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NANO-STRUCTURED CVD TUNGSTEN CARBIDE COATING PROTECTS AGAINST WEAR AND CORROSION

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ABSTRACT

Drilling tools operate in extremely abrasive, erosive and corrosive environments which reduce tool life, especially in the case of sour well applications. This paper discusses a new family of low temperature Chemical Vapour Deposition (CVD) Tungsten Carbide coatings proven to increase tool life and thus reduce expensive downtime and drilling operation costs particularly in new frontier, harsh and difficult drilling conditions.

The coating consists of Tungsten Carbide nano-particles dispersed in a metal Tungsten matrix which results in enhanced hardness and abrasion resistance. The coating can be produced up to 100 microns thick, which is unique for hard CVD coatings. As a nano-structured material, it demonstrates outstanding toughness, crack and impact resistance.

The gas-phase CVD process enables the coating of internal surfaces and complex designs such as valves, hydraulic components and pump cylinders. The pore-free coating is resistant to acids and aggressive media. This combination of wear resistance and chemical resistance makes CVD Tungsten Carbide coating an attractive solution to coat critical components in high wear and/or aggressive media environments including downhole tools, mud-driven hydraulic systems, pumps for abrasive fluids, valves and aerospace applications. CVD Tungsten Carbide coating is an attractive replacement for Hard Chrome, which is to be phased-out due to environmental and health and safety considerations.

KEYWORDS:

Hard coating, CVD, Tungsten Carbide, wear resistance, erosion resistance, acid resistance, toughness, nano-structured material, downhole tools, sour well tools, Hard Chrome replacement.

INTRODUCTION

A number of hard coatings and surface treatments are successfully used to increase the life of tools and critical components. Plasma and thermal spray coatings, hard chrome plating, PVD (Physical Vapor Deposition) and CVD coatings, Nitriding and Boronizing are among the most widely used surface engineering techniques. However, each of these well established processes has its limitations. In particular the currently used PVD and CVD processes produce very thin coatings of less than 5 microns, which cannot resist abrasive or erosive conditions[1,2,3]. Meanwhile chrome plating is under pressure for environmental reasons and although spray coatings are considered as a prospective alternative to chrome, they are not suitable for internal surfaces. Most of these treatments do not protect substrate against chemically aggressive media.

This article presents the new advanced CVD Tungsten Carbide/Tungsten coating called Hardide™[1], which offers a unique combination of properties. It has already proven successful as an enabling material in applications including downhole tools, valves and pumps handling abrasive and chemically aggressive fluids. The coating provides resistance to both wear and aggressive and corrosive chemicals such as acids. As it is applied from the gas phase, it can uniformly coat complex shaped parts and internal surfaces. The CVD Tungsten Carbide coating was commercialized in 2003 when our company established the first production centre in Oxfordshire, UK following a number of years of research and development.

COATING STRUCTURE AND COMPOSITION

Types of CVD Tungsten Carbide/Tungsten Coatings

There are four types of coatings, as detailed in Table 1 below:

TABLE 1.
TYPES OF CVD TUNGSTEN CARBIDE/TUNGSTEN COATINGS

Type	Hardness	Toughness	Thickness	Applications
Type T (Tough)	1100 – 1600 Hv	Excellent	Typically 50 µm	Oil tools, pumps, valves, actuators
Type A	800 – 1200 Hv	Excellent	Typically 50-100 µm	Developed as a hard chrome replacement, primarily for aerospace applications
Type M (Multi-Layer)	1200 – 2000 Hv	Good	Typically 50 µm	Abrasion/Erosion-resistance
Type H (Ultra-Hard)	3000 – 3500 Hv	Satisfactory	5-12 µm	Self-sharpening blades

All of these coatings consist of a tungsten carbide / tungsten composition produced by CVD. Unlike most other tungsten carbide coatings CVD Tungsten Carbide coating does not use cobalt or nickel metal matrix binder. The hardest coating type H, consists of pure tungsten carbides, which are extremely hard but have only 'satisfactory' toughness. The multi-layer coating type M, includes layers of various hardness. By varying the ratio between the thickness and properties of each individual layer, one can adjust the overall coating characteristics to meet specific application requirements. The most widely used type of coating is T which consists of tungsten carbide nano-particles dispersed in a tungsten matrix, this structure gives it a unique combination of properties: ultra-high hardness (varied from 1100 Hv up to 1600 Hv) is combined with excellent toughness, impact and crack-resistance. This combination is important for practical applications. These coatings are produced by low temperature CVD. The process temperature is between 480 and 550 degrees C which facilitate the coating of a wide range of metals including various types of steel, stainless steel, Ni-based and Co-based alloys and titanium. The lower process temperature also reduces stresses in the coating. This produces a hard coating with a typical thickness of 50 microns – uniquely thick among CVD hard coatings.

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CVD coatings are crystallised from gas-phase atom-by-atom. This enables the coating of internal and shaped "out of line-of-sight" surfaces, for example the inside surface of a cylinder. The coating can be polished to a mirror-like finish and its surface is pore-free. Due to its uniform structure, CVD Tungsten Carbide coating retains its finish which prevents the wear of counterparts made of softer metals or elastomeric materials.

Nano-Structure of CVD Tungsten Carbide Coating Type T

Coating type T is an advanced nano-structured material which consists of a metallic tungsten matrix with dispersed tungsten carbide nano-particles, typically between 1 and 10 nanometres. Figure 1 presents a high resolution electron microscopy image of CVD Tungsten Carbide coating T showing a tungsten carbide inclusion of 1-2 nanometres.

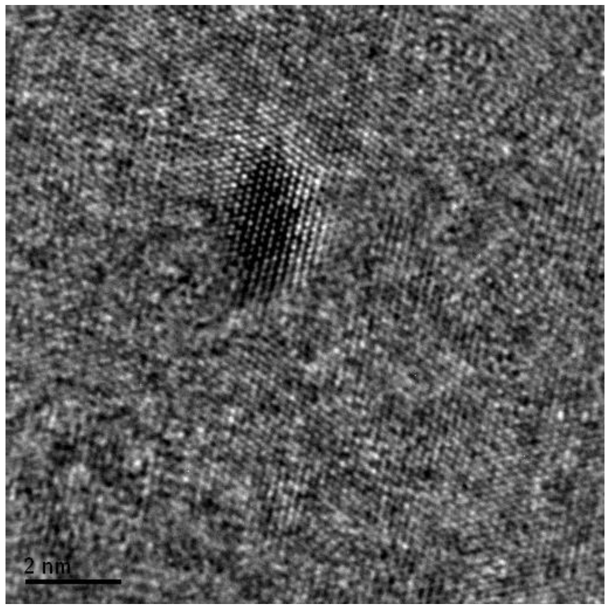

FIGURE 1 - High Resolution Electron Microscopy image of precipitate in CVD coating type T deposited on Cu substrate. The atomic distances (1.49 and 1.76Å) directly taken from the precipitate region are matched best to the lattice constants of W_2C (110- 1.49 Å and 102 – 1.74 Å).

The coating type T shows enhanced hardness in excess of 1100 Hv, and abrasion resistance up to 12 times better than hard chrome (ASTM[(2)] G65 abrasion-resistance testing). The coating can be produced on stainless steel, low alloy and some tool steels, Ni-, Co- and Cu-based alloys, titanium, typically with thickness of 50 microns, which is unique for hard CVD coatings. As a nano-structured material, it demonstrates outstanding toughness, crack and impact resistance by withstanding 3000 microstrain deformations without any damage; this deformation will crack or chip any other thick hard coating.

CVD Tungsten Carbide Coating Porosity

Due to the deposition mechanism, CVD Tungsten Carbide coating shown on Figure 2 is free from through porosity from a thickness of less than 1 micron. The coating is crystallised from the gas-phase atom-by-atom; the highly mobile reaction products fill micro-pores and defects in the coating as it grows. The porosity, measured as the difference between theoretical and actual material density, is less than 0.04%. Pore-free tungsten/tungsten carbide coating has high chemical resistance and

[(2)] ASTM International (ASTM), 100 Barr Harbor Dr., West Conshohocken, PA 19428 protects the substrate from attacks by aggressive media[4]. These protective properties were demonstrated in the coatings testing in corrosive and chemically aggressive conditions, described below.

Traditionally used coatings like flame-spray or hard chrome can have micro-pores and micro-cracks which may open when the substrate deforms under load which allows the solution to attack the substrate. These pores are often sealed using epoxy or other organic sealants with low viscosity which penetrate into the open pores and then polymerise to seal them. These sealed coatings have several disadvantages. Firstly, the use of organic sealant limits the temperatures to which the coatings can be

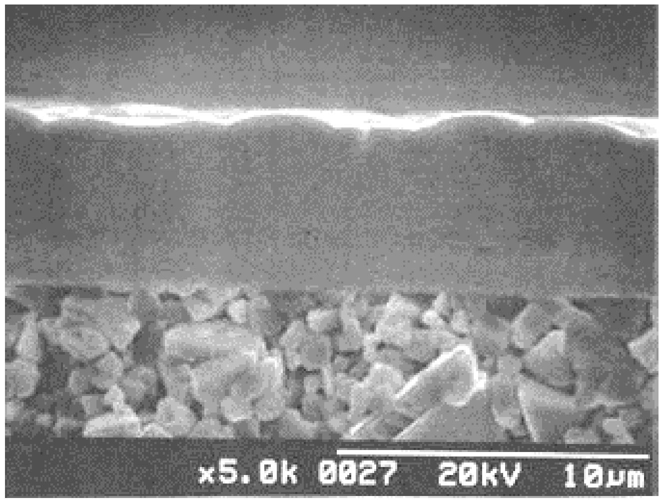

FIGURE 2 - SEM image of a cross-section of CVD coating layer on cemented carbide substrate. The coating as deposited has exceptionally low porosity and it can isolate substrate material against attacks of aggressive media, such as acids.

exposed as many sealants would decompose or oxidise above 200 degrees C. The second problem is that the sealants can only seal pores which are open to the surface and when the coating gradually wears when the coated parts are used, the deeper concealed pores could open – which were not sealed and allowing corrosion of the substrate. In contrast, the CVD Tungsten Carbide coating has exceptionally low porosity as applied and does not require additional sealing in most applications.

KEY PROPERTIES OF CVD TUNGSTEN CARBIDE COATINGS

Chemical and Corrosion Resistance

The resistance of the CVD Tungsten Carbide coating to corrosion and aggressive media has been extensively tested by methods including neutral salt spray tests, sulphide stress cracking test and immersion into various acids.

Salt Spray Corrosion Testing. It is important that we benchmark CVD Tungsten Carbide coating performance against other coatings. To compare its corrosion protective properties with hard chrome and other coatings we independently commissioned salt spray tests on mild steel plates coated with CVD coating type T, commercially sourced hard chrome plating and High-Velocity Oxy-Fuel (HVOF) coating. The 480 hour tests were conducted in accordance with ASTM standard B117-07 “Neutral Salt Spray Test”. Figure 3 shows samples of each of the three coatings after testing. The hard chrome plated samples were badly corroded and had to be removed from test after just 288 hours exposure. HVOF-coated samples showed heavy rust stains and the coating cracked due to the intensive corrosion of the steel plate beneath. The CVD coating samples showed only light staining.

Unlike various paints and soft anti-corrosion coatings, CVD Tungsten Carbide offers the additional benefit of enhanced wear and erosion resistance. It can also be used at temperatures up to 400^{O}C - where organic coatings and sealants have temperature limitations.

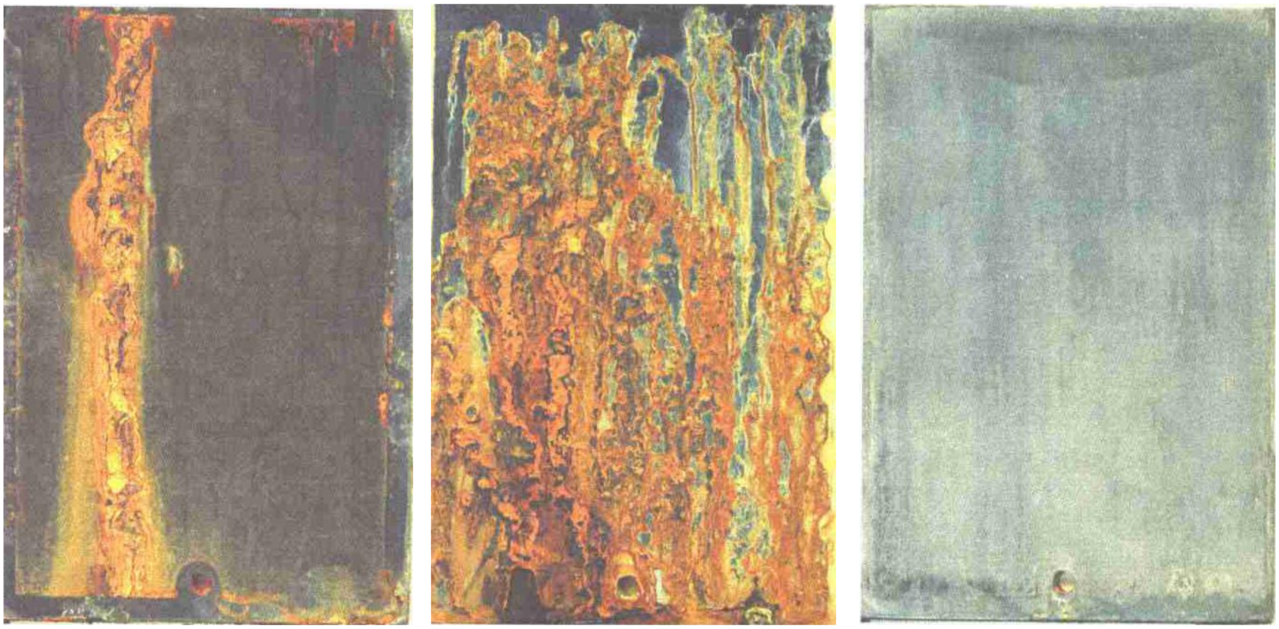

FIGURE 3 - Samples of three different coatings after salt spray corrosion tests: left - HVOF after 480 hours; centre – Hard Chrome after 288 hours; right – CVD coating type T after 480 hours.

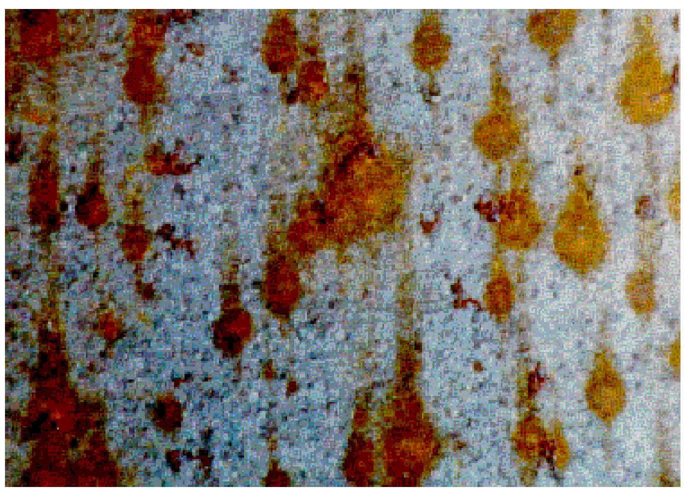

FIGURE 4 - Corrosion Damage to Unsealed HVOF WC/Co Coating

In the unsealed thermal spray coatings the cobalt metal binder is prone to corrosion, as shown on Figure 4 below. CVD Tungsten Carbide coating does not contain cobalt metal binder, so the coating itself was not affected by corrosion during the salt spray testing. As CVD Tungsten Carbide coating is free from through porosity it effectively protects the mild steel substrate from the corrosion attack without the need to seal the coating.

Resistance to Sulphide Stress Cracking. CVD Tungsten Carbide coating was tested by Bodycote Materials Testing [(3)] for resistance to Sulphide Stress Cracking in accordance with the NACE[(4)] standard TM0177-2005 / ASTM G39 "30 Day Sulphide Stress Cracking Test"[5] – Method B (1 bara H_2S**)** in a solution of 5% NaCl, 0.5% Acetic acid, saturated with H_2S, results presented in a report[6]. Samples of 17-4PH and 316L stainless steels as well as Inconel 625 were tested in 4-point bent beam stress conditions strained to 0.2%, 0.25% and 0.3%. Figure 5 shows four samples of 17-4 PH stainless steel after the 30 day test: the top dark plate is a control uncoated sample which cracked across the full 20 mm width and shows extensive micro-cracking and pitting. The three bottom lighter samples were coated with CVD Tungsten Carbide coating type T and show no cracking or degradation after the same test.

FIGURE 5 - Stressed faces of Uncoated (top) and CVD-coated (N 2, 3 and 4 from the top) samples of 17-4 PH stainless steel after 30 days Sulphide stress cracking test (photo from report [6]).

Due to its deposition mechanism, CVD Tungsten Carbide coating is free from through porosity from a thickness of less than 1 micron. Pore-free coatings have high chemical resistance and protect the substrate from attacks by aggressive media[4]. Traditionally used coatings like flame-spray or hard chrome have micro-pores and micro-cracks which can open when deformed under load and allow the solution to attack the substrate.

Similar results were observed on CVD-coated 316L stainless steel and Inconel 625 specimens, strained to 0.2%, 0.25% and 0.3%. As shown on Figure 6 the CVD Tungsten Carbide coating prevented stress corrosion cracking of these samples. None of the coated samples displayed any evidence of coating cracking, degradation or de-lamination after the 720hr exposure period.

[3] Bodycote Materials Testing, LTD. Midlands Laboratory.182 Halesowen Road.Netherton Dudley.West Midlands. DY2 9PL, UK

[4] NACE International, 1440 South Creek Drive, Houston, Texas 77084-4906 USA Houston, TX, USA

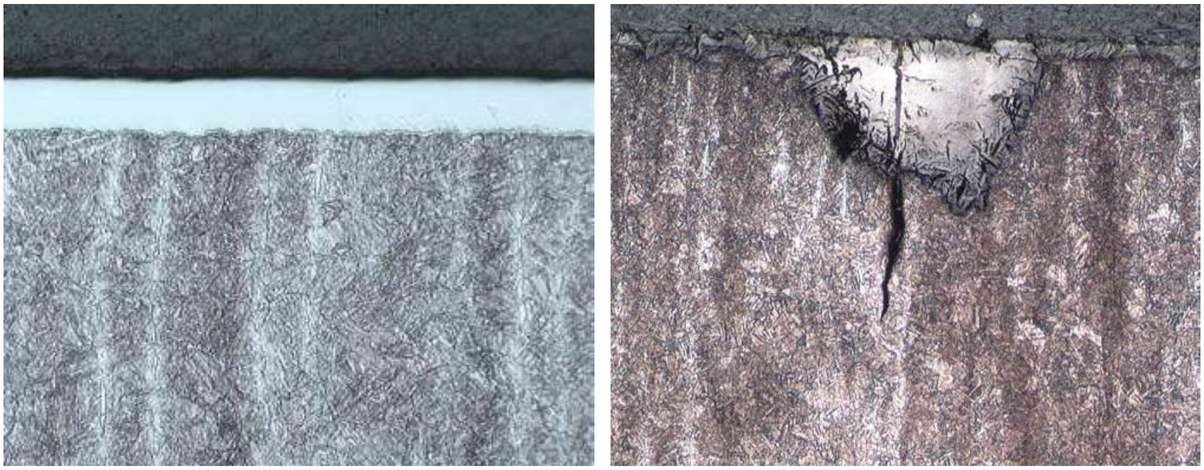

FIGURE 6 - Left: Photomicrographs showing the coating and substrate at the sectioned stressed face of specimen 498 (17-4PH, 0.2%) after 30 days in solution of NaCl, Acetic Acid and H2S, magnification x100. Pore-free CVD Tungsten Carbide coating protects 17-4 stainless steel substrate against aggressive media attacks; Right: Photomicrographs showing one of the finer 'secondary' cracks at the stressed face of the uncoated 17-4PH specimen 496, strained to 0.2%, magnification: 50X (micro-photographs from report [6]).

Acid Resistance. CVD Tungsten Carbide coating is particularly effective at protecting against mineral acids, including HCl and H_2SO_4. It will even resist Aqua Regia at room temperature; particularly notable as this mixture of hydrochloric and nitric acids is capable of dissolving noble gold.

CVD Tungsten Carbide coating was tested alongside a WC/Co detonation coating for resistance to nitric acid. Figure 7 below shows two CVD coated samples: one untested and one tested for 113 hours in 20% nitric acid. The CVD Tungsten Carbide coating sample is a yellowish colour due to slight surface oxidation, meanwhile its dimensions have not changed, the weight loss was not measurable – it was less than 0.001 g, and its surface roughness remained the same as before testing - 0.10 micron Ra, that all indicated that the coating has not been attacked.

FIGURE 7 - CVD Tungsten Carbide-coated 316 stainless steel samples: untested (left) and tested for 113 hours in 20% Nitric acid (right).

In the same test the detonation coated sample has changed colour to dark grey, while the acid solution became rose color due to Cobalt leaching from the sample. The weight loss of the WC/Co sample after 46 hours 40 min was approx. 0.3 g, Roughness of detonation sample before testing was 0.10 microns Ra, after testing in 20% acid increased to 0.41 microns Ra due to metal binder leaching. As a result of the roughness increase the detonation coating exposed to aggressive media can become extremely abrasive for seals and packing.

Figure 8 below shows 4140 steel test ring coated with 50 microns CVD coating type T, which was immersed into uninhibited 28% Hydrochloric acid for 24 hours. This sample appearance has not changed, no measurable weight loss or surface roughness change were detected.

FIGURE 8 - 4140 steel test ring with 50 microns CVD Tungsten Carbide coating type T after 24-hours immersion in uninhibited 28% HCl – no appearance change or weight loss were detected.

Mechanical Properties of CVD Tungsten Carbide Coatings

Wear Resistance. Hardness, wear and abrasion resistance are the key characteristics of CVD Tungsten Carbide coatings which have been extensively tested in the laboratory and proven in industrial environments. Figure 9 presents the results of abrasion resistance tests performed in accordance with the ASTM G65 standard - Procedures A and B [7]. The results showed that the CVD Tungsten Carbide coating wear rate is 40 times lower than abrasion resistant steel AR-500, 12 times lower than hard chrome and four times lower than thermal spray WC.

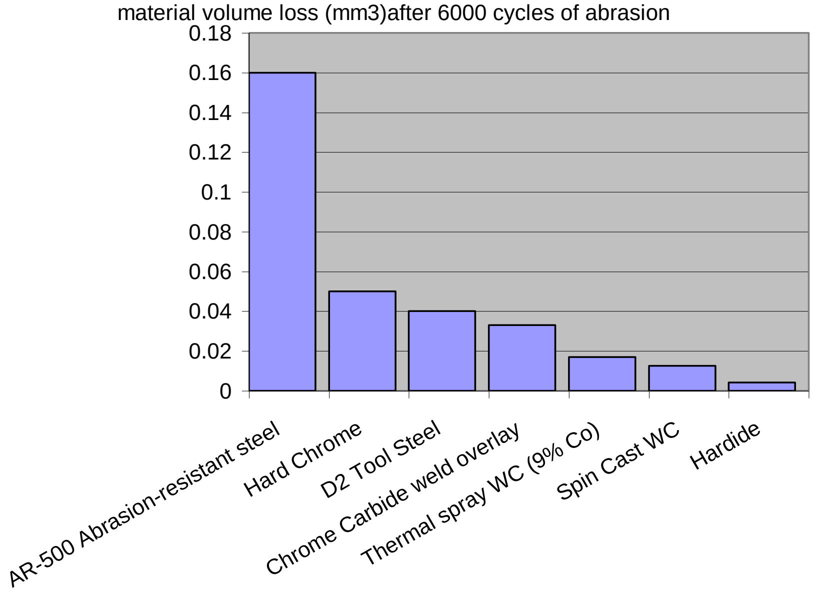

FIGURE 9 - Results of ASTM G65 tests of CVD Tungsten Carbide coating abrasion resistance as compared to the results for other hard materials.

<u>Erosion Resistance.</u> Erosion resistance tests were performed in accordance with ASTM G76-95[8]; velocity was 70 m/sec and aluminium oxide (particle size 50 µm) was used as the erosive material. Table 2 and Figure 10 below present the test results and comparative results for other hard materials at various angles of impact - 90°, 60°, 45° and 30°. CVD Tungsten Carbide coating erosion rate was 0.017-0.019 mm^3/g which is significantly better than the erosion rate of the tested types of cemented carbide, white iron, hard chrome and chrome carbide weld overlay. CVD Tungsten Carbide coating resists erosion by alumina particles at 70 m/sec; three times better than steel and more than two times better than cemented carbide (hardmetal). CVD Tungsten Carbide coating also significantly exceeded various currently used hard materials in a sand/water erosion test.

TABLE 2.
EROSION RESISTANCE TEST G76-95: EROSION BY ALUMINA PARTICLES IMPINGEMENT IN GAS JET AT 70 M/SEC.

Angle of target, °	Erosion Rate, $mm^3/g*1000$					
	CVD Tungsten Carbide coating	Chrome Carbide Weld Overlay	White Iron	Abrasion-resistant steel	WC cladding	Hard Chrome
30	17					
45	19	71	76	53	36	25
60	18	66	64	48	41	26
90	18	60	40	40	50	30

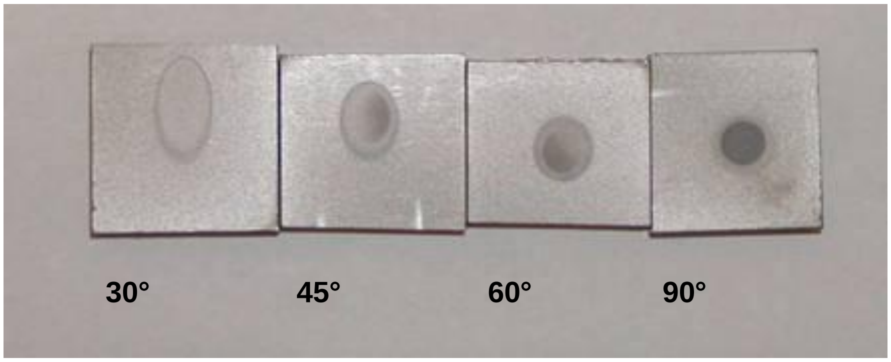

FIGURE 10 - CVD Tungsten Carbide coating samples after ASTM G76-95 erosion tests with Alumina particles at 70 m/sec under different angles.

CVD Tungsten Carbide coating wear and erosion resistance are superior to the tested materials despite the fact that some of them have higher hardness. This enhanced performance of CVD Tungsten Carbide coating can be explained by its excellent toughness and fatigue resistance. Micro-cracking and chipping are the main mechanisms of wear and erosion of hard materials like flame-spray tungsten carbide or hard chrome. A tougher material will better resist this degradation.

Toughness, Resistance to Impact and Deformations. Toughness, resistance to impact and deformations are properties of significant practical importance, especially for applications involving shock loads and impact. Brittleness and poor impact resistance are among the few drawbacks of traditional WC/Co hardmetals. HVOF WC/Co coatings are known to crack and spall under high load and high cyclic fatigue conditions [9]. These drawbacks restrict the use of cemented carbides and spray coatings on tools and wear parts operating in conditions where shock loads and impact may cause fracture and catastrophic failure. CVD Tungsten Carbide coating can provide a solution to these problems. One of this coating users, a producer of valves for the oil and gas industry, developed a valve seat which deformed in operation. Traditional coatings like HVOF spray were not suitable as they crack or chip under this deformation. CVD Tungsten Carbide coating type T is proven to withstand deformations of 3000 microstrain without micro-cracking and has now been tested and approved for this application. This confirmed the theoretical expectation that nano-structured materials can show unique toughness, crack and impact-resistance.

Figures 11, 12, 13 below illustrate the CVD Tungsten Carbide coating ability to survive impact, significant substrate deformations and shock loads without spalling or cracking. The coated parts retain integrity and can continue operating under harsh conditions.

FIGURE 11 - Micro-photo of a 1 mm diameter indentation (left) and the scratch test (right) of 50 microns thick CVD Tungsten Carbide coating type T on steel. Absence of cracking, chipping or spalling demonstrate coating's unique toughness and flexibility.

FIGURE 12 - Steel test ring with 50 microns CVD Tungsten Carbide coating crushed to test coating adhesion and toughness – no flaking or coating separation from substrate

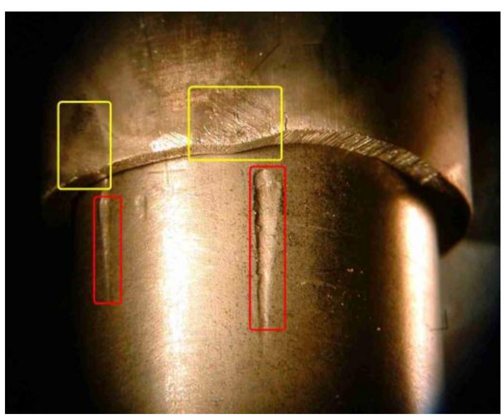

FIGURE 13 - CVD-coated Ni-based alloy parts survived intense repeated hammer impacts without fracture or flaking despite significant deformations of the substrate (magnification 5X).

Ability to Coat Internal Surfaces and Complex Shapes. CVD Tungsten Carbide coatings are deposited from the gas phase, this allows the coating of complex shapes and internal surfaces [10, 11, 12]. This ability illustrated by Figure 14 is important for applications with parts like actuator threads, hydraulic cylinders, valves and pumps.

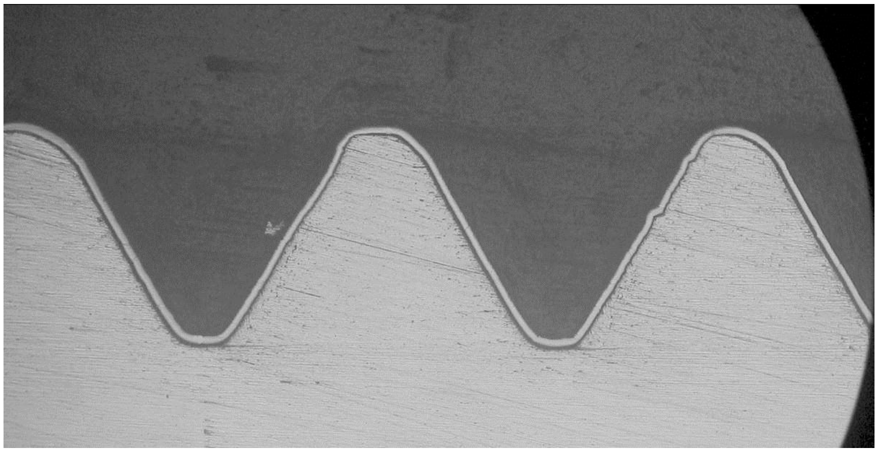

FIGURE 14 - A micro-photograph of a cross-section of 50-microns thick CVD Tungsten Carbide coating type T on thread. The uniform coating follows the substrate; even slight imperfections are accurately followed (magnify. 20X).

CVD TUNGSTEN CARBIDE COATING APPLICATIONS

CVD Tungsten Carbide coating has proven itself as a problem-solving material for applications with a broad variety of components operating in abrasive and erosive environments, including critical components of downhole tools, metal seated ball valves, pumps handling abrasive fluids.

Applications with Ball Valves

Ball valves similar to those shown on Figure 15 will suffer from abrasion by sand or stone chippings present in the fluids or from erosion by accelerating flow when the valve is being closed/opened. CVD Tungsten Carbide coatings make the valve parts scratch-proof and able to resist abrasion and erosion. This significantly increases the valve life.

FIGURE 15 - Ball valves coated with CVD Tungsten Carbide coating.

A UK producer of ball valves started using the CVD Tungsten Carbide coating in 2003. Most of the CVD-coated valves are used in topside applications in the oil and gas industry – these are in service in the UK, Norway and South Africa as well as in high pressure oil refinery applications. The CVD-coated valves have been in service for between one and two years with no failures reported.

In an instant coffee manufacturing application, hard chrome plated ball valves suffered from intensive abrasion and erosion and had to be replaced every few days. Since being CVD-coated, they have been in continuous service for over 18 months.

CVD Tungsten Carbide - coated ball valves are also used successfully in speciality chemicals manufacturing where chemical resistance is required. In these cases, the coated valves have been in service for more than six months while previously the valves were failing every few days or weeks. CVD-coated valves are also in use in cryogenic equipment controlling liquid Helium at temperature of -196^{o}C and pressure 200 bar; an application which is very abrasive for valves.

After two years of working in co-operation and impressive slurry test results, CVD Tungsten Carbide coating has been approved for use on a new line of ball and seats by one of the leading providers of flow control products. The CVD Tungsten Carbide coating enabled this customer to offer 316 stainless steel as the base metal for use in severe service applications that require metal to metal seating, including abrasive and slurry applications. In the slurry tests CVD Tungsten Carbide coating coated 316 balls and seats remained operational after more than 70,000 cycles in slurry where Co-based alloy parts failed in 29,000 cycles.

Applications with Downhole Tools

CVD Tungsten Carbide coatings are used successfully in several advanced down-hole tools including:

- Mud-driven hydraulic parts for directional drilling tools;
- High loading bearings pins;
- Grippers for down-hole tractors.

In each of these applications the CVD-coated parts are operating in a highly abrasive and erosive drilling mud environment. In some cases the mechanical abrasion is combined with the chemical attack by acidic fluids and H_2S. CVD Tungsten Carbide coating extended the life of critical parts for these tools and reduced the downtime costs.

Applications in Pumps

CVD Tungsten Carbide coating type T is used on inside cylinder and outside piston of a positive displacement pump handling abrasive viscous fluids at the pressure up to 2800 psi. In this application the main coating advantages were the ability to coat internal surfaces, enhanced wear-resistance and also reduced wear of packing counter-surfaces. The coating has tripled the pump life.

CVD Tungsten Carbide coating as a Hard Chrome Replacement

CVD Tungsten Carbide coating is an attractive replacement for hard chrome, which could be phased-out due to environmental and health and safety considerations. Hard chrome plating is widely used as a wear resistant and anti-galling coating with some degree of corrosion protection, but the hexavalent chrome salt solutions used in the coating production, and the process effluents, are known carcinogens which represent major health, safety and environmental problems[13]. Restrictive pollution control legislation, such as EU REACH, 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, we developed a new type of coating, CVD Tungsten Carbide coating type 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 to switch to CVD Tungsten Carbide coating type A. As this coating is free from micro-cracks typical of hard chrome, it has much better corrosion-resistance – see Figure 3. Applied by CVD technology, the coating 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 CVD Tungsten Carbide 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 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. The ability to coat internal surfaces and complex shapes opens new potential applications for hard coatings with critical parts. Being pore-free, the coating protects the substrate from attacks by aggressive media.

These properties are realised in various applications of CVD Tungsten Carbide coating 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 CVD Tungsten Carbide coating enables the advanced design of engineering systems operating in abrasive and corrosive environment and under shock loads.

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