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CORROSION OF NICKEL-MOLYBDENUM DISULPHIDE ELECTRO COMPOSITES

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Electrochemical and non electrochemical methods are used to evaluate the corrosion behaviour of nickel-molybdenum disulphide electro composites in acidified chloride solutions. The presence of MoS_2 decreased the corrosion resistance of electro-deposited nickel in acetic acid salt spray and in acidified chloride solutions.

Key words: Corrosion, electro composites, Ni - Mos_2 composites

INTRODUCTION

When soft particles, having a low shear strength are dispersed in a metal matrix, the resulting composite coating may be expected to possess good antifriction properties. Electrodeposited Ni-MoS_2 composites have low internal stress and adhesion properties compared to nickel coatings [1, 2]. Recently Ni-MoS_2 coatings have been reported from fluoborate bath and found to have superior hardness and self lubricating properties [3]. Although the nickel coated steel components exhibit good corrosion resistance, the influence of the co-deposited MoS_2 particles on the corrosion behaviour was not studied. Hence to explore the possibility of using Ni-MoS_2 composites for corrosion protection as well as for antifriction requirements, a study of the corrosion behaviour of Ni-MoS_2 composites in various environments was made. In the present investigation, the nonelectrochemical and electrochemical methods of evaluation of the Ni-Mos_2 composites for their corrosion behaviour in 1N HCl and 5% NaCl solutions of pH 3.0 and 6.5 are discussed and compared with that of electro-deposited nickel coatings. The results will throw light on the applicability of such coatings in chloride environments.

EXPERIMENTAL

40 $g.l^{-1}$ MoS_2 particles (5.3 μ) were kept in suspension in the fluoborate bath containing nickel fluoborate 280 $g.l^{-1}$, sodium lauryl sulphate 0.1 $g.l^{-1}$, free fluoboric acid 5 $g.l^{-1}$ and boric acid 30 $g.l^{-1}$. The pH of the bath was maintained at 3.0 ± 0.1. The plating was carried out at 323 k with a fully regulated DC power supply using nickel anodes and steel cathodes of 1:1 area.

The corrosion behaviour of the electrodeposited Ni-MoS_2 (35.5 volume %) composites were studied in 1N HCl solution, 5% NaCl solution acidified with acetic acid (pH 3.0) and 5% NaCl solution only (pH 6.5). The tests were also carried out with bare steel substrates and electrodeposited nickel for comparing their performance with that of Ni-MoS_2 composites.

Non electrochemical methods

Weight loss method: One side of the steel specimens ($7.5 \times 5.0 \times 0.1$ cm^3) were plated with nickel or Ni-MoS_2 composites. They were cleaned, weighed and suspended in the test solutions using glass hooks. After the test period, the specimens were removed, rinsed in distilled water, dried and weighed. The weight loss was determined and the corrosion rate (CR) in mpy was obtained. The i_{corr} was calculated [4] using the equation.

$$i_{corr}\ (\mu\ A{\cdot}cm^{-2}) = \frac{CR \times \text{density of the specimen}}{0.128 \times \text{equivalent weight of the coating}} \qquad (1)$$

Salt spray exposure test: Nickel and Ni-MoS_2 composite deposits of 10 to 30 μm thickness were tested in 5% NaCl solution acidified with acetic acid (pH 3). The edges and the top unplated portions were sealed with two successive coats of the lacquer. The specimens were degreased and suspended in a PVC salt spray chamber using glass hooks. The test was conducted upto 144 hours at the rate of 8 hours spraying per day and 16 hours rest successively. The extent of corrosion was assessed after every 8 hours of spraying [5]. A rating below 7 for either protection or appearance was considered unsatisfactory. Three specimens under identical conditions were subjected to the test.

Electrochemical methods

For polarisation studies, a three electrode cell assembly was used. The specimens were masked with lacquer to expose only one cm^2 area to be used as the working electrode. A platinum foil of 2.5×2.5 cm^2 was used as counter electrode with SCE as reference electrode.

Potentiodynamic polarisation method: The corrosion measurement system (PAR-USA) was employed in which the potential of the electrode was varied by the universal programmer (Model 175, PAR) through the potentiostat (Model 173, PAR). The electrodeposit was introduced into the test solution and was allowed to attain a steady value. The steady state polarisation (1 $mv.s^{-1}$) was carried on either side of corrosion potential (± 200 mV) and from the resultant E-log 1 curves the i_{corr} and E_{corr} values were obtained.

Impedance method: Impedance measurements were carried out at the corrosion potential using the AC impedance system (PAR model 368, USA). An amplitude of 10 mV was impressed over a wide frequency range 10^{-3} $C.s^{-1}$ to 1 $KC.s^{-1}$. The values of solution resistance (Rs) and charge transfer resistance (Rt) have been obtained from the Nyquist plot and the i_{corr} values were obtained using Stern-Geary equation [6].

RESULTS AND DISCUSSIONS

Studies on weight loss indicate that the incorporation of MoS_2 in nickel enhance the corrosion rate of the composite deposit. (Table I). In salt spray exposure studies the corrosion protection rate was found to decrease with MoS_2 addition. The appearance of the deposit was also get deteriorated in the presence of MoS_2 (Table II).

The potentiodynamic polarisation curves for the corrosion of electrodeposits in chloride solutions of different pH's revealed that the inclusion of MoS_2 does not shown any significant change in corrosion behaviour. The corrosion currents were obtained by

TABLE-I: Corrosion rates, i_{corr} Obtained from weight loss method

System	i_{corr} (μA.cm^{-2}) IN HCl	NaCl (pH 3)	NaCl (pH 6.5)
Mild steel	479.0	35.0	11.0
*Electro-deposited nickel	167.0	14.0	5.5
*Ni - MoS_2 (35.5 vol %)	219.8	25.8	9.3

*Thickness of deposit = 30 μm

TABLE-II: Acetic acid salt spray exposure test results

System		Deposit thickness (μm)	Rating number protection	appearance
Nickel		10	7.5	7.2
Ni-MoS_2	(23.3 vol %)	10	6.8	6.3
	(29.5 vol %)	10	7.1	6.0
	(35.5 vol %)	10	7.1	6.0
Nickel		20	8.5	8.2
Ni-MoS_2	(23.3 vol %)	20	7.3	6.6
	(29.5 vol %)	20	7.5	6.8
	(35.5 vol %)	20	7.7	7.0
Nickel		30	9.4	9.0
Ni-MoS_2	(23.3 vol %)	30	8.2	7.3
	(29.5 vol %)	30	8.5	7.5
	(35.5 vol %)	30	8.6	7.5

extrapolating the linear segments of the anodic and cathodic curves to corrosion potential (Tables III–V)

TABLE-III: Corrosion Behaviour 1n 1n HCl Solution

	Potentiodynamic method		Impedance method
System	E_{corr} (V)	i_{corr} (μA.cm^{-2})	i_{corr} (μA.cm^{-2})
Mild Steel	– 0.510	500	846
* Electro deposited nickel	– 0.490	180	228
*Ni – MoS_2 (35.5 vol %)	– 0.445	250	258

*Thickness of deposit = 30 μm.

TABLE-IV: Corrosion Behaviour In 5% NaCl Solution (pH 3.0)

	Potentiodynamic method		Impedance method
System	E_{corr} (V)	i_{corr} (μ A · cm^{-2})	i_{corr} (μA · cm^{-2})
Mild steel	– 0.568	40	65.7
*Electro-deposited nickel	– 0.510	12	30.6
*Ni-MoS^2 (35.5 vol %)	– 0.535	35	55.0

*Thickness of the deposit = 30 μ m

V vs SCE

TABLE-V: Corrosion Behaviour In pH 6.5 NaCl Solution

	Potentiodynamic method		Impedance method
System	E_{corr} (V)	i_{corr} (μA · cm^{-2})	i_{corr} (μA · cm^{-2})
Mild steel	– 0.660	14	27.8
*Electro-deposited nickel	– 0.440	7	12.6
*Ni-MoS_2 (35.5 vol %)	– 0.580	10	18.3

*Thickness of deposit = 30 μm

V vs SCE

The corrosion currents obtained from the faradaic impedance method were compared that from potentio-dynamic polarisation method. The corrosion current values obtained from weight loss method and potentiodynamic methods are comparable.. This is because these measurements were carried out for about 30 minutes whereas the impedance measurements were carried out over hours. The enhanced corrosion rates may be due to the longer period of exposure of the surface to the corrosive environment.

The corrosion of nickel electrodeposit in HCl solutions was found to involve the dissolution of nickel and evolution of hydrogen as anodic and cathodic reactions respectively. The observed anodic Tafel slope of 50 ± 10 mV/decade in all solutions upto pH 6.5 suggests that

$$
\begin{aligned}
Ni + Cl^- &\rightleftharpoons NiCl_{ads} + e \\
NiCl_{ads} + H^+ &\longrightarrow NiCl\,H^+ \\
NiCl\,H^+ + Cl^- &\rightleftharpoons NiCl_2 + H^+ + e \\
NiCl_2 &\rightleftharpoons Ni^{2+} + 2\,Cl^-
\end{aligned}
$$

This is similar to earlier observation [7].

The observed cathodic Tafel slope of 105 mV/decade suggests that

$$
\begin{aligned}
&H^+ + e \longrightarrow H \\
&H + H \longrightarrow H_2 \text{ or } H^+ + H + e \longrightarrow H_2
\end{aligned}
$$

with first electron transfer as the rate determining step. The observed increase in corrosion current in presence of MoS_2 with the same anodic Tafel slope for nickel dissolution suggests that the mechanism of dissolution of nickel remains unaffected. The cathodic reaction, viz., hydrogen evolution may have been favoured in 1N HCl and NaCl solutions of pH 3.0 and 6.5. The MoS_2 sites in the deposit would have offered more favourable condition by lowering overpotential for H_2 evolution reaction may be responsible for the observed increase in corrosion rate. The influence is significant in acidic solutions and marginal in neutral chloride solutions.

CONCLUSIONS

The investigated methods to assess the corrosion behaviour of Ni-MoS_2 composite deposits revealed that the presence of MoS_2 decreases the corrosion protection rate in acetic acid salt spray and enhances the corrosion in acidic chloride solutions.

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