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Corrosion resistance and lubricated sliding wear behaviour of novel Ni–P graded alloys as an alternative to hard Cr deposits

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Abstract

Alternative process to hexavalent chromium, substitute materials and new designs are urgently needed owing to the requirement of “clean” manufacture. This comparative study was conducted to systematically investigate the corrosion resistance and lubricated sliding wear behavior of graded Ni–P alloy deposits produced from a single plating bath by electrodeposition and hard Cr deposits, using potentiodynamic polarization and reciprocating ball-on-disc tribometer. Results showed that Ni–P deposits heat-treated at 400 °C with maximum hardness exhibited more than two orders of magnitude higher corrosion resistance than hard Cr deposits in 10 wt.% HCl solution. The Stribeck curves for the heat-treated Ni–P gradient deposits and hard Cr under lubrication conditions were obtained with accurate control of normal load and sliding speed during the wear process, three main different regimes corresponding to different lubrication mechanism were identified. Heat-treated Ni–P gradient deposits showed relatively poor wear resistance than hard Cr deposits under the lubrication conditions, which may be attributed to superior oil-retaining surface structure and the unique “nodular” effect of hard Cr in wear process.

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1. Introduction

Electrodeposition as an industrial activity has been practiced for over 150 years. Nowadays, the electro-deposition industries are undergoing fundamental changes due to the environmental problems. Huge environmental pressures increasingly require that

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certain established plating processes be substituted by more environmental friendly technologies. The development of “clean” technologies in the electroplating industry is today an essential task required and initiated by environmental laws of countries around the world [1,2]. Undoubtedly, from an environmental point of view, chromium electrodeposition, which has a wide range of industrial applications in the automotive, aerospace, mining and petrochemical fields [3,4], is one of the most critical electrodeposition processes. In all environmental regulations, chromic acid (CrO_3), which is mainly used in hard Cr plating have been recognized as both highly toxic and carcinogenic chemicals, and was identified by the U.S. Environmental Protection Agency (EPA) as one of 17 “high priority” toxic chemicals. Consequently, the use of hexavalent chromates will require special waste disposal methods and expensive breathing apparatus, and exhaust systems must be employed to deal with emissions during processing [5]. For these reasons, alternative process, substitute materials and new designs have been under study for many years. Alternatives such as composite coatings and trivalent chromium deposits have been investigated in recent years. Alloy electrodeposits including Ni–W, Ni–P, Co–W and ternary or quaternary alloys have been considered to replace the conventional hard chromium deposits [6,7]. Unfortunately, extremely limited deposits could completely replace the conventional hard chromium owing to the comprehensive properties Cr deposit possesses, such as high hardness, low friction coefficient, excellent wear and corrosion resistance.

A possible approach for the preparation of such kind of Ni-based alloy coatings as an alternative to hard chromium is to introduce the new concept of functionally graded deposits (FGDs), which originally evolved from the application of functionally graded materials (FGMs), since the property gradient in the FGMs is caused by a position-dependent chemical composition, microstructure or atomic order [8–10]. It has been found in our previous research work that functionally graded Ni–P deposits (Ni–P FGDs) exhibited much better adhesive strength, smaller thermal stress induced by heat treatment and high wear resistance when compared to ungraded Ni–P deposits. The hardness of graded Ni–P alloys after heat treatment at 400 °C are close to or even higher than that of conventional hard chromium and heat-

treated Ni–P gradient deposits exhibited better wear resistance than hard Cr deposit both at dry sliding wear and high temperature wear conditions [11]. Consequently, gradient design of alloy composition inside the deposits could solve the classic hard chromium problems to adapt the properties of the coatings to special demands. In some cases hard Cr deposits was often used in oil-lubricated wear conditions and even provide excellent protection against corrosion in petrochemical fields. Therefore, further investigations on the corrosion resistance of newly developed Ni–P gradient deposits and the tribological behaviour under the oil-lubricated conditions are needed.

The aim of present work is to systemically investigate the corrosion resistance and oil-lubricated wear behavior of the heat-treated Ni–P gradient deposits and to compare their behaviour to that of conventional hard chromium deposits.

2. Experimental

Ni–P deposits were deposited on AISI-1045 steel substrates by direct current electrodeposition process. The anode was a pure Ni plate. The basic compositions of the electrolyte are as follows: 240 g/l nickel sulfate, 30 g/l nickel chloride, 30 g/l boric acid and 20 g/l phosphorous acid. The temperature of the plating bath was kept at 70 °C. The pH of the plating bath was 1.5 adjusted by ammonia water or dilute sulfuric-acid. Prior to the deposition, the substrates were mechanically polished to a 0.10–0.12 μm surface finish, then a sequence of cleanings were performed to remove contamination on the substrate surface, the steel substrates were activated for 20 s in a mixed acidic bath, then rinsed with distilled water. The Ni–P gradient deposits (Ni–P FGDs) with six layers were electrodeposited by gradually changing the current density from 5 to 30 A/dm^2 . The detailed controlling parameters are seen in Ref. [11].

Hard Cr deposits with microhardness in the range of 980–1050 HV and approximately 40 μm in thickness was also deposited on steel substrates from a conventional plating bath mainly containing chromium trioxide and sulfuric acid, similar to what is widely used in industry.

Microstructure investigation of cross-sectioned deposits was performed using a JSM-5600Lv scanning

electron microscopy (SEM). The P content in the direction of deposits thickness was measured using a Kevex sigmaTM energy dispersive X-ray spectroscopy (EDS) analysis tool coupled to the SEM. The phases in the coatings were determined by means of X-ray diffraction (XRD) techniques. Microhardness of the deposits was determined using a Vicker's microhardness indenter. The final value quoted for the hardness of a coating was the average of 10 measurements.

To evaluate the corrosion resistance and possible passivation behavior of the graded Ni–P and hard Cr deposits, potentiodynamic anodic polarization curves were acquired and the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined using the Tafel extrapolation method. Measurements were respectively performed in 10 wt.% HCl and 10 wt.% NaOH solutions at a temperature of 20 °C, using a CHI660A Potentiostat/galvanostat system. A conventional three-compartment plastic cell was used for the electro-chemical investigations. The samples with defined area of 0.24 cm² were exposed to the electrolyte solution. A saturated calomel electrode (SCE) was used as the reference electrode whereas a platinum electrode served as the counter electrode. The specimen was first immersed in the corrosion solution until a stable open-circuit potential (E_{ocp}) was reached before dynamic scanning at 10 mV/s. After getting the stable E_{ocp} , the upper and lower potential limits of linear sweep voltammetry (LSV) were set at 30 mV more positive and negative than E_{ocp} .

The wear tests under oil-lubricated sliding conditions at room temperature were performed on a reciprocating ball-on-disc UMT-2MT tribometer (Center for Tribology, Inc., California, USA) in air. The lubrication oil used in this study was CF-4 diesel oil, which is commercially available from Great Wall Lubricant Corporation of China. Si₃N₄ ceramic balls of 3 mm diameter were used as the counter body. The normal load in the wear tests was in the range of 2–100N, whereas the sliding speed was between 2.2 and 33 cm/s. The friction coefficient and sliding time were recorded automatically during the test. The wear volume was measured using a surface profilometer, the wear rates of all the deposits were calculated using the equation of $K = V/SF$, where V is the wear volume in mm³, S the total sliding distance in m and F is the normal load in N. For each set of experimental

conditions, three tests were repeated and the results given below refer to average values.

3. Results and discussion

3.1. Structure and composition

The cross-sectional micrograph of the Ni–P FGDs which had a total thickness of approximately 36 μm is shown in Fig. 1. It can be clearly observed that the Ni–P FGDs exhibited a dense structure and strong bonding between the deposit and steel substrate was achieved. Moreover, Ni–P FGDs exhibited perfect compatibility between the six sublayers and no obvious interface between sub-layers can be seen. The distribution of P contents in as-deposited Ni–P FGD and after heat treatment at 400 °C in the direction of thickness is shown in Fig. 2 [11]. It is evident that the P content decreases gradually from the coating-substrate interface to the top surface, which is in accordance with the experimental design of the Ni–P gradient deposits. In addition, the graded composition of Ni–P gradient deposits was not changed after heat-treated at 400 °C.

Previous study has shown that as-deposited Ni–P FGDs became increasingly amorphous with increasing the distance from the surface. After annealing at 400 °C for 1 h, diffraction peaks corresponding to the Ni₃P and nickel phase in the XRD pattern were observed simultaneously [11], indicating the precipitation of dispersed hard Ni₃P intermetallic compounds

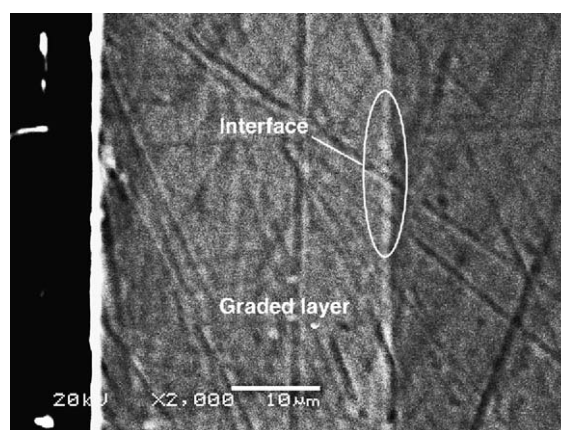


Fig. 1. The cross-sectional SEM morphology of the electrodeposited Ni–P FGDs.