Technical paper:

CVD coatings good choice for nuclear valves

EDF Energy recently specified CVD tungsten carbide coating to increase the life of the boiler feed steam valves at the Hinkley Point B nuclear power station in Somerset, UK. The coatings offer the nuclear industry a unique combination of protective properties including wear and erosion resistance, and protection against aggressive chemicals and corrosion.

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Graham Young, Steam & Rotating Plant Engineer, EDF Energy Nuclear Generation Ltd, owner and operator of Hinkley Point B nuclear power station explained: "Hardide CVD coatings offered a very cost-effective, high-performance solution to extend the life of the 15 MW boiler feed pump steam valves in the plant at Hinkley Point B. We evaluated four options, including other hardface coatings, before making our choice based on several technical and financial reasons. The coating's ability to coat internal surfaces evenly, its performance in testing and the ease of implementation and maintenance made Hardide the solution of choice. It has enabled us to continue to use the existing equipment which would be very expensive to replace, as well as require validation and safety case development, and will allow us to operate smoothly between planned outages."

"There were technical challenges in applying the coating process to the large stellite 6 valve covers and we needed to work with a supplier that could provide troubleshooting support and deliver the parts on time so as not to affect the availability of the power plant equipment." Spare valve cover guide sleeves were also delivered to EDF Energy at the end of 2012 and Hardide is being evaluated for other applications within the energy company.

EDF carried out tensile tests which revealed that the CVD coating achieved extremely high adhesion to components.

Tough, cobalt-free coatings

Hardide coatings consist of tungsten carbide nano-particles (1-2 nanometers across) dispersed in a tungsten matrix.

The coatings, which are typically 50 microns thick, are crystallised from the gas phase atom-by-atom by a process called chemical vapour deposition (CVD). This enables the uniform coating of internal surfaces and complex shapes, where other coatings such as HVOF, D-gun and PVD cannot be used. No grinding or other expensive finishing operations are required to achieve a good finish of 0.3-0.2 μm Ra due to the smooth and uniform 'as coated' surface. The coatings can be applied to a wide range of metals including various grades of stainless steel, tool and alloy steels, nickel, cobalt and copper-based alloys and titanium.

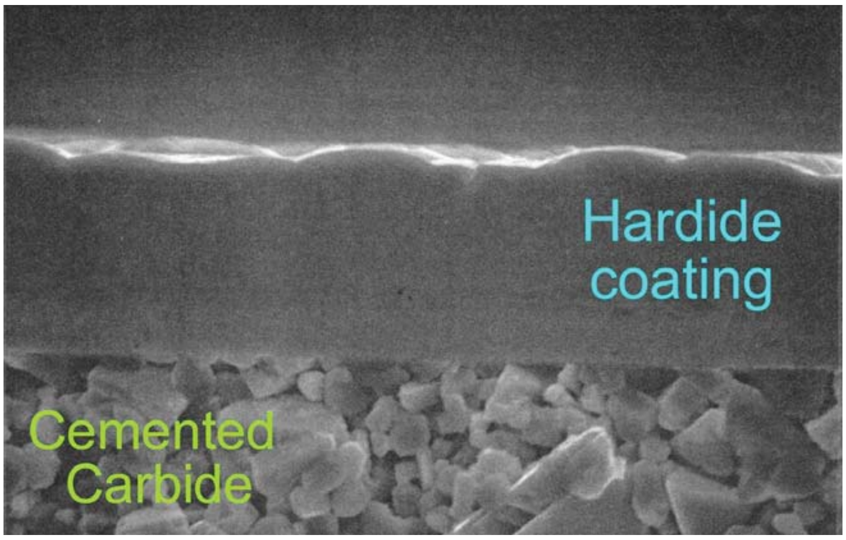
As the coatings are free from cobalt, this is an important advantage for nuclear applications where cobalt-containing alloys and hard-facing can be hazardous. Even corrosion- and wear-resistant Co alloys produce small amounts of Co-containing debris which can be carried with the coolant fluids into the reactor zone. Neutron irradiation can produce radioactive Co^{60} isotope, which is a strong emitter of highly penetrating gamma-radiation with a half-life of 5.27 years. Highly radioactive Co^{60} can be absorbed from the coolant flow into the surface of the primary system components making them a source of occupational radiation exposure. Attempts to develop cobalt-free hard-facing with good tribological properties and enhanced resistance to wear, erosion, corrosion and also cavitation started in the 1960s and are still continuing today. CVD coatings have good potential to become an attractive solution to this problem.

The CVD coatings are free from porosity and micro-cracks, so they can effectively protect the substrate from corrosive and chemically aggressive media. In comparative salt spray corrosion testing, a Hardide-coated mild steel plate showed no signs of corrosion after 480 hours, while both HCP and HVOF thermal spray coated plates showed heavy rust stains and some coating delamination. Further salt spray tests of up to 2000 hours duration showed no corrosion.

The coating also provides especially effective protection against acidic media and has successfully passed the NACE Sulphide Stress Cracking test. In this test, specifically designed to replicate high H_2S sour oil and gas conditions, a batch of various strained coated and uncoated steel samples were immersed for 30 days in a corrosive solution of salt and acetic acid saturated with H_2S. After this test, the surface of the control uncoated 17-4 stainless steel sample changed colour to black and showed extensive micro-cracking induced by H_2S. One of the cracks went through the full sample width. In contrast, Hardide-coated samples showed no change at all; both visual and metallographic examination confirmed that the media had not affected the coating and that the coating completely isolated the substrate from attack. This demonstrated that the coating can help extend the life of the valves controlling sour oil and gas in both upstream and downstream applications.

Nano-structure

The nano-structure of CVD coatings enables enhanced toughness and ductility. Valve and pump components can be deformed under high pressure and can experience shock loads in operation. Brittle hard facing materials under these conditions can chip or



Hardide CVD coating on cemented carbide.

CVD coatings can be used on internal surfaces and complex shapes impossible to reach using traditional methods.

fracture which can lead to catastrophic equipment failure. Even in normal operation, in erosive or abrasive environments, brittle, hard material will suffer from micro-cracking and fatigue erosion, which can lead to premature failure. Therefore, toughness and ductility are very important in practical applications of hard materials. In reality, hardness and toughness are often incompatible characteristics. Most traditional materials can be described as either hard (but brittle, like glass) or tough and ductile (but soft, like copper). CVD coatings are nano-structured materials consisting of a metallic tungsten matrix with dispersed nano-particles of tungsten carbide. Nano-structured materials can have a combination of properties (like hardness and toughness) that are not common in macro or micro-structured materials. Hardide coatings are a good example, combining extremely high micro-hardness with enhanced toughness, and crack and impact resistance. This combination helps achieve exceptional resistance to wear and erosion.

Strong adhesion bond of the coating to the substrate is very important and when evaluating various solutions to the boiler-feed valve problem, EDF tested the coating's adhesion by test-quenching samples in cold water from a nominal operating temperature of 350°C and 375°C. Thermal shock into a hard coating is considered to be a very effective method of qualitatively assessing the adhesion of the coating. The coating passed this quench test without any damage. Tensile tests of the coating's adhesion showed the bond strength as being better than 70 MPa (10,000 psi). This value represents the ultimate strength of the epoxy adhesive used in the ASTM C633 bond strength testing so the actual bond strength of the Hardide coating remains unknown as it is stronger than the strongest adhesive available for such a test.

Past history

Previously Hardide coatings have been used on valve trims within the UK nuclear sector e.g., by British Energy at the Hartlepool & Heysham Power Stations and by Costain Oil Gas & Process, which operates the Sellafield Evaporator 'D' Project. At the Hartlepool & Heysham Power Stations, coated valves with a bore size ranging from 0.5" – 3" were used on the Emergency Shutdown CO_2 Cooling System and were exposed to radioactive carbon dioxide. These are Class 600 Top Entry Valves, made of 316 stainless steel and coated with Hardide-T type coating.

The Sellafield Evaporator 'D' valves with 1" – 3" bore sizes were used to process some of the waste materials. These are also Class 600 Top Entry (2-Way or 3-Way) Valves, made of either 316 or 304 stainless steel and also coated with Hardide-T type coating.

The coatings are used successfully by the leading oilfield service companies in advanced down hole tools and typically extend the life of critical parts by factor of four.They have also proven successful in applications on metal-seated ball valves and pumps. Ball valves can suffer from abrasion by sand or stone chippings present in fluids and from erosion by accelerating flow when the valve is being closed/opened. The CVD coatings make the valve parts scratch-proof and capable of resisting abrasion and erosion. In one case, the coating was approved for use on a new line of balls and seats by Flowserve after successful slurry test results. The coating allows Flowserve to offer Type 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 Flowserve slurry tests, Hardide-coated 316 balls and seats remained operational after more than 70,000 cycles in slurry where a Co-Cr wear-resistant failed in 29,000 cycles. Testing of several other applications of the coatings on valves and pumps handling abrasive and chemically aggressive fluids is currently underway.

In summary, Hardide CVD coatings offer the nuclear industry a unique combination of protective properties including wear and erosion resistance, and protection against aggressive chemicals and corrosion. The ability to coat internal surfaces and complex shapes enables the coating of parts that are impossible by many traditional coating methods. The use of these CVD coatings enables advanced valve design for valves operating in abrasive and corrosive environments and under shock loads. The coatings are a useful addition to the range of advanced materials and processes available for nuclear industry designers and engineers.