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CVD HARDIDE Coatings Protect Internal Surfaces and Complex Shaped Parts against Wear and Erosion

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Introduction

This paper presents the emerging CVD Hardide coating technology and reviews its place among other coatings and surface engineering methods.

Surface engineering treatments and hard coatings are widely used to extend the life of industrial equipment like valves, pumps, tools operating in abrasive, erosive, corrosive and chemically aggressive environments. Thermal spray coatings, Hard Chrome plating and PVD coatings are among the most widely used surface treatments. For Designers and Engineers it is important to know the specific strengths and limitations of each of these technologies, which determine their most suitable applications. Thermal Spray coatings can build a very thick and durable layer, with enhanced load-bearing capacity, but they cannot be applied to internal surfaces and require post-coating grinding which limits their applications. Hard Chrome plating combines wear resistance with corrosion protection, but is under pressure from REACH and OSHA pollution control regulations. PVD coatings can produce an extremely hard layer with accurately controlled thickness, but are best suited to coating external surfaces and have limited load-bearing capacity.

Hardide™ is a new family of nano-structured CVD Tungsten Carbide/Tungsten coatings, consisting of nano-particles of Tungsten Carbide dispersed in a metal Tungsten matrix. This structure gives it a unique combination of ultra-high hardness (1100-1600 Hv) with excellent toughness, crack and impact resistance. Advanced CVD coating technology enables control of the hardness and toughness of the coating and thus to achieve optimum protection against wear and erosion. The coating hardness inhibits the micro-cutting mechanisms of wear and erosion while its toughness, ductility, residual compressive stresses and homogeneous micro-structure prevent fatigue micro-cracking/chipping and platelet mechanisms of erosion.

The coating is typically 50 microns thick – exceptionally thick for CVD – and withstands 3000 microstrain deformations without any damage; this deformation will crack or chip most other thick hard coatings. The gas-phase CVD process enables the uniform coating of internal surfaces and complex shapes such as pump cylinders, impellers, extrusion dies or ball valves. The need for post-coat grinding is eliminated in the majority of applications thereby reducing cost and turnaround time compared to traditional coating methods.

The Hardide coating is pore-free and protects parts from corrosion, acids and aggressive media. It is an attractive replacement for Hard Chrome, which is being phased out due to environmental legislation, especially for coating complex shapes and internal surfaces.

The coating can be applied on steel, stainless steel, Ni, Cu, Co alloys, Titanium.

The following key features of Hardide CVD coatings define the position of this technology among other surface engineering technologies:

- Ability to coat uniformly complex shaped items, including both internal and external surfaces;
- A combination of ultra-hardness with enhanced toughness and ductility;
- Sufficient thickness of the coating to provide load-bearing capacity independent from the substrate metal strength;
- Pore-free coating protects substrates against corrosion and chemically aggressive media, acids.

These key features of Hardide coatings are further illustrated below:

Coating complex shapes and internal surfaces

The CVD Hardide coatings are particularly suitable for coating complex shaped parts with precise dimensions, or where internal surfaces need protection against wear and erosion.

For many coating technologies, internal surfaces or items of a complex shape are very difficult or even impossible to coat, due to the line-of-sight nature of the coating processes. For example, spray coatings (including HVOF, Plasma Spray, D-gun) can be applied to the external surfaces, easily accessible for the spray gun so that the spray nozzle can be kept at a distance to prevent part overheating. When spray-coating complex shaped items, it is difficult to avoid building a thicker coating layer on the more exposed edges while applying a thinner layer in the “shadowed” areas, this can distort part shape. Similar limitations exist for PVD coatings, where planetary rotation of the parts being coated helps achieve coating uniformity on the external surfaces but the coatings cannot be deposited uniformly inside deep holes. Electrolytic processes such as Hard Chrome plating can coat inside but often build a thicker layer on the edges where current density is higher, creating the “dog-bone” shape. As a result, complex shaped items such as a pump impeller, a hydraulic cylinder or an extrusion die cavity could not be coated by these traditional methods.

Hardide coatings are applied from gas media at a low pressure by Chemical Vapour Deposition technology. The coating is crystallised atom-by-atom from the gas phase on every hot surface in contact with the reactive gas mixture, so if this mixture is pumped through a hydraulic cylinder bore, the coating will grow uniformly inside the part. To illustrate this important ability, Fig.1 below shows some examples of complex shaped items coated with Hardide. Fig.2 shows a magnified section of M5 thread with 50 microns thick Hardide coating. The coating is not only uniform on the edges and between the threads, it also accurately follows imperfections in the steel surface. This ability to coat uniformly internal, as well as external, surfaces and complex shapes, opens many new applications where previously hard coating was impossible.

A uniform coating also facilitates the finishing of Hardide-coated parts: in most applications, a good finish can be achieved by polishing, without the need for expensive and complicated grinding operations.

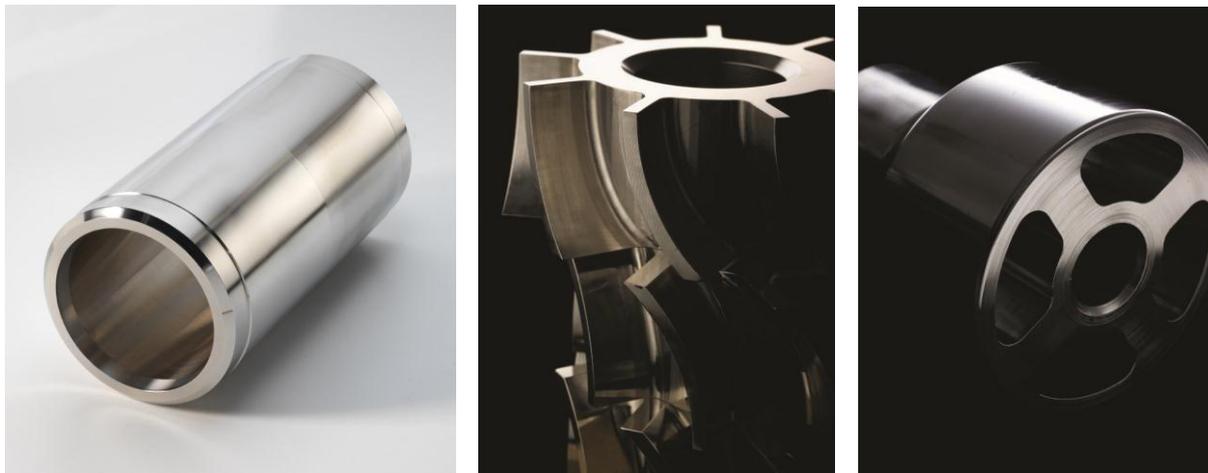


Fig.1. Examples of complex shape parts coated with Hardide: a pump cylinder coated inside (left), an impeller (center), and a flow diverter (right).

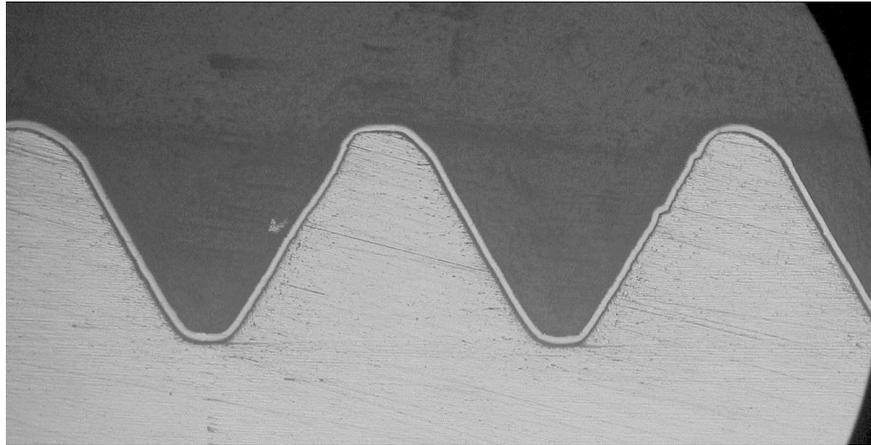


Fig.2. Hardide coating on an M5 thread shows ability to coat complex shape items uniformly; even slight imperfections in the substrate are accurately followed.

Combination of Ultra-high Hardness with Toughness and Ductility

Parts of oil drilling tools, pumps or metalworking tools can suffer from impact or shock loads in operation; the parts can be deformed under load. If these actions cause fracture or chipping of the hard materials this may lead to a catastrophic equipment failure. Even in normal operation in erosive or abrasive environments, brittle hard material would suffer from micro-cracking and fatigue erosion which could lead to premature failure. For these reasons, toughness and ductility are very important for practical applications of hard materials. In reality, hardness and toughness are often contradicting characteristics. Most traditional materials can be described as either hard (but brittle – like glass or cemented carbide) or tough and ductile (but soft – like copper).

The Hardide advanced CVD coating technology enables control of the hardness and toughness of the coating. Hardide-T coating is a nano-structured material which consists of a metallic tungsten matrix with dispersed nano-particles of Tungsten Carbide typically between 1 and 10 nanometres in size. Nano-structured materials can combine properties which are not compatible in macro- or micro-structured materials, like hardness and toughness. Hardide-T is a good example as it has extremely high hardness (1100-1600 Hv) while demonstrating unique toughness, crack and impact resistance. The coating can withstand 3000 microstrain deformation without any damage; this deformation will crack or chip any other thick hard coating. Hardide-T coated onto a component manufactured out of a tough alloy gives an unprecedented combination of surface wear resistance and the ability to survive impacts and shock loads. Fig.3. below shows a crater left after a shock impact on a Hardide-T-coated sample, Fig.4 shows a coated steel ring crushed in a vice. The coating survived the impact and the deformation without cracking or chipping.

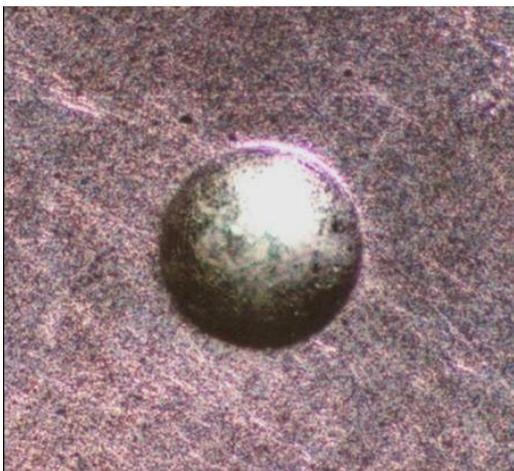


Fig.3. (Left): Micro-photograph of a crater (diameter approx. 1 mm) made by impact into 50 microns thick Hardide-T coating. Fig.4. (Right) Steel test ring with 50 microns Hardide coating crushed to test coating adhesion and toughness – no flaking or coating separation from substrate

The combination of ultra-high hardness with enhanced toughness achieves optimum protection against wear and erosion. The coating hardness inhibits the micro-cutting mechanisms of wear and erosion while its toughness, ductility, residual compressive stresses and homogeneous micro-structure prevent fatigue micro-cracking/chipping and the platelet mechanisms of erosion. This optimised wear and erosion resistance of Hardide-T coatings is proven by extensive laboratory and field testing of coated components.

Coating thickness

PVD or PE CVD coating technologies can produce very hard but thin coatings, such as Titanium Nitride and Carbonitride, DLC and Chrome Nitride which are all typically just 3...4 microns thick, the thickest advertised are up to 10 microns. These coatings give excellent results in tribological applications, but are so thin that a point load (such as when a grain of sand is pressed against the coated part) can deform the substrate and "plough" through the coating. Although the coating is much harder than sand, it requires the substrate to be hard enough to support the thin coating, otherwise it will be abraded very quickly.

There is an empirical rule that the coating should have a thickness which is 10% of the typical abrasive particle size to be able resist abrasion or it will behave like an eggshell e.g. pressure from a loaded particle will easily break through it. Coarse Arizona Road Dust (ARD) is often used in tests modelling abrasive or erosive conditions, ISO standard defines nominal ARD grain size up to 180 microns. The empirical rule would suggest that coatings with thickness >18 microns should perform better when compared to thinner coatings against ARD. In testing, we compared abrasion and erosion resistance of 50 microns thick Hardide-T type coating against a much harder 10 microns thick coating. The tests confirmed this empirical rule and the thicker coating resisted abrasion much better than the extremely hard but thin coating.

The importance of sufficient coating thickness was demonstrated during testing of an application in an oil drilling tool. A thick Hardide coating on a Copper component resisted the extremely erosive and abrasive high speed flow of drilling mud with sand and rock chippings. Uncoated Copper being very soft would be eroded away in a matter of seconds, but with 50-100 microns thick Hardide, the Copper parts last as long as the drilling tool itself. At a microscopic level, when a grain of sand impacts this thick coating, the deformations in the coating layer dampen the effect and spread the point load over a sufficiently large surface area of the copper substrate to prevent plastic micro-deformations and thus protect against erosion.

Pore-free Hardide Coating Protects against Chemically Aggressive Media

The CVD Hardide coatings have exceptionally low porosity, measured at less than 0.05%. The coating completely covers the substrate without any through pores starting from just 1 micron thickness. This absence of porosity is explained by the coating crystallisation mechanism: highly mobile reaction products fill pores and defects in the coating as it grows. Unlike sprayed Tungsten Carbide, Hardide does not use Cobalt which can be affected by acids; this is especially important for processing sour oil. Tungsten and Tungsten Carbide have high resistance to many aggressive chemicals, in particular to acids (including H₂S). As a result, the pore-free coating is resistant to aggressive chemicals and can protect critical parts and tools from corrosion and chemical attack.

Fig.5 below shows the results of comparative Neutral Salt Spray corrosion tests to ASTM B117-07. Mild steel plates were coated with three coatings: Hard Chrome, HVOF WC/Co and Hardide. Hard Chrome samples were badly corroded and removed from test after just 288 hours exposure. HVOF-coated samples showed heavy rust stains and the coating blistered due to the intensive corrosion of the steel plate beneath. The Hardide samples showed only light staining. Unlike various soft anti-corrosion coatings, Hardide offers the additional benefit of enhanced wear and erosion resistance. Hardide can be used at temperatures up to 400°C - where organic coatings and sealants cannot.

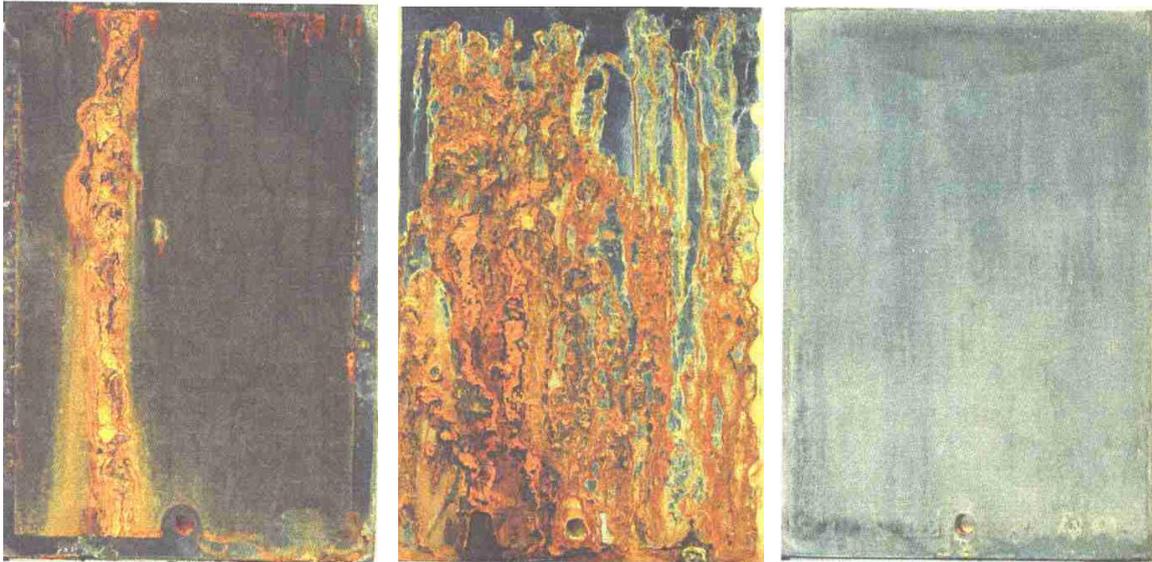


Fig.5. Samples of three different coatings after salt spray corrosion tests: left - HVOF after 480 hours; centre – Hard Chrome after 288 hours; right – Hardide coating after 480 hours.

Hardide-T was tested by Bodycote Materials Testing for resistance to H₂S in the NACE Sulphide Stress Cracking test in a solution of 5% NaCl, 0.5% Acetic acid, saturated with H₂S. Samples were tested in 3-point bent conditions with coating elongation up to 3000 microstrain. During the 30 day test the uncoated control sample cracked across the full 20 mm width and suffered from extensive micro-cracking and pitting while the same substrate coated with Hardide-T showed no micro or macro-cracking or degradation after the same test. This confirmed the non-porous structure of Hardide-T, as under 3000 micro-strain deformation any existing micro-cracks or defects would open up channels for the aggressive fluid to attack the substrate.

The zero porosity of Hardide-T is important for applications with gas valves where any porosity can result in gas diffusion through the coating layer leading to a potentially explosive mixture.

Hardide coating applications

Hardide coatings are the result of many years of research and development and are now in commercial use around the world in a diverse range of harsh environment and critical component applications including oil and gas drilling, power generation, chemical refinery and food manufacture - applications where part failure can cause hugely expensive downtime or have catastrophic impact.

The CVD Hardide coatings are particularly suitable for complex shaped parts with precise dimensions, or where internal surfaces need protection against wear and erosion. These applications are often difficult to coat by other technologies and Hardide coatings often complement rather than replace other coatings thus expanding the range of surface engineering applications.

In a drilling tool application for one of the largest global oilfield services providers, the coating has increased the life of critical components three-fold. Hardide-T appeared to be the only suitable solution for this application as traditional hard materials were too brittle and difficult to machine due to the complex part geometry, while other coating technologies were not able to reach the important hidden surface areas.

Hardide coatings are widely used on severe service metal-seated ball valves, pistons and cylinders of positive displacement pumps, industrial tooling and bearings. Longer-lasting coated parts reduce expensive downtime and enhance the reliability of expensive equipment such as directional oil and gas drilling tools. Reduced wear of critical components helps maintain optimum performance for longer and optimises the equipment design making it more competitive.

In other sectors, the coating is being used in the power, chemical and food manufacturing industries and in aerospace by BAE Systems on the Eurofighter Typhoon.

Hardide is an attractive replacement for Hard Chrome, which is to be phased-out due to environmental and health and safety considerations. The hexavalent Chromium salts used in the Hard Chrome plating coating production are known carcinogens which represent major health, safety and environmental problems. Restrictive pollution control legislation, such as REACH in Europe and OSHA in the US, applies further

pressure on the plating companies which increases the cost and reduces the availability of Hard Chrome plating. In response to this, some of the large users of Chrome plating such as aircraft manufacturers launched programs to identify new and more environment-friendly replacement technologies. HVOF thermal spray coatings are often selected as a suitable replacement but they can't be applied to internal surfaces, they have a very rough finish and require expensive and complicated grinding which is not possible on complex shaped parts. To meet industry demand for an alternative solution, Hardide has developed a new type of coating, Hardide-A, specifically for aerospace applications. This coating has hardness similar to Hard Chrome (800...1200 Hv) and can be applied with the same thickness as Hard Chrome (typically between 50 and 100 microns). This makes it easier for Hard Chrome users to adapt drawings and specifications and reduces the cost of a switch to Hardide-A. As Hardide-A is free from micro-cracks typical of Hard Chrome, it has much better corrosion-resistance – see Fig.5, and also shown excellent fatigue properties. Airbus is one of the prospective customers conducting qualification testing of Hardide-A coating as a replacement for Hard Chrome. As with the other Hardide coatings, Hardide-A is applied by CVD technology, so is particularly suitable for the coating of internal surfaces and complex shapes which are difficult to coat by spray coating technologies.

Summary and Conclusions

The nano-structured Hardide coatings offer a unique combination of protective properties including wear and erosion resistance, protection against aggressive chemicals and corrosion, as well as toughness, impact and crack resistance. The ability to coat internal surfaces and complex shapes opens new potential applications for hard coatings on critical parts. The coating can be applied to a broad range of substrate materials including stainless steel, some grades of tool and carbon steel, Nickel and Cobalt-based alloys and Titanium. Being pore-free, the coating protects the substrate from attacks by acids.

These properties are realised in various applications of Hardide with downhole tools, pumps and valves operating in oil and gas facilities, food manufacturing, refineries, cryogenic equipment and power generation. Typically, the coating triples the operational life of critical parts in abrasive conditions. The use of Hardide enables the advanced design of engineering systems operating in abrasive and corrosive environment and under shock loads.