Fe-Cr Compositionally Graded Films by Use of Electroplating

Sachio Yoshihara, Kenji Kubota, Namio Kudoh, Wataru Oikawa**

*Utsunomiya University, *Nippon Platec Co., Ltd.*

Graduate School of Engineering, Utsunomiya University (7-1-2 Yoto, Utsunomiya-shi, Tochigi 321-8585)

**NIPPON PLATEC Co., Ltd (7-334 Nishimishima, Nishinasuno-machi, Nasu-gun, Tochigi 329-2756)*

Fe-Cr alloy plating shows superior resistivities for abrasives. But sometimes thus plated films shows inferior resistivities for heat shock or inferior adhesion strength. The origin for above mentioned disadvantages is perhaps attributed to their internal stress of plated films. So, for the purpose of relaxation of the internal stress, we tried to fabricate the Fe-Cr compositional graded films by successive stepwise electroplating technique. The plating current density was stepwise increased during deposition, initially 10 mA/cm^2 to finally 50mA/cm^2. Thus prepared film showed quite superior resistivities for heat shock test.

For more informations, contact:
Assoc. Prof. Dr. Sachio Yoshihara
Department of Energy & Environmental Science,
Graduate School of Engineering, Utsunomiya University,
7-1-2 Yoto, Utsunomiya, Tochigi 321-8585, Japan
Phone & Fax: +81-28-689-6150,
E-mail: sachioy@ees.utsunomiya-u.ac.jp

1. Introduction

Iron alloy plating is often used as one of the surface hardening processing of aluminum alloys[1]. Especially Fe-Cr alloy plating film shows superior hardness and superior resistivities for abrasives, so they are applied to aluminum brake disk for motorcycles.

As for this Fe-Cr alloy plating, wider application will be desired.
Improvements of corrosion-resistance, adhesion strength, *etc* are desirable.

Specifically It is important to avoid the crack of the film which is caused by the difference of hardness or thermal expansion coefficient between the substrate aluminum and the plated Fe-Cr alloy film. Here we report the improvement of adhesive strength by composition graded structure.

Continuous change of the deposition potential and current density makes the compositional or structural graded film [2,4]. Then, the content of Cr, Vickers hardness, *etc* could be controlled by current density in case of Fe-Cr alloy deposition [5].

The current density was changed stepwise with the passage of time and the composition graded Fe-Cr alloy film has been fabricated. The purpose of this graded film is to fabricate of the plated film with both superior resistivities and superior adhesion strength.

2. Experimental

2.1 The dependence of deposition current on the content of Cr in the Fe-Cr alloy plating film

The Fe-Cr alloy plating film was deposited by constant current electrolysis by use of galvanostat (Hokuto denko Co. Ltd, HB-304), and deposition rate, surface morphology, the content of Cr, the hardness of the plated film for thus deposited film was evaluated. Electrolyte supplied by Atotech Japan Co. Ltd consists of 40g/dm^3 iron sulfate, 120g/dm^3 basic chromium sulfate, 55 g/dm^3 ammonium formate, 10g/dm^3 ammonium oxalate, 54g/dm^3 potassium chloride, 54g/dm^3 ammonium chloride, 40g/dm^3 boric acid.

The deposition current density was varied in the range of 10-60mA/cm^2, the bath temperature was maintained at 45 °C and stirred at a rotation speed of 300 rpm. The working electrode was Au-QCM (Quartz Crystal Microbalance) electrode with the surface area of 1.37 cm2 (the resonance frequency: 5 MHz, MAXTEC Inc.) and counter electrode was carbon.
The resonance frequency of the QCM electrode was checked by a frequency counter (MAXTEC Inc., PM700). The deposition rate was calculated from the mass change measured with QCM. The surface morphology of the deposited film was evaluated by FE-SEM (Hitachi Inc., S-4500) and content of Cr in the plating film was checked by EDX (Horiba Co. Ltd., EMAX -5770W).

As for the measurement of the hardness, Vickers hardness tester (Shimadzu Co. Ltd., HMV-1T) was used.

2.2 Preparations of composition graded Fe-Cr alloy plating film

By building up several layers with different Cr content the composition graded Fe-Cr alloy plating could be fabricated. 3 layered graded film was fabricated on the Au QCM electrode under different current density.

The thickness of each layer was controlled as 1 μm by controlling the deposition period for each current density. The current density was varied stepwise (3 steps), from 10 mA/cm^2 for 120 min to 50 mA/cm^2 for 5min through 25 mA/cm^2 for 20min. The cross sectional distribution of the Cr content for thus prepared film was evaluated by EPMA (JEOL Co. Ltd.,

2.3 Evaluation of adhesion strength of the composition graded Fe-Cr alloy plating film.

The adhesion strength of the film was examined by two ways, heat shock test and bending test.

Above mentioned graded film was compared with the Fe-Cr alloy film fabricated by conventional way, which was prepared under constant current density (50 mA/cm^2 for 44 min). The thickness of each film is ca. 13 μm, which is calculated from QCM data.

The electrolysis condition for graded film was shown in Table 1. Initially the lowest current density was applied to the substrate so as to deposit the "soft" alloy layer, and the current was increased stepwise, so finally the highest current density was applied so as to obtain the surface with high hardness. The substrate was aluminum alloy (A1100P) with a thickness of 1 mm, the substrate was degreased, washed by acid, etched by alkaline solution, and followed by smut removal process, zincate treatment, immersion into Nitric acid, finally zincate treatment again. The solution for zincate treatment was supplied by Atotech Japan Co. Ltd.

Table 1 Conditions of Electrolysis time at preparation Fe-Cr alloy film with composite graded structure

Current Density(mA/c ㎡)	Electrolysis time(min)	Thickness(μm)
10	128	2
15	42	2
20	24	2
25	16	2
30	7	1
35	6	1
40	5	1
45	4	1
50	3	1

Heat shock test was applied, e.g. heated specimen in the muffle furnace (YAMATO Scientific Co. Ltd, FP32) at the temperature of 400℃ for 30 min was abruptly cooled by immersion into water at room temperature.

Bending test cited in JISH3504 was applied, e.g. the plated specimen was bent once by 90 °. The surface of the specimen after above test was observed by FE-SEM and it observed the delaminating of the film and the state of the division.

3. Result and discussions

3.1 The characteristic of the Fe-Cr alloy plating film

Fig. 1 shows the deposition rate calculated from the resonance frequency change of QCM electrode. It was found that the deposition rate of the Fe-Cr alloy film was proportional to the

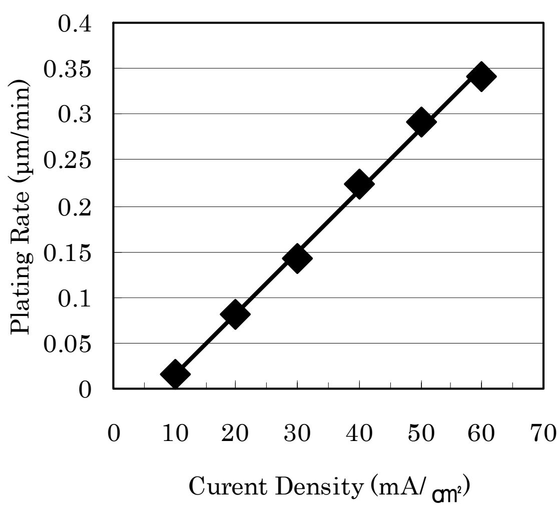

Fig.1 Relationship between current density and plating rate.

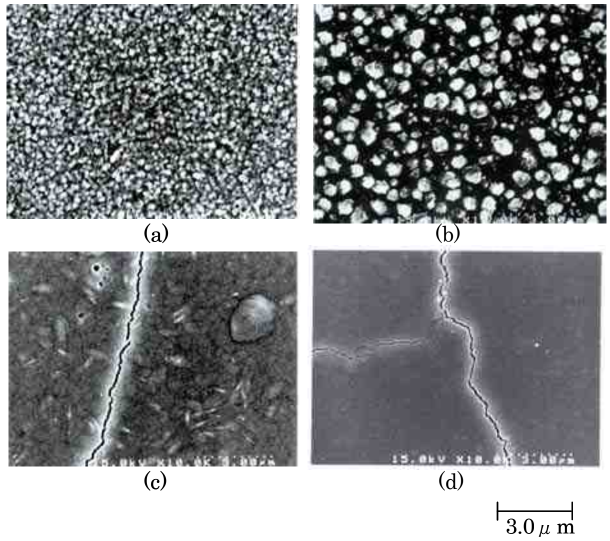

Fig.2 Effect of current density on the morphology
Current density. (a)10mA/cm^2 (b)25mA/cm^2 (c)50mA/cm^2 (d)60mA/cm^2.

deposition current density, which means the overall current efficiency was about the same in this current range. The electrolysis period for fabricating each layer of composition graded film was determined by using this data. Thus prepared surface morphology of and Fe-Cr plating film was shown in Fig.2.

The surface prepared under higher current density, e.g. 50mA/cm^2, 60mA/cm^2, was relatively smooth, and have some cracks. It was also found that the film prepared under lower current density (< 25 mA/cm^2) showed granular surface.

The Cr content of the Fe-Cr alloy plating film and the Vickers hardness of the plated film prepared under various deposition current densities were shown in Fig.3 and Fig. 4, respectively. The Cr rich alloy plating film deposited under higher current densities had a higher Vickers hardness. The film prepared under current density of 10 mA/cm^2 consisted of iron only, but the one prepared under 60 mA/cm^2 contained 15 wt% Chromium. The Vickers hardness of this film

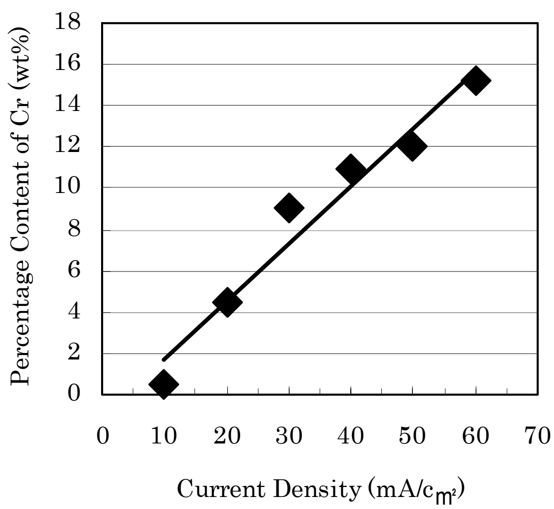

Fig.3 Relationship between current density and Percentage content of Cr.

was ca. 800 Hv. On the other hand prepared film deposited under 25 mA/cm^2 showed a Vickers hardness of 500 Hv. So the Vickers hardness of the plated film was strongly influenced by deposition current density.

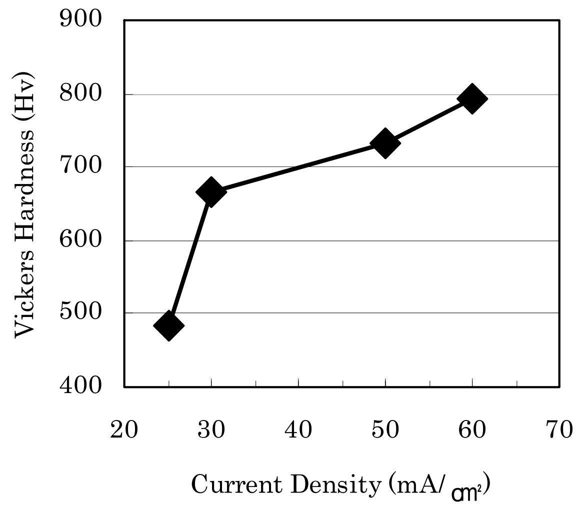

Fig.4 Relationship between current density and Vickers hardness.

So it was suggested that one could fabricate the film with Cr content graded or with hardness graded by changing the deposition current density with the passage of deposition time.

3.2 Fabrication of the composition graded Fe-Cr alloy plating film

EPMA analysis for the cross-cut of the specimen prepared by stepwise deposition mention in Section 2.2 was shown in fig. 5. Because the current density was stepped 2 times, three zones with different Cr content were observed. Low Cr content zone was observed near the aluminum substrate, and high Cr content zone was observed near the surface. It was confirmed that Cr composition graded Fe-Cr alloy plating film could be fabricated by changing deposition current density, step by step inn this way.

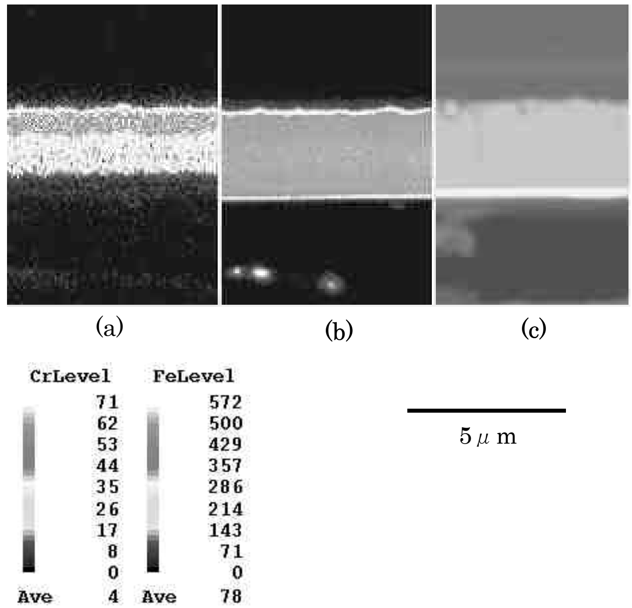

Fig.5 Cross sectional EPMA maping image & SEM image of the Fe-Cr alloy film with composite graded structure. (a)EPMA maping image of distribution of Cr. (b)EPMA maping image of distribution of Fe. (c)SEM image.

3.3 Adhesion strength of Cr composition graded plating film

The SEM image of each specimen after heat shock test was shown in Fig.6. As for Fe-Cr alloy plated specimen (not with graded structure) contains wider cracks on its surface. The width of the crack observed on graded film is smaller than that for not graded one.

As for specimen prepared under constant current density of 50 mA / cm^2, apparent cleavage of the film was observed after the bending test as shown in fig. 7. And several part of the surface was peeled off. On the other hand on the surface of the composition graded film the delaminating of the film was hardly seen.

So the improvement of adhesion strength of the film was established by the gradient of the Cr content. It was suggested that such a graded structure could relax the internal stress of the plated film, so prevented from cracking, peeling, *etc*.

Conventional plating film   Composite graded plating film

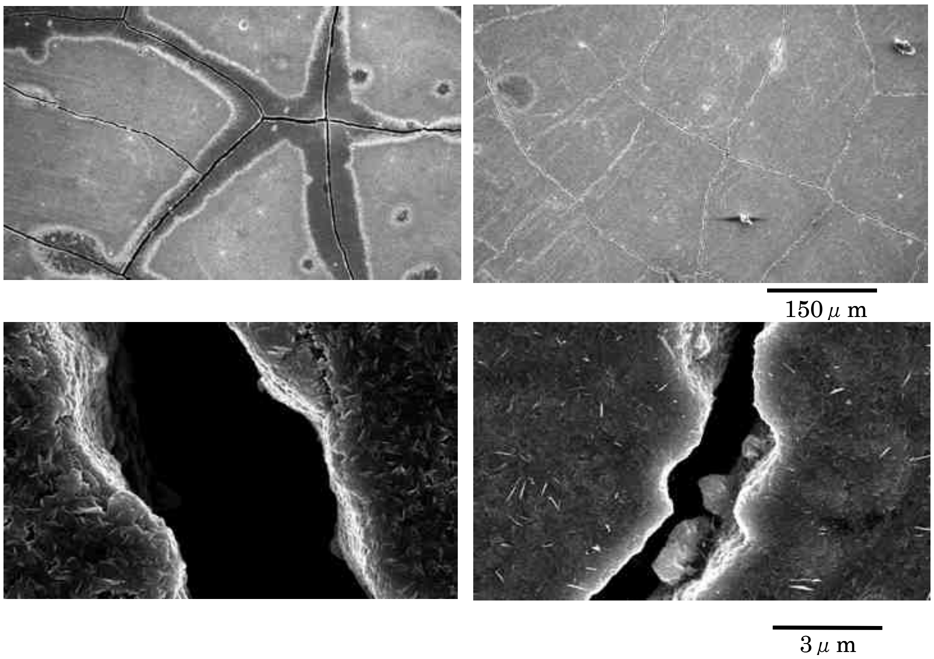

Fig.6 SEM images of the Fe-Cr film surface after the thermal shock test.

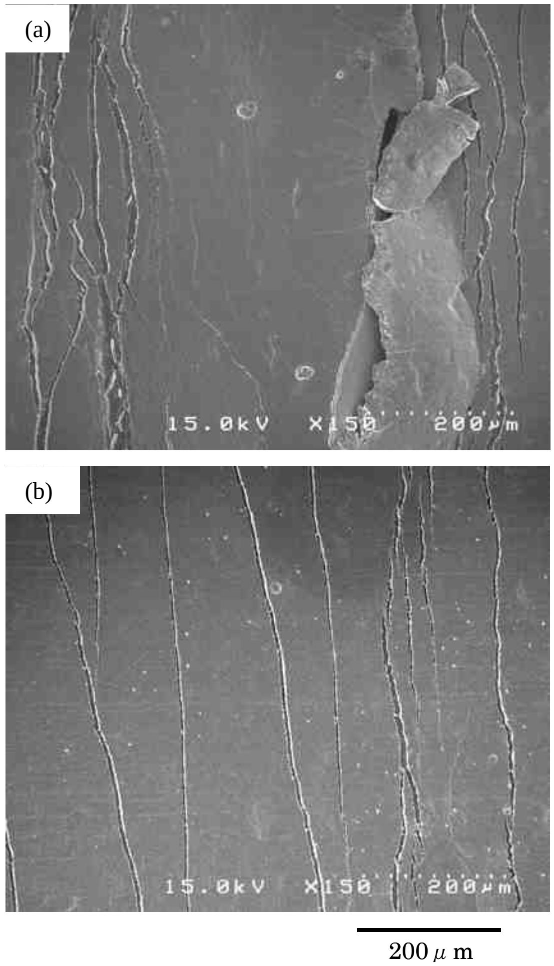

Fig. 7 SEM images of the Fe-Cr film surface after the bending test. (a) conventional plating film (b)composite graded plating film

4. Summary

By changing the deposition current density step-by-step, the Cr composition graded Fe-Cr alloy plating film could be fabricated.

As for the graded plating film contains Cr-poor layer with low hardness near the substrate, and Cr-rich layer with high hardness near the surface, it showed superior adhesion strength. It was also suggested that the plated inside layer with low Vickers hardness relaxed the internal stress

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5. References

1) Surface Finishing Society of Japan, Hyomen Gijutsu Binran, Nikkan Kogyo Shinbun-sha (1998)

2) Y. Tanaka, N. Yamada, K. Kato, Jpn Patent-H9-296292 (1997)

3) T. Watanabe, M. Kakegawa, *Hyomen Kagaku*, **14**, 565 (1993)

4) M. Matsunaga, *J. Surf. Fin. Soc. Jpn*, **46**. 1079 (1995)

5) K. Kubota, Y. Nobumoto, S. Yoshihara, T. Shirakashi, W. Oikawa, N. Kudoh, *Proc. of 108th meeting of the Surface Finishing Society of Japan*, 66 (2003)