电化学和光谱法研究镍镀层表面肉豆寇酸配合物膜

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【摘 要】用加速化学和电化学腐蚀实验（LSV）研究了一系列有机缓蚀剂在镍镀层表面形成的配合物膜的耐蚀性，结果表明，肉豆寇酸在镍镀层表面形成的膜耐蚀效果最佳。采用XPS和AES研究了配合物膜层的结构与性能，以及在金属表面的成键特征和波谱变化，探讨了配合物膜的组成、性能、结构、化学状态和形成机理。配合物膜由镍的氧化物和镍的肉豆寇酸配合物组成，其中Ni和O分别呈+2、+3和-2价。

【关键词】电化学；光谱；镍镀层；肉豆寇酸配合物膜

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Electrochemical and Spectroscopy Investigations on the Myristic Acid Coordination Compounds Films on Nick Plate Surface

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Abstract: Through accelerated chemical and electrochemical corrosion tests, we studied the anticorrosive effects of the coordination compound films formed by a series of organic inhibitiors on nick plate surface. Results have shown that the films formed by myristic acid got the best corrosion-resistant result. XPS and AES determinations were carried to investigate the bonding features and spectral changes of the coordination compound films. The mechanism for films formation and the relationships between these films structure and the observed inhibition behavior are discussed. The films are found to actually be the mixture of nickel oxide and the myristic acid coordination compounds, and Ni existed as Ni(II) and Ni (III), O as -2 valence states.

Key words: Electrochemical; Spectroscopy; Myristic acid coordination compounds films

0 Introduction

The nick plate process has generated a wide variety of applications in aerospace, automotive, lec-tronics, computer, machinery, nuclear, oil and gas pr-odution and valve industries due to the excellent chemical, machinical and physical properties of nick plate. The mostly used chemical for passivation is chromates for the exemplary protecting effect of the mixed chromium/substrate metal oxide coating formed. However, it is recognized over the past decade that chromates are both highly toxic and carcinogenic. Through accelerated chemical and electrochemical corrosion tests, we studied the anticorrosive effects of the coordination compound films formed by a series of organic inhibitiors on nick plate surface.XPS and AES determinations were carried to investigate the bonding features and spectral changes of the coor-

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dination compound films.The mechanism for films formation and the relationships between these films structure and the observed inhibition behavior are discussed.

1 Experimental

Steel specimens were polished with MgO powder, degreased with acetone, etched at room temperature in 1% solution of H_2SO_4 and rinsed with distilled water.The steel was plated in the bath ($NiSO_4.7H_2O$, 30g.L^{-1}; $NaH_2PO_2.H_2O$, 25g.L^{-1}; pH=9; T=50℃), rinsed again with distilled water, passivated by im-mersing in 0.002 mol.L^{-1} solutions of a series of organic inhibitiors at 50℃~55℃ for 5 minutes, then washed by distilled water and dried.The organic inhibitiors applied for passivation include: stearic acid ($C_{17}H_{35}COOH$), lauric acid ($C_{11}H_{23}COOH$), rosin acid ($C_{19}H_{39}COOH$), myristic acid ($C_{13}H_{27}COOH$), 2-mercaptobenzothiazole, benzotriazole, 1-phenyl-5-mercaptotctrazole, hydroxybcnzotriazolc, tetrazole.

LSV tests were conducted on EG&G PARC M273 at 25℃, The accelerated corrosion tests were performed by incubating the specimens in 10% NaCl solution at room temperature, the accelerated tarnish tests were done at room temperature in a stoppered glass vacuum desiccator in which the concentration of H_2S was 1%.XPS and AES measurements were made on a Perkin-Elmer PHI 550 ESCA SAM photoelectron spectrometer.

2 Results and Discussion

2.1 The Anticorrosive Effects of the Coordination Compound Films

Nick plate on Fe substrate were examined with salt water dipping and H_2S accelerated tarnish tests before and after passivation, the results are summarized in table 1.The results showed that myristic acid are the most effective among the compounds tested to treat nick plate.

Table 1 Results of the coordination compound films accelerated corrosions and tarnish tests

Inhibitors	Salt water/hr(A)	H_2S tarnish test/min(B)
none	3(3) – 5(4)	0.5(4)
stearic acid	72(0)-109(1)	500(0)-700(1)
lauric acid	61(0)-98(1)	502(0)-621(1)
rosin acid	67(0)-78(1)-98(3)	508(0)-600(1)
myristic acid	98(0)-132(1)	602(0)-861(1)
2-mercaptobenzothiazole	77(1)-121(3)-148(4)	301(0)-550(3)-630(4)
benzotriazole	56(1)-79(3)-121(4)	300(1)-350(3)-430(4)
1-phenyl-5-mercaptotctrazole	58(1)-89(3)-120(4)	261(1)-305(3)-410(4)
hydroxybcnzotriazolc	65(1)-99(3)-117(4)	285(1)-310(3)-530(4)
tetrazole	85(1)-99(3)-130(4)	350(1)-410(3)-480(4)

(A) Parenthetical numbers mean 0-no muddy; 1-faint muddy; 2-light muddy; 3-obvious muddy; 4-serious muddy;

(B) Parenthetical numbers mean 0-no tarnish; 1-faint tarnish; 2-light tarnish; 3-obvious tarnish; 4-serious tarnish

2.2 LSV Investigation on the Coordination Compound Films

The threshold limit anodic voltages of nick plate passivated by different compounds listed in table 2 show that passivation by myristic acid exhibits the highest ability against electrochemical corrosion (the LSV curves).It is reasonable to deduce that the impedance is attributed to the hydrophonity of the film formed on nick plate surface which can block the transport of aggressive inos and make nickel ion difficult to be hydrorized.

Table 2 The threshold limit anodic voltages of nick plate passivated by different compounds

Compounds	Potential/V	Compounds	Potential/V	Compounds	Potential/V
none	0	stearic acid	0.56	lauric acid	0.46
rosin acid	0.52	myristic acid	0.67	2-mercaptobenzothiazole	0.37
benzotriazole	0.42	1-phenyl-5-mercaptotctrazole	0.36	hydroxybcnzotriazolc	0.38
tetrazole	0.29				

2.3 Survey XPS and AES investigation of the films formed by myristic acid

The survey XPS generated for the myristic acid treated nick plate surface showed clearly C_{1s},Ni(A), Ni_{3p},Ni_{2p},O_{1s} and O(A) bands.This suggested the existance of nickel oxide films and films formed by myristic acid.The spectrum of Auger electron indicated apparently the appearance of nickel,oxygen and carbon,the film is composed of nickel oxide and myristic acid coordination compound.

2.4 High Resolution XPS of Ni_{2p}, C_{1s} and O_{1s}

High resolution XPS of Ni_{2p},C_{1s} and O_{1s} form the prefilmed specimen are listed in table 2.The peak at 852.3 eV indicated the exitance of nickel in oxide state 0.And the peaks of Ni2p at from 860.7 eV to 855.6 eV manifested the presentation of nickel in oxide state +2 or +3.The 530.8 eV peak of O_{1s} showed the oxygen oxide state was -2. Therefore,the myristic acid treated nick plate surface can probably be described as the structure Ni-myristic acid/Ni_xO_y/Ni.

Table 3 Binding energies of Ni_{2p}, O_{1s} and C_{1s} in the films formed by myristic acid

	Binding energy Ni_{2p}/eV	Binding energy O_{1s}/eV	Binding energy C_{1s}/eV
Before sputtering	855.6,860.7(Ni :-2 or -3)	530.8(O : -2)	285.1
Sputtering 10 min	855.5,860.8(Ni :-2 or -3)	530.7(O : -2)	285.0
Sputtering 30 min	855.6,860.9(Ni :-2 or -3)	530.8(O : -2)	285.1
Sputtering 60 min	852.3,855.6,860.7(Ni :0,-2 or -3)	530.6(O : -2)	285.0

3 Conclusion

Results have shown that the films formed by myristic acid got the best corrosion-resistant result. XPS and AES determinations were carried to investigate the bonding features and spectral changes of the coordination compound films. The mechanism for films formation and the relationships between these films structure and the observed inhibition behavior are discussed. The films are found to actually be the mixture of nickel oxide and the myristic acid coordination compounds, and Ni existed as Ni (II) and Ni (III), O as -2 valence states.

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