy that the nitrogen-sintered (10 kPa) sample is by a factor of 4 better

![FIGURE 7 Polarisation curves indicating the current density of sintered samples with respect to applied potential in an NaCl (1 wt%) electrolyte solution measured at room temperature [Color figure can be viewed at wileyonlinelibrary.com]](image-url)

**TABLE 6** OCP of sintered samples in an NaCl (1 wt%) electrolyte solution after 600 s

| Sample          | Vacuum – 200°C | 10 kPa, N₂ – 200°C | 10 kPa, N₂ – 540°C | 40 kPa, N₂, DCT – 200°C | 50 kPa, N₂ – 200°C | 80 kPa, N₂ – 200°C |
|-----------------|----------------|--------------------|--------------------|-------------------------|-------------------|-------------------|
| OCP (V)         | −0.59          | −0.51              | −0.51              | −0.55                   | −0.49             | −0.59             |

Abbreviations: DCT, deep cryogenic treatment; OCP, open circuit potential.
than the sample processed in a nitrogen atmosphere at 80 kPa. The vacuum-sintered sample had a mean breakdown potential of 117 ± 9 mV, which is lower than that of the nitrogen-processed (10 kPa) sample. However, tempering the nitrogen-sintered (10 kPa) sample at a higher temperature of 540°C resulted in poor resistance to pitting with a breakthrough potential of −97 ± 15 mV. Moreover, the nitrogen-sintered (40 kPa) sample subjected to DCT and tempered at 200°C gave the best overall breakdown potential of 142 ± 11 mV.

Table 7: Threshold breakdown potential of sintered and heat-treated samples at a current density of 100 µA/cm²

| Specimen | $T_{\text{AUS}}$ (°C) for 30 min | Quenching medium | $T_{\text{TEMP}}$ (°C) for 2 h | Breakdown potential, $E_b$ (mV/SCE) at 100 µA/cm² |
|----------|-------------------------------|------------------|-----------------------------|--------------------------------------------------|
| Vacuum   | 1150                          | Oil at 25°C      | 200                         | 117 ± 9                                          |
| 10 kPa, N₂ | 1100                         | Oil at 25°C      | 200                         | 126 ± 7                                          |
| 10 kPa, N₂ | 1100                         | Oil at 25°C      | 540                         | −97 ± 15                                         |
| 40 kPa, N₂ | 1150                         | DCT at −196°C    | 200                         | 142 ± 11                                         |
| 50 kPa, N₂ | 1000                         | Oil at 25°C      | 200                         | 63 ± 8                                           |
| 80 kPa, N₂ | 1000                         | Oil at 25°C      | 200                         | 31 ± 3                                           |

Abbreviation: DCT, deep cryogenic treatment.

Figure 8 depicts the area percent and micrographs of corroded pits on the steel surfaces after the completion of both the forward and the reverse scans of the potentiodynamic polarisation. The experimental fraction of surface pits on each sample was obtained from image processing of four micrographs with an area of 4.31 mm². The surface area fraction of the pits on the samples shown in Figure 8a corroborates their breakdown potentials ($E_b$) (Table 7). The pit area fraction increases with decreasing breakdown potential. For the samples oil-quenched and tempered at a low temperature (200°C), the vacuum-sintered sample had the lowest corroded pit area of 0.25 ± 0.07%, whereas the nitrogen-sintered (80 kPa) had the highest pit area of 0.90 ± 0.14%. Despite the fact that the nitrogen-sintered (10 kPa) sample has a higher breakdown potential than the vacuum-sintered sample, the mean surface pit area fraction is measured to be 0.45 ± 0.05%, which is slightly higher than on the sample processed in vacuum. Considering the sample processed in nitrogen at 10 kPa and subjected to different tempering, the pit area on the sample tempered at 540°C is measured to be 1.12 ± 0.13%, which is 2.5 times higher than the pit area percent measured on the same sample tempered at 200°C. Figure 8b shows the surface of the nitrogen-sintered (10 kPa) sample, tempered at 540°C, after the potentiodynamic polarisation test with evidence of

**Table 7** Threshold breakdown potential of sintered and heat-treated samples at a current density of 100 µA/cm²

| Specimen | $T_{\text{AUS}}$ (°C) for 30 min | Quenching medium | $T_{\text{TEMP}}$ (°C) for 2 h | Breakdown potential, $E_b$ (mV/SCE) at 100 µA/cm² |
|----------|-------------------------------|------------------|-----------------------------|--------------------------------------------------|
| Vacuum   | 1150                          | Oil at 25°C      | 200                         | 117 ± 9                                          |
| 10 kPa, N₂ | 1100                         | Oil at 25°C      | 200                         | 126 ± 7                                          |
| 10 kPa, N₂ | 1100                         | Oil at 25°C      | 540                         | −97 ± 15                                         |
| 40 kPa, N₂ | 1150                         | DCT at −196°C    | 200                         | 142 ± 11                                         |
| 50 kPa, N₂ | 1000                         | Oil at 25°C      | 200                         | 63 ± 8                                           |
| 80 kPa, N₂ | 1000                         | Oil at 25°C      | 200                         | 31 ± 3                                           |

Abbreviation: DCT, deep cryogenic treatment.
corrosion pits. A magnified view of the corrosion pits labelled A and B in Figure 8b shows that the steel matrix is preferentially attacked and dissolved into the electrolyte during the corrosion test, as seen in Figure 8c,d. The M7C3 carbides and the MX carbonitrides are seen to form a part of the edge around the pits.

Figure 9 shows the cross-sections of a typical corrosion pit on the heat-treated steel surfaces after potentiodynamic polarisation experiment. A porous layer is observed at the surface of the vacuum-sintered sample, as evident in Figure 9a,b. This indicates pitting owing to the corrosion attack of the steel matrix having the dispersion of fine MX precipitates. In addition to pitting, dissolution of the subsurface matrix is dominant in the cross-section of the other corroded samples, as observed in Figure 9c–f. More so, a porous structure, similar to that of the vacuum-processed sample (Figure 9b), is also observed in the cross-section of the nitrogen-sintered (10 kPa) sample, tempered at 540°C, as depicted in Figure 9d. The dissolution around the M7C3 carbides is evident in the cross-sections as these carbides bound the pit region and impede further dissolution of the matrix. As the pitting progressed into the matrix, the dissolution of subsurface matrix beneath the dispersed carbides and carbonitrides occurs, which results in the disconnection of these precipitates from the steel matrix. This is evident in the cross-section of the corroded samples as the pit becomes wider at the subsurface region with loose carbides/carbonitrides having no matrix to hold them, as seen in Figure 9e,f. However, the cross-section of the nitrogen-sintered (40 kPa) sample subjected to DCT and tempered at 200°C shows that minimal pitting has occurred during the corrosion test, as seen in Figure 9g,h. Despite minimal surface pitting, the dissolution of the region around the M7C3 carbides at the subsurface region is seldomly observed, as seen in Figure 9h. Hence, the steel matrix is preferentially

**FIGURE 9** Cross-section of a typical corroded pit on the surface of sample: (a) vacuum-sintered; (b) magnified view of the red box in (a); (c) N2-sintered 10 kPa, tempered at 200°C; (d) N2-sintered 10 kPa, tempered at 540°C; (e) N2-sintered 50 kPa, tempered at 200°C; (f) N2-sintered 80 kPa, tempered at 200°C; (g) and (h) N2-sintered 40 kPa, deep cryogenic treatment and tempered at 200°C [Color figure can be viewed at wileyonlinelibrary.com]
dissolved during the corrosion test to form pits and the dissolution severity is linked to the manufacturing process conditions of the samples.

4 DISCUSSION

4.1 Microstructural evolution

The essence of the development of martensitic stainless steels is to produce parts with high strength and strong resistance against the simultaneous degradation actions by surface contact deformation, wear and corrosion loadings. Thus, it is essential to achieve a steel microstructure with quench-hardened martensitic matrix containing a reasonably high content of Cr and other elements (Mo and N) that promote corrosion resistance and the dispersion of reinforcement phases such as carbides and carbonitrides. However, the thermal history and other manufacturing processing conditions affect the desired microstructure and mechanical properties of the parts formed using these martensitic stainless steels. Previous studies have shown that nitrogen soluted in the matrix of stainless steel resulted in an enhancement of its corrosion resistance, especially to pitting corrosion. Hence, the main aim of this study was to evaluate the influence of nitrogen uptake and heat treatment on the corrosion performance of X190 martensitic stainless steel.

On the basis of thermodynamic computations, it was predicted that the nitrogen uptake of the X190 steel increases with increasing nitrogen partial pressure applied (Figure 1a), which is in agreement with the microstructural observations of the densified steel samples (Table 4). The high uptake is strongly dependent on the affinity of vanadium for nitrogen and carbon to form carbonitrides. The volume of the Cr- and V-rich carbonitrides (MX) increases as the nitrogen partial pressure applied during sintering increases. An increase in the frequency of the MX precipitates (size range, 1.5–2.5 μm) is observed with an increasing nitrogen partial pressure applied during sintering (Figure 3). It was predicted that the microstructure of the densified steel sample should comprise majorly austenite matrix, carbides (M7C3 and M23C6) and MX carbonitrides. However, for industrial applications, the as-sintered microstructure is not useful, as the hardness of the densified samples is always very low, hence possessing a low resistance against surface contact deformation loads. This makes heat treatment essential for the austenite matrix of the densified steel samples to be transformed to a hardened martensitic matrix. Upon heat treatment, as specified for each sample (Table 3), the transformation of the matrix to martensitic occurred. As for the heat-treated, vacuum-sintered sample, the microstructure is comprised of martensitic structure and fine MC-type carbides, as observed in a previous study. However, as for the heat-treated, nitrogen-sintered sample, the matrix structure is characterised by martensitic laths, as observed in the SEM micrographs (Figure 2) with eutectic M7C3 carbides, near-spherical MX carbonitrides and fine carbides of M23C6 and M6C types present in the microstructure. However, the full transformation of the austenite matrix to martensite cannot be achieved, as retained austenite was observed in the optical micrographs of the heat-treated samples. The retained austenite was seen as bright halos around the eutectic carbides and carbonitrides (Figure 4). It may be inevitable not to have the retained austenite colony around the carbide precipitates. These regions are locally enriched with elements such as Cr, Mo, C and N, which partitioned from the alloy carbides into the surrounding austenite matrix during solidification after densification and austenitisation. As Cr and Mo possess much lower diffusivities when compared with that of the interstitial elements (C and N), the microsegregated Cr and Mo will not fully homogenise during the duration of austenitisation. The increasing content of these elements lower the martensite start temperature, such that the enriched regions are austenite-stabilised after quenching to room temperature. As a low-temperature tempering at 200°C was adopted to relieve the internal stress in the martensite, the retained austenite colonies remained undecomposed or transformed, as seen in Figure 4a–c,e,f. However, fine precipitates, seen in Figure 4d, are formed during tempering at high temperature (540°C). The formation of the fine precipitates is associated with the consumption of the carbide/carbonitride-forming elements such as Cr, V, Mo, C and N in the retained γ-Fe present in the matrix of the steel samples. More so, there is a possibility of slight element partitioning during the formation of the martensite laths, which results in carbon-enriched regions in between adjacent laths. These carbon-enriched regions remained as austenite and became untransformed after the heat treatment. The presence of the retained austenite is observed in the X-ray diffractograms of all the samples (Figure 5). However, there is a low reflection of the austenite phase while the most prevalent reflection is for the α′-Fe(110), indicating a significant transformation of the matrix to martensite.

It is worth noting that the heat treatment procedure is important to achieve the desired properties of the X190 densified steel. The austenitising temperature, at which the steel sample was treated, determines the degree of the element partitioning from the dispersed carbides and carbonitrides into the matrix. This affects the transformation kinetics of the matrix from austenite to martensite.
The rate of transformation and volume of matrix transformed are dependent on the quenching medium employed to achieve the rapid cooling required. This influenced the matrix transformation of the nitrogen-sintered (40 kPa) sample to martensite after austenitising at 1150°C and quenched in oil. The steel matrix is highly enriched with austenite-stabilising elements at 1150°C, which resulted in a reluctance in the transformation of the matrix to martensite when oil-quenched. This was confirmed by the X-ray diffractogram of the oil-quenched nitrogen-sintered (40 kPa) sample with its matrix predominantly austenitic (Figure 6). However, when this sample (nitrogen-sintered, 40 kPa) was subjected to DCT by quenching in liquid nitrogen at −196°C, the transformation from austenite to martensite became prevalent.

Moreover, the properties of the X190 martensitic stainless steel are dependent on the microstructure achieved in the steel. The microstructure is dependent on the heat treatment procedure deployed. As it is desired to produce steel with high resistance against surface contact deformation and corrosion, it is important to employ a heat treatment that enhances significantly the partitioning of elements Cr and N into the steel. This is expected to enhance the resistance of the steel to corrosion. In addition, a significant transformation of the matrix from austenite to martensite is important and should be simultaneously achieved by the heat treatment employed.

4.2 | Hardness

The ability of the densified X190 martensitic stainless steel to resist surface contact deformation is reliant on the hardness of the steel. To enhance the hardness of the steel, it is necessary to employ the appropriate heat treatment steps. The best appropriate heat treatment, especially the austenitising/quench-hardening temperature, to achieve an enhanced hardness of the steel is dependent on the matrix chemistry. It is desirable to have a significant portion of the steel matrix to be transformed into martensite. The austenite–martensite transformation is determined by the martensite start, $M_s$, temperature and is affected by the steel matrix chemistry (Equation 2). Thus, it is necessary to achieve a matrix chemistry through austenitising that gives a high $M_s$ temperature; otherwise, deep cooling below room temperature may become necessary. With a high $M_s$ temperature, the transformation of the matrix to martensite upon oil quenching starts earlier before ambient room temperature is reached. For samples oil-quenched and tempered at 200°C, the obtained hardness value ranged between 700 and 760 HV10, with exception to the nitrogen-sintered (10 kPa) sample which had a slightly lower mean hardness of 689 HV10. The low hardness of the nitrogen-processed (10 kPa) sample, tempered at 200°C, is attributed to a high fraction of retained austenite ($\gamma$-Fe), which was higher in the nitrogen-processed sample, as observed in the diffractograms of these samples in Figure 5. However, the nitrogen-sintered (10 kPa) sample, tempered at a higher temperature of 540°C, possessed the highest mean hardness of 769 ± 4 HV10. The enhancement in hardness of this sample is attributed to the formation of fine carbides/carbonitrides (Figure 4d) due to the decomposition of the retained austenite after quenching at 1100°C. It is worth noting that oil quenching provides a reasonable degree of rapid cooling to allow martensitic transformation and hardening of the steel matrix, based on their austenitising/quenching temperature.

The $M_s$ temperature was calculated based on the matrix chemistry obtained when different nitrogen partial pressures were applied during processing and different austenitising temperatures employed during heat treatment. With the martensite start ($M_s$) temperature of the samples indicated on the $M_s$ temperature–nitrogen gas pressure curves plotted for different austenitising temperatures (Figure 10), the nitrogen-sintered (40 kPa) sample has the lowest $M_s$ temperature when subjected to austenitising temperature of 1150°C. This indicates that the austenite matrix possesses the highest stability against martensitic transformation owing to the maximum amount of nitrogen dissolved in it. The conventional oil quenching to room temperature is not suitable to achieve a significant amount of the austenite matrix transformed to martensite. Thus, it is necessary for DCT to be employed to achieve a significant austenite–martensite matrix transformation, as depicted in

![Figure 10](wileyonlinelibrary.com)
its X-ray diffractogram (Figure 6). The DCT to temperature below the room temperature is essential for this steel sample owing to its matrix chemical composition.[23] This results in a mean hardness of 738 ± 4 HV10 after it has been subjected to tempering at 200°C.

4.3 Corrosion resistance

The overall corrosion performance of the martensitic stainless steel is dependent on its microstructure achieved through the processing history and the heat treatment. It is known that nitrogen is beneficial to enhance the corrosion performance of stainless steels.[6,9] The X190 martensitic steel powder employed in this study has a significantly high nitrogen uptake capability. It is anticipated that this characteristic can help to improve its pitting corrosion performance. In this study, the nitrogen soluted in the steel powder during the densification process promoted the in situ synthesis of chromium- and vanadium-rich carbonitrides. The volume of carbonitrides increases as the nitrogen partial pressure applied during densification increases (Figure 4). However, it is known that nitrogen soluted in the steel matrix is beneficial rather than having it as carbonitrides in the steel. Thus, this study examines the influence of heat treatment after densification on the corrosion performance of the densified X190 steel.

After the potentiodynamic polarisation test, it is clear that the pitting corrosion resistance of X190 steel is sensitive to the densification atmosphere employed during processing and heat treatment. Nitrogen soluted in the steel during densification led to the formation of the carbonitrides; also, part of this nitrogen soluted in the steel matrix. Owing to computational thermodynamics, it is expected that the carbides, the carbonitrides and the matrix making up the steel microstructure should be in equilibrium with one another in terms of their chemistry. This is achieved by having the densified steel to slowly cool down in the furnace to room temperature. However, with heat treatment, the chemistry of the matrix can be modified by having the partitioning of elements from the carbides and carbonitrides into the steel matrix before rapid cooling by quenching in a medium. It is worth noting that in this study, the aim of the heat treatment was to make the steels possess maximum hardness combined with best corrosion resistance. The enhancement of the resistance of the steel against pitting corrosion is strongly dependent on the content of some essential elements, especially Cr, N and Mo, in the steel matrix. The content of these elements in the matrix can be manipulated by the heat treatment given to the steel samples. By evaluating the PREN of the steel matrix using the content of these elements, the corrosion performance of the steel samples can be appraised. From the corrosion test results, the nitrogen-sintered (40 kPa) steel sample, subjected to austenitising temperature of 1150°C, DCT and tempering at 200°C, possessed the best corrosion performance by having the highest breakdown potential (Table 7). On the basis of thermodynamic computation, the PREN value of the steel matrix was calculated with respect to the nitrogen partial pressure applied during densification and the austenitising temperature during heat treatment, as depicted in Figure 11a. The triangular points in Figure 11a indicate the PREN values of the sintered samples in this study with exception to the maximum point indicated using a small red circle. The maximum PREN value is achieved when nitrogen partial pressure applied is 40 kPa, irrespective of the austenitising temperature employed. The PREN is highest when the austenitising temperature is 1150°C. This corroborates the experimental results, as the nitrogen-sintered (40 kPa) sample, subjected to an austenitising temperature of 1150°C, possessed the highest breakdown potential. The amount of chromium

![Figure 11](https://example.com/figure11.png)

**Figure 11** (a) Curves of pitting resistance equivalent number for the steel at different austenitisation temperatures with respect to the nitrogen gas pressure applied; (b) calculated Cr and N contents of the sintered steel matrix processed under different atmospheres and quenched at different austenitisation temperatures [Color figure can be viewed at wileyonlinelibrary.com]
and nitrogen in the austenite matrix of the densified steel matrix, as calculated, is depicted in Figure 11b. The steel matrix of nitrogen-sintered (40 kPa) sample has a significantly higher amount of nitrogen and chromium content when compared with the matrix of other samples. Nitrogen promotes the stability of the passive film formed by the chromium formed on the surface of the nitrogen-sintered (40 kPa) sample, austenitised at 1150°C, to delay corrosion by pitting during the polarisation test than other samples. This reflects in the cross-section of the corroded samples, as the matrix of the nitrogen-sintered (40 kPa) samples suffered less corrosion attack when compared with other samples (Figure 9).

Increasing austenitising temperature of any of the steel sample significantly leads to an increase in the PREN value as there is an upward shift in the PREN curve, as seen in Figure 11a. Increasing austenitising temperature from 1000°C to 1150°C promotes a greater supersaturation of the passive film-forming elements (Cr, Mo and N) in the steel matrix due to the dissolution of the carbides and carbonitrides before quenching. However, employing a higher tempering temperature is not beneficial to the corrosion performance, as it is reflected in the wide difference in the corrosion performance of the nitrogen-sintered (10 kPa) sample tempered at 200°C and 540°C. Tempering is done either to relieve the internal stresses in the martensite after quenching, which can be brittle and make it tough, or to promote secondary hardening. Thus, tempering the nitrogen-sintered (10 kPa) sample at 540°C promoted secondary hardening, and it is evident as the sample had the highest hardness (Table 5). The formation of fine carbides/carbonitrides from the retained austenite during high-temperature tempering led to the secondary hardening of the steel sample. Thus, the consumption of the passive film-forming elements such as Cr and Mo in the matrix to form fine carbides resulted in a very low resistance to pitting for the nitrogen-sintered (10 kPa) sample, austenitised at 1100°C and tempered at 540°C (Figure 7).

Moreover, the microstructural heterogeneity is a significant factor that affects corrosion performance of the martensitic stainless steel employed in this study. Being a multiphase material system, the possibility of galvanic corrosion is high. Thus, galvanic couples can be formed among the Cr-rich carbides and its Cr-depleted surrounding matrix owing to the electrochemical potential differences. The Cr-rich carbides/carbonitrides act as the cathode, whereas the surrounding matrix serves as the sacrificial anode. Hence, the oxidation of the anodic sites is promoted, leading to the dissolution of the matrix around these precipitates during the polarisation test. The presence of the Cr-rich fine precipitates in the steel matrix is suggested to have resulted in a galvanic couple, which allows the preferential dissolution of the matrix to form the porous structure observed in Figure 9b,d. More so, the matrix region at the precipitate/matrix interfaces is prone to reduced Cr content when compared with the nominal matrix content. This makes the region susceptible to localised pitting corrosion with the pit growing to the subsurface region, as seen in Figure 9. Besides, there is a possibility for the discontinuity, variation in thickness and low stability of the passive layer formed on the surface of the sample due to the heterogeneity of the steel. As the volume of MX precipitates increases with increasing nitrogen partial pressure applied during the densification process (Table 4), the degree of microstructural heterogeneity of the nitrogen-sintered samples increases. The increase in the microstructural heterogeneity contributes to the increase in the area fraction of the corroded pit on the surface of the nitrogen-sintered samples (Figure 8). The nitrogen-sintered (10 kPa) sample, tempered at 540°C, has the highest corroded pit percentage, which is attributed to the lean content of Cr, Mo and N in the matrix and an increase in the microstructural heterogeneity due to the fine carbides.

Hence, the empirical PREN is a reliable guide to rank the produced sintered X190 steel densified in different atmospheres in terms of their resistance to pitting corrosion. However, it does not take into consideration the impact of tempering at different temperatures and microstructural morphology on the resistance to corrosion by pitting. Summarily, the densification of the pre-alloyed steel X190 powder in a nitrogen-pressurised furnace at 40 kPa, austenitised at a higher temperature of 1150°C and subjected to DCT in liquid nitrogen, is helpful to the resistance of the steel against corrosion as well as its contact deformation resistance. Employing a higher austenitising temperature increases the soluted Cr, N and Mo in the steel matrix to enhance its resistance against pit initiation and growth. Most important, a low-temperature tempering is recommended for the steel to relieve the internal stress after rapid quenching in liquid nitrogen without resulting in the formation of fine carbides. These fine carbides increase the microstructural heterogeneity, as they are formed by the consumption of the Cr in the matrix, thus making the matrix less noble when compared with the Cr-rich carbides, which leads to poor pitting corrosion resistance.

5 | CONCLUSION

The influence of the nitrogen uptake during the densification of the pre-alloyed steel X190 powder in a nitrogen-pressurised environment at different partial pressures on its resistance against corrosion by pitting has been successfully explored with the following deductions:
(i) Despite an increase in the degree of microstructural heterogeneity in the nitrogen-sintered (40 kPa) sample, it exhibited a better corrosion performance when compared with the vacuum-sintered sample, quench-hardened at the same austenitising temperature of 1150°C and tempered at 200°C. This clearly shows the positive influence of nitrogen solved in the tool steel matrix on its resistance against pitting corrosion.

(ii) The pitting corrosion resistance of the X190 steel densified in a nitrogen atmosphere is strongly dependent on the chromium, nitrogen and molybdenum soluted in the steel matrix. This is directly dependent on the choice of the austenitising temperature.

(iii) A nitrogen-sintered sample densified under a partial pressure of 40 kPa, austenitised at 1150°C, subjected to DCT in liquid nitrogen (−196°C) and tempered at 200°C had the highest breakdown potential of 142 ± 11 mV/SCE and hardness of 738 ± 4 HV10. The steel matrix of the sample suffers the least corrosion attack.

(iv) Tempering at low temperature is advantageous towards resistance against corrosion by pitting for the nitrogen-processed samples, as sample densified with a low-pressure (10 kPa) nitrogen atmosphere possessed a higher breakdown potential of 126 ± 7 mV/SCE when tempered at 200°C, whereas the same sample tempered at a higher temperature, 540°C, had the lowest potential of −97 ± 15 mV/SCE.

(v) The combination of thermodynamic and empirical calculations is a suitable approach for predicting microstructural characteristics, and it allows the determination of appropriate austenitising temperatures in the context of SLPS.

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CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

AUTHOR CONTRIBUTIONS

Peter K. Farayibi: Conceptualisation; methodology; software; formal analysis; investigation; data curation; writing—original draft; writing—review and editing; visualisation; funding acquisition. Frederic van gen Hassend: Conceptualisation; methodology; software; validation; writing—review and editing. Michael Blüm: Conceptualisation; methodology; software; validation; writing—review and editing. Sebastian Weber: Conceptualisation; methodology; software; validation; writing—review and editing; resources; supervision; funding acquisition; project administration.

PEER REVIEW

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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REFERENCES

[1] P. Niederhofer, S. Huth, W. Theisen, Wear 2015, 332–33, 1059.
[2] H. Hill, S. Weber, S. Siebert, S. Huth, W. Theisen, Metall. Mater. Trans. A 2010, 41A, 686.
[3] P. K. Farayibi, M. Blüm, S. Weber, Mater. Sci. Eng., A 2020, 777, 139053.
[4] S. Giménez, C. Zubizarreta, V. Trabadelo, I. Iturriza, Mater. Sci. Eng., A 2008, 480, 130.
[5] P. K. Farayibi, M. Blüm, W. Theisen, S. Weber, J. Mater. Eng. Perform. 2019, 28, 1833.
[6] M. O. Speidel, Materwiss. Werkstech. 2006, 37, 875.
[7] F. Van gen Hassend, S. Weber, Steel Res. Int. 2019, 91(1900481), 1.
[8] P. K. Farayibi, M. Blüm, S. Weber, J. Heat Treat. Mater. 2020, 75, 48.
[9] H. Leda, J. Mater. Proc. Technol. 1995, 53, 263.
[10] J. L. Li, C. T. Qu, S. D. Zhu, L. Liu, Z. Q. Gao, Anti-Corros. Methods Mater. 2014, 61, 387.
[11] M. Seifert, D. Wieskämper, T. Tonfeld, S. Huth, Mater. Corros. 2015, 66, 1290.
[12] I. Taji, M. H. Moayed, M. Mirjalili, Corros. Sci. 2015, 92, 301.
[13] H. Yoon, H.-Y. Ha, T.-H. Lee, S.-D. Kim, J. H. Jang, J. Moon, N. Kang, Metals 2019, 9, 930.
[14] M. C. Bignozzi, L. Calcinelli, M. Carati, L. Ceschini, C. Chiavari, G. Masi, A. Morri, Met. Mater. Int. 2019, 26, 1318.
[15] G. Petzow, Metallographisches, Keramographisches, Plastographisches Ätzen, 6, Überarbeitete, Gerbrüder Borntraeger, Stuttgart, Germany 1994, p. 239.
[16] P. J. Uggowitzer, R. Magdowski, M. O. Speidel, La Metallurgia Italiana 1994, 86, 347.
[17] K. Ishida, J. Alloys Compd. 1995, 220, 126.
[18] ASTM G150-9, Standard Test Method for Electrochemical Critical Pitting Temperature Testing of Stainless Steels, ASTM International Standard Organisation, West Conshohocken, PA 2014.
[19] P. K. Farayibi, M. Blüm, S. Weber, Metall. Mater. Trans. A 2020, 51, 5818.
[20] T. N. Baker, Mater. Sci. Technol. 2009, 25, 1083.
[21] I. I. Gorbachev, V. V. Popov, A. Y. Pasynkov, Phys. Met. Metallogr. 2014, 115, 69.
[22] G. Roberts, G. Krauss, R. Kennedy, Tool Steels, 5th ed., ASM International, Materials Park, OH 2000.
[23] B. Podgornik, I. Paulin, B. Zajec, S. Jacobson, V. Leskovsek, *J. Mater. Proc. Technol.* **2016**, *229*, 398.

[24] T. E. Abioye, P. K. Farayibi, D. G. McCartney, A. T. Clare, *J. Mater. Proc. Technol.* **2016**, *231*, 89.

[25] M. V. Boniardi, A. Casaroli, *Stainless Steels*, Gruppo Lucefin Research and Development, Dipartimento Di Meccanica, Politecnico Di Milano, Milano, Italy **2014**.

[26] S. Peissl, G. Mori, H. Leitner, R. Ebner, S. Eglsäer, *Mater. Corros.* **2006**, *57*, 759.

[27] A. F. Candelaria, C. E. Pinedo, *J. Mater. Sci. Lett.* **2003**, *22*, 1151.

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