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Electroplating Technology of Trivalent Chromium Nickel Composite Coatings

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Abstract

In this paper, the commercial BSC16 trivalent chromium hard chromium plating solution was used as the base solution, nickel sulfate or nickel sulfonic acid was added, and the chromium-nickel composite metal deposit was prepared by periodically adjusting the constant current density. The test was conducted by Hall chamber experiment, scanning electron microscope and metallographic experiment. The experimental results showed that the composite chromium-nickel metal could be produced by periodically adjusting the constant current density. The width and number of cracks in Cr-Ni composite coatings become narrower, which may improve the protective properties of CR-Ni composite coatings. In the case of mechanical bending, the interlayer fracture occurs, which may improve the tough-plastic properties of CR-Ni composite coatings.

Keywords

Trivalent Chromium, Nichel, Composite Coating, Plating

1. Introduction

Hard chromium plating is an indispensable supporting process of the modern manufacturing industry. In machinery manufacturing, the shipbuilding industry, aerospace and other fields have been widely used, but the current chromium plating industry is generally used as the main component of the plating solution. Hexavalent chromium is a serious pollution of the environment, toxic and harmful, but also the environmental regulations of various countries strictly monitor and restrict the use of chemical substances [1]-[4]. For many years, people have been studying the use of trivalent chromium instead of hexavalent chromium plating, trivalent chromium toxicity is only 1% of hexavalent chromium, and can reduce electroplating wastewater more than 70%, the current efficiency is higher than hexavalent chromium plating, but the brittleness of trivalent chromium plating is relatively large, easy to form penetrative cracks, cannot meet the needs of many mechanical products. To improve the mechanical and protective properties of the coating, the chrome-nickel multilayer structure was prepared by periodically adjusting the electrodeposition current density [5].

2. Preparation Principle and Experimental Method of Chromium-Nickel Coating Structure

Reference [5] introduces the preparation of nickel-chromium multilayer structure in a trivalent chromium solution of chloride system, but the prepared coating is thin, and there is a certain distance to meet the engineering application. It has been introduced that trivalent chromium coatings can also be prepared when the content of nickel ions in a trivalent chromium sulfate system can reach a high concentration. The current density of chromium coating in a sulfate trivalent chromium plating solution system must reach 15 to 20 amps or more, but nickel ions can be deposited into nickel metal at current density below 5 amps. Above 35 amps, the deposited metal coating is chromium metal. Therefore, if the current density is set at a certain time interval, the nickel-chromium multilayer coating can be deposited. That is, the nickel-chromium multilayer coating can be prepared by periodically adjusting different current densities. As shown in the picture below:

In the low current density area, chromium metal will not be deposited, but nickel metal will be deposited, in the high current density area, the deposited coating is composed of chromium, through X-ray diffraction analysis, chromium content reaches more than 90%. The chromium-nickel composite coating structure was prepared.

3. Experimental Method and Experimental Equipment

3.1. Base Working Solution

The selection of trivalent chromium hard chromium base working solution is also the key to successfully preparing chromium-nickel composite coating. After comparing various trivalent chromium working fluids on the market, BSC16 trivalent chromium hard chromium plating was adopted. Because the plating bath is composed of chemical reagents with excellent stability, the flushing water of the parts after electroplating can be directly added to the bath, and even zero discharge of hard chromium electroplating can be achieved, which not only saves water and metal materials, but also protects the environment. Under the best electroplating conditions, the current efficiency can reach more than 30%, which is about three times the efficiency of conventional hexavalent chromium plating, and the deposition rate is about five times that of hexavalent chromium plating [6]-[9]. To reduce a metal chromium ion, the hexavalent chromium ion requires six electrons, and the trivalent chromium ion only requires three electrons, so the production of the same hard chromium coating, deducting the higher solution resistance to the current consumption, electroplating the same thickness of hard chromium plating, trivalent chromium hard chromium plating at least saves about 30% energy consumption than the hexavalent chromium hard chromium plating. This type of hard chromium plating technology is stable, insensitive to impurities such as iron, nickel, and hexavalent chromium ions, and easy to maintain, and can be added to the plating solution to prepare chromium nickel and other composite coatings, significantly improving the toughness and corrosion resistance of the coating. The coating produced by this type of hard chromium electroplating technology has good polishing performance, reduces the friction coefficient of copper-chromium friction pair, and improves the wear resistance. The comprehensive cost of this type of hard chromium plating technology is lower than that of hexavalent chromium plating, about 50% of that of hexavalent chromium plating, especially reducing the cost of wastewater treatment, environmental maintenance (such as no need to install chromium fog absorption recovery tower, strong exhaust at the plating site), and greatly improving the operating environment of the plating site. With the popularization and use of this technology and scale effect, the production cost has the prospect of reducing. The product conforms to ROSH law and relevant environmental protection regulations at domestic and abroad and belongs to energy-saving green environmental protection and safety electroplating technology [10]. The trivalent chromium concentrates working liquid developed by Beijing Blue Chemical Centre was used, the content of metal chromium ion was 25 g/l, and 2 g/l metal nickel ion was added. The Hull experiment was conducted on the brass Hull cell test plate with a special chrome-plated Hull chamber. The electroplating was conducted for one minute at a current density of 10 amps, a temperature of 45 degrees Celsius and a pH2. See **Figure 1** for the Hull slot test piece.

Figure 1. Hull cell test piece, ten amps, 42˚C with iridium-tantalum DSA anode, plating time 1 minute.

3.2. Modulate Current Method

Electroplating equipment that can modulate current is used to prepare chrome-nickel composite coatings with different thickness ratios according to different current modulation methods.

Metal content measurement of composite coating the chromium layer and the metal content in the nickel layer of the Cr-Ni composite coating were measured by X-ray respectively at different current densities.

Electron metallography the fracture and surface metallography of multi-layer structures were observed by electron microscope.

Mechanical properties the brittleness of the coating is measured by indentation method. Mechanical bending method was used to check the brittleness and fracture morphology of the coating.

4. Experimental Results and Analysis

4.1. Hull Cell Experiment

Standard Hull cell test, the temperature is 45 degrees Celsius, the current is ten amps, plating time is 1 minute.

It can be seen from the above picture of the Hall Chamber experiment that there is basically no chromium metal precipitation in the current density interval below 10 amps/cm^2, but nickel metal can be precipitated in the interval of 10 amps/cm^2, so the chrome-nickel composite metal deposit layer can be prepared by periodically controlling the deposition current density.

4.2. Experiment of Modulated Current Multilayer Structure and Electron Metallography of Chrome-Nickel Composite Coating Structure

The modulated current electrodeposition experiment was conducted after 20 g/L nickel sulfate was added into the base bath and fully dissolved.

We used 35 A/dm^2 per minute for chromium and 8 A/dm^2 for nickel, respectively (see **Figure 2**).

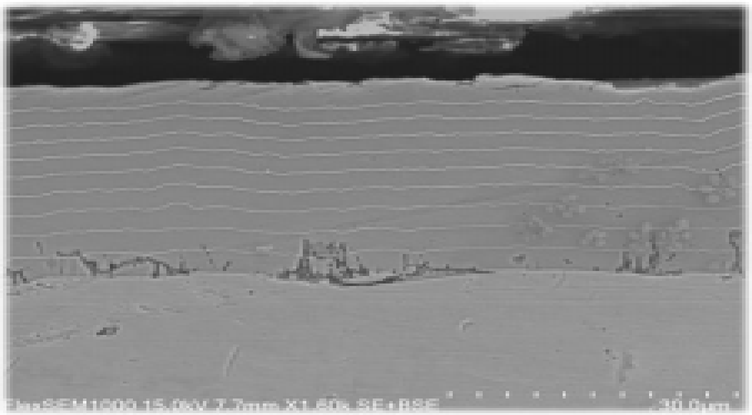

Figure 2. Electron metallography of chromium-nickel composite coating (11 layers).

Chromium 40 A/dm[2] for 30 seconds, nickel 5 A/dm[2] for one minute (see **Figure 3**).

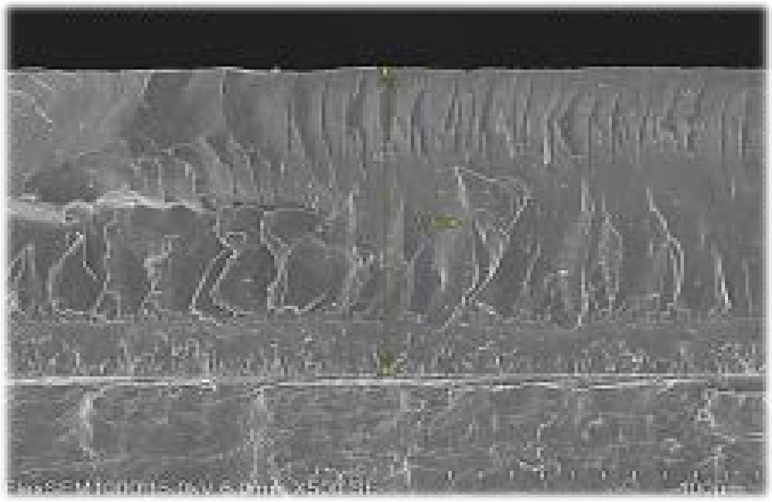

Figure 3. Electron metallography of trivalent chromium.

Multi-layer chromium-nickel deposition experiments were conducted by period-modulated current.

From the metallographic diagram (**Figures 2-3**), it can be found that the chrome-nickel multilayer structure is indeed prepared, but it is still not enough to reduce the brittleness of the chromium coating, and the internal stress still causes penetration cracks, but the cracks are less than that of single-layer chromium plating.

4.3. Fracture Morphology of Chrome-Nickel Composite Coating Structure

Figure 4. Fracture morphology of chromium nickel composite coating.

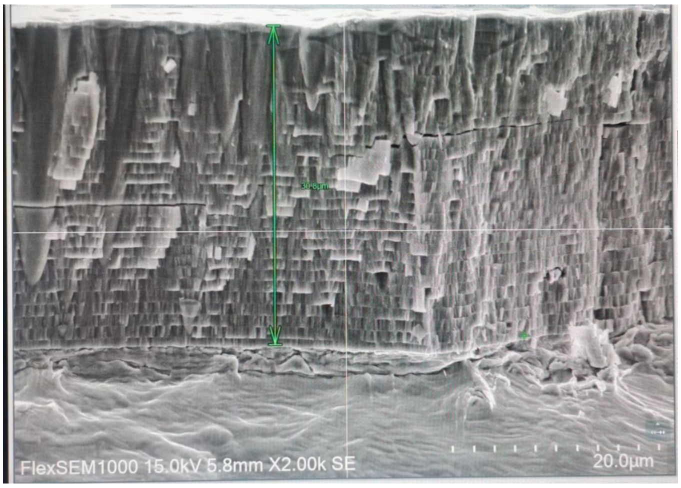

Figure 5. Fracture morphology of chromium-nickel composite coating.

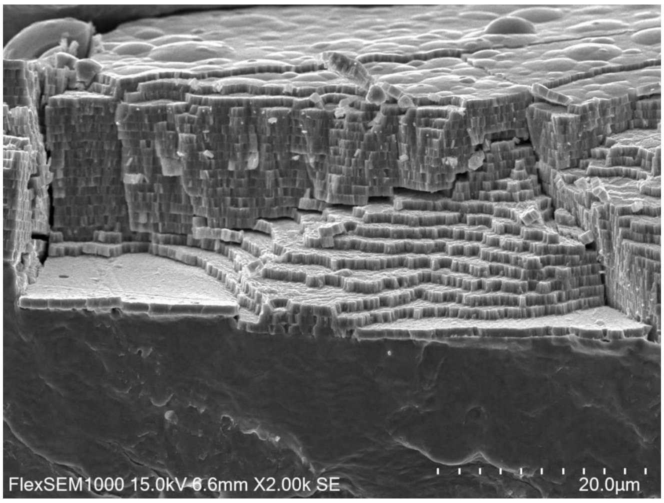

Figure 6. Fracture morphology of chromium-nickel composite coating.

The prepared chromium nickel composite coating was subjected to destructive bending experiments, and the fracture morphology was observed with an electron microscope, and it was found that the layered fracture was helpful to reduce the fracture brittleness (Figures 4-6).

4.4. Composition Analysis of Chromium-Nickel Composite Coating Structure

By X-ray diffraction analysis, the content of metal chromium in the chromium layer is more than 90%, and the content of metal nickel in the nickel layer is also more than 90%, indicating that the preparation of chromium-nickel composite electrodeposition layer is indeed realized.

4.5. Preparation of Microcrack Chromium-Nickel Composite Coating Structure

Previous experiments show that the thickness of the nickel layer is still not enough to relieve the electrodeposition stress of chromium. Therefore, the following micro-cracked chromium-nickel deposition layer is obtained by adjusting the modulated current electrodeposition parameters (**Figure 7**).

Figure 7. Microcrack metallography of Cr-Ni composite coating.

4.6. Chromium Nickel Composite Plating Sample and Rockwell Hardness Indentation Test

By adjusting the modulated current parameters and the composition of the solution, the chromium-nickel composite metal of the rod-like material (30CrMnSi) was electrodeposited (**Figure 8**), and the chromium-nickel composite coating without cracks was obtained (**Figure 9**). The indentation experiment shows that it has excellent toughness. The indentation test of single-layer trivalent chromium coating showed many cracks (**Figure 10**). It is proved that good toughness of chromium-nickel composite coating can be obtained by careful selection of modulated current parameters and other process parameters.

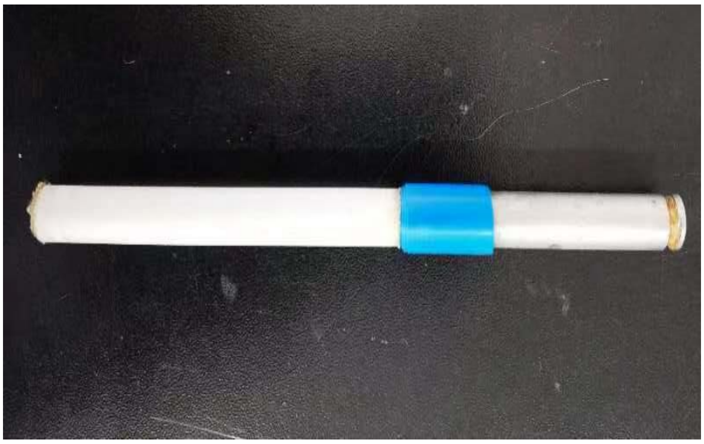

Figure 8. Chromium-nickel composite coating on 30CrMnSI steel with upper, middle, and lower thickness of eighty microns, seventy microns and one hundred microns, respectively.

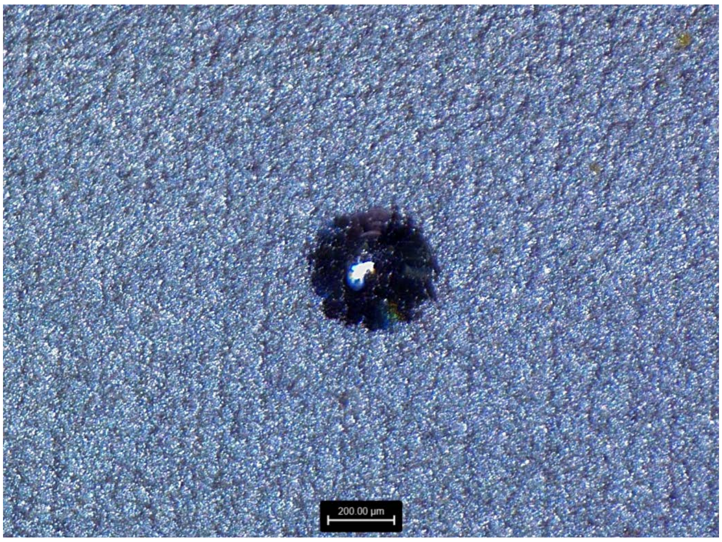

Figure 9. Chromium-nickel composite coating 60 kg Rockwell hardness indentation test.

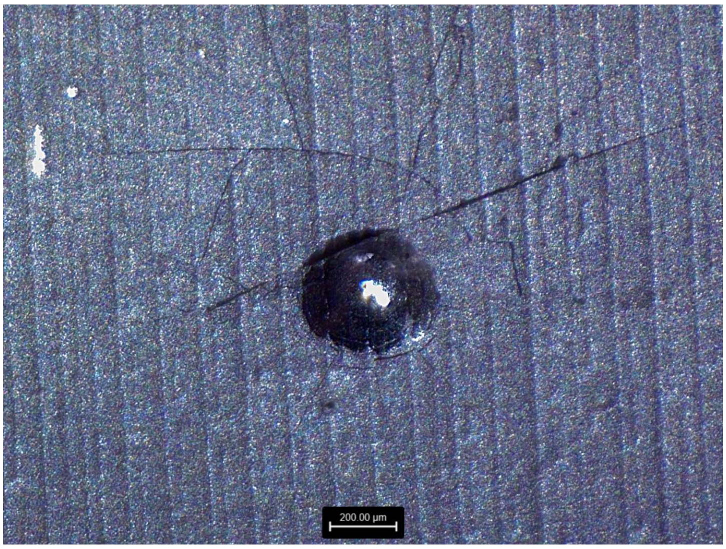

Figure 10. 60 kg rockwell hardness indentation test of trivalent chromium coating.

5. Conclusion

The chromium-nickel composite coating can be prepared in the solution developed by the modulated current method. Using appropriate modulated current parameters and solution composition, microcrack chromium-nickel composite coating can be prepared. Microcrack chromium-nickel composite coating has good tough-plastic properties and predictable corrosion.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Kvashnin, A.G., Oganov, A.R., Samtsevich, A.I. and Allahyari, Z. (2017) Computa-

tional Search for Novel Hard Chromium-Based Materials. *The Journal of Physical Chemistry Letters*, **8**, 755-764. https://doi.org/10.1021/acs.jpclett.6b02821

[2] Liang, A., Li, Y., Liang, H., Ni, L. and Zhang, J. (2017) A Favorable Chromium Coating Electrodeposited from Cr(III) Electrolyte Reveals Anti-Wear Performance Similar to Conventional Hard Chromium. *Materials Letters*, **189**, 221-224. https://doi.org/10.1016/j.matlet.2016.12.022

[3] Castro-Rodríguez, A., Carro-Pérez, M.E., Iturbe-Argüelles, R. and González-Chávez, J.L. (2014) Adsorption of Hexavalent Chromium in an Industrial Site Contaminated with Chromium in Mexico. *Environmental Earth Sciences*, **73**, 175-183. https://doi.org/10.1007/s12665-014-3405-4

[4] Liu, S., Mishra, S.B., Zhang, Y. and Qi, L. (2017) Uptake of Hexavalent Chromium in Electroplating Wastewater by Hydrothermally Treated and Functionalized Sand and Its Sustainable Reutilization for Glass Production. *ACS Sustainable Chemistry & Engineering*, **5**, 1509-1516. https://doi.org/10.1021/acssuschemeng.6b02185

[5] Huang, C.A., Chen, C.Y., Chen, C.C., Kelly, T. and Lin, H.M. (2014) Microstructure Analysis of a Cr-Ni Multilayer Pulse-Electroplated in a Bath Containing Trivalent Chromium and Divalent Nickel Ions. *Surface and Coatings Technology*, **255**, 153-157. https://doi.org/10.1016/j.surfcoat.2014.03.062

[6] Li, J.Z., Li, Y.J., Tian, X.H., Zou, L., Zhao, X., Wang, Y.F. and Wang, S.G. (2017) The Hardness and Corrosion Properties of Trivalent Chromium Hard Chromium. *Materials Sciences and Applications*, **8**, 1014-1026. http://www.scirp.org/journal/msa

[7] Liao, C., Lee, H., Hou, K., Jian, S., Lu, C. and Ger, M. (2016) Characterization of the Cr-C/Si_3N_4 Composite Coatings Electroplated from a Trivalent Chromium Bath. *Electrochimica Acta*, **209**, 244-253. https://doi.org/10.1016/j.electacta.2016.05.084

[8] Schopphoven, T., Gasser, A., Wissenbach, K. and Poprawe, R. (2016) Investigations on Ultra-High-Speed Laser Material Deposition as Alternative for Hard Chrome Plating and Thermal Spraying. *Journal of Laser Applications*, **28**, Article ID: 022501. https://doi.org/10.2351/1.4943910

[9] Li, J., Li, Y., Tian, X., Zou, L., Zhao, X., Wang, S., *et al.* (2017) The Hardness and Corrosion Properties of Trivalent Chromium Hard Chromium. *Materials Sciences and Applications*, **8**, 1014-1026. https://doi.org/10.4236/msa.2017.813074

[10] Li, J.Z., Mao, Z.L., Ding, Y., *et al.* (2012) Research of Trivalent Chromium Plating. *Planting & Finishing*, **34**, 14-17.