

**FLUID TIGHT LOW FRICTION COATING SYSTEMS FOR
DYNAMICALLY ENGAGING LOAD BEARING SURFACES**

Field of the Invention

[0001] The present invention generally relates to low friction, fluid impermeable novel protective coatings for a variety of applications. Particularly, the coatings offer low friction and enhanced fluid impermeability for engaging surfaces of gate and seat components.

Background of the Invention

[0002] Gate valves are typically used when a straight-line flow of fluid and minimum flow restriction are required. Gate valves are an integral part of wellhead assemblies and piping systems utilized in various supply and pump lines, including oil and gas exploration and production where pressures may range from 5,000 to 30,000 psi or greater. Gate valves consist of a valve body located axially in piping through which fluid flows. Within the valve body is a gate, which is typically a solid metallic component with an aperture extending through the component. In operation, the gate typically slides between two seats, which are circular annulus components having an inside diameter approximately equal to the diameter of the aperture in the gate. The seats are coaxially aligned with and directly or indirectly attached to the ends of the pipe or tubing and in a fixed position thereto, within which the valve is located. When the aperture in the gate is aligned with the holes in the seats, the gate valve is fully open, and the fluid flows freely through the valve. The term "fluid" as used herein and throughout the specification is intended to refer to a liquid, slurry, gas or vapor. When the aperture in the gate is partially or completely misaligned with seats, the gate valve is partially or fully closed, and the fluid flow is impeded or interrupted. When the valve is partially or fully closed, fluid pressure on the upstream side of the valve also presses the gate against the seat on the downstream side.

[0003] An actuator is typically utilized to enable sliding of the gate between the seats. The actuation can be manual, hydraulic or pneumatic. The actuation must be able to generate a sufficient amount of force to overcome static

and dynamic frictional forces between the seats and the gate. The gate and seat components have a tendency to stick, adhere or cold weld to each other, thereby resulting in high frictional forces. Additionally, the frictional forces can become even larger at higher fluid operating pressures for oil and gas supply and pump lines.

[0004] Wear and corrosion is also a problem for oil and gas applications. As a result, the gate valve must be made of corrosion resistant materials, particularly the seats and gate where corrosion of the surfaces exacerbates wear and frictional problems.

[0005] As a result of the tendency for such gate valves to be exposed to harsh conditions which can degrade its structural integrity, various protective coatings have been employed. For example, lubricative coatings have been utilized on the sealing faces of the gates and/or seats. Polymeric materials such as thermoplastics have been applied onto at least one of the surfaces to reduce friction and impart lubricity. However, such coatings have proven unacceptable, as frictional problems may develop over time and eventually increase to an enhanced level that can result in sticking or uneven movement of the valve gate during operation. The loss of lubrication can lead to unacceptable valve torques which may lead to local deformation and/or galling of mating surfaces.

[0006] Wear resistant coatings such as WCCrCo are another type of protective coating routinely utilized. While the wear resistant coatings have proven successful at lower operating pressure regimes of 15,000 psi or less, they are typically inadequate as the oil supply and pump lines approach higher pressures. In particular, gas leakage through the coatings can occur. Additionally, the coatings lose their lubricity and exhibit galling, thereby rendering such coatings inadequate.

[0007] Failure to utilize a coating having adequate fluid impermeability, in combination with adequate wear resistance and lubrication of the gate and seats components can, among other problems, lead to unacceptable galling and potential localized deformation, thereby causing leakage of fluid through the coating and eventually through the valve.

[0008] In view of the drawbacks of conventional coatings, there is an unmet need for an improved protective coating system that offers superior performance over conventional coating materials for gate and seat components, including improved wear resistance, lubricity and sealing properties over a wide range of operating pressures and temperatures.

Summary of the Invention

[0009] The invention may include any of the following aspects in various combinations and may also include any other aspect of the present invention described below in the written description.

[00010] In a first aspect, a protective coating system is provided. A protective coating system comprising: an underlying carbide-based thermal spray compositional layer overlying at least one or more sealing surfaces; a low friction layer applied onto an outer portion or free surface of said underlying carbide-based thermal spray composition, said low friction layer having a predetermined thickness; a polymeric or non-polymeric sealant compatible with said low friction layer and said underlying carbide-based thermal spray composition, said polymeric sealant penetrating into the predetermined thickness of the diamond-like carbon layer and optionally into at least a portion of the underlying carbide-based thermal spray composition; wherein said coating is characterized by fluid-tight impermeability and a reduced coefficient of friction at elevated operating pressures.

[00011] In a second aspect, a protective coating system prepared by the process comprising: thermal spraying a carbide-based coating layer onto a sealing surface; applying a diamond-like carbon layer by WC-CoCr, WC-Co, WC-Ni, and Chromium Carbide-NiCr; impregnating the diamond-like carbon layer with a polymeric or non-polymeric sealant; and forming a fluid impermeable coating.

[00012] In a third aspect, A surface treated apparatus comprising: a gate valve including a cavity and a flow passage extending along an interior of said body and traversing said cavity; said valve further defined at least in part by a seat and a gate, said seat affixed to the body at a location defined by an intersection of

said cavity and said flow passage; said gate having an engaging face that slidably engages with a corresponding face of said seat; wherein at least one of said engaging face of gate and seat is coated with a protective coating system comprising a carbide-based thermal spray composition; said coating further comprising a diamond-like carbon layer applied onto an outer portion of said carbide-based thermal spray composition, said diamond-like carbon layer having a predetermined thickness; and said coating further comprising a polymeric or non-polymeric sealant penetrating into the predetermined thickness of the diamond-like carbon layer and optionally at least a portion of the carbide-based thermal spray composition.

[00013] Other aspects, features and embodiments of the disclosure will be more fully apparent from the ensuing description and appended claims.

Brief Description of the Drawings

[00014] The objectives and advantages of the invention will be better understood from the following detailed description of the preferred embodiments thereof in connection with the accompanying figures wherein like numbers denote same features throughout and wherein:

[00015] Figure 1 shows a cross-sectional view of a gate valve with the gate disengaged from the seat to allow fluid flow through the passageway;

[00016] Figure 2 shows a test set-up of a twist compression test employed to replicate frictional behavior incurred by opening and closing of gate valves;

[00017] Figure 3 shows a test set-up employed to replicate high pressure leakage which may be encountered by gate valves utilized in oil and gas applications;

[00018] Figure 4 shows an unsealed Super D-gun® coating (deposited from a powder comprising tungsten carbide-cobalt-chromium material and 5 to 35 weight percent of a cobalt alloy) that exhibited leakage through the coating at less than 1,000 psi pressure during testing performed as described in Comparative Example 1;

[00019] Figure 5 shows an unsealed Super D-gun® coating (deposited from a powder comprising tungsten carbide-cobalt-chromium material and 5 to 35 weight percent of a cobalt alloy) and with a diamond-like carbon layer that exhibited leakage through the coating at an applied pressure of less than 1,000 psi during testing performed as described in Comparative Example 2;

[00020] Figure 6 shows a protective coating composition of the present invention (Super D-gun® coating deposited from the powder comprising tungsten carbide-cobalt-chromium material and 5 to 35 weight percent of a cobalt alloy with a diamond-like carbon layer which was then sealed after application of the diamond-like carbon layer) that exhibited an absence of leakage through the coating at an applied pressure of 10,000 psi during testing performed as described in Example 1;

[00021] Figure 7 shows a graphical relationship of the effects of coefficient of friction upon incorporating a diamond-like carbon material into a thermal spray coating whereby the diamond-like carbon material was applied over a WC-CoCr HVOF coating and tested against a WC-CoCr HVOF coating at 10 ksi contact pressure with no grease;

[00022] Figure 8 shows a graphical relationship of the effects of coefficient of friction upon incorporating a diamond-like carbon material into a thermal spray coating, whereby the diamond-like carbon material was applied over a WC-CoCr HVOF coating and tested against a WC-CoCr HVOF coating at 30 ksi contact pressure with grease;

[00023] Figure 9 shows a graphical relationship of the effects of coefficient of friction when utilizing a coating of the present invention, whereby a diamond-like carbon material was applied over a Super D-gun® coating deposited from a powder comprising tungsten carbide-cobalt-chromium material and 5 to 35 weight percent of a cobalt alloy and tested against a WC-CoCr HVOF coating at 10 ksi contact pressure with no grease; and

[00024] Figure 10 shows a graphical relationship of the effects of coefficient of friction when utilizing a coating of the present invention, whereby a diamond-like carbon material was applied over a Super D-gun® coating

(comprising tungsten carbide-cobalt-chromium material and 5 to 35 weight percent of a cobalt alloy) and tested against a WC-CoCr HVOF coating at 30 ksi contact pressure with grease.

Detailed Description of the Invention

[00025] The disclosure is set out herein in various embodiments, and with reference to various features and aspects of the invention. The disclosure contemplates such features, aspects and embodiments in various permutations and combinations, as being within the scope of the disclosure. The disclosure may therefore be specified as comprising, consisting or consisting essentially of, any of such combinations and permutations of these specific features, aspects and embodiments, or a selected one or ones thereof.

[00026] Unless indicated otherwise, all compositions herein are in weight percent, not including unavoidable trace contaminants.

[00027] The present invention relates to novel protective coatings which are defined at least in part by their low friction and fluid impermeability for a variety of applications. The coatings are particularly suitable for maintaining structural integrity of load bearing surfaces, such as the gate and seat surfaces of a gate valve. The coatings offer improved and sustained wear resistance, corrosion protection and the ability to create and maintain lubricity and a substantially impermeable seal through the coating and along one or more load bearing surfaces which, during operation, engage with other sealing surfaces at elevated service pressures, such as for example, 5,000 psi to 30,000 psi or more. In this regard, the present invention represents a significant improvement over conventional coatings and coating systems for gate and seat components, both of which are susceptible to leakage during service, and therefore not able to maintain a seal. As today's oil and gas applications continue to require higher operating pressures and temperatures, conventional coatings and coatings systems are unable to create and maintain the necessary seal and lubricity on the engaging surfaces of a gate and seat that are subject to ever increasing loads for prolonged periods of time.

[00028] In one embodiment of the present invention, a protective coating system is provided having various constituents, including a carbide-based thermal spray composition; a low friction layer of material; and a polymeric sealant. Each of the constituents is chemically and physically compatible with each other, thereby eliminating deleterious degradation reactions which could potentially affect the structural integrity of the protective coating system. It should be understood that the term “layer” as used herein and throughout the specification is intended to refer to one or more layers which can be discrete or continuous.

[00029] The carbide-based thermal composition overlies a sealing surface of a substrate. The carbide-based thermal composition is characterized as a hardened layer that provides wear resistance and corrosion resistance. In a preferred embodiment, the carbide-based composition is derived from a powder blend of a tungsten carbide-cobalt chromium material and a metallic cobalt alloy (i.e., carbide-cobalt), whereby the tungsten carbide-cobalt-chromium material has a formulation that comprises tungsten carbide-5% to 20% cobalt and 0% to 12% chromium, and more preferably about 8% to 13% cobalt and 0% or 4% to 10% chromium. Details of the tungsten carbide-cobalt chromium material blended with the metallic cobalt alloy (i.e., carbide-cobalt) are described in U.S. Patent No. 6004372, which is incorporated herein by reference in its entirety. Other carbide-based compositions are also contemplated by the present invention.

[00030] The metallic alloy is preferably a cobalt alloy with a formulation which comprises 27% to 29% chromium, 7% to 9% tungsten, 0.8% to 1.2% carbon and the balance cobalt. More preferably, the cobalt alloy comprises cobalt-28% chromium-8% tungsten-1% carbon. Other metallic alloys are contemplated by the present invention, including, but not limited to, a metallic alloy composition comprising 25% to 31% molybdenum, 14% to 20% chromium, 1% to 5% silicon, less than 0.08% carbon, and the balance cobalt. Still further, another metallic alloy is a cobalt alloy having a formulation of cobalt-28% molybdenum-17% chromium-3% silicon-less than 0.08% carbon. Various carbide-cobalt thermal spray compositions are contemplated, including those

selected from the group consisting of WC-CoCr, WC-Co, WC-Ni, and Chromium Carbide-NiCr.

[00031] Preferably, the blend comprises 5% to 35% metallic cobalt alloy, and more preferably 10% to 30% metallic cobalt alloy. The tungsten carbide-cobalt-chromium material can be made by various suitable processes, including, by way of example, a cast and crush powder manufacturing technique which is preferred when the chromium content is approximately 0%. Alternatively, a sintering process is preferred when the chromium content is from about 2% to 12%. The metallic cobalt alloy may be produced by any known method, including vacuum melting and inert gas atomization.

[00032] The carbide-based thermal composition can be applied onto any type of substrate. Preferably, the composition is the carbide-cobalt blended powder, which is applied onto a sealing surface of a substrate by a suitable thermal spray processes. The thermal spray process may include a detonation gun deposition process, such as a D-gun™ or Super-D gun® processes which are used to produce the coating onto the sealing surface of the substrate. Details for the detonation processes are described in U.S. Patent Nos. 4626477; 4826734; 4902539; 4999255; 5326645; 5652028; 5700423; and 5741556, each of which is incorporated herein by reference in its entirety. The carbide-cobalt powder is preferably sized to less than 325 U.S. standard screen mesh (44 micrometers) and the metallic cobalt alloy sized to less than 270 mesh (60 micrometers), but greater than 325 mesh (44 micrometers) by screening. It should be understood that other thermal spray deposition techniques can be utilized with the present invention.

[00033] The second constituent of the protective coating system is a low friction coating. In a preferred embodiment, the low friction coating is a diamond-like carbon layer (DLC). The DLC is applied onto an outer portion or free surface of the carbide-based thermal coating composition to thereby create a DLC coating region overlying the carbide-based thermal composition. The DLC has a predetermined thickness, which ranges from about 1 to 4 microns, preferably from about 1 to 3 microns, and more preferably from about 2 to 3 microns. Incorporation of the DLC at the predetermined thickness substantially

lowers the friction of the underlying carbide-based thermal composition in a manner that imparts lubricity to the exposed regions of the protective coating system without deleteriously impacting wear resistance and corrosion resistance properties of the carbide-based thermal composition. The result is a reduction in friction between the gate and seat components. Representative examples of DLC materials include, but are not limited to, hydrogenated amorphous carbon (designated as "a-C:H") and hydrogenated tetrahedral amorphous carbon (designated as "ta-C:H"). DLC coatings may be deposited by any suitable technique, and advantageously at temperatures not exceeding 400 F so as to not affect substrate and coating material properties.

[00034] The present invention has discovered that a low friction material, such as a DLC, in combination with a carbide-based thermal composition does not adequately create and maintain a fluid-tight (i.e., substantially impermeable) seal of a gate valve (as shown by the representative example in Figure 1) during its service life. The inability to form a fluid-tight seal can be more problematic when service or operating pressures increase beyond 5000 psi to moderate levels or elevated levels approaching 30,000 psi or greater. Additionally, corrosive fluids and sustained service life (i.e., repeated cycles of opening and closing of gate valve 11) exacerbates the problem. As will be shown in the working examples, coatings which incorporate a DLC cannot form an impermeable fluid-tight seal at moderate or elevated pressures.

[00035] In this regard, the protective coating system of the present invention is formulated with a specific type of polymeric or non-polymeric sealant. The sealant is impregnated into the low friction layer and optionally the carbide layer. Preferably, the sealant layer is impregnated into both the low friction layer and the carbide layer. The sealant flows within the pores of the low friction layer and penetrates into the low friction layer and, preferably, the carbide based thermal sprayed layer. The sealant is able to penetrate from the outer free surface of the low friction layer and into the pores, thereby not increasing the overall thickness of the coating system. The end result is a fluid-tight protective coating system that is achieved without compromising lubricity of the low friction

layer. The working examples that will be discussed below quantify the improved performance of the protective coating system of the present invention in comparison to conventional coatings and coating systems.

[00036] Sealants suitable for the present invention include polymeric (i.e., thermoplastic or thermoset) as well as non-polymeric sealants. Typical organic sealants useful in this invention, include but are not limited to, epoxies (e.g., Bisphenol A, Bisphenol F, Novolac, Aliphatic, and Glycidylamine), silicones, phenolics, polyamide-imides, fluoro-resins, urethanes and vinyls. Typical inorganic sealants useful in the present invention include, but are not limited to, phosphates, chromates, silicates and chromic acid. Preferably, the sealant is Bisphenol A based epoxy resin.

[00037] Selection of a suitable sealant is dependent upon several factors, including chemical and physical compatibility of the sealant with the low friction layer; the specific type of carbide-based thermal spray coating; the gate valve service temperature; and the degree of porosity of the low friction layer.

[00038] The sealant is considered the third constituent to be added into the low friction layer and/or underlying carbide-based layer. The sealant is added after formation of each of the underlying carbide-based layer and the low friction layer. The sealant is preferably applied onto the low friction layer by brushing or dipping followed by curing at room temperature for a minimum of 8 hours.

[00039] The protective coating system of the present invention is suitable for any substrate surface, including, by way of example, and not intending to be limiting, aviation components in which the cylinders or their mating surfaces (bushings or bearings) are at least partially coated. Additionally, the coating systems of the present invention are particularly suitable for metallic load bearing surfaces, including, but not limited to, gate and seat components of the gate valves for the oil and gas industry. Referring to Figure 1, the coating system can be applied to the engaging surfaces 2 and 3 of both seats. Alternatively, the coating system can be omitted from the gate 1 or engaging surfaces 2 and 3 of both seats. Unlike conventional materials, the coating systems of the present invention achieves and prevents fluid leakage through the coating, without adversely

impacting lubricity, wear resistance and corrosion resistance during the service life of the gate valve 4. In operation, when moving the gate 1 across the faces 2 and 3 of the seats, the protective coating system provides for a reduced coefficient of friction, reduced wear, and galling prevention while creating and maintaining a fluid-tight seal through the coating when the gate valve 4 is moved down into the closed position with seat faces 2 and 3. As the working examples will show, such properties remain even after numerous cycles.

[00040] Preferably, the coating system of the present invention is applied onto the engaging faces of the seats 2 and 3 and the gate faces 1a and 1b. Specific pairings on the faces 2 and 3 of the seats and the gate faces 1a and 1b can include a Super D-gun® coating that is derived from a powder blend of a tungsten carbide-cobalt chromium material and a metallic cobalt alloy applied to a seat surface in combination with a HVOF (high velocity oxygen fuel) deposited tungsten carbide-cobalt chromium coating applied to a gate surface.

[00041] It should be understood that variations are contemplated. For example, the protective coating system may be applied onto either of the faces 2 and 3 for the seats and gate 1 while the other face is coated with only a carbide-based thermal spray composition that is optionally coated with a low friction layer. Alternatively, the protective coating system of the present invention can be applied to one of the surfaces with the other surface including no protective coating.

[00042] As will be shown and discussed below in the Working Examples, several experiments were performed to compare the protective coatings of the present invention with other conventional materials. The criteria for a successful protective coating system were dependent upon its ability to achieve and create a fluid tight impermeable seal while maintaining a low coefficient of friction.

[00043] The experiments simulated high pressure conditions typically encountered by gate valves utilized in oil and gas applications. A twist compression test was used to replicate frictional behavior incurred by opening

and closing of gate valves. The friction behavior of different coating systems was investigated using a twist compression test at 10,000 psi contact pressure with no lubrication and at 30,000 psi contact pressure with grease lubrication. The schematic of the test-up is shown in Figure 2. The coating to be tested was applied between the annular sample substrate and the flat sample substrate as shown in Figure 2. The test was performed with an annular cylinder which was driven by a hydraulic motor brought into contact with a flat sample. When the desired pressure had been generated, the annular sample was rotated. Torque transmission between a rotating annular cylinder and a flat sample was measured. Data was collected electronically and the coefficient of friction was calculated from the ratio of transmitted torque to applied pressure.

[00044] A second test set-up as shown in Figure 3 was used to replicate high pressure leakage, which may be encountered by gate valves utilized in oil and gas applications. High pressure leak testing was used to investigate the gas leakage through the coating. The test consisted of subjecting a portion of a coated sample to nitrogen at a pressure of 10,000 psi for a minimum of 10 min as shown by the arrows in Figure 3 while another portion of the coated sample was submitted to atmospheric pressure and covered with a thin layer of soapy water. If the coating was permeable to the nitrogen gas, bubbles were observed on the coating surface during the test.

COMPARATIVE EXAMPLE 1 (leak test for carbide-based thermal spray composition – fig4)

[00045] A powder blend of a tungsten carbide-cobalt chromium material and a metallic cobalt alloy was employed to produce a coating using a Super D-gun® coating process. The coating was applied to the test sample having a diameter of approximately 2.8 inches and a thickness of approximately 1.5 inches. No low friction layer was applied, and no sealant was impregnated into the coating system.

[00046] A high pressure leak test was conducted. A significant amount of bubbles was observed along the periphery of the test sample as shown in Figure 4

at an applied pressure of less than 1,000 psi. The large amount of bubbles was an indication of the inability of the coating to prevent leakage at low pressures. No sealant was impregnated into the coating.

COMPARATIVE EXAMPLE 2 (leak test for carbide-based thermal spray composition + DLC – fig 5)

[00047] A powder blend of a tungsten carbide-cobalt chromium material and a metallic cobalt alloy was employed to produce a coating using a _Super D-gun® coating process. The coating was applied to the test sample having a diameter of approximately 2.8 inches in diameter and a thickness of approximately 1.5 inches. Next, a low friction layer of DLC was applied to the sample by a Plasma activated chemical vapor deposition (Pa CVD) process. No sealant was impregnated into the coating system.

[00048] A high pressure leak test was conducted to the resultant coating. A significant amount of bubbles was observed along the periphery of the tested sample as shown in Figure 5 at an applied pressure of less than 1000 psi. The large amount of bubbles was an indication of the inability of the coating with DLC to prevent leakage at low pressures.

COMPARATIVE EXAMPLE 3 (Friction test for carbide-based thermal spray composition (HVOF) at 10,000 psi – fig 7 red line)

[00049] The frictional behavior of a thermal spray coating system was evaluated using the twist compression test at 10,000 psi contact pressure with no lubrication. The coating to be tested was a HVOF WC-CoCr coating, which was applied to both the annular sample substrate and the flat sample substrate. When a pressure of 10,000 psi was generated, the annular sample was rotated. Torque transmission between a rotating annular cylinder and a flat sample was measured, and the coefficient of friction was calculated from the ratio of transmitted torque to applied pressure.

[00050] Figure 7 shows the results in a graphical format. The coating system exhibited a stabilized coefficient of friction of about 0.720, which was considered unacceptably high for intended applications.

COMPARATIVE EXAMPLE 4 (friction test for carbide-based thermal spray composition (HVOF) + DLC at 10,000 psi – fig 7 orange line)

[00051] The frictional behavior of the thermal spray coating system of Comparative Example 3 with the addition of a DLC onto the HVOF coated annular sample was evaluated using the twist compression test at 10,000 psi contact pressure with no lubrication. The DLC was applied onto the surface by Pa CVD. When a pressure of 10,000 psi was generated, the annular sample was rotated. Torque transmission between a rotating annular cylinder and a flat sample was measured, and the coefficient of friction was calculated from the ratio of transmitted torque to applied pressure.

[00052] Figure 7 shows the results in a graphical format. The coating system stabilized to a coefficient of friction value of about .585. This was notably lower than that of Comparative Example 3. The results indicated that the DLC served as a low friction layer that reduced the overall coefficient of friction of the coating system. However, the coefficient of friction was still considered inadequate.

COMPARATIVE EXAMPLE 5 (friction test for carbide-based thermal spray composition (HVOF) at 30,000 psi – fig 8 red line)

[00053] The frictional behavior of a thermal spray coating system was evaluated using the twist compression test at about 30,000 psi contact pressure with grease. The coating to be tested was a HVOF WC-CoCr coating, which was applied to both the annular sample substrate and the flat sample substrate. When a pressure of 30,000 psi was generated, the annular sample was rotated. Torque transmission between a rotating annular cylinder and a flat sample was measured, and the coefficient of friction was calculated from the ratio of transmitted torque to applied pressure.

[00054] Figure 8 shows the results in a graphical format. The coefficient of friction between the annular substrate and flat sample substrate exponentially increased without stabilizing during the test.

COMPARATIVE EXAMPLE 6 (friction test for carbide-based thermal spray composition (HVOF) + DLC at 30,000 psi – fig 8 orange line)

[00055] The frictional behavior of the thermal spray coating system of Comparative Example 4 with the addition of a DLC onto the HVOF coated annular sample was evaluated using the twist compression test at 30,000 psi contact pressure with grease. The DLC was applied onto the surface by PaCVD. When a pressure of 30,000 psi was generated, the annular sample was rotated. Torque transmission between a rotating annular cylinder and a flat sample was measured, and the coefficient of friction was calculated from the ratio of transmitted torque to applied pressure.

[00056] Figure 8 shows the results in a graphical format. The coating system gradually increased to a value of .140. At 30,000 psi grease was used, while at 10,000 psi test was performed at dry conditions. The results indicated that the DLC served as a low friction layer that reduced the overall coefficient of friction of the coating system.

COMPARATIVE EXAMPLE 7 (friction test for carbide-based detonation gun thermal spray composition (Super D-gun) at 10,000 psi – fig 9 red line)

[00057] The frictional behavior of a thermal spray coating system was evaluated using the twist compression test at 10,000 psi contact pressure with no lubrication. The coating to be tested was a Super D-gun® coating derived from a powder blend of a tungsten carbide-cobalt chromium material and a metallic cobalt alloy. The Super D-gun® coating was deposited onto the annular sample substrate. The other coating was a HVOF WC-CoCr coating that was deposited onto the flat sample substrate. When a pressure of 10,000 psi was generated, the annular sample was rotated. Torque transmission between a rotating annular

cylinder and a flat sample was measured, and the coefficient of friction was calculated from the ratio of transmitted torque to applied pressure.

[00058] Figure 9 shows the results in a graphical format. The coating system gradually increased in coefficient of friction during the course of the test.

COMPARATIVE EXAMPLE 8 (friction test for carbide-based detonation gun thermal spray composition (Super D-gun) at 30,000 psi – fig 10 red line)

[00059] The frictional behavior of a thermal spray coating system was evaluated using the twist compression test at about 30,000 psi contact pressure with grease. The coating to be tested was a Super D-gun® coating derived from the powder blend of a tungsten carbide-cobalt chromium material and a metallic cobalt alloy. The Super D-gun® coating was deposited onto the annular sample substrate. The other coating was a HVOF WC-CoCr coating which was deposited onto the flat sample substrate. When a pressure of 30,000 psi was generated, the annular sample was rotated. Torque transmission between a rotating annular cylinder and a flat sample was measured, and the coefficient of friction was calculated from the ratio of transmitted torque to applied pressure.

[00060] Figure 10 shows the results in a graphical format. The coating system exponentially increased in its coefficient of friction during the course of the test.

EXAMPLE 1 (leak test for present invention – fig 6)

[00061] A powder blend of a tungsten carbide-cobalt chromium material and a metallic cobalt alloy was employed to produce a coating using a Super D-gun® coating process. The coating was applied to the test sample having a diameter of approximately 2.8 inches and a thickness of approximately 1.5 inches. A low friction layer of DLC was applied onto the underlying coating. The DLC was applied by PaCVD.

[00062] A high pressure leak test was conducted. No bubbles were observed along the periphery of the tested sample as shown in Figure 6 at an applied pressure of 10,000 psi after 10 minutes of testing. The lack of bubbles at high pressure was an indication of the ability of the coating with DLC and with sealant to prevent leakage.

EXAMPLE 2 (friction test for present invention at 10,000 psi – fig 9 orange line)

[00063] The frictional behavior of the inventive thermal spray coating system was evaluated using the twist compression test at 10,000 psi contact pressure with no lubrication. The coating to be tested was a Super D-gun® coating derived from a powder blend of a tungsten carbide-cobalt chromium material and a metallic cobalt alloy. The Super D-gun® coating was deposited onto the annular sample substrate. The other coating was a HVOF WC-CoCr coating which was deposited onto the flat sample substrate. A low friction layer of DLC was applied onto the underlying Super D-gun® coating. The DLC was applied by the Pa CVD process.

[00064] When a pressure of 10,000 psi was generated, the annular sample was rotated. Torque transmission between a rotating annular cylinder and a flat sample was measured, and the coefficient of friction was calculated from the ratio of transmitted torque to applied pressure.

[00065] Figure 9 shows the results in a graphical format. The coating system maintained an acceptably low coefficient of friction of .090 during the entire duration of the test.

EXAMPLE 3 (friction test for present invention at 30,000 psi – fig 10 orange line)

[00066] The frictional behavior of an inventive thermal spray coating system was evaluated using the twist compression test at 30,000 psi contact pressure with grease. The coating to be tested was a Super D-gun® coating derived from a powder blend of a tungsten carbide-cobalt chromium material and a metallic cobalt alloy. The Super D-gun® coating was deposited onto the annular sample substrate. The other coating was a HVOF WC-CoCr coating, which was deposited onto the flat sample substrate. A low friction layer of DLC was applied onto the underlying coating Super D-gun® coating. The DLC was applied by a PaCVD process.

[00067] When a pressure of 30,000 psi was generated, the annular sample was rotated. Torque transmission between a rotating annular cylinder and a flat sample was measured, and the coefficient of friction was calculated from the ratio of transmitted torque to applied pressure.

[00068] Figure 10 shows the results in a graphical format. The coating system maintained an acceptably low coefficient of friction of .100 during the entire duration of the test.

[00069] While it has been shown and described what is considered to be certain embodiments of the invention, it will, of course, be understood that various modifications and changes in form or detail can readily be made without departing from the spirit and scope of the invention. It is, therefore, intended that this invention not be limited to the exact form and detail herein shown and described, nor to anything less than the whole of the invention herein disclosed and hereinafter claimed.

CLAIMS

1. A protective coating system comprising:
 - an underlying carbide-based thermal spray compositional layer overlying at least one or more sealing surfaces;
 - a low friction layer applied onto an outer portion or free surface of said underlying carbide-based thermal spray composition, wherein said low friction layer is a diamond-like carbon material (DLC) having a predetermined thickness;
 - a polymeric or non-polymeric sealant compatible with said low friction layer and said underlying carbide-based thermal spray composition, said polymeric sealant penetrating into the predetermined thickness of the diamond-like carbon layer and optionally into at least a portion of the underlying carbide-based thermal spray composition;
 - wherein said coating is characterized by fluid-tight impermeability and a reduced coefficient of friction at elevated operating pressures; and
 - wherein said coating is coated on a sealing surface and a second coating is applied onto a corresponding sealing surface, wherein said second coating is selected from the group consisting of WC-CoCr, WC-Co, WC-Ni, Chromium Carbide-NiCr and cobalt-based metallic alloys.
2. The protective coating system of claim 1, wherein said carbide-based thermal spray coating consists essentially of powder blend of a tungsten carbide-cobalt chromium material and 5 wt% to 35 wt% of a metallic cobalt alloy.
3. The protective coating system of claim 1, wherein said at least one or more sealing surfaces are a gate component or a seat component.
4. The protective coating system of claim 1, wherein said carbide-based thermal spray composition is selected from the group consisting of WC-CoCr, WC-Co, WC-Ni, Chromium Carbide-NiCr and cobalt-based metallic alloys.

5. The protective coating system of claim 1, wherein said DLC has a thickness of 1 to 4 μm .
6. A surface treated apparatus comprising:
 - a gate valve including a cavity and a flow passage extending along an interior of said body and traversing said cavity;
 - said valve further defined at least in part by a seat and a gate, said seat affixed to the body at a location defined by an intersection of said cavity and said flow passage;
 - said gate having an engaging face that slidably engages with a corresponding face of said seat;
 - wherein said engaging face of gate and seat are coated with the protective coating system of any one of the preceding claims.