

Evolution and Anticorrosion Properties of Ni-Cu Thin Film Coatings on Low Carbon Steel

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Nickel-copper alloys electrolytic co-deposited on carbon steel and their recrystallization thermal permanence under various processed parameter were investigated. The influence of plating variables such as time of deposition, current, bath composition and pH on the coating properties, structural modification and electrochemical oxidation were investigated with the help of SEM/EDS and potentiodynamic polarization technique. The adhesion and strengthening behaviour on the coating was evaluated by diamond based Dura scan micro-hardness tester. The thermal stability was studied at 180 °C. From the result, modified morphology with perfect crystal growth was obtained. The corrosion resistance as well as micro-hardness of Ni-Cu alloy coatings improved significantly above the substrate and the annealed deposit. After thermal analysis, the surface structure of the deposited sample affirms the presence of pinhole which was attributed to the furtherance of oxidation process leading to internal cracks.

Keywords: Corrosion, Microstructure, Thermal oxidation, Thin films.

INTRODUCTION

Nickel extensive application for advancement of technological materials is enormous due to their predominant characteristic such as good corrosion properties, wear resistance and improve hardness. The electrodeposits of nickel on mild steel possess crucial application because of their passive thin film layer properties and oxidation stability at ambient temperature application [1-6]. At present, several efforts has been made in advancing the unique properties of nickel-copper plated alloys through inoculation and liquid melt technique; composite induced coating [6-12]. Although several researchers has worked on the mechanism of this electrolytic co-deposition and their photo-characterization since the properties of thin film deposited layers significantly depend on the structural behaviour [11-15].

Most recent development is the study of the behaviour of alloy beyond the ambient region. It is expected that some co-deposition coating perform above their room application. It has been recognized that the influence of heat treatment has a great impact on the microstructural recrystallization, thermal stability and the micro hardness trend of the coating [3,16-19]. However, in this study, an attempt was made to verify thermomechanical properties, microstructure, anticorrosion resistance and micro hardness response of Ni-Cu alloy after thermal treatment at 180 °C.

EXPERIMENTAL

Prepared mild steel sheet with accurate dimension of 40 mm × 20 mm × 1 mm were used as substrate, mechanically polished with 1200, 2000 grade level and further degreased immediately, cleaned with ethanol and dried. The anode was zinc sheets of 30 mm × 20 mm × 1 mm. The cathode mild steel specimens have a weight composition as described in Table-1 and zinc anode composition of (99.99 %).

The mild steel substrate prepared was dipping into 10 % HCl solution for 10 s followed by rinsing in distilled water. All chemical used are analytical analaR grade chemicals and deionized water were used in all processes to prepare the plating solution at 40 °C. The bath formulation used was described for Ni-Cu alloy coating is shown in Table-2. The prepared cathode and anodes were connected to the direct current *via* a rectifier at current density of 1-5 to 2 A for 10 min. The distance between the anode and the cathode and the immersion depth was kept constant. Thereafter, the samples were rinsed in water and dry. The coating samples were taken for structural studies and elemental analysis of the plated samples using a TESCAN scanning electron microscope with an attached energy dispersive X-ray analyzer (SEM/EDS) and an optical microscope (OM). Energy dispersive X-ray analyzer point analysis was used to observe the elemental composition. The adhesion and topography of coated surface was observed

TABLE-1
NOMINAL CHEMICAL COMPOSITION (wt %) OF MILD STEEL SUBSTRATE

Element	C	Mn	Si	P	S	Al	Ni	Fe
Composition (%)	0.15	0.45	0.18	0.01	0.031	0.005	0.008	Balance

with the help of atomic force microscope. In addition to this, is the heat treatment process of the coated alloy at 180 °C for 2 h to improve the mechanical properties and attest to the stability behaviour of the materials using diamond based duramicrohardness tester. The measurements were done on the coated and heat-treated coated alloy at five intervals for 20 μm distance and after which the average were obtained.

TABLE-2
BATH COMPOSITION OF Ni-Cu ALLOY CO-DEPOSITION

Composition	Mass concentration (g/L)
CuSO ₄	100
Boric acid	10
Glycine	10
NiSO ₄	100
pH	4.8
Voltage	1.5-2.0 A
Time	5, 10 min
Temperature	40 °C

TABLE-3
FORMULATED BATH COMPOSITION OF Ni-Cu COATING

Sample order	Material sample	Time of deposition (min)	Current density (A/cm ²)
Blank	–	–	–
Sample 1	Ni-Cu	10	2.0
Sample 2	Ni-Cu	5	2.0
Sample 3	Ni-Cu	10	1.5
Sample 4	Ni-Cu	5	1.5

The diamond based Dura-scan microhardness tester was used to evaluate the mean value microhardness of the deposit in an equal interval range. Further on this is the electrochemical study with Autolab PGSTAT 101 Metrohm potentiostat/galvanostat. The electrochemical behaviour of the deposited sample and as-received mild steel are tested in 3.65 wt. % NaCl solution. The surface area of working cathode is 1.2 cm² with a fixed run potential between -1.5 V to + 1.5 mV with scan rate of 0.016 V/s.

RESULTS AND DISCUSSION

Structural and thermal stability: Fig. 1 shows the surface morphology of prepared as-received mild steel sample. Figs. 2 and 3 revealed electrodeposited Ni-Cu induced additive under prepared formulation in Table-2. From the SEM/EDX images, a strong alloy formation with good surface finish was observed in both Ni-Cu 5 min at 1.5 A and Ni-Cu 10 min at 1.5 A in the presence of the admixed additive.

The surface structures of Ni-Cu 10 min at 1.5 A/cm² deposited show a preferred and visible crystal in the presence of boric acid and glycine. The evidence of attested adhesion and fine grain in Fig. 3 against Fig. 2 with 5 min time of deposition was quite obvious taking reference from [16-18] previous studies; that coating variable such as time of deposition and potential undoubtedly influence crystal distribution and the

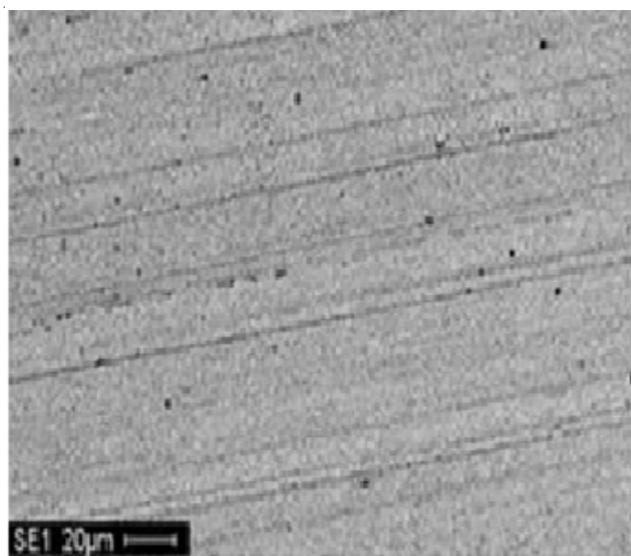


Fig. 1. SEM micrographs of as-received sample

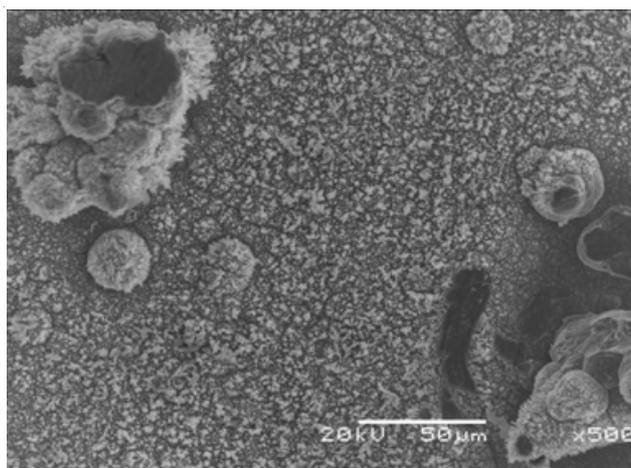


Fig. 2. SEM micrographs of [a] Ni-Cu 5 min at 1.5 A at X500 magnification

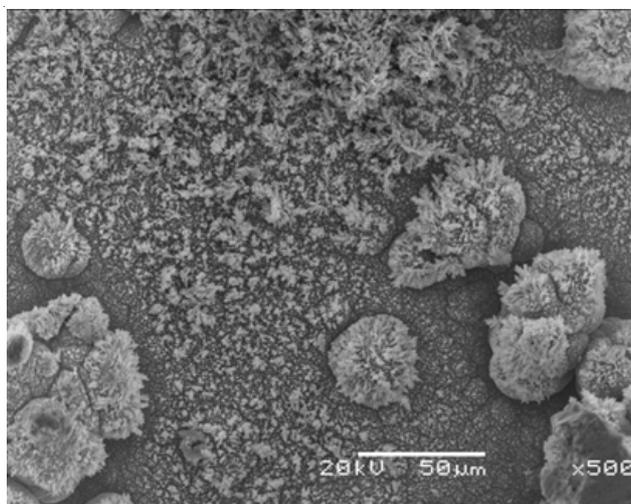


Fig. 3. SEM micrographs of Ni-Cu 10 min at 1.5 A at X500 magnification

morphological orientation of coating dispersed within prepared surfaces [13-16]. The homogeneous and consistence of the crystal particle in Fig. 3 are attributed to a good throwing power.

In addition to this, the expectation to see a crack deposit and poor adhesion behaviour in Fig. 2 but the reverse was the case instead, preferred surface diffusion rate as a result of this low potential convincingly results into build-up of atom with inhomogeneous nucleation rate. Although, unstable atom with different nucleation growth were found on the surface of the deposited sample in Fig. 2 as compare to that of Fig. 3 which are traceable to the deposition rate, less potential, effect of surfactant additive (glycine) and the metal ion arising from adsorbing metal ion provide a strong adsorption within particulate toward mild steel substrate [15,16].

In other hand, SEM study of the fabricated nickel alloy indicated obviously re-crystallization and thermal instability of the coated sample at 10 min (Fig. 4). In general the coating could not exhibit a consistence better surface adhesion as expected but rather a predominant pinhole and stress propagation within the interface. Though, the reason for this studies which is to checkmate and explore mechanical thermal failure mechanism of the coating at 180 °C might have been seen but the process of the thermal degradation and the cause of quick degeneration can be observed. In view of this, we observed that the adsorption of the additive in the bath that could generate a strong bond over the substrate was rather in sufficient to withstand thermal realignment and orientation without severe hole and crack. Secondly, the inconsistency of electron transfer rate during plating might as well results into this defect which is reported by Gomes *et al.* [16] that the effects of electron transfer rate of coating include blocking of active site by the sufficient or additives.

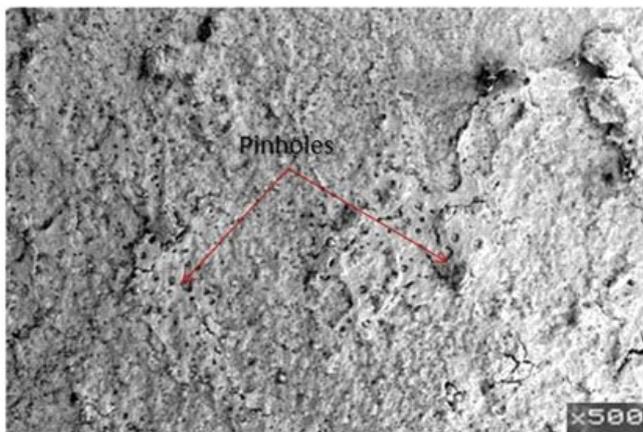


Fig. 4. SEM micrographs of heat treated Ni-Cu 10 min at 1.5 A at X500 magnification

Subsequently, Fig. 5 shows the effect of Ni-Cu at different applied current of 1.5 and 2.0 V in 5-10 min on mild steel. From the result, there is an increase in micro-hardness for sample deposited in 10 min-1.5 A/cm² against other coated sample and over the as-received. The indispensable reason for the pronounced improvement may be due to the modification in the structural trend and the influence of the low current density. Though, Srivastava *et al.* [1] affirmed that the mechanism of co-deposition can be trace to the fact that at lower

current density, the time to obtain a given thickness is more compared to the higher current density. With this fact, the crystal growth and preferred improved adhesion of 10 min-1.5 A/cm² over other is not dependent on throwing rate influence of current density but as well as the correlation of the time of deposition [1,2].

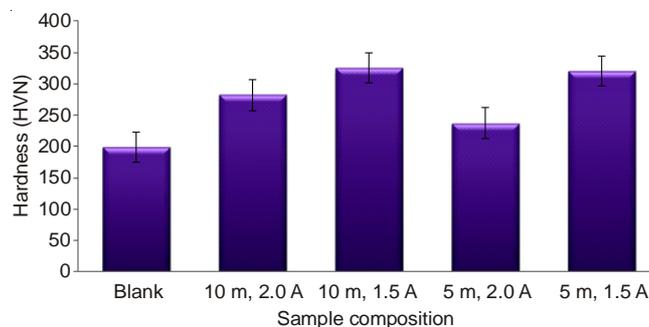


Fig. 5. Variation of micro-hardness of sample deposited at various time of deposition and current density

Besides the hardness properties of the coated sample at different degree of plating parameter is the effect of thermal induced hardness behaviour at 180 °C (Fig. 6). It is quite obvious to see a non-improvement of the hardenability of the coated heat-treated sample but rather a slight reduction. Though, it might be expected to envisage an increase in mechanical behaviour due to the thermal treatment and porosity found within the alloy surface. Meanwhile from open literature it was gathered that the compression stress could significantly improve the micro-hardness when it is much less than the ultimate strength of the coating.

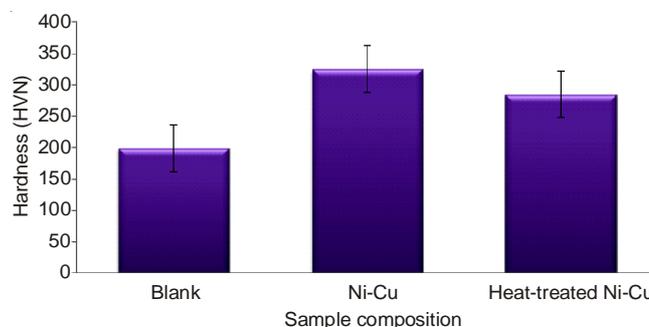


Fig. 6. Micro-hardness variation of coated and heat treated Ni-Cu 10 min at 1.5 A deposited for 180 °C

However, in another report [17] a new insight was unveiled that the defect such as porosity, macro-particle at the alloy surface will have detrimental effect on the mechanical properties. In this regards, our dependent factor for slight reduction can be linked to the poor adhesion of the coated sample and non-incorporation of particles to enhance and support the bath additive which could have been entrap by the cathode and forcefully provide hard coating [1].

Electrochemical studies: The linear potentiodynamic polarization electro-oxidation behaviour was assessed in 3.65 % sodium chloride medium for the coated and un-coatings sample as shown in Fig. 7 with tafel data shown in Table-4. It was obvious to see a successful improvement of corrosion resistance of all coated sample against the as-received substrate.

TABLE-4
LINEAR POTENTIODYNAMIC POLARIZATION PLOT OF COATED AND UNCOATED SAMPLES IN 3.65 % NaCl SOLUTION

Sample	b_a (V/dec)	b_c (V/dec)	E_{corr} , Obs (V)	j_{corr} (A/cm ²)	C_r (mm/y)	R_p (Ω)
10 min 1.5 A	0.049916	0.050579	-0.50953	4.39×10^{-9}	5.10×10^{-5}	2.49×10^6
5 min 1.5 A	0.042447	0.035509	-0.89415	2.19×10^{-5}	0.25416	463.43
10 min 2.0 A	0.027934	0.064379	-0.92366	2.93×10^{-5}	0.34023	383.09
5 min 2.0 A	0.031224	0.041489	-0.98922	3.30×10^{-5}	0.38321	288.95
Control	0.056793	0.26525	-1.0534	4.38×10^{-5}	0.50938	125.10

In general, the potential of the developed alloy resulted in an increased corrosion potential of -0.50953 mV doubled the as-received sample at -1.0534 mV. The corrosion rate and current density of the entire coated sample decreased significantly down the trend. This indicates that the admixed coatings matrixes are promising for the substrate material, if developed and deposited at certain potential of coating to enforce adequate adhesion.

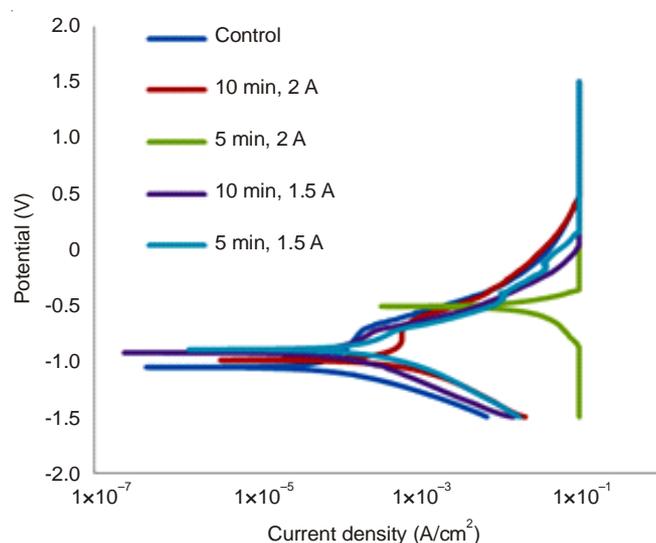


Fig. 7. Linear potentiodynamic polarization curve of coatings and uncoated samples in 3.65 % NaCl solution

More interestingly is the trend to which the coated material polarized. Although, corrosion resistance behaviour is connected to the morphological characteristic of a develop alloy [Gomes]. However, the anticorrosion resistance are tailored toward modify growth and passive layer derived from the deposit. The polarization resistance of the entire coated sample improved in the following trend $3 > 4 > 1 > 2 >$ as-received with the R_p values of $2.49E + 06 \Omega$, 463.43Ω , 383.09Ω , 288.95Ω , 125.10Ω and CR value of 5.10×10^{-5} mm/y, 0.25416 mm/y, 0.34023 mm/y, 0.38321 mm/y and 0.50938 mm/y, respectively.

Conclusion

This study represented the coating, thermal mechanism, corrosion stability and photo-structural behaviour of Ni-Cu that was thermally induced at 180°C .

• Ni-Cu coating exhibit a higher value of micro-hardness behaviour and slightly generated at 180°C compared to un-heat treated electrodeposited sample.

• From the morphological, hardness and electrochemical studies, Ni-Cu 10 min at 1.5 A/cm^2 alloy coating have demonstrated better performance than other coatings in terms of hardness and surface appearance.

• The electrochemical oxidation behaviour of coated sample performed excellently well at lower current density.

• The porosity and macro-crack observed at the interface of the heat-treated plated sample are as a result of thermal oxidation that arise as a result of insufficient additive or conditioning particle that could enhance block active site and enforce strong adhesion.

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