

# A novel electrodeposited Ni–P gradient deposit for replacement of conventional hard chromium

Liping Wang<sup>a,b</sup>, Yan Gao<sup>a</sup>, Qunji Xue<sup>a</sup>, Huiwen Liu<sup>a</sup>, Tao Xu<sup>a,\*</sup>

<sup>a</sup>State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

<sup>b</sup>Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China

Received 3 September 2004; accepted in revised form 8 October 2004

Available online 2 December 2004

## Abstract

In this paper Ni–P gradient deposits with a graded change of P content in the direction of thickness were prepared from a single plating bath using an electrodeposition method. The tribological properties of the heat-treated Ni–P gradient deposits at room temperature compared with ungraded Ni–P after heat treatment at 400 °C was investigated using a ball-on-disc tribometer. Also, tribological properties of heat-treated Ni–P gradient deposits against a silicon nitride ball were examined in the temperature range from room temperature to 600 °C with a comparison to conventional hard Cr deposits. Results show that the wear resistance of graded Ni–P alloys was approximately two times that of ungraded deposits. In addition, graded Ni–P deposits exhibited better wear resistance and lower friction coefficient than that of hard Cr deposits both at room and high temperature wear conditions. The main reason may be that the formation and propagation of through-thickness cracks within heat-treated Ni–P deposits during the wear process were effectively inhibited due to the introduction of graded composition and structures.

© 2004 Elsevier B.V. All rights reserved.

*Keywords:* Gradient; Ni–P alloy; Chromium replacement; Wear resistance; Electrodeposition

## 1. Introduction

Hard chromium deposits, which have the advantage of high hardness, excellent wear resistance and low coefficient of friction, have been widely used in the automotive, aerospace, mining and general engineering industries for application such as internal combustion engine components, hydraulic cylinders, rolls and machine tools [1–3]. However, conventional hard chromium is now considered to be a significant problem due to the environmental concerns. Chromates have been recognized over the past 10 years as both highly toxic and carcinogenic 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 [4]. Hence, investigation and development of alternative deposits or processes that do not involve hexavalent chromium are of great importance from the point of view of industrial applications.

Alloy electrodeposits including Ni–W, Ni–P, Co–W and ternary or quaternary alloys have been considered as the best materials to replace the conventional hard chromium deposits [1,4,5]. Among these, Ni–P alloys with widely different compositions and microstructures have been extensively studied because of their high hardness, excellent wear, corrosion resistance and their relatively stable electrolyte [6,7]. It has been established that the hardness of Ni–P alloys after heat treatment at high temperature are close to or even higher than that of conventional hard chromium, however, the brittleness and the reduced integrity of alloy deposits after heat treatment restricted their applications for the replacement of hard chromium, especially for anti-wear applications with higher thickness of deposits in a progressive environment, such as under the conditions of high

\* Corresponding author. Tel./fax: +86 931 496 8169.

E-mail address: [pingsingwlp@hotmail.com](mailto:pingsingwlp@hotmail.com) (T. Xu).

speed and heavy load, in which significant through-thickness cracking is observed [1,8,9].

In our present work, a novel Ni–P gradient alloy with the graded change of P content in the direction of deposit thickness was electrodeposited. The microstructure, friction and wear resistance of the resulting gradient Ni–P deposits after heat treatment were investigated compared with ungraded Ni–P alloys. The high temperature friction and wear properties of graded Ni–P deposits compared to conventional hard chromium were also measured.

## 2. Experimental

### 2.1. Electrodeposition

Ni–P deposits were deposited on AISI-1045 steel substrates by conventional 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 coatings with six layers were electrodeposited by gradually changing the current density from 5 to 30 A/dm<sup>2</sup>. The detailed controlling parameters are shown in Table 1. Each experiment was carried out on a fresh solution.

Hard Cr 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, similar to what is widely used in industry.

### 2.2. Characterization

Microstructure investigation of cross-sectioned coatings was performed using a JSM-5600Lv scanning electron microscopy (SEM). The P content in the direction of coatings thickness was measured using a Kevex sigma™ energy dispersive X-ray spectroscopy (EDS) analysis tool coupled to the SEM. The phases in the coatings were deter-

mined by means of X-ray diffraction (XRD) techniques. Microhardness of the coatings was determined using a Vicker's microhardness indenter. The final value quoted for the hardness of a coating was the average of 10 measurements.

### 2.3. Friction and wear tests

The wear tests at room temperature were performed on a reciprocating ball-on-disk UMT-2MT tribometer (Center for Tribology, California, USA) in air with a relative humidity of 45–55% under dry sliding conditions. All tests were performed under a load of 20 N while high temperature ball-on-disc wear tests were conducted on a THT07-135 tribometer at temperature of 25, 100, 200, 400, 600 °C under dry sliding conditions. Si<sub>3</sub>N<sub>4</sub> ceramic balls of 3-mm diameter were used as the counter body both in room temperature and high temperature wear tests. All high temperature wear tests were performed under a load of 10 N, a sliding speed of 0.4 m s<sup>-1</sup>, a contact radius of 5 mm for a total sliding distance of 500 m. 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 alloy deposits were calculated using the equation of  $K=V/SF$  where  $V$  is the wear volume in mm<sup>3</sup>,  $S$  is the total sliding distance in m and  $F$  is the normal load in N.

## 3. Results and discussion

### 3.1. Gradient composition analysis

The Ni–P gradient deposits were deposited according to the electrodeposition conditions listed in Table 1. The composition of the electrodeposited Ni–P deposits was easily controlled by the change in the current density during the electrodeposition process. The deposition time at each current density was controlled accurately in order to obtain the sub-layers with the same thickness. Fig. 1 shows the cross-sectional SEM morphology of the Ni–P gradient deposit which had a total thickness of approximately 36 µm. It can be seen that the Ni–P gradient deposits exhibited a dense structure and strong bonding between the deposit and steel substrate was achieved. Moreover, no obvious interface between sub-layers can be seen, which indicated that the gradient structure had no sharp interfaces and produced graded alloy deposits free of macrodefects.

The distribution of P contents in as-deposited Ni–P gradient deposit and after heat treatment at 400 °C in the direction of thickness is shown in Fig. 2. 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. Based on the

Table 1  
Electrodeposition conditions of Ni–P gradient deposits

Current density $D_k$ (A · dm <sup>-2</sup> )	Electroplating time (min)
5	15
10	6
15	5
20	4
25	3
30	2