JMEPEG (1992) 1: 359-362

Electroplating of Ni-Cr on Steel with Pulse Plating

K-L Lin, C-J Hsu, I-M Hsu, and J-T Chang

It has been difficult to electrolytically obtain crack-free chromium plating because of the high stresses caused by several factors. Accordingly, electroplating of nickel-chromium also encounters a similar problem. Cracks in chromium-containing plating was ascribed, in a certain sense, to the formation of a hydride formed through hydrogen adsorption from the electrolyte. A periodical pulse reverse plating current would enhance the release of hydrogen and hence the elimination of cracking. The present work describes a successful process for obtaining crack-free nickel-chromium plating and the effects of experimental variables on plating compositions.

1. Introduction

THE major interest in developing chromium alloy platings is the possible formation of a passive film of chromium, which enables the plating to be quite corrosion resistant. Previous studies have investigated the experimental parameters such as pH, current densities, bath compositions, and temperatures on current efficiency, plating composition, as well as on hardness of the platings.[1-5] An investigation of the microstructure and surface morphology has also been reported.[5]

A number of studies have been reported on the electrodeposition of nickel-chromium alloys since 1960.[6-14] It was reported that lower plating temperatures[9-12] and greater current densities[9,10,13] tend to enhance the chromium content of the alloy plating. Nickel-chromium alloy plating exhibits good corrosion resistance in a chloride medium.[14] A plating containing chromium, however, exhibits high stress, which could cause the plating to crack. Cracking is induced by the decomposition of chromium hydrides that form during electroplating. For chromium plating, cracking readily occurs when the plating thickness is greater than 0.5 μm. It was reported in the mid-1980s that a smooth crack-free nickel-chromium plating could be achieved with the application of pulsating current. It was found, however, in the present work that incorporation of pulse reversing current seems to be able to achieve crack-free plating with a high chromium content.

2. Experimental

Electroplating of the nickel-chromium alloy was applied on carbon steel in a solution composed of 100 g/l $CrCl_3 \cdot 6H_2O$, 30 g/l $NiCl_2 \cdot 6H_2O$, 15 g/l NaBr, 50 g/l NH_4Cl, 30 g/l H_3BO_3, 80 g/l $C_3H_4(OH)(COONa)_2 \cdot 2H_2O$, and 35 ml/l 98% HCOOH. The pH value of this solution was 4. The carbon steel was anodically cleaned at 5 A/dm^2 in an alkaline solution made up with 55 g/l NaOH, 18 g/l sodium carbonate, 10 g/l sodium silicate, 6 g/l sodium phosphate, and 1 g/l sodium acetate, followed by acidic cleaning in a solution of 30 wt.% HCl and 10 wt.% H_2SO_4.

The anode was a 75 by 37 by 5 mm graphite plate, whereas the carbon steel was 40 by 80 by 1 mm. The volume of the plating bath was 1.5 l in a container of 200 by 200 by 80 mm, of which the temperature was controlled to be within 1° of the desired temperature. The total applied electrical current was kept constant. The bath was strongly mechanically stirred during electroplating. Electroplating was conducted on one side of the substrate by taping the other side. Periodic reverse plating was performed with a Dynatronix pulse reverse power supply, which is capable of providing a 1-ms period of power. Investigation of the surface morphology, as well as of the cross section, to determine plating thickness was conducted with an optical microscope. For composition analysis, a piece of the plating was dissolved along with the substrate in a 60-ml 4 *M* HNO_3 solution followed by diluting to 1000 ml. The nickel and chromium concentrations of the solution were analyzed with inductive coupled plasma (ICP). The plating was characterized for the microstructures with a Rigaku X-ray diffractometer.

3. Results and Discussion

It is generally known that electroplating of chromium will give rise to crack plating when the thickness of the plating is greater than 0.5 μm. This phenomenon was ascribed to the formation of chromium hydride, which tends to decompose during electroplating. The decomposition of the chromium hydride to produce chromium and release hydrogen causes a 15% volume reduction, which introduces tensile stress and results in cracking. It has been reported[14] that the application of on-off pulse plating is capable of eliminating the cracks in chromium plating. The effect of pulse plating on crack elimination was explained through the earlier release of hydrogen during the off-period. As such, the hydrogen was released before a critical thickness was reached.

In the case of nickel-chromium alloy plating, it would also be expected, for similar reasons, that cracking would occur after a certain thickness was reached. Figures 1(a) and (b) show that the plating surface of the nickel-chromium plating obtained at 20 and 30 °C, respectively, contains high-density cracking. The thickness of these platings, investigated cross sectionally, is around 15 μm. It is also of interest that the smoothness of the plating surface is enhanced by increasing the plating temperature. This observation may be attributed to the better surface diffusion of the adatoms at higher temperatures.

Attempts at obtaining crack-free nickel-chromium plating with on-off pulse plating were not successful. Figures 2(a) and (b) illustrate platings obtained at around 70% (5 ms on-time, 2 ms off-time) and 50% (5 ms on-time, 5 ms off-time), at 20 °C,

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K.-L. Lin, C.-J. Hsu, I.-M. Hsu, and **J.-T., Chang,** Department of Materials Engineering, National Cheng Kung University, Tainan, Taiwan, Republic of China.

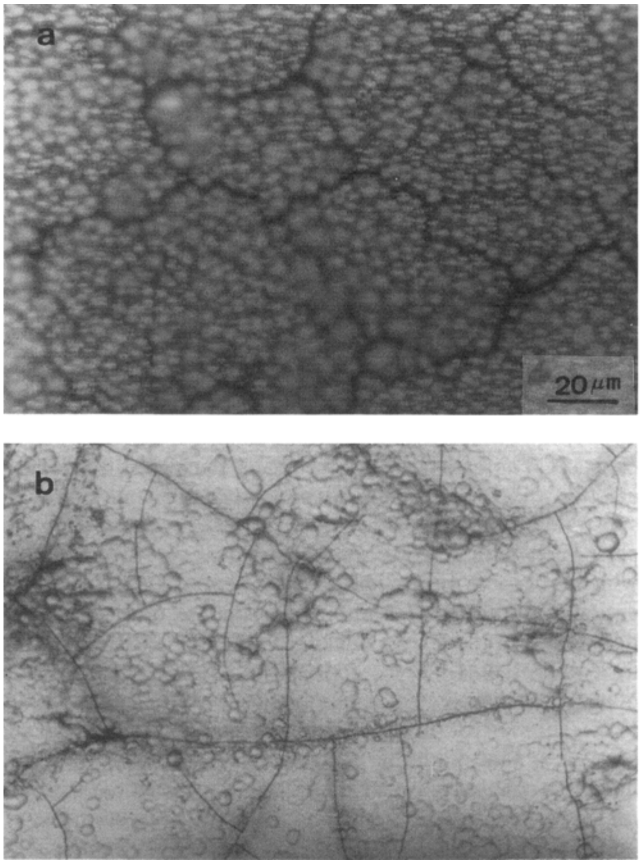

Fig. 1 Nickel-chromium plating obtained with direct current at (a) 20 °C and (b) 30 °C.

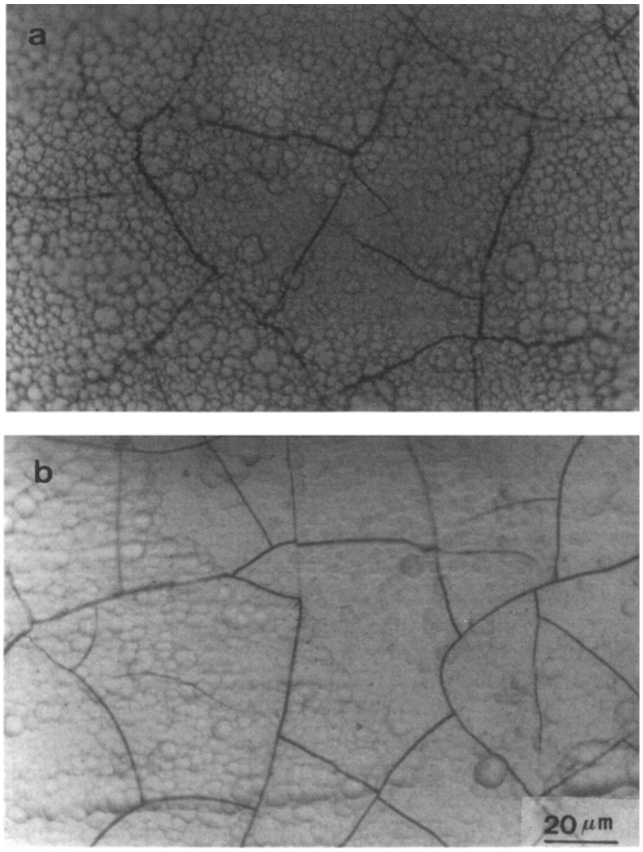

Fig. 2 Nickel-chromium plating obtained with pulse-off current at 20 °C. (a) On 5 ms, off 2 ms and (b) On 5 ms, off 5 ms.

respectively, which are typical examples of platings obtained with on-off pulse plating. It was found in the present work that, by fixing the on-time at 5 ms, manipulation of the off-time periods from 1 to 5 ms was not able to eliminate surface cracking. However, comparison of Fig. 2(a) and (b) would indicate that a longer off-period tends to improve surface smoothness.

The incapability of obtaining crack-free plating with on-off pulse plating indicates the inefficiency of hydrogen relief in nickel-chromium plating. This may be due to the alloying that occurs between the nickel and chromium, which requires further energy to enforce the decomposition of any hydride formed during plating. Thus, the application of a suitable reverse period to further provide anodic current for dissolution and hence decomposition is a possible alternative to achieving crack-free plating. A typical example of a crack-free plating is presented in Fig. 3 for platings obtained at 20 °C, with combinations of forward and reverse periods of (+5, −1), (+5, −2), and (+5, −3), with thickness of around 12, 8, and 5 μm, respectively. It clearly shows the fascinating effect of incorporating the reverse process in producing crack-free plating.

In the present work, the goal is to achieve nickel-chromium co-deposition for corrosion or oxidation protective purposes. The performance of these platings has not been investigated in the present work. Nevertheless, the plating would be of interest provided that the co-deposition of nickel and chromium is actually achievable. The composition analysis with ICP (inductive coupled plasma) did show the co-deposition of these elements, as described below. X-ray diffractive investigation (Fig. 4) further shows that the plating exhibits both a nickel phase and a nickel-chromium co-existing phase when plated with a (+5, −3) pulse-reverse process. The possibility of producing a crack-free plating by incorporating the reverse process relies on the decomposition of the alloy hydride formed during plating. The decomposition process may be accompanied by the dissolution of the alloy content. Thermodynamically, nickel is easier to dissolve compared to chromium. Accordingly, it is expected to produce platings with increasing chromium contents with a longer reverse period. This was evidenced by the composition analysis of platings, which had chromium contents of around 65 and 6% obtained at reversing the period of 3 and 1 ms, respectively, with a fixed forward period of 5 ms.

4. Conclusion

Nickel-chromium platings contain high-density cracking when obtained with dc and on-off pulse plating processes. The application of pulse-reverse plating was able to reduce cracking density via lengthening the reverse period. A crack-free nickel-chromium alloy plating was obtained at electroplating periods of 5 ms forward and 3 ms reverse. The chromium con-

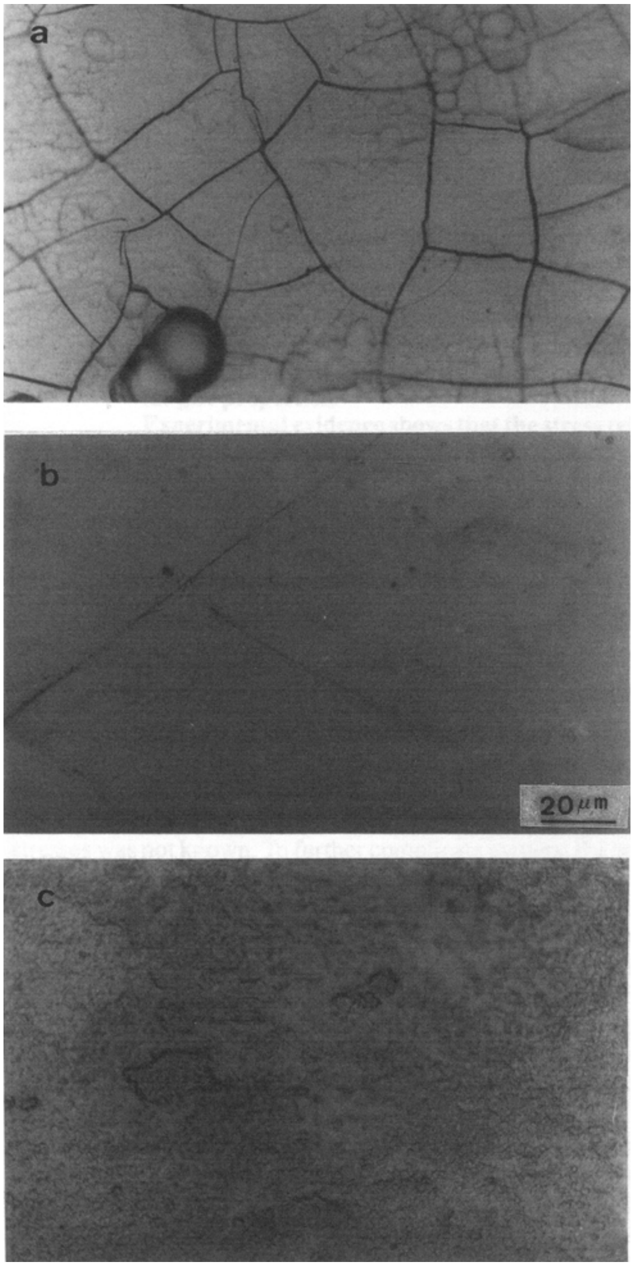

Fig. 3 Nickel-chromium plating obtained with pulse-reverse current at 20 °C. (**a**) On 5 ms, off 1 ms. (**b**) On 5 ms, off 2 ms. (**c**) On 5 ms, off 3 ms.

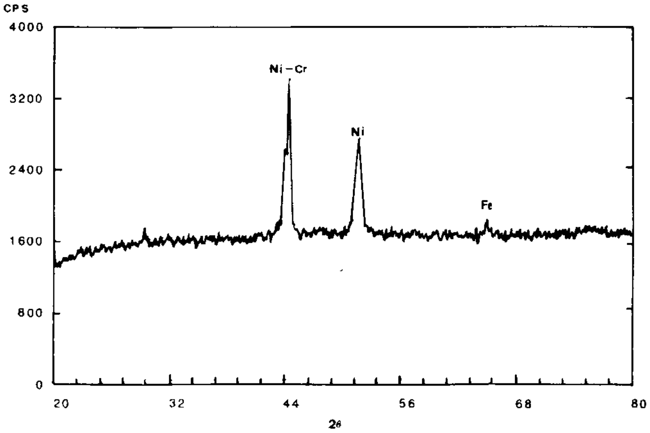

Fig. 4 X-ray diffraction analysis of a nickel-chromium plating obtained with pulse-reverse current at 20 °C (–5 ms, –3 ms).

tent of the plating is increased via a longer period of the reverse process.

Acknowledgment

The financial support of the present work from the National Science Council of the Republic of China under project NSC79-0405-E006-23 is gratefully acknowledged.

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