Nickel coating on high strength low alloy steel by pulse current deposition

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Abstract. Nickel is a silvery-white metal mostly used to enhance the value, utility, and lifespan of industrial equipment and components by protecting them from corrosion. Nickel is commonly used in the chemical and food processing industries to prevent iron from contamination. Since the properties of nickel can be controlled and varied over broad ranges, nickel plating finds numerous applications in industries. In the present investigation, pulse current electro-deposition technique has been used to deposit nickel on a high strength low alloy (HSLA) steel substrate. Coating of nickel is confirmed by X-ray diffraction (XRD) and EDAX analysis. Optical microscopy and SEM is used to assess the coating characteristics. Electrochemical polarization study has been carried out to study the corrosion behaviour of nickel coating and the polarisation curves have revealed that current density used during pulse electro-deposition plays a vital role on characteristics of nickel coating.

1. Introduction
Refinement of grains is an important aspect that improves the mechanical properties such as strength, wear and impact resistance [1-3]. However, the effect on corrosion resistance due to variation in grain size is still not much explored. Also in many cases, contradictory conclusions have been drawn that decrease in grain size can either increase or decrease corrosion resistance [4-7]. The nanostructured materials with significant amount of surfaces and interfaces have attracted much interest because of their demonstrated unique properties compared to conventional materials [8]. The coating of nanocrystalline deposit on steel leads to significant improvement of corrosion resistance [9-11]. As such, there are various nano-coating processing techniques. In this work, pulse-current electro-deposition has been used with an attempt to deposit finer grains as compared to which is obtained by conventional electroplating technique. An optimum amount of saccharin has been used in the nickel bath as grain refinement agent. Till date, this area is not much explored and there is lots of scope to work further. Corrosion, a deteriorating phenomenon of materials, particularly in metals, often dictates the life span of a product. By careful observations and proposing newer methods to inhibit corrosion, material life of any product could be improved and thus preventing loss to the society. Usually corrosion resistance of metals and alloys can be achieved by applying coatings over them, just as nickel films which have been proved suitable in this regard [12-17]. In the present research the corrosion behavior of the coating is evaluated with the help of potentiodynamic polarization tests. The resistance of the coatings towards corrosion is evaluated on the basis of the corrosion parameters obtained from the polarization curves viz. corrosion potential, corrosion current density, charge transfer resistance, double layer capacitance, corrosion rate, etc. Experiments have been done to analyze the effect of pulse current parameter such as current density on surface texture of the Nickel coating [18-20].
2. Experimental Procedure

2.1. Material.
A high strength low alloy (HSLA) steel used in this investigation was obtained from TATA Steel, Jamshedpur in plate form of thickness 6.0 mm. The composition of this alloy is given in Table 1. The alloy plate was hot rolled and the hot rolling parameters of the HSLA were: soaking temperature 1185 °C, finish rolling temperature 910 °C and coiling temperature 580 °C.

| C   | Mn  | Si   | P    | S    | Al  | Ti  | V   | Nb  | Cr  | Fe  |
|-----|-----|------|------|------|-----|-----|-----|-----|-----|-----|
| 0.08| 0.95| 0.024| 0.013| 0.006| 0.04| 0.025| 0.01| 0.04| 0.021| balance |

2.2. Specimen Preparation.
The coupons of HSLA steel of approximate dimensions of 15 mm x 15 mm were prepared. The surface of the specimens was polished by SiC emery paper ranging from grit size of 220-1500. The samples were then further cloth polished using alumina abrasives to get scratch free mirror-like surface. Washing with ethanol or acetone helps to remove any dust or grease on the surface of the specimen. The specimen was wrapped in the Teflon tape exposing only the polished area. Over the Teflon, an organic polymer (nail polish) coat was put on in order to completely insulate every part of the specimen except the polished portion. Then electroplating on the sample was carried out in glass beaker containing the electrolyte/bath using a Potentiostat.

2.3. Pulse-current electro-deposition technique.
Pulse electro-deposition (PED) is a novel technique for producing nano-structured coatings on metallic substrates. It is associated with many advantages such as reduction in porosity, low level of inclusions, and higher rate of deposition as compared to conventional direct current (DC) electro-deposition process. There is much more flexibility involved in varying three basic parameters such as pulse peak current density, pulse frequency, on time and off time in pulse electro-deposition resulting into unique composition and microstructure of the coating being deposited.
Pulse current electro-deposition (PED) is done using a Potentiostat/Galvanostat/FRA unit of model PARSTAT 2273 manufactured by Advanced Electrochemical Systems. The electro-deposition is carried out at room temperature in a nickel bath. The composition of the bath is given in Table 2. The set-up for pulse current electro-deposition showing all the three electrodes inserted in a glass beaker is connected to Potentiostat as shown in Figure 1. Terminals of the Potentiostat/galvanostat/FRA e.g. working electrode was connected to sample, counter electrode with 99% pure nickel strip and a saturated calomel electrode (SCE) as a reference electrode. The pulse frequency is 5 Hz and the on and off time is 1 s each.

| Substrate   | Nickel Bath (gm l⁻¹) | Bath Temp(°C) | pH |
|-------------|----------------------|---------------|----|
| HSLA Steel  | Nickel sulphate     | 200           | 25 | 4  |
|             | Sodium chloride     | 20            | 30 | 1.5|
|             | Boric acid          | 30            | 25 | 4  |
|             | Saccharin           | 1.5           | 4  |    |

The pulse current electro-deposition was performed at different current densities of 7 A/dm² - 50 A/dm². The solution/electrolyte used for carrying out nickel deposition was prepared as given in Table 2.
2.4 Observation of microstructures of the substrate and nickel deposits.

A Leica DM2500M optical microscope with an in-built QWIN3 image analyser and a scanning electron microscope (SEM) model Hitachi S-3000N were used to observe the microstrutures of the HSLA steel and the nickel deposits.

2.5 X-Ray Diffraction (XRD).

X-ray diffraction (XRD) was carried out to acquaint with the phases present in the alloy of different tempers. XRD study was carried out using a PANalyticalX Pert Pro Basic X-ray diffractometer. A scanning electron microscope (SEM) model HITACHI S-3000 N with an EDAX attachment unit is used for microstructural observation of nickel coating and for elemental analysis as well.

2.6. Electrochemical study.

Electrochemical polarisation study was carried out on the nickel coated HSLA steel at room temperature using a computercontrolled potentiostat/galvanostat/FRA model of PARSTAT 2273 Advanced electrochemical systems model with an inbuilt Power suite software. The experiments were performed at room temperature in 3.5 wt. % NaCl solution which is a standard saline solution used to study the corrosion behaviour of steel and Al-alloys. The standard three electrodes configuration: saturated calomel electrode (SCE) as a reference, platinum electrode as counter and the sample as the working electrode have been used for potentiodynamic polarisation study of the nickel coated steel in 3.5 wt. % NaCl solution. Polarisation scan was carried out towards more noble value at a scan rate of 0.5mV/s, after 10 minutes of immersion of sample into the electrolyte or allowing a steady state potential to develop. Polarisation tests for each sample were repeated at least twice to confirm the reproducibility of the test results.

3. Results and Discussions

3.1. Optical Micrographs.

Figure 2 shows the microstructure of the HSLA steel (as-received HSLA alloy plate was solutionised at 1050°C for 3 hours followed by air cooling). Microstructure reveals mostly fine ferrite grains and a small amount of very fine pearlite at the grain junctures. Figures 3 and 4 show the micrographs of the nickel deposit carried out at pulse current density 10 A/dm²and the coating thickness, respectively. The micrograph (Figure 3) displays fine grains structure containing a few numbers of pits as well.
3.2. **SEM and Energy Dispersive X-Ray Analysis.**

Figure 4, the SEM micrograph displays the coating thickness approximately 100 μm produced by the pulse current metal deposition. The figure 5 and figure 6 exhibit the SEM microstructure of the nickel coating at current densities of 30 A/dm² and 50 A/dm². The microstructures shown in the figures 4-5 reveal that the coating consists of polyhedral grain of nickel. Further, there is presence of prominent cracks (Figure 6) in the coating done at current density 50 A/dm², but the tendency of cracking of less when pulse coated at current density of 30 A/dm², although a very few fine cracks are visible (Figure 4). This suggests that pulse current electro-deposition using a proper and appropriate current density will results in producing submicron and or nano-structure nickel deposit on steel substrate.

Figure 7 shows the EDAX analysis done at different positions on the nickel coating. EDAX analysis confirms the presence of nickel, carbon, oxygen, manganese and iron. The presence of nickel is evident in all the points as shown in the figures 7(b-e).
The percentage of the nickel is quite high as compared to other elements present, which is as obvious. Line scan EDAX analysis was made as shown in figure 8(a-b). The figure 8b also shows the presence of all these elements, and the nickel count is the maximum amongst all the other elements. Small quantity of Mn and Fe present in the coating may be considered as impurities. Further, the nickel coating is not uniform enough and contains numerous cracks as well and these account the peaks of Fe and Mn arisen from the substrate.
Table 3. Weight percentage of elements obtained by EDAX analysis

| Element | C   | O    | Mn  | Fe   | Ni  |
|---------|-----|------|-----|------|-----|
| Point 1 | 0.47| 5.69 | 0.00| 10.45| 83.39|
| Point 2 | 0.39| 18.04| 0.47| 8.00 | 73.09|
| Point 3 | 0.40| 2.3  | 0.08| 9.00 | 88.21|
| Point 4 | 0.00| 8.92 | 0.09| 8.00 | 82.99|

Figure 7. EDAX: Nickel percentage at four different points.

Figure 8. EDAX line scan on the (a) microstructure of nickel coating and (b) elemental counts of the coating.
3.3 X-Ray Diffraction (XRD).

Figure 9 shows the X-ray diffractograms using CuKα radiation of the coating done at different current densities. The diffractograms showing the peaks of Ni(111) and Ni(002) confirms the presence of nickel in the coating.

![X-ray diffraclgram](image)

**Figure 9.** X-ray diffractograms of nickel deposits produced by pulse electro-deposition

3.4 Potentiodynamic Polarization.

Figure 10 shows the potentiodynamic polarization curves of the nickel deposit coated by different pulse current electro-deposition technique on HSLA steel in 3.5 wt. % NaCl solution. The shape of the polarization curves (Figure 10) is similar for all the nickel deposits at different densities. In all the cases, the cathodic and anodic branches of the curves show typical E-i characteristics of a metal and or alloy in 3.5 wt.% NaCl solution at near neutral pH. The cathodic branches of the polarization curves showed the typical Tafel behaviour enabling to evaluate cathodic slope or Tafel constant ($\beta_\text{c}$) as well as corrosion current density ($i_{\text{corr}}$) by Tafel extrapolation method. The anodic branch of the polarization curves in 3.5 wt. % NaCl and 3.5 wt.% NaCl solutions exhibited typical active metal dissolution behaviour with an initial sharp increase of corrosion current density with applied anodic overvoltage. These polarisation curves clearly display that the corrosion current density ($i_{\text{corr}}$) is very low when the deposition was carried out at 20 A/dm$^2$ compared to pulse deposition carried out at other current densities. This could be attributed to the fact that the nickel deposition at the 20 A/dm$^2$ of current density is free from cracking. However, the higher corrosion current ($i_{\text{corr}}$) for the nickel deposits at other pulse current deposition is due to the fact that the deposits are not free from cracking, as observed in figure 4 & 5. Thus, it can be inferred from the polarisation curves and SEM micrographs that an optimum pulse current density will result in producing defect free micro and/or sub-micron nickel deposit with an improved corrosion resistance.
Figure 10. Potentiodynamic polarization curves of nickel coating in 3.5 wt. % NaCl solution.

Table 4. Electrochemical data of the Ni-coating on HSLA steel in 3.5 wt. % NaCl solution.

| Coating Current Density | Environment       | $E_{\text{corr}}$ vs SCE (mV) | $i_{\text{corr}}$ (µA/cm$^2$) | $\beta_c$ (mV/dec$^{-1}$) | $\beta_a$ (mV/dec$^{-1}$) |
|-------------------------|-------------------|-------------------------------|-----------------------|----------------|------------------|
| 7                       | 3.5 wt. % NaCl solution | -444                          | 34.53                 | -453           | 260              |
| 10                      |                   | -388                          | 20.67                 | -920           | 60               |
| 20                      |                   | -417                          | 0.02                  | -394           | 20               |
| 30                      |                   | -515                          | 89.5                  | -648           | 138              |
| 50                      |                   | -462                          | 31.7                  | -490           | 210              |

$E_{\text{corr}}$ is the corrosion potential and $i_{\text{corr}}$ is the corrosion current density at $E_{\text{corr}}$ determined by Tafel extrapolation technique and $\beta_c$ and $\beta_a$ Tafel constants.

4. Conclusions
Pulse current electro-deposition method at different current densities in a suitable nickel bath exhibited micro-or sub-micron nickel deposit over a HSLA substrate. Electro-deposition at current densities of 20-30 A/dm$^2$ was found out to be crack free compared to coating deposited at higher current densities.
densities. The coating done at lower current density also does not seem to be very prominent enough as the deposit is becoming very thin. XRD and EDAX analyses confirmed the presence of nickel deposit. Potentiodynamic polarisation study of the nickel coating in 3.5 wt. % NaCl solution exhibited characteristics $E-i$ curves. Further, it has been observed that the corrosion rate is least of the nickel coating when pulse electro-deposition was performed at current density of 20 A/dm$^2$.

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