Analysis of Functional Chromium Electrodeposits

Dr. Allen R. Jones and Chris Ringholz, Atotech USA, Rock Hill, SC

Accurate analysis of deposit quality starts with an understanding of the basic procedures for deposit qualities such as: adhesion, microhardness, microcrack density, and cross sections. These procedures will be reviewed. Deposit qualities are affected by the electroplating chemistry and conditions. Sample preparation and incorrect analysis can lead to the conclusion that the deposit is not acceptable. For example, when a cross section of a functional chromium deposit is made, a few pick-outs occur; sometime they are incorrectly identified as voids in the chromium. Errors made during the analysis of deposit properties will be reviewed.

For more information contact: Allen R. Jones Staff Chemist Atotech USA Inc. 1750 Overview Drive Rock Hill, SC 29730

 Phone:
 803/817-3568

 Fax:
 803/817-3502

 Email:
 ajones@atousa.com

Introduction

To accurately evaluate a functional chromium deposit's quality a basic understanding of the analytical procedures is required. Procedures including adhesion, microhardness, microcrack density, and cross sectional microscopic evaluation will be reviewed. Most chromium specifications discuss adhesion and microhardness properties. A few customers specify microcrack densities. Some mistakes in sample preparation and interpretation will be identified. From a practical point of view, a bright chromium deposit, as plated, is usually acceptable with respect to microhardness and microcrack density.

Adhesion

If a chromium deposit does not have good adhesion then the rest of its deposit qualities are not relevant. The most important factors that influence adhesion are the substrate and pretreatment. Adhesion is usually adequate if it exceeds the substrate or chromium cohesion (assuming the deposit is bright). Jones¹ discusses adhesion of chromium electrodeposits in detail.

Qualitative adhesion testing determines the weakest link of the coating-substrate system. This could be the chromium, substrate, or adhesion. Specifications such as ASTM B 571 describe qualitative adhesion tests. This specification describes the bend, chisel, file, grind, impact and pushout tests, among others. These tests damage the coating and interface in an attempt to delaminate the coating from the substrate. The ASTM B571 grind test is outlined below:

- 1. Force sample into rough emery wheel
- 2. Grind should be from substrate into the coating
- 3. Lifting or peeling is evidence of unsatisfactory adhesion.

This and most specifications do not sufficiently describe the detailed evaluation of the grind area required.

The sample should be examined at low magnification (<40X) to determine if chromium remains on the substrate near the interface. Chromium is not ductile and cohesive failure should occur before the adhesive failure. Chromium will fracture (cohesive failure) in the test area, but this does not mean that the adhesion is poor. Figure 1 shows what poor, good, and excellent adhesion would look like in a cross section of the damaged area. A coating with poor adhesion (a) will have exposed substrate visible for a large area and the chromium coating will have a vertical edge. Good adhesion (b) will be manifested in the damaged area by islands or shards of chromium and the edge of the chromium will taper up to its full thickness. A coating with excellent adhesion (c) will have no substrate visible and the chromium will taper from the defect area to the full chromium thickness. A severely damaged area from an impact test may appear to not have a thin coating of chromium on it. By tilting the sample so that the damaged area is perpendicular to the line of sight of the microscope, the reflective chromium will be visible if the coating has good adhesion. Figure 2 shows a view of the surface for samples exhibiting excellent and poor adhesion after the grind test. At high magnification (Figure 2c), fractured chromium is observed in the test area for the samples with good adhesion. Conversely, the steel substrate is visible for the sample with poor adhesion (Figure 2d).



Figure 1. Cross section of an adhesion test sample depicting poor, good, and excellent adhesion.



c. Excellent adhesion 250X

d. Poor adhesion 250X

Figure 2. Grind test results showing excellent adhesion (a and c) and poor adhesion (b and d).

Common mistakes in adhesion testing can be made in performing the tests, using the wrong test or in the interpretation of the results.

Common mistakes:

- Emery wheel was to fine of grit
- Emery wheel did not penetrate the chromium layer
- Coating was to thin or thick for the test
- Chromium cohesion failure is interpreted as an adhesion failure
- Substrate cohesion failure is interpreted as an adhesion failure.

If to fine of grit is used on the wheel in the grinding test or the chromium layer is not penetrated then insufficient force is applied to the interface. The test must be suited to the coating thickness, for example the grind test is well suited to thicker deposits (>25 μ m) whereas the scribe-grid test is only useful for thinner coatings (<25 μ m). During most adhesion tests the chromium will flake off during the test, this does not mean that the adhesion is poor. If only substrate is observed after an adhesion test, then the adhesion is poor or the substrate cohesion is poor. If tape is applied to the chromium surface and the area is tested, then the backside of the chromium flakes can be examined for iron with the aid of copper sulfate. A dilute acidic copper sulfate solution will form an immersion layer of copper on most ferrous substrates and make the iron more discernible from the chromium. An immersion time of a few seconds followed by a rinse should be used. Grey cast iron can have a tensile strength less than the chromium adhesion. Cast iron can also be damaged during machining to produce a weak rubble layer.

Microhardness

A deposit's microhardness is an indicator of its, quality, wear resistance, and toughness. Variance in the microhardness measurements is due to the variance in the deposit hardness and measurement itself. Figure 3 shows the variation of microhardness with chemistry, temperature, current density and ratio for hard chromium deposits from two different baths^{2, 3}. Greater variation is observed for the deposits plated in the conventional chemistry than for the deposits plated in the high efficiency etch free chemistry^{*}. In fact, there is not a statistical difference in hardness for any of the high efficiency etch free deposits, but there is a statistical difference between the deposits from a conventional bath.

Common chromium specifications refer to the following microhardness specifications: ASTM B 578 (US), ISO 4516 (EU), and JISZ 2244 (Japan). The method is reviewed in several references^{4, 5}. The microhardness method uses one of two shapes of diamond indenters and the load typically used for hard chromium is 100g. A Knoop indentation is narrower and only one half as deep as a Vickers indentation, which is reported to be more tolerant of surface irregularities. The Vickers indenter is not the same as the macro indenter, DPH (diamond pyramid hardness).

Horner reports the results of a round robin tests that show the variation between equipment and operators⁶. Samples were prepared by a single person and sent to the participants, who measured the microhardness with various loads and two indenters. The range for tests with a Knoop indenter was 200 compared to a 325 range for tests with the Vickers indenter. He concluded that the measurements might not be in statistical control. Figure 4 shows the variation in microhardness by Knoop indentation as a function of different operators making readings on the same five indents, as determined in our laboratory. Standard deviation in this case was between 26 and 52.

^{*} HEEF 25, Atotech USA Inc. Rock Hill, SC.



Figure 3. Microhardness vs. chemistry and conditions for conventional and high efficiency etch free deposits (95% confidence intervals shown).

The ASTM B 578 is outlined below:

- 1. Over plate coating with a coating of a different color but similar hardness
- 2. Cut the sample
- 3. Mount and polish a cross section according to ASTM E 384
- 4. Test the cross section with a Knoop indentation parallel to the interface
- 5. The coating thickness is at least 25 μ m
- 6. Make indentation near center of cross section
- 7. Cracked or non symmetrical indentions (>10%) are invalid
- 8. Report the range, mean, standard deviation, and coefficient of variation of at least five indentations

This document states that if a nondestructive test is necessary, then a surface indentation can be used if the thickness is at least 0.7 times the length of the Knoop indentation. If the coating is not sufficiently thick then the softer substrate can decrease the apparent coating hardness. This effect is called the anvil effect. For a coating with a hardness of about 1000 HK₁₀₀ (100g load) this corresponds to a thickness of about 25 μ m. It also states that values obtained from surface indentations may not be equivalent to cross sectional values and therefore cannot be reported. Others claim that the coating must be 15 times thicker than the indentation depth to prevent the anvil effect⁷. This would correspond to a thickness of about 18 μ m for a coating with a microhardness of 1000 HK₁₀₀. Surface indentations must be performed on a flat polished surface.

The data in Figure 5 (measured in our laboratory) shows that for deposit thicknesses of 18 μ m and 30 μ m, there is no statistical difference between surface and cross sections measurements of microhardness on flat panels of O-1 tool steel under the conditions of the tests. The average substrate hardness was HK₁₀₀ 226.



Figure 4. Variation in microhardness as a function of the operator reading the same indents in a high efficiency etch free deposit (95% confidence intervals shown).



Figure 5. Microhardness measurements of deposits plated from a high efficiency etch free chemistry onto flat O-1 steel (95% confidence intervals shown).

Specifications are sometimes given in Rockwell C, which is a macrohardness scale. The documents, ASTM E 384 and BAC 5709⁸ both reference different hardness conversion tables. The lightest load in the document referenced by E 384 is 500 g, which is much higher than the 100 g load usually used for testing functional chromium deposits by Knoop or Vickers indentation. Horner recommends against conversion to other units since the loads can have a significant effect on the measured value and coatings are usually tested using a microhardness measurement, but not a macrohardness measurement.

Common Mistakes

The variance of microhardness values can be significant even when the analytical procedure is performed correctly. There are many mistakes related to sample preparation and testing that can result in inaccurate microhardness values. Some of these mistakes are listed below and the effect on microhardness is shown.

Common Mistakes:	Resulting Microhardness Value
• Over heating while cutting the sample	Low
• Over heating while polishing the sample	Low
• Sample preparation leading to sample porosity	Low
Vibration	Low
• Sample holder	High

During sample preparation, the sample must be cut one or more times so that the cross section can be tested. Typically, the sample should be cut slowly with cooling. The substrates of chromium-plated samples are typically hardened and require the use of an abrasive (SiC) cut-off saw. Often sparks can be observed during this process. The mistake of cutting too rapidly or without cooling could lead to excessive heating and therefore causing the chromium to become softer. The document, E 384 cautions against "excessive heating" during sample preparation. Figure 6 shows the affect of heat treatment on chromium microhardnesses. The hardness can be decreased significantly and is a function of the temperature and time.





Figure 6. Microhardness vs. heat treatment temperature for high of a efficiency etch free deposits (95% confidence intervals shown).

Figure 7. Polishing artifact in a cross section chromium plated steel substrate. The steel was moved into the chromium layer during polishing.

An abrasive cut-off saw is basically a grinding tool. Shaw⁹ discusses grinding temperatures in great detail. The grit-chip interface temperature was determined to be 1260°C for iron and 1593°C for chromium (which is greater than the melting point of chromium). This can occur due to the time required for the structural change due to melting. After the metal sparks contact air (oxygen) they explode and glow. The substrate near the grinding area can reach temperatures of between 500 and 600°C. Shaw measured the temperature in the bottom of a hole 20 μ m from the ground surface. The

dry grinding produced temperatures between 500 and 1000°C, while with coolant temperatures between 90 and 1100°C were measured. This data shows that even with coolant, the peak temperature can be very high during grinding. Sparks are observed using a cut-off saw with coolant to cut chromium-plated shafts.

Polishing during sample preparation can generate heat. The use of a long nap cloth, low lubricant, high force, and excessive time can generate heat and polishing artifacts. Polishing has deformed steel and caused it to move the chromium coating. This is shown in Figure 7. This amount of deformation indicates significant heat was generated during the sample preparation and this could make the chromium softer.

Porosity can be generated in the surface of the cross section during sample preparation. The section on cross sectional evaluation discusses apparent porosity from pick outs in greater detail. If the indent hits a pick out, then the measured hardness is lower than its actual value. A few pick outs are present in most samples, and care should be taken to avoid them for indentation measurements.

Excessive vibration of the instrument during the test has been known to cause low microhardness values. Vibration dampening table or pads should be used to minimize this effect. Do not locate the instrument near vibration sources⁵.

Inaccurate and high microhardness values are obtained if the mount moves during the indentation. This was observed in one case when a thin bent metal plate was used to support the sample. During indentation the metal moved and the full force of the load was not applied to the sample. The microhardness values where about 30% higher than the real values.

Variations of microhardness are due to the variations of the actual hardness of the deposit and the testing process. Variations of actual microhardness are minimized by using a high efficiency etch free process. There is no statistical difference in cross sectional versus surface measurements when the chromium is sufficiently thick. Finally, several common mistakes can lead to obtain incorrect microhardness values, including specimen preparation technique mistakes that alter hardness and procedural mistakes that lead to erroneous readings.

Microcrack Density

Jones^{2, 10} studied microcracks in functional chromium deposits in detail. Microcrack density shows some correlation to microhardness² and wear properties¹⁰. Microcracks are not voids, but deposits of chromium that are more electrochemically active than the bulk of the deposit. None of the common chromium specifications discuss microcrack density. There are two main procedures used in industry to measure microcrack density. They are the Electrolytic (Atotech) method and the Chemical (VW) method. The Electrolytic method uses an anodic etch in an alkaline solution while the Chemical method is a chemical etch in an alkaline solution of potassium ferricyanide. The Electrolytic method develops about twice as many microcracks as the Chemical method.

The Electrolytic method is described below:

- 1. Place part in boiling water for 30 minutes.
- 2. Clean part to water break free surface.
- 3. Anodically etch the part in a solution that contains100 g/l of sodium hydroxide for two minutes at 46.5 A/dm², rinse and dry the part.
- 4. Examine the part under sufficient magnifications so that between 10 and 20 cracks intersect a reference line on a grid. Count all of the cracks intersecting several lines and several perpendicular lines. Measure the cracks in three different areas on the same part.

5. Based upon the number of cracks, length of the lines in the grid and the magnification, calculate the average microcracks/cm to the nearest 100.

Boiling the parts causes the outer layer of chromium to microcrack. The anodic etch time and current is designed to obtain a steady state microcrack density. Excessive etching does not result in a higher microcrack density, because the outer layers are being completely dissolved. A typical microcrack distribution for five samples plated from the same bath under identical conditions is shown in Figure 8. Microcracks are shown in Figure 9. The plating conditions, chemistry, impurities, substrate, and post finishing effect the microcrack density.



Figure 8. Microcrack variation on replicate samples plated from a high efficiency etch free chemistry (95% confidence intervals shown).



Figure 9. Microcrack pattern after etching the surface of a chromium deposit.

Common mistakes

Figure 8 shows that there is significant variance in the microcrack density of replicate samples. Common mistakes related to microcrack density analysis can lead to low values of the microcrack density.

Common mistakes:

- Sample was not clean
- Sample was tested before post finishing was performed
- Chromium was too thin for the standard test
- Magnification was too low

When the sample is not properly cleaned before anodic etching, some sample areas are masked during a portion of the etching cycle. This will decrease the measured microcrack density. Under those conditions, the etch appears non-uniform or blotchy. After etching, the sample will usually be darker if there are a high number of microcracks. Post finishing will microcrack the outer layer and passivate the surface so that the etching will reveal more microcracks. The anodic etch will dissolve about 7 μ m of chromium, therefore on thin deposit all or most of the chromium will be dissolved and an accurate microcrack density will not be obtained. A shorter etch time can be used but should be specified with the results. If this shorter etch is used consistently, then trends or

changes in microcrack density can be detected. If the magnification is too low, then some of the smaller microcracks may not be observed.

Monitoring microcrack density is not difficult and this property reflects the general quality of the chromium deposit. Low microcrack density can indicate that the chemistry is contaminated or out of the recommended ranges or that the operating conditions are not in normal ranges.

Cross Sectional Evaluations

Microscopic evaluations of cross sections are performed on samples to examine the microhardness, thickness, and structure of the deposit. When the structure of the deposit is to be examined, a short anodic etch (a few seconds at 6V) is used to develop the microcracks. The proper etch of a cross section is more of an art than a science since the chromium area is small and steel or substrate is also exposed. A typical functional deposit before and after etching is shown in Figures 10 and 11. Short etch lines indicate a high microcrack density; longer microcracks can span the entire chromium thickness if the microcrack density is very low.



Figure 10. Pick outs from a cross section of a chromium deposit. Figure 11. Etched cross section of a chromium deposit.

Common Mistakes

Figure 10 shows a normal unetched chromium cross section. All such cross sections show a few dark areas that are pick outs from samples preparation. Occasionally, longitudinal sections in contrast to cross-sections of chromium-plated shafts will be made to examine the case depth along a shaft. Artifacts of longitudinal sections can be very unusual.

Common mistakes:

- Incorrect polishing can generate an excessive number of pick outs.
- Assuming pick outs are voids in the chromium deposit.

• Making a longitudinal cross section (a few percent off of the diameter) and observing transverse microcracks and assuming that these unusual cracks are a problem.

A chromium deposit with a high microcrack density will have a few pick outs in the cross section. Good polishing techniques are necessary to avoid excessive quantity of pick outs. The dark areas shown in Figure 10 will look like the surface shown in the SEM in Figure 12. This shows that the dark area observed with an optical microscope are small pick outs that do not reflect light back perpendicular to the surface.

The drawing in Figure 11 shows how the pick outs are formed. They are not observed in the surface of a chromium part only in a cross section. In the cross section the microcracks can form small areas that are not held together well. Area "A" in Figure 13 shows that when two microcracks meet near the surface of the cross section a small area can be picked out from the surface by the polishing forces. The polishing forces can pick out area "B" where a microcrack is almost parallel to the surface of the cross section.



Figure 12. SEM of a pick out showing that it is not a void, but just a small area of chromium that was removed



Figure 13. Schematic of pick outs from a chromium deposit.

When longitudinal sections are made in contrast to cross sections as shown in Figure 14, the section must be made at the full diameter of the rod. If it is off the full diameter by as little as 5% then transverse cracks are observed and are normal. Transverse cracks are microcracks that are not perpendicular to the substrate. If a section of the microcracks shown in Figure 13 is made that is not perpendicular to the surface then the section will be a combination of the surface and the cross section and will have transverse cracks. Figure 15 shows transverse cracks obtained from sections that are off the diameter by 5 and 25%.



Figure 14. Schematic of a cross and longitudinal section.

Figure 15. Longitudinal sections at A. 95% diameter and B. 75% diameter

Artifacts can be generated from polishing cross sections or from making longitud inal sections not on the full diameter of the rod. Both of these artifacts are due to the unique microcrack structure of functional chromium electrodeposits.

Conclusions

Qualitative adhesion tests of functional chromium deposits are easy to perform, however careful analysis of the damaged areas must be undertaken to prevent incorrect conclusions. Microhardness and microcrack density measurements have large variances. Errors can result in higher variances and inaccurate values for these properties. Careful sample preparation and measurements can minimize the variance and improve the accuracy of the results. Artifacts can be generated during sample preparation. Understanding potential artifacts and their causes can minimize their occurrences.

References

- 1. "Adhesion Testing of Hard Chromium Electrodeposits," Allen R. Jones, Seiho Sugawara, and Jack Enloe *Proc. AESF SUR/FIN 2000*, June (2000).
- 2. A.R. Jones, Plating & Surface Finishing, 76, 62 (April 1989).
- 3. K.R. Newby & A.R. Jones, 25th Annual Aerospace/Airline Plating & MF Forum, March (1989).
- 4. *Metals Handbook Desk Edition*, 2nd Ed, J.R. Davis, Ed., ASM International, Metals Park Ohio, p.1315 (1998).
- 5. Hardness Testing, H.E. Boyer, Ed., ASM International, Metals Park, Ohio, p. 67 (1987).
- 6. J.D. Horner, *Testing of Metallic and Inorganic Coatings*, ASTM STP 947, W.B. Harding & G.A. De Bari, Eds, American Society for Testing and Materials, Philadelphia, 1987, pp. 96-110.
- 7. *Electroplating and Engineering Handbook*, 3rd Ed, A.K. Graham, Ed., New York, Van Nostrand Reinhold Co. p. 411 (1971).
- 8. Boeing Process Specification, Rev. "L" 10-4-83, Boeing Aircraft Corp. Seattle, WA.
- 9. Principles of Abrasive Processing, M.C. Shaw, Calrendon Press, Oxford pp. 211-260 (1996).
- 10. A.R. Jones, Trans. Inst. Metal Finish, **70**, 8 (1992)