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Phase Transformation, Mechanical Properties and Corrosion Behaviour of 304L Austenitic Stainless Steel Rolled at Room and Cryo Temperatures

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ABSTRACT

The present work investigates the effect of rolling (90% thickness reduction) on phase transformation, mechanical properties, and corrosion behaviour of 304L-austenitic stainless steel through cryorolling and room temperature rolling. The processed steel sheets were characterised through X-ray diffraction (XRD), electron backscattered diffraction (EBSD), and vibrating sample magnetometer (VSM). The analysis of XRD patterns, EBSD scan, and vibrating sample magnetometer results confirmed the transformation of the austenitic phase to the martensitic phase during rolling. Cryorolling resulted in improved tensile strength and microhardness of 1808 MPa and 538 VHN, respectively, as compared to 1566 MPa and 504 VHN for room temperature rolling. The enhancement in properties of cryorolled steel is attributed to its higher dislocation density compared to room temperature rolled steel. The corrosion behaviour was assessed via linear polarisation corrosion tests. Corrosion resistance was found to decrease with increasing rolling reduction in both room temperature rolled and cryorolled specimens.

Keywords: Cryorolling; Room temperature rolling; 304L austenitic stainless steel; Phase transformation; Mechanical properties; Corrosion behaviour

1. INTRODUCTION

Austenitic stainless steels (ASS) are a significant stainless steel family that finds a wide range of applications in varied industrial sectors such as oil and gas, chemical, petrochemical, nuclear, biomedical, transportation, and many more[1,2]. Wide applications of these steels are mainly attributed to their outstanding resistance to oxidation (corrosion) and superior malleability. However, ASS owes moderate strength, resulting in limited technological applications range because of the soft austenite phase (γ) presence, having face-centered cubic (FCC) structure[2,3]. Continuous efforts have been made to improve the strength of these steels. Improved strength in this class of stainless steels can be achieved by altering in grain size (grain refinement), work hardening, and solid solution strengthening[4,5]. Room temperature rolling can lead to the strengthening of the material; however, concurrent dynamic recovery phenomenon during rolling, resulting in the loss of strength[4,6]. To circumvent the dynamic recovery phenomenon, cryogenic rolling (i.e., rolling under sub-zero temperature) is done, during which the dislocations generated are retained up to room temperature that contributes to the necessary strengthening of the material[7].

The effect of cryorolling specifically on ferrous alloy systems has not been investigated much. Singh[6], *et al.* studied the impact of cryogenic rolling on 304 austenitic steel and reported an increase in deformation-induced martensite transformation with increasing cryo deformation. After 90% deformation, the hardness value increased to twice its counterpart with ultimate tensile strength (UTS) of 1956 MPa. Roy[8], *et al.* reported the evolution of martensite (the result of deformation) and improved mechanical properties of the 304L steel when processed at -153 °C. Mallick[9], *et al.* reported the effect of rolling temperatures (0 and -196 °C) on microstructure and mechanical properties in deformed austenitic steel (40% reduction in thickness). A higher value of strength is reported at relatively lower deformation for cryo-deformed specimens, as the amount of strain-induced martensite is higher when compared to deformation at 0 °C. Steels subjected to deformation are eventually more resistant to oxidation/corrosion under a corrosive atmosphere as compared to the annealed specimens[2]. Tanhaei[2], *et al.* too studied the impact of cold rolling on 316L steel and reported an increased rate of corrosion with increasing deformation. Shukla[10], *et al.* studied the effect of cold working over AISI 202 steel in NaCl solution (3.5% concentration) and reported cold working resulted in increased dislocation density in the steel, which resulted in decreased film resistance and a consequent decrease in corrosion resistance of cold-worked steel. Tandon[11], *et al.* reported the influence of martensite content and dislocation density over the passivating film in an acidic medium of cold-worked 316L austenitic steel. Tandon[12], *et al.* studied the influence of cold working on the electrochemical behaviour of 316L steel and illustrated that with increased cold working,

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the corrosion rate decreases, which can be ascribed to martensitic transformation and increased dislocations density during cold deformation of the material. Kurc[13], *et al.,* and Monrrabal[14], *et al.* reported the influence of cold rolling over 304 austenitic steel and reported, with increasing deformation, corrosion potential value decreases resulting in rapid corrosion of steel. In this present research study, an effort has been made to investigate the effect of rolling temperature (room temperature and cryo-condition) on mechanical behaviour, the transformation of austenitic phase, and corrosion behaviour of 304L austenitic steel.

2. EXPERIMENTAL METHODOLOGY

In this study, commercially available 304L austenitic stainless steel (elemental composition as listed in Table 1) has been used for carrying out the research. Specimens of 50 mm × 25 mm × 3 mm were sectioned and rolled at both room temperature and cryo conditions up to 90% reduction in the thickness. To attain cryo-temperature conditions, specimens were kept in a vessel containing liquid nitrogen for 20-30 minutes before each rolling pass. XRD and VSM studies were performed to investigate phase transformation after room temperature rolled (RTR) and cryo (CR) specimens. XRD studies were conducted using a Rigaku Smartlab diffractometer. EBSD measurements were conducted on small coupons of 10 mm × 10 mm using FEI-Nova Nano SEM equipped with an EBSD detector. The EBSD data was analysed using TSL OIM software.

To investigate the effect of rolling temperature on mechanical properties, tensile tests and hardness tests were performed. Tensile specimens were fabricated according to the ASTM E8 standard. Tensile tests were performed at room temperature using a BISS tensile testing machine with a constant crosshead movement of 0.05 mm/min. For each condition, five tests were conducted. UHL-VMHT microhardness tester was used to record Vickers hardness values at room temperature, using a load of 500 g and dwell time of 15 seconds. Hardness measurements were taken at evenly spaced intervals along a straight line over the surface. Corrosion behaviour of RTR and CR steel specimens was investigated via polarisation tests using the AUTOLAB potentiostat-galvanostat. NOVA software was used to analyse the results of the corrosion tests.

Table 1. Chemical composition of ASS-304L (Weight %) used in the study

Elements	C	Cr	Ni	Mo	Mn	Si	P	S	Fe
Content (wt.%)	0.03	18.22	8.09	0.14	1.70	0.19	0.035	0.007	Bal

The electrochemical cell (three-electrode system) of volume 250 ml designed for flat samples with an exposed area of 1 cm^2 was used to conduct all corrosion tests at room temperature. Also, Ag/AgCl reference electrode, platinum mesh as a counter electrode, processed steel (with varied thickness reductions) as working electrode, and 3.5% NaCl solution as an electrolyte were used to perform the corrosion tests. Before measurements, samples were kept in the test solution for 1 h to obtain stabilised open circuit potential (OCP) value.

3. RESULTS AND DISCUSSION

3.1 Phase Analysis

XRD patterns of ASS 304L samples subjected to room temperature rolling and cryorolling for thickness reduction of 30, 50, 70, and 90% are shown in Figs. 1(a) and 1(b). The undeformed steel (0% RTR and CR) samples show a predominantly austenite phase. The small intensity of BCC-ferrite was also observed. Peaks of α'-martensite phase (deformation-induced martensite) appear after rolling at room temperature and cryo-temperature. The intensity of the austenite phase starts disappearing and martensitic peaks emerge, indicating the transformation of the martensitic phase with increasing rolling reduction. Though both rolling conditions resulted in phase transformation, however, RTR seems to result in less amount of deformation-induced martensite, which can be seen from the intensities of the martensitic phase α' at (110), (200), and (211). Comparing XRD results of 30% RTR and 30% CR condition, 30% CR steel sample shows more increase in the intensities of α' phase. On further cryorolling, the intensity of α' phase increases, such that beyond 50% reduction in CR specimens only α' phases is present.

XRD results of the RTR and CR steel show the presence of both austenitic and martensitic phases. The extent of transformation is dependent on the amount of strain developed during processing and martensitic transformation can be identified using magnetisation curves. The austenite phase is

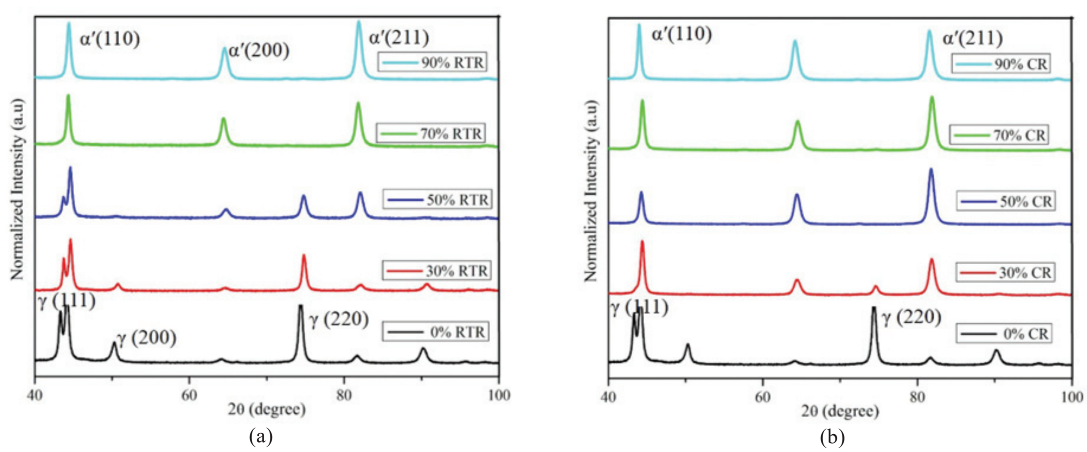


Figure 1. XRD patterns of 304L austenitic steel after (a) RTR and (b) CR

non-magnetic at ambient conditions, i.e., it shows nearly zero saturation magnetisation, while on the contrary α′-martensite is ferromagnetic[2,6]. VSM study was performed, to detect α′-martensite presence in the austenitic matrix. The values of saturation magnetisation from VSM characterisation were used to determine α′-martensite volume fraction. Figures 2(a) and 2(b) show the change in saturation magnetisation, the volume fraction of austenite and α′-martensite as a function of % rolling reduction for RTR and CR specimens, respectively. α′-martensite volume fractions obtained using saturation magnetisation shows a monotonic increase, while for cryorolled specimens, an upsurge in the increase is observed, indicating a higher extent of α′-martensite transformation (Fig. 2(b)).

Strain-induced phase transformation is an important feature of large strain deformation. Austenite is metastable, working at room temperature and subzero conditions result in the appearance of strain-induced martensite[15]. Regions of deformation-induced martensite are areas of large strain gradients such as vicinities of grain boundaries and micro shear bands. Figure 3 shows the inverse pole figure (IPF) map of the undeformed steel. The EBSD images shown in Figs. 4 and 5 represent the IPF map and the phase map of the RTR and CR steel , respectively. Both room temperature rolling and cryorolling resulted in the transformation of parent austenite (red) to deformation-induced or strain-induced α’-martensite (green) as visible in Figs. 4(b) and 4(d), as well in Figs. 5(b) and 5(d). The fraction of austenite and α’-martensite obtained from phase maps are found to be 0.987 and 0.013, respectively

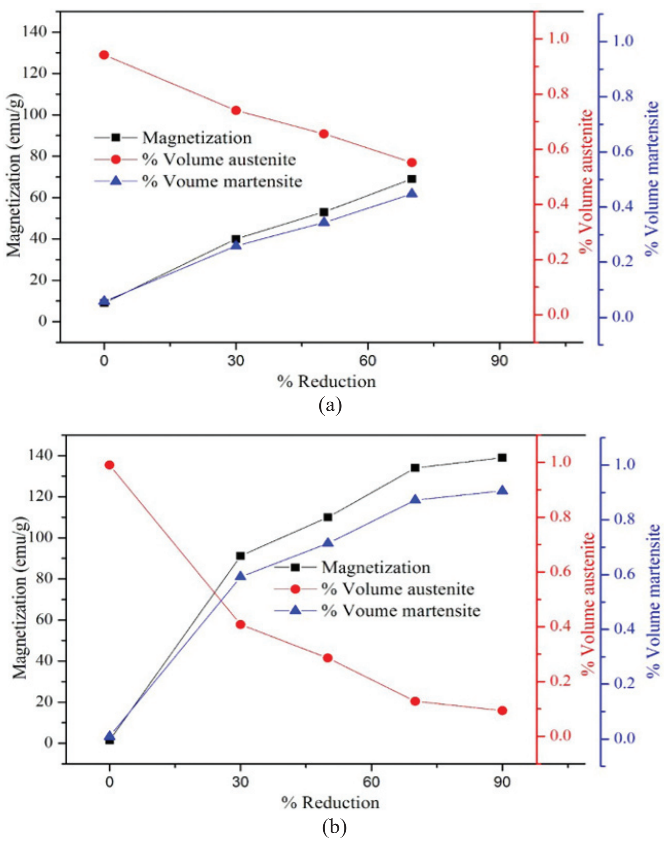


Figure 2. VSM analysis showing saturation magnetisation, austenite fraction, and martensite fraction after RTR (a), and CR (b) of 304L austenitic steel.

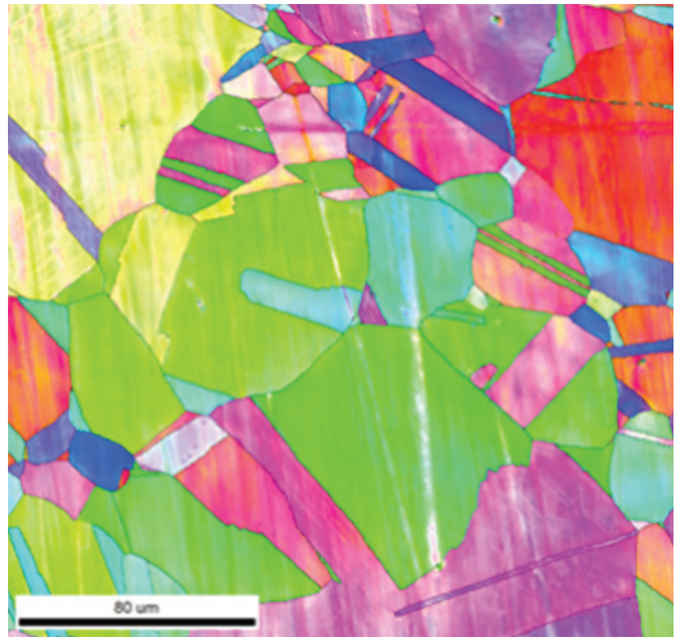


Figure 3. EBSD micrographs of undeformed 304L austenitic steel.

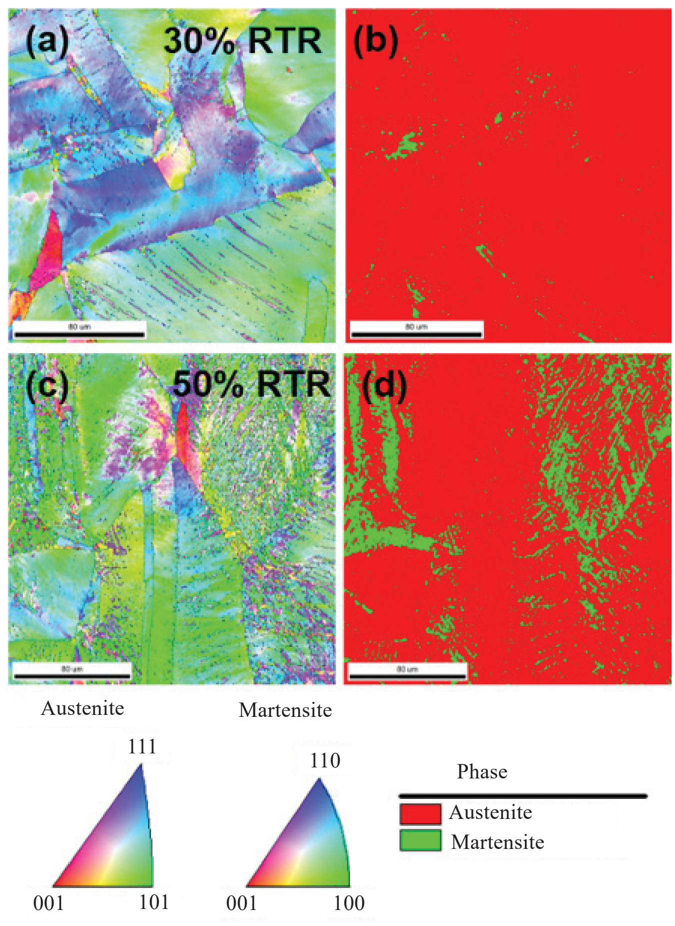


Figure 4. The IPF of RTRed 304L austenitic stainless after 30% deformation (a), after 50% deformation (c); and corresponding phase maps of aforementioned are represented in (b) and (d).

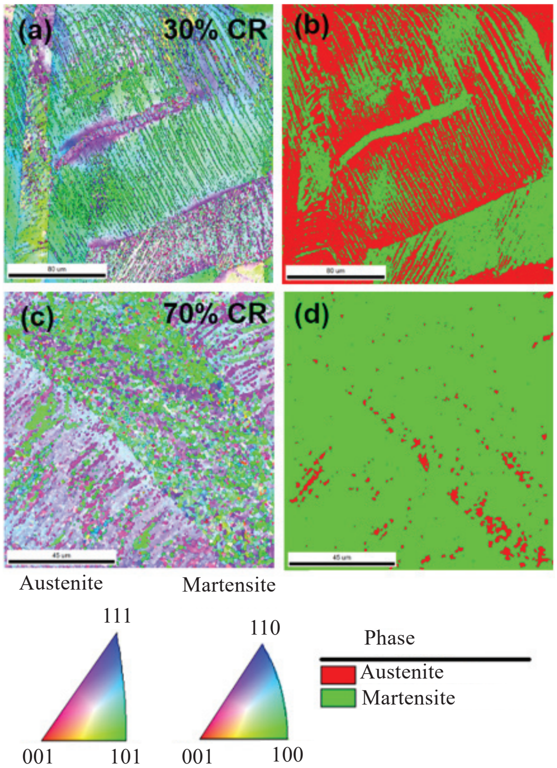
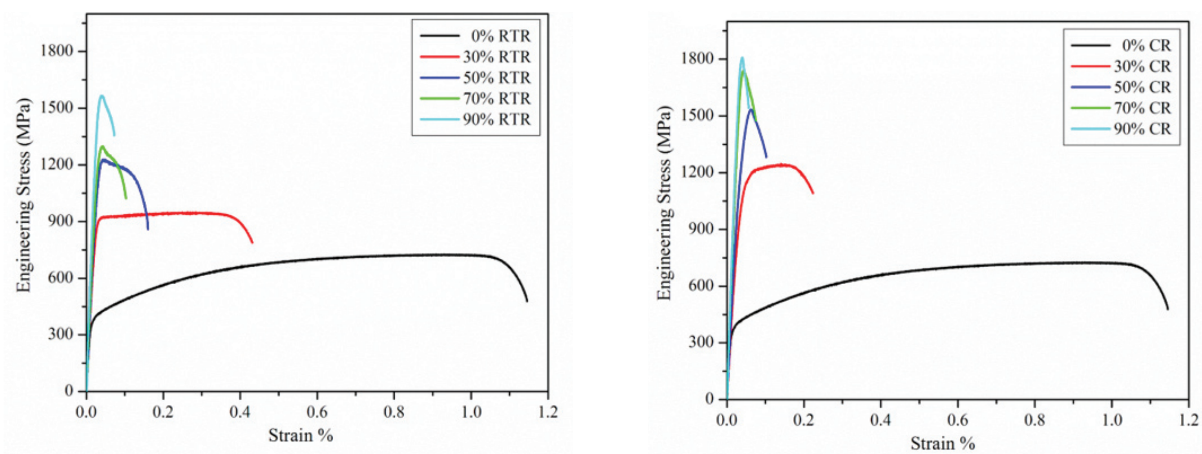


Figure 5. The IPF of cryorolled 304L austenitic stainless after 30% deformation (a), after 70% deformation (c); and corresponding phase maps of aforementioned are represented in (b) and (d).

for 30% RTR; 0.836 and 0.164, respectively for 50% RTR. Similarly, for CR samples, the fractions of α'-martensite and austenite for 30% CR are found to be 0.583 and 0.417, respectively; and for 70% CR, 0.960 and 0.040, respectively. Figure 3 shows an IPF map of undeformed steel which reveals the presence of course grain structure. With rolling (RTR & CR) formation of subgrains within the grains can be noticed. Figures 4(a) and 4(c) as well Figs. 5(a) and 5(c) show the formation of subgrains represented by the gradient of colour within the grain. The EBSD results affirm α'-martensite fraction increased with an increase in the rolling reduction both at room temperature and cryo temperature. Similar results have been reported by other studies as well[9]. Cryorolled steel shows higher values compared to room temperature rolled steel specimens. Phase maps give clear information on phase transformation.

3.2 Mechanical Property Assessment

Figures 6(a) and 6(b) show the engineering stress-strain curve of RTR and CR steels, respectively. The mechanical properties have been tabulated in Table 2. Rolling at room temperature as well as rolling at cryo temperature conditions enhanced the ultimate tensile strength (UTS). The UTS of undeformed steel (i.e., 0% RTR) is improved from 726 MPa to 1566 MPa (approx. 115% increase) after a 90% rolling reduction. Similarly, for cryorolling, UTS is enhanced from 726 MPa to 1808 MPa (approx. 149% increase) after a 90% rolling reduction. However, ductility loss is noticed in both the RTR and CR steels. The average hardness value is also shown



(a) (b)

Figure 6. Engineering stress-strain plots of 304L austenitic steel after (a) RTR and (b) CR for different rolling reductions.

Table 2. Mechanical properties obtained from the tensile and hardness tests for RTR and CR specimens for different rolling reductions

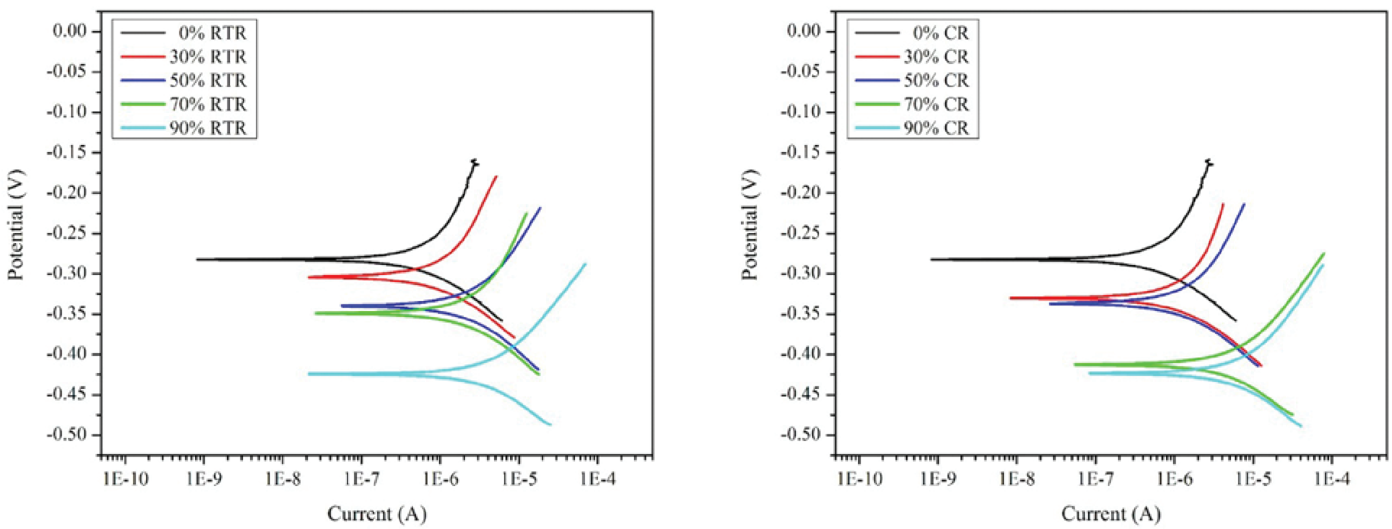
Percentage rolling reduction	Room temperature		Cryogenic temperature	
	Ultimate tensile strength (MPa)	Microhardness (VHN)	Ultimate tensile strength (MPa)	Microhardness (VHN)
0	726	244	726	244
30	949	350	1246	438
50	1229	421	1534	488
70	1299	432	1736	499
90	1566	504	1808	538

in Table 2 for the undeformed steel (0% RTR & 0% CR) and the RTR and CR steels for different rolling reduction. It shows an increase in the hardness values with an increase in rolling reduction. The hardness value measured was found to increase from 244 VHN to 504 VHN (gross increase 106%) after a 90% rolling reduction at room temperature. Similarly, an increase of 120 % in hardness value is observed for 90% CR specimen. The hardness values have increased from 244 VHN to 538 VHN. Remarkable improvement in values of both UTS and hardness are noticed in the initial stage rolling reduction i.e., 30% for RTR and CR condition; however, the rate of increase in strength and hardness decreased with further increase in rolling reduction.

Improvement in tensile and hardness values for cryorolled steel specimens is primarily because of suppression of dynamic recovery increasing dislocation density; however, higher dynamic recovery in RTR specimens resulted in relatively lower values of hardness and tensile strength as compared to CR specimens. The other factor responsible for the enhancement in UTS and hardness values is the evolution of strain-induced martensite phase and material strain hardening during cryorolling. In general, during cryorolling hardness increases as deformation progresses and this increment in hardness values is quite prominent in the initial deformation (30%). The increase in hardness is progressive with deformation but the rate of increase decreases with further increase in deformation.

3.3 Corrosion Behaviour

Figure 7 shows the linear polarisation plots of room temperature rolled and cryorolled samples in the 3.5% NaCl solution. Results from the analysis of polarisation plots (corrosion parameters) are listed in Table 3. According to obtained results, I_{corr} (corrosion current) increases sharply from 1.24 µA for 0% RTR to 5.63 for the 90% RTR. In contrast, R_p (polarisation resistance) decreases from 27.88 Ω (0% RTR) to 4.18 Ω (90% RTR). Similarly, for cryorolled condition, the I_{corr} value increased from 1.24 µA to 10.6 µA, and the R_p values decreased from 27.88 Ω to 2.6 Ω. The corrosion rate was found to increase for both the RTR and CR steel specimens. The corrosion rate was found to be relatively higher for CR steel specimens.



(a) (b)

Figure 7. Linear polarisation curves of 304L steel rolled at different temperature condition: (a) room temperature and (b) cryo-temperature.

Table 3. Corrosion parameters obtained from linear polarisation curves for RTR and CR specimens at various percentage thickness reduction

Specimen condition	OCP	E_{corr} (mV)	β_a (mV/dec)	β_c (mV/dec)	I_{corr} (µA)	Corrosion rate (mm/Yr)	Polarisation resistance (Ω)
0% RTR	-0.259	-282.31	105.42	327.73	1.2423	0.014435	27.885
30% RTR	-0.294	-307.08	178.74	229.30	2.5053	0.029111	17.41
50% RTR	-0.319	-339.88	121.52	184.20	4.0362	0.0469	7.87
70% RTR	-0.326	-348.77	119.43	264.61	4.3636	0.050705	8.19
90% RTR	-0.388	-424.26	100.35	118.45	5.6324	0.065488	4.188
30% CR	-0.315	-330.22	106.92	408.06	2.289	0.026598	16.075
50% CR	-0.315	-336.68	110.46	238.02	2.3893	0.027764	13.714
70% CR	-0.376	-412.42	99.612	119.03	7.1043	0.082552	3.3151
90% CR	-0.391	-423.35	113.46	156.81	10.618	0.12338	2.69

The presence of lattice defects like dislocations and low angle grain boundaries results in a decrease in corrosion resistance. The atoms near the defect regions tend to have higher surface energy and prone to corrosion because of their less stable crystalline domain. With the increase in density of lattice defects, the corrosion rate increases because of the increase in the concentration of reactive spots. The corrosion rate is also proportional to the amount of α′-martensite phase formed, which, in turn, is directly proportional to the degree of deformation. Several studies[12-16] have reported a similar behaviour when the austenitic steels are subjected to cold rolling.

4. CONCLUSIONS

In the present study, room temperature rolling and cryorolling has been carried out on 304L austenitic steel for various thickness reduction. Both rolling methods resulted in improved strength and hardness. Ultimate tensile strength increased by 115% for room temperature rolled specimen and 149% for cryorolled specimen after 90% thickness reduction. Whereas the hardness values showed an increase of 106% and 120% after 90% rolling reduction at room temperature and cryo temperature, respectively. Austenite to martensite transformation was observed with an increase in the rolling reduction for RTR and CR specimens. However, CR specimens showed a relatively higher extent of martensitic transformation as confirmed through XRD, EBSD, and VSM measurements. Both room temperature rolling and cryorolling resulted in decreased resistance to corrosion.

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He helped in the interpretation of EBSD results, reviewed the work, helped in drafting the manuscript, and provided suggestions to improve quality of work.

Mr Biraj Sahoo is working as a Scientist in Materials Science and Technology Division, CSIR-National Metallurgical Laboratory, Jamshedpur.
He contributed to conducting EBSD characterisation and its analysis.

Dr Sandip Ghosh Chowdhury is working as Chief Scientist and Head in Material Science and Technology Division, CSIR-National Metallurgical Laboratory, Jamshedpur, India.
He contributed to providing the facility of EBSD characterisation, along with valuable suggestions in the current study.

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The research work has been deemed possible owing to his valuable comments and supervision.