The Study on Microstructure and Wear-resistance Mechanism of A Chromium Replacement Coating

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ABSTRACT

A new chromium replacement coating has been developed. This paper investigates this new coating's microstructure at different temperature using X-ray diffractometer, transmission electron microscope and surface analytical apparatus. The results revealed that the new coating is composed of amorphous and microcrystalline matrix and intermetallic compounds. Such a microstructure is very beneficial to improving its wear resistance.

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1. INTRODUCTION

Among the wear-resistance electroplated metals, chromium plating coating is most widely used, because the radius of its atoms is relatively small and the atoms can be bonded with each other very closely, chromium coatings have high lattice energy and hardness. However, the chromium ions (Cr^{6+}) are poisonous. It has been reported that the chromium ions can case cancer and also harmful to the agricultural production and microbe[*].

Since 1930s, electroplating researchers around the world have been studying various chromium replacement coatings and have achieved great success. The electroplating of Sn-Co alloy is the most promising example. It has excellent corrosion resistance and a beautiful outlook, but its serious drawback is its low hardness and poor wear resistance (~ 50% that of chromium)[**].

Other than the So-Co alloy, some other new products have also been developed, including trivalent chromium electroplating; electrodeposition Fe-Cr, Ni-W-B, Ni-W-P, Co-W, Ni-P and Ni-P-SiC. So far none of the above can universally replace electrodeposited chromium when wear resistance, corrosion resistance, complexity of the process and costs are all considered.

To overcome the disadvantages of these chromium replacement coatings, we have developed a new generation of chromium replacement coating-METTEX 6, which has excellent properties and simpler plating process.

This paper attempts to investigate the microstructure of this newly developed coating and reveal its mechanism of wear resistance.

1. EXPERIMENTAL METHODS

(1) Materials of Micro-analyses

The 1018 plain carbon steel with dimensions of 100x20x3 mm^3 was used as the substrate. After grinding, 30 μm chromium replacement alloy coating was plated. The composition of plating coating is Ni 68%, Co 30% and X 2% (selecting X member from IIIA group of periodic table of the elements). Then this steel plate was cut into small pieces of 15x10x3 mm^3 for X-ray and TEM analyses.

Table 1 Regimes of Heat Treatment

Sample No.	0	1	3	4	5	7
Heat temp. (^oC)	Room temp.	100	300	400	500	700
Holding time (hr).	1	1	1	1	1	1
Cooling rate	Cooling in furnace	Cooling in furnace	Cooling in furnace	Cooling in furnace	Cooling in furnace	Cooling in furnace

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[*] "The Toxicity of Chromium and Inorganic Chromium Compounds", *HSE Toxicity Review* TR31 HMSO (1989)

[**] George Shahin. CEF., "Alloys are Promising as Chromium Cadmium Substitutes.", *Plat. & Surf. Finish.*, 1998,85(8):8-14

(2) Heat Treatment

In order to understand the plating coating’s amorphous structure behavior, the samples for TEM analyses were heat-treated in a vacuum furnace with the regimes as shown in Table 1.

(3) Analyses of Microstructure

AD/max-RA model X-ray diffractometer was employed for analyses of phase constitution (Cu target, λ=1.5418A, tube potential 40KV, beam current 120mA), and a JEM 200-EX model Transmission Electron Microscope was used for analysis of microstructure.

2. RESULTS AND DISCUSSIONS

(1) The Phase Constitution Of Alloy Plating Coating

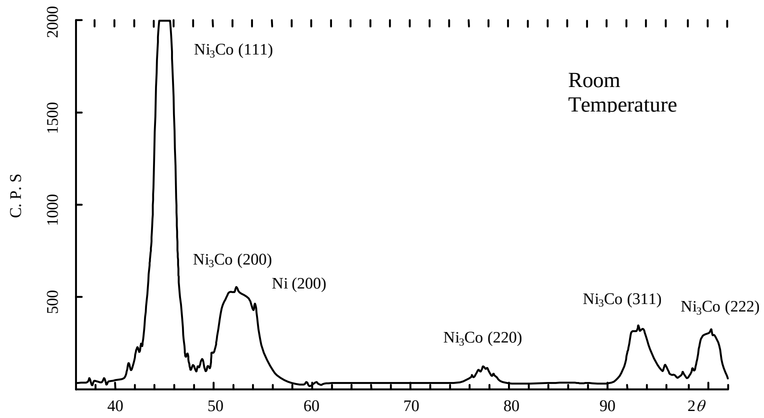

Figure 1 X-ray Diffraction Pattern of Chromium Replacement Alloy Coating at Room Temperature

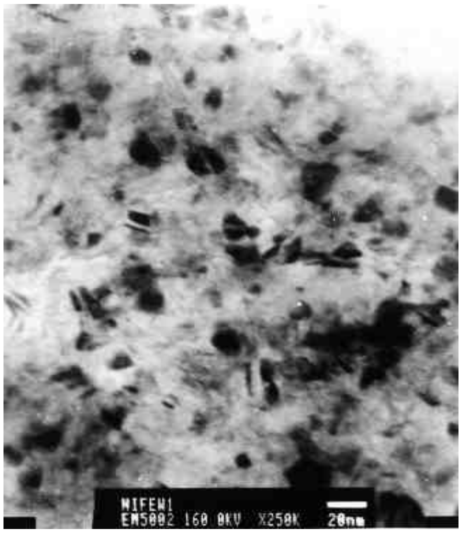

Figure 2 The TEM Morphology of Chromium Replacement Alloy Coating

Figure 1 shows the results of X-ray diffraction of chromium replacement alloy coating at room temperature. It is composed of nickel based solid solution containing cobalt and X, and intermetallic compound Ni_3Co, Ni_2X, and Co_2X. The peak profiles of Ni_3Co, Ni_2X and Co_2X are broad, and that of the solid solution is diffuse, resulted from the scattering of its microcrystals and amorphous structure.

Figure 2 shows the TEM morphology of the alloy coating. There are many finely dispersed precipitates, about 10 nm in size, present in the matrix.

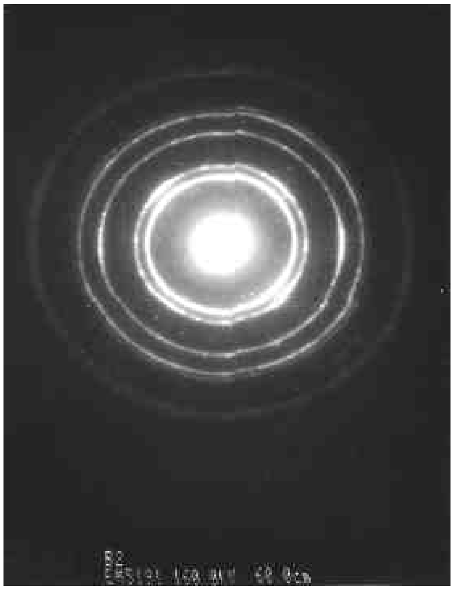

Figure 3 Electron Diffraction Pattern of Chromium Replacement Alloy Coating

The selected area diffraction pattern (*Figure 3*) shows diffraction rings characteristic of a microcrystal structure. The distribution of spots on the rings suggests that the main contribution to this diffraction pattern comes from an ordered FCC structure with a lattice constant of 0.356 nm (i.e.,Ni_3Co).

When the chromium replacement alloy coating was heated at 100^oC, its X-ray diffraction spectrum did not show any difference to those samples without heat treatment. Because the alloy coating is still in relaxation stage, the atoms can move only in local area, thus presents a high degree of short- range ordering.

Figure 4 shows the X-ray diffraction spectra of the chromium replacement alloy coating after heat-treated at 200^oC. There appeared many small diffraction peaks on the main wide peaks. However, they are neither Ni, Co nor Ni_3Co, but something that cannot be easily identified according to the present ASTM cards.

A local magnified diffraction ring of the No.2 Sample is shown in *Figure 5*. It is obvious according to the distribution of diffraction spots on the ring that the structure is not composed of a single but several substances, the lattice constants of which show only a little difference within 5%. Such a phenomenon is in accordance with the results of the X-ray diffraction (*Figure 4*).

The crystallization process of amorphous structure always starts from the formation of a sub-stable transition phase[*]. Therefore, we believe that the small diffraction peaks in *Figure 4* (or diffraction spots on the rings in *Figure 5*) probably come from the formation of a sub-stable phase Ni_xCo_y (or Co_xNi_y).

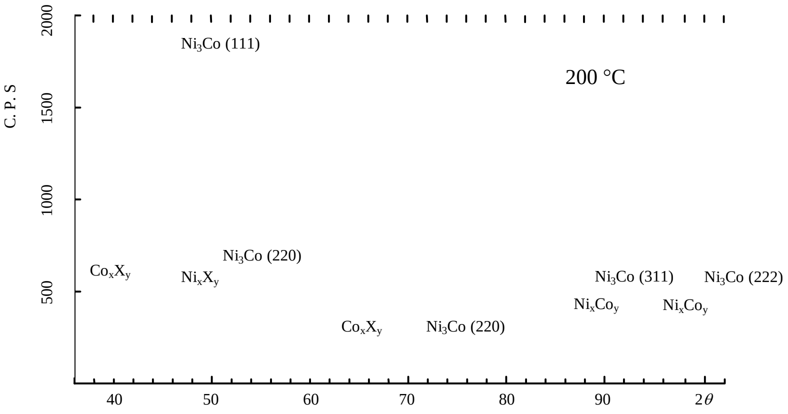

Figure 4 X-ray Diffraction Pattern of Chromium Replacement Alloy Coating at 200°C

In order to examine the changes of properties in the crystallization process of the chromium replacement alloy coating, hardness were also tested at different temperature levels. The results are shown in Table2.

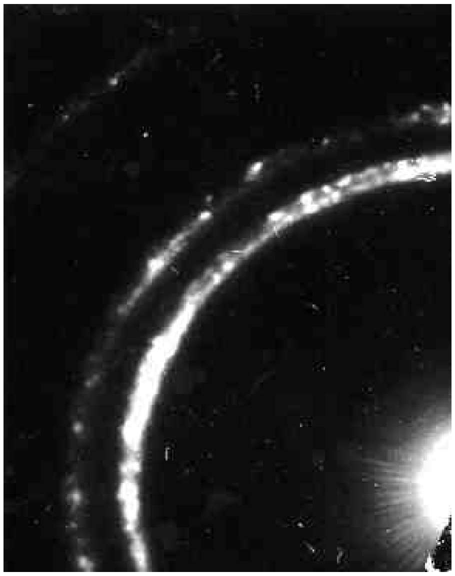

Figure 5 Enlarged Image of Electron Diffraction Pattern of Chromium Replacement Alloy Coating

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[*] Wenhua Hui, and Jiajun Liu, The Study on Microstructure of Ni-Fe-W-P Brush Plating Layer. Proceeding of the International Symposium on Tribology.1993(10):696-703

Table 2 Hardness of Plating Coating at Different Temperatures

Heat treatment temp.(^{o}C)	Room temp.	100	200	300	400	500	600	700
Hardness (Hv_{50})	910	910	1120	900	780	710	630	420

The table indicates that maximum hardness appears after heat-treated at 200^{o}C. This result corresponds to the fact that there are more small diffraction peaks as shown in *Figure 4* and more diffraction spots on the ring in *Figure 5*.

Based on the analyses of microstructure, the strengthening mechanisms of the chromium replacement alloy coating can be explained from two aspects: First, the role of grain boundaries. As shown in *Figure 2*, the grain boundaries are almost invisible due to the too small grain sizes of matrixes. It is estimated at about 2 nm according to the TEM analyses. Such a structure with so fine grain must be greatly strengthened by its grain boundaries.

The other one is the role of dispersively distributed intermetallic compound Ni_3Co, $Ni_2X$and Co_2X, which can strengthen the material to a considerable extent due to the coherency of precipitated with the matrix.

(2) Industry testing

This chromium replacement alloy coatings were plated onto rotogravure cylinders are typically plated with 6-8 μm of chromium to enhance their wear resistance and increase their service life. The properties of the chromium replacement alloy coated cylinders were then tested by a leading manufacturer in plating equipment manufacturing. According to them, this replacement coating outrun the chromium plated cylinders by three times. This performance is better than our own laboratory tests, which shows a 200% increase in wear resistance. According to this manufacturer, after 3,000,000 revolutions, the tested cylinder had two fine scratches around it in an non-engraved area. Typically, the service life of a chromium-plated cylinder under the same conditions is 600,000 to 1,000,000 revolutions[*]

In the printing process, a doctor blade pressure of 6 kg was used on the cylinder surface to scrape off the ink. This is a most typical fatigue wear. Fatigue wear may happen when a surface is loaded cyclically with repeated sliding, rolling or impact. Fatigue wear, in general, is caused by repeated stress and unstress that produces cracks at or just below the surface. Further cycles cause the cracks to grow, line up and eventually break through to the surface, thus produce discrete wear debris particles. The chromium replacement alloy coating has a good wear resistance largely because of its intermetallic compounds - hard particles. When fatigue wear occurs, the cracks on intermetallic compound initiate, grow, and line up, but they still cannot break through from its surface because it is surrounded by soft nickel based solid solution intermetallic compounds. Also, such a structure can effectively prevent cracks to grow and decrease the wear rate.

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[*] Wenhua Hui, METTEX 6 –A Chromium Replacement Coating Process and Technology, Gravure, 2000(1):54-59

3. CONCLUSIONS

- The structure of the chromium replacement alloy coating consists of an amorphous matrix, including some microcrystals containing dispersed Ni_3Co, Ni_2X and Co_2X precipitates.
- Such a microstructure can greatly reduce fatigue wear because the solid solution can passivate the cracks to grow on intermetallic compounds.
- Its strengthening mechanisms are caused by grain boundaries and coherent precipitated fine particles.
- Industry tests show that it is an excellent and practical chromium replacement.

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