Progress in Developing Electrodeposition for Substitute Hard Chromium

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Abstract

The latest progress in substitute processes for hard chromium plating in recent years is reviewed. The researching status and developing trends of amorphous alloy, nanometer electrodeposition and alloy coatings in this field. The results show that the electrodeposition is superior to hard chromium in performance and environmental protection.

Keywords: Electrodeposition; Substitute chromium coating; Alloy electroplating; Composite deposits

1 Introduction

Hard chromium plating is also called Wear resistance chromium. Hard chromium plating has a high rigidity plus a low friction coefficient, after plate chrome, the ability of resisting abrasion is enhanced, so the longevity of components is prolonged[1]. However, the hard chromium plating can lead to serious environmental protection, such as the chromate used in hard chromium plating can bring liquid waste and acid mist with chrome , in addition, it has some other drawbacks: rigidity decreases with the increases of the temperature; the plating layers exits micro cracks; the speed of sediment is very slow etc[2]. Compared with metal plating, alloy plating may be much more level off、brightness and crystal particularity. If the component and proportion is appropriate, alloy plating may be more abrade-resistant and erode-resistant than metal that composed of the alloy. Amorphous material is a new material that undergo a fast development in recent 20 years, whereas the amorphous film plating is paid much attention because of its high erode-resistant as well as high intensity. Composite deposits is a composite material that base on metal, its performance changes greatly because the embed of tiny particulate, so it's application is enlarged in many field[3]. Hard chromium plating can be substituted by developing excellent alloy plating, amorphous alloy plating and composite deposits.

2 Binary alloy electrodeposition

2.1Ni-W

When the amount of W in Ni-W alloy plating is over 44 percent, then amorphous plating can be obtained. The Ni-W alloy has a comparable high melting point, rigidity, heat-resistant, abrade-resistant and erode-resistant. It can be used as substitute hard chromium. The amount of W in the plating is increased with the increase of electroplating solution， it will go to a certain value finally，unless the temperature of the liquid is above 50℃, it can obtain amorphous plating; in addition, high electric current density is also good to the form of amorphous plating; when the PH value is between 5 and 7, we will get amorphous. Ni-W amorphous plating has good stability，it can keep amorphous structure under 400 ℃ [4]. When 2-butyne-1,4-diol is applied, we can get a whole lucent Ni-W plating, but 2-butyne-1,4-diol can reduce the amount of W and also has an effect on electric current density than reduce the efficiency of electric current[5]. Some literature figure out that when the amount of W in the plating is between 30 percent and 32 percent, the rigidity is between 450 and 500℃. After the heat treatment between 350 and 400℃, its rigidity can come to between 1000 and1200HV, which is the same as chrome plating[6].

Gradient coating method and enhance the liquid temperature and electric current density gradually, we can get nano-crystalline Ni-W plating with grads, the W amount increases gradually along the plating growth direction, the grain size decreases from 10.9 nm to 7 nm, crystal lattice aberration increases gradually, the plating become amorphous configuration from nano-crystalline configuration, which arranges with continuous grads. The study of thermal strain characteristic suggests that the continuous grads configuration along the direction of thickness of plating can relieve thermal distribution in the grain boundary effectively, so the thermal stress can be relieved. By analyzing the section, we can draw a conclusion that the toughness from surface layer to the inside increases step by step and distributing with grads[7].

BMüller studied the process of oxidation in steel-based Ni-16%W. He found out that before oxidation, the plating is composed of nano-crystalline Ni particle which the crystal lattice constant is 3.782À. During oxidation ,with the diffusion of oxygen, the surface layer is NiO, whereas the inside layer is NiO plus $NiWO_4$ composition, under the oxidation layer, there is supersatured W, Fe, O and Ni , above the base is the Ni-W-Fe sediment with full Fe. Ni^{2+}, O^{2-}, the diffusion of element, the configuration of Ni-Fe-W plus the degree of Ni nano-crystalline are the factor that affecting oxygenation[8].

Because of the difference of configuration and characteristic of the substrate, the ingredient, appearance, erode characteristic on Ni-W is different, Ni-based alloy and Ni-W amorphous plating on stainless-steel show a good exterior characteristic and erode-resistant, A3 steel

and the plate on it have plenty crack, the ability of protection is bad. So we can pre-plate nickel on the base material[9,10].

2.2 Ni-Co

The nickel has a comparable low rigidity, abrade-resistant ability is poor, if we put some Co in it and form Co-Ni alloy, beside attain the physical chemistry characteristic of the Ni-plating, it has another two advantages: rigidity is enhances greatly, and its rigidity can keep in high temperature. In addition, its chemistry stability is very well, especially the thermal stability and abrade-resistant under high temperature enhanced greatly[11,12].

Now we will study the electrodeposit Ni-Co alloy that with glucide and without glucide. When we put some glucide in the plating, the enhance of electrical current density will lead to the grain growth of Ni/Co alloy electrodeposit and it'll become thick crystal. After analysing we know that the decrease of transfer resistance and ion diffuse and also the prevention of electrochemistry adsorption that lead to this result. The addition of glucide in the plating groove can finer the Ni/Co alloy plating, the glucide prevent the taper growth of grain so that we can get smooth surface easily[13].

The electrodeposit of Ni/Co ally is a kind of abnormally co-aggradations. The Co salt increases with the increase of concentration of Co liquid, and the tiny increase of concentration will result in the increase of the Co amount. If the Co amount is a little high, the inner stress of the plating will increase, the performance of it will be affected. With the increase of electrical current density in the cathode, the amount of Co will decrease. When the temperature of the liquid increases, the Co amount will increase too, meanwhile the inner stress can be reduced, but if the temperature is too high, the hydrolyze of ion will be accelerated, so the quality of the plating will worse. We can control the PH value at an appropriate (4-5) so that we can get a good quality of plating[14-16].

The configuration of Ni-Co alloy is changed from fcc to hcp with the great increase of Co amount. Under the condition of friction， the fcc Ni-Co alloy plating has a comparable high friction coefficient and bad abrade-resistant ability. However, hcp alloy plating play a role of reducing abrade and abrade-resistant, its friction coefficient decrease to about 1/3 , the abrasion rate decrease over 10 percent[17-18].

2.3 Co-W

The thick of Co-W alloy plating is increase with the increase of plating voltage, but when the voltage is above 12V, the increase rate of plating layer become slow. When the voltage is 12V and the movement rate of anode is 10 m per minute, the rigidity of the plating is highest. Co-W alloy plating has a good thermal stability, after temper at high temperature, the rigidity will increase greatly because of the separate out of Co3W. Co-W alloy plating has a good oxygenation-resistant ability under 500℃, its oxygenation-resistant ability is superior to 3Cr2W8V steel even when the heat up temperature is 700℃[19].

3 Multi-alloy electrodeposition coating

3.1 Ni-W-B

Ni-W or Ni-W-B(P) amorphous alloy is paid much attention because of its good erode-resistant ability and high rigidity. In recent years, plenty of papers covered the characteristic of this kind of plating. These two plating have a very good erode-resistant ability and high rigidity, and the electrical current efficiency and disperse ability are better than chrome plate. So, these two plating are hoped to the substitution for hard chromium[20].

The addition of B can eliminate micro crack effectively, the erode-resistant ability and the protection ability to the basal body of Ni-W-B amorphous alloy plating is superior to Ni-W amorphous alloy, and after the addition of B, the oxygenation-resistant ability performs much better. When 31wt. percent of W and 1wt. percent of B are used to form amorphous alloy plate, the rigidity can even reach to 900, which basically accord with the need of rigidity of hard chromium plating. After the heat treatment, the rigidity value of Ni-W-B is higher than Ni-W amorphous alloy evidently, which is changeless at 400℃, and when the heat preservation temperature reach to 400℃, the Ni_4W fine grain is appeared in the amorphous alloy. If the heat temperature is enhanced, the grain will grow up, and the rigidity value will decrease accordingly. Besides, the limited rigidity value of Ni-W appears when the heat treatment temperature is 500℃, whereas the limited value of Ni-W-B appears at 700℃.

3.2 Ni-W-P

The characteristic can be enhanced ulteriorly if metalloid P is added in Ni-W amorphous alloy plating. By employing some technics and use the method of electrodeposit , we can obtain Ni-W-P ternary alloy plating. When the liquid temperature is below 60℃, the plating that we get is crystal configuration; while the temperature is above 60℃, the plating is amorphous alloy correspondingly. With the increase of PH and DK , the W amount of plating increases and the tiptop value of it is as high as 55.2 percent. If decrease the amount of P and Ni, with the increase of PH, the erode-resistant ability is decrease firstly and then will increase; whereas with the increase of DK, the erode-resistant ability of the plating is increase slightly[23-25].

Using pulse plating method, we obtain the Ni-P-W alloy plating with multilayer which has cycle modulate configuration, by studying the effect of cycle modulate configuration to the rigidity, heat stability and abrade-resistant of the plating, we found out that the rigidity of alloy film is increase with the decrease of modulate wavelength, this electrophoresis is more remarkable when the wavelength is below 120nm. If the heat treatment is between 500 and 600℃, the rigidity can reach to between 1000 and 1100.This nano-crystalline alloy has a good characteristic of abrade-resistant ability, this is because the multilayer boundary can block the appearance of crack effectively[26].

With the increase of the temperature ,the plating of Ni-W-P changes from amorphous alloy(below 300℃) to mix crystal(400℃) and then to crystal alloy(above 500℃

). The heat treatment method plays an important role in the erode-resistant ability and the rigidity value. After 400℃ heat treatment , the rigidity value reaches limited value, and the erode-resistant ability is not than good, and when the treatment temperature is 600℃, the erode-resistant ability will increase obviously and rigidity value decrease somehow. The erode rate of plating amorphous alloy Ni-W-P increases gradually with the increases of heat treatment temperature, its value reaches highest at 500℃, the highest erode rate of Ni-W-P is 0.17mg per cm2*h[27,28].

3.3 Fe-Co-Ni

The rigidity, erode-resistant ability and surface lucency degree of Fe-Co-Ni alloy is very close to hard chromium plating, so it can replace hard chromium plating to some degree in order to reduce environment pollution . The study of constant voltage electrodeposit of Fe-Co-Ni ternary alloy suggests that with the addition of certain amount of organic compound, under the condition of liquid temperature is between 50 and 60℃, the PH value between 3.0 to 4.5 and the voltage of cathode is -1.2 V , we can obtain a Fe-Co-Ni ternary alloy plating with luminant , splendid erode-resistant ability as well as high micro rigidity value ,whose integrated performance is close to the hard chromium plating[29,30].

3.4 Ni-Fe-W-P-S

Electro-deposit of Ni-Fe-W amorphous alloy have good performance，this is because W can strengthen the mechanical performance of effectively without changing its basic structure. Electro-deposit of Ni-Fe-W-P-S amorphous alloy has the same flamboyant color The good corrosion resistance and Excellent wear resistance as, at the same time， it can also offset some defects of ，The plating possess both the wear resistance close to hard chromium plating，and well corrosion resistance.

4 Electrodeposition composite coating

4.1 Ni-Co-YZA

The aim is to develop an economical composite coating with high thermal stability. Ni–Co alloys are found to possess better thermal, physical and mechanical properties compared to Ni. Also, oxide particles as distributed phase can impart better thermal stability. Hence, particulates of composite Yttria stabilised zirconia, a commonly used high temperature material and alumina (YZA) were reinforced in various Ni–Co alloy matrices through electrodeposition. The influence of YZA on the microhardness, tribology and corrosion behaviour of Ni–Co alloys with Co contents of 0 wt.%, 17 wt.%, 38 wt.% and 85 wt.% was evaluated. Optical and Scanning Electron Microscopy (SEM) confirmed the presence of YZA particles and Energy Dispersive X-ray Analysis (EDX) revealed the composition. Tribology testing showed that composite containing 38 wt.% Co displayed better wear resistance. It was found from the immersion corrosion studies that Ni–17Co–YZA coating displayed improved corrosion resistance. Thermal stability studies showed that Ni－85Co－YZA coating retained its microhardness at temperatures of 600℃. Thus, these coatings can be tailored for various applications by varying the cobalt content[33].

4.2 （Ni-W）-SiC

The codeposition process of SiC solid particles with nickel and tungsten to form Ni-W-SiC wear resistant composite coating was studied. Ni-W-SiC composite coating containing 47.2~51.0wt% W was obtained[34]. The effects of concentration of SiC particle suspended in the plating bath，temperature. cathodic current density of the bath and agitation speed on the codeposition amount of particle in the composite coating were discussed[35]. The hardness and wear resistance of the composite coating were examined. The results demonstrated that the SiC particle dispersed in Ni-W alloy coating increased obviously the hardness and wear resistance of the coating[36].

4.3 Ni-W-ZrO_2

n-ZrO_2 particle can be set into the coating, if n-ZrO_2 particles can be deal with. Because that n-ZrO_2 particle can easily reunite. N-ZrO_2 particle dispersed uniformly on the surface of composite coating in proper PH values and current densities. The proper PH values and current densities are 4~5 and 2.5A/dm^2. 5.5 Percents N-ZrO_2 particle dispersed uniformly on the surface of composite coating when the temperature of electroplating solution is 60 degree[37,38]. Amorphous composite coating with 40~52 percents of W and 3~10 percent of Zr can be able to get through join in n-ZrO_2 particle. Amorphous composite coating with more W and few Zr can be get by higher temperature[39].

4.4 Co(W)-Ni-Al_2O_3

The technology of electrodepositing Ni-W-$A1_20_3$ is studied and the effects of $A1_20_3$ particles on the hardness and wear resistance are discussed[40,41]. The results show that the hardness of N-W-$A1_20_3$ layer is raised by the addition of the $A1_20_3$ particles, but the wear resistance is greatly increased.Ni-Co/$A1_20_3$ composite coating was prepared by direct current electrodeposit technique. The hardness and wear resistance of the composite coating improve with the increase of the $A1_20_3$ particle content in the range of this experiment. The codeposition of Al_2O_3 particles in Co-Ni alloys cannot change the phase structure of solid solution, only affects the growth and orientation of crystal planes and mostly increases the d value of lattice. The high-temperature properties of the Co-Ni-$A1_2O_3$ coatings, including hardness, wear resistance, oxidation resistance, coefficients of thermal expansion and thermal conductivity at high temperature were also investigated. The results show that Co-Ni-$A1_2O_3$ composite coatings have good performance of wear resistance and oxidation resistance at the high temperature. Furthermore, the composite coatings with high-cobalt content show lower coefficients of thermal expansion and higher thermal conductivity than coatings with low-cobalt content do[42-45].

4.5 Ni-W-B-ZrO_2

The relationship of the electroplating conditions to the composition, structure and fault plane appearance of the Ni-W-B amorphous composite films with ZrO_2 particle is studied. The Ni-W-B-ZrO_2 amorphous composite films show a good resistance to oxidation corrosion and wear[46].

5 Conclusions

The replacing is still developing, The mentioned above can partly replace the traditional. Compared to present hard chromium plating, it has many merits, but it also has some limitations. Achieve alloy or composite plating with better wear resistance, corrosion resistance and high-temperature oxidation resistance, Based on studying the mechanism of alloy or composite plating deeply. While optimize its craftwork conditions. Of course, there are lots of problems still unsolved and waiting for further discussion.

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