# Microribbons in Hard Chromium Electrodeposits

#### Allen R. Jones and Craig V. Bishop, Atotech WW R&D

The term "microcracked chromium" was used in the 1960s to describe new decorative chromium coatings and related process chemistry was later used for hard chromium deposits. During plating, microcracks occur and subsequent plating fills in the cracks to form microribbons (films or inclusions). These ribbon-like inclusions are more electrochemically active than the bulk of the chromium. Microribbon densities influence corrosion and wear resistance. Low voltage scanning electron microscopy (SEM) images show only the surface microcracks visible in optical microscopes, while high voltage SEM images reveal underlying microribbons. The structure and composition of microribbons will be described using data from instrumental methods including: compositional and topographic SEM, Field-Emission Scanning Auger Microprobe (FE-SAM), nanoindentation, Time-of-Flight Secondary Ion Mass Spectrometry (ToF SIMS) show differences in composition near the microribbons compared to the bulk chromium areas, and focused ion beam (FIB).

For more information contact: Allen R. Jones, Ph.D. Atotech Worldwide R&D 1750 Overview Drive Rock Hill, SC 29730 USA Phone: 803-817-3568 ajones@atousa.com

#### Introduction

The term hard chromium or functional chromium is used to describe chromium electrodeposits that have a coating thickness greater than approximately 1.2  $\mu$ m. Typical coating thicknesses are greater than 15  $\mu$ m. Hard chromium deposits are non homogenous, they contain heterogeneities normally referred to as microribbons or microcracks. The term microcracked is misleading when used to describe hard chromium deposits. Articles in the 1920s discussed cracks and fissures in chromium deposits. Films and inclusions in chromium structures were reported in the literature from the 1940s. The term "microcracked chromium" was used in 1960 to describe new decorative chromium coatings and later used for hard chromium deposits. During plating, microcracks occur and subsequent plating fills in the cracks to form microribbons (films or inclusions). These inclusions are like a ribbon, long with a narrow dimension and a wider dimension perpendicular to the substrate surface. The microribbons are more electrochemically active than the bulk of the chromium. A few microcracks may exist on the surface of chromium deposits. Anodic or chemical etching dissolves the ribbons and form more visible microcracks. Microribbons have a slightly different composition than the bulk of the chromium deposit.

Microribbons form during deposition when the tensile stress exceeds the cohesive strength of the chromium. The stress may be due to the decomposition of chromium hydride in the deposit. This change may be accompanied by a 15% reduction in the volume of the coating.

Commercially, hard chromium is deposited from three types of baths; conventional, fluoride<sup>\*</sup> (mixed-catalyst), and high-efficiency etch-free<sup>\*\*</sup> baths. All of the baths contain sulfate  $(SO_4^{-2})$  and chromium (VI) oxide commonly referred to as chromic acid  $(CrO_3)$ . The sulfate and fluoride compounds act as catalysts. The high-efficiency etch-free bath contains a non-halide catalyst. Chromium cannot be electrodeposited from an aqueous chromic acid solution unless one or more catalysts are present. Depending on which catalysts are present and the plating parameters, between 10 and 30% of the cathodic current will be used to reduce hexavalent chromium (Cr<sup>6+</sup>) to chromium metal. In the fluoride process a high concentration of fluoride compound must be used to obtain a high microribbon density; unfortunately this causes severe substrate etching in the low current density areas.

The importance of microribbon (microcrack) density was first recognized in the development of channel or porous chromium in the 1940's. Channel chromium uses the etched microribbon channels to retain oil for improved operating characteristics and was developed for the Army Air Forces and Navy during WWII. Coyle<sup>1</sup> examined conditions needed to obtain the correct plateau size for these processes. Numerous photomicrographs show different microribbon densities, but he made no attempt to quantify the microribbon density. Plateau size is inversely proportional to the microribbon density. Guffie<sup>2</sup> discussed the effect of sulfate to chromic acid ratio on microribbon density in his book published in 1986.

In the 1980's new chromium plating chemistries were developed and the supplier reported microribbon densities in their technical information<sup>3</sup>. Minimum microribbon densities are specified by some manufactures of piston rings and shock/strut rods. Jones<sup>4</sup> studied

<sup>\*</sup> HCR 840 Chromium Plating Process, Atotech

<sup>\*\*</sup> HEEF 25 Chromium Plating Process, Atotech

Microribbon formation in detail and a correlation of microhardness with microribbon density was reported. This author also demonstrated improved sliding wear with increased microribbon density<sup>5</sup>.

A corrosion study was conducted to determine the effect of temperature and microribbons (mrb) on corrosion resistance. Ten samples were plated from an etch-free bath under identical conditions at both 60 and 70°C and then tested in a neutral salt spray test (NSST) according to the specification ASTM B117. The samples had a chromium thickness of 25  $\mu$ m and were not post finished. Table 1 shows that for deposits plated in an etch-free bath, as the microribbon density increases, the deposits corrosion resistance increases significantly. The anodic etch method used to develop microribbons is described on page 9. It is normal for the microribbon density and the conditions move to a regime that is out side of the bright plating range. Figure 1 shows that in different plating chemistries, as the microribbon density increases the deposits corrosion data used in this plot is from prior studies by Newby<sup>6</sup> and the microribbon density data was estimated from the plating conditions using data from Jones<sup>4</sup>. This data shows that microribbon density is an important factor in determining a plated products corrosion resistance.

Microribbons are an important and beneficial attribute of chromium deposits. They improve the wear and corrosion resistance of hard chromium deposits. Deposits with low microribbon densities will have inferior wear and corrosion performance compared to deposit that has a high microribbon density. Deposits with very low or no microribbons can have high stress and may form macrocracks that proceed from the substrate to the surface of the chromium.

Temperature	Current Density	Mrb Density	Ave. NSST	
°C	A/dm <sup>2</sup>	Mrb/cm	Hours	
60	62	1400	>144	
70	62	400	84	

Table 1. Etch-free deposits corrosion resistance.



Figure 1. Corrosion resistance of 25-µm thick deposits without post finishing after 200 hrs. vs. Microribbon Density.

Numerous studies have characterized the structure of microribbons. Morisset<sup>7</sup> reported and reviewed many of these studies. He reports that researchers conclude that microribbons are cracks or empty voids or filled with hydrides or chromic oxide,  $Cr_2O_3$ .

Cymboliste<sup>8</sup> examined the cross-sectional structure of more than 300 conventional deposits plated from various concentrations of chromic acid, sulfate, metal ions, and anions at various temperatures and current densities. The majority of the samples exhibited microribbons in the cross-sections. Cymboliste used the term "inclusions" to describe the microribbons. Depending upon the plating chemistry and conditions, the number of microribbons range from "few" to "numerous" to "a great many". As the microribbon density increased, the deposits' corrosion resistance to sulfuric, hydrochloric and chromic acid increased and the deposits' hardness increased.

Microribbons, or films, were isolated and analyzed by Cohen<sup>9</sup> from conventional deposits. After baking the deposits at 482°C for two hours they were anodically etched in 10% chromic acid solutions. The films were 0.05% by weight of the chromium coating. X-ray diffraction analysis showed that the films consisted of  $Cr_2O_3$ . The films were photographed after a layer of carbon was deposited on the surface and are described as "fence-like" structures on the chromium surface. The analysis of the films may have been compromised due to the baking

and anodic etching of the deposit. The baking conditions would have removed 90% of the hydrogen from the coating. Anodic etching in chromic acid could oxidize the species present in the microribbon. Snavely<sup>10</sup> also photographed similar inclusions or films after baking and anodic etching.

Jacquet<sup>11</sup> and Bastien and Popoff<sup>12</sup> have described fan like structures. The fan like structures reported by Jacquet may be due to the oblique sections that he examined. Abnormal microribbon structure will be observed if one examines any surface other than a cross section or surface of a chromium deposit. An oblique section, or a transverse section off the exact diameter of a rod, will exhibit a microribbon structure that is a mixture of the surface structure and a cross section structure<sup>13</sup>. The fan like structure could be an artifact of the oblique section made of the chromium deposit. The fans described by Bastien are due to the extreme coating thickness; 20,000 µm. These structures are not relevant to commercial coating thicknesses that are usually less than 100 µm.



Figure 2. 3-D and 2-D representations of spatial and temporal distributions of microribbons from a film recorded during electrodeposition in a conventional solution. The microribbon at time 0 was at the start of recording, microribbons are shown at 2, 5 and 15 minutes.

Jones<sup>4</sup> filmed microribbons in a conventional solution. This data was used to generate the 2-D and 3-D representations of microribbons shown in Figure 2. These graphs show the spatial and temporal distributions of microribbons in a conventional chromium deposit. Four microribbon episodes are represented. The deposit contained 170 microribbons/cm based upon anodic etching of the sample. The films showed copious quantities of hydrogen gas emanating from or coalescing at the microribbons. At a magnification of 650x when the current was monetarily turned off, the gassing ceased and the microribbons were not visible. Prior microribbons were visible in the chromium surface.

### Microribbon Characteristics

Various experiments were conducted to better elucidate the characteristics and nature of microribbons. Photomicrographs were taken of the as-plated chromium surface, after various periods of anodic etching, and after post finishing or buffing. The microribbon densities were determined for conventional and etch-free deposits plated at various conditions. The etched microribbon width distributions were determined for these samples.

## **Optical Photomicrograph**

As-plated deposits exhibit many microribbon episodes on the chromium surface. Figure 3 shows at least three layers of microribbons. The outer most microribbon (#1) may contain a crack and the deepest (#3) is filled in and plated over and leaves a faint "foot print" in the chromium deposit.



Figure 3. As-plated chromium samples from an etch-free bath. At least three microribbon layers are visible; #1 is the outer most, #2 is deeper, and #3 is the deepest. (0410a00137)

## Microribbons After Anodic Etching

A study was completed to determine if the most visible microribbons are the first to be etched and widest after anodic etching is used to develop the microribbons. Microhardness indents were used as landmarks so that photographs could be taken after the etching process. The sample used for this testing was a 25-µm thick etch-free deposit plated from a solution containing 250 g/l of chromic acid, 3.2 g/l sulfate, and catalyst at 60°C and 30 A/dm<sup>2</sup>. The substrate used was AISI 1018 hexagonal bar. The anodic etch was performed in a 100 g/l sodium hydroxide solution at 31 A/dm<sup>2</sup> for 1, 2, and 3 minutes. The results are shown in Figures 4-7. The most visible microribbons in the as-plated sample are the first to be developed by the anodic etching and become more pronounced with increased etching. As the etching is continued more microribbons are developed.



Figure 4 As-plated etch-free deposit.



Figure 5. After anodic etching for 1 minute at 31 A/dm<sup>2</sup>.



Figure 6. After anodic etching for 2 min at 31 A/dm<sup>2</sup>.



Figure 7. After anodic etching for 3 min at 31 A/dm<sup>2</sup>.

# Microribbons After Buffing

Kobayshi, et al<sup>14</sup> reported that microribbons could be removed or cloaked with post finishing and that this was accomplished more readily with etch-free deposits, which contain more microribbons. This was confirmed using a manual post finishing method. The chromium deposit used for these tests was taken from a different area of the sample used in the above-mentioned anodic etching tests. Microhardness indents were used as landmarks so that photographs could be taken after the buffing process. The sample was buffed using green compound on a hard muslin wheel for 5 and 10 seconds. As shown in Figures 8-10 the microribbons are diminished after 5 seconds of buffing and not visible after 10 seconds. Ultrasonic treatment after buffing did not make the microribbons more visible. This indicates that the microribbons were not just filled with compound but that metal was possibly smeared over the microribbons. The length of the indents decreases with buffing; indicating that metal was removed during the buffing process or chromium metal was moved into the indent.







Figure 8. As-plated sample

Figure 9. After 5 sec of buffing.

Figure 10. After 10 sec of buffing & 2 min ultrasonic.

# Microribbon Densities of Conventional and Etch-Free Deposits

Samples were plated on precisionground AISI O-1 oil hardenable steel rods, 9.52 mm in diameter and 152 mm long. Sample preparation included: abrasive cleaning, cold water rinse, alkaline cleaner immersion for 15 seconds, cold water and deionized water rinse. The samples were then dried and weighed. The plated area was 0.252 dm<sup>2</sup> and 84 mm long. Samples were plated from solutions containing 250 g/l of chromic acid, sulfate, as indicated in Table 2, and mist suppressant. The bath volume was 3.4 l with low agitation and the temperature was thermostatically controlled to  $\pm 0.5^{\circ}$ C. The current was ramped up to the plating current, which was under current control with a low ripple rectifier during the plating cycle. The etch-free chromium deposits also contained a non-halide catalyst. The plating times were adjusted to obtain a constant coating thickness of 25 µm for all samples. Additional plating

	Temp	$[SO_4]$	Current	Sample	Mrb	Std.
			Density		Density	Dev.
	°C		A/dm <sup>2</sup>		Mrb/cm	Mrb/cm
Conv.	55	2.5	15	M1	250	55
				M2	220	89
			30	M4	120	35
				M5	110	37
Etch-free	60	3.2	30	M7	1600	206
				M8	1600	263
			60	M10	1500	278
				M11	1500	165
			75	M13	1600	236
				M14	1500	135
Etch-free	65	3.2	30	M16	1200	116
				M17	1100	105
			60	M19	970	310
				M20	1000	122
			75	M22	1000	135
				M23	940	136

Table 2. Microribbon densities for various samples

conditions are shown in Table 2. Duplicate samples were prepared for each condition.

The microribbon densities were developed and determined using an anodic etch process. After cleaning, the sample was anodically etched in a solution that contained 100 g/l of sodium hydroxide for two minutes at 46.5 A/dm<sup>2</sup>, rinsed and dried. The part was examined under sufficient magnification so that between 10 and 20 microribbons intersect a reference line on a grid. All of the microribbons intersecting several lines were counted in three different areas on the same part. The microribbon densities are calculated based upon their number per unit length and the magnification. The microribbon densities are shown in Table 2 and Figure 11, each value is the average of nine measurements. The microribbon densities of the conventional deposits are much lower than the densities for the etch-free deposits and as the current density increases the microribbon densities of the conventional deposits decreases. The microribbon densities of the etch-free deposits plated at 60°C are more than 10 times higher than the microribbon densities of the conventional deposits. The microribbon densities of the etch-free chromium deposits do not vary with changes in current density, but higher plating temperatures decrease the microribbon density. As indicated by the 90% confidence interval error bars in Figure 11, there is considerable uncertainty in microribbon densities. This means that microribbon densities of 1400 and 1600 mrb/cm may not be statistically different values.



Figure 11. Microribbon density vs. current density for conventional and etch-free deposits. The error bars are based on 90% confidence intervals.

Figures 12, 13, and 14 show the etched surface of conventional sample M5 and etch-free samples M7 and M16, plating conditions are shown in Table 2. The conventional deposit has very few microribbons and they are wide. The etch-free deposits have many microribbons after etching and many of these microribbons are very narrow.



Figure 12. Etched surface of conventional deposit M5 at 400x.

Figure 13. Etched surface of etchfree deposit M7 at 1000x.

Figure 14. Etched surface of etchfree deposit M16 at 1000x.

### Microribbon Width Distributions after Etching

To better understand microribbons, the width of the etched microribbons were measured. The distributions of the widths for several samples are shown in Figures 15-19. These figures show the frequency or number of microribbons in a specific width range; for example, between 1 and  $2\mu m$ , or 3 and  $4\mu m$ , etc.

Since the conventional deposits contain so few microribbons, the data from samples M4 and M5 were combined to produce a larger microribbon sample size. The frequency axis and values for the conventional deposits are much smaller than the axis and values for the etch-free deposits. The software used to measure the etched microribbon widths is limited to values greater than  $0.8\mu m$ . Microribbons widths of less than  $0.8\mu m$  were assigned values of  $0.5\mu m$ .

There is a significant difference in the distributions between conventional chromium deposits and etch-free chromium deposits. The conventional deposits have a majority of microribbon widths of >4  $\mu$ m where as etch-free deposits have a majority of widths <3  $\mu$ m. The microribbon width distributions for etch-free deposits plated at 30 A/dm<sup>2</sup> and 60 A/dm<sup>2</sup> are very similar, however the distribution of the deposit plated a 75 A/dm<sup>2</sup> has a slight shift to intermediated microribbon widths.

Figure 19 shows a more detailed distribution of the data from Figure 16 for sample M7. This data shows at least three different microribbons episodes. The deepest episode is represented by the narrowest ribbons; <0.9 and 0.9-1.1  $\mu$ m. The next layer is delineated by microribbons with widths of 1.9-2.1  $\mu$ m, and a third layer exhibits ribbon widths of 3.1-3.2  $\mu$ m. There may yet be another layer with ribbon widths of 4.1-4.3 or 4.7-4.9 $\mu$ m. The outer most layers may be less distinct because the ribbons are wide and may overlap with other ribbons.



Figure 15. Etched microribbon width data for conventional deposits M4 and M5.



*Figure 16. Etched microribbon width data for etchfree deposit M7.* 



*Figure 17. Etched microribbon width data for etch-free deposit M10.* 



*Figure 18. Etched microribbon width data for etch-free deposit M14.* 



Figure 19. Etched microribbon width data for etch-free deposit M7.

### **Microribbon Chemical and Structural Analyses**

Instrumental techniques were used to determine the composition and physical properties of microribbons compared to the bulk chromium. These techniques include: scanning electron microscopy, using different contrast modes, to differentiate atomic numbers and topography; field-emission scanning auger microprobe to show compositional differences; nanoindentaions to detect mechanical differences; and Time-of-Flight Secondary Ion Mass Spectrometry (ToF SIMS) show differences in composition near the microribbons compared to the bulk chromium areas.

### SEM Compositional and Topographic Contrast Images

Figures 20 and 21 show scanning electron micrographs (SEM) of the same sample of an etchfree deposit as plated. The SEM used was a LEO 430 with an EDAX (CDU, LEAP) detector. Both images were recorded with the same accelerating voltage, magnification, tilt, and working distance. The high contrast four quadrant backscatter detection compositional (atomic number) mode image in Figure 20 shows microribbons and some of the surface details. The backscatter coefficient is proportional to the atomic number. Thus, in the compositional mode, brighter areas represent higher atomic number elements like chromium. This figure shows that all of the surface microribbons terminate when they meet another microribbon. This results in intersections of three microribbons but is only true for microribbons in the same layer. Microribbons in different layers can appear to have four microribbons intersecting as in Figure 3 for ribbons #1 and #2. The topographic backscatter contrast mode, from the same detector, image in Figure 21 shows very faint ridge and valley lines corresponding to the microribbons and shows the topographical features of the surface in greater detail.



Figure 20. Composition mode, unetched. (12150402) Figure 21. Topographical mode, unetched. (12150409)

These images show that even the surface microribbons may be filled in and are not cracks in the surface to any significant depth. Additional images using secondary electron detection show more microribbons as the accelerating voltage is increased. In these images the under lying microribbons were visible at higher accelerating voltages. Topographical mode shows the topography of the surface in greater detail than the composition mode, thus if the microribbons

were cracks, they should be more visible in the topographical mode. The microribbons are more apparent in the compositional mode, which indicates that the microribbons are chemically different than the bulk of the chromium deposit. The darker microribbons in Figure 20 may be due to the presence of elements with an atomic number less than chromium. Those elements would include: hydrogen, carbon, oxygen, and sulfur, with hydrogen and oxygen the most likely elements in the microribbons.

### FE-SAM Analysis

Microribbons of an etch-free deposit plated on brass were analyzed using Field-Emission Scanning Auger



Figure 22. SEM image of 25-µm etch-free deposit.

Microprobe (FE-SAM). The FE-SAM used is Perkin-Elmer PHI 680 located at CASE Western Reserve University in the Department of Materials Science and Engineering. The plating conditions for this sample were the same as the conditions used for sample M7, in Table 2. The areas analyzed are shown in Figure 22, a bulk chromium area (#1) and a microribbon area (#2). Area #2 will etch more rapidly in a chemical or an anodic etch, than the bulk chromium. FE-SAM spectra in Figure 23 showed no difference in composition between the areas. This technique will not detect hydrogen. These results were not expected since Jones<sup>5</sup> reported that the bulk oxygen content of conventional deposit is 0.36% and etch-free deposit is 0.84%. The source of the additional oxygen in the etch-free deposits was theorized to be from the increased amount of microribbons. Analysis of chromium deposits on steel substrate also showed no compositional difference between the bulk and microribbon areas. The surface crack in Figure 22 appears to have a width of approximately 0.2  $\mu$ m, after sputtering.



Figure 23. FE- SAM of 25-µm etch-free deposit on brass.

### Nanoindentation Testing

The sample used for these tests was plated from an etch-free chemistry under conditions identical to sample M10 in Table 2, on a polished AISI 1018 hexagonal bar. Nanoindentations were performed using a Hysitron Triboscope Nanomechanical Test Instrument interfaced to a Digital Instruments (Veeco Metrology Group) Dimension 3100 atomic force microscope (AFM). A Berkovich diamond indenter (three-sided pyramidal tip, total angle included 142.3° deg, average radius of curvature 100 nm) was used. The instrument load frame compliance and indenter tip area function were calibrated with a vendor-supplied fused silica specimen assuming a contact depth independent elastic modulus. Nanoindents were made on the surface of bulk chromium and in

microribbons to determine if the mechanical properties of the two areas are different. Figure 24 shows three nanoindents in a microribbon and four in the bulk chromium. Figure 25 shows four



Figure 24. Test #1 nanoindents.



Figure 25. Test #2 nanoindents.

nanoindents in a microribbon and six in the bulk chromium. The differences in Young's modulus values compared to the average bulk value in each test are shown in Figure 26. This data shows that in 90% confidence intervals, Young's modulus values for the microribbons are statistically higher than the values for the bulk chromium. The scatter in the data may be due to the difficulty of placing the nanoindent in the microribbons or due to the presence of underlying microribbons. This data shows that the material in the microribbons is a different composition or crystal structure.



Figure 26. Change in Young's modulus for microribbon areas vs. bulk chromium areas.

### Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) Analyses

The samples used for these tests were plated from an etch-free chemistry under conditions identical to sample M8 in Table 2, on polished AISI 1018 hexagonal bar. A cross-section was prepared in a cold epoxy medium and cured for 24 hours and then polished using silicon carbide and diamond paste to a surface finish of 0.25 micrometers. The ToF-SIMS studies were conducted at Surface Science Western (The University of Western Ontario, Canada) using a Cameca ToF-SIMS IV instrument. The ToF-SIMS technique has ultra-high sensitivity that can

detect atomic concentrations down to the parts per million level. The chromium samples were tested in the as-plated condition and after a heat treatment at 400°C for 4 hours in argon. The SIMS images have a lateral resolution down to 100 nanometers for elements. The samples were sputtered for 30 minutes prior to analysis to remove any contamination from sample mounting or polishing.

The results in Figures 27 and 28 depict the dramatic effect of microribbons and heat treatment on the chemical distribution in the chromium deposits. Concentration SIMS image maps are shown in Figure 28 for Cr, H, O, and  $CrO_2$  for the as-plated and heattreated chromium deposits. The iron substrate



Figure 27. Field Emission secondary electron micrograph etch-free deposit.

is located at the top of each image and the mounting medium is at the bottom of the images. The dark areas near the mounting medium in the heat-treated images are due to topography and are considered to be artifacts of the sample. The as-plated sample shows that near the microribbons the concentrations of Cr and H are elevated where as in the bulk the concentrations of O and  $CrO_2$  are increased. The chromium deposits contain > 99% chromium<sup>5</sup>. During plating copious quantities of hydrogen emanate from the microribbons. After heat treatment the chemical composition of the chromium coating is very uniform. The heat treatment temperature is not high enough to reduce the deposits microhardness.

This data demonstrates that the microribbons are not chromium oxide rich areas and definitely contain higher concentrations of hydrogen than the bulk areas. The microribbons affect the chemistry of the areas that surrounds them. They can alter the chemistry in an area about 10 times their actual area. This sphere of altered chemistry may explain why etching widens the microribbons and the "footprints" of microribbons. Depending upon the microcrack density the microribbons can alter the chemistry of a small fraction of the coating or can alter the chemistry of the entire chromium deposit.

## As-plated chromium deposit.



Figure 28. ToF-SIMS images of etch-free deposits. The as-plated image sizes are 35 micrometers by 35 micrometers. The heat- treated image sizes are 19 micrometers by 19 micrometers.

#### Conclusions

The presence of a significant number of microribbons improves a chromium deposit's corrosion and wear resistance. Optical photomicrographs appear to show a crack on the outer surface of unetched chromium deposits. Plated over microribbons of prior cracks are also visible, as "footprints" of prior cracks. During anodic etching the outer most crack is etched first and becomes the predominate microribbons. The "footprints" of plated over microribbons also etch but are narrower and less predominate than the outer most microribbons. The surface microribbons are not visible after buffing.

In another paper at this conference, additional detail on structure of hard chromium including microribbons suggests that ribbon structure is finer grained and of a different crystallographic orientation from the bulk chromium. This would explain the different etch rates.

The microribbon densities of etch-free deposits are about 10 times higher than the microribbon density of conventional deposits. A high plating temperature significantly reduces the microribbon density of etch-free deposits. After anodic etching the microribbon widths are narrower for etch-free deposits than for conventional deposits. A plating current density of 75 A/dm<sup>2</sup> produces etch free deposits that have a microribbon width distribution that is intermediate

between lower current density etch-free deposits and conventional deposits.

SEM compositional contrast images show what appear to be surface microcracks, however topographic contrast images show greater topographical details and only show very faint microribbons. The compositional image cracks must be inclusions of elements with a lower atomic number than chromium. Additional images using secondary electron detection show more microribbons as the accelerating voltage is increased. In these images, the under lying microribbons were visible at higher accelerating voltages. Field-Emission Scanning Auger Microprobe analysis did not detect any compositional differences between the bulk and microribbon chromium areas. Indicating that any compositional difference between these areas must be due to hydrogen, undetectable by conventional Auger methods, in the microribbon. During the plating process copious quantities of hydrogen evolve or coalesce at the microcracks.

Nanoindentation experiments have shown that Young's modulus values of the microribbons are different than the bulk chromium values. This indicates that the material in the microribbons is of a different composition and/or crystal structure.

ToF-SIMS data demonstrates that the microribbons are not chromium oxide rich areas and definitely contain higher concentrations of hydrogen than the bulk areas. This is in agreement with the FE SAM and SEM compositional contrast images. The microribbons affect the chemistry of the areas that surrounds them.

#### Acknowledgements

The authors acknowledge the nanoindentation work done by Dr. Charles McFarland and the ToF-SIM work done by Dr. Sridhar Ramamurthy of Surface Science Western, The University of Western Ontario, Canada.

# **References.**

- 1. T. G. Coyle, Proc. Amer. Electroplaters' Soc., Vol. 43, 1944, p 20-76
- 2. R. K. Guffie, Hard Chromium Plating, Gardner Pub. Inc., 1986, p 22
- 3. Technical Information: HEEF 25 Chromium Plating Process, Sheet No. P-CR-HEEF-25, 2/87, M&T Chemicals Inc.
- 4. A. R. Jones, Plat. Surf. Finish., Vol 76, (No. 4), 1989, p 62-66
- 5. A. R. Jones, Trans. Inst. Metal Finish., Vol 70, (No. 1), 1992, p 8-13
- 6. K. R. Newby, Interfinish 92 Surface Finishing Congress Sao Paulo, 1992, p 1089-1103
- 7. P. Morisset, Chromium Plating, Robert Draper, 1954, p 198-203
- 8. M. Cymboliste, T. Electrochem. Soc., Vol 73, 1938, p 353-363
- 9. J. B. Cohen, T. Electrochem. Soc., Vol 86, 1944, p 441-456
- 10. C. A. Snavely, T. Electrochem. Soc., Vol 92, 1947, p 537-577
- 11. P. A. Jacquet and A. R. Weill, Chrome Dur, 1949, p 4-19
- 12. P. Bastien and A. Popoff, Chrome Dur, 1948, p 13-20
- 13. A. R. Jones and C. Ringholz, Proc. AESF SUR/FIN 2002, June 2002
- 14. S. Hoshino and T. Midorikawa, 2<sup>nd</sup> International Colloquium Hard & Decorative Chromium Plating, April 1998