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HARDIDE Nano-Structured Tungsten - Tungsten Carbide CVD Coating as Enabler for Engineering Systems

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1. Abstract.

Hardide™ is a family of low-temperature Chemical Vapour Deposition coatings composed entirely of Tungsten and Tungsten Carbide. Nano-structure gives the material a combination of hardness with toughness and flexibility. Pure tungsten metal can be applied to copper substrates for electrical applications, or to diamond particles for corrosion resistance and improved bonding to other metals. Pure tungsten carbide can be applied to items such as paper cutting blades, were wear resistance is far more important than corrosion or impact resistance. However, Hardide-T™ - a composite of tungsten carbide nano-particles in a tungsten matrix - has the widest range of applications. This unique system exhibits wear resistance typical of extremely hard materials, but is also physically durable enough that it will dent rather than crack under severe impact. Because of the low coating temperature, Hardide is suitable for application to stainless steel, Inconel, 4140, copper, and many other metals.

2. Introduction.

Cemented Carbide WC/Co (also called Hardmetal) is widely used in industry for over 70 years for manufacture of metal cutting tools, drill bits and wear parts as a bulk material and more recently - as a spray coating, and proven as one of the best wear- and abrasion-resistant materials. Meanwhile these materials and coatings also have a number of properties which restrict or complicate their usage, one of them is brittleness, poor resistance to impact, shock loads and deformations. Several additional problems are associated with the use of Cobalt metal binder, which suffers from corrosion or chemical attacks. Use of powder metallurgy liquid phase sintering results in the pressed compact shrinkage to almost half its volume during sintering due to pore elimination [1]. This shrinkage is often non-uniform and complicates manufacturing of precision components of complex shape.

An advanced nano-structured pore-free Tungsten Carbide – based coating Hardide helps resolve these issues and open new applications for Tungsten Carbide, in particular for complex shape and precision components [2] and parts operating under shock load. The coating is produced by a patented [4] low-temperature Chemical Vapour Deposition (CVD) process as a dense layer with thickness between 5 and 100 microns.

The article presents results of the ASTM G65 and ASTM G75 abrasion and erosion resistance tests, as well as the NACE H_2S corrosion testing and examples of Hardide applications with engineering systems operating in abrasive environment, including valves, oil industry down-hole tools and pumps.

3. Structure and Key Properties of Hardide Coating.

3.1. Nano-Structure of Hardide-T coating.

Hardide-T consists of a metallic tungsten matrix with dispersed tungsten carbide nano-particles with size typically between 1 and 10 nanometers. Fig. 1 presents a high resolution electron microscopy image of Hardide-T showing a Tungsten Carbide inclusion of 1-2 nanometers.

Dispersed Tungsten Carbide nano-particles give the material enhanced hardness of between 1100 and 1600 Hv_{50}, and abrasion resistance up to 12 times better than Hard Chrome. Nano-structured materials can show unique toughness, crack and impact-resistance and Hardide-T has proven this by withstanding 3000 microstrain deformations without any damage – this deformation will crack or chip any other thick hard coating.

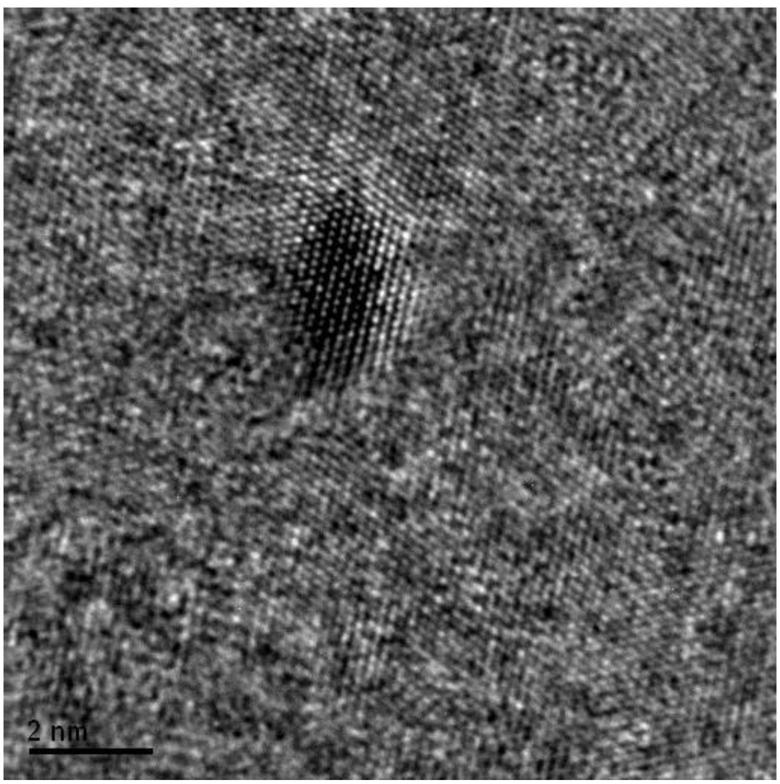


Fig.1 HREM micrograph of precipitate in Hardide-T deposited on copper substrate.   The atomic distances (1.49 and 1.76Å) directly taken from the precipitate region are matched best to the lattice constants of W_2C (110- 1.49 Å and 102 – 1.74 Å).   (The micrograph was produced at the Oxford University Department of Materials)

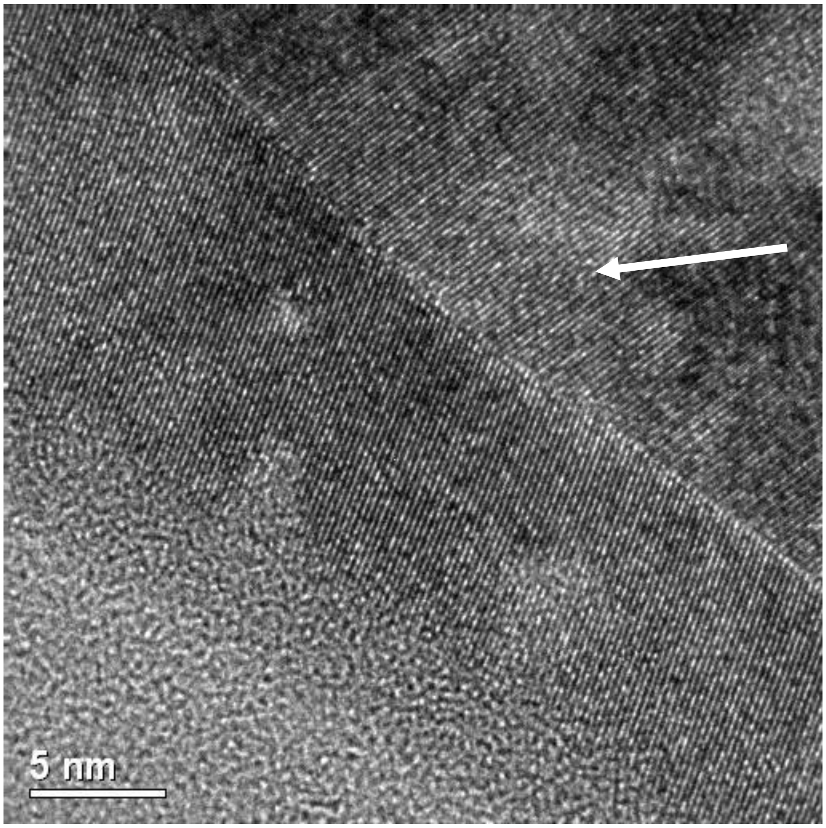


Fig.2 HREM micrograph of the grain boundary in Hardide-T deposited on copper substrate only very small contrast changes are seen along the grain boundary between the two grains indicating that there are no extensive amounts of carbon or carbide precipitates. (The micrograph was produced at the Oxford University Department of Materials)

3.2. Hardness, wear and erosion resistance.

Hardness, wear and abrasion resistance are the key characteristics of Hardide-T important for most engineering applications, these properties have been extensively tested in the laboratory and proven in industrial environments.

Hardness of pure metal Tungsten is measured at 350 Hv_{50}. The dispersed Tungsten Carbide nano-particles give Hardide-T significantly higher hardness which can be controlled and tailored to give a typical range of hardness between 1100 and 1600Hv_{50}, and with other types of Hardide™ coating up to 3500 Hv_{50} – that exceeds hardness of traditional pure Tungsten Carbide WC made by reaction between tungsten and carbon [5].

Fig. 3 presents the results of abrasion resistance tests performed in accordance with the ASTM G65 standard - Procedures A and B [3]. The results showed that the Hardide™ 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.

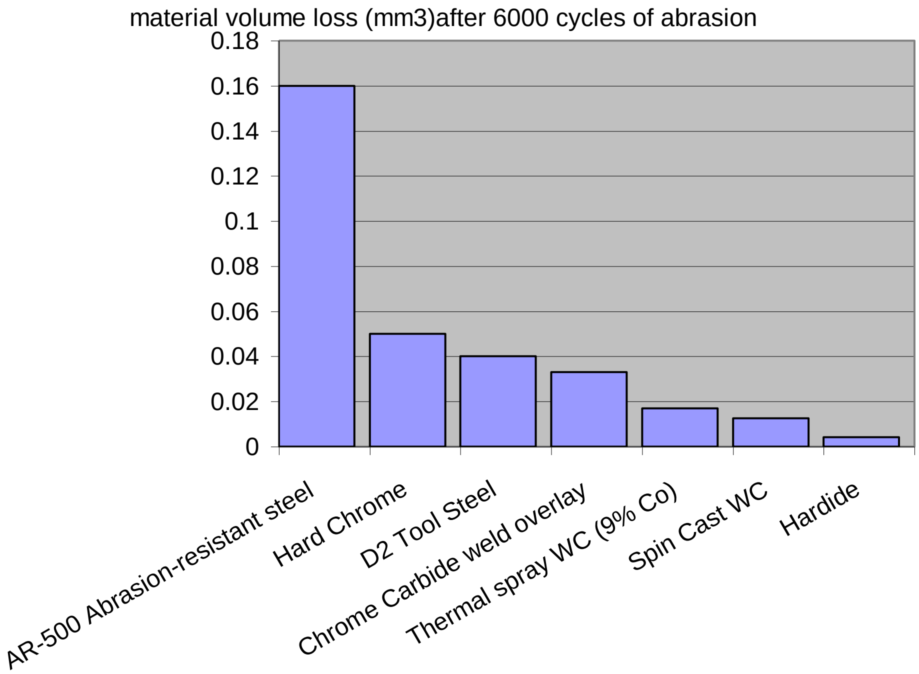


Fig. 3. Results of ASTM G65 tests of Hardide coating abrasion resistance as compared to the results for other hard materials.

Erosion resistance tests were performed in accordance with ASTM G76-95; aluminium oxide (particle size 50 µm) with velocity 70 m/sec were used as the erosive material. Angles of impact for erosion tests were 90°, 60°, 45° and 30°. The results summarised in Table 1 below, Hardide's erosion rate was 0.017 - 0.019 mm^3/g which, again is significantly better than the erosion rate of the tested types of cemented carbide, white iron, hard chrome and chrome carbide weld overlay. Hardide™ resists erosion by Alumina particles at 70 m/sec three times better than steel and more than two times better than cemented carbide (hardmetal). Hardide™ also significantly outperformed various currently used hard materials in a sand/water erosion test.

Table 1. Erosion resistance test ASTM G76-95: erosion by Alumina particles impingement in gas jet at 70 m/sec.

Angle of target, °	Erosion Rate, $mm^3/g*1000$					
	Hardide	Chrome Carbide Weld Overlay	White Iron	AR-500 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

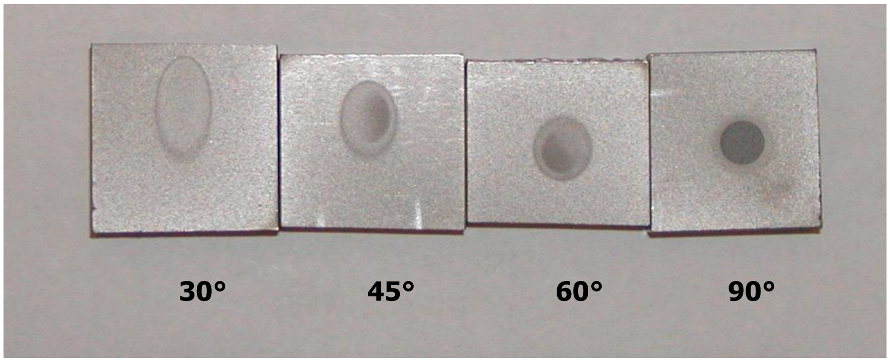


Fig.4. Hardide-coated samples after ASTM G76-95 erosion tests with Alumina particles at 70 m/sec under different angles.

Hardide-T wear and erosion resistance are superior to the tested materials despite the fact that some of them have higher hardness. This enhanced performance of Hardide-T can be explained by its outstanding 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.

3.3. Ability to coat internal surfaces and complex shapes

Hardide™ coatings are deposited by Chemical Vapour Deposition (CVD) technology from the gas phase, that allows the uniform coating of complex shapes and internal surfaces [4]. Fig.5 below illustrates this as it shows a cross-section of thread coated with 50-microns thick Hardide, which follows and repeats accurately even small imperfections in the substrate. Most other coating technologies used in valve applications either are not able to coat internal surfaces (HVOF spray, D-gun), or cause thicker coating build-up on sharp edges (hard Chrome).

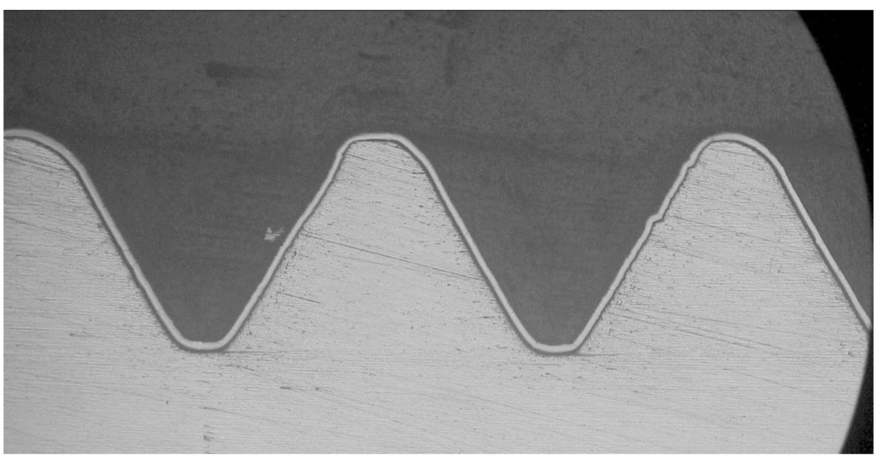


Fig.5. A micro-photograph of a cross-section of 50-microns thick Hardide-T coating on thread. The uniform coating follows the substrate; even slight imperfections are accurately followed.

This opens new applications for Tungsten Carbide coatings with precision parts and parts of complex shape. Such parts could be difficult or even impossible to manufacture out of WC/Co hardmetals due to its shrinkage during sintering and also brittleness and difficulties of machining. Instead such parts can be made out of tough and inexpensive steel and coated with Hardide coating, the resulting parts would combine surface wear-resistance exceeding one of hardmetals with toughness or a steel component.

3.4. Protection against aggressive media

Unlike sprayed or sintered Tungsten Carbide, Hardide does not use Cobalt which can be affected by corrosion. Binder-free Hardide™ resists attacks of salts, acids, H_2S, molten metals and many other aggressive media. This is especially important for the petrochemical industry processing sour oil.

Due to its deposition mechanism, Hardide™ is free from through porosity from a thickness of less than 1 micron. 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 [6] and protects the substrate from attacks by aggressive media. Traditionally used coatings like flame-spray or Hard Chrome have micro-pores and micro-cracks which open when the substrate deforms under load and allow the solution to attack the substrate.

Hardide™ was tested by Bodycote Materials Testing for resistance to aggressive media in accordance with the NACE Sulphide Stress Cracking test in a solution of 5% NaCl, 0.5% Acetic acid, saturated with H_2S [7]. Stainless steel 17-4 and 316 and Inconel 625 samples coated with Hardide™ were tested in stress conditions of up to 3000 microstrain.

Fig.6 shows two samples of 17-4 PH stainless steel after the 30-days test: the top dark plate is a control uncoated sample which cracked across the full 20 mm width and shown extensive micro-cracking and pitting. The bottom, lighter sample was coated with Hardide and shown no cracking or degradation after the same test.

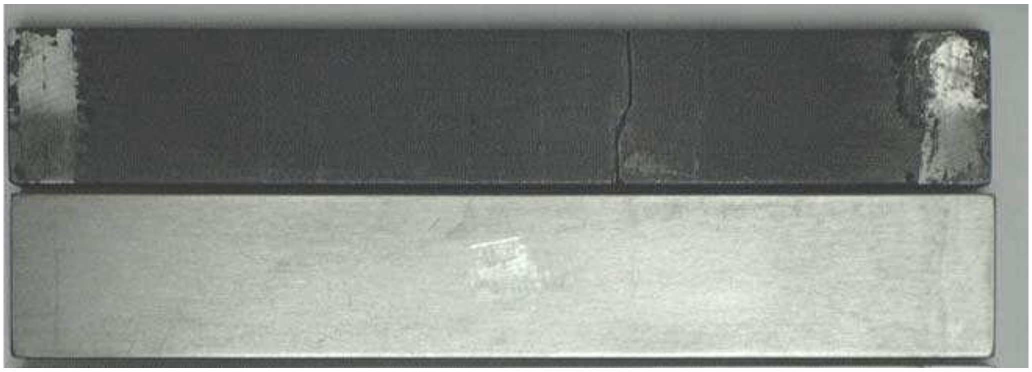


Fig.6. Uncoated (top) and Hardide-coated (bottom) samples of 17-4 PH stainless steel after 30 days Sulphide stress cracking test (photograph from Bodycote report [7]).

Fig. 7. Pore-free Hardide™ coating protects the substrate against aggressive media attacks; a micro-graph of a Hardide-coated sample of 17-4 stainless steel after 30 days in solution of NaCl, Acetic Acid and H_2S (micro-photograph from Bodycote report [7]) .

3.5. Toughness, resistance to impact and deformations.

Brittleness and poor impact resistance are among the few drawbacks of traditional WC/Co hardmetals, there are properties of significant practical importance which restrict use of Tungsten Carbide with tools and wear parts operating in conditions where shock loads and impact may cause fracture and catastrophic failure. Hardide coating can provide a solution to these problems. One of Hardide's customers – a producer of valves for the oil and gas industry - developed a valve seat which deformed in operation. Traditional coatings like HVOF spray are not suitable as they crack or chip under this deformation. Hardide 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.

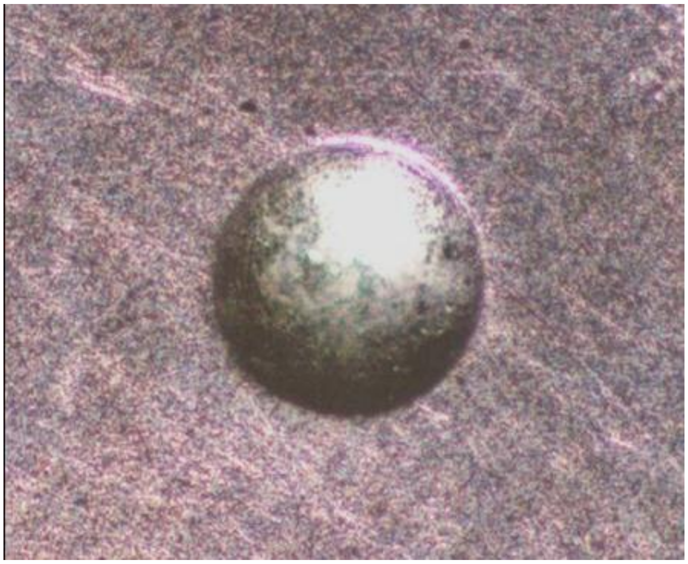


Fig.8. Micro-photo of a 1 mm diameter crater made by a ball impact into 50 microns thick Hardide-T coating on steel. Absence of cracking, chipping or spalling demonstrate coating's unique toughness and flexibility.

Fig.9. Steel test ring with 50 microns Hardide coating crushed to test coating adhesion and toughness – no flaking or coating separation from substrate

4. Hardide™ applications

Hardide™ has proven very successful for applications with a broad variety of components operating in abrasive and erosive environments, including critical components of downhole tools used in the oil and gas industry, valves and pumps handling abrasive fluids such as paints.

4.1. Abrasion- and erosion-resistance.

Ball valves similar to those shown on Fig.10 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. Hardide™ coatings make the valve parts scratch-proof and able to resist abrasion and erosion. This significantly increases the valve life.

Fig.10. Ball valves coated with Hardide™.

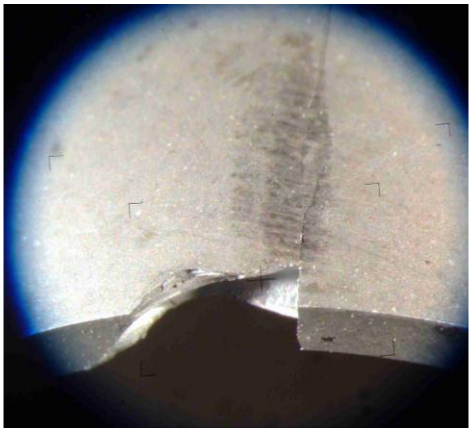
LG Ball Valves Ltd, a UK producer of ball valves is a Hardide customer which started using the coating in 2003. Most of the Hardide-coated LG Ball Valves' valves are used in topside applications in the oil and gas industry – these are in service in the UK, Norway and South Africa as well as in high pressure oil refinery applications. The Hardide-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 Hardide-coated, they have been in continuous service for over 18 months.

Hardide-coated LG Ball Valves' 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. Hardide-coated valves are also in use in cryogenic equipment controlling liquid Helium at temperature of -196oC and pressure 200 bar; an application which is very abrasive for valves.

4.2. Flexibility and toughness

Hardide™ can be applied as a tougher substitute to brittle cemented carbide WC/Co for parts suffering from impact. Fig. 11 shows a hardmetal bush fractured after light impact, failure of this part caused catastrophic failure of an expensive tool used in oil industry. As an alternative solution Hardide-coated Inconel parts survived repeated impact without fracture, this made the tool much more resistant to operate under shock loads.



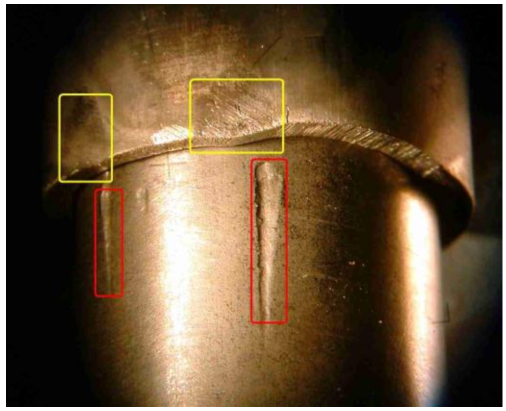


Fig.11. Left: Brittle cemented carbide bushes fracture after light impact. Right: Hardide-coated Inconel parts survived intense repeated hammer impacts without fracture or flaking.

4.3. Facilitated finishing

Hardide™ solves another practical problem for producers of complex shaped components where hardness and wear-resistance is required. If a spray coating is applied to such parts they have to be machined to restore the shape after coating. This can be a very complicated and expensive operation in some cases even practically impossible due to the complex shape, that limits such coatings applications. Hardide™ coating, as applied, is very smooth and uniform; coated valve parts usually require only polishing to achieve a finish of typically 0.3 microns Ra. This vastly streamlines finishing operations, especially for complex shaped parts.

Ease of finishing, ability to coat complex shapes uniformly and Hardide's unique flexibility therefore open new opportunities for valve design where traditional brittle hard coatings and materials cannot be used.

5. Summary and Conclusions

The nano-structured Hardide-T coating is an advanced material which offers a unique combination of protective properties, including ultra-hardness, wear and erosion resistance as well as toughness, impact and crack resistance. These properties are utilised in various application of Hardide with valves operating in oil and gas facilities, food manufacturing, refineries, cryogenic equipment and power generation, where valve operation life was increased many-fold. A number of Hardide properties are unique to Hardide: absence of porosity, flexibility and facilitated finishing and ability to coat complex shapes uniformly. The use of Hardide opens new applications for the use of Tungsten and Tungsten Carbide enabling advanced design of engineering systems operating in abrasive environment and under shock loads.

6. References:

[1] Petersson, Anders, Cemented Carbide Sintering: Constitutive Relations and Microstructural Evolution, 2004, KTH, Materials Science and Engineering

[2] Eureka, November 1999, p.21 “Super-Hard Coating goes deep inside”.

[3] ASTM G65-94, Standard test for measuring abrasion using the dry sand/rubber wheel apparatus, 1996 Annual Book of ASTM Standards, Volume 03.02, ASTM

[4] TUNGSTEN CARBIDE COATINGS AND PROCESS FOR PRODUCING THE SAME, Patent PCT/RU/99/00037, filed 11.02.1999, published WO 00/47796 (17.08.2000 Gazette 2000/33), Applicant: Hardide Ltd

[5] Characterisation of Tungsten Carbide Coatings produced by Chemical Vapour Deposition”, Davide Di Maio PhD Thesis, Department of Materials, University of Oxford, England, April 2005.

[6] Website http://www.tungsten.com/tungcorr.html

[7] Bodycote Materials Testing test report: 30 DAY SULPHIDE STRESS CRACKING (SSC) TEST TO NACE TM0177-2005 / ASTM G39 – Method B (1 bar H2S)