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## **Hardide™: advanced nano-structured CVD coating**

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**Abstract:** Hardide™ is a family of new low-temperature Chemical Vapour Deposition (CVD) Tungsten/Tungsten Carbide coatings. Coating consists of Tungsten Carbide nano-particles dispersed in metal Tungsten matrix, that give the material enhanced hardness of between 1100 Hv and 1800 Hv, and abrasion resistance up to 12 times better than Hard Chrome. Nano-structured materials show unique toughness, crack and impact-resistance. The coating is resistant to acids and aggressive media, can be produced on steel, including stainless steel and some tool steels, with coating thickness varied from 5 microns to 100 microns. Gas-phase CVD process allows coating internal surfaces and items of complex shape like dies, moulds, pump cylinders. Homogeneous pore-free structure facilitates finishing by honing, polishing, mirror finish can be achieved with suitable substrate. Use of Hardide with cutting tools for paper and plastics makes them self-sharpening. Application of Hardide increases life of tools and critical components and reduces down-time.

**Keywords:** CVD; Tungsten Carbide; hard coating; wear-resistance; erosion-resistance; acid-resistance; nano-structure; non-stick coating.

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**Biographical notes:** Zhuk graduated with Honours from the Lomonosov Moscow State University, where he received PhD Degree in Plasma Physics and Chemistry. Since 1992, he was involved in technology commercialisation, has successfully accomplished a number of projects with ICI, GM, Johnson & Johnson and Samsung. In 1999 in cooperation with Flintstone Plc., he co-founded Hardide Ltd. and has managed its growth and development from laboratory experiments to an ISO-certified AIM-listed technology company supplying international customers. He is a Technical Director of Hardide Plc. responsible for the technology and products development, patenting and commercialisation.

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### **1 Introduction**

A number of hard coatings and surface treatments are successfully used to increase life of tools and components, thin PVD and CVD coatings on cemented carbide metal cutting tools, hard Chrome plating of moulds, spray coatings and Nitriding are most widely used techniques. Meanwhile each of these well-established surface engineering processes has its limitations, in particular the currently used PVD and CVD processes produce very thin

coatings typically less than 5 microns (Bloyce, 2000; [http://www.richterprecision.com/richter\\_precision\\_FAQ.htm](http://www.richterprecision.com/richter_precision_FAQ.htm); <http://www.ionbond.com>), which can not resist abrasive or erosive conditions. Chrome plating is under pressure for environmental reasons, HVOF spray coating is considered as a prospective alternative to Chrome but it is not suitable for internal surfaces. Most of these treatments do not protect tools against aggressive media.

Hardide™ is a new coating material which offers a unique combination of properties making it a promising material for applications with tools and components (di Maio, 2005)<sup>1</sup>. Hardide was introduced into full-scale commercial use in 2003 when Hardide Ltd., established the first production centre in Oxfordshire, UK, resulting from many years of research and development.

There are several types of Hardide coatings, one of them Hardide-T consists of Tungsten Carbide nano-particles dispersed in Tungsten matrix that gives it a unique combination of properties. Hardide-T has a combination of ultra-high hardness which can be varied from 1100 HV up to 1800 HV, with toughness, impact and crack-resistance important for practical applications. It can be applied with thickness up to 50 microns and on some substrate materials – up to 100 microns, which is unique among CVD hard coatings.

Hardide is crystallised from gas phase atom-by-atom, which allows to coat internal and shaped “out of line-of-sight” surfaces, such as a die cavity or a mould of a complex shape.

Hardide™ can be polished to mirror-like finish, its surface is pore-free (porosity less than 0.04%). Thanks to its uniform structure Hardide retains its finish that prevents wear of the counterparts made of softer metals or elastomeric materials.

## **2 Structure and key properties of Hardide coating**

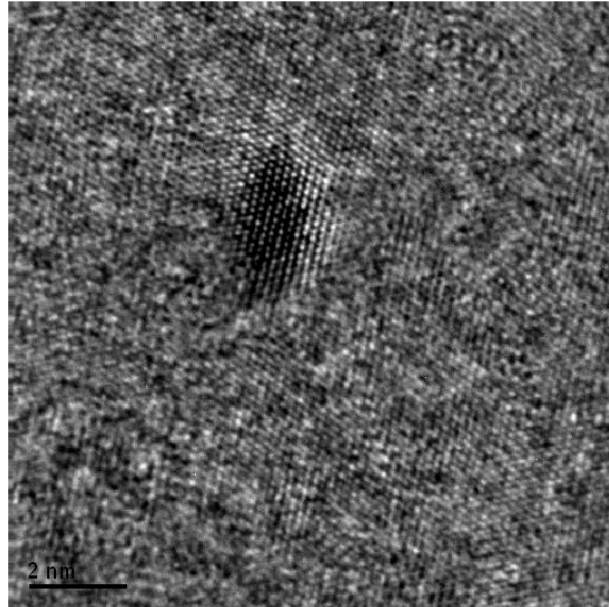
### *2.1 Nano-structure of Hardide-T*

Hardide-T is an innovative material, which consists of a metallic tungsten matrix with dispersed tungsten carbide nano-particles with size typically between 1 and 10 nanometers. Figure 1 presents a high resolution electron microscopy image of Hardide-T showing a Tungsten Carbide inclusion with size 1–2 nanometers.

Figure 2 shows the high resolution electron microscopy image of the grain boundary in Hardide-T sample. There are only minor variations on the image contrast in the boundary area that demonstrates that the Tungsten Carbide or Carbon precipitates are not formed in this area. This feature of Hardide-T structure is beneficial for its mechanical properties.

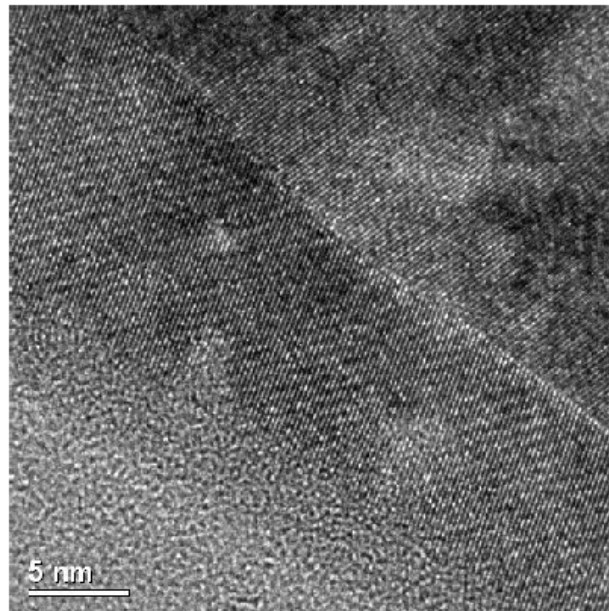
The coating is virtually pore-free, the difference between the actual material density and the theoretical density is below than 0.04%.

**Figure 1** HREM micrograph of W<sub>2</sub>C nano-particle precipitate in Hardide-T coating



*Source:* The micrograph made at Begbroke Science Park of Oxford University Department of Materials

**Figure 2** TEM micrograph of grain boundary in Hardide-T sample

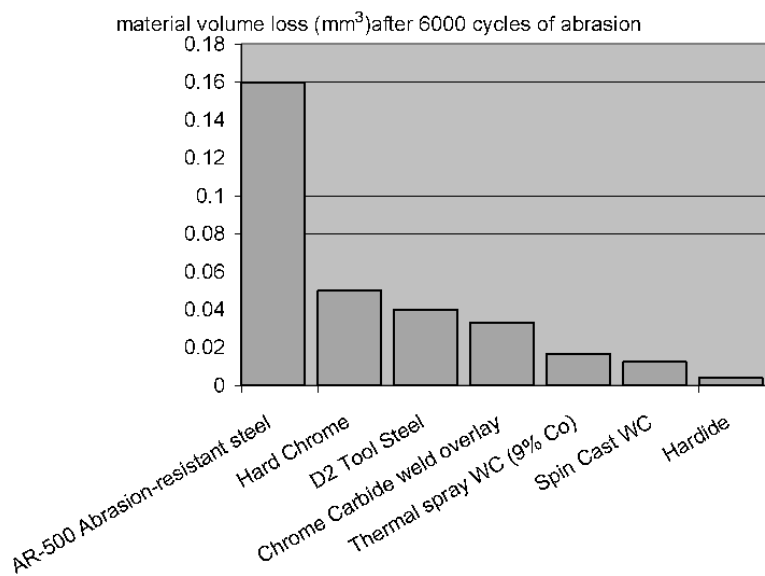


*Source:* The micrograph made at Begbroke Science Park of Oxford University Department of Materials

## 2.2 Hardness and wear resistance

Hardness, wear and abrasion resistance are the key characteristics of Hardide™, which were extensively tested in laboratory and proven in industrial environment. Figure 3 presents the results of abrasion resistance tests performed in accordance with ASTM G65 standard. Abrasion resistance tests were performed in accordance with ASTM G65 Procedures A and B (ASTM G65-94, 1996). These tests shown that Hardide wear rate is 40 times lower than abrasion resistant steel AR-500, 12 times lower than hard Chrome, four times lower than thermal spray WC.

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

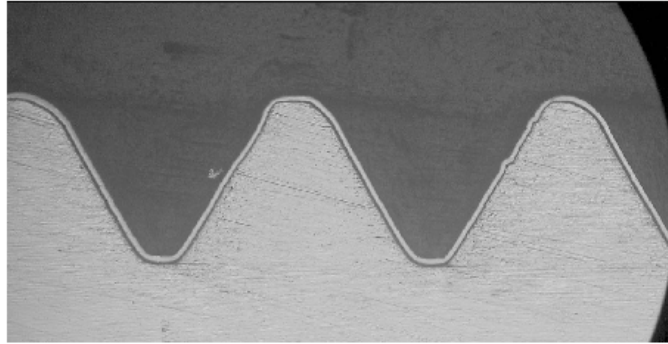


Erosion resistance tests were performed in accordance with ASTM G76-95, velocity was 70 m/sec, aluminium oxide (particle size 50  $\mu\text{m}$ ) was used as the erosive material. Angles of impact for erosion tests were 90°, 60°, 45° and 30°. Hardide's erosion rate was 0.017–0.019  $\text{mm}^3/\text{g}$ , that again is significantly better than 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, more than two times better than cemented carbide (hardmetal).

## 2.3 Ability to coat internal surfaces and complex shapes

Hardide coating is deposited by CVD technology from the gas phase, which allows coating items of complex shape and internal surfaces (di Maio, 2005).<sup>1</sup> This is important for applications with some types of tools, such as extrusion dies for plastics and ceramics.

**Figure 4** 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 (made by Hardide Coatings Ltd)



### 3 Hardide applications

#### 3.1 Components operating in abrasive environment: pumps, valves, down-hole tools for oil and gas industry

Hardide had proven very successful for applications with a broad variety of components operating in abrasive and erosive environment. The critical components of down-hole tools used in oil and gas industry, pumps handling abrasive fluids such as paints, metal- and elastomer-seated ball valves are a few examples.

Ball valves similar to shown on Figure 5 can be easily scratched by grains of sand or stone chippings trapped between the ball and the seats, the scratches can quickly develop into leaks. Hardide coating makes the valve parts scratch-proof and able to resist erosion by accelerating flow when the valve is being closed/opened. This significantly increases the valve life, in one application where previously hard-Chrome plated ball valves suffered from intensive abrasion and erosion and have to be replaced with the intervals of just few days now Hardide-coated valves are in continuous service for over 18 months without any failures.

**Figure 5** Ball valves coated with Hardide (made by Hardide Coatings Ltd)



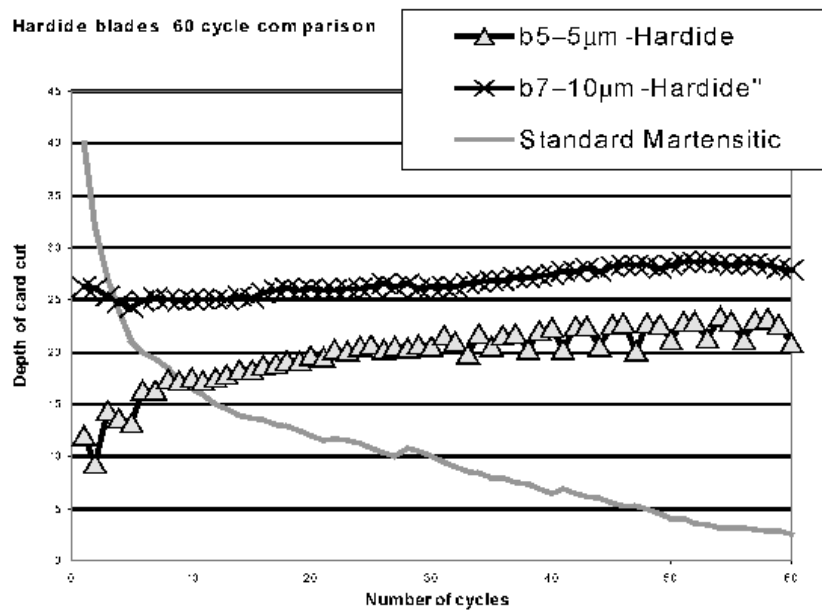
Similar effects were achieved by Hardide coating of the pistons and cylinders of positive displacement pumps handling paints with high content of abrasive mineral pigments.

### 3.2 Self-sharpening cutting tools

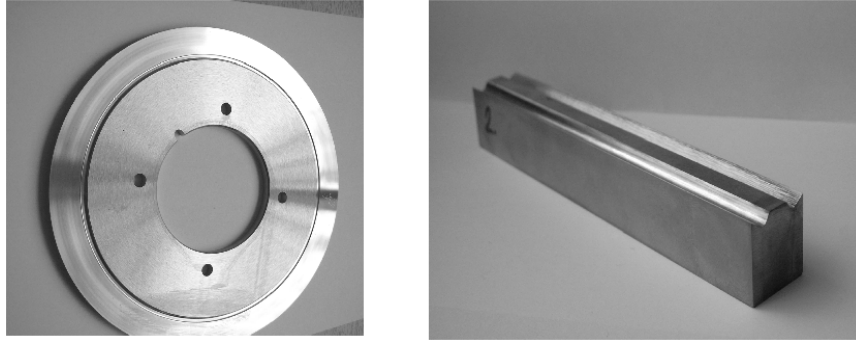
Hardide is used to make self-sharpening cutting tools for paper and plastics. To achieve this thin coating is applied to one side of the blade. When the blade cuts its uncoated side is worn much faster than the coated side, the coating edge is exposed and forms sharp cutting edge.<sup>2</sup> This effect was confirmed by laboratory tests performed at CATRA Report 957921 (2002) (UK) and in the industrial conditions.

CATRA tested martensitic stainless steel blades for sharpness and life to ISO 8442.5 The blades were mounted in the ISO cutting test machine to cut through 10 mm wide strips of manila card with 5% of silica, which increased the blade wear rate during cutting. The blade was cycled back and forth over a distance of 40 mm at a speed of 50 mm/second under a load of 50 N. The amount of card cut/cycle being recorded, this is a measure of the blade sharpness all the blades were subjected to 60 cycles initially. The results for two Hardide-coated blades are presented on Figure 6 compared to standard uncoated blade. The depth of cut of a standard blade is degrading very quickly, after 50 cuts reduced down to 1/10 of the initial depth. Meanwhile Hardide-coated blades shown opposite effect: the depth of cut is even increasing with the number of cuts. One of the Hardide-coated blades shows oscillating results, this reflects the mechanism of the effect: the coating becomes exposed at the tip as the base metal side of the edge is worn away, gradually making the blade sharper. After a certain time the coating collapses leaving a fractured and a blunt tip. This cycle then repeats itself over a significant number of cycles.

**Figure 6** Results of the testing of cutting depth of various blades vs. number of cuts. Standard martensitic blade very quickly loses its sharpness, while two blades with various Hardide coatings even increase the depth of cut thanks to self-sharpening effect



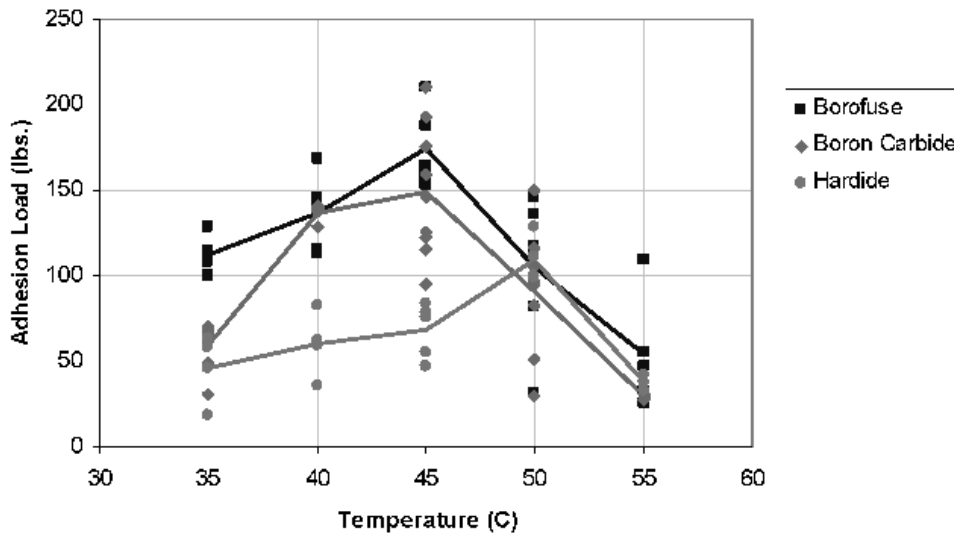
**Figure 7** Hardide-coated rotary paper knife (left) operated without sharpening for 10 weeks – instead of 12 hours. Hardide-coated knife for ultra-high molecular weight Polyethylene film (right) worked without re-sharpening for 3 months – instead of 1 day (made by Hardide Coatings Ltd)



### 3.3 Ceramics forming moulds

Hardide being chemically inert homogeneous material with low friction shown non-stick properties against green ceramics paste, plastics. One of the tests was performed with Hardide-coated moulds forming green ceramics paste, the adhesive force was measured as various temperatures. Figure 8 shows comparison to Borofuse and Boron carbide coated tool steels, in typical working temperatures range Hardide reduced the sticking by factor 3. Reduced sticking prevents the pieces of formed material being left on the mould that results in manufacturing rejects, down-time to clean the mould. Durable non-stick coating can substitute use of spray fluid lubricants and increase productivity of moulding machines.

**Figure 8** Sticking of green ceramics paste to Hardide-coated tools as compared to Borofuse and Boron Carbide. Hardide reduced the sticking force by factor of 3



### 3.4 Tools for powder compaction

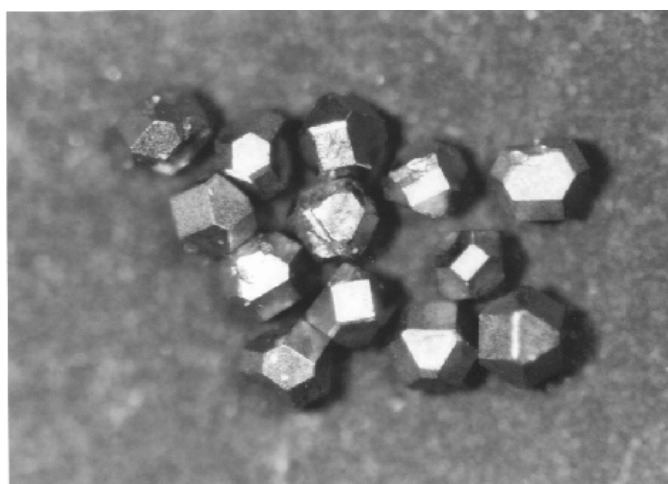
Hardide coating has been tested with punches and dies used for tableting. Powders used in pharmaceutical and food supplements and vitamins are often highly abrasive. The modern tools for production of medical tablets are precision tools made out of tough steels with very high surface finish. Wear and corrosion of the tools affects quality of the medical tablets and requires change of the tools increases down-time. Use of hard coatings reduces wear and allows maintaining the surface finish of the punches and dies.

Hardide coating is used with good effect on the working tips of tableting punches.

### 3.5 Hardide coating for diamond tools

Hardide coating on diamonds (see Figure 9) plays a specific function: as the coating has strong chemical bond to diamond crystals as well as good wettability by metal bonds it increases crystal retention in tool matrix.<sup>3</sup> Hardide coating has also filled micro-defects and cracks in diamond crystals, as a result the average strength of the crystals has been increased. As a result diamond tools become more durable and enhanced cutting rate can be achieved.

**Figure 9** Hardide-coated diamond crystals will last longer in diamond tools



## 4 Summary and conclusions

Nano-structured Hardide-T coating offers a unique combination of protective properties, including ultra-hardness, wear- and erosion-resistance as well as toughness, impact- and crack-resistance. The coating can be applied to a broad range of substrate materials, including steels, some grades of tool steel can be coated due to low process temperature of 500 C. The ability to coat internal surfaces and complex shapes opens new potential applications for hard coatings with tools and dies.

Hardide became enabling technology that already had impact on the design of tools, to makes them more durable and better performing.



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## Notes

- <sup>1</sup>*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.
- <sup>2</sup>*Cutting Tool with Hard Coating*, Patent PCT/GB2003/001219, filed on 21/Mar/2003, Applicant: Hardide Ltd.
- <sup>3</sup>*Adhesive Composite Coating for Diamond and Diamond-Bearing Materials, and Process for its Application*, PCT/RU00/00086, filed on 15/03/00, publication N WO 01/68559, Applicant: Hardide Ltd.

## Websites

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- <http://www.ionbond.com>.
- <http://www.tungsten.com/tungcorr.html>.