Eliminating Substrate Defects

By Dr. Allen R. Jones, CEF

Substrate defects are a main cause of pits and nodules in hard chromium deposits. Nodules are primarily caused by substrate slivers, while pits are mostly caused by substrate pits or inclusions. Substrate preparation methods, including grinding, chemical polishing and electrochemical polishing, were investigated for their effectiveness in reducing plating defects. Surface roughness was measured for each of the substrate preparation methods. Case studies of reduction of pitting in cast aluminum and cast iron are outlined in this edited version of a presentation from the AESF Chromium Colloquium, held in January 1994, at Orlando, FL. The presentation was selected as the "Best Paper" on the program.

Substrate defects cause nodules and pits in chromium electrodeposits[1]. Many tests have shown that corrosion resistance can be improved by decreasing the nodules in the chromium deposit. A chromium deposit with nodules is shown in Fig. 1.

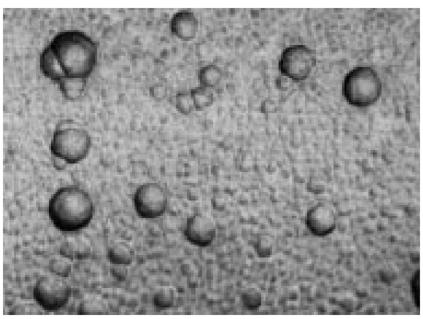

Fig. 1—Nodules on a chromium plated steel rod.

The size and number of nodules can be reduced by better preparation of the basis metal, if the proper chemistry and plating conditions are used. Decreased nodularity of the chromium deposit will allow quicker and better finishing. Compared to steel substrates, cast iron and cast aluminum have different problems with basis metal and chromium plating. Pits are sometimes produced when cast materials are plated. An example of a pit in chromium plated cast iron is shown in Fig. 2. Impurities in the substrate usually cause pitting in cast materials, although other factors have been implicated. Pits in chromium plated cylinders, or piston rings, are undesirable, because they can result in the loss of compression in an operating engine.

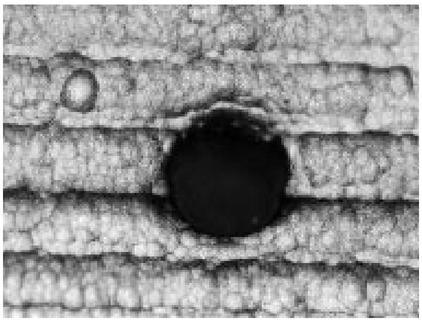

Fig. 2—A pit in a chromium plated cast iron part.

Steel Substrate Finishing

Basis metal prefinishing processes occur before plating. These include grinding, polishing, electrocleaning and etching. All machined surfaces are damaged. Machining- and grinding-produced defects are magnified by chromium plating, especially on thick deposits. Because leveling does not occur in chromium plating solutions, the plated part is never smoother than the substrate. The surface should be free from tool marks, slivers, gouges and inclusions. Removing substantial stock from the steel will significantly improve the substrate. A good book on prefinishing is *Grinding and Polishing; Theory and Practice.*[2]

The finishing wheel grit act as small plows as they remove material, forming ridges at the grooves. This "plowing" often leaves metal slivers on the surface. Prefinishing should progressively proceed with finer and finer grit material, to produce a less damaged surface, and smaller slivers. Eventually, the metal slivers will be removed, or reduced to an insignificant size. Metal slivers may be removed, during chemical or electrochemical activation of the steel, before plating.

One key to good prefinishing is the selection of the initial and final grit sizes. The initial grit size should be coarse enough to remove all machining lines, unevenness, pores and surface oxides. The final grit size should produce a surface that is suitable for plating, or polishing, if required. Basis metal improvement may occur in electrocleaning and etching, before plating. The grain, or grit size of the intermediate steps must be appropriate to remove the scratches and slivers of the proceeding step, and produce finer defects for the next step to remove or reduce. Each grinding step should be perpendicular to the grinding direction of the prior step, to obtain optimum results.

During the grinding process, plastic deformation of the steel occurs, and metal is bent over and embedded into the substrate. Chips that are not removed can cause slivers in the basis metal. The plastic condition caused by the high pressures of grinding can also cause grit material to be embedded into the substrate, resulting in base metal defects.

Grit material should be as uniform as possible. Cost is usually related to quality. Cheap media (wheels, belts) may allow larger grit material to mix in with the finer media. Low quality media will produce a poor quality finish. It is also possible to contaminate media, and important to prevent coarse media from contaminating fine media.

Fig. 3—A single grinding cut.

Fig. 3 shows a single grinding cut in a steel substrate. Most of the chip is removed, but the edges show plastic deformation and ridges or burrs. A section of a chip could stay attached to form a sliver. Fig. 4 shows a cross section of a

Fig. 4—Proper finishing with three grit sizes.

Fig. 5—Improper finishing with two grit sizes and a light etch.

substrate with proper finishing, using three grit sizes—A, B and C. Grit B removes all traces of scratches from grit A, and grit C removes all traces from grit B. Fig. 5 shows the cross section of the substrate, omitting grit B. Slivers were formed when grit C was used on the rough surface produced by grit A. Etching causes the slivers to stand up, and will cause significant nodules during plating. Although the luster, or brightness, of the substrate in 4C may be about the same as the substrate produced in step 5C, after substrate 4C will be much brighter than 5C. Brightness is not always a good measure of basis-metal quality.

Mechanical Finishing

The table below shows that a bright substrate is not necessarily a good substrate. The parts represented are motorbike shocks.

R_A microinches

	Appearance	Before Plating	After Plating
Factory Finish	bright	3.1	18
Finish with 400 & 600 grit SiC paper	semi-bright grind lines visible	3.3	5.6

The factory-finished part, and the part refinished with 400 and 600 grit paper, had about the same R_A before plating. The refinished part, however, had a much smoother finish, and fewer nodules, after plating. The surface finish R_A is of great importance in obtaining a good chromium plated part. The R_A does not, however, measure slivers that have been bent over into the substrate.

Deposit quality is a function of basis-metal smoothness and freedom from defects. A finer media produces a smoother surface, and, as a result, a brighter finish. When prepared properly, a good bright sample should have a R_A of less than 2.0 microinches. The R_A is the average roughness, while the R_Z is the average of five peak-to-valley maxima, one in each of five sample lengths.

Etching in Chromic Acid

The anodic (reverse) etch of parts in a chromic acid solution, or in the plating bath, will influence the nodularity of the chromium deposit. Reduced nodularity will occur with a very low coulomb (short time in low current) etch, or a high coulomb (moderate time and high current) etch. An electrocleaner will cause the slivers to extend, as will a moderate etch. A very light (low coulomb) etch will not extend slivers. A long etch, typically 60 A/dm^2 for one min, will extend slivers and etch them away. High-current-density causes the solution to act as an electropolish. A long or short etch will produce the smoothest surface, after plating. Etch intensity has a dramatic effect on the surface roughness. The finish on samples ground with 400 and 600 grit paper, for example, improves as the etch increases. The photomicrographs in Fig. 6 show that a longer etch produced an almost nodule-free surface on samples with comparable R_A values.

The following experiments show the effect of pretreatment cycle, or etch, on surface roughness and corrosion resistance. Two pretreatments were used:

Pretreatment A:
- Anodic electroclean for two min at 10 A/dm^2;
- Cold water rinse;
- Immersion in five-percent sulfuric acid at room temperature for 15 sec;
- Cold water rinse.

Pretreatment B:
- Anodic electroclean for one min at 15 A/dm^2;
- Cold water rinse;
- Etch in bath for one min at 60 A/dm^2.

The parts were plated in a high-efficiency, etch-free chromium solution to a thickness of 35 microns (1.3 mils). Samples were plated at 60 °C and 45 A/dm^2 (3 A/in.^{2}). The accompanying table shows the basis metal finish, and the finish of parts processed with pretreatments A and B. Also shown are results of a neutral salt spray (NSS) test for corrosion. Corrosion resistance and surface finish improved as nodules were decreased. No finishing was completed after plating. Post finishing usually improves corrosion resistance.

	Substrate	Pretreatment A	Pretreatment B
R_A (microinches)	5.2	21	7
R_Z (microinches)	42.5	155	68
Hours in NSST		24-48	96-122

Chemical and Electrochemical Finishing

Chemical and electrochemical polishing can be used to improve the substrate before plating. These processes are designed to remove metal and make the substrate smoother. The chemical solution involved is a proprietary solution[a] containing 10 percent by volume of the concentrate, and 10 percent by volume of 35-percent hydrogen peroxide. Parts were immersed in this solution for five min at room temperature.

The electropolish contained 15 percent acid, 63 percent phosphoric acid (85 percent), 10 percent chromic acid, and 12 percent water. The solution was used at a temperature of 70 °C for six minutes, at 45 A/dm^2 (3 A/in.^{2}). After the chemical or electrochemical polishing, the rods were plated to a thickness of 50 microns.

The chemically polished rod appeared less bright after plating than a rod that had been mechanically polished with the one micron aluminum oxide compound. The chemical polish removed most grinding lines, but a few nodules were present after plating. The after-plate R_A and R_Z were 14 and 98 microinches, respectively. The surface appeared only slightly smoother than the as-received plated sample, and similar to the rod finished with 600 grit paper. The appearance of the chemically polished plated rod is shown in Fig. 7.

After plating, the electrochemically polished rod was bright, with few nod-

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[a] *KEMGLO™ FE-42, ATOTECH USA, Inc., Somerset, NJ.*

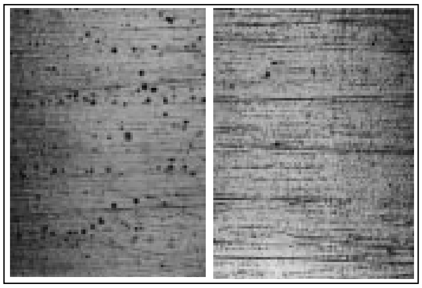

Fig. 6—Photomicrographs of chromium plated motorbike shocks, prefinished with 400 and 600 grit paper. The chromium thickness is 20 microns. At left is the sample (R_A = 9.4) with an etch of seven sec at 15 A/dm.^{2} At right is the sample (R_A = 7.4) with an etch of 50 sec at 60 A/dm^2 (100x).

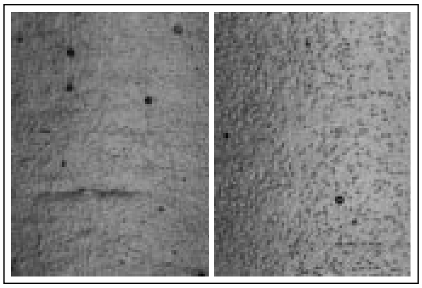

Fig. 7—Photomicrographs of chromium plated rods that were chemically (left) and electrochemically polished (right). The rods were plated with 50 microns of chromium (100x).

Fig. 8—Photomicrograph of a chromium plated cylinder. The bright area is the defect. The chromium is thin in this area, and it did not get postfinished properly (50x).

ules, but some indentations. This rod had the smallest number of nodules observed on any of the mechanically or chemically polished rods in the study. A finish such as this, with a good etch in chromic acid, will produce a deposit with very few nodules. The after-plate R_A and R_Z were 7.3 and 64 microinches, respectively. Fig. 7 shows the appearance of this sample.

Cast Aluminum & Cast Iron Substrate Defects

Cast materials are subject to the same grinding and finishing defects as steel substrates. Cast materials, however, are more likely to have inclusions and voids than are non-cast steels.

Aluminum

Chromium plated cast aluminum cylinders had defects as shown in Fig. 8. This accounted for a 10- to 50-percent defect rate, depending on the part number. Examination of the substrate showed no defects on the as-machined surface.The etched or pretreated surface, however, showed voids. Because aluminum is ductile, machining smeared aluminum over the voids, which were opened after the pretreatment.

A comparison of laboratory and factory casting quality highlights sources of aluminum substrate defects. For example, Fig. 9 shows a sample of aluminum melted in a laboratory, and aluminum melted in factory pots. The laboratory-cast sample had no voids or inclusions, while the plant-cast material had many inclusions. The aluminum was contaminated in the casting process. The sources of voids in the casting department considered significant were:

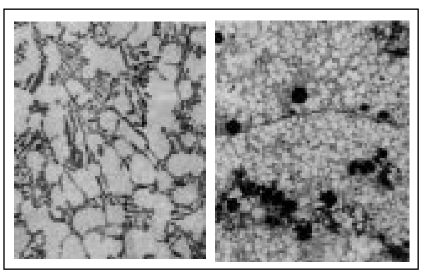

Fig. 9—Photomicrograph of aluminum castings prepared in the laboratory (left) and factory (right). The factory casting shows many inclusions. The samples were polished and etched in hydrofluoric acid (380x).

- Putting oily scrap into the pots;
- Contacting the aluminum directly with flame in the pot;
- Infrequent cleaning of the bottom of the pot;
- Not emptying the ladle on each run.

By eliminating these practices, rejects were reduced to less than two percent.

Cast Iron

Chromium-plated cast iron can show pits in the plate as shown in Fig. 2. When these pits are cross sectioned, they usually reveal pits in the cast iron. A four-micron-wide pit in the basis metal will cause a pit in the chromium. Electroplated chromium has very good microthrowing power. It can plate down in very small cracks. When the defect becomes too large, chromium cannot bridge over, or fill it, so a pit in the chromium occurs. Because graphite or carbon particles in cast iron have low hydrogen overvoltages, hydrogen is formed at the graphite particle before chromium is electrodeposited. A graphite particle on the cast iron surface could, therefore, cause a pit in the chromium deposit. Pitting can be caused by voids or inclusions.

A large cast iron surface was examined and suspected basis metal defects were located. These defects were suspected as the cause of pits in the chromium plate. After plating, the surface was reexamined for pits. The pits that were observed, however, did not occur at the previously identified basis metal defect sites. If inclusion of sulfur occurred on the surface, it could overcatalyze the localized area and prevent plating. In a fluoride-based plating system, low-current-density etching could occur to form a pit at the point of sulfur inclusion. The pit may appear to be caused by a basis-metal pit, but may be caused by a surface inclusion instead.

Cast iron contains voids that are caused by several factors, such as:

- A graphite nodule being removed from the surface;
- Tom metal because of dull machine tools;
- Microshrinkage.

Microshrinkage occurs during casting and can cause the formation of small cracks in cast iron.

Inclusions in cast iron can cause pits. Inclusions of non-metallic dross will cause pits, because the dross will not be plated. Magnesium silicate dross has also been observed in cast iron. Graphite can become segregated from the surface and cause pitting. Voids and inclusions can be controlled by casting procedures and control of cast iron chemistry.

Correcting Defects

Prefinishing techniques were shown to cause postplate defects in chromium plated substrates. Identifying and optimizing these prefinishing methods improved the basis metal of steel, cast aluminum, and cast iron, resulting in improved chromium plated parts. Appropriate mechanical finishing, and an anodic etch, produce a surface that can be plated with a minimum of nodules. Optimum casting practices can produce substrates with a minimum of voids and inclusions, resulting in acceptable plated parts. o

Acknowledgments
The author acknowledges J. Corsentino, ATOTECH USA, Inc., for sample preparation, and O. Igel, ATOTECH Deutschland GmbH, for corrosion data.

References:
1. A. Jones, *Sources of Nodules and Pits in Hard Chromium Electrodeposits,* AESF Hard Chromium Plating Workshop (1992).
2. W. Burkart and K. Schmotz, *Grinding and Polishing Theory and Practice,* England Portcullis Press, Ltd., 1981.

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Prior to joining ATOTECH USA, Inc., Jones performed research and development on zinc and zinc alloy electrodeposits at Republic Steel (LTV Steel), Cleveland, OH. He performed research in electrochemistry while obtaining a PhD in physical chemistry at Rensselaer Polytechnic Institute, Troy, NY, and a BA in chemistry at Linfield College, McMinnville, OR. He holds several patents, and has published numerous papers involving research in electrochemistry and metal finishing.