# The Effects of Plasma Nitriding on the Structure And Properties of Electrodeposited Chromium Film

By J.P. Ge

**The structure and properties of electrodeposited chromium films after plasma nitriding were studied. The following results were obtained: (1) plasma nitriding caused the network cracks to disappear; (2) a chemical compound layer (CrN, Cr$_2$N) formed in the outer part of the chromium film and chemical compound diffusion layer at the interface of the chromium film/substrate during plasma nitriding; (3) plasma nitriding made the surface microhardness increase and corrosion resistance markedly improve, but the critical load, Lc, experienced a small decrease.**

Electrodeposited chromium films, because of their higher hardness and good wear resistance, are used to make a wide variety of mechanical components for industry, but they do not provide good corrosion protection, as a result of the tendency for cracks to appear in the film, and their hardness decreases with increasing service temperature; therefore, their useful range is definitely limited.

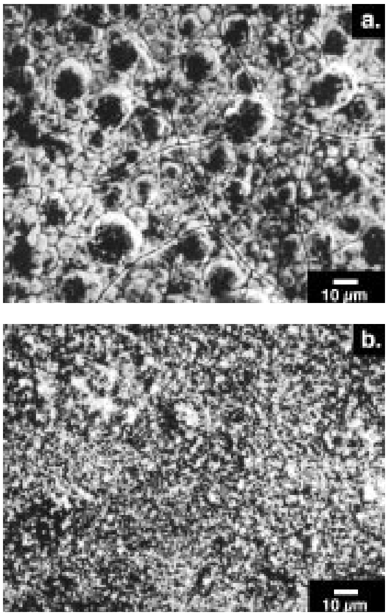

*Fig. 1—SEM photographs of an electrodeposited chromium surface: (a) 600 ℃ for 4 hr heat treatment; (b) 600 ℃ for 4 hr plasma nitrided.*

The surface modification technique for electrodeposited chromium films has been developed in an attempt to apply them more successfully.In this technique, the studies of the effect of nitrogen ion implantation on hard chromium coatings have gained the attention of industry and the research community.[1-4] The results indicated that nitrogen-ion-implanted chromium coatings showed remarkable surface hardness, as well as wear and corrosion resistance; this duplex surface engineering technique has been applied successfully to tools and components.[5,6] Because the depth of penetration of nitrogen ion is too shallow (0.1 to 0.5 µm), the microstructural and compositional evolution are not completely understood. There are brief reports about the combined treatments of excimer laser irradiation and chemical heat treatment of electrodeposited chromium films,[7] but the structure and the properties of the combined treatment layer are not known. In this paper, an investigation of the effect of plasma nitriding on the microstructure and properties of electrodeposited chromium films is described, as an attempt to find a new technique available for hard chromium film.

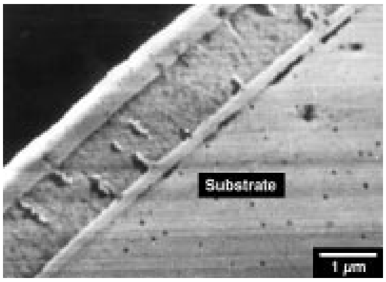

*Fig. 2—SEM micrograph showing the substrate profile (plasma nitrided at 550 ℃ for 4 hr).*

## Experimental Procedure

The substrate material used in the experiments was commonly gray cast iron. The chromium films were deposited from a solution containing 250 g/L CrO$_3$ and 2.5 g/L H$_2$SO$_4$, at 50 °C and 50 A/dm$^2$ current density. The electrodeposited chromium samples were dipped in TiCl$_3$ solution for 10 sec to remove the passivation films of chromium before plasma nitriding.

Plasma nitriding experiments were carried out in a plasma nitriding unit with 3 mbar cracked ammonia (NH$_3$) at a variety of temperatures for various times.

The surface and profile morphology of the duplex-treated samples was observed by scanning electron microscopy. The structural evolution during plasma nitriding was analyzed using an X-ray diffractometer with Cu-Kα radiation and a vanadium filter. The C, N, Cr distribution on depth profiles was determined by an electron probe.

The microhardness tests were conducted with a Vickers instrument at a loadof 10 g to limit penetration depth of the indenter and to measure more appropriately the hardness contribution of the shallow combined-treatment layer. The adhesive force was measured by a scratching test, which caused a film crack, based on drawing a diamond stylus over the sample surface under a continuously increasing load, with

### Table 1
### Effect of Plasma Nitriding Temperature On Layer Thickness

| Process Conditions | Film | Outer Layer | Inter-layer | Inner Layer |
|---|---|---|---|---|
| | µm | | | |
| 550 °C, 4 hr | 26.4 | 2.6 | 22.8 | 1.0 |
| 600 °C, 4 hr | 23.1 | 6.6 | 14.5 | 2.0 |
| 650 °C, 4 hr | 26.4 | 9.2 | 12.9 | 4.3 |

### Table 2

**Surface Hardness (10 g load)**

| Process | Microhardness, HV Treated | Microhardness, HV Untreated | Hardness Increase, % |
|---|---|---|---|
| 550 °C, 4 hr | 1221 | 536 | 228 |
| 600 °C, 4 hr | 1259 | 498 | 255 |
| 650 °C, 4 hr | 1314 | 486 | 270 |

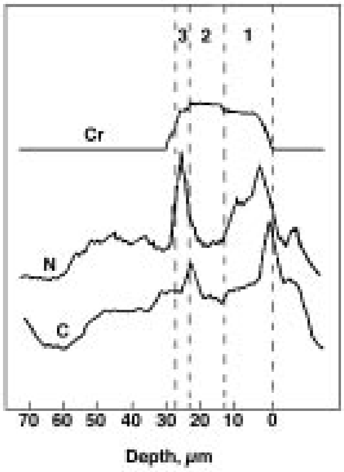

Fig. 3—Distribution of C, N, Cr in combined treated chromium film (600 °C, 4 hr, plasma nitriding).

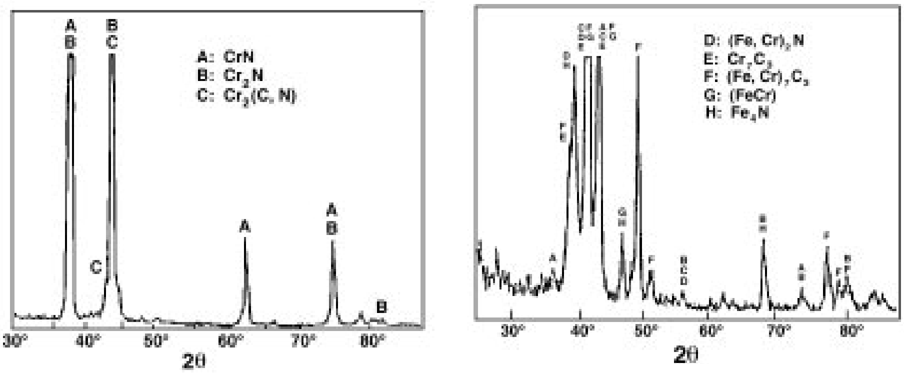

Fig. 4—Diffracted X-ray intensity vs. Bragg Angle 2θ (plasma nitriding at 650 °C, 4 hr, recorded using characteristic Cu-Kα radiation).

the critical load Lc used as the adhesive force. The corrosion resistance was investigated with an electrochemical corrosion meter in a solution of 7-percent HCl for 20 min. The corrosion velocity $V = \Delta m/s * t$, where Dm is weight loss, s is corrosion surface area, and t is corrosion time.

## Results

### Surface Observation

Figure 1 consists of SEM photographs of electrodeposited chromium samples, heat-treated and plasma nitrided at 600 °C for 4 hr. In Fig. 1a, the nodular protrusion characteristics are seen similar to the original morphology of electrodeposited chromium, where the network of cracks is more visible than before heat treatment. After plasma nitriding, the nodular protrusions and network cracks have disappeared (Fig. 1b). The facts observed were the same as the previously obtained results,[1,2] but there were also opposite results (*i.e.*, after nitrogen implantation, new cracks were formed).[3,4]

### Characterization of Profile

During plasma nitriding, three layers were generally developed in the chromium films (*i.e.*, the slow-etching “white” outer and inner layers, and a “gray” interlayer (Fig. 2).

The experimental results revealed that the profile morphology was dependent on film thickness and such plasma nitriding process parameters as temperature, time, gas composition, etc. Table 1 lists the effect of plasma nitriding temperature on the thickness of each layer. The results indicate that the higher the temperature, the thicker the outer- and inner-layers are.

The distribution of C, N, and Cr in the combined treated films was determined as a function of depth by applying electron probe microanalysis. Figure 3 shows the results. It is clear that the higher carbon and nitrogen content occurs in the outer and inner layers, but the highest chromium content is in the interlayer. It was found also that the distribution of C, N, and Cr over the combined films, treated at other temperatures and plasma nitriding times, is the same.

### X-ray Diffraction Analysis

The experimental results above show that three layers formed over the electrodeposited chromium films during plasma nitriding. The major microstructural phenomena are as follows: Figure 4a shows the result of X-ray diffraction of the surface of the combined treated film (chromium film thickness 28.1 µm). After 650 °C and 4 hr of plasma nitriding, the outer-layer thickness is 13. 5 µm, the interlayer 10.6 µm, and the inner-layer 4 µm. According to current experimental conditions, the depth of X-ray irradiation is 4.8 to 11.9 µm. From Fig. 4a, it can be seen that there are CrN. $Cr_2N$ and $Cr_2(C, N)$ in the outer-layer. Figure 4b shows the X-ray diffraction pattern of the inner-layer and substrate. The result reveals that there are $(Fe, Cr)_2N$, $(Fe,Cr)_7C_3$, FeCr and $Fe_4N$, etc.

Microhardness results for the combined treated film are listed in Table 2. It can be seen that the higher the plasma nitriding temperature, the higher the surface hardness. This hardening effect can be explained by the well-known processes of solid solution, precipitation strengthening and compressive residual stresses. In this study, the major strengthening mechanism may be by formation of CrN and $Cr_2N$ compound layers, because they have a hardness of about 2000 kg/mm$^2$.

### Adhesive Force (Critical Load Lc)

Table 3 shows the critical load Lc of a nitrided and non-nitrided electrodeposited chromium sample. When samples are not subjected to plasma nitriding, the Lc is increased as the heat treatment temperature increases. It is perhaps the result of relief of internal stress and at the interface (chromium film/substrate) transformation from mechanical joint to metallurgical joint. The critical load Lc is relatively decreased after nitriding, however, resulting from a sample surface easy to crack under diamond stylus scratching because of formation of chromium nitrides.

### Table 3

| Process | Critical Load Lc (N) | |
|---|---|---|
| | No Nitriding | Nitriding |
| 25 °C | 24 | - |
| 200 °C, 4 hr | 54 | - |
| 400 °C, 4 hr | 60 | - |
| 550 °C, 4 hr | - | 25 |
| 600 °C, 4 hr | - | 41 |

### Table 4

| Process | Corrosion Velocity (g/m$^2$ * min) | |
|---|---|---|
| | No Nitriding | Nitriding |
| 25 °C | 4.218 | - |
| 200 °C, 4 hr | 1.087 | - |
| 400 °C, 4 hr | 2.302 | - |
| 500 °C, 4 hr | 3.720 | - |
| 550 °C, 4 hr | - | 0.284 |
| 600 °C, 4 hr | 3.782 | 0.009 |

### Corrosion Resistance

The corrosion velocity for combined treated layers is summarized in Table 4. It can be seen that, for the pure electrodeposited chromium samples, the corrosion resistance is greater for the sample heat treated at 200 °C for 4 hr. Then, corrosion resistance decreases with increase of heat treatment temperature. After plasma nitriding, the chromium film displays excellent corrosion resistance, which increases with the nitriding temperature. This differed from the tendency in electrodeposited film that was heat-treated, but not nitrided.

Figure 5 shows SEM photographs of surface corrosion of two combined treated samples. For the chromium film + heat-treated sample, the corrosion occurred at the network cracks, and the cracks changes thicker than before corrosion (Fig. 5a). For the chromium film + plasma nitriding sample, however, the network cracks disappeared and corrosion occurred over the whole sample surface (Fig. 5b).

## Conclusions

1. Plasma nitriding caused the cracks to disappear.
2. The chromium film is developed in three layers during plasma nitriding; the outer layer consists of chromium nitrides (CrN, $Cr_2N$), the inner layer is a compound diffusion layer.
3. Plasma nitriding produced a significant hardening effect and a corrosion-resistant layer, but the critical load Lc showed a small decrease.

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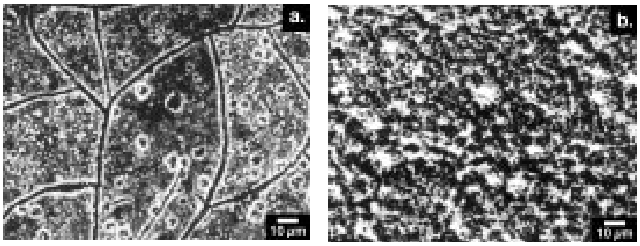

*Fig. 5—SEM micrographs of combined treated samples: (a) chromium film, heat treated at 600 °C , 4 hr; (b) chromium film, heat treated at 600 °C, 4 hr, plasma nitriding.*

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