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SURFACE HARDENING OF AISI 304, 316, 304L AND 316L SS USING CYANIDE FREE SALT BATH NITRIDING PROCESS

T. Kumar[1], P. Jambulingam[2], M. Gopal[3] and A. Rajadurai[4]
[1]*Department of Mechanical Engineering, S R M Engineering college, Kattankulathur. 603 203.*
[2]*Hi – Tech Processes Limited, Chennai.600 110.*
[3]*DMI College of Engineering Chennai.*
[4]*Department of Production Technology, MIT campus, Anna University, Chennai. 600 044.*

ABSTRACT

In this study, salt bath nitrocarburizing and oxidizing of 304, 316, 304L and 316L were experimented. The salt bath nitrocarburizing experiment was carried out at a temperature of 560^0C and for a time period of 120, 150 and 180 minutes. The oxidation process was carried out at a temperature of 373^0C and for duration of 60 minutes. Vickers' micro hardness and salt spray test were carried out for the above-mentioned stainless steels before and after diffusion hardening. It was found that salt bath nitrocarburizing effectively increases the hardness of stainless steels 304, 316 304L and 316L. From the microstructure of the nitrocarburized and oxidized specimens, the case depth was measured. The depth of diffusion layer could be attributed to the attraction between the alloying elements Molybdenum and Nitrogen. Also the corrosion resistance of nitrocarburized and oxidized steels is observed to be superior to the untreated specimens.

Key words: *nitriding, stainless steels, micro hardness, case depth* and *corrosion resistance.*

1 INTRODUCTION

1.1. Stainless Steels

Iron and the most common iron alloy steel are, from a corrosion view point, relatively poor materials as they rust in air, corrode in acids and scale in furnace atmosphere. In spite of this there is a group of iron base alloys, the iron-chromium-nickel alloys known as stainless steels, which are resistant to concentrated acids, alkalis and which do not scale under temperatures up to 1100^0C. The usage of stainless steels is small compared with that of carbon steels but exhibits a steady growth, in contrast to the constructional steels. Based on their crystalline structure, stainless steels are classified into three basic groups such as austenitic, ferritic and martensitic[1]. The most widely used stainless steels are the austenitic 18/8 type steels, i.e. AISI 304 and AISI 304L, which form more than 50% of the global production of stainless steels. The next most widely used grades are the ferritic steels such as AISI 410 followed by the molybdenum-alloyed steels AISI 316 and AISI 316L. Together these grades make up over 80% of the total tonnage of stainless steels.

Stainless steels with their excellent corrosion properties have a very broad application range. This extends to Chemical plants, Dairy and Food processing industries, Nuclear power plants, Heat exchangers, Laboratory benches and Equipments.

1.2. Passivity

The reason for the good corrosion resistance of stainless steels in oxidizing environments is the thin passive oxide film. As chromium is added to steel, a rapid reduction in corrosion rate is observed to around 10% because of this protective film or passive layer. Passivity increases fairly and rapidly with increasing chromium content up to 17%. This is the reason why many stainless steels are containing17 – 18% chromium[2]. The film is rapidly self-repairing in the presence of oxygen and damage by abrasion, cutting or machining is quickly repaired[3].

1.3. Sensitization of stainless steels

Sensitization is a process whereby chromium carbides ($Cr_{23}C_6$) precipitate at the grain boundaries even at elevated temperatures, typically between 450 – 850 ^{0}C. As a result, some chromium is lost and eventually reduces the corrosion resistance property of the Stainless steels[4]. This results in reduced ductility, toughness and aqueous corrosion resistance. Except the 'L' grade stainless steels all the other stainless steels are easily susceptible to sensitization. Those stainless steels cannot be case hardened directly since the addition of carbon on the further induces the problem of sensitization in the stainless steels. Therefore a case hardening process must be chosen so that the final stainless steel that is obtained after treatment must possess increased hardness without losing its corrosion resistance.

1.4. Significance of surface hardening of stainless steels

Industrial applications require a hard wear resistance surface called the 'case' and relatively soft, tough inside called the 'core'. In general, stainless steels have a good combination of strength and corrosion resistance, but they lack in wear resistance. The low hardness of stainless steels being the order of 200 – 300 kp mm^{-2} and the large wear in abrasively stressed parts lead to short life times that could be prolonged with improved tribological properties[5]. There exist several established processes for increasing hardness and reducing wear in stainless steels. These processes operate at elevated temperatures necessary to obtain treatment depths of several tens of micrometers in a reasonable time. These surface hardening processes include *Carburizing, Nitriding,* and *Carbonitriding or Cyaniding*. These methods change the chemical composition of the steel, *Carburizing* by the addition of carbon, *Nitriding* by the addition of nitrogen and *Cyaniding* by the addition of both carbon and nitrogen. Surface hardening could also be performed by *plasma assisted diffusion processes.*
Suh and Lee[6] *plasma carburised* AISI 316L SS and obtained uniform case depth of about 40 μm with hardness values above 700 VHN. El-Hossary et al.,[7] subjected AISI 304SS to *RF plasma carbonitriding* and obtained a very high surface hardness value of 1715 VHN. Liang. W.[8] *plasma nitrided* AISI 304 austenitic stainless steel and achieved a hardness value of 1600 Hv. Li. C. X and Bell. T[9] *plasma nitrided* AISI 316 stainless steel and obtained a hardness of 1220 $Hv_{0.05}$. Mandl. S. et. al.,[5] *nitrided* austenitic stainless steels [X6CrNiMo Ti17.12.2 – AISI 316 Ti] with PIII and achieved an increase in the hardness up to a factor of 4, improved wear behaviour by 1 – 2 orders of magnitude and retained corrosion resistance.

1.5. Reason for selecting the nitriding for the study

It is known that surface hardness of the steels can be increased by the addition of carbon and nascent nitrogen. In carburizing hardness is increased only by sacrificing the corrosion resistance property of the material. During the carburizing process, the carbon atoms diffuse through the surface and occupy lattice sites of the stainless steels. These excess carbon atoms have the affinity to react with the chromium present in stainless steels and form chromium carbide ($Cr_{23}C_6$). So as explained the sensitization property of the stainless steels comes into the picture. But in nitriding, the problem of sensitization is not encountered. Instead, diffusion of nitrogen into surface layers of steel promotes the formation of hard nitrides. In case of stainless steels, it is expected that the complex hard Fe-Cr nitrides form on the surface, which in turn could improve the wear resistance. Nitrogen is very strong austenite stabilizer and strongly promotes an austenite structure. So the advantages of nickel addition / alloying to promote an austenite structure can also be obtained by the case hardening stainless steels by nitriding. It also increases the mechanical strength substantially. Hence the case hardening process of nitriding is chosen for this study.

1.6. Nitriding

Nitriding is a class of low temperature thermo chemical treatment. It is undertaken in an atmosphere capable of supplying nitrogen into the surface of the components being treated. At temperatures between 400^0C and 590^0C, the nitrogen supplied diffuses into the work piece surface to a depth depends on time and temperature. The nitrogen may come from the decomposition of ammonia gas or from a nitrogen / hydrogen atmosphere activated by plasma. Nitrogen combines with nitriding forming elements such as Cr, Al, V, Ti and Mo, forming fine scale precipitates, which strengthen the surface region.

1.7. types of Nitriding

lassification is based on the phase of steel in which the case hardening is performed namely *Ferritic phase nitriding* and *Austenitic phase nitriding.*

1.7.1. Ferritic Phase Nitriding

As the name indicates, is done in the ferritic phase at around 500 – 650^0C. Normally salt bath nitriding is carried out in this phase. The higher the nitriding temperature, the lower the hardness of the nitrided case and the greater its thickness. Molten salt bath containing 85% of salt (consisting of 40%KCNO or Sodium Cyanide and 15% $NaCo_{3)}$ is considered for this purpose through which dry air is passed. This treatment produces a thin layer of carbide – nitride of 7 to 15 microns on the surface of the steel.

1.7.2. Austenitic Phase Nitriding

The austenitic phase nitriding can be done at around 800–1000^0C where the steel possesses an austenitic structure. So, the thickness of the case is higher than that at low temperature, but the hardness is lower due to the solid solutioning of nitrogen rather than compound formation. Of the above two processes, ferritic nitrocaburising is chosen because higher value of hardness is the aim of the study. The problem of decreasing corrosion resistance can be overcome by controlled oxidation process. So a combined property of increased hardness and corrosion resistance is possible to be obtained.

1.8. Benefits of Nitriding

(i) Nitriding produces compressive stress within the nitrided case and this can be beneficial in preventing surface initiated fatigue failures. (ii) Nitrided parts retain hardness up to 500^0C. (iii) Distortions and Cracks are low. (iv) Further heat treatment is not necessary. (v) Very smooth surface finish is obtained.

2. EXPERIMENTAL STUDY

2.1. Experiment

Different types of Nitriding processes include Salt bath Nitriding, Gas Nitriding and Ion Nitriding. Among these processes salt bath nitriding was considered first, for preliminary study. This salt bath nitrocarburising diffusion treatment was carried out on 304, 316, 304L and 316L grade stainless steel specimens.

2.2. Nitrocarburising and Oxidizing Parameters

Nitriding process	: Ferritic Nitrocarburising
Operation Temperature	: 560 °C
Operation Time	: 120 min. 150 min. and 180 min.
Oxidizing Temperature	: 373 °C
Oxidizing Time	: 60 minutes
Salt Bath Used	:Mixture of Sodium and Potassium cyanate and Carbonates

The beneficial aspect of the nitriding process used is that a very thin single-phase layer of epsilon nitride is formed. Nitrogen diffuses fast when compared to carbon. So the nitrogen diffuses into the stainless steel at the operating temperature (500°C). The epsilon nitride layer formed has excellent wear and anti-scuffing properties. Cyanide free baths are used since they are not hazardous.

2.3. Pickling

Pickling or chemical descaling was performed to remove tightly adherent oxide films resulting from hot forming, heat-treating, welding and other high temperature operations. A descaling solution of nitric and hydrofluoric acids was used. Mechanical alternatives such as sand blasting or wheel abrading may also be performed.

2.4. Operation

Electrically heated furnace with stainless steel pot (AISI 304) was used to carry out the processing. Initially base salt was filled up in the pot and heated to 560- 570 °C. After the initial aging of 24 hours to saturate the pot, the bath chemistry was checked and brought to normal by the addition of regenerator salt. Thus the bath was made ready for operation. The components were pre heated, degreased and soaked in the furnace for required time durations and then quenched in oil. After quenching, the components were washed in hot water and conditioned with oil after inspection.

2.5. Bath Composition

2.5.1. Base salt

The base salt consists of alkaline cyanates and carbonates of potassium and sodium mixed in certain composition. The base salt was used to make up new baths and to maintain the level of the bath of the bath in continuous operation. This salt heated to 560- 570 °C becomes effective source of nitrogen and effectiveness is maintained in continuous operation with the addition of a regenerator salt.

2.5.2. Regenerator Salt

The regenerator salt is an organic product which was added periodically to maintain the constant nitriding potential of the bath. The addition of regenerator salt does not involve change in volume but reacts with the base salts to convert carbonates back to cyanates to maintain the nitriding potential of the bath by way of chemical reaction.

2.6. Chemical reaction and source of nitrogen

The sources of nitrogen are mainly due to nitrogen generated because of the dissociation of cyanates present in the base salt and oxidation of cyanates.

$$4NCO \longrightarrow CO_2 + CO + 2N + 2CN$$
$$XFe + N \longrightarrow Fe_xN$$
$$2CN + O_2 \longrightarrow 2NCO \text{ (Regeneration of CN-)}$$
$$3CO_2 + \text{regenerator} \longrightarrow 6NCO + xH_2O$$

2.7. Oxidising

The nitrided steel usually oxidized to compensate for any reduction in corrosion resistance of the specimen and to increase the corrosion resistance of the same to a greater magnitude.

2.8. Testing Procedures

The hardness test used for measuring the micro hardness of untreated and treated specimens was carried out in Zwick micro hardness tester. A load of 100gms was applied for 10 seconds and the indentation is measured. From the tables available with the hardness tester it was easy to measure the micro hardness of the samples. Corrosion resistance was evaluated using Salt-Spray test, in which 5% salt (sodium chloride) solution. The Salt-Spray test was performed as per ASTM-B117. The surface morphologies and cross sectional micrographs were examined using metallurgical microscope. The treated specimens were viewed under a metallurgical microscope with suitable magnification and the case depth was measured from the difference in structure observed.

3. RESULTS AND DISCUSSION

The stainless steel specimens that are nitro-carburized for duration of 180 min were tested for surface hardness, microstructure and corrosion rate. The results of these experiments are given below.

3.1. Hardness Test

The surface hardness of the untreated and diffusion hardened steel specimens are listed in Table 2. For an easy comparison Fig. 1 shows the hardness bars of the untreated and diffusion hardened steels. From Table 2 and Fig. 1 it is evident that nitro-carburising causes a high increase in the surface hardness. The percentage increase in surface hardness ranges between 350 to 460 %. A very high hard case of 1200 VHN is obtained in the case of 316 grades stainless steel, whereas 304 grades exhibited a surface hardness of only 870 VHN.

The high hardness values observed in the 316 grades in comparison with 304 grades could be attributed to the formation of complex (Fe, Mo) nitrides. Even in the case of nitridable carbon steels small additions of Al, Cr and Mo are made in order to obtain surface hardness of 1200 VHN[10].

3.2 Microstructure and case depth measurement

The microstructures of the nitrocarburized (180 min) stainless steels 304, 316, 304L & 316L are shown in Figs. 2(a) to 2(d) respectively. Table 3 lists the case depth measured in the various grades of stainless steels.

From Figs. 2(a) to 2(d), it is evident that the case depths are fairly uniform and thin, which is the hallmark advantage of the nitriding process. The case depths observed in 316 grades is comparatively thicker than that observed in 304. This observation could be attributed to the attraction between the alloying elements Mo with Nitrogen.

3.3. Corrosion rate

The corrosion rate of the untreated and diffusion hardened & oxidized specimen was tested using salt spray method and the results in mpy are listed in Table 4. Also for easier comparison the Fig. 3 shows the corrosion rate bars of the untreated and nitrocarburized and oxidized samples.

From Table 4 and Fig.3 it can be seen that the corrosion rate has decreased drastically after performing the diffusion hardening followed by the oxidizing process for all the three grades of the stainless steels. The decrease in corrosion rate is observed to be about 87% to 95%. Though the nitriding process may decrease the corrosion resistance of the steel, the increase in corrosion resistance could be attributed to the oxidizing that is being done after the diffusion hardening process.

4. CONCLUSION

In this study, salt bath nitro-carburizing of stainless steels 304, 316, 304L and 316L was experimented. From the experiments, it was found some improvements in corrosion resistance, wear resistance, and hardness property of the nitrided stainless steels could be achieved at an acceptable cost. The major conclusions are as follows.

1. Salt bath nitro-carburizing effectively increase the surface hardness of stainless steels of 304, 316, 304L and 316L grades.
2. A very high surface hardness of 1200 VHN could be obtained on 316grades, whereas a hardness value of 870 VHN could be obtained in 304 grades.
3. For the given treatment parameters of 560°C and 180 minutes the case depth were found to be 50 and 60 microns for 304 and 316L steels respectively.
4. The corrosion resistance of nitro-carburized and oxidized steels is superior to that of the untreated specimen.

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TABLES

Table 1: Composition of the selected stainless steel grades considered for the study.

Alloy Grades	C	Mn	P	S	Si	Cr	Ni	Mo	Others
SS304	0.040	1.580	0.024	0.040	0.400	18.35	8.040	0.070	-
SS304L	0.010	1.638	0.023	0.002	0.412	18.56	8.138	0.364	-
SS316	0.080	2.000	0.045	0.030	1.000	16.80	11.20	2.500	-
SS316L	0.020	1.390	0.024	0.080	0.480	16.80	10.22	2.080	-

Table 2: Hardness of the untreated and salt bath nitrided specimen for 180 min.

S.No	GRADE	SURFACE HARDNESS (VHN)		% INCREASE
		Untreated	Salt Bath Nitrided (180 min)	
1.	304	220	870	395
2.	304L	260	920	350
3.	316	250	900	360
4.	316L	260	1200	460

Table 3: Case depth in 304, 304L 316 and 316L grade stainless steels.

S. No.	GRADES	CASE DEPTH (microns)
1	304	47
2	304L	44
3	316	63
4	316L	51

Table 4: Corrosion Rate of the untreated and Diffusion hardened stainless steels

S. No	GRADE	CORROSION RATE (mpy)		% DECREASE
		Untreated	Diffusion hardened	
1.	304	0.5	0.062	87.6
2.	304L	0.495	0.0495	90
3.	316	0.488	0.0371	92.4
4.	316L	0.485	0.02475	94.8

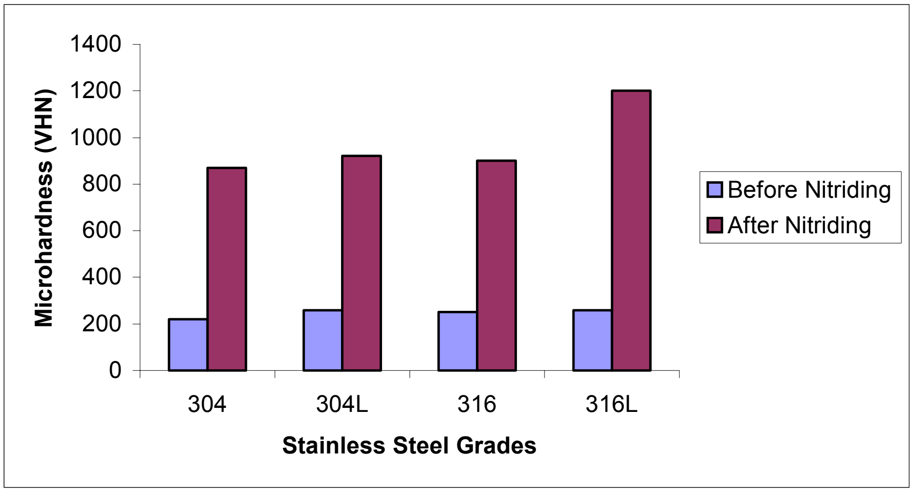

Figure. 1. Hardness of the untreated and salt bath nitrided specimen for 180 min.

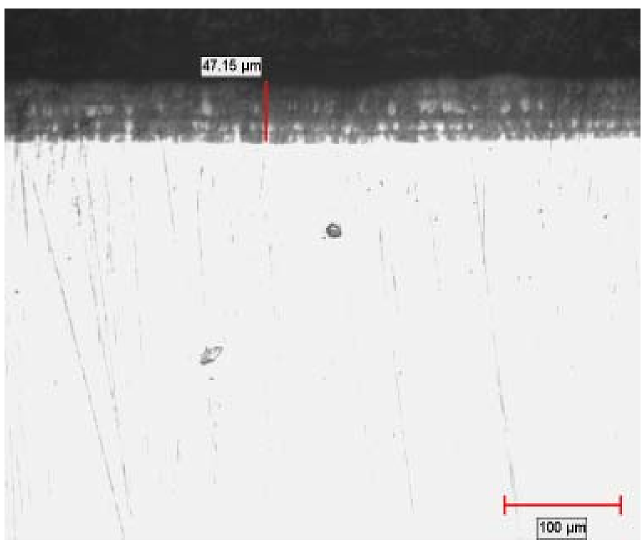

Fig. 2.(a) Microstructure of SS304 showing an average case depth of 47 Microns

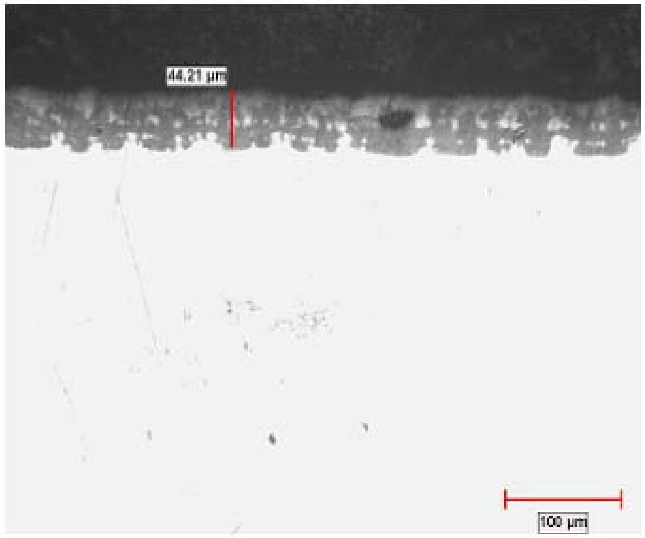

Fig. 2.(b) Microstructure of SS304L showing an average case depth of 44 Microns

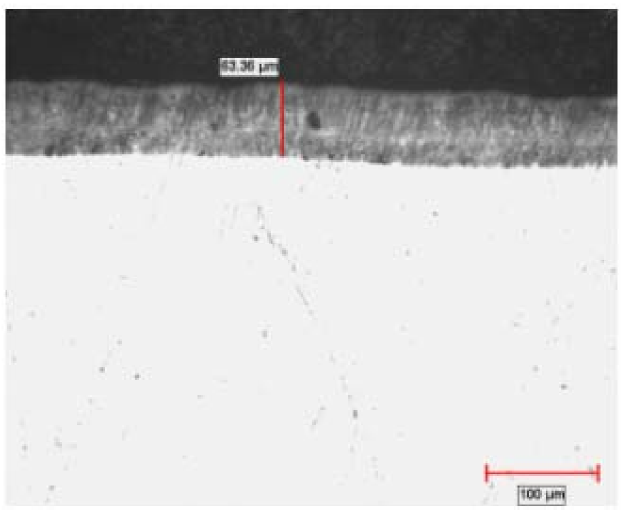

Fig. 2(c) Microstructure of SS316 showing an average case depth of 63 microns

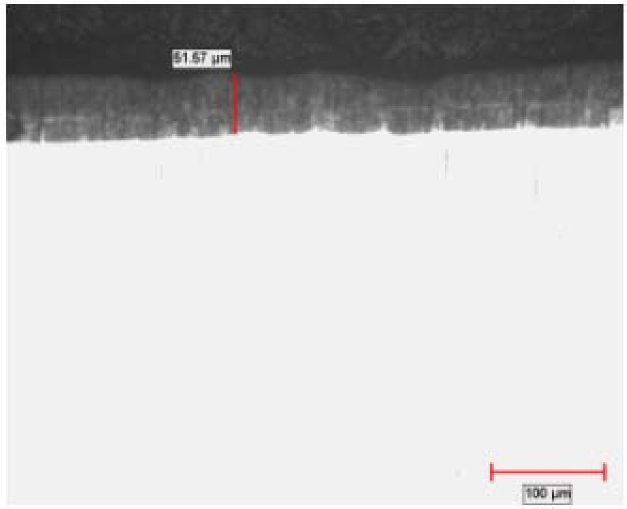

Fig. 2. (d) Microstructure of SS316L showing an average case depth of 51 Microns

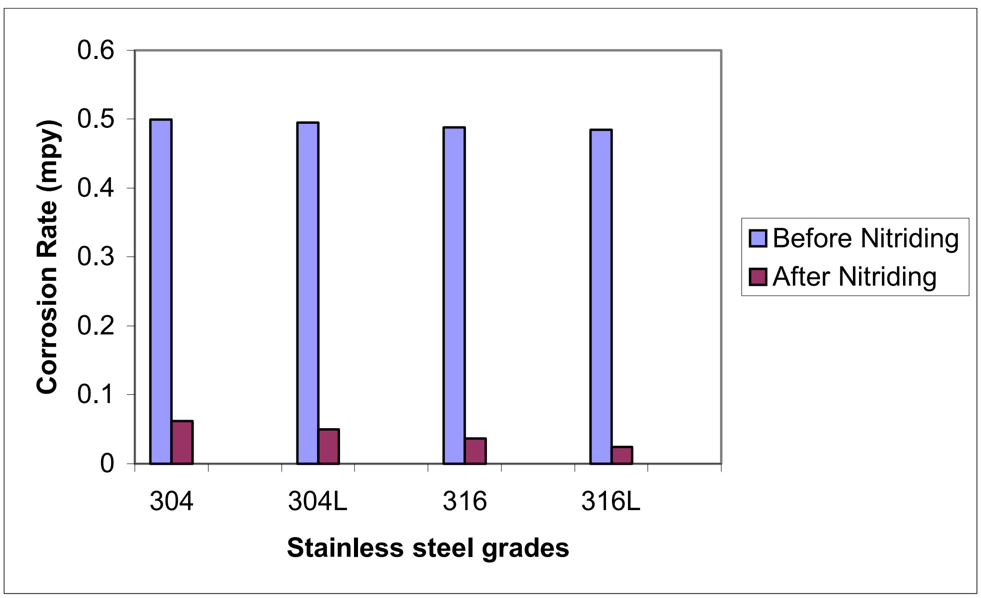

Figure 3: Corrosion rate of the untreated and diffusion hardened stainless steels