

**IN SITU MONITORING OF THE ELECTROPLATING
PROCESS AND ITS PHOTOCATHODIC PROTECTION
FROM CORROSION OF Fe-Cr ALLOY BY THE USE OF
QUARTZ CRYSTAL MICROBALANCE**

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INTRODUCTION

Recently aluminum alloys are widely used for the chassis materials for motorcycles, and quite recently they have been gradually adapted as that for special automobiles, for example hybrid vehicles, which need sufficient lightweight properties. Generally aluminum alloys shows good durability for corrosion and they also shows good heat sinker. So most motorcycles aware the engine block made of aluminum alloy. We wanted to apply this aluminum alloy material to the rear brake disk for motorcycle. But there are some problems before using such aluminum alloy for brake disk, aluminum alloys doesn't have such a high wear resistance. So surface finishing has to be made on the surface of aluminum brake disk. Already we have presented that the iron-chromium alloy plated aluminum alloy possessed quite high Vickers hardness more than 1,000, by after treatment of nitridation.¹⁾ Even as-deposited samples show Vickers hardness of 700. The hardness depends on the composition of the alloy, namely the content of chromium. In this report we investigated the mechanism of the iron-chromium alloy plating on the aluminum substrate by use of quartz crystal microbalance, which can detect nano-scale mass change of the sample.

In the end of this paper newly developed photocathodic protection from corrosion of thus prepared Fe-Cr alloy will be presented.

EXPERIMENTAL

The substrate for quartz crystal microbalance (hereinafter denoted as QCM) was an AT cut crystal (Maxtek Inc., SC501), which was coated with aluminum pure metal by use of vacuum deposition. The QCM apparatus consists of three parts, frequency counter (PM-700), sensorhead and accessing computer hardware. Conventional three-electrode-type electrochemical set-up was adopted by use of carbon rod as counter electrode (Anode), saturated calomel electrode as reference electrode.

The electrodeposition were controlled under the galvanostatic conditions at 7.5, 25.5, 43.8 mA/cm². The composition of the electrolytic bath was shown in the **table 1**.

Table 1 The main composition of the bath for Iron-chromium alloy plating.

FeSO ₄	40g/dm ³
Cr ₂ (SO ₄) ₃	120g/dm ³
HCOONH ₄	55g/dm ³
(NH ₄) ₂ C ₂ O ₄	10g/dm ³
KCl	54 g/dm ³
NH ₄ Cl	54 g/dm ³
H ₃ BO ₃	40g/dm ³

Zincate pre-treatment of the aluminum electrode was performed.

The morphologies of thus deposited film were investigated by use of Scanning electron microscope (S-4500, Hitachi Co. Ltd.).

It has been reported that the relationship between the mass change and the frequency change, named "sauerbrey equation" as shown in the following.

$$\Delta m/A = -N \rho \Delta f / f_0^2$$

Where Δm : mass change[g], A: electrode area[cm³], Δf : frequency change[Hz], N: constant coefficient[cm · Hz], ρ : density of quartz[g/cm³], f_0 : Original resonant frequency of the sample quartz[Hz]

From this equation the mass change can be calculated from the frequency change of the QCM electrode.

RESULTS AND DISCUSSION

The time dependence of the mass change in the case of constant current mode at 7.5 mA/cm² was shown in **figure 1**.

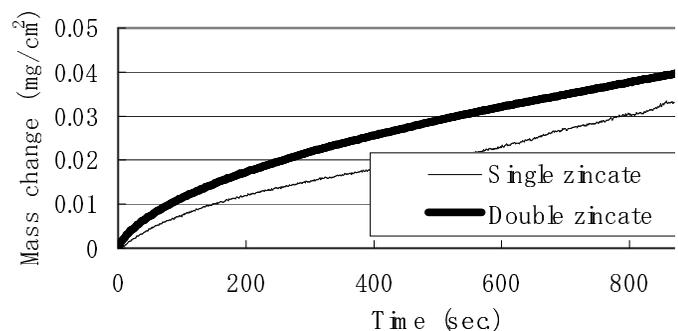


Fig. 1 Time dependence of mass change under the current density of 7.5 mA/cm²

From this figure we can evaluate the effect of double zincate treatment, which accelerate the plating. But in the case of higher current density, 43.8 mA/cm², the effect of acceleration

was not so obvious.

Under low current density region clear difference could be observed between the sample in the case of double zincate treatment and the one in the case of single zincate one. But under high current density region such a difference could not be observed between them. From above results it was suggested that double zincate treatment was important especially at the position where local current density was lowered, for example in the concave region.

Under the lower current density the chromium content of the obtained plated films is lower, which is reasonable considering that the supposed potential of polarization will be more positive in the case of lower current densities. (The standard redox potentials are -0.744 V vs. NHE, for Cr^{3+}/Cr , -0.44 V for Fe^{2+}/Fe , respectively.) And in the case of double zincate treatment the content of chromium is somewhat higher than in the case of the single zincate treatment. Perhaps the potential of the polarization in the case of double zincate treatment will be slightly more negative than that in the case of single zincate treatment, perhaps due to the decrease of exchange current density at the surface where the double zincate treatment has been applied, which will increase the overpotential for metal plating, because the electric conductivity of zinc is slightly lower than the one of aluminum. But this difference is not so clear.

Thus prepared Fe-Cr alloy will not be so resistant to the corrosion. So photocathodic protection from corrosion have been tried. RF sputtered Titanium Dioxide film was used for the photoanode. The photoanode was directly connected to the Fe-Cr plated QCM electrode in 1% NaCl aqueous solution. And the effect of the photocathodic protection has been investigated quantitatively by the use of QCM.

REFERENCE

1) Sachio YOSHIHARA, Kei-ichiro MOTOI, Akio CHIBA, Takashi SHIRAKASHI, Namio KUDOH, Wataru OIKAWA, Proceedings of 100th Meeting of the Surface Finishing Society of Japan, 58 (1999)