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Microstructure, Hardness and Corrosion Resistance of Surface Modified Ni - Hard 4 Cast Iron with Nitrogen using Gas Tungsten Arc

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Abstract: ***The change in microstructure, hardness and corrosion rate of Ni-Hard 4 cast iron were studied after surface modification with Nitrogen mixed the Argon shielding environment. The microstructure of the modified layer was grains with the presence of nitrogen, observed under the optical microscope. An average of 1.37wt% of Nitrogen was observed in the modified layer during EDAX analysis. The presence of Nitrogen in the modified layer has formed FeN, Ni_3N and Cr_2N phases. The formation of nitride phases were confirmed during XRD spectral analysis. The hardness of the modified layer was taken along the depth direction. The hardness of the modified layer was improved from 578HV of the substrate to 1735HV of the modified layer. The electrochemical polarization test was conducted at a 3.5wt. % saline (NaCl) solution in both the substrate and the modified layer. The modified layer forms a protective layer over the surface and reduced the corrosion rate than the substrate***

Index words: ***Ni-Hard 4 Cast Iron, Nitrogen, Hardness, Corrosion Resistance***

I. INTRODUCTION

The cast iron was used in the field of mining, minerals and iron processing industries. Ni-Hard 4 Cast Iron (NH4CI) was a high strength material with the alloying element of Nickel (Ni) and Chromium (Cr). NH4CI is a category of white cast iron and it has an extreme abrasion resistance and fracture resistance compared to the cast iron category of Ni-Hard1 and Ni-Hard 2 materials. The 4.5 – 6.5 wt% of Ni and 8 – 9 wt% of Cr has decided to the grade 4 of this material. The carbon content of this material is compromised between abrasion resistance and toughness. The experiment on NH4CI is conducted and adding alloying element like titanium and vanadium atoms has been mixing with the carbon content to form titanium carbide and vanadium carbide. These formations of the carbide contain high amount of strength and the properties was huge improved.

The experiment on NH4CI with 2 wt. % of vanadium powder as a reinforcement and observe the mechanical properties. It was reported that the properties like hardness and wear resistance were improved because of the refinement of Chromium carbide and the formation of vanadium carbide [1]. Effect of titanium addition to the Ni Hard White Cast Iron (NHWCI) and the properties of the newly developed alloy were investigated. The result showed that the addition of 2 wt. % of titanium to the alloy formed titanium carbide and found that the properties of the material improved significantly [2]. The high Cr cast iron and NH4CI material have added elements like tungsten particle and molybdenum to the bulk alloy. Due to the effect of the tungsten and molybdenum the properties like hardness, impact toughness is increased in high Cr cast iron and NH4CI [3] – [4]. The NH4CI were subjected to an erosive wear behavior of the mining operation to find optimum condition using an L9 orthogonal array. The angle 30° degrees of implement shows the less removal of material [5]. NH4CI reinforcement with Titanium. The Titanium 1.3 wt% attains the maximum hardness of 963HV and the wear resistance was improved [6]. The formation of titanium carbide and Cr carbide formation the hardness and the wear resistance was improved. The types of NH4CI were subjected to heat treatment. It was reported that the NH4CI samples were subjected to annealing at 790°C for the duration of 4-8 hours. It was inferred that the NH4CI hardness were improved by 22.5% [7]. The heat treatment process like destabilization was carried out 820°C for 4 hours and subcritical treatment were carried out at three different temperatures. Strong correlations were found between the abrasion resistance and equivalent hardness of the test alloy [8]. The AISI 304 stainless steel with surface modification with commercially pure titanium sheet of 0.3mm thickness were performed with GTA. The hardness was improved from 265HV to 2098HV and wear rate was decreased in the modified layer [9]. The AISI 304 stainless steel, alloyed with titanium using GTA to form the alloyed layer on the surface. The heat treatment was performed for 6 hours. The hardness was found to be improved on the heat treated and modified area [10]. The Fe18Cr8Ni steel alloyed with tungsten under nitrogen atmosphere has improved the hardness and wear resistance due to the formation of Nitrides and the dispersion strengthening when alloying tungsten [11]. The effect of titanium as alloying element to the surface on 0.2 wt. % C, 0.4 wt. % C and 1.1wt. % C steel was carried out with GTA. The result showed that the properties were improved by six times in 1.1 wt% C, four times increased in 0.4 wt% C and two times increased in 0.2 wt. % C content.

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It was reported that the enhancement of the properties was attributed to the TiC formation [12]. The Ti-6Al-4V alloy subjected to nitriding and followed by surface modification. In that, the modified area under a depth of 1.2mm forming the phase like
titanium nitrides was analysed. The wear resistance and hardness properties were improved on the modified area [13]. AISI 4340 stainless steel subjected to surface modification using 64Cr-80Si-6.84C-26.84Fe hypereutectic alloy powder on surface of the steel through GTA. The hardness was improved and the abrasive wear resistance was increased on the coating layer [14]. The surface cladding on Spheroidal graphite cast iron using TiC powder was performed using laser source. The experiments were conducted between 700, 1000 and 1500W. At 700W the maximum hardness 1350HV is attained on the cladding area [15]. Nitrogen and carbon are interstitial elements in relation to the iron crystal lattice and may be kept in solid solution in the austenite and martensite phases and precipitates in the matrix as nitrides or carbonitrides. Carbon gives better phase stability than nitrogen in austenite, but carbon forms many precipitates such as carbide and carbonitrides. The addition of nitrogen is reported to delay carbide precipitation, and in high nitrogen steels results in the disappearance of carbide phases [16]. The Nitrogen is an interstitial alloying element is well known for its beneficial effects in high Cr and Ni steel. Phase stability, high strengthening effect and corrosion resistance have made nitrogen an attractive candidate for high temperature and corrosion resistance applications [17]. 18/8 SS usually exhibits pitting corrosion in sulfuric acid containing ferric chloride. Once started, however, a pit penetrates the metal at an ever-increasing rate. 18/8 SS also exhibits galvanic corrosion when it is treated with unpolluted seawater [18]. The corrosion resistance of Ti and electroless nickel coated layer was improved by the formation of chemically inert titanium oxides and Ti–Ni phases [19]. The electro zpolarization technique was used to evaluate the corrosion resistance of the varying coating thickness of TiN on SS under 5% NaCl and 1N H2SO4 + 0.05 KSCN. The effect of coating thickness and the packing factor plays the effective role in the corrosion resistance of the coated samples [20]. The addition of bicarbonates to the saline (NaCl) solution has influenced in reduction of pitting corrosion on 304 Stainless Steel [21].

Pervious works have been done on NH4CI material and reinforced with Titanium, vanadium, and molybdenum in bulk modification process. The results were observed and the properties are improved. No study has been done with a surface modification properties of NH4CI. In the present study, the Nitrogen is added over the surface using GTA technique to the NH4CI to investigate the surface properties.

II. EXPERIMENTAL PROCEDURE

The sand casting method was used to make NH4CI. Induction furnace was used for making NH4CI with the melting point between 1460°C to 1480°C. The cast specimen was made in a form of bar with the dimension of 100 × 30 ×30mm. Arc Emission Spectroscopic test was carried to observe the wt. % of Ni and Cr. The chemical composition of NH4CI was shown in Table – 1. Gas Tungsten Arc heat source was used for surface modification under nitrogen gas mixed with argon shielding environment. The surface modification was performed on all the 4 sides of bar at 180A of current, 3mm of 2% thoriated tungsten electrode, 2mm standoff distance, 2mm/s of travel speed, with Nitrogen mixed with Argon flow at 12L/Min. After the modification process, the substrate and the alloyed layer were sliced and polished with different grades of emery paper followed by diamond polisher and cleaned with acetone to remove dirt’s and inclusion. The polished surface was etched with freshly prepared etchant. The optical microstructural examination was taken on the etched surface using Lyzer Instruments optical microscope. The elemental composition of the modified layers was determined by HITCHUI SU 6600 EDS. The existence of intermetallic particles were determined using UTIMMA IV X-Ray diffractometer. The microhardness test was carried under 100 Kgf for 15 Sec along the depth direction on all the four samples and the average results are reported. Electrochemical Polarization (ECP) method was used to investigate the corrosion behaviour of the substrate and the alloyed layer. The specimens were cut to dimensions of 50 mm × 5 mm × 4 mm and then insulated except the area which is exposed to the testing solution. An electrochemical workstation (CH Instruments, Inc.) was used in conjunction with the substrate and surface modified specimens, platinum wire and saturated Calomel solution used as the working, counter and reference electrodes, respectively. The test was carried out in a glass beaker with 30 ml of saline solution at 28°C room temperature as per ASTM G5-94 standard. The potential was scanned from −0.7V to 0.3V with the sweeping rate of 1 mV/s. Corrosion current (i_{corr}), corrosion potential (E_{corr}) and corrosion rate (C_{rate}) were calculated by Tafel exploration method

Table 1 Chemical Composition of NH4CI

Elements	C	Cr	Ni	Si	Fe
Wt%	3.66	8.48	4.59	0.87	Balance

III. RESULTS AND DISCUSSIONS

A. MICROSTRUCTURE

NHWCI has a microstructure consisting of martensitic – austenitic or martensitic matrix and carbides, due to the presence of carbon, Ni, Cr and silicon in the cast iron. NH4CI is a white cast iron designed to give a structure with rod or blade like eutectic ((Cr, Fe) $_7C_3$) carbides and the matrix which is free from perlite in the cast condition. Figure 1 shows the microstructure of the as-cast NH4CI. The desires carbide structure is resulted as the effect of the balanced carbon, Cr, Ni, and silicon content. NH4CI has low carbon content than the NH1CI and NH2CI. The as-cast matrix structure consists of about equal amount of martensite, austenitic and secondary carbides. The presence of nitrogen has refined the rod like eutectic carbide structure into uniaxied grain with the presence of nitrides in the grains boundaries. In Fe-Cr-N alloys, some regions have a high dislocation density while in some other areas eutectic twins were formed. Figure 2 shows the microstructure of the surface modified layer.

The presence of N_2 has enriched Cr content. 10% - 20% Cr alloy absorbs larger amounts of nitrogen, the lower the temperatures, equilibrium is attained. The presence of enormous amount of δ-ferrite in NH4CI because of high Cr equivalent and low Ni equivalent. The addition of nitrogen in martensitic stainless steel effectively reserved δ-ferrite,

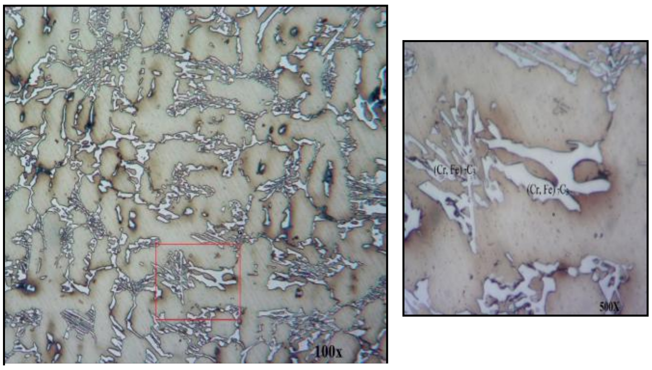


Figure 1 Microstructure of As-Cast NH4CI

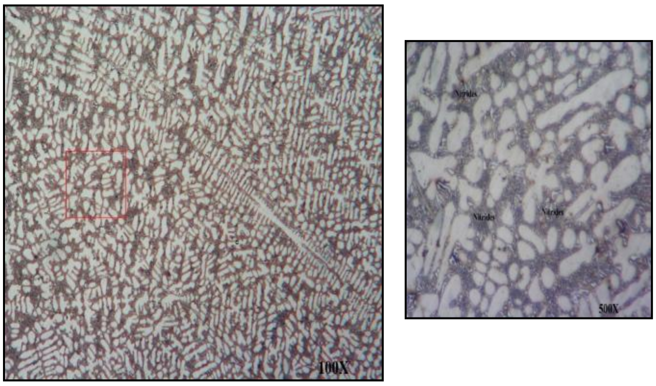


Figure 2Microstructure of the surface modified NH4CI layer

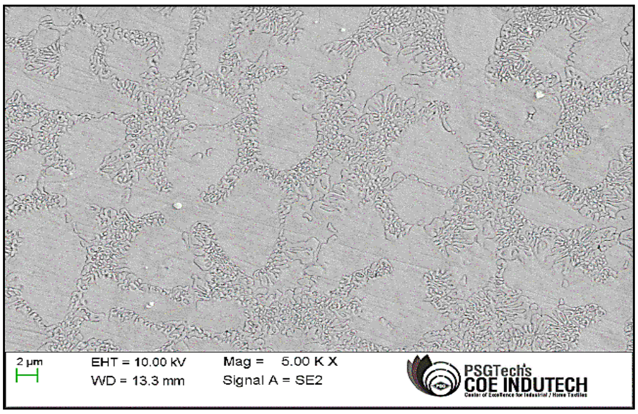
because of the strong stabilizing nature of N_2. N_2 existed as randomly distributed precipitates in high N_2 martensitic stainless steels. Besides, the main precipitates in steels containing nitrogen up to 0.24 wt.% were $M_{23}C_6$, and the further addition of nitrogen substantially converted the main precipitates to be M_2N [22].

B. PHASE IDENTIFICATION

The microstructural observation revels the change in surface microstructure and the presence of nitride phases in the surface modified layer. The amount of nitrogen in solution in austenite increases as the temperature is decreased until the nitride becomes stable. From this point on the solubility limit of nitrogen in martensite steel decreases with decreasing temperatures. The N_2 content dissolved in austenite structure was observed by EDAX analysis. Figure 3 shows the EDAX spectrum of the surface modified layer. EDAX spectrum gives the elemental composition of the surface modified layer. Table – 2 shows the elemental wt. % on the surface modified layer. During the surface modification at higher temperature the Cr got evaporated and the remaining Cr absorb N to for Cr_2N phase. The elemental mapping revels the distribution of N_2 all along the surface modified layer which is showed in Figure 4. Further, to have a clear transparency in the phase formation between Fe, Cr, Ni and Si with N_2 X-ray Diffraction spectrum was taken. The XRD spectrum was analysed using X'Pert high score software to get the intermediate phases, which confirms the formation of FeN, $Fe_2Cr_{14}C$, Ni_3N, and Cr_2N with the peak score of 56, 31, 17, and 11 respectively. The peaks values were cross referenced with the ICDD –JCPDS data, the JCPDS pdf data 87-2146, 02-3782, 24-2586, and 79-1004, confirms the peaks values with the intermetallic phases formed in the surface alloyed layer. Figure 5 shows the XRD spectrum of the surface alloyed layer

Table 2 Elemental Wt. % of the surface alloyed layer

Element	Cr	Ni	C	Si	N	Fe
Wt.%	11.50	4.04	8.46	1.05	1.37	68.66



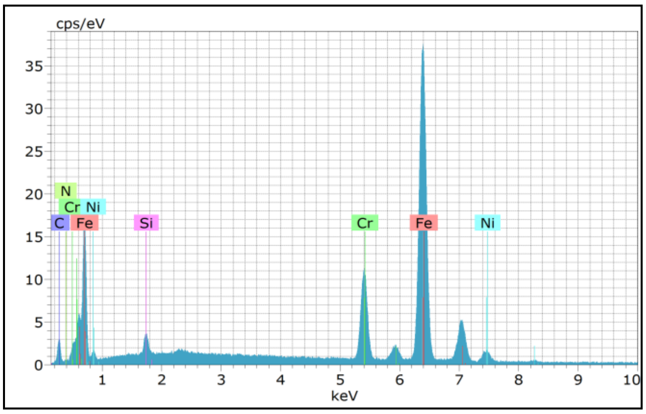


Figure 3EDAX spectrum of the surface alloyed layer

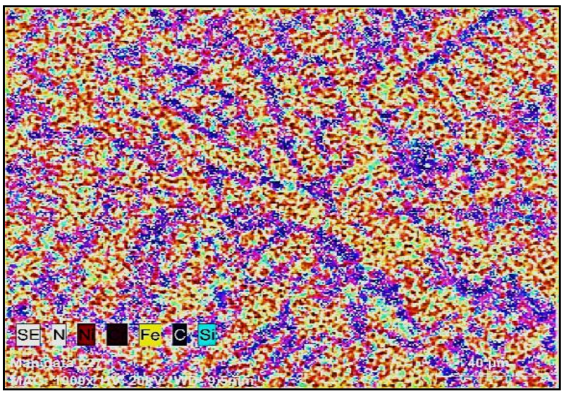


Figure 4Elemental Mapping of the surface alloyed layer

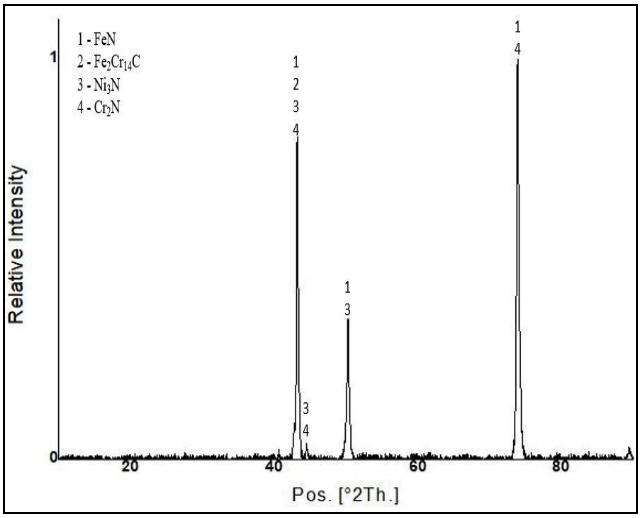


Figure 5XRD spectrum of the surface alloyed layer

C. Hardness

The microhardness of the surface alloyed layer was found on the cross sectional layer of the surface alloyed layer. The external force applied was 100kgf for 15 seconds. The refined rod like eutectic carbide structure with the hard Cr_2N, ((Fe, $Cr_7)_2$ C_3) intermetallic phases. The hard phases restrict the dislocation motion and improved the hardness of the surface alloyed from 587HV to 1738HV. Figure 6 shows the harness along the depth direction. Figure 6 revels the existence of gradient due to the temperature distribution along the depth direction. The hardness is increased because of fine grain structure and hard phases like Iron carbide, Nickel nitride, chromium nitride, and chromium carbide were formed on the modified layer

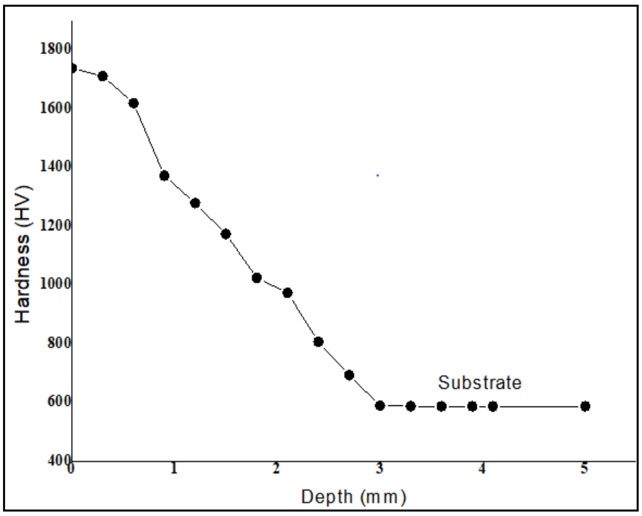


Figure 6 Hardness along the depth direction

D. CORROSION RESISTANCE

The ECP test was performed to evaluate the cathodic and anodic behaviour of the substrate and the modified layer. The TAFEL polarization curves of the substrate and modified specimens in 3.5 wt. % NaCl solution is shown in Figure 7. The corrosion potential (E_{corr}), the equilibrium corrosion current density (i_{corr}) and the corrosion rate of various specimens were determined by Tafel extrapolation method. Moreover, increased surface hardness in modified specimen, especially the formation of intermediate phases on the surface, may also significantly improve the corrosion resistance of the specimen. It is observed from the results that the corrosion potential of the modified specimens shifted cathodically from – 0.319mV to – 0.208mV. This indicates that the modified specimens has better corrosion resistance in the saline environment (3.5 wt. % NaCl) in which the measurement were carried. Similarly, the corrosion current density of the modified specimen was about 49 % lower than that of the substrate, indicating substantial improvement in the corrosion resistance. Tafel curves of both the substrate and the modified specimen show an initial anodic passivation, followed by strong localized corrosion, and further passivation. The modified surface passivates at much higher

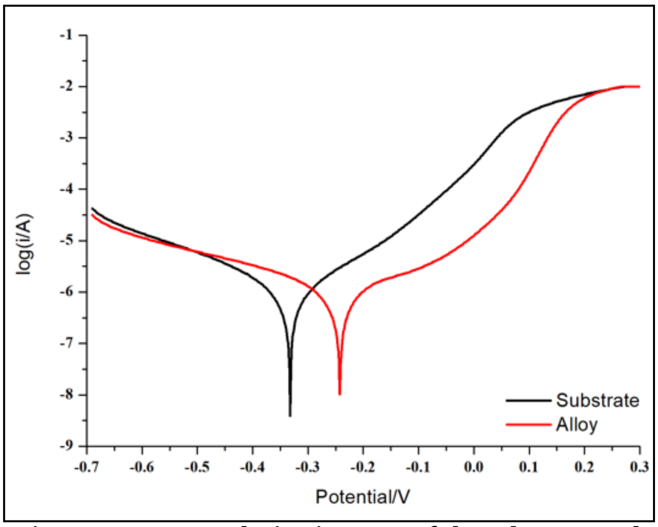


Figure 7 TAFEL polarization cure of the substrate and the modified layer

corrosion currents, though for a slightly lower potential window. Eventually, all the SEM results portrays a stable protective film developed on the surface modified specimen. Hence, GTA treatment under nitrogen atmosphere has a positive influence on the corrosion behaviour of the NH4CI. It is found from the TAFEL analysis that corrosion rate of the modified specimen (0.1271 mmpy) is much lower than that of substrate (0.2443 mmpy). Figure 8 shows SEM images of pit formation after corrosion test on the substrate and the formation of corrosion products which acts as a protective layer in the modified layer. It was noticed that the pit formation was reduced for modified surface as compared to the substrate. The reduction in the pit is due to the formation of oxide layer such as Fe_2O_3, SiO_2, and Cr_2O_3 which is confirmed by XRD spectrum and the ICDD – JCPDS data 24 – 0072, 33 – 1161, 84 – 3872 and 38 – 1479 strengthen the formation of Fe_2O_3, SiO_2, NiO, and Cr_2O_3, respectively. Figure 9 shows the XRD spectrum of the modified layer. Using ECP, the modified layer which acts as a passive layer, attributes to

the reduction in the surface pitting. The pits formed over the surface shows an irregular shape for both modified and base metal surfaces.

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Figure 8 SEM image of the corroded (a) Substrate and (b) surface modified specimen

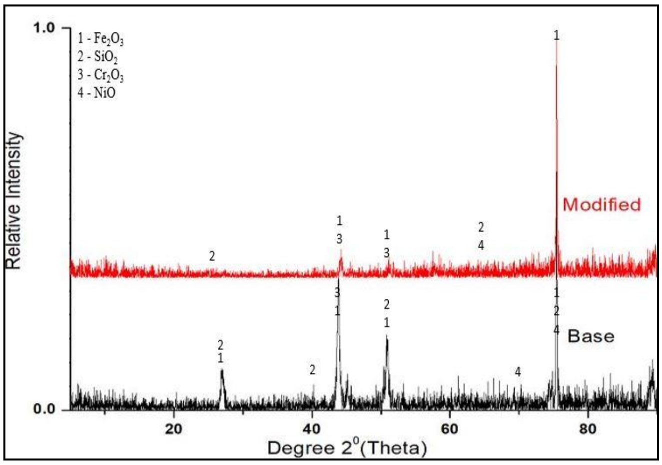

Figure 9 XRD Spectrum On The Protective Layer On The Substrate And The Modified Layer

IV. CONCLUSION

The influence of gas tungsten arc surface modified under Nitrogen atmosphere on the hardness, wear rate, and corrosion behavior of Nickel Hard – 4 Cast Iron have been systematically investigated.

The following conclusions are drawn:

- Surface modification of Nickel Hard – 4 Cast Iron under Nitrogen atmosphere were achieved. The SEM image of the modified layer reveals the formation of fine grains in the modified layer.
- The hardness on the surface of the modified layer was found to be 1738HV for modified layer under Nitrogen atmosphere which is much higher compared to the substrate of 587 HV.
- In Saline solution, an improvement in the corrosion resistance was observed for the modified layer.
- The rate of corrosion of the modified layer was reduced to 49 % when compared to the substrate, which is mainly influenced by the nature of the surface films, the alloy composition, the process parameters and the time of immersion in the Saline solution.
- A formation of oxides decreases the corrosion rate of the modified layer

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