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Experimental Research on Hard and Crack-Free Electrodeposited Chromium Coatings

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Abstract. In order to eliminate cracks in the chromium coating, a novel method named flexible extrusion assisted chromium electroplating was proposed. The bright and crack-free chromium coatings were electrodeposited by using the perturbation and extrusion of hard and insulating particles. The prepared deposits were characterized by scanning electron microscope (SEM) and three-dimensional topography. The testing results showed that the surface was very smooth and there was no micro cracks in the coating. Micro hardness of the electrodeposited layer was also tested. It was confirmed that the chromium coating electrodeposited with rotating cathode in hard particles had high micro hardness as to 850HV and the micro hardness could be controlled by the process parameters. The rule of the micro hardness was concluded by analyzing current density and rotating speed. In addition the results of salt spray test and electrochemical polarization curve showed that the coating deposited by new method had higher corrosion resistance than that by traditional method.

Introduction

Chromium is one of the most important metal electroplated. Hard chromium plating is a widely spread technique to enhance the wear and corrosion resistance of industrial parts. It is applied widely in the automotive, aerospace, mining and general engineering industries for application such as internal combustion engine components, hydraulic cylinders and rolls. Conventional electrodeposited chromium possesses an extremely fine structure with built in oxide, hydroxide and hydride inclusions together with high levels of internal stress which combine to give a crack network throughout the coating. However, the presence of cracks in the coating can have a deteriorating effect on its corrosion resistance and air tightness. The cracks can provide a suitable path for penetration of corrosive agents to the interface of the base material and the chromium deposit [1]. In order to overcome this problem, crack-free chromium plating has been suggested. Some researchers obtain crack-free chromium coating at high electrolyte temperature and low current density [2]. It is also possible to produce crack-free chromium plates by direct current，pulse electroplating and pulse reversal current electroplating[3–7]. In addition many researchers are absorbed in addition agents. The using of additives can obtain phosphorus-containing amorphous deposits and chromium-carbon deposits to improve the poor corrosion resistance [7]. But electroplaters are faced with many problems and often achieve undesirable results on chromium depositions. For example crack-free chromium electrodeposits have a certain disadvantage which the hardness of these deposits is considerably lower than the hardness of regular chromium deposits. The efficient of plating is lower such as pulse reversal current electroplating, or the range of deposition conditions is limited such as pulse electroplating[1,5,8]. In order to obtain crack-free and hard chromium deposit, a new method by using the perturbation of hard particles named flexible extrusion assisted chromium electroplating has been studied in this paper.

Mechanism analysis

Fig.1 shows the schematic view of polishing affection of hard particles. Isolating and hard particles are filled between the electrodes in the process of electroplating, they touch the surface of moving cathode tightly and random move with the motion of the cathode simultaneously. While cathode moves, the particles will polish and impact the surface of cathode continuously. Ions of H_3O^+ near the cathode are difficult to close the cathode by the perturbation of hard particles, so the reaction of $H_3O^+ + e \rightarrow H_{吸} + H_2O$ will be hindered. Because of the discharging retardation of hydrogen ions, the hydrogen evolution overpotential is increased. Thus, with the decreasing of the precipitation quantity of hydrogen, the quantity of hydrogen into chromium coating is less than that by traditional method. The micro cracks will be eliminated due to the decreasing of internal stress[9]. Simultaneously, the particles can roll and polish the surface of deposit, and reduce the degree of roughness and irregularity.

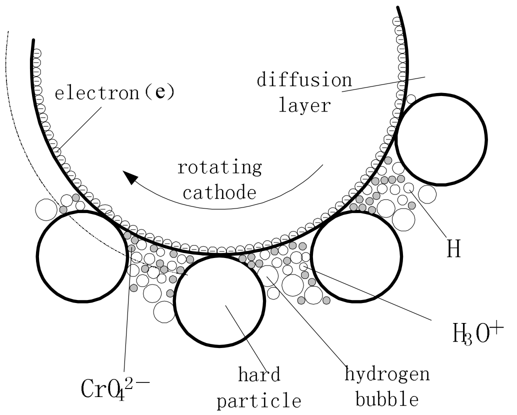

Fig.1 Schematic diagram of flexible extrusion assisted electroplate

Experiment and testing method

Fig.2 shows the schematic diagram of the experimental setup. A cylinder mandrel droved by a motor rotated inside a cylinder through carved basket as cathode. Isolating and insoluble little hard particles filled the space between the cathode and the basket wall. Anodes were placed paralleling the cathode. While the cathode rotates, the particles will be forced to move around and slightly polish the surface of deposition layer simultaneously. Ceramic beads with diameter of Ø 1–1.2 mm were chosen as the hard particles. 30CrMnSi was chose as the material of cathode. Before deposition, the mandrel was mechanically polished, degreased and rinsed. The electrolyte contained CrO3 150-400 g/l, H2SO4 5-20 g/l, pH 1–2.5, T = 35-550C.

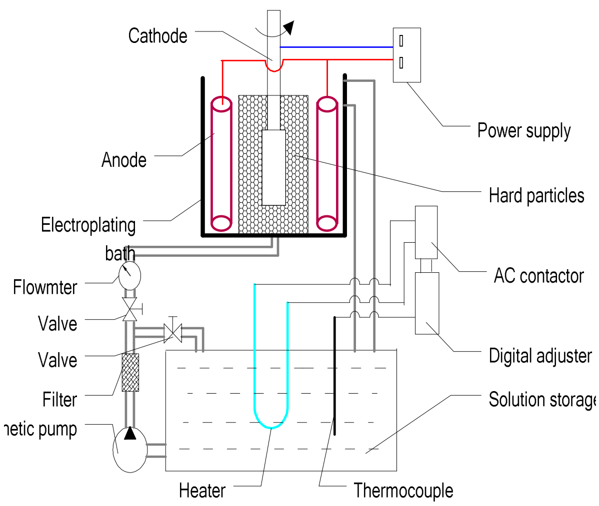

Fig.2. The schematic diagram of experimental setup.

At the end of the process, the cathode was immediately withdrawn, washed with distilled water, dried and then subjected to further characterization measurements. A HXS-1000A Vickers micro hardness tester was used as the device of micro hardness measurements. The surface morphology of the deposits was examined by a LEO-1530VP FEG-SEM. three-dimensional topography of Micro XAM was used to characterize the surface of the deposits.

Experiment and result

Surface morphology of the deposits

Fig.3 shows the surface morphology of two typical chromium deposits electroplated. The SEM photos of the two deposits appear with different morphology. It can be seen that the surface of the coating plated with traditional technique was chapped due to the high internal stress and the coating seems to have a rough surface. The main reason is that much hydrogen produced in the process of plating, some of which entered into the coating inducing crystal lattice distorted as a result of cracks produced. By comparison, at the same condition the surface of the sample plated from the bath with hard particles was smooth without any sign of cracks on the surface. It can also be seen that the deposit plated with hard particles represents distinct abrasion marks and the crystal is too fine to discern. It appears that hard particles can polish the surface of the deposits and sweep off the nodules during electroplating.

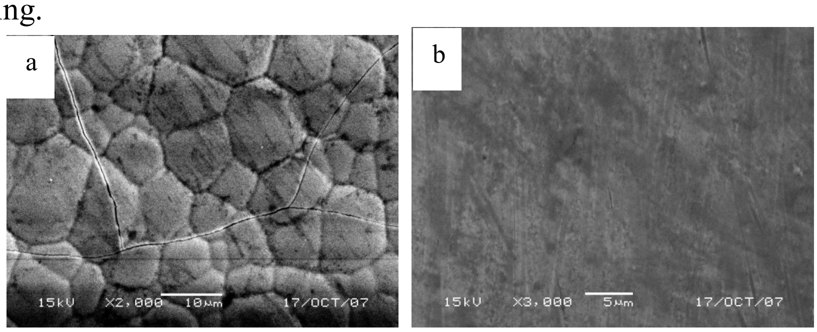

Fig3. SEM micrographs:(a)without hard particles and (b) with hard particles.

The surface roughness was measured by a Mahr perthometer M1 tester and the magnitude is about 0.2μm obvious lower than the deposit by traditional method. These results imply that the hard particles between the cathode and anode can obviously prevent hydrogen from adhering to the cathode surface. Simultaneously, the particles can polish the surface of deposit, and reduce the degree of roughness.

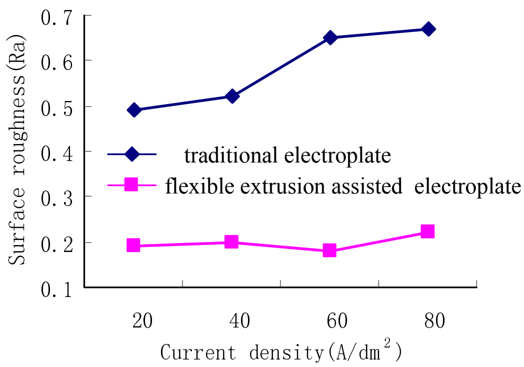

Fig. 4. Surface roughness of different coatings

Fig.5 shows the three-dimensional topography of different coatings. It can be seen that the surface of the coating plated with traditional technique was very rough covered with many spikes like pyramid. By comparison, at the same condition the surface of the sample plated by new method is very smooth. The results as stated aboved imply that the hard particles between the cathode and anode can obviously prevent hydrogen from adhering to the cathode surface. Simultaneously, the particles can polish the surface of deposit and reduce the degree of roughness.

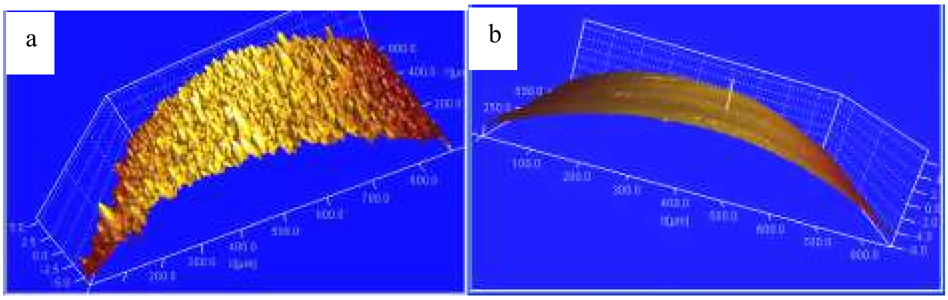

Fig.5. Three-dimensional images of two different chromium coatings
(a) without hard particles and (b) with hard particles.

The micro hardness of deposits

Fig. 6 shows the trend in micro hardness of deposits with current densities temperature of the electrolyte. The micro hardness of the deposits is measured using a 25g load. The electrodeposited samples are ultrasonically cleaned and degreased prior to testing. The result of hardness measurement shows that the micro hardness value of the chromium deposit from the bath with hard particles is beyond 800HV at the current density less than 30A/dm^2. In addition, the higher the current density is, the lower the micro hardness of deposit is. Fig.7 shows the relation of the micro-hardness and rotating speed. It can be seen that the micro hardness value of the crack-free chromium deposit from the bath with hard particles declines with the augment of rotating speed. When increasing the rotating speed, the effects of extrusion and polishing will be strengthen. The dynamical hard particles can effectively impede the adherence of H^+ and drive the hydrogen bubbles formed into the solution to eliminate deposition defects and decrease internal stress, so the micro hardness of deposits will be decreased with the increasing of rotating speed.

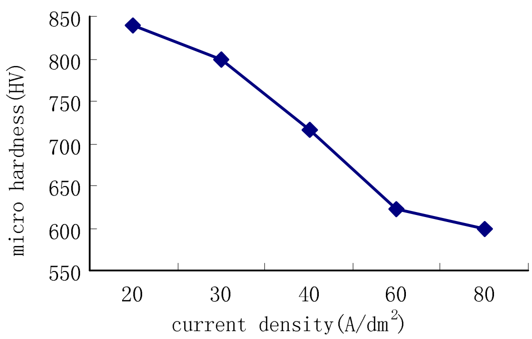

Fig.6. The relation of the current density and micro hardness (40^o C)

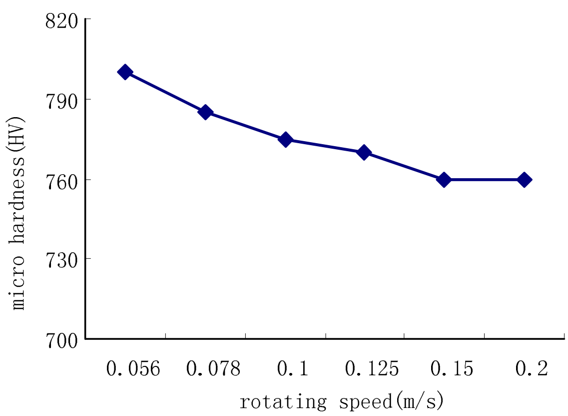

Fig.7. The relation of rotating speed and micro hardness

The corrosion resistance of deposits

The neutral salt fog spray test (NSFST) is performed by the medium of 5%NaCl solution according to the standard of ASTM B117. Fig. 8(b) is the surface deposited by new method after 200h NSFST. The result shows that chromium layer by new method has no rust stains. However, as shown in Fig.8(a) more corrosion products exist on the chromium layer after 5h NSFST with relatively cracks that was observed by SEM. The coating deposited by new method with few inner cracks should be better NSFST life.

Fig. 8 Corroded surface of chromium layers after neutral salt fog spray test:
(a) with traditional method and (b) with new method.

Fig. 9 shows electrochemical polarization curves for electrodeposited chromium in 5%NaCl solution. Scanning speed is 5mV/s. The curves display the active passive behavior between -1 and 0 V. It indicates that the mechanism of activity and passivation is similar in essence for different electrodeposits. However the corrosion potential of deposit by new method is -0.4745V which shifts positively 98mV compared with that by traditional method and the corrosion current density is 1.501e-7 A·cm-2 which decrease the moment to 87% as shown table1. The results are matched with the phenomenon of NSFST.

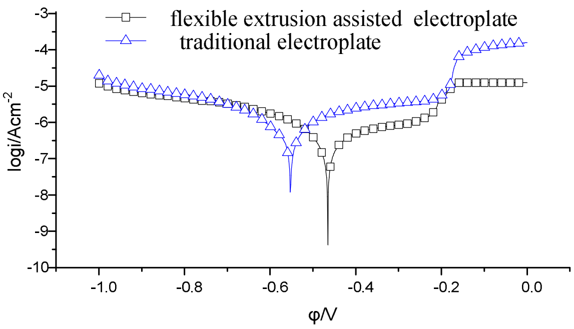

Fig. 9. Polarization studies of different coatings in 5%NaCl electrolyte.

Table 1 Corrosion parameters obtained from polarization studies in 5%NaCl electrolyte.

samples	Vcorr /V	Icorr/A·cm-2
New method	-0.4745	1.501e-7
Traditional method	-0.5728	1.155e-6

Summary

In this paper, a new technique has been developed, in which the disturbing of hard particles in the bath could obviously improve the external appearance and microstructure, which resulted in smooth and crack-free deposits. Vickers micro-hardness of the coating attained to around 850 HV. In comparison with traditional electroplating technique, the results of salt spray test and electrochemical polarization curve showed that the coating had higher corrosion resistance. Therefore it comes to a conclusion that crack-free chromium coatings can be obtained by flexible extrusion assisted chromium electroplating.

Acknowledgements

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