Choosing a Hard Chrome Alternative

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What is wrong with chrome plating?
Chrome plating has been in use since the 1940’s and is a powerful, simple and cheap process. The plating solution is very simple (chromic acid, sulfuric acid, and sometimes brighteners and other additives) and the process is quite forgiving. Unfortunately chromic acid (CrO₃) is a hexavalent chromium (Cr⁶⁺) compound, and the process is quite inefficient, with most of the current going to hydrolyze the water, producing copious amounts of hydrogen and oxygen bubbles. When they rise to the surface these bubbles burst, throwing a fine mist of hexavalent chrome into the air. To protect workers and the environment, this mist has to be sucked away in an efficient air-handling system.

Chrome plating generates several different waste streams:

- Cr⁶⁺ mist air emissions – worker health and safety issue in the plant, air pollution issue outside, must be trapped in scrubbers
- Cr⁶⁺-contaminated waste water – must be treated before release to public treatment plants or water courses
- Solid wastes – must be disposed of as hazardous waste:
  - Cr⁶⁺-contaminated sludge and masking material
  - Cr⁶⁺-contaminated air filters, solids and water from air-handling systems
- Groundwater contamination from leakage and spills (this is rarely a problem with modern plants, which have double-containment, but used to be a serious source of contamination in older brown-field plants).

Note that the problem with chrome plating is the deposition process. Chrome plating itself is benign.

Over the last decade emissions from chrome plating plants in the US have become very small as plating shops have had to meet the very stringent EPA Clean Air Act emission requirements. They have done this through a combination of stringent engineering controls and the use of PFOS fume suppressants in plating tanks. However PFOS is a long chain fluorinated hydrocarbon that has been found to be very persistent in the environment, and is being phased out, leaving the plating shops to control emissions by engineering controls (scrubbers, tank lids, etc.).

What is hard chrome plating used for?
Hard chrome is used throughout manufacturing industry for a very large number of wear resistant applications in industrial equipment and vehicles, and for almost all metal fabricating tooling except cutting tools (which are usually carbide tools with very hard CVD or PVD thin coatings):

1. Wear resistance – Put down by OEMs on hydraulic actuators, shaft journals, railway engine shafts, aircraft landing gear, and thousands of other components for wear resistance (and to provide a
measure of corrosion protection). Almost all hydraulic actuators on earth movers, snow plows, road repair equipment, backhoes, car transporters, farm machinery, mining equipment, etc. are chrome plated. In vehicles most stems on all of the engine valves are chrome plated, as are many shock absorbers.

2. Industrial tools – Rolls for producing steel, aluminum, and other alloys, as well as most other materials that come in sheets, such as paper and plastic sheet, stamping tools and dies for everything from tiny electrical connectors to car doors, molds for manufacturing almost anything in plastic. In short, almost everything that is manufactured from metal, plastic, or even paper relies on chrome plating for its production.

3. Reclamation and rebuild – Chrome plate is used by overhaul shops in the mining and aircraft industry to bring worn or corroded parts back to dimensional tolerances, so that they can be repaired rather than having to be replaced. This is done on many components that are never plated by the OEM, as well as plated components whose plating has become worn or scored.

4. Decorative uses – Hexavalent chromium plating is also very commonly used in the form of a very thin coating for decorative chrome on car and truck trim, motorcycles, kitchen and bathroom appliances such as faucets drains, and numerous other items that require a bright, shiny appearance. Trivalent chromium plating can be used (and is used) on many decorative items, but it is not as easy to do and does not always look identical to hex chrome coated surfaces.

**Hard chrome plating alternatives**

There are several hard chrome plating alternatives that are now used, depending on the application and on whether it is an OEM part or a component to be repaired:

- Thermal sprays (HVOF) – Primary replacement for most commercial and military aircraft repair, and for large actuators on mining equipment. Best performance. Cannot be used for deep internal diameters and high strain fatigue applications.

- Electro and electroless plates (usually based on Ni or Co) – Good for internals.

- Vacuum coatings – OEM applications only. Not for rebuild.

- Heat treatments – OEM applications only. Not for rebuild.

- Laser and weld coatings – Localized repair.

See below for more detailed descriptions of these alternatives.

**Thermal spray and HVOF**

The most commonly used technology for replacing hard chrome plating is thermal spray (primarily, but not exclusively, HVOF). While this is the technology of choice for most applications it is not necessarily the best choice for all.

There are a large number of companies around the US and the world who supply thermal spray services, and the equipment and supplies (thermal spray powders) are available from a number of international companies.

Thermal spray is the general term for a number of processes in which particles of coating material are heated and sprayed using high speed gas onto the surface to be coated. It is a fully commercial industrial process that is used for coating everything from bridges and radar towers to aircraft parts and prosthetic knee joints. Since thermal spray coatings are readily sprayed up to 0.020’’ (500 microns) thick, they are good for rebuilding worn components, which is the primary use for hard chrome plate.

If you are currently using hard chrome plating you will find thermal spray to be a considerable culture shock.
Thermal spray is not all that difficult, but it means doing things in a very different way.

- If done well, thermal spray will give you a higher quality, more reliable coating with much longer service life. If done poorly, coatings will flake off or be very porous, or they will turn into efficient cutting tools that tear up seals and mating surfaces.

- Unlike hard chrome, where there are only minor choices of plating additives and hard chrome is what you always get, there is a large choice of coating materials, starting powders, gases, types of equipment and deposition conditions. The most common coating materials for chrome replacement are chrome carbide-nickel chrome \((\text{Cr}_3\text{C}_2-\text{NiCr})\) and tungsten carbide-Co \((\text{WC-Co} \text{ and } \text{WC-CoCr})\). (Note that the Cr in these materials is not hexavalent, despite the misinformation in the California CARB regulations.)

- Hard chrome plating is very forgiving and makes acceptable coatings without a lot of attention. Thermal sprays require proper process definition and careful control.

- Workers require a lot more training and skill to do thermal spray reliably that to do chrome plating.

- You cannot always use the same finishing methods. Chrome plate is usually ground with an aluminum oxide wheel to a finish of about 16\(\mu\)m \(Ra\) for bearing surfaces, but the carbide sprays must be ground with a diamond wheel or belt, and sometimes superfinished with a stone or belt to <6\(\mu\)m \(Ra\).

- If you need to coat internal diameters or complex shapes, HVOF is not a good choice, and you may need to use plasma spray for larger diameters or alternative electroplates or electroless nickel for smaller diameters.

- The way thermal spray fits into the production system is different. Chrome plating requires products to be cleaned and masked, then left in the plating bath for a day or more. Large items are sprayed one at a time for 15-60 minutes, while batches of small items can be sprayed at the same time in special fixtures. Thus thermal spray is much faster, but requires constant attention.

Because most users are not very familiar with all these choices, we offer consulting assistance to make the best choices, as well as training and coating optimization for a consistently high quality product.

**Electroplates, electroless nickel and composite plating**

As drop-in replacements for chrome plating, electroless- and electro-plates have the advantage that they are bath processes able to be done with the same sort of technology with which chrome plating users are familiar. Most non-chrome hard electroplates are based on nickel, although there are some plates that are based on other materials:

- Ni-W, Ni-W-B and Ni-W-B with SiC (the Takada process). All of these are alloy coatings, which typically are more complicated to deposit than the simple elemental coatings. Coatings with particles co-deposited (such as SiC, diamond, PTFE, etc.) are particularly difficult as particle suspension and deposition uniformity are difficult to control, and in some cases the particles have been known to wreak havoc with air handling systems.

- Cobalt-based electroplates avoid the Ni ESOH problems, although Co is a more expensive metal and often termed a strategic metal because its sources lie mostly in unstable areas of the world, with little available in North America or Europe. Co-based electroplates include Co-P nanophase alloys developed specifically as chrome replacements and only just now becoming commercially available, and Co-SiC composites, which have been used in some aircraft engine applications for some years in the UK.

Electroless nickel (often just called EN) is a standard and widely available plating process. There are a great many platers offering electroless Ni, and the plating equipment and solutions are commercially available.
Unlike chrome plating and other electroplating methods, which use an electric current to deposit the coating, electroless Ni is an “autocatalytic” process – i.e. the Ni deposits out of the bath onto the parts just because they are there, without any need for anodes and robbers, and all the associated fixturing used in electroplating. This makes it a very flexible process, able to coat even very complex parts and small internal spaces easily and uniformly. But because the bath is a delicate balancing act of keeping the Ni in solution, but allowing it to deposit onto anything put into the bath, it requires careful attention to bath chemistry and cleanliness of the surface being coated. Unlike chrome plating baths, which last essentially for ever, electroless Ni baths typically require complete replacement periodically.

There are several types of electroless Ni available commercially:

- **Electroless Ni-P** is the most common type, with a typical hardness up to.
- **Electroless Ni-B** is used for some aerospace and other specialized applications. It is much less widely available than Ni-P. Because lead or thallium are required for the bath chemistry, Ni-B coatings usually contain from 0.1-1wt% of these toxic materials. Therefore these coatings are not always RoHS-compliant.
- **Electroless Ni-P composite coatings** are available with a variety of additions to the base Ni-P coating. These include SiC or diamond for wear resistance, PTFE for lubricity, or even both for a hard, lubricious coating.

Because it is a plating process electroless Ni is not a big step for most companies used to using chrome plating, although it is a much less forgiving process:

- **Electroless Ni** is not usually as wear resistant as hard chrome and must be heat treated at 400°C (750°F) to create the phosphide precipitates that give the coating its hardness. As-deposited the hardness of electroless Ni-P is 500-700 HV as deposited and up to 1,100 HV after heat treating, while Ni-B is typically 650-750 HV as-deposited and up to 1,200 HV after heat treating. This makes it unsuitable for alloys and products that cannot take this temperature.
- The coating is very corrosion resistant as-deposited, provided there are no holes or scratches, but loses some corrosion resistance on heat treating.
- It is usually a thin coating (<0.003” (75mm), although some bath chemistries now allow coatings that are much thicker), and so it is not usually used for rebuilding worn items, which is the primary use for hard chrome.
- **Electroless Ni coatings** can take a very smooth finish, and are often used for mirrors and very smooth dies and molds. The coating is not microcracked as hard chrome is.
- Electroless Ni is most useful for small components, although some companies are able to plate items several feet across weighing several tons. While small components can usually be cleaned and plated fairly easily, it is often difficult to prepare and clean large items perfectly over their whole surface. As a result large components frequently exhibit small poorly adhered areas.
- Because the process requires a fine chemical balance it is critical to maintain bath chemistry accurately. Some users set up systems to do this automatically to maintain consistent quality.
- Especially with large items the cleanliness and finish of the surface to be plated is critical as contamination can prevent the autocatalytic reaction and leave holes in the coating.

The presence of Pb in electroless Ni-B coatings makes them non-compliant with RoHS. The alternative, thallium, is not covered under RoHS, but it is also a heavy metal cumulative poison. Neither of these materials is used in EN-P.

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Vacuum Coatings

For most of the applications for which chrome plating is used, vacuum coatings are not the answer because of their relatively high cost and their inability to build the dimensions of worn or damaged components back to spec. However, for some applications these types of coatings can be cost-effective, especially for small components that must last a long time.

There are two primary types of vacuum deposition methods:

1. Physical vapor deposition (PVD) – In this method the coating material is created from a solid, either evaporated by an electric arc or an electron beam, or sputtered. It goes through a plasma (to allow the ions to be accelerated) and lands on the component surface, forming a very thin but very hard layer.

2. Chemical vapor deposition (CVD) – CVD processes have a lot in common with PVD, including cost and the size of items that can be coated. However, in the CVD method the coating material comes from gases that combine on the hot surface to form a coating.

These types of coatings are usually expensive because they are relatively complex technologies that require vacuum chambers. This limits the sizes of products that can be coated to less than a foot or so (30cm).

Facts about PVD coatings:

- PVD coatings are usually deposited at temperatures of 250°C (480°F). They can be deposited at lower temperatures, but, depending on the method coating quality and adhesion tend to suffer at low temperature. This limits the alloys that can be readily coated.

- PVD coatings are highly sensitive to contaminants on the surface being coated, which must be scrupulously clean and must not expose the vacuum to water, oils, paints, or other contaminants that will contaminate the process.

- They are only a few microns thick (typically 3 microns, or 0.0001”) and cannot be used for rebuilding worn components. Thick PVD coatings often have such high stress internal stress that they spall off. Some Japanese automotive companies do, however, make PVD CrN coatings 60mm (0.0025”) thick.

- PVD nitride and carbide coatings are hard – 2,000 - 3,000 HV (three times as hard as chrome plate), and some can even be up to 5,000 HV (half as hard as diamond). For this reason they are used as erosion coatings in some aircraft engines.

- PVD is not in general a good method for coating internals, although some techniques have been developed specifically to coat the insides of tubes, pipes and gun barrels.

- Among the most commonly-used PVD coatings are TiN, CrN, and the various diamond-like coatings (DLCs).

- PVD nitride coatings are essentially inert and do not corrode, but they do not provide any protection once scratched or damaged.

- IVD (Ion Vapor Deposition) aluminum is an example of a PVD process that is used quite widely in the aircraft industry. While there have been attempts to modify the method to deposit hard coatings, none of these have gone beyond the R&D stage.

- PVD coatings are often used for decorative surfaces, to create “lifetime coatings” on door hardware and plumbing fixtures. Many of the nitrides have gold or other attractive colors.

- PVD is environmentally benign in that the only gases that go through the process generally are nitrogen and argon, and the source materials are solid metals, although some processes do use
methane or acetylene gas. Vacuum chambers do have to be cleaned, and care must be taken to avoid worker exposure to fine metal dusts.

Facts about CVD coatings:

- CVD is used to create many of the same hard nitride coatings as PVD, with similar hardness.
- The primary advantage of CVD coatings is that, because they use gases, they can be used to coat very complex objects, including internals, even down to micron sizes.
- For CVD coatings to grow on a surface the surface must usually be red hot (around 1,000°C, 1,830 °F), which limits what types of alloys it can be used to coat. As a result it is seldom used for coating high strength alloys, which are heat-sensitive. CVD can be done at lower temperatures by using plasmas or more expensive metalorganic gases. This lowers to temperature to around 500°C (930°F), which is still above the tempering temperature of many alloys.
- Coatings are usually a few microns thick, although the method can be used to create materials several centimeters thick (such as infrared windows).
- CVD materials are usually hazardous (some highly so) – poisonous, pyrophoric, explosive, or combine with water vapor in the air to create hazardous fumes such as HCl. The process must therefore be used with proper safety systems and methods of trapping the used gas.

If you are used to using chrome plating, you will find adopting vacuum coating methods to be very challenging. Very few companies outside the cutting tool industry use CVD coatings because of the safety issues. PVD coatings have been brought in-house by manufacturers of plumbing products and some aircraft engine parts manufacturers and overhaulers. However, the cost of equipment can be very high ($1-3 million for a coating system, with additional costs for a cleaning line). Running a coating operation also requires a sophisticated workforce able to handle and troubleshoot vacuum systems, cooling systems, gas handling systems and electronics. PVD coatings require very careful attention to cleanliness, both of the product to be coated and of the vacuum chamber, which requires proper equipment and a well-trained workforce.

In general, unless production volumes are high, most users will find it most cost-effective to a coating service vendor rather than bringing the process in-house. Vendors can be found in most areas of the world.

**Heat Treatments**

Heat treating is the general name for a set of technologies in which the product is heated to give the proper alloy properties (tensile strength, hardness, toughness) or to modify the surface. These types of technologies are also known as diffusion treatments when they also involve the diffusion of metal atoms from a packed bed into the surface – primarily Al, Cr and B.

The most widely used surface modifications are nitriding, carburizing and nitrocarburizing. Older processes used to involve the use of molten salt baths (frequently cyanides) or packed beds, but these methods have been largely displaced by gas methods of nitriding, carburizing and nitrocarburizing, and by plasma nitriding. New technologies such as ion implantation have been adopted into the surface treatment industry from the semiconductor industry, but have found only small niches.

Because they cannot be used to build up worn material, heat treatments are not used in repair. Their primary usage is to create wear-resistant surfaces on products (carburizing of gears, for example), or to make surfaces resistant to corrosion or oxidation (e.g. boiler tubes, hot section turbine blades). The exception to this is ion implantation, which is a room temperature process in which ions are fired into the surface to form a very thin (0.1 mm) layer. Although the layer affected is extremely thin, the process appears to change the wear mechanism so that it has an impact on wear long after the thin surface has been worn away.

Facts about heat treatments:
- Heat treatments generally take place at temperatures of 500-1,000°C (930–1,830°F). This limits the alloys and products that can be treated.
- At these temperatures, some alloys can grow as they go through phase changes, and products can distort.
- These treatments are not coatings. They cannot come off as coatings can, but they also cannot be used to build up worn surfaces.
- Not all alloys can be nitrided or carburized. These processes are usually used on nitridable or carburizable steels, but can be used on some other alloys.
- The exception to this is ion implantation, which is done at room temperature, usually using nitrogen ions. It has very limited market niches (medical prostheses such as hip and knee joints, certain molds, dies and metal forming tools). The method has been shown to reduce wear in hard chrome plate, and so some companies have used the process to improve the life of plated products.

Nitriding, carburizing, ferritic nitrocarburizing and implantation are clean processes and the surfaces are RoHS-compliant. Metallizing treatments (chromizing, aluminizing, boronizing) can produce chlorine and HCl gas and leave the packed bed a hazardous waste that must be disposed of properly. Some newer metallizing methods have been developed to alleviate these problems.

**Laser and Welding Methods**

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<th>Alternative</th>
<th>Compliance</th>
<th>Usage</th>
<th>Notes</th>
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<tr>
<td>Laser cladding</td>
<td>RoHS, WEEE, ELV, OSHA Cr</td>
<td>Turbine blades, worn shafts</td>
<td>Localized high temperatures. Can build very thick and near-net structures.</td>
</tr>
<tr>
<td>Weld cladding</td>
<td>RoHS, WEEE, ELV, OSHA Cr</td>
<td>Rebuilding turbine engine blades and other parts</td>
<td>High surface heating. Some alloys must be re-heating treated after processing. Good for large areas. Note: welding of stainless steel can be an OSHA Cr problem.</td>
</tr>
<tr>
<td>Explosive bonding</td>
<td>RoHS, WEEE, ELV, OSHA Cr</td>
<td>Thick cladding under evaluation for gun barrels</td>
<td>Old technique enjoying a resurgence for cladding gun barrels and joining dissimilar metals.</td>
</tr>
<tr>
<td>Electrospark deposition (alloying)</td>
<td>RoHS, WEEE, ELV, OSHA Cr</td>
<td>Aircraft engine part repair, repair of corroded or damaged areas</td>
<td>Very low deposition rate. Useful for small area repair of nicks and damage. Not used for fatigue-critical parts</td>
</tr>
</tbody>
</table>

Some of these welding methods have been in use for many years – weld cladding has long been a simple do-it-yourself method for repairing and reducing wear of farm machinery, while explosive welding used to be used for welding railroad track. However, these methods have been modernized and some of the newer technologies, such as laser cladding, are beginning to make headway as hard coating and repair methods in place of chrome plate.

**Laser cladding** is a technology that has only become industrially viable on a large scale in the past few years as more robust and reliable lasers, such as diode lasers, have become widely available. The technique uses a laser to melt a powdered metal onto the surface. This heats the surface but not the bulk of the material, so it does...
not have the limitations of most heat treatments, but this can an issue for aerospace parts.

**Electrospark deposition** (alloying) (ESD, ESA) is a microwelding technique in which an electrode is used to weld coat the surface or fill in small damage areas. It is often used to repair dies and molds, but has been adopted in some other limited applications. The heat-affected zone is very small and the method is used for repairing some aircraft engine components that are not fatigue-critical. Its primary use is the repair of damage and wear in molds and dies. The equipment is very inexpensive and easy to use with minimal training, and there are several suppliers around the world.

Facts about laser and weld methods:

- Welding involves melting the material to be welded. This limits the alloys and products that can be treated to materials that can be welded and products that can withstand the heating involved or can be heat treated back to their original properties.
- The various standard torch and electric arc welding methods input the most heat. They are ideal for large items. However, welding of stainless steel can generate Cr$^{6+}$ in significant quantities because of evaporation from the weld rod.
- Laser welding is best for external surfaces. It can be highly controlled and automated and can even be used to produce 3-dimensional near net shapes.
- ESD can be done in such a way that it has almost no effect on fatigue. It is a very small area, slow deposition process and is primarily used for repair rather than coating.

These methods are all RoHS-compliant. Weld coating with any Cr-containing electrode material or laser cladding with Cr-containing powder could be OSHA non-compliant.

**What option is best?**

It depends on the application, the item being plated, whether it is contracted or done in-house, and how the process needs to fit with your production system.

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<tr>
<th>Treatment</th>
<th>Typical applications</th>
<th>Pros and Cons</th>
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</thead>
<tbody>
<tr>
<td>Thermal spray (HVOF, etc.)</td>
<td>Aircraft landing gear, hydraulic rods for most purposes, industrial rolls</td>
<td>Harder and more wear resistant, can rebuild. Not for IDs, must be superfinished.</td>
</tr>
<tr>
<td>Electro and electroless plating</td>
<td>Anywhere hard chrome is used, internals (esp electroless Ni)</td>
<td>Mostly easy to use for internals and externals. Generally no better than chrome.</td>
</tr>
<tr>
<td>Heat treats</td>
<td>Hydraulic rods, gears, bearings</td>
<td>Almost any size and shape, cannot delaminate. Cannot be used for rebuild, cannot be used for heat-sensitive materials.</td>
</tr>
<tr>
<td>Vacuum coatings</td>
<td>Typically small, high value items, molds and dies</td>
<td>Extremely hard and wear resistant. Complex and expensive.</td>
</tr>
<tr>
<td>Welding methods</td>
<td>Rebuild of worn or corroded items</td>
<td>Good for thick coatings, mostly on externals. Not for heat sensitive materials, must be refinshed.</td>
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