

Research Article

Comparison of Corrosion Behavior of Electrochemically Deposited Nano-Cobalt-Coated Ni Sheet

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Corrosion behavior of nano-cobalt-coated Ni sheet was compared with pure Ni and 20% Fe-Ni alloy sheet using potentiodynamic polarization and linear polarization technique in 0.1 M NaCl solution at room temperature. Results showed that corrosion resistance properties of nano-Co-coated Ni sheet were almost same as that of pure Ni sheet, however corrosion resistance of 20% Fe-Ni sheet was decreased significantly. Pitting potential of 20% Fe-Ni sheet was subsequently decreased as compared to pure Ni sheet as well as nano-cobalt-coated Ni sheet. SEM/EDS analysis of the corroded surfaces showed that both pure Ni and nano-cobalt-coated Ni sheet did not show any appreciable corrosion however significant corrosion was observed in the case of 20% Fe-Ni sheet.

1. Introduction

Among different alloys used for coating applications, Ni-based alloys are very successful owing to their remarkable mechanical, adhesion, tribological, and corrosion properties as well as good thermal stability. Cobalt, as an alloying element in Ni-base alloys, is considered to contribute in many different ways, in improving their properties [1] and also these alloys can be prepared using simple methods such as electrodeposition technique. This method can be used in the development of Ni-Co nanostructured coatings with improved properties. It is preferred because it is scalable, can easily overcome shape limitations, is economically viable, and produces pores-free and high purity nanostructures [2].

There have been few investigations on binary Ni-Co systems along with ternary additions, such as oxides [3, 4], nitrides [1, 5], carbides [6–8], and carbon nanotubes [9]. Some researchers also successfully produced Ni-Co nanowires [10]. However, there are not many investigations on the corrosion performance of such alloys and possible ways to improve their performance in variety of environments. For example a lot of work has been done and still being done to understand the corrosion behavior of passive metals by investigating the passive films formed on their surface at

nanoscale. Passive films found in Fe-Cr alloys and high-speed steels show superior resistance than carbon steels because of the presence of spheroidal nanoparticles of ~40 nm [11, 12]. Same has been reported for many other alloys such as for Al-Mg alloys; it has been found that the nanoprecipitates of Al_3SiC can significantly affect the passivity of these alloys [13, 14]. Also thermally sprayed coatings of stainless steel, nickel, and nickel alloys are being used to maximize the corrosion resistance. It is clearly observed from the extensive studies on steels and Ni-based alloys that the best corrosion resistance was found on nickel with small particle size of 16–44 μm .

With coatings on microscale, pitting and erosion-corrosion is a serious issue, and it is expected that if a nanocrystalline coating of nickel is applied, even a higher resistance to corrosion can be achieved [15]. Nano-sized $\beta\text{Ni}(\text{OH})_2$ electrolyte exhibits an excellent electrochemical performance which is markedly superior to spherical $\beta\text{Ni}(\text{OH})_2$ [16]. It has been reported that electrodeposited amorphous alloys has better corrosion resistance and amorphous Ni-Co-based alloy which showed better pitting corrosion resistance [17]. In Ni-Co-P amorphous alloy system, presence of Co showed a significant effect in improving the corrosion resistance of the alloy [18] and another study suggested that nanostructured

TABLE 1: Chemical composition of bath used for electrodeposition of nano Co-coated Ni sheet.

Chemical Addition	Amount (g/L)
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	30
H_3BO_3	15
NaCl	10

electrodeposited Co and Co-P alloy can improve the corrosion behavior significantly [19].

Therefore, it is an important area of investigation, and the objective of this study was to investigate the corrosion behavior of electrodeposited nano-Cobalt-coated Ni sheet, pure Ni foil, and 20% Fe-Ni in terms of corrosion rate values as well polarization resistance (R_p).

2. Experimental Details

Three different materials, that is, pure Ni, nano-cobalt coated Ni, and 20% Fe-Ni, have been investigated for their corrosion performance during this study. The followings are the details of different techniques used for material preparation as well as electrochemical investigations.

2.1. Material Preparation. Nano-Co-coated Ni sheets were prepared with electrodeposition technique using different applied currents densities and additives in the deposition path. The bath temperature was maintained at 35°C , and electrolyte-containing beaker was placed for about 20 minutes in the bath before testing, to assure thermal equilibrium. A magnetic stirrer was operated throughout the process to facilitate dispersion of the electrolyte. Two anodes were used consisting of 99.95% Co and 99.95% Ni. Table 1 shows the base composition of the bath used in these experiments to prepare nano-cobalt-coated Ni sheet.

The pH measurements were constantly performed using a calibrated digital pH (meter). Pulsed current was used in order to avoid any stress buildup in the coatings as well as to promote the nucleation of grains. Duty cycle was fixed at 50% (pulse on time and off time was set to 5 ms). Bath composition (Table 1) was used with an average current density $\sim 2 \text{ A/dm}^2$. A well-polished Ni cathode was used for depositing the nano-Co film to prepare nano-cobalt-coated Ni sheet.

2.2. Electrochemical Investigations. Potentiodynamic polarization along with linear polarization technique was used to evaluate the corrosion performance of the prepared coatings. Experiments were carried out in a three electrode flat cell (K0235, Princeton Applied Research). An Ag/AgCl electrode was used as a reference electrode, and counter electrode was made of platinum. The investigations were carried out with an exposed working electrode area of 1 cm^2 in 0.1M NaCl solution at room temperature. Specimens were degreased in benzene and cleaned ultrasonically in DI water prior to electrochemical experiments. The experiments were performed using PCI4/750 Gamry potentiostat and repeated several

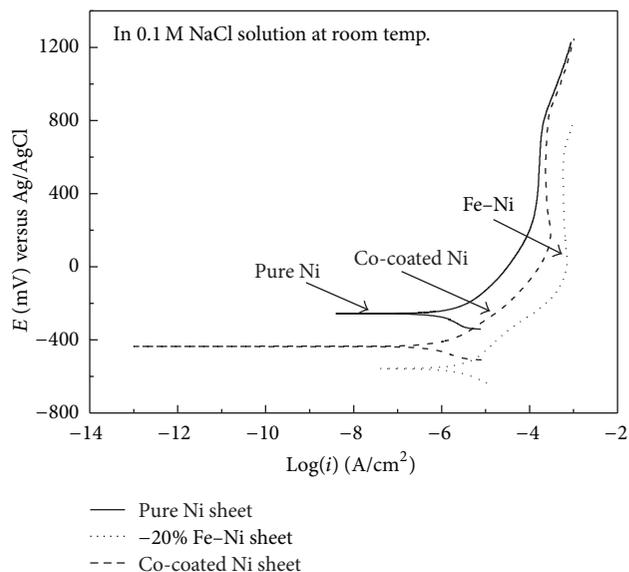


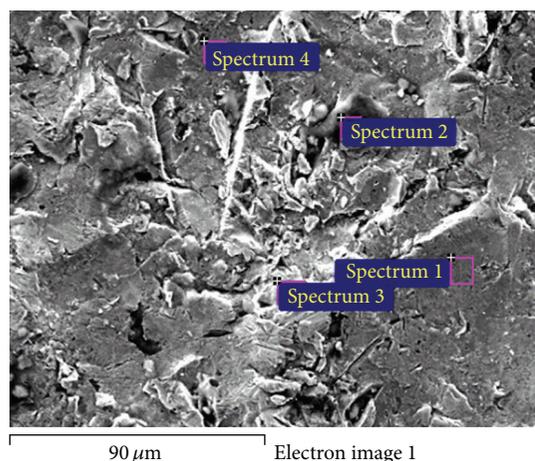
FIGURE 1: Potentiodynamic polarization response of the alloys in 0.1 M NaCl solution at room temperature.

times to ensure the reproducibility of the data. DC105 corrosion software was used to analyze the data, and polarization experiments were performed at a scan rate of 0.1 mV/s to measure the polarization resistance values (potentials were -20 mV and $+20 \text{ mV}$ versus open circuit corrosion potential (OCP)). SEM/EDS analysis was carried out after corrosion tests to investigate the chemical composition of corrosion products and their morphology.

3. Results and Discussion

3.1. Potentiodynamic Polarization Response of the Alloys. Figure 1 shows the potentiodynamic polarization response of the three alloys in 0.1 M NaCl solution at room temperature. Pitting potential (E_{pit}) value was taken at the potential, where there was a sudden and substantial increase in corrosion current density of the alloys. Overall all the alloys showed a stable passive range; however at higher potentials current has started to increase slowly. So those critical points were taken as pitting potential of the alloys. It was found that pitting potential was almost similar for pure Ni sheet and that of nano-Co-coated Ni sheet, that is, $1560 \text{ mV}_{\text{Ag/AgCl}}$, followed by 20% Fe-Ni sheet, which was the lowest, that is, $798 \text{ mV}_{\text{Ag/AgCl}}$. Evidently, pure Ni sheet and nano-Co-coated Ni sheet exhibited higher resistance to localized corrosion as compared to 20% Fe-Ni in terms of pitting potential. These results demonstrate that the resistance to pitting corrosion or the pitting potential of the alloys was not affected by coating with nano-Cobalt alloy; rather it performed almost similar to that of pure Ni alloy. However the addition of iron decreased the corrosion resistance.

The corrosion potential of pure Ni sheet is higher than rest of the alloys (Ni sheet = $-256 >$ nano-Co-coated Ni sheet = $-436 >$ 20% Fe-Ni = -557) $\text{mV}_{\text{Ag/AgCl}}$, respectively. These results are in agreement with already reported findings



Spectrum	C	O	Ni	Total
Spectrum 1	1.22	1.57	97.21	100
Spectrum 2	6.64	5.28	88.08	100
Spectrum 3	1.89	1.61	96.5	100
Spectrum 4	1.17	1.54	97.29	100

FIGURE 2: SEM/EDS of the pure Ni sheet after corrosion tests in 0.1 M NaCl temperature.

that corrosion potential of materials is related with Ni content of the alloys. As Ni is a noble element and hence will increase the corrosion potential, as shown in Figure 1 [20]. The stage of pitting includes passive film breakdown, metastable pitting, initiation and repassivation, and stable pit growth. The metastable pitting stage is thought to be the most important stage because only pits that survive this stage could become stable growing pits. Comparison of the passive current density showed similar trend observed for pitting potential. Passive current density of pure Ni and that of nano-Co-coated Ni sheet was almost similar. However the addition of iron increased the passive current density of 20% Fe-Ni sheet, suggesting a less stable and less protective film on this alloy as compared to rest of the alloys.

These results of potentiodynamic polarization were further confirmed by polarization resistance experiments in Section 3.2.

3.2. Comparison of the Polarization Resistance. Linear polarization resistance experiments were performed for all three samples, that is, pure Ni sheet, 20% Fe-Ni, and nano-Co-coated Ni sheet, and subsequently data was analyzed. Table 2 showed the polarization resistance (R_p) as well as corrosion rate values of these specimens.

It is clear from the results presented in Table 2 that pure Ni has the highest corrosion resistance in 0.1 M NaCl solutions, having polarization resistance (R_p) value of 106.9 K Ω . It was followed by nano-Co-coated Ni-sheet with R_p value of 102.6 K Ω and 34.2 K Ω for 20% Fe-Ni foil, respectively. The comparison of corrosion rate values showed that both the pure Ni sheet and nano-Co-coated sheet have very similar

TABLE 2: Comparison of polarization resistance and corrosion rate of three samples after corrosion tests in 0.1 M NaCl solution.

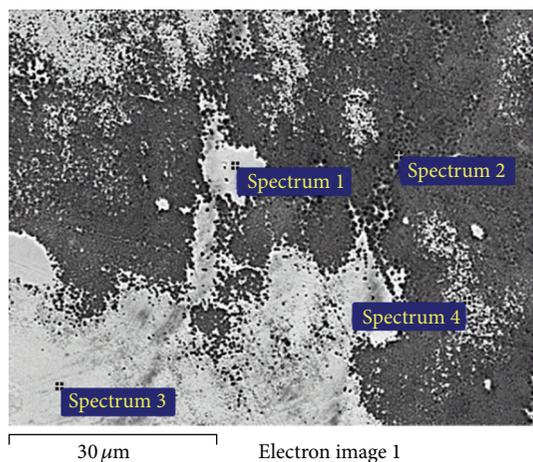
Materials	Polarization Resistance (K Ω)	Corrosion Rate (mmpy)
20% Fe-Ni sheet	34.26	0.3
Pure Ni sheet	106.9	0.003
Nano-Cobalt coated Ni sheet	102.6	0.003

corrosion resistance, that is, 0.003 mmpy for both of the above materials. However 20% Fe-Ni foil showed high corrosion rate value, that is, 0.3 mmpy as compared to the other two materials.

These results suggest that nano-Co-coating of a Ni sheet did not decrease the corrosion resistance properties of pure Ni, while addition of iron in Ni decreased its corrosion resistance properties as compared to pure Ni and nano-Co-coated Ni sheet. These results can be further confirmed based on SEM/EDS analysis of the specimens after corrosion tests.

Figure 2 shows the surface of pure Ni sheet after electrochemical corrosion tests in 0.1 M NaCl solution. The Ni sheet looks in very good shape and there is no visible degradation as can be confirmed from SEM image. EDS data presented in Figure 2, showed that composition of the surface remains almost same at all locations. Some oxides of nickel are present; however Nickel oxides are good considering their corrosion resistance behavior. It has been reported [21, 22] that the passive film on Ni composed of duplex layered structure with the inner NiO and outer Ni(OH)₂, which contribute in improving the corrosion resistance properties. Ni is not only an important austenite stabilizing element in stainless steels, but also has effects on the corrosion resistance of the alloy. It is known that Ni can lower the critical current density and elevate the pitting potential of austenitic alloys. Stress corrosion cracking susceptibility of Fe-Cr-Ni alloy is significantly dependent on Ni content. The photocurrent spectra for the passive films formed on Fe-20Cr-15Ni alloys showed very similar behavior to that for the passive film on Fe-20Cr at low photon energy region below 5 eV, showing that the base structure of the passive films formed on Fe-20Cr-15Ni was found to be Cr-substituted γ -Fe₂O₃. However, the photocurrent spectra for the passive films formed on Fe-20Cr-15Ni exhibited additional spectral components induced by Ni oxide (NiO). Regardless of the composition of alloys, the Mott-Schottky plots for the passive films showed *n*-type semiconductivity with shallow and deep donors, which are associated with oxygen vacancy and Cr⁶⁺ ions, respectively. Comparing with the passive film of Fe-20Cr, the density of shallow donor was decreased by addition of Ni and density deep donor was increased, which means corrosion resistance properties were increased considerably, due to incorporation of Ni²⁺ by substituting Fe³⁺ in spinel structure of γ -Fe₂O₃.

Figure 3 shows the SEM/EDS of the nano-Co-coated Ni sheet after the corrosion tests. It is to be emphasized that Co is very intact on the Ni sheet and no significant damage is caused by the corrosion tests under given conditions. Cobalt was above 90% on all areas on the surface. Some oxidation



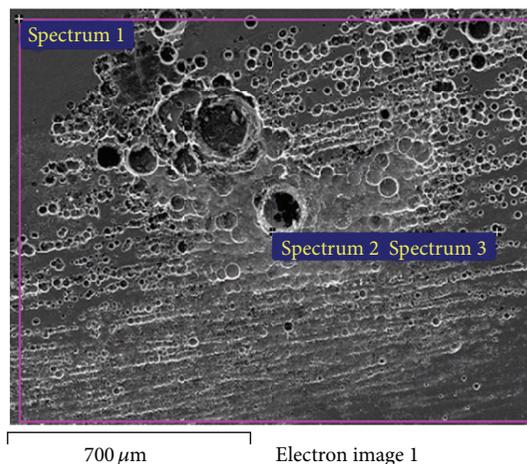
Spectrum	C	O	Co	Total
Spectrum 1	0.27		99.73	100
Spectrum 2	1.82	6.96	91.22	100
Spectrum 3	0.28		99.72	100
Spectrum 4	0.62	6.07	93.31	100

FIGURE 3: SEM/EDS of the nano-Co-coated Ni sheet after corrosion tests in 0.1 M NaCl solution.

occurred; however cobalt oxide has good corrosion resistant materials [21, 22]. Also it appears that there might be some randomly distributed metastable sort of pits, which died away by repassivation, and surface is almost completely covered with cobalt coating [23].

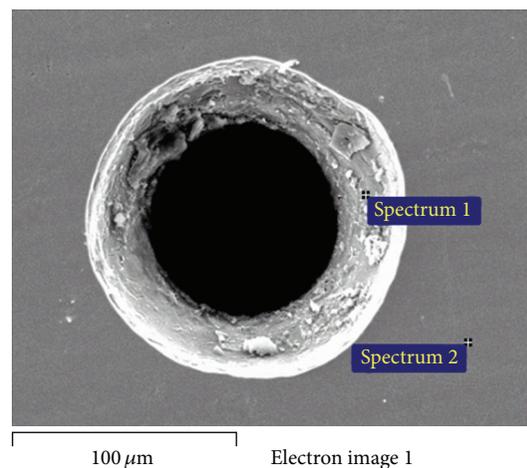
Figures 4(a) and 4(b) show the SEM/EDS of 20% Fe-Ni foil after corrosion tests. Significant corrosion has been observed at different locations and it was mainly iron oxide. It is clear from Figure 4(b) that pits were interconnected, which has increased the corrosion rate/dissolution rate of this coating. These results are in agreement with those presented in Section 3.2, where it was concluded that pure Ni and nano-Co-coated Ni sheet both exhibited good corrosion resistance properties. However the induction of Fe in Ni decreased the corrosion resistance properties as was clear from Figure 4.

Another important comparison is of free corrosion potential, and it was found from Figure 1 that nano-Co-coated Ni sheet has the lowest E_{corr} (-0.48 V SCE), followed by 20% Fe-Ni sheet (-0.38 V SCE) and pure Ni sheet (-0.20 V SCE), respectively. Similar results have been reported previously by Aledresse and Alfantazi [24], and they observed the E_{corr} ; for nanocrystalline Co (-0.574 V_{Ag/AgCl}) specimen was more cathodic than that of the conventional polycrystalline Co, which was in contrast to the nanocrystalline pure Ni system studied by Rofagha et al. [25]. The authors [25] reported that there is a significant anodic shift in E_{corr} for the nanocrystalline Ni with respect to its conventional crystalline counterpart. This was interpreted to be the result of the enhanced catalysis of the hydrogen reduction reaction at the surface of nanocrystalline Ni due to the large quantity of intercrystalline defects such as grain boundaries and triple



Spectrum	C	O	Fe	Ni	Total
Spectrum 1	1.07	4.99	21.08	72.86	100
Spectrum 2	1.05	9.59	18.38	70.98	100
Spectrum 3	1.57	5.46	20.75	72.22	100

(a)



Spectrum	C	O	Fe	Ni	Total
Spectrum 1	1.54	18.32	19.69	60.46	100
Spectrum 2	0.39		22.75	76.85	100

(b)

FIGURE 4: (a) SEM/EDS of the 20% Fe-Ni sheet after corrosion tests in 0.1 M NaCl solution and (b) SEM/EDS of pit morphology and composition in 20% Fe-Ni sheet after corrosion tests in 0.1 M NaCl.

junctions. This inconsistency is probably due to the difference in crystalline structure between Ni and Co. Like many other transition metals, the cobalt surface is covered by a native barrier film, which consists mainly of CoO or hydrated oxide CoOH_2O [26]. Indeed, the potentiodynamic polarization of the polycrystalline cobalt and cobalt-based alloys has been reported on numerous occasions. For example, Badawy et

al. [27] studied the anodic polarization of the conventional cobalt in acidic, neutral, and alkaline solutions. They considered that in acidic solutions, the passive film is unstable, and hence higher rates of corrosion were recorded. This corrosion process is preceded by a pure chemical dissolution of the native cobalt oxide (CoO) or the hydrated oxide (CoOH₂O). There are no significant differences between the chemical compositions of the nanocrystalline and polycrystalline Co, so it can be speculated that the cathodic shift of nanocrystalline Co may be due to the microstructural differences (i.e., intercrystalline volume fraction) between the nanocrystalline and conventional polycrystalline Co. In the low potential region, corrosion attack is initiated more easily at defects sites (i.e., grain boundaries and triple junctions). The higher volume fraction of the intercrystalline constituent in nanocrystalline materials provides active sites due to the fact that grain boundaries and triple junctions possess higher energies than the crystal surface.

So based on above discussions and experimental results presented, it can be suggested that electrochemically deposited nano-Co coatings can be very useful in improving the corrosion performance, and results here have shown that their performance was almost similar to that of pure Ni sheet. On the other hand, iron in an alloy will degrade the corrosion performance.

4. Conclusions

Results of this work can be concluded as follows:

- (1) Both pure Ni sheet and nano Co-coated Ni sheet exhibited very good corrosion resistance properties measured in terms of pitting potential (E_{pit}) and polarization resistance (R_p).
- (2) Corrosion resistance of 20% Fe-Ni sheet was decreased significantly as many pits appeared after corrosion tests.
- (3) SEM/EDX analysis showed no appreciable corrosion of pure Ni sheet as well as of nano-Co-coated Ni sheet; however 20% Fe-Ni exhibited significant corrosion.

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