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Effect of deformation and sensitization on corrosion behavior of 304LN and 316 LN austenitic stainless steel

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Abstract

The present work was concerned with the effect of sensitization and deformation on the corrosion behavior of 304LN and 316LN austenitic stainless steel before and after hot rolling. Specimens were subjected to mechanical deformation and heat treated at 650°C for 5hrs, 6.5 hrs and 8 hrs. Detailed micro-structural analysis using optical metallurgical microscope and hardness testing by Vicker's hardness tester were carried out to investigate the hardness of the specimens. X-ray Diffraction (XRD) was used to explain the phenomena qualitatively. The electrochemical technique such as the potentio-dynamic cyclic polarization measurement was performed to investigate and analyze pitting and protection corrosion resistance properties and also double loop electrochemical potentio-kinetic reactivation measurement technique was also performed for detecting degree of sensitization.

Key words: Sensitization, Deformation, Austenitic stainless steels, Corrosion resistance.

1. Introduction

Austenitic stainless steels have wide applications especially in chemical, petrochemical and nuclear industries due to superior mechanical, fabrication and chemical properties (Dayal et al., 2005). These iron-based alloys contain a high level of chromium which forms protective oxide film on the surface hence resisting corrosion. The oxide film regenerates when damaged, making the steel 'stainless'. However, carbide precipitation due to heat treatment can cause the occurrence of chromium-depleted zones at the boundaries, leading to a phenomenon known as sensitization, in which the depleted zones become the focus of the intense corrosion.

The microstructure of austenitic stainless steel is predominantly austenitic γ phase. It has low stacking fault energy (SFE) which plays an important role to control the formation of shear bands which is an important criterion for the formation of nucleation sites of the α martensite phase. Change in chemical composition and working temperature will change the stacking fault (Talonen and Hänninen, 2007; Kurc et al., 2010).

Austenitic grades are those alloys which are commonly in use for stainless applications. The most common austenitic alloys are iron chromium- nickel steels and are widely known as the 300 series. The austenitic stainless steels, because of their high chromium and nickel content, are the most corrosion resistant of the stainless group providing unusually fine mechanical properties. The austenitic stainless steels become more susceptible to sensitization in the temperature range from 425 to

850^{O}C. It is usually attributed to the precipitation of chromium rich carbides (Fe, $Cr)_{23}C_6$ at the grain boundaries. If the chromium content near grain boundaries drops under the passivity limit (12 wt%), making the material susceptible to inter-granular corrosion (Parvathavartini and Dayal, 2002; Trillo and Murr, 1999). In that condition, tendency of inter-granular corrosion (IGC) and inter-granular stress corrosion cracking (IGSCC) increases rapidly and can cause premature failure. So sensitization temperature is a very important consideration for isothermal heat treatment, hot working processes and heat treatments in the heat affected zones of welds (Nishimura R., Maeda, 2003; Wasnik et al., 2002).

Although austenitic stainless steel is highly resistant against general corrosion like rusting, but they are not liable for chloride containing environments because they suffers local corrosive attacks like stress corrosion cracking and pitting corrosion (Lu et al., 2005; Ningshen and Mudali, 2010).

To reduce inter-granular corrosion, many attempts were made like prevention of precipitation of Cr-carbides and Cr-carbonitrides along the grain boundaries (Kim et al., 2011). By decreasing the C and N content and alloying with Ti and Nb, inter-granular corrosion can also be controlled. This happens due to the higher affinity of Ti and Nb for C than Cr and therefore formation of titanium carbides and niobium carbides forms instead of chromium carbides (Kim et al., 2010). As a result, sufficient amount of Cr will be in the solution for corrosion resistance.

2. Experimental

The 304LN and 316LN stainless steels were obtained in the form of bars and details(dimensions, approximate weight; and chemical compositions) are shown in the table 1 and table 2 respectively. The samples were 20% hot rolled and testing and observations were done.

The XRD analysis was done to determine the phases present before and after deformation and sensitization. Standard polished samples were subjected to XRD analysis. Cu Kα (0.154056 nm) radiation at 40 kV and 30 mA at 2^{0}/min was used for X-ray diffraction using Rigaku X-ray Diffractometer, in the 2θrange of 0º to 80º.

After polishing, the samples were etched with 10% HNO_3 + 30% HCl + 60% distilled water solution. To etch these samples, they were washed in acetone and plunged into the etching solution, agitated vigorously for 2-3 minutes. The specimens were then very quickly transferred to running water, in order to wash away the etchant as rapidly as possible. They were then examined with naked eye, to see what extent etching has taken place. The effectively etched surface became dull. After this, the specimens were observed under optical microscope (LEICA 2700 M) for metallographic examination.

All the samples were mirror polished and cleaned ultrasonically to remove any dust or dart prior to corrosion testing. Potentio-dynamic polarization was carried out using three electrode systems. Graphite was taken as an auxiliary electrode, and calomel electrode was taken as reference. Gamrypotentiostat 600 TM instrument was used for corrosion test and the curves were analyzed by Echem Analyst software.

Hardness tests were done Vicker Hardness test methods by using LEICA LM 248 SAT hardness tester.

Table 1:Sample dimensions and approximate weight.

Sl. No.	Sample	Length (mm)	Breadth (mm)	Thickness (mm)	Approx. Wt. (Kg)
1	304 LN	215.0	172.0	28.0	8.3
2	316 LN	242.5	147.5	31.0	8.9

Table 2 (a, b & c) :Chemical Composition of the steel samples (wt %).

Sl. No.	Sample	Cr	Ni	Mo
1	304 LN	19	Nil	Nil
2	316 LN	17	2.0	2.0

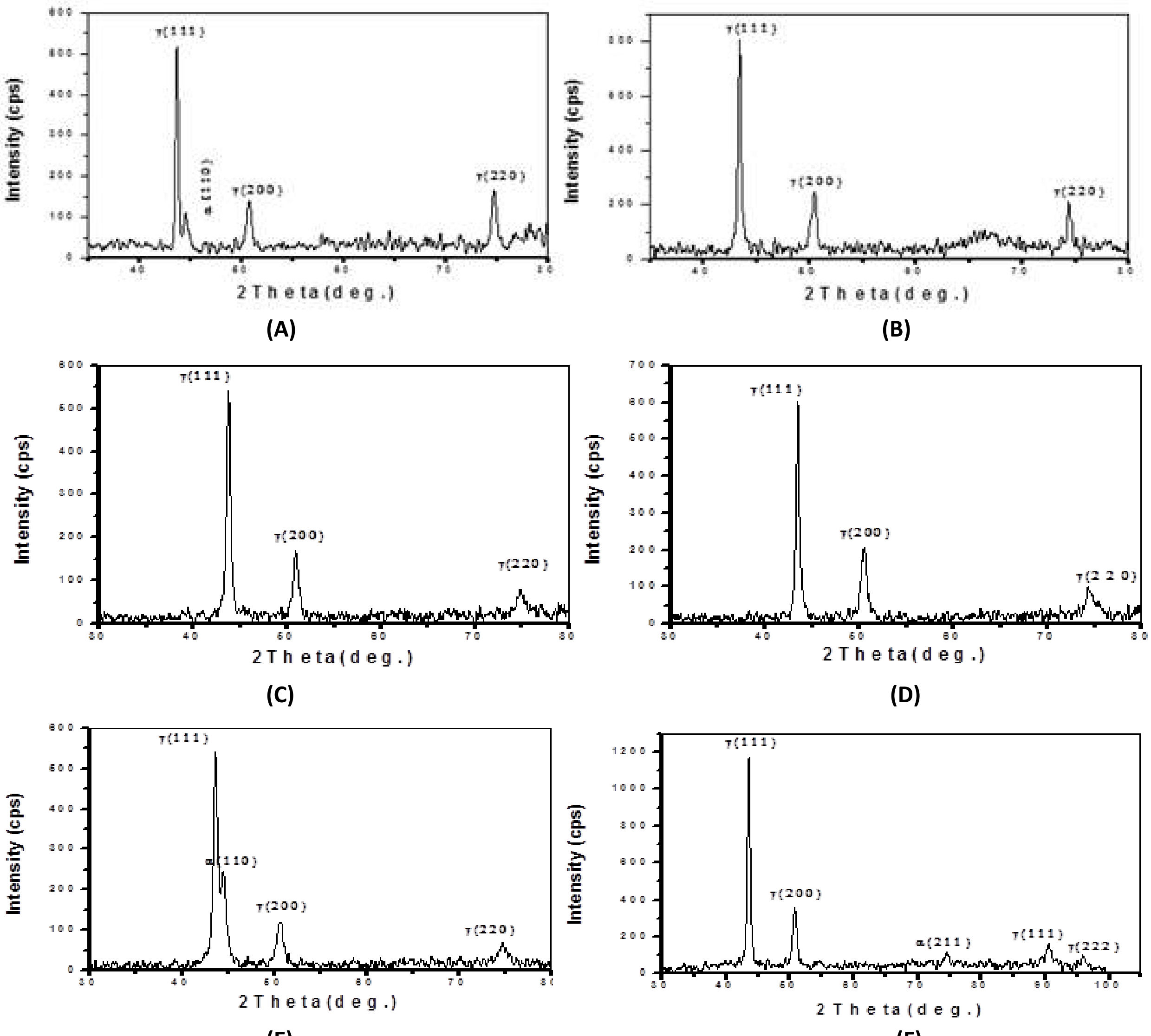
Sl. No.	Sample	Mn	C	N
1	304 LN	2.0	0.04	0.08
2	316 LN	1.8	0.02	0.10

Sl. No.	Sample	Si	P	S	Iron
1	304 LN	0.75	0.045	0.03	Balance
2	316 LN	1.0	0.03	0.03	Balance

3. Result and Discussion

3.1 X-ray diffractions:

X-ray diffractions were carried out for as received as well as worm worked sensitized specimens. As received specimens of 304LN shows mixture of α ferrite and γ austenite where as 316 LN specimens shows pure γ phase.



(A) **(B)** **(C)** **(D)** **(E)** **(F)**

Figure 1: (A) 304 LN (0.08%N_2) sample without any heat treatment
(B) 316 LN (0.1%N_2) sample without any heat treatment
(C) Warm worked 304 LN (0.08%N_2) sample (Sensitized at 650°C for 5 Hrs)
(D) Warm worked 316 LN (0.1%N_2) sample (Sensitized at 650°C for 5 Hrs)
(E) Warm worked 304 LN (0.08%N_2) sample (Sensitized at 650°C for 6.5 Hrs)
(F) Warm worked 316 LN (0.1%N_2) sample (Sensitized at 650°C for 6.5 Hrs)

3.2 Optical Microscopy:

Optical microscopy revealed that there is significant change in microstructure due to 20% hot rolling and heat treatments. Due to straining and heat treatments, chromium and carbon combines and deposited along grain boundaries. Formation of chromium carbide particles in the grain boundariesdepletes the chromium in the solid solution and reduces corrosion resistance of austenitic steel. As a result preferential chemical attack occursalong the grain boundaries.

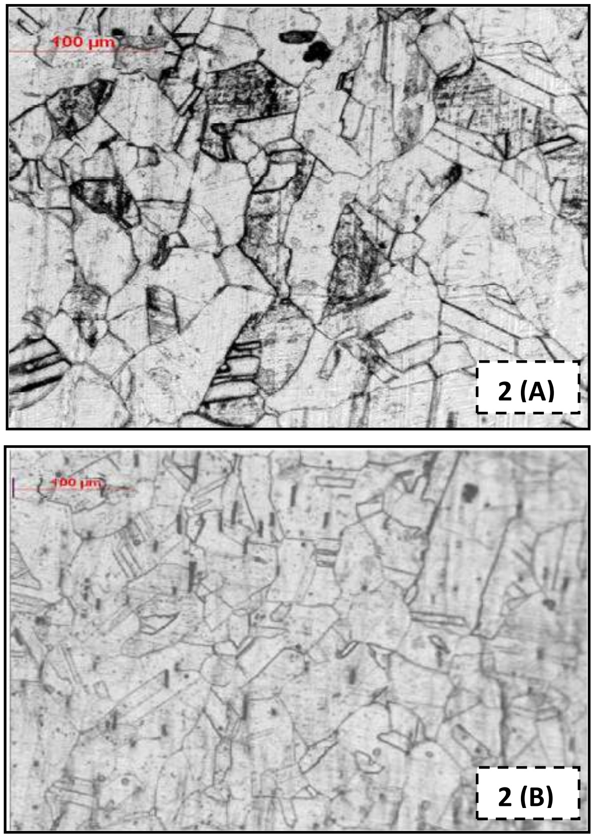
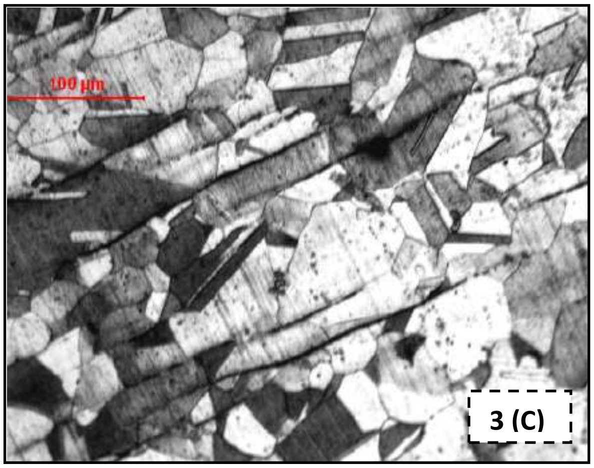


***Figure 2: Microstructure : Austenitic Stainless Steel Sample without any heat treatment; (A)304 LN (0.08%N_2) and (B) 316 LN*(0.1%N_2)**



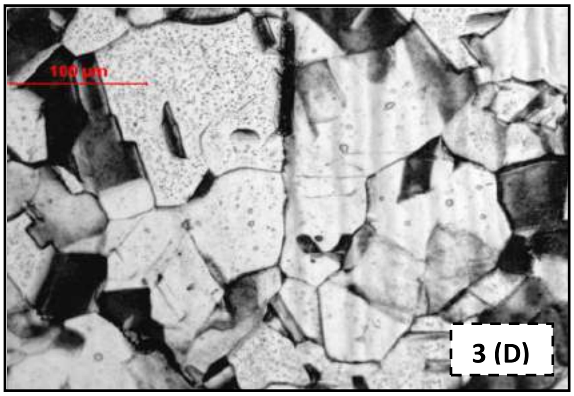


***Figure 3: Microstruture : Warm Worked Austenitic Stainless Steel Sample (Sensitized at 650^{o}C for 5 Hrs); (C) 304 LN (0.08%N_2) and (D) 316 LN*(0.1%N_2).**

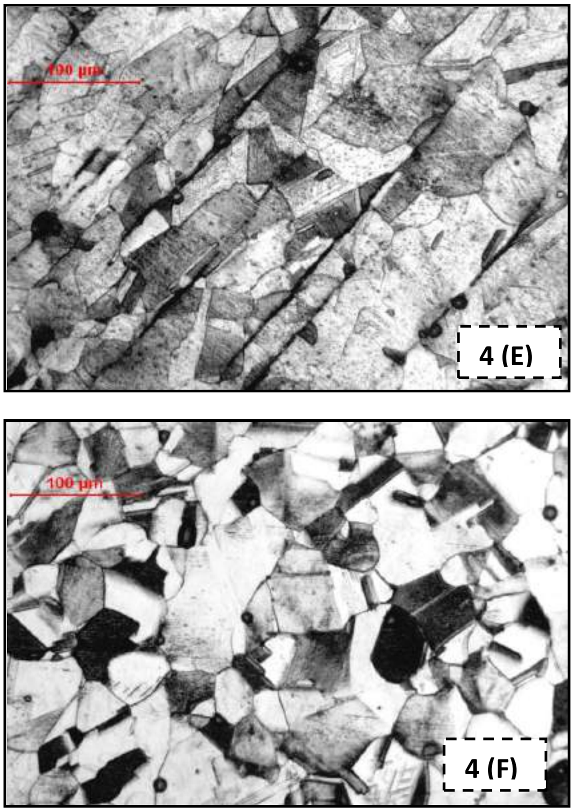


***Figure 4: Microstructure : Warm Worked Austenitic Stainless Steel Sample (Sensitized at 650^{o}C for 6.5 Hrs); (E) 304 LN (0.08%N_2) , and (F) 316 LN*(0.1%N_2).**

3.3. Vickers hardness testing:

Vickers hardness testing using a load of 50 gm was carried on the samples. The results are given in Table 3.

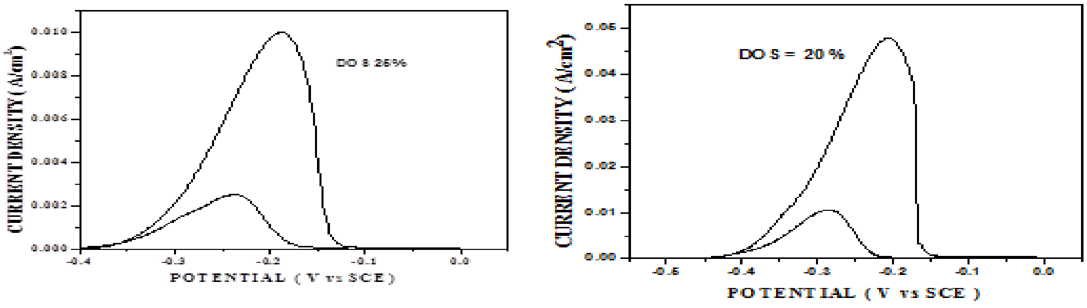
Table 3: Vickers hardness of 304 LN and 316 LN at different conditions.

Sl. No.	Sample	Condition	VHN
1	304 LN	As received	175
		Sensitized at 650°C for 5 Hrs	378
		Sensitized at 650°C for 6.5 Hrs	383
2	316 LN	As received	183
		Sensitized at 650°C for 5 Hrs	351
		Sensitized at 650°C for 6.5 Hrs	353

Due to the combined effect of rolling and heat treatment, hardness of the specimens increases significantly. This is due to the combined effects of slip and precipitation hardening of the specimens. There is no significant increase of hardness for sensitization for extended period of time (5 hours and 6.5 hours).

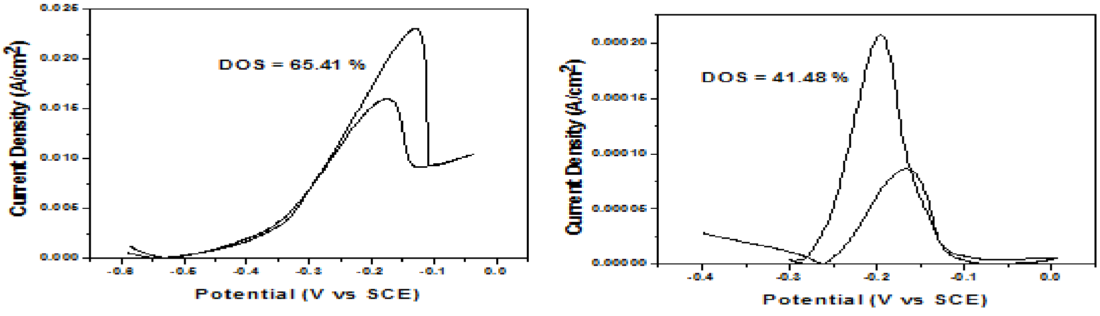
3.4 DL-EPR Test:

Double Loop Electrochemical Potentiokinetic Reactivation **(**DL–EPR) test were carried out for detecting degree of sensitization for undeformed, warmed worked (20%) and sensitized samples with different sensitization hours (0, 5, and 6.5hrs.). They are shown in figure.



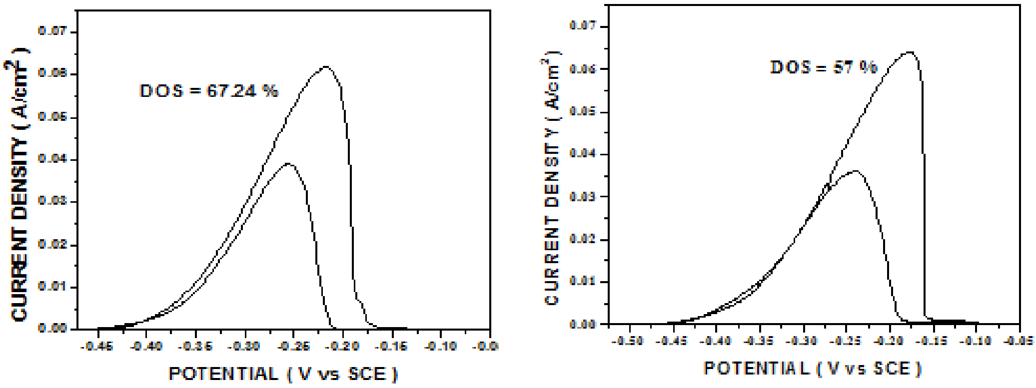
(5A) **(5B)**

Figure 5 (A-B): DL-EPR curves for as received Austenitic Stainless Steel
(5A) 304 LN (0.08%N_2) (5B) 316LN (0.1% N_2)



(6A) **(6B)**

Figure 6 (A-B):DL-EPR curves for worm worked Austenitic Stainless Steel Samples Sensitized at 650°C for 5 Hrs: (6A) 304 LN (0.08%N_2) (6B) 316LN (0.1% N_2).



(7A) **(7B)**

Figure 7(A-B): DL-EPR curves for Warm Worked Austenitic Stainless Steel Samples (Sensitized at 650°C for 6.5 Hrs: (7A) 304 LN (0.08%N_2) (7B) 316LN (0.1% N_2).

Table 4: Results of degree of sensitization of 306 LN and 316 LN Austenitic Stainless Steel Samples.

Sl. No.	Sample	Condition	Degree of sensitization (DOS) (%)
1	304 LN	As received	25.00
		Sensitized at 650°C for 5 Hrs	65.41
		Sensitized at 650°C for 6.5 Hrs	69.00
2	316 LN	As received	20.00
		Sensitized at 650°C for 5 Hrs	41.48
		Sensitized at 650°C for 6.5 Hrs	57.00

3.5 Pitting Potential and Protection Potential Measurements:

From the curves initial estimates of the pitting potential and protection potential were made which were followed up by current transient method and current transient scratch methods. The values are given in Table 5.

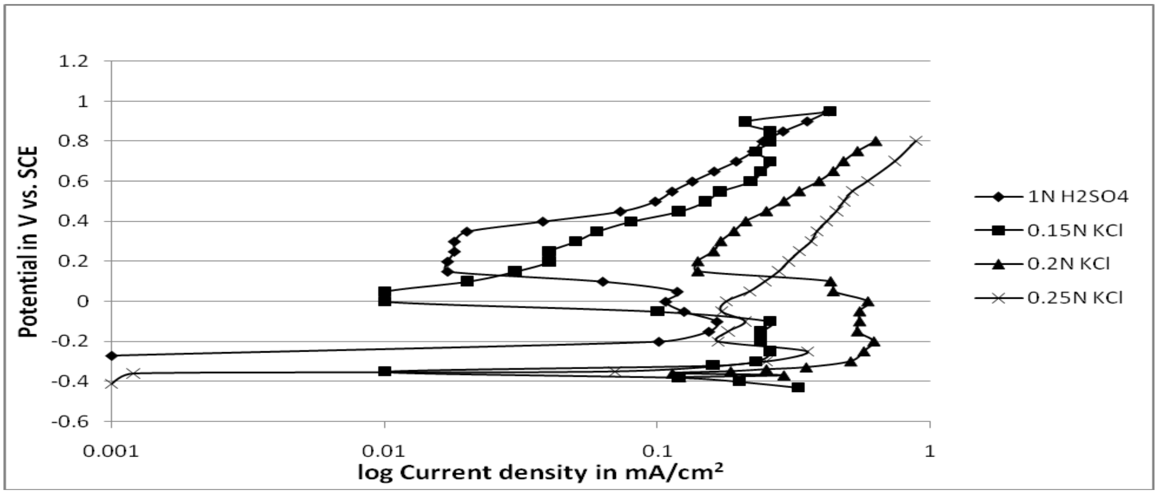


Figure 8: Polarization curves of 304LN (0.08 %N) in 1N H_2SO_4 with and without Cl^-.

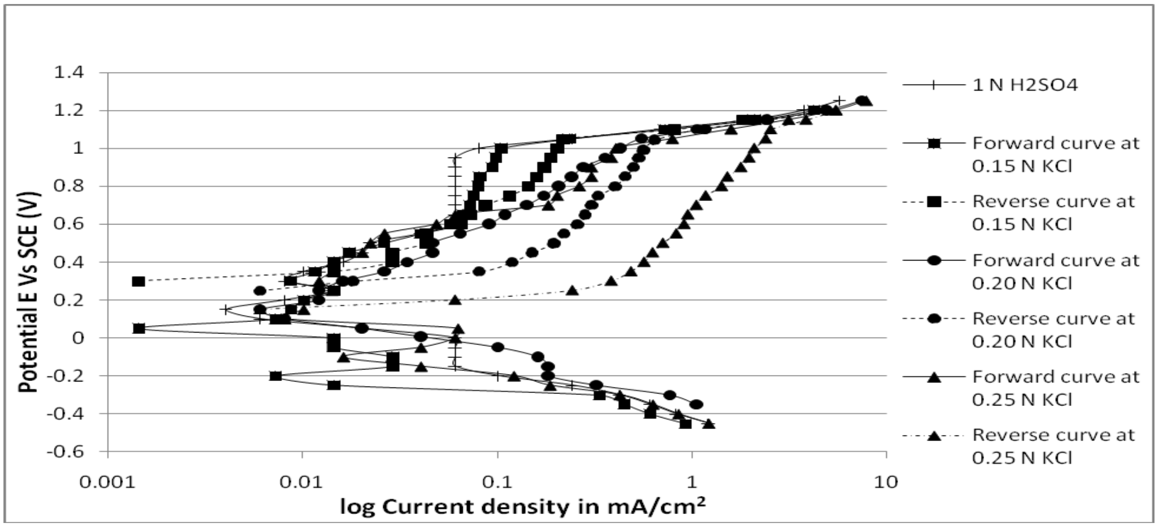


Figure 9:Polarization curves of 316LN(0.1 %N_2) in 1N H_2SO_4 with and without Cl^-

Table 5: Pitting Potential & Protection Potential.

Sample	**Concentration of solution**	**Pitting Potential in Vvs. SCE**	**Protection Potential in V vs. SCE**
304 LN (0.08%N_2)	1 N H_2SO_4+0.15 N KCl	0.45	0.375
	1 N H_2SO_4+0.20 N KCl	0.35	0.240
	1 N H_2SO_4+0.25 N KCl	0.10	0.070
316 LN (0.1%N_2)	1 N H_2SO_4+0.15 N KCl	0.95	0.345
	1 N H_2SO_4+0.20 N KCl	0.92	0.564
	1 N H_2SO_4+0.25 N KCl	0.90	0.675
Sample	**Concentration of solution**	**E_{CORR}Vs SCE**	**I_{CORR} mA/cm^2**
304 LN (0.08%N_2)	1 N H_2SO_4	0.20	0.034
	1 N H_2SO_4+0.15 N KCl	-0.06	0.046
	1 N H_2SO_4+0.20 N KCl	0.16	0.13
	1 N H_2SO_4+0.25 N KCl	-0.20	0.16
316 LN (0.1%N_2)	1 N H_2SO_4	0.08	0.0020
	1 N H_2SO_4+0.15 N KCl	0.06	0.0055
	1 N H_2SO_4+0.20 N KCl	0.04	0.0080
	1 N H_2SO_4+0.25 N KCl	-0.12	0.0250

Both pitting potential and protection potentials of both the steels increased with increase in chloride ions in the solution. It is interesting to note that both pitting potential and protection potential of 316 L is much superior to 304 LN (0.08 % N_2)

Conclusion

Metallographic investigation shows that the degree of sensitization increases with increase in holding time of sensitization. Due to the formation of chromium carbides during sensitization there is significant increase in hardness of the steels.I_{CORR} values of 316 LN (0.1%) were superior to 304 LN (0.08%N_2) and increased with increase in chloride content. Pitting potential and protection potentials of both the steels increased with increase in chloride ions in the solution. Both pitting potential and protection potential of 316 LN(0.1%) is much superior to 304 LN (0.08 %N_2).

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