Adhesion Testing of Hard Chromium Electrodeposits

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Qualitative adhesion testing is preferred to quantitative methods primarily because of the ease of specimen preparation and testing. With either method, failure can occur at the interface, in the substrate, or within the chromium, therefore, care must be used to correctly interpret the results. A three-point bend test was developed to obtain semi-quantitative adhesion data without overplating or sample machining. In this test, adhesion is inversely proportional to the distance between the cracks in the bent sample. Use of this and other adhesion test methods will be discussed for hard chromium plating.

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Introduction

Hard chromium electrodeposits must be adherent so that the beneficial wear and corrosion properties of chromium are manifested in the plated product. Hard chromium electrodeposits are normally plated only on metal substrates, therefor adhesion on non-metal substrates will not be discussed. For most chromium plating processes and substrates the adhesion is adequate and greater than the cohesive strength of the chromium or substrate.

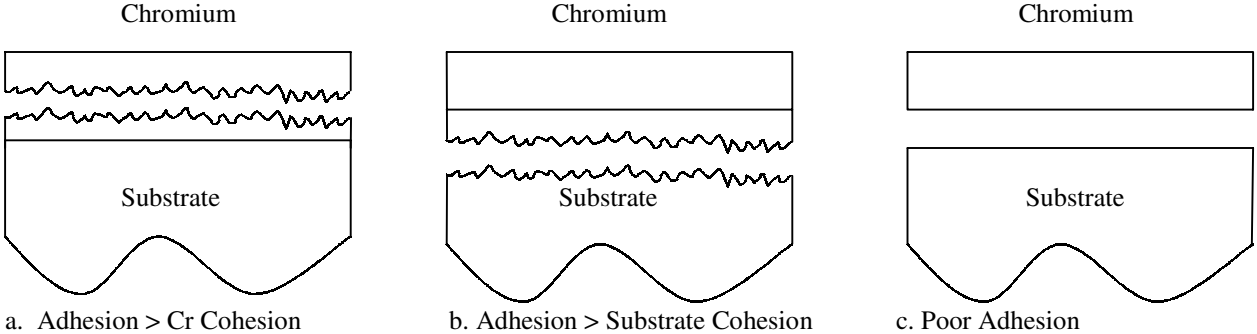
Adhesion of chromium to the substrate is achieved through metal-to-metal bonds formed at the atomic level. The bond strength is about the same as the tensile strength of the substrate or chromium. This metal-to-metal bond is in excess of that required for normal applications. Since the adhesion is from atom-to-atom interactions and not mechanical keying, the surface roughness is not a factor in bond strength. Chromium plated on polished substrate has the same adhesion as on a rougher, vapor-blasted surface. Epitaxial crystal growth is not necessary for good adhesion[1]. A substrate contaminated with oils or oxides will not have good adhesion to the chromium coating.

The goal of adhesion testing is to apply stress to the interface to cause failure of the bond, coating, or substrate. In one technique, the coating is "attacked with a hammer and chisel at the interface"[2]. A variety of mechanical mayhems are used to deform the interface. Chromium is not ductile and usually has a cohesive or tensile strength less than the strength of the adhesion or substrate cohesive strength and will flake off in the damaged (test) area. The chromium cohesion will effect the results of the test. Typically, the chromium cohesion will be the weakest part of the coating. An adhesion test of the chromium coating with low cohesion may appear good, but since the chromium cohesion is low, less stress will be applied to the interface. Careful and detailed interpretation must be made of the interface to assess the coating's mode of failure and adhesion.

Microscopic examination of the damaged (test) area is required to correctly assess the coatings adhesion. A stereomicroscope that can magnify up to 30 times is adequate. If the damaged area shows mostly chromium, then the adhesion is generally good. If only substrate is observed, then the adhesion is poor or the substrate cohesion is poor. These three cases are shown schematically in Figure 1. 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[3].

Figure 2 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,

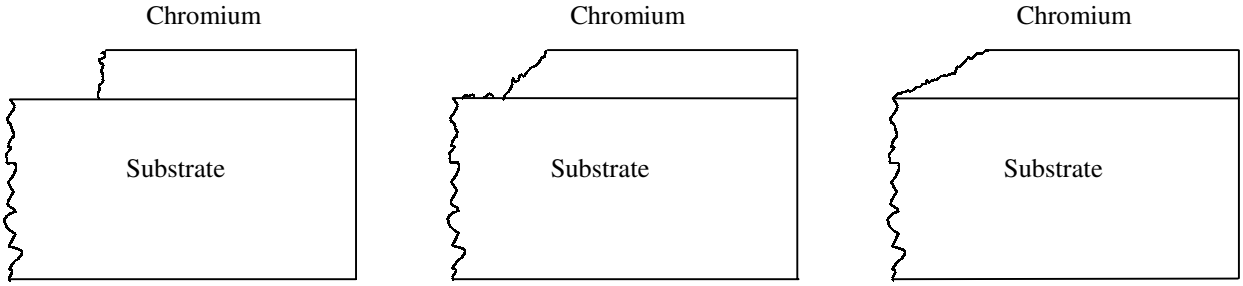
Figure 1. Failure modes of the damaged area of an adhesion test.



a. Adhesion > Cr Cohesion b. Adhesion > Substrate Cohesion c. Poor Adhesion

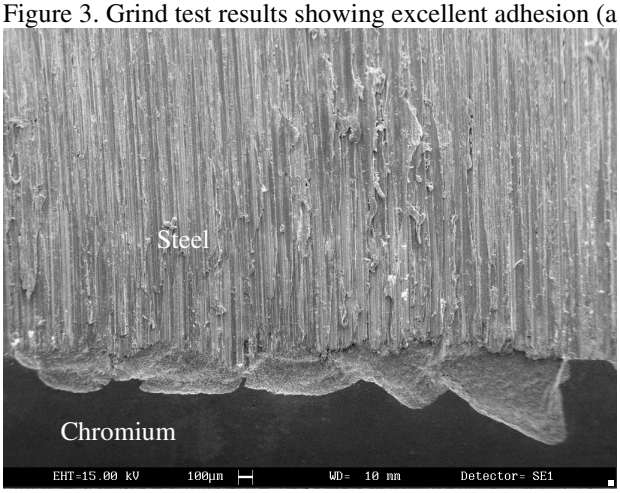
the reflective chromium will be visible if the coating has good adhesion. Figure 3 shows a view of the surface for samples exhibiting excellent and poor adhesion after the grind test. At high magnification (Figure 3c), fractured chromium is observed in the test area for the samples with good adhesion. Conversely, the steel substrate is visible for the sample with poor adhesion (Figure 3d). Figure 4. shows a twisted oil ring with excellent adhesion. There are many chromium shards in the damaged area. A coating with good adhesion will satisfy most commercial applications.

Figure 2. Cross section of an adhesion test sample depicting poor, good, and excellent adhesion.

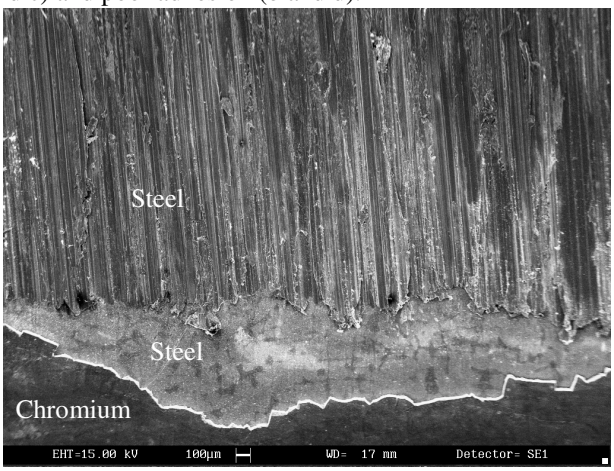


a. Poor adhesion. b. Good adhesion. c. Excellent adhesion .

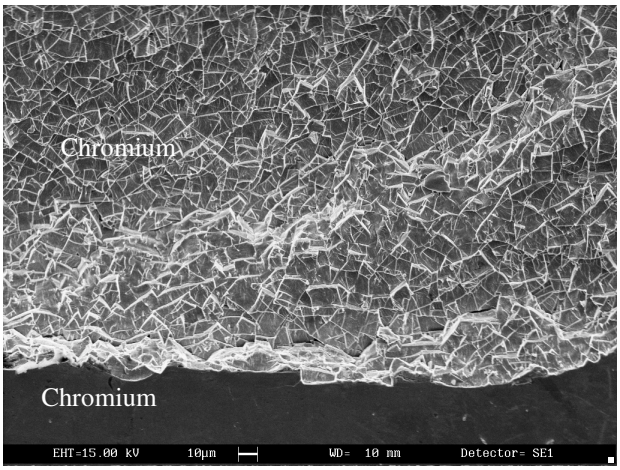
Figure 3. Grind test results showing excellent adhesion (a and c) and poor adhesion (b and d).



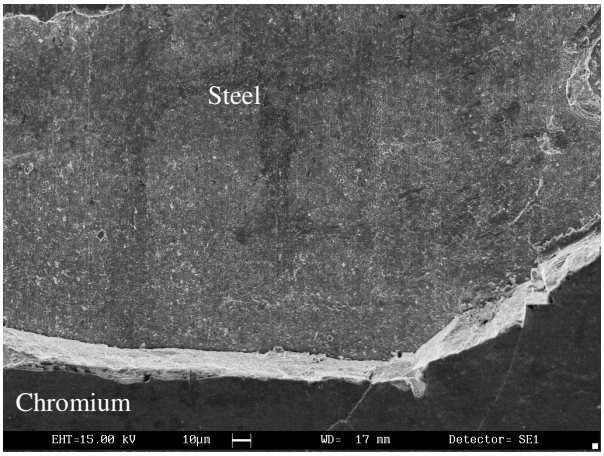
a. Excellent adhesion 20X



b. Poor adhesion 20X

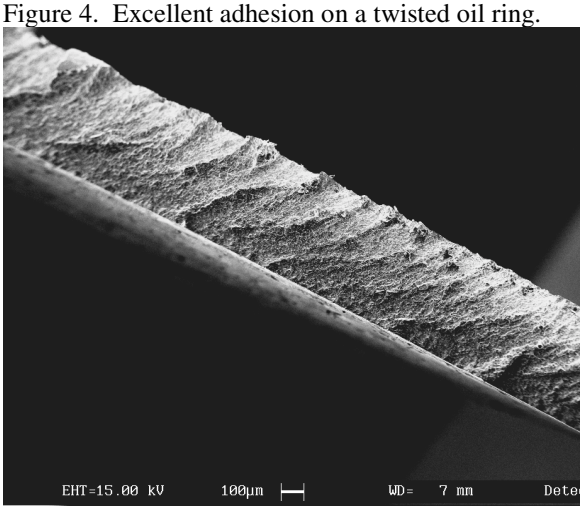


c. Excellent adhesion 250X



d. Poor adhesion 250X

Figure 4. Excellent adhesion on a twisted oil ring.



Obtaining Good Adhesion

Good cleaning and activation will produce good adhesion on most substrates. Cycles for various substrates are described in Electroplating Engineering Handbook[1]. Etching or activation is required for most parts to obtain good adhesion. Anodic etching, more commonly referred to as reverse etching, is usually performed in chromic acid or sulfuric acid. The advantages of anodic etching in chromic acid compared to sulfuric acid include: better control (etching only occurs when the current is on), minimal or no rinsing after etching, chemical compatibly with the plating process, and elimination of flash rusting of ferrous substrates during transfer to the plating tank. The duration of anodic etching in chromic acid can range from a few seconds to many minutes depending upon the alloy that is being plated. Anodic etching at a high current density ($\approx 60 A/dm^2$) will: electropolish the part, leave less smut, reduce the plated parts roughness, and improve its corrosion resistance[4]. The slight smut from an anodic etch will not decrease adhesion. The chromium undercuts the smut.

Adhesion strength is probably not linearly proportional to the anodic etch time. If the optimum etch time is 60 seconds, then a 30 second etch at the same current density will probably produce an adhesion strength much greater than 50% of the optimized adhesion strength.

A hydrogen wash in the plating bath at a very low current density can improve adhesion. During a hydrogen wash, hydrogen is evolved without chromium being deposited. The hydrogen mechanically cleans the surface, reduces oxides and activates the steel. This is a good technique to use on highly polished surfaces such as molds that can not be anodically etched because the etching will ruin the surface finish.

As with any process, problems can occur during pretreatment and plating. Poor adhesion can occur if the part is large and not heated to the plating temperature prior to anodic etching. Inadequate etch is also obtained if voltage control is used and the trivalent chromium is significantly increased or the anode to cathode gap is increased. High efficiency processes start plating chromium at lower voltages compared to the conventional (sulfate) process, and therefore lower voltages must be used to produce a hydrogen wash. A rectifier with a high ripple can also cause poor adhesion. The high ripple can be caused by one leg of a three-phase line being open. A large stainless steel part was chromium plated and exhibited macrocracks. Chromium was extending over one edge of the part and when it was dislodged from the substrate with a hammer and chisel the chromium delaminated as is represented in Figure 2a. Poor adhesion is one of several causes of macrocracks. Lead is added to some steels to improve their machinability. Leaded steels require special activation to remove the lead from the surface to get good adhesion. Air supplies to the vapor blaster or tank agitation should be free from oil since this could decrease adhesion.

The most common reasons for poor adhesion are poor cleaning or improper anodic etch. Special alloys or difficult to plate substrates are also a problem. Surprisingly, another main problem is that of unknown substrates. In many cases, platers do not know the composition of the substrate they are trying to plate.

Adhesion Measurements

Adhesion tests are often prescribed by chromium specifications. The actual processing of chromium plated parts after plating can indicate poor adhesion. Qualitative adhesion testing is often performed in production. Quantitative adhesion testing is rarely used and adhesion values are very limited. Only adhesion test methods used or applicable to chromium will be discussed. Adhesion test methods are described in detail in several references[5-7].

Table 1 shows chromium specifications and the required adhesion test. Many of the specifications refer to specific adhesion test specifications. All of the adhesion tests are qualitative. The Japanese specification gives a lot of details on how to perform the tests. All of the specifications are deficient in their descriptions of how to analyze the test results. As noted earlier, analysis of the adhesion test area is very important.

Table 1. Chromium Specifications

Source	Specification	Adhesion Specification	Tests and Comments
US Federal	QQC 320	---	Knife and Bend
SAE	AMS 2406H	ASTM B571	Chisel, Draw, Grind, Heat, Impact, Push
Boeing	BAC 5709	---	Chisel and Bend
Japan	JIS H 8615	JIS 8504	As B571 with cathodic test and more details

Thermal or mechanical processing of parts after plating can reveal adhesion failures, although processing is usually a less severe adhesion test as compared to distructive qualitative tests. Heat treating of struts or other parts for hydrogen release can reveal poor adhesion by the presence of blisters. Hydraulic rods are often plated in long lengths and then cut to size after plating. Poor adhesion is sometimes noticed as chromium delamination at the cut edge. Grinding or superfinishing of rolls, struts, or shocks cold cause delamination of a coating with poor adhesion. Likewise, lapping of piston rings could reveal poor adhesion.

Qualitative Testing

Mechanical mayhem is performed on the coating and substrate to evaluate the coatings adhesion. Adhesion testing can be done periodically on inexpensive parts or for more expensive parts a coupon of the same alloy, surface finish, pretreatment and plating can be used to asses adhesion. In some tests the force to the coating can be applied reproducibly. Even in test where the force is not reproducible, the coatings adhesion can be rated as in Figure 2 as being poor, good, or excellent. If the substrate and coating thickness and plating conditions are held constant, then qualitative testing can discern significant changes in pretreatment. Qualitative testing may distinguish between a one second and a one-minute anodic etch, if the adhesion is changed from poor to good or excellent. Some tests can produce a number that is related (not necessarily proportional) to the adhesion. If the coating and substrate are held constant, then these semi-quantitative methods can differentiate the coatings adhesion for different pretreatment methods. Usually, microscopic examination (described in the introduction) is used as part of the qualitative testing to identify the failure mode.

The following adhesion tests are listed from simpler to more complex methods. Many of the techniques are simple, but have modifications that make them more complex. The test areas should be inspected as described on pages 2 and 3 to determine adhesion characteristics.

Cut/File/Chisel Test

The part is cut and then the interface is attacked with a coarse mill file or chisel. The file is moved from the substrate towards the chromium in an attempt to lift the chromium from the substrate. The chisel can also be used to make a pattern in the shape of a ladder on the part and look for delamination. This test is often used on chromium plated aluminum cylinders. These tests are used on medium to thick chromium deposits.

Engraver Test

For thin coatings an engraver can be used to punch through the chromium and deform the substrate.

Grind Test

The part is thrust into and moved along the edge of a coarse grinding wheel. A more severe test is to use the grinder to make a “V” on the part with the wheel coming out of the substrate on the inner edge of the “V”. The interface where the wheel was passing from the substrate to the chromium is examined. The tip of the “V” is the most severe area of the test area. This method is used for thicker coatings.

Push Out/Back Cut Test

The push out test was designed for testing chromium plated cast iron liners. The cast iron is drilled out to near the interface and then the remaining cast iron and chromium is punched out with a rod and a press or hammer. The perimeter of the hole and the button are examined for adhesion characteristics. A modification of this method is to cut through most of the substrate and then break the substrate and chromium by bending the part. This modified test is not as severe as the push out test. These techniques are good for thicker chromium deposits.

The part is made a cathode at an elevated temperature and high current density. Hydrogen gas diffuses through the chromium and can accumulate at the interface and cause blisters in a coating with poor adhesion.

Bend/Twist Test

In this test the substrate is bent or twisted until the chromium flakes off. This test can be applied to pipe that is plated on the internal diameter with chromium. About 350^{o} around the pipe the substrate and chromium are cut and then the remaining sections are bent away from each other. This test can be made reproducible by bending the part around a mandrel. Bending the part on a 3 or 4 point-fixture with a tensile testing machine can attain even more reproducibility. This test is semi-quantitative and is described in additional detail on pages 11 and 12.

Impact Test

The simplest form of this test is to strike the edge of the chromium and substrate with the edge of a hammer and cause a dent in the ductile substrate. This method has been refined to use a dropping or swinging weight to strike the part that is held in a fixture. This test has also been refined[8] into a dynamic test where a smaller specific load is repeatedly impacted on the surface of the chromium.

Heat Treatment Test

Heating the part may cause blisters if there is poor adhesion due to the pressure from gasses or liquids trapped at the interface. A more severe test involves the sudden heating or cooling of the sample. Differences in the thermal expansion coefficients between the chromium and substrate can cause strong forces at the interface that can delaminate the chromium if the adhesion is poor. This is a nondestructive adhesion test if the temperatures do not cause harm to the substrate.

Rockwell C Test

A Rockwell C indenter deforms the surface of the chromium and substrate. This method applies a reproducible load and then the test area is inspected for adhesion characteristics.

Scratch Test

The surface of the chromium and substrate are scratched with a diamond stylus under an increasing load while the sample is moved at a constant rate normal to the applied force. Adhesion and cohesion numbers can be obtained. The force of the load when full delamination occurs is recorded. Delamination is detected visually after plating or acoustically during

Cathodic Hydrogen Charging Test.

the test the load rate and sample movement are controlled. Additional details are given on page 10.

Qualitative tests very from simple to complex. One of the most inexpensive methods of applying reproducible damage is the dropping or swinging impact tester. The equipment cost can be as inexpensive as a hammer or an instrument costing tens of thousands of dollars.

Quantitative Testing

The ideal test method would reproducibly measure adhesion by applying a force normal to the interface on any sample or part without extensive machining of the part before or after plating. The difficulty in attaining this goal lies in the inability to grip the chromium so that it can be pulled off the substrate. Adhesives and solders are generally limited to 700 kg/cm^2. Solders could also heat-treat the chromium, thus altering the adhesion. Most quantitative methods require extensive plating times and sample machining. The best methods use some means of automatic alignment so that the force is exactly normal to the surface. Any non-alignment of the force will cause shearing failure and will produce adhesion values that are lower than the true values. Some quantitative tests apply a load normal to and away from the substrate while other tests apply force in different directions. The test areas must be examined to determine where the failure occurred.

Normal to surface and away from the substrate:

Ollard Test

In this test, the end of a rod is electroplated with a thick deposit. The rod is subsequently machined to leave an overhanging coating. The rod is then forced through a close fitting die to detach the coating.

Tapered Pin Test

This method uses small tapered pins (1-mm diameter at the tip) that fit exactly into a block. The tip of the pin is flush with the block. Both the pin and block are plated and the pin is then pulled out of the block. Adhesion is measured as the force required to remove the pin. The pin and the block require precise machining. This can create a problem since pretreatment solutions could bleed out from the slight gap between the pin and block. Pitting could also occur in this area.

Ultracentrifuge Test

In this test, a rotor is plated and then very rapidly revolved. The coating is detached by centrifugal force if the speed is fast enough. A 0.022cm rotor was rotated at speeds up to 10^6 revolutions per minute. A thicker coating has more mass and can apply more force to the interface. The equipment is complex and expensive.

Other test methods:

Ring Shear

A cylindrical rod is chromium plated and then over-plated with copper. Groves are machined through the copper and chromium and just into the substrate. The rod is forced through a die and the coating or substrate is delaminated. This test measures the shear strength of the coating. Many tests can be done on one plated rod. Dini and Johnson[7] reported the effect of rod diameter and crosshead speed on the measured ring shear strength of nickel.

Dennis and Such[5] and Dini and Johnson report the sample preparation and plating thicknesses required for several quantitative adhesion tests. The required plating time for chromium is between five and 200 hours and would require between 20 minutes and four hours of machining and between 10 minutes and one hour for testing. The ring shear test was selected by Sandia Laboratories as the preferred adhesion test method because "it can be done in a shorter time and is less costly"[7].

Literature Adhesion Data

Ring Shear Test

Zmihorski[9] studied the effects of etch chemistry, plating current density, chromium thickness, plating chemistry, substrate hardness, and heat treatment on shear strength. In his paper, there is no discussion of failure mode (cohesive or adhesive). Some of the data is shown in Table 2. No etch times or etch current densities are reported. The data suggests that etching in sulfuric acid produces better shear strength than etching in a chromium plating bath and that the shear strength is dependent upon the coating thickness. The etch time and etch current density may not have been optimized for both etch chemistries. The thickness effect may be an artifact of the test, since Dini and Johnson observed a similar increase in shear strength with an increase in the sample to die clearance gap. A smaller gap and a thicker coating will both have more support on the die. The author suggests that the 20% decrease in shear strength observed with increasing plating current density is due to more hydrogen accumulating at the interface and the resulting stress. This argument may not be valid since the higher current density will plate at a higher efficiency and will have a shorter plating time; thus the hydrogen exposure would not be significantly different for the two different current densities. The lower current density probably produced brighter or tougher chromium than the higher current density.

Zmihorski data on the shear strength for three different plating chemistries: conventional, used conventional, and fluoride is shown in Table 3. The very high concentration of impurities in the used solution decreased the shear strength by producing a more brittle deposit. The deposit from the conventional bath at 35 A/dm^2 had a shear strength equal to the deposit from the fluoride bath plated at 50 A/dm^2. The lower current density gives a better deposit than the higher current density in the conventional solution.

Table 2. Shear strength as a function of etch chemistry and plating current density from Zmihorski.

Etch chemistry	Plating Current density A/dm^2	Shear strength*, kg/cm^2		
		Coating thickness, microns		
		60	150	350
CrO_3 200g/l, H_2SO_4 2g/l	35	5400	3300	
54^{o}C	50	4200	2600	1800
H_2SO_4 53^{o}Bé (66%w/w)	35	7000	4100	
Room temperature	50		3400	2000

*Average of two measurements.
Plating conditions: CrO_3 250g/l, H_2SO_4 2.5g/l, 54^{o}C.

Table 3. Shear strength as a function of plating current density and chemistry after Zmihorski.

Plating Current density A/dm^2	Shear strength*, kg/cm^2		
	Plating chemistry, g/l		
	CrO_3: 250 H_2SO_4: 2.5 other: -	250 2.5 Fe 10, Cr^{3+} 15	250 1.5 H_2SiF_6 4
35	5400	3400	
50	4200	2400	5400

*Average of two measurements.
Etch conditions: CrO_3 200g/l, H_2SO_4 2g/l, 54°C.
Heat treated 60-micron thick chromium samples for 1 hour at 200°C.

Steel rods with different hardness' were plated to 60 microns of chromium at 35 A/dm^2 in a conventional chromium bath (CrO_3 250g/l, H_2SO_4 2.5g/l, 54°C) using a chromic acid etch. After plating the rods were heat treated for one hour at 200°C. The results were as follows:

Substrate Hardness Rockwell C	Shear Strength kg/cm^2
26	5800, 6500
58	5300, 5500

The author concluded that the softer steel could better accommodate the stress of the heat treatment than the hardened steel. There is no indication that the reverse etch was optimized for the different steels. The author showed that heat treatments of 200 and 580°C had no or minimal effect, on the shear strength. A heat treatment of 850°C has a very significant effect on the shear strength. Of course temperatures of 580 and 850°C are going to decrease the deposits microhardness.

Tapered Pin

Hasegawa et al.[10] used a tapered pin to measure the effect of pretreatments on chromium adhesion. The data is shown in Table 4. Etching improves the adhesion. The authors claim that hydrogen over voltage and surface roughness affect adhesion. The sample that was etched produced adhesion comparable to the samples in the Zmihorski study.

Table 4. Adhesion as a function of pretreatment process after Hasegawa.

	Surface Roughness	Adhesion Strength, kg/cm^2		
Pretreatment	R_a, microns	at 40 A/dm^2	Average*	Standard Deviation
Buffing	0.029	1200	1200	300
Polishing	0.036	1900	1600	270
Polishing	0.080	1900	1600	270
Polishing	0.130	1300	1400	180
Grinding	0.088	1000	1000	180
Etching◆	0.032	4500	3800	510

*Average of data from samples plated at 20, 40, 60, and 80 A/dm^2.
◆ In CrO_3 250g/l, H_2SO_4 2.5g/l, at 40 A/dm^2 for 30 seconds at 50°C.
Plating chemistry is the same as the etching.
All samples were prepared as follows after the pretreatment:

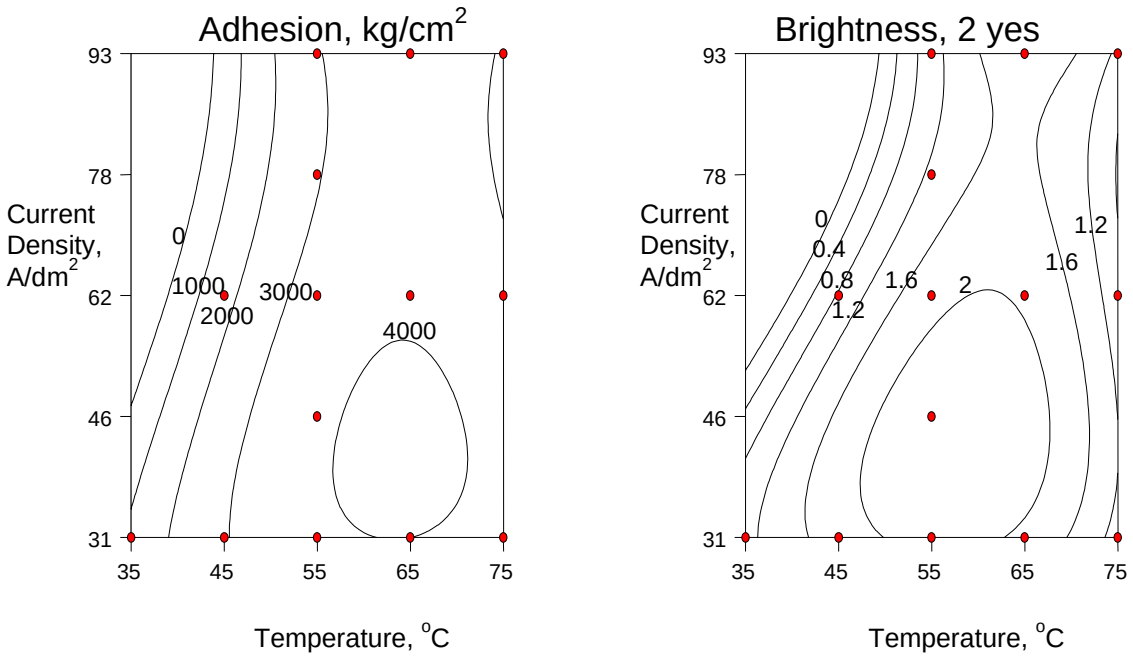
- cathodic and anodic eletroclean
- cold water rinse
- 10% H_2SO_4 for 3 seconds
- cold water rinse
- sample held 1 V cathodic while adjusting to plating temperature.

Ultracentrifuge

Dancy and Zavarella[11] studied chromium adhesion as a function of plating temperature, current density, chemistry, pretreatment and heat treatment using the ultracentrifuge method developed by Beams[12]. The method suspends a plated rotor in vacuum in a magnetic field and then a drive coil spins the rotor at speeds that produce a force up to 10^9 time greater than gravity. No clear differentiation between cohesive and adhesive failure was noted for most of the samples in these tests. Figure 5 shows the adhesion and brightness of deposits plated in a 400 g/l chromic acid bath containing 10g/l of sulfate as a function of temperature and current density. The better adhesion coincided with the brighter deposits. Dancy and Zavarella found better adhesion/cohesion at chromic acid to sulfate ratios lower than 100:1.

The effect of pretreatments is shown in Table 5. An anodic etch in chromic acid and an electropolish improved the adhesion/cohesion of the deposits. Photomicrographs show that as the adhesion strength increased, less base metal is observed after the test. The sample with electropolish and anodic etch showed failure in the chromium coating adjacent to the interface. Data indicates that in these tests the reverse etch is primarily removing damage substrate. Table 6 shows the effect of heat treatment on adhesion for 300-micron thick deposits plated from a solution of 250 g/l chromic acid containing 2.5 g/l of sulfate. Some heat treatments increased the adhesion by 33% compared to the as plated sample. Beams reported that Dancy and Kuhlthau showed that a 15 second anodic etch nearly eliminated the deleterious effect of a motor oil immersion on adhesion.

Figure 5. Average adhesion strength and deposit brightness as a function of current density and temperature after Dancy and Zavarella. Their data was used to develop a model. The adhesion model was a reduced cubic equation with and excellent fit (R^2= 0.99 and adjusted R^2= 0.97). The brightness model was a cubic equation with a good fit ($R.^2$= 0.90 and adjusted R^2= 0.69). This is a good fit if you consider that the bright sample were given values of two and the other samples were given values of one.



Sample preparation:

- AISI 4140 with a surface roughness of 0.25-0.5 microns
- Degrease in carbon tetrachloride (CCl_4)
- Dry in warm air
- Cathodic/anodic alkaline clean
- Warm water rinse
- Anodic etch at 30 A/dm^2 for 30 seconds in chromic acid.

Table 5. Adhesion as a function of pretreatment from Dancy and Zavarella.

Pretreatments	Anodic etch in plating bath minutes	Adhesion, kg/cm^2	
		As processed	With anodic etch
CCl_4 and alkaline clean	1	2520	3400
CCl_4, alkaline clean, and vapor hone	5	2520	3170
CCl_4, electropolish, and alkaline clean	5	3420	3670

Table 6. Average adhesion strength after heat treatment at given temperature for 30 minutes with gradual cooling after Dancy and Zavarella.

Heat Treatment	Adhesion, kg/cm^2
as plated	3377
400^{o}C	3406
500^{o}C	4469
600^{o}C	3943
700^{o}C	2968

Conclusions

Adhesion strength data from the ring shear, tapered pin, and ultracentrifuge test are in fair agreement. The highest values were obtained for thin coatings in the ring shear test while the lowest values were obtained from the tapered pin tests on substrates without anodic etching. Ultracentrifuge tests showed that even without anodic etching the failure is a combination of adhesive and cohesive failure.

In House Adhesion Tests

As mentioned earlier, the quantitative tests investigated to date for hard chromium suffer from difficult sample preparation. This limits the number of tests that can be performed practically. The present work evaluated two tests with simple specimen preparation that show some promise of providing quantitative information related to adhesion strength. The first test, the adhesion scratch test, was performed by an outside laboratory on flat samples prepared by the authors. The three-point bend test was performed in the authors' laboratory on similar samples.

Scratch test

A vendor measured chromium adhesion using their scratch tester. This instrument has been described in the literature.[13,14] The initial samples were 125 microns thick and the scratch indenter could not penetrate the chromium. Additional samples were plated to a thickness of 10 microns on flat AISI O-1 oil hardened steel. The substrate was 25.4 mm wide, about 130 mm long, and 1.19 mm thick. The plated area was 19 mm wide and 103 mm long. The samples were prepared for plating by pumice scrubbing, cold water rinse, alkaline cleaning, cold water rinse, and anodic etching. The plating cell consisted of a thermostatically controlled 1.4 liter beaker The cathode was placed in a PVC shield and placed in the cell opposite a lead alloy anode. A low ripple constant current rectifier supplied the current. Two chemistries were used. One was a 25% efficient etch free process* which will be called "Process A". This solution contained 250g/l of chromic acid, 2.5 g/l of sulfate, and a proprietary catalyst and the samples were plated at 62 A/dm^2 and 60^{o}C. The other chemistry was a 40% efficient etch free process** and will be called "Process B". This solution contained 250g/l of chromic acid, 2.5 g/l of sulfate, and proprietary catalyst and the samples were plated at 62 A/dm^2 and 55^{o}C. Process B can produce deposits with poor adhesion unless a strong anodic etch such as 78 A/dm^2 for 5 minutes is used before plating. The Process A can attain very good adhesion with an etch as mild as 15 A/dm^2 for 5 seconds.

Adhesion Results

The scratch test results are shown in Table 7. The results show the correct trends with respect to the chemistry and etch conditions. The force needed for full delamination according to the vendor increased from 120 N to 140 N when the etch was increased from 15.5 A/dm^2 for 5 seconds to 62 A/dm^2 for 30 seconds for the Process A samples. An additional increase in etch time did not increase the force for full delamination of the coating. The Process B samples required much less force, 60 N for full delamination.

* HEEF 25 Atotech
** HEEF 40 Atotech

The vendor reported remarkably high precision for replicate scratches on the same sample. For some samples, only three scratch values were reported even though there were 10 scratches on the same sample. Copper sulfate on the scratches to differentiate the substrate from the chromium. During examination of the scratches, a distinct transition to full delamination was not observed. On the Process A sample full delamination was observed at a force of 80 to 100 N, although the vendor indicated adhesive failure occurred at 140 N. The Process A sample also showed first signs of delamination at about 40 N, while the Process B sample showed first signs of delamination at about 0 N.

An overall observation from these tests is that the scratch test method does not appear to provide a well-defined endpoint for hard chromium samples. Moreover, full delamination could be misleading, since chromium particles can become embedded in the substrate by the indenter. From these observations, it appears that a simple grind test may provide semi-quantitative information similar to that gleaned by the complicated scratch test for hard chromium samples.

Table 7. Scratch adhesion tests by vendor on 10-micron thick chromium coatings.

Coating	Anodic etch		Full delamination*
	A/dm^2	sec	N
Process A	15.5	5	119, 121, 121
Process A	62	30	140, 141, 141
Process A	62	60	134, 135, 137
Process B	15.5	5	60, 61, 62

*The results were rounded to two or three significant figures from four or five.
Test preformed by CSEM instruments on a REVETEST instrument.
Test Conditions:

- loading rate: 100 N/min
- scratch length: 15 mm
- indenter: Rockwell 200 micron
- delamination: detected visually

Bend test

The samples were analyzed for adhesion using a three-point bend test. This test has been described in the literature[7, 15, 16]. Hu and Evans have shown that for brittle coatings:

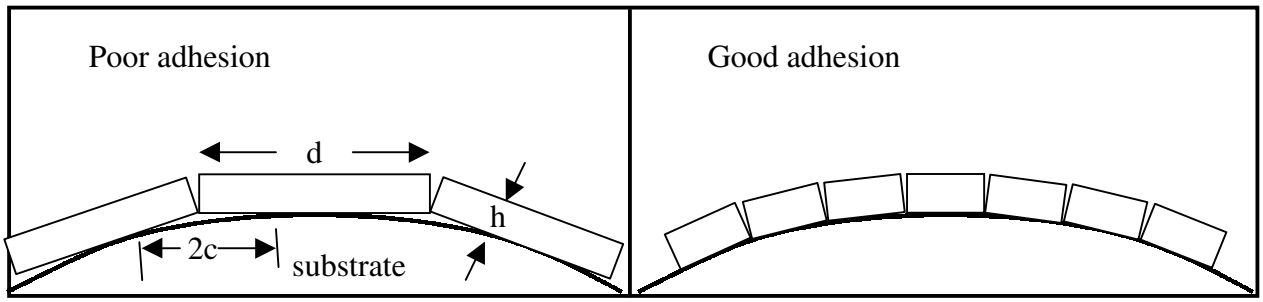
$$\Omega_c = \pi F(\Sigma) + 2\int_0^{c/h} \frac{E^f G_d}{\sigma^2 h}\, d(c/h) - \frac{2E^f G_d}{\sigma^2 h}(c/h)$$

where Ω_c is a critical cracking non-dimensional parameter, c is the decohesion length and h is the coating thickness. The rest of the parameters are described in the footnote*. The critical cracking parameter decreases as adhesion increases. They showed that the critical cracking number is a function of the relative decohesion length:

$$\Omega_c = f(c/h)$$

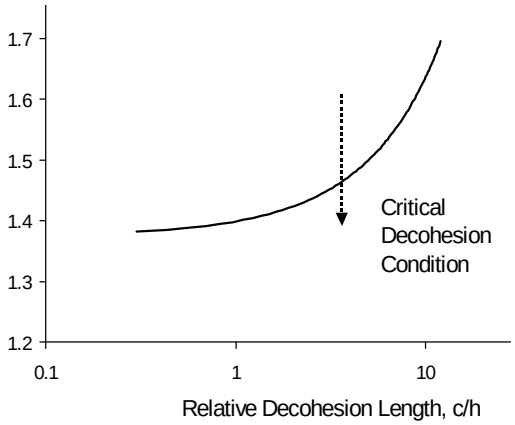
Figure 6 shows c, the decohesion length and d, the distance between cracks. As shown in Figure 6 as the adhesion strength increases the values of d and c decrease. A large distance between cracks indicates poor adhesion and a small distance between cracks indicates good adhesion. As the substrate is bent, stress is applied to the interface. For a coating with poor adhesion, decohesion (delamination) occurs reducing the stress and the spacing between cracks is large. For a coating with good adhesion, the stress cracks the coating and the spacing between the cracks is small. Figure 7 shows their data for the relationship between the critical cracking parameter Ω_c and the relative decohesion length, c/h for brittle coatings. As the coatings' adhesion decreases, the value of 2c approaches d. For coatings with good adhesion, 2c is less than d.

Figure 6. Decohesion length, c and spacing between cracks, d.



* F(Σ) is the elastic modulus ratio of Young's modulus of the film, E^f to that of the substrate, E^s. G_d is the energy release rate of decohesion and σ is the total tension in the coating.

Figure 7. Critical cracking parameter Ω_c vs. relative decohesion length c/h after Hu and Evans.



The samples preparation and size were described in the scratch test section. The samples were bent on a three point bend fixture with the lower heads at a distance of 65 mm and the crosshead speed was 2.00 mm/min. The samples were bent 32.5 mm in the test to form a 90° angle. The distance between the cracks was measured on a microscope.

Adhesion results

The results shown in Table 8 are consistent with qualitative testing of the deposits. The Process A samples showed good adhesion and were much better than the Process B samples. Qualitative testing has shown that for Process B samples, striking is preferred to ramping the current to promote good adhesion. The relative decohesion lengths are in good agreement with the theoretical data in Figure 7.

The three-point bend test appears to give reliable semi-quantitative adhesion data based upon the limited testing completed to date. Testing need to be done on thinner deposits and deposits with less anodic etching for the Process A. The use of thinner deposits would reduce the testing time. The cracks are easy to count and the calculations are simple.

Conclusions

There are many qualitative and quantitative adhesion tests but they need careful examination after the test to determine the cause of the failure. Many qualitative tests can yield semi-quantitative adhesion information. Quantitative tests are time consuming and expensive, but give good data that is consistent from one type to another. The scratch test samples appeared to give poorly defined adhesion end points for hard chromium. Three-point bend test results appear reliable and the test is simple to carry out.

Table 8. Sample conditions and d/2h values.

Coating	Anodic Etch		Current Applied	**h** thickness	**d** distance between cracks	**d/2h**
	A/dm^2	sec	by:	microns	microns	
Process A	77.5	5	ramp	125	165	**0.65**
Process A	77.5	30	ramp	125	202	**0.8**
Process B	77.5	60	strike	125	510	**2.0**
Process B	77.5	60	ramp	125	1750	**7**

References

1. Lawrence J. Durney, Editor, *Electroplating Engineering Handbook*, 4th ed., Van Nostrand Reinhold, New York, N.Y. 1984; p 59 and pp. 174 – 205

2. Fredrick A. Lowenheim, Editor, *Modern Electroplating*, 3rd ed., John Wiley & Sons, New York, 1974 p 692

3. H. Chessin, E.C. Knill, and E.J. Seyb Jr., *Plating and Surface Finishing*, **70**, February p 24, March p 52 (1983)

4. Allen R. Jones, AESF *Chromium Colloquium,* Cleveland, Ohio 1996

5. J.K. Dennis and T.E. Such, *Nickel and Chromium Plating*, Butterworths, London, 1986 pp. 144 – 152

6. R.W. Polleys, *Proc. Am. Electroplaters' Society*, **50**, 54 (1963)

7. K.L. Mittal, Editor, *Adhesion Measurement of Thin Films, Thick Films, and Bulk Coatings* ASTM Special Tech. Pub. 640, Philadelphia, PA 1978; pp. 305-326

8. W. Heinke, A. Leyland, et al; *Thin Solid Films*, **270**, 431 (1995)

9. E. Zmihorski, *J. Electrodepositors' Tech. Soc*., **23**, 203 (1947-48)

10. Y. Hasegawa, S. Hanasaki, and S. Ohmagari, *Hyomen Gijutsu*, **37**(9), 123 (1986)

11. William H. Dancy Jr. and Arthur Zavarella, *Plating*, **52**, 1009 (1965)

12. J.W. Beams, *AES 43rd Technical Proceedings*, **56**, 211 (1956)

13. A.J. Perry, *Thin Solid Films*, **107**, 167 (1983)

14. C. Julia-Schmutz and H. E. Hintermann, *Surface and Coating Technology*, **48,** 1 (1991)

15. M.S. Hu and A.G. Evans, *Acta metall*., **37**(3), 917 (1989)

16. H. Ollendorf, D. Schneider, et al, *Surface and Coatings Technology*, **84**, 458 (1996)