Electrochemical Deposition and Characterization of Co-P Alloy Coatings for Better Corrosion Protection

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Abstract: The present study reports the electrochemical deposition and characterization of Co-P alloy coatings from an electrolytic bath having sodium hypophosphite (NaH_2PO_2) and cobalt chloride ($CoCl_2$) as salts, potassium sodium tartrate (PST) as complexing agent, NH_4Cl as conducting salt and glycine as the brightener. Bath composition and operating variables were optimized by conventional Hull cell method for bright and uniform coating. Co-P alloy coatings were developed at varied current densities (1.0 A dm^{-2} to 4.0 A dm^{-2}), keeping pH at 8.5. The corrosion behaviors of Co-P alloy coatings were evaluated by electrochemical AC and DC methods in 3.5% NaCl solution. Scanning electron microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and X-ray diffraction (XRD) techniques were used to study the surface morphology, chemical composition and phase structure of alloy coatings, respectively. The electrodeposited alloy coatings are characterized by the presence of cracks on its surface. The compositional data revealed that wt. % of P in the deposit has increased with deposition current density. The XRD study demonstrated that solid solution of Co and P were formed, irrespective of the current density at which they are deposited. The observed facts stand for the reason that bath follows induced type of codeposition in the range of experimented current density. Corrosion study validated that Co-P alloy coating deposited at 1.0 A dm^{-2} is the most corrosion resistant, compared to all other current densities. The highest corrosion stability of Co-P alloy corresponding to 1.0 A dm^{-2} is attributed to the relatively compact structure, and inhibition effect of corrosion product formed on the surface, demonstrated by SEM and cyclic polarization study, respectively. Increase of corrosion rate towards high current density was analyzed in the light of composition, surface morphology and phase structure of alloy coatings, and results are discussed.

Keywords: Co-P alloy coatings, corrosion study, SEM, XRD and cyclic polarization study.

Introduction

Electrodeposition has numerous advantages including precise control over the thickness and microstructure of the film, a low operating temperature, and a low cost. This method has the potential to create alloy and particle-re-inforced composite coatings. The operational variables involved in electrodeposition, are like current control type, cathode current density, electrolyte pH, temperature etc. have a significant impact on the final properties of electrodeposit[1]. Cobalt (Co) and its alloys [2,3,4] formed either by electroless[5,6] or electrochemical deposition (ECD) methods have been investigated extensively for years, owing to their enhanced physical, chemical and magnetic properties. These properties are mainly used in the application of corrosion, wear resistance, soft magnetic materials for magnetic recording and electrocatalysts for hydrogen evolution and oxidation reactions. Due to excellent mechanical and wear-resistant properties of nano-crystalline Co and Co-based alloy coatings, they have recently been identified as a promising candidate materials for the replacement of hexavalent-Cr coating[6]. Recently, electrochemical deposition of Co-based alloy coatings have gained interest in both basic and applied research[7]. Co-P alloy coatings find extensive technological applications due to its appealing appearance, good corrosion and wear resistance.

Generally, physico-mechanical properties of binary alloy coatings, including their corrosion protection efficacy largely depends on their homogeneity and uniformity. Therefore, in the present study glycine was used as the additive to improve the uniformity, and in turn the corrosion resistance behavior of electrodeposited Co-P alloy coatings. The added glycine is expected to impart better brightness and uniformity to alloy coatings by bringing a significant change in nucleation process, and grain refining action. Therefore, the novelty of present work lies in understanding the effect of addition of glycine on the electro-crystallization of Co-P alloy coatings, and hence to study the effect of current density on corrosion protection efficacy of those alloy coatings. At the same time, it is well known that elements, such as P, Mo and W, cannot be electrodeposited by themselves independently from their electrolyte solution. However, these elements can be codeposited with Fe-group metals, like Fe, Co, Ni and Mn. This phenomenon is called induced codeposition, introduced first by Brenner[8]. Generally, deposition of Co-P alloy coating can be accomplished, using sodium hypophosphite (NaH_2PO_2) by two methods: i) electroless method where hypophosphite act as reduction agent, and ii) electrodeposition method where it acts as source of phosphorous[9]. The main disadvantage of electroless deposition is that the plating bath is inherently unstable. Hence, a delicate balance must be struck between the desire to have a stable bath and, yet, allow reasonably high rates of deposition. The rate of electroless deposition cannot be controlled as readily as the rate of electroplating, although some control can be achieved by varying the concentration of the reducing agent in the bath, and by controlling the rate of mass transport and the temperature. In addition, it is established that electrolyte solutions without NaH_2PO_2 are not suitable for electrodeposition of Co-P because of lower deposition rate and poor quality of the coatings. Thus, due to inevitability of using sodium hypophosphite (NaH_2PO_2) for getting satisfactory coatings, Brenner and his co-workers attempted for electrodeposition of Co-P alloy coatings using sodium hypophosphite(NaH_2PO_2) as a source of P ions, than it as a reducing agent. This procedure has improved the quality of coating by imparting change in mass transport process, rate of deposition and temperature, etc. Thus, electrodeposition of Co-P alloy coatings was made possible using less quantity of expensive sodium hypophosphite (NaH_2PO_2), compared to that in electroless plating. Consequent to this advancement initiated by Brenner and his co-workers, enormous amount of research publications are reported in the literature on electrodeposition of P alloys with Fe-group metals [8, 10,11].

In this direction, present study is to optimize a new electrolytic bath for electrodeposition of Co-P alloy on copper for its high corrosion resistance, using sodium hypophosphite (NaH_2PO_2) as the source of P (than as a reducing agent), using glycine as the additive. Here, Co-P alloy coatings have been developed at different current density, and their corrosion performances have been evaluated. Current density, the driving force of electroplating has been used as the tool to develop Co-P alloy coatings of highest corrosion resistance, using sodium hypophosphite (NaH_2PO_2). The compositional data, phase structure and surface morphology of the alloy coatings corresponding various current densities were characterized using SEM, EDX and XRD techniques. The experimental results of investigations were correlated with the morphology, chemical and phase composition of the coatings. Here, the work is mainly focused on the galvanostatic development of Co-P alloy coatings on copper at different current densities, and to optimize the current density for development of alloy coatings for better corrosion protection, to test in 3.5% NaCl solution (to mimic the intense corrosion medium).

1. Experimental

A new Co-P alloy bath having cobalt chloride, sodium hypophosphite, potassium sodium tartrate (Rochelle salt), ammonium chloride and glycine as bath constituents has been proposed. Individually, all chemicals were dissolved in double distilled water, then mixed thoroughly on stirring to ensure complete dissolution. The pH of bath was maintained to be 8.5 (on adding either dil. H_2SO_4, or NH_4OH depending on the requirement) using Micro-pH Meter (Systronics-362). The composition and operating variables were optimized for deposition of smooth, bright and uniform Co-P alloy coatings by conventional Hull cell method, as reported elsewhere [11]. The bath conditions and plating variables of

Table 1- The composition and operating variables of optimized Co-P alloy bath

Bath Ingredients	*Composition (g L^{-1})*	*Operating Variables*
Cobalt chloride ($CoCl_2$)	13.2	Anode: Graphite
Sodium hypophosphate (NaH_2PO_2)	22.5	Cathode: Copper sheet
Potassium sodium tartrate (PST) ($KNaC_4H_4O_6.4H_2O$)	104.5	Temp: 303 K
Ammonium chloride (NH_4Cl)	49.5	pH: 8.5
Glycine (NH_2-CH_2-COOH)	4.4	Current density range: 1.0-4.0 Adm^{-2}

optimized bath, arrived after Hull-cell experiment is reported in Table 1.

Thin coatings of Co-P alloy have been accomplished on copper substrate using optimized electrolyte, in a 200 mL capacity cubic cell (made of PVC material). A direct current (DC) power source (DC Power Analyzer, Agilent N6705A, USA) was used to drive the process of electrodeposition. Copper plates having dimensions of 7.5 cm × 2.5 cm × 0.2 cm were metallurgically polished to obtain a mirror finish, and then degreased with trichloroethylene (TCE), as solvent. During deposition, the anode and cathode were kept parallel at a distance of 5 cm. All depositions were carried out on same active surface area of (3.0 × 3.0 cm^2), keeping other part masked using cellophane tape at 303 K, and pH = 8.5 for 10 minutes, for comparison purpose. The polished substrate was electro-cleaned before plating, and then pickled in 0.5 M HNO_3. After deposition, coatings were rinsed multiple times with distilled water, and then dried in hot air, and finally desiccated, until further testing. The anti-corrosion behavior of all electrodeposited Co-P alloy coatings were studied by electrochemical AC and DC methods in 3.5% NaCl solution, to mimic aggressive corrosion environment. All electrochemical investigations of Co-P alloy coatings were carried out using a computer controlled Electrochemical Workstation, Potentiostat/Galvanostat (Biologic SP-150, Biologic Science Instruments, France), in a three-electrode cell by having the electrodeposited Co-P alloy as working electrode, platinum foil (having same active surface area as that of working electrode) as counter electrode, and saturated calomel electrode (SCE) as reference electrode. Electrochemical impedance spectroscopy (EIS) technique has been used as a powerful tool to explore information with regard to the electrode processes such as double layer capacitance, solution resistance and polarization resistance, etc. This technique basically consists of studying the impedance (AC resistance) over a range of frequency, on passing AC current of small amplitude[12]. The EIS study was made using AC pulse of small amplitude (±10 mV) in the frequency range of 100 kHz to 10 mHz. The corrosion rates (CR) of Co-P alloy coatings were evaluated by potentiodynamic polarization method in the potential window of ± 250 mV, around open circuit potential (OCP) at a scan rate of 1 mVs^{-1}, using Tafel's extrapolation method. In EIS technique, the best adaptable tool for studying the corrosion behavior of electrodeposited coatings is the Nyquist plot; and it has been used in the present study. The relative EIS responses of different Co-P alloy coatings were used to find their polarization resistance (Rp) values, using Nyquist plots.

The change in surface morphology and composition of alloy coatings with deposition current density were examined using Scanning Electron Microscopy (SEM) technique, interfaced with Energy Dispersive X-ray Spectroscopy (EDS) facility. The variation in the phase structure of alloy coatings with current density were analyzed through X-Ray Diffraction (XRD) technique (Rigaku, Miniflex 600, with CuK_α radiation having θ = 1.5418 Å, as the X-ray source).

3. Results and Discussions

The electrodeposition of Co-P alloy coatings was carried out using optimal bath at different current densities. *i.e.* from 1.0 A dm^{-2} to 4.0 A dm^{-2}. A sound, bright, and homogeneous Co-P alloy coatings were obtained in the experimented range of current density. It is well known that in case of induced type of codeposition, there is no consistent trend for change of reluctant metal content in the deposit, with change of current density. Consequently, structure-property relationship of Co-P alloy with change of current density is also quite vagarious. Keeping this in mind, in the present study of Co-P alloy coatings corresponding to different current density were first characterized for their basic properties, like, composition, surface morphology, phase structure and corrosion resistance.

3.1 Compositional analysis

The change of composition, thickness and corrosion rate (CR) of electrodeposited Co-P alloy coatings with deposition current density are analyzed, and are reported in Table 2.

From the composition data, it may be noted Co content of the deposit decreased and with increase of current density. Variation in the Wt% of Co and P in the deposit with current density, in relation to their content in the bath is shown in Fig. 1. The composition reference line (CRL) corresponding to the Wt% of Co and P in the bath (based on the weight of salt in the bath) is shown by horizontal perforated lines.

Thus, it may be noted that Wt% Co in the deposit is much higher than that in the bath, whereas Wt% P is much lower than that in bath. Further, change in the Wt. of both metals (Co and P) with current density is also found to be very minimal, as shown in Fig. 1. This marginal change of metal contents in the deposit, with current density may be attributed to ongoing induced type of codeposition. It may be recalled that in induced type of codeposition, effects of the plating variables (current density, stirring, temperature etc.) on the composition of the alloys are more vagarious and unpredictable than in other types of codeposition[8].

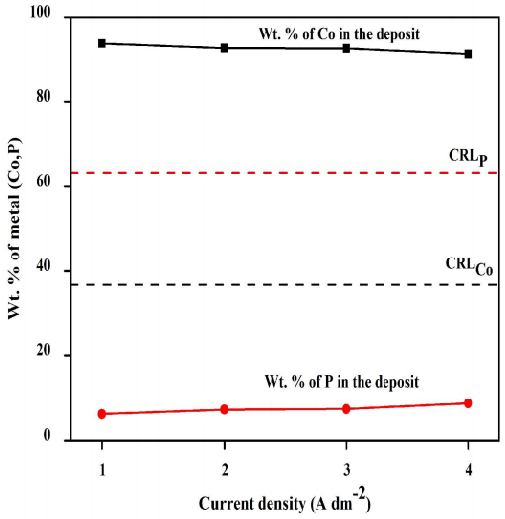


Fig. 1- Variation in the Wt% of Co and P in Co-P alloy deposit with current density. The composition reference line (CRL) corresponding to Wt% of Co and P in the bath are shown as horizontal perforated line

Table 2 - Change of composition, and corrosion rates (CR) of Co-P alloy coatings with current density deposited from optimized bath

Deposition Current density (A dm^{-2})	Co content in the deposit (Wt. %)	P content in the deposit (Wt. %)	Thickness of coating (μm)	E_{corr} (V vs. SCE)	i_{corr} (μA cm^{-2})	CR (×10^{-2} mmy^{-1})
1.0	93.8	6.2	6.0	-529.9	28.9	34.9
2.0	92.7	7.3	8.2	-527.1	35.6	43.7
3.0	92.6	7.4	10.3	-576.4	36.9	45.2
4.0	91.3	8.7	12.0	-540.0	37.5	46.5
In the bath	36.6	66.4				

The observed increase of corrosion rates (CR) of Co-P alloy coatings with increase of P in the deposit (Table 2) may be attributed to the low limiting current density (i_L) of Co in the bath. Here, it is appropriate to recall that limiting current density is the maximum current density at which rate of deposition of a particular metal is maximum. Moreover, limiting current density of a particular metal is constant for a given bath composition. Hence, in a given bath any attempt to increase the voltage/current beyond its limiting current density value of a particular metal, it lead to evolution of excessive H_2 gas on cathode, at the cost of quality of coating by decreasing that metal's content in the deposit. In other words, at higher current density, it leads the coating to become more porous, with decreased metal content. Accordingly, in the present study, limiting current density of Co is rather low (due to less Co content in bath). Hence, on increasing the current density the evolution of H_2 gas has increased by decreasing noble metal (Co) content in the deposit. This resulted in development of a more porous Co-P alloy coating having higher P content. Therefore, increased corrosion rates of Co-P alloy coatings at higher current density is due to increased porosity of alloy coatings, and it is evident from their SEM micrographs shown in Fig. 2. Thickness of electrodeposited Co-P alloy coatings were measured using digital Thickness Tester (Coat Measure M&C), and it was further verified from Faraday's law and they are found to be in the range of 6 - 12 μm as shown in Table 2.

3.2 Surface morphology

The microstructure of Co-P alloy coatings deposited at different current densities are shown in Fig. 2. From the surface morphology of alloy coatings deposited at current density from 1.0 A dm^{-2} to 4.0 A dm^{-2}, one can make out that current density has significant role on the process and pattern of electrodeposition.

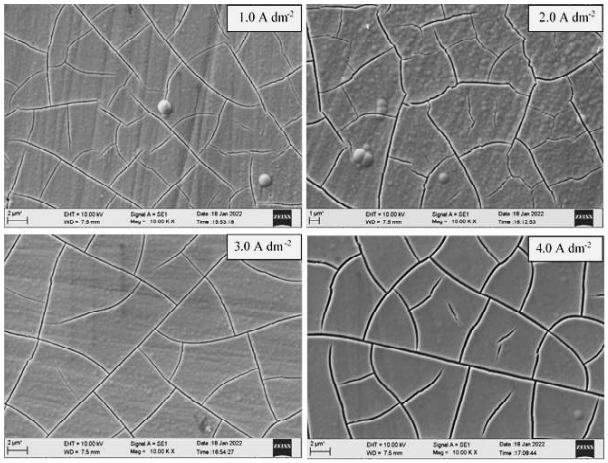


Fig. 2 - Micrographs of Co-P alloy coatings showing dependency of deposition current density on surface morphology of deposits. A characteristic cracks having specific patterns, found growing with increase of current density may be seen.

It may be seen that the surface structure of Co-P alloy coatings obtained at different current densities are characterized by the presence of crack, with few spheroids on its surface. It is important to note that these cracks of specific patterns are characteristic feature of binary alloys of Fe-group metals with W and P. The characteristic cracks having specific patterns were found to growing with increase of current density. The cracks of Co-P alloy coatings may be attributed to hydrogen embrittlement, affected due to simultaneous liberation of H_2 on cathode during deposition. Accordingly, as the current density is increased, liberation of H_2 on the surface of cathode has also been increased. The increase in liberation of H_2, due to increase of current density made the depth and width of cracks to grow more, which is evident from SEM micrographs of alloy coatings shown in Fig. 2.

3.3 X-Ray diffraction study

XRD technique was used to determine the phase structure of Co-P alloy coatings at different c.d.'s. The characteristic XRD peaks of Co-P alloys deposited at 1.0 A dm^{-2} to 4.0 A dm^{-2} is presented in Fig. 3. Sharp signals of X-ray reflections confirm that Co-P alloy coatings is crystalline in nature.

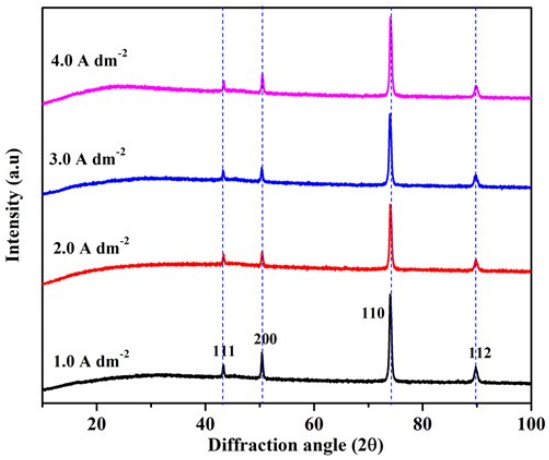


Fig. 3 - X-ray diffraction peaks of Co -P alloy deposited at different current densities from optimal bath. Constancy of phase angles of coatings corresponding to different current density indicate the formation of solid solution of Co with P.

The XRD peaks at 2θ = 43.3°, 50.4°, 73.9° and 89.7° represents the phase angles of Co-P alloy coatings electrodeposited at different current densities, corresponding to the planes (111), (200), (110), and (200), respectively. It may be seen that intensity of peaks corresponding to different scattering angles remained to be almost constant even with change of current density. This stands for the reason that change of composition of alloys is minimal with current density, and is supported by composition data in Table 2. It may also be seen that phase angles corresponding to different reflections of all coatings remains constant regardless of the current density at which they are deposited. This constancy of phase angles of Co-P alloy coatings corresponding to different current densities indicates the formation of solid solution of Co with P[13]. Here, it may be recalled that in solid solution the chemical components (metals) remain in a single homogeneous phase in all proportions of constituents [14].

3.4 Corrosion study of Co-P alloy coatings

The electrochemical corrosion behavior of Co-P alloy coatings was examined using Electrochemical Impedance Spectroscopy (EIS) and potentiodynamic polarisation techniques, and the experimental results are reported below.

3.4.1 EIS Study

In the most popular Nyquist plots, impedance (Z) is represented as complex number, having real impedance part (Z') and imaginary impedance part (Z"), and such representation is provided with provision to distinguish the contribution of polarization resistance (R_p) verses solution resistance (R_s) of a test electrode[15]. Accordingly, Nyquist plots of Co-P coatings deposited at different current densities are shown in Fig. 4. It may be noted that impedance responses of Co-P alloy coatings decrease with increase of deposition current density. In other words, polarization resistance (R_p) value of coatings decreased with current density. Change of impedance corresponding to the different Co-P alloy coatings in full scale is shown in the inset of Fig. 4. Thus on the basis of highest polarization resistance value, observed in Co-P alloy coating deposited at 1.0 A dm^{-2}, it may be inferred that it is the most corrosion resistant coatings, compared to all other coatings.

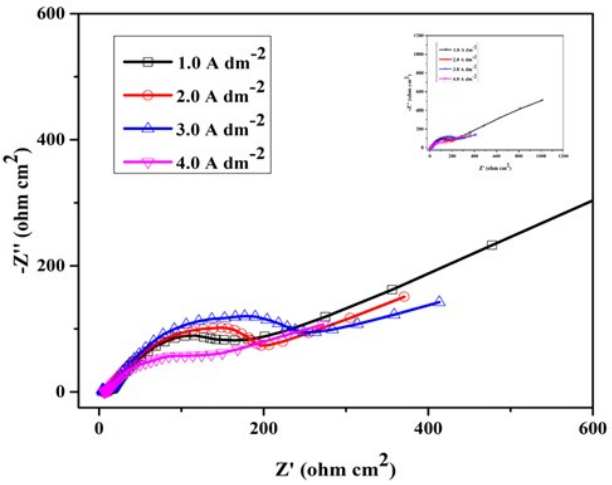


Fig. 4 - Nyquist plots of Co-P coatings deposited at different current densities. Highest polarization resistance (R_p) of Co-P coating corresponding 1.0 Adm^{-2} may be seen, compared to other coatings. In the inset is given impedance spectrum of all coatings in full scale.

3.4.2 Potentiodynamic polarization study

The corrosion behavior of Co-P alloy coatings was evaluated quantitatively by potentiodynamic polarization method. The potentiodynamic polarization behavior of Co-P alloy coatings deposited at various current densities are shown in

Fig. 5 table2 shows the corrosion data of all alloy coatings, evaluated using Tafel's extrapolation method. The corrosion rate values of different Co-P alloy coatings, reported in Table 2 reveals that Co-P alloy deposited at 1.0 A dm^{-2} is the most corrosion resistant, compare to all other coatings, and is in agreement with the trend observed in case of EIS study. From the nature of anodic polarization curve of all coatings, shown in Fig. 5, it may be pointed out that Co-P alloy coating continues to dissolve rapidly in the beginning, and then forms passive film at higher potential. This indicate to propose the possibility of better corrosion protection of Co-P alloy coatings due to formation of corrosion product to act as barrier between coating and corrosion medium. Thus it may be summarized that among the Co-P alloy coatings deposited at different current density, Co-P alloy corresponding to 1.0 A dm^{-2} is the most corrosion resistant, and is attributed to its highest metal (Co) content. Further, small change in corrosion rates of alloy coatings with current density is due to marginal change in its composition.

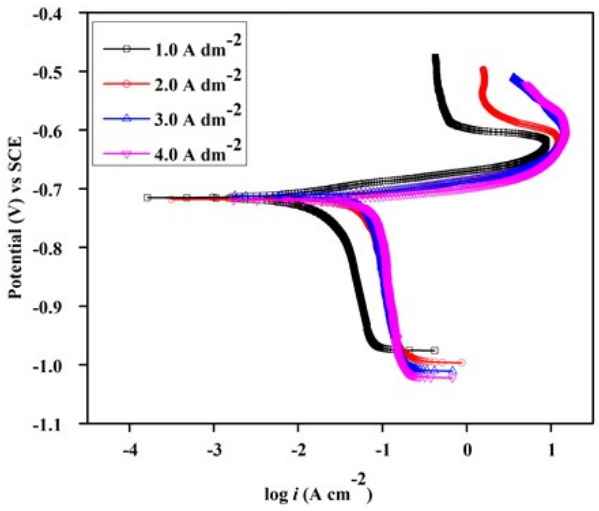


Fig. 5 – Potentiodynamic polarization behavior of Co-P alloy coatings deposited at different current densities. Tafel plot corresponding to 1.0 A dm^{-2} showing different behavior, compared to other current density may be seen.

3.4.3 Cyclic polarization study

The highest corrosion resistance exhibited by Co-P alloy coating, deposited at 1.0 A dm^{-2} was tried to understand better by cyclic polarization study in a potential ramp from -1.0 V to 0.1V, and is shown in Fig. 6. In the forward scanning, the value of current increased from negative to positive, which showed that the oxidizing reaction of passivation film occurred with increasing potential. During backward scanning, the value of current decreased from positive to negative, indicating that reduction reaction of the high valence oxide in the passivation film occurred with the falling potential. It may be noted that in the range of -0.1V to -0.6V, the current of backward scanning is higher than that of the forward scanning (it may be seen at a given potential shown by horizontal line in Fig. 6), indicating that the dissolving of oxide film has better corrosion protection compared to the alloy coatings. In addition, E_{corr} value corresponding to corrosion product is found to be shifted to higher (nobler) value compared to that of electrodeposited alloy as seen in Fig. 6.

It indicates that the corrosion product by being nobler acts as a barrier, and gives better protection to the substrate. Thus cyclic polarization study demonstrates that very high corrosion stability of Co-P alloy coating deposited at 1.0 A dm^{-2} is due to the inhibition effect of corrosion products formed on the electrode surface, where they act as barrier between metal and the medium.

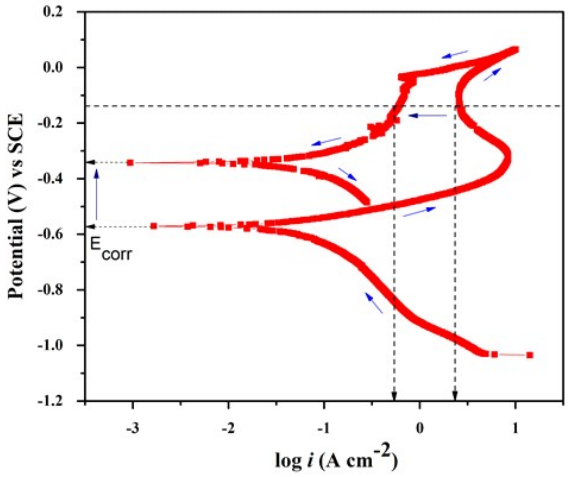


Fig. 6 - Cyclic polarization behavior of Co-P alloy coating deposited at 1.0 A dm^{-2}. Decreased current corresponding to corrosion product of at given potential indicates the better corrosion stability of Co-P alloy coatings is due to barrier protection of corrosion product

4. Conclusions

An electrolytic bath of Co-P alloy has been proposed for electrodeposition of highly corrosion resistant coatings, using glycine as the additive and following conclusions are made:

1. Very bright and sound coatings of Co-P alloy was obtained from a new bath at different current densities (1.0 A dm^{-2} to 4.0 A dm^{-2}).
2. The compositional data of electroplated alloy coating revealed that bath follows induced type of codeposition in the entire range of current density studied.
3. The constancy of phase angles of all Co-P alloy coatings, demonstrated by XRD study indicates the formation of solid solution of Co and P at all current densities studied.
4. Experimental study demonstrated that among Co-P alloy coatings deposited at different current density, Co-P alloy corresponding to 1.0 A dm^{-2} is the most corrosion resistant.
5. The highest corrosion protection of Co-P alloy coatings corresponding to 1.0 A dm^{-2} is due to high Wt% of Co in the deposit and lesser cracks on its surface.
6. Increase of corrosion rate of Co-P alloy coatings towards high current density is attributed to their decreased Co content and increased porosity.
7. Least corrosion rate of Co-P alloy coatings at 1.0 A dm^{-2} may be ascribed to the inhibition effect of corrosion product formed on the surface, demonstrated by cyclic polarization study**.**

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