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Electroplating process of amorphous Fe-Ni-Cr alloy①

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[Abstract] A novel process of electroplating amorphous Fe-Cr-Ni alloy in chloride aqueous solution with Fe(Ⅱ), Ni(Ⅱ) and Cr(Ⅲ) was reported. Couple plasma atomic emission spectrometry (ICP-AES), X-ray diffractometry(XRD), scanning electronic microscopy(SEM), microhardness test and rapid heating-cooling method were adopted to detect the properties of the amorphous Fe-Ni-Cr deposit, such as composition, crystalline structure, micrograph, hardness, and adherence between deposit and substrate. The effects of the operating parameters on the electrodeposit of the amorphous Fe-Ni-Cr alloy were discussed in detail. The results show that a 8.7 μm thick mirror-like amorphous Fe-Ni-Cr alloy deposit, with Vicker's hardness of 530 and composition of 45%~55% Fe, 33%~37% Ni, 9%~23% Cr was obtained by electroplating for 20 min at room temperature(10~30 ℃), cathode current 10~16 A/dm^2, pH = 1.0~3.0. The XRD patterns show that there only appears a broad hump around 2θ of 41°~47° for the amorphous Fe-Ni-Cr alloy deposit, while the SEM micrographs show that the deposit contains only a few fine cracks but no pinholes.

[Key words] amorphism; Fe-Ni-Cr alloy; electroplating; trivalent chromium; chloride
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1 INTRODUCTION

The amorphous alloys are a new kind of materials with short-range order and long-range disorder. They display macroscopic uniformity and isotropy. Because of their excellent physical, chemical and mechanical properties, the research and development of the amorphous alloys becomes wider and deeper in such fields as decoration, corrosion-resistance, repairing of mechanical components and parts, preparation of super-hard materials, production of magnetic materials, semi-conducting materials, electrochronic chromatic materials and electronic materials[1~4].

Few reports about the study of electroplating amorphous Fe-Ni-Cr alloy can be found[5~7], and there are some problems which also exist in the common electroplating of Fe-Ni-Cr alloy to be solved[6, 8, 9]. Theoretically, the amorphous stainless steels have both the advantages of the smelted stainless steels and especially excellent corrosive pitting resistance. Therefore, it is theorectically and practically important to study the process of electroplating amorphous Fe-Ni-Cr alloy deposits.

Combined with the previous results of electroplating amorphous Cr and Fe-Ni alloy[10~14], the authors systematically studied the effects of operating parameters on electroplating mirror-like amorphous Fe-Ni-Cr alloy in chloride equeous solution at room temperature.

2 EXPERIMENTAL

The electrolyte composition listed in Table 1 was adopted to study the process of electroplating amorphous Fe-Ni-Cr alloy. All the agents used are analytically pure or chemically pure. The solutions were prepared using distilled water. The test anode is insoluble titanium net(40 mm × 50 mm × 1.5 mm); the substrate is pretreated copper plate(20 mm × 20 mm) prepared using 0.2mm thick pure copper film (99.95% purity).

The appearance quality was evaluated by range estimation; the bonding force was analyzed by bending tests and rapid heating-cooling tests; the average thickness of the deposits was calculated from the mass difference before and after electroplating; the microhardness values were measured with an HV-50 microhardness tester[10, 11, 13, 15].

The determination of the composition, the analysis of the crystalline structure and the observation of the micrographs of the Fe-Ni-Cr alloy deposits were performed by P6-6 couple plasma atomic emission

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Table 1 Electrolyte composition for Electroplating amorphous Fe-Ni-Cr alloy

Component	Concentration/ (g•L^{-1})
$CrCl_3 \cdot 7H_2O$	120
$[Fe^{2+}]/[Ni^{2+}]$	0.08
H_3BO_3	35
KBr	15
KF	0.10~ 0.20
H-L(Complexing agent)	80
H-W(Stabilizer)	80
T1(Additive 1)	0.06~ 0.10
T2(Additive 2)	0.05~ 0.20
Wetting agent	0.04~ 0.20

spectrometer, Rigaku D/max-rA10 X-ray diffractometer and Hitachi S-570 scanning electron microscope.

3 RESULTS AND DISCUSSION

3.1 Effect of cathod current density on deposit composition

The effect of cathod current density on deposition composition is shown in Fig. 1. It can be seen that, with increasing cathod current density, the content of Cr increases sharply, and when the cathod current density reaches 14 A/dm^2, it decreases slightly; the content of Fe decreases with increasing cathod current density and tends to be stable; the content of Ni almost does not change with the cathod current density.

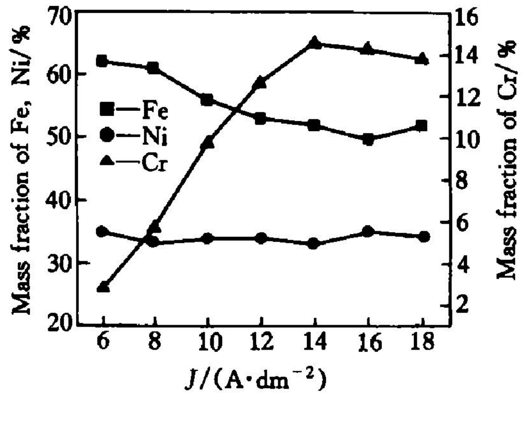

Fig. 1 Effect of cathod current density on composition of Fe-Ni-Cr deposit
(pH= 2, θ= 20 ℃, t= 20 min)

The rise of current density helps to raise the content of Cr in the Fe-Ni-Cr deposit, but when the cathod current density surpasses 18 A/dm^2, the Fe-Ni-Cr deposit is apt to turn white and dark; if the electroplating time is prolonged, then the deposit is easy to crack and peel off. On the contrary, if the cathod current density is too low, then the content of Cr in the deposit will be lower than just enough, thus it is difficult to meet the requirement of stainless steel that the content of Cr must be higher than 12%. It is known from comprehensive analysis that the proper cathod current density is 10~ 16 A/dm^2, and the corresponding content of Cr in the deposit is 9.7% ~ 14.5%.

3.2 Effect of electrolyte temperature on deposit composition

The effect of electrolyte temperature on deposit composition is shown in Fig. 2. It can be seen that, with increasing electrolyte temperature, both the contents of Fe and Cr increase gradually, while the content of Ni decreases rapidly. When the temperature is higher than 40 ℃, the content of Cr in the deposit is below 5%.

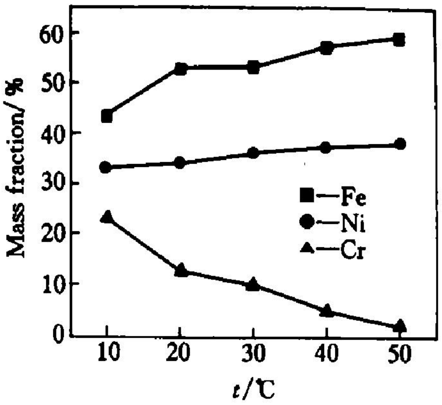

Fig. 2 Effect of electrolyte temperature on composition of Fe-Ni-Cr deposit
(J= 12 A•dm^{-2}, pH= 2, t= 20 min)

On one hand, the rise of electrolyte temperature can raise the diffusion and migration rate of the ions and weaken the cathod polarization; on the other hand, it can raise the energy of ions so as to promote the electroplating reactions of Fe^{2+}, Ni^{2+} and Cr^{3+} ions, thus accelerating the electroplating of the Fe-Ni-Cr alloy. But the rise of electrolyte temperature affects the reaction rates of Fe^{2+}, Ni^{2+} and Cr^{3+} ions with different electrode potentials to different extents. The electrode potentials for the electroplating reactions of Fe^{2+} and Ni^{2+} ions are similar and far larger than those for the Cr^{3+} ions, therefore the effects of the rise of electrolyte temperature on the elctroplating reactions of Fe and Ni are similar and larger than that of Cr. As a result, the contents of Fe and Ni increase with the electrolyte temperature but that of Cr decreases on the contrary. However, over high temperature will accelerate the olation of Cr^{3+} ions, thus affecting the appearance of the Fe-Ni-Cr alloy deposit and the content of Cr[8, 13, 14, 16, 17]; at the same time over high temperature will make the Fe^{2+} ions in the electrolyte rapidly oxidize into the

Fe^{3+} ions to deteriorate the deposit quality[18]. Additionally, too low temperature will inevitably slow down the electroplating reactions. Furthermore, both need additional heating or refrigeration apparatus, thus raising the operating costs. Therefore, the proper electrolyte temperature is 10~ 30 ℃.

3.3 Effect of pH value of electrolyte on deposit composition

The effect of pH value of the electrolyte on the deposit composition is shown in Fig. 3. With increasing pH value of the electrolyte, the content of Cr in the deposit first gradually then rapidly decreases, while that of Ni changes contrarily. The content of Fe increases gradually when $pH < 3$ and decreases gradually when the $pH > 3$.

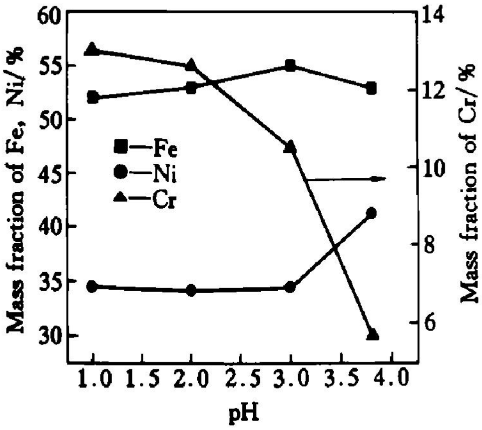

Fig. 3 Effect of pH value of electrolyte on composition of Fe-Ni-Cr deposit
($J = 12\ A\cdot dm^{-2}$, $\theta = 2$ ℃, $t = 20\ min$)

The required pH values for the formation of $Cr(OH)_3$, $Ni(OH)_2$ and $Fe(OH)_2$ are 4.6, 6.9 and 7.6 respectively[17]. Therefore, the effect of the pH value of electrolyte on the electroplating process of Cr is the greatest[16]. When the pH value of the electrolyte reaches a certain value, the effect of pH value on electroplating Cr becomes stronger and stronger as the pH value rises, and the content of Cr begins to decrease rapidly.

Because of the presence of H-W stabilizer, the Cr^{3+} ions in the electrolyte mainly exist in the form of highly active compounding ions such as $[Cr(H_2O)_6]^{3+}$ and Cr(Ⅲ) ~ (H-W)[14, 16, 19], and their concentration changes have little effects on the electroplating behavior of Cr(Ⅲ) when the pH value of the electrolyte is relatively small. But when the pH value is over 3, as the electroplating reaction progresses, the local pH value and temperature at the electrode/solution interface will further rise, which will accelerate the olation of Cr^{3+} ions and rapidly decrease the content of Cr in the deposit. As a result, the deposit quality will become worse. Therefore, the proper pH value is 1.0~ 3.0.

3.4 Composition and crystalline structure of deposit

Based on the above analyses, it can be known that the proper electroplating parameters when using the electrolyte composition in Table 1 are temperature of 10~ 30 ℃, and pH value of 1.0~ 3.0. The appearance and color of the Fe-Ni-Cr deposit prepared by electroplating for 20 min under the above conditions are similar to those of the mirror-like stainless steels. The deposit has a thickness of 8.7 μm, and a microhardness of about HV530. The contents of Fe, Cr and Ni in the deposit are 45% ~ 55%, 33% ~ 37% and 9% ~ 23% respectively, and all the elements display amorphous structures. The results of bending tests and heating-rapid cooling tests show that, the bonding between the deposit and the substrate is good, and there occurs some peeling off only when the appearance of the deposit turns white or grey.

SEM observations (Fig. 4) show that the surface

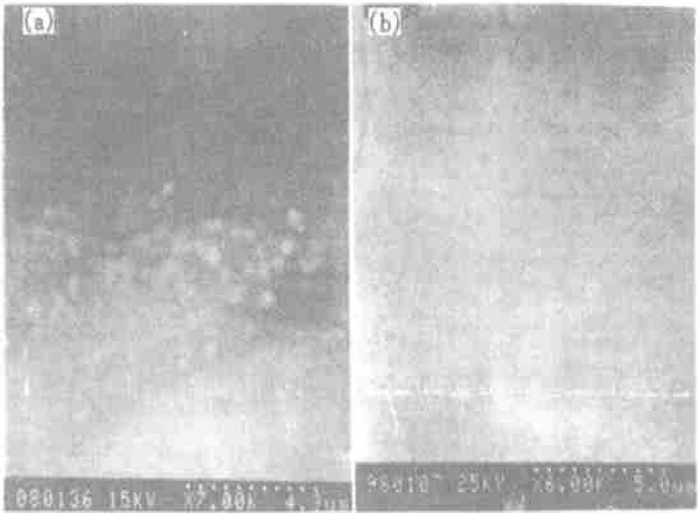

Fig. 4 SEM micrographs of amorphous Fe-Ni-Cr electrodeposits
(a) —$J = 12\ A/dm^2$, $t = 20\ min$; (b) —$J = 12\ A/dm^2$, $t = 40\ min$

of the deposit is flat and smooth and there are not any pinholes; only when the electroplating time is too long (> 40 min), there will occur some small cracks on the Fe-Ni-Cr deposit surface but no pinholes, which is similar to the cases of amorphous Cr and Fe-Cr electrodeposits[10, 11, 13].

The results of X-ray diffraction in Fig. 5 show that there are not any characteristic diffraction peaks of Fe, Ni, Cr and Fe-Ni alloy ($2\theta = 20° \sim 120°$)[12, 13, 20] and there is only a broad bump around 2θ of 41° ~ 47°. This indicates that the Ni-Fe-Cr electrodeposits have amorphous crystalline structures, which may be due to the reduction reactions among the H-W stabilizer, compounding agent H-L, additive T1 and T2[6, 10, 13], and the presence of the other elements such as B, C, H and O[5, 6, 10, 13, 20].

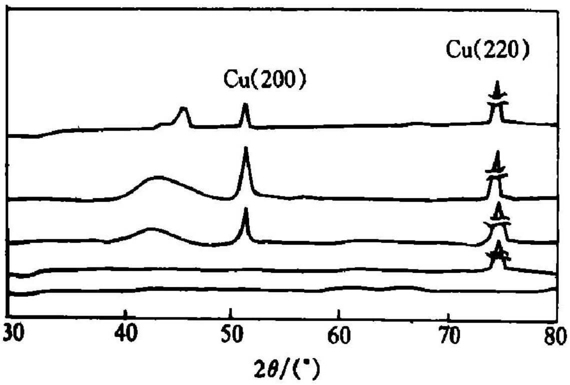

Fig. 5 X-ray diffraction patterns of amorphous Fe-Ni-Cr electrodeposits
(Cu K_α, voltage 50 kV, current 100 mA)

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