MECHANICAL PART WITH A NANOSTRUCTURED TiO2-Cr2O3 CERAMIC COATING AND METHOD FOR DEPOSITING A NANOSTRUCTURED TiO2-Cr2O3 CERAMIC COATING ON A SUBSTRATE

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Abstract
There is provided a method for depositing a TiO2-Cr2O3 ceramic coating on a substrate. The method includes mixing a powder of sprayable nanostructured titanium(IV) oxide (n-TiO2) and a powder of chromium(III) oxide (Cr2O3), thereby obtaining a n-TiO2-Cr2O3 powder blend. The method also includes thermal spraying particles of the n-TiO2-Cr2O3 powder blend on the substrate at an in-flight particle temperature of 2350°C and a particle in-flight velocity of or greater than 350 m/s, thereby obtaining a coated substrate.
MECHANICAL PART WITH A NANOSTRUCTURED TiO2-Cr2O3 CERAMIC COATING AND METHOD FOR DEPOSITING A NANOSTRUCTURED TiO2-Cr2O3 CERAMIC COATING ON A SUBSTRATE

CROSS-REFERENCE TO RELATED APPLICATIONS


TECHNICAL FIELD

[0002] This invention generally relates to the field of thermal spray coatings, and more particularly to nanostructured ceramic thermal spray coatings having a good resistance to abrasion, erosion or corrosion, as well as methods for their production and use.

BACKGROUND

[0003] Ceramics are known for being hard and stiff materials. Ceramic thermal spray coatings have been extensively used as anti-wear coatings, and are important to protect various mechanical parts of machines from harsh abrasive conditions encountered in corrosive processes such as Pressure Oxidation (POx) and High Pressure Acid Leach (HPAL), notably in hydrometallurgy applications.

[0004] Over the last two decades, metal-seated ball valves (MSBV) have become the industry standard for hydrometallurgy application, providing tight, reliable shut-off in this critical service which facilitates maintenance and contributes to a safe working environment. Typical MSBV design for this application consists of a floating ball in contact with a fixed seat. Ball and seats are manufactured with either titanium or duplex stainless steel substrates and protected with a ceramic coating. The primary function of the ceramic coating is to enhance the load carrying capacity and the tribological performance of the base material in order to extend the in-service life of the equipment, especially during ball motion phases.

[0005] Many thermal ceramic coatings have already been developed for protecting mechanical parts from harsh abrasive conditions. For example, conventional Cr2O3 applied by Air Plasma Spray (APS) was the coating selected 20 years ago to protect MSBV’s against the extreme abrasion, pressure and elevated temperature inherent to the Pressure Oxidation (POx) recovery process used for gold wherein the ore is mixed with oxygen and sulfuric acid into an autoclave. Over the years, silicon dioxide and titanium dioxide have been gradually added to the originally pure Cr2O3 in order to improve its ductility and toughness.

[0006] Conventional titanium(IV) dioxide (TiO2) and nanostructured titanium(IV) oxide (n-TiO2) coatings have also been proposed but they show limited mechanical and tribological performances, leading to high wear rates. Additionally, it has also been shown that blends of conventional TiO2 and Cr2O3 (TiO2-Cr2O3) offer superior tribological performances compared to TiO2, mainly due to the presence of Cr2O3. Optimized balance between the hard and brittle Cr2O3 phases and the soft and ductile conventional TiO2 phases yields to higher abrasion, sliding and galling resistance.

[0007] However, despite the developments in thermal spray coatings, maintenance costs on coated parts such as balls and seats of industrial valves remain high. There is therefore still a need for an improved technology.

SUMMARY

[0008] According to a general aspect, there is provided a method for depositing a ceramic coating on a substrate, the method comprising: mixing a powder of sprayable nanostructured titanium(IV) oxide (n-TiO2) and a powder of chromium (III) oxide (Cr2O3), thereby obtaining a n-TiO2-Cr2O3 powder blend; and thermal spraying particles of the n-TiO2-Cr2O3 powder blend on the substrate at an average in-flight particle temperature of or greater than 2350° C. and an average particle in-flight velocity of or greater than 350 m/s, thereby obtaining a coated substrate.

[0009] In some implementations, the substrate is a metal substrate.

[0010] In some implementations, the metal substrate comprises one of titanium, a titanium alloy, stainless steel, steel, a high-performance nickel alloy, a high-performance cobalt alloy, bronze and a copper alloy.

[0011] In some implementations, the metal substrate comprises one of titanium and stainless steel.

[0012] In some implementations, the powder of sprayable n-TiO2 comprises nanosized constituents agglomerated and/or sintered in microsized n-TiO2 particles.

[0013] In some implementations, the nanosized constituents have a size ranging from 50 nm to 500 nm.

[0014] In some implementations, the microsized n-TiO2 particles have a diameter distribution ranging from 4 μm to 100 μm.

[0015] In some implementations, the n-TiO2-Cr2O3 powder blend comprises 40 wt % to 70 wt % of n-TiO2 and 30 wt % to 60 wt % of Cr2O3.

[0016] In some implementations, the n-TiO2-Cr2O3 blend comprises 50 wt % to 60 wt % of n-TiO2 and 40 wt % to 50 wt % of Cr2O3.

[0017] In some implementations, the n-TiO2-Cr2O3 blend comprises 53 wt % to 57 wt % of n-TiO2 and 45 wt % to 47 wt % of Cr2O3.

[0018] In some implementations, the n-TiO2-Cr2O3 blend comprises about 55 wt % of n-TiO2 and about 45 wt % of Cr2O3.

[0019] In some implementations, the thermal spraying is air plasma spraying (APS).

[0020] In some implementations, the average in-flight particle temperature is 2350° C. to 2800° C.

[0021] In some implementations, the average in-flight particle temperature is 2400° C. to 2800° C.

[0022] In some implementations, the average in-flight particle temperature is 2500° C. to 2800° C.

[0023] In some implementations, the average in-flight particle temperature is of about 2590° C.

[0024] In some implementations, the average particle in-flight velocity is greater than 400 m/s.

[0025] In some implementations, the average particle in-flight velocity is greater than 450 m/s.

[0026] In some implementations, the average particle in-flight velocity is about 457 m/s.

[0027] According to another general aspect, there is provided a mechanical part coated with a nanostructured tita-
nium(IV) oxide-chromium(III) oxide (n-TiO₂-Cr₂O₃) coating, the coating having a microhardness of at least 1000 HV and a dry abrasion volume loss of less than 15 mm³.

[0028] In some implementations, the microhardness is of at least 1150 HV.

[0029] In some implementations, the dry abrasion loss is less than 8.4 mm³.

[0030] In some implementations, the microhardness is between 1150 and 1250 HV and the dry abrasion loss is between 7 and 8.4 mm³.

[0031] In some implementations, the n-TiO₂-Cr₂O₃ coating comprises 40 wt % to 70 wt % of n-TiO₂ and 30 wt % to 60 wt % of Cr₂O₃.

[0032] In some implementations, the n-TiO₂-Cr₂O₃ coating comprises 50 wt % to 60 wt % of n-TiO₂ and 40 wt % to 50 wt % of Cr₂O₃.

[0033] In some implementations, the n-TiO₂-Cr₂O₃ coating comprises 53 wt % to 57 wt % of n-TiO₂ and 43 wt % to 47 wt % of Cr₂O₃.

[0034] In some implementations, the n-TiO₂-Cr₂O₃ coating comprises about 55wt % of n-TiO₂ and about 45wt % of Cr₂O₃.

[0035] In some implementations, the mechanical part is a valve element of a valve.

[0036] In some implementations, the valve element is a ball valve.

[0037] In some implementations, the ceramic coating is deposited using the method of described above.

[0038] According to another general aspect, there is provided a powder blend for use in thermal spraying for coating a substrate, the powder blend comprising 40 wt % to 70 wt % of n-TiO₂ and 30 wt % to 60 wt % of Cr₂O₃.

[0039] In some implementations, the powder blend comprises 50 wt % to 60 wt % of n-TiO₂ and 40 wt % to 50 wt % of Cr₂O₃.

[0040] In some implementations, the powder blend comprises 55 wt % to 57 wt % of n-TiO₂ and 43 wt % to 47 wt % of Cr₂O₃.

[0041] In some implementations, the powder blend comprises about 55 wt % of n-TiO₂ and about 45 wt % of Cr₂O₃.

BRIEF DESCRIPTION OF DRAWINGS

[0042] FIG. 1 includes FIG. 1A, 1B and 1C. FIG. 1A is a scanning electron micrograph showing a sprayable nanostructured n-TiO₂ powder; FIG. 1B is an XRD pattern of the sprayable nanostructured n-TiO₂ powder; and FIG. 1C is a graph representing the particle size distribution of the sprayable nanostructured n-TiO₂ powder.

[0043] FIG. 2 includes FIG. 2A and FIG. 2B. FIG. 2A is a x150 scanning electron micrograph of an electronic conventional prior art Cr₂O₃ coating; and FIG. 2B is a x1000 scanning electron micrograph of the same Cr₂O₃ coating.

[0044] FIG. 3 includes FIG. 3A and FIG. 3B. FIG. 3A is a x150 scanning electron micrograph of a conventional prior art TiO₂-Cr₂O₃ coating; and FIG. 3B is a x1000 scanning electron micrograph of the same TiO₂-Cr₂O₃ coating.

[0045] FIG. 4 includes FIG. 4A and FIG. 4B. FIG. 4A is a x150 scanning electron micrograph of a conventional prior art n-TiO₂ coating; and FIG. 4B is a x1000 scanning electron micrograph of the same n-TiO₂ coating.

[0046] FIG. 5 includes FIG. 5A and FIG. 5B. FIG. 5A is a x150 scanning electron micrograph of a n-TiO₂-Cr₂O₃ coating according to the invention; and FIG. 5B is a x1000 scanning electron micrograph of the same n-TiO₂-Cr₂O₃ coating.

[0047] FIG. 6 is a graph showing EDS spectra of Cr₂O₃, Cr₂O₃-TiO₂, n-TiO₂ and n-TiO₂-Cr₂O₃ coatings.

[0048] FIG. 7 is a graph showing and comparing the coefficient of friction as a function of the sliding distance for the Cr₂O₃, Cr₂O₃-TiO₂, n-TiO₂ and n-TiO₂-Cr₂O₃ coatings.

[0049] FIG. 8 is a graph showing and comparing the wear rate for the Cr₂O₃, Cr₂O₃-TiO₂, n-TiO₂ and n-TiO₂-Cr₂O₃ coatings.

[0050] FIG. 9 shows x50 photographs comparing the wear tracks after pin-on-disc tests for specimens coated with Cr₂O₃, Cr₂O₃-TiO₂, n-TiO₂ and n-TiO₂-Cr₂O₃.

[0051] FIG. 10 shows photographs comparing the wear tracks after dry abrasion tests for specimens coated with Cr₂O₃, Cr₂O₃-TiO₂, n-TiO₂ and n-TiO₂-Cr₂O₃.

[0052] FIG. 11 shows photographs comparing wear tracks after wet abrasion tests for specimens coated with Cr₂O₃, Cr₂O₃-TiO₂, n-TiO₂ and n-TiO₂-Cr₂O₃.

[0053] FIG. 12 shows a photograph and a schematic representation of the custom-designed and automated variable temperature galling tester used to measure the variable temperature galling resistance.

[0054] FIG. 13 is a graph showing and comparing the galling resistance of self-mated specimens after variable temperature galling resistance. Mass loss is given between 0 (initial mass) and 100 cycles (i.e. after step 0).

[0055] FIG. 14 includes FIG. 14A to FIG. 14H and shows photographs comparing wear patterns after variable temperature galling tests for fixed or rotating specimens coated with Cr₂O₃, Cr₂O₃-TiO₂, n-TiO₂ and n-TiO₂-Cr₂O₃.

DETAILED DESCRIPTION

[0056] A method for depositing a ceramic coating on a substrate is described. The method includes mixing a powder of sprayable nanostructured titanium(IV) oxide (n-TiO₂) and a powder of chromium(III) oxide (Cr₂O₃), thereby obtaining a n-TiO₂-Cr₂O₃ blend. The method also includes thermal spraying particles of the n-TiO₂-Cr₂O₃ blend on the substrate at an in-flight particle temperature greater than 2350°C and a particle in-flight velocity greater than 350 m/s, thereby obtaining a coated substrate.

[0057] As usual, the in-flight particle temperature and the particle in-flight velocity is measured at the spray distance i.e. the linear distance between the thermal spray torch nozzle and the substrate surface.

[0058] It should be understood that "thermal spraying" refers to a technique wherein melted (or heated) materials are sprayed onto a surface. The feedstock (or coating precursor) is heated by electrical (plasma or arc) or chemical means (combustion flame). The feedstock may be in the form of a powder, wires or a liquid/suspension containing the material to be sprayed. Thermal spraying includes different variations, such as air plasma spraying, detonation spraying, wire spraying, flame spraying, high velocity oxy-fuel spraying, warm spraying and cold spraying. Typically, a thermal spray system includes: a spray torch for performing the melting and acceleration of the particles to be deposited; a feeder for supplying the feedstock (powder, wire or liquid) to the torch, for example through tubes; and media supply such as gases or liquids for the generation of the flame or plasma jet, and optionally a carrier gas for carrying the powder feedstock, when applicable.

[0059] In some implementations, the substrate is a metal substrate. The metal substrate may include one of titanium, a titanium alloy, stainless steel, steel, a high-performance
nickel alloy, a high-performance cobalt alloy, bronze and a copper alloy. In some implementations, the substrate is a mechanical part which may be used in a mechanical assembly or a mechanical device. In some implementations, the mechanical part is of the type to be subjected to harsh abrasive conditions such as Pressure Oxidation (POx) and/or High Pressure Acid Leach (HPAL). For example, the mechanical part may be a ball or a seat of a ball-valve, or a valve element of a valve which is subjected to wear due to friction with other parts of the valve during movement. It is understood that the valve may be an industrial valve or any other type of valve. It is also understood that the mechanical part may be a suitable mechanical part used for example in autoclaves or other apparatus which can be subjected to harsh abrasive conditions.

Other non-limiting examples of mechanical parts include sucker rod couplings, autoclave impellers and pumps.

[0060] It should be understood that a “powder of sprayable nanostructured” component refers to the component in the form of a powder having microparticles comprising nanosized constituents, the particles being suitable for being thermally sprayed on a substrate. A “sprayable” component may also refer to a suspension (or slurry) including particles which are to be sprayed. In the case of a suspension, the liquid containing the particles is directly sprayed to form the coating. The liquid is evaporated under the effect of the high temperatures and the suspended particles can thereby form the coating.

[0061] In some implementations, the powder of sprayable n-TiO₂ comprises nanosized constituents agglomerated and/or sintered in microstructured TiO₂ particles, as can be seen in FIG. 1. The nanosized constituents may have a size ranging from 50 nm to 500 nm, and the microsized n-TiO₂ particles may have a diameter distribution ranging from 4 μm to 100 μm.

[0062] In some implementations, the powder of n-TiO₂ and the powder of Cr₂O₃ are mechanically mixed in order to obtain the n-TiO₂-Cr₂O₃ powder blend.

[0063] In some implementations, the n-TiO₂-Cr₂O₃ powder blend includes 40 wt% to 70 wt% of n-TiO₂ and 30 wt% to 60 wt% of Cr₂O₃. The n-TiO₂-Cr₂O₃ powder blend may also include 50 wt% to 60 wt% of n-TiO₂ and 40 wt% to 50 wt% of Cr₂O₃, or 30 wt% to 50 wt% of n-TiO₂ and 40 wt% to 50 wt% of Cr₂O₃. For example, the n-TiO₂-Cr₂O₃ blend may include 55 wt% of n-TiO₂ and 45 wt% of Cr₂O₃.

[0064] In some implementations, the thermal spraying is air plasma spraying (APS). Various parameters of the torch can be tuned so as to control the in-flight particle temperature and the particle in-flight velocity. The parameters of the torch can be tuned according to the Argon flow, H₂ flow and N₂ flow, as well as the current and spraying distance. While these parameters are dependent on the torch used, they help controlling the in-flight particle temperature and the particle in-flight velocity, which are the physical parameters of the particles during spraying.

[0065] As mentioned above, it is understood that the in-flight particle temperature and the particle in-flight velocity are both measured at the spray distance. By “measured at the spray distance”, it is meant the linear distance between the thermal spray torch nozzle and the substrate surface.

[0066] In some implementations, the in-flight particle temperature is greater than 150°C. For example, the average in-flight particle temperature may be 250°C to 2800°C, 240°C to 2800°C, 250°C to 2800°C, or about 2590°C. With a sample standard deviation of about 200 to 300°C, i.e. more or less 100°C, which represent the instrument error of the measuring instrument.

[0067] In some implementations, the average particle in-flight velocity is greater than 350 m/s, greater than 400 m/s, or greater than 450 m/s. For example, the average particle in-flight velocity may be about 457 m/s with a sample standard deviation of about 50 to 100 m/s, i.e. more or less 5 m/s, which represent the instrument error of the measuring instrument.

[0068] A substrate coated with a nanostructured titanium (IV) oxide- chromium(III) oxide (n-TiO₂-Cr₂O₃) coating is also described. The n-TiO₂-Cr₂O₃ coating may be deposited on the substrate using the method described above. These coatings have certain improved properties compared to the Cr₂O₃ coatings, conventional TiO₂-Cr₂O₃ blend coatings, or n-TiO₂ coatings known in the art.

[0069] For example, the n-TiO₂-Cr₂O₃ coating has a microhardness of at least 1000 HV and a dry abrasion volume loss of less than 15 mm³. In some implementations, the n-TiO₂-Cr₂O₃ coating has a microhardness of at least 1150 HV. In some implementations, the dry abrasion loss is less than 8.4 mm³. In some implementations, the microhardness is between 1150 and 1250 HV and the dry abrasion loss is between 7 and 8.4 mm³.

[0070] The values of microhardness are obtained as follows. Microhardness measurements were performed on coating polished cross-sections with a Bueller Micromet II Tester (Vickers Tip) under 100 gf load. For each specimen, a minimum of 12 indentations was performed (straight line pattern, at the center of the coating cross-section), and the highest and lowest values removed from the dataset.

[0071] The dry abrasion loss was measured as follows. Coating dry abrasion resistance was tested through dry sand/ rubber wheel abrasion test (ASTM G65/Procedure D-modified, 45 N, 2000 wheel revolutions, Durometer A-60 wheel). Two samples were tested for each coating type. Prior testing, the sample surfaces were ground with diamond wheel to produce a surface finish of about 0.2-0.3 μm i.e. more or less 0.05 μm, which represent the instrument error of the measuring instrument. Evaluation of the sample volume loss due to the test was performed with an optical profilometer.

EXAMPLES

Example 1

[0072] Base Materials

[0073] Experiments were performed by preparing several powders and powder blends to be used for Air Plasma Spray (APS) coating. An n-TiO₂-Cr₂O₃ powder blend was manufactured for coating substrates. Three (3) comparative powders/powder blends were also manufactured for coating substrates and for comparison with the properties of the n-TiO₂-Cr₂O₃ powder blend.

[0074] The following powder materials were selected, and obtained by mixing when applicable.

[0075] Comparative Material A: Cr₂O₃ powder supplied by Velan supplier.

[0076] Comparative Material B: TiO₂-Cr₂O₃ powder supplied by Velan supplier and obtained by mechanically mixing conventional TiO₂ powder with Material A.

[0077] Comparative Material C: nanostructured n-TiO₂ powder supplied by Millydine. This nanostructured n-TiO₂ powder is formed of nanosized constituents agglomerated
and sintered in bigger microsized particles to allow spraying. The n-TiO2 microstructure, XRD pattern and size distribution are shown in FIG. 1.

[0078] Material D: n-TiO2-Cr2O3 powder. Material D was obtained by mechanically mixing 55 wt% of n-TiO2 (Material C) with 45 wt% of a Cr2O3 powder (Metco™ 106). Metco 106 is a fused, sintered and crushed Cr2O3 powder.

Example 2

[0079] Deposition of the Materials

[0080] Experiments were performed to coat substrates with materials A, B, C and D of Example 1. All coatings were deposited by Air Plasma Spraying (APS). All coatings were applied onto titanium grade 5 coupons (compliant with ASTM B348) that were previously grit blasted (Al2O3—grit 24). A nominal coating thickness of 0.020" (500 μm) was targeted.

[0081] Materials A and B were deposited using an SG100 plasma spray torch from Praxair. Material C was deposited using a high power Mettech Axial III APS torch. The spraying parameters for coatings A, B and C are shown in Table 1 below.

### TABLE 1

<table>
<thead>
<tr>
<th>Torch</th>
<th>Cr2O3</th>
<th>TiO2—Cr2O3</th>
<th>n-TiO2—Cr2O3</th>
<th>Mettech Axial III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar flow (lpm)</td>
<td>53</td>
<td>53</td>
<td>37.5</td>
<td></td>
</tr>
<tr>
<td>H2 flow (lpm)</td>
<td>—</td>
<td>—</td>
<td>37.5</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 1-continued

<table>
<thead>
<tr>
<th>Torch</th>
<th>Coating A</th>
<th>Coating B</th>
<th>Coating C</th>
<th>Coating D</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-TiO2</td>
<td>Cr2O3</td>
<td>TiO2—Cr2O3</td>
<td>n-TiO2—Cr2O3</td>
<td>n-TiO2—Cr2O3</td>
</tr>
<tr>
<td>Torch</td>
<td>SG-100</td>
<td>SG-100</td>
<td>Mettech</td>
<td>Mettech</td>
</tr>
<tr>
<td>N2/He flow (lpm)</td>
<td>41 He</td>
<td>41 He</td>
<td>75 N2</td>
<td>75 N2</td>
</tr>
<tr>
<td>Current (A)</td>
<td>800</td>
<td>800</td>
<td>230*</td>
<td>230*</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>−42</td>
<td>−42</td>
<td>152</td>
<td>152</td>
</tr>
<tr>
<td>Power (kW)</td>
<td>33.6</td>
<td>33.6</td>
<td>105</td>
<td>105</td>
</tr>
<tr>
<td>Net Power (kW) or</td>
<td>—</td>
<td>—</td>
<td>15.0 kJ/L</td>
<td>15.0 kJ/L</td>
</tr>
<tr>
<td>Enthalpy (kJ/L)</td>
<td>—</td>
<td>—</td>
<td>3.8*</td>
<td>3.8*</td>
</tr>
</tbody>
</table>

*Current per electrode set—3 electrode sets in the torch.

**The standard deviation corresponds to the sample distribution, and not the experimental error.

***Approximation; velocity higher than the standardized range.

[0082] For Material D, the gas flows, current and spraying distances were varied in order to produce coatings with different structures and properties. The different spraying parameters used (coatings D1 to D4) are presented in Table 2 below. In-flight particle temperature and velocity are measured by the thermal spray sensor DPV 2000 (Tecnar Automation).

### TABLE 2

<table>
<thead>
<tr>
<th>Torch</th>
<th>Coating D1</th>
<th>Coating D2</th>
<th>Coating D3</th>
<th>Coating D4</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-TiO2</td>
<td>Cr2O3</td>
<td>TiO2—Cr2O3</td>
<td>n-TiO2—Cr2O3</td>
<td>n-TiO2—Cr2O3</td>
</tr>
<tr>
<td>Torch</td>
<td>Mettech Axial III</td>
<td>Mettech Axial III</td>
<td>Mettech Axial III</td>
<td>Mettech Axial III</td>
</tr>
<tr>
<td>Ar flow (lpm)</td>
<td>37.5</td>
<td>37.5</td>
<td>62.5</td>
<td>75.0</td>
</tr>
<tr>
<td>H2 flow (lpm)</td>
<td>37.5</td>
<td>37.5</td>
<td>62.5</td>
<td>30.0</td>
</tr>
<tr>
<td>N2/He flow (lpm)</td>
<td>75</td>
<td>75</td>
<td>125 N2</td>
<td>45.0</td>
</tr>
<tr>
<td>Current (A)</td>
<td>230*</td>
<td>230*</td>
<td>230*</td>
<td>230*</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>205</td>
<td>205</td>
<td>205</td>
<td>205</td>
</tr>
<tr>
<td>Power (kW)</td>
<td>141</td>
<td>141</td>
<td>141</td>
<td>141</td>
</tr>
<tr>
<td>Net Power (kW) or</td>
<td>18.2 kJ/L</td>
<td>18.2 kJ/L</td>
<td>18.2 kJ/L</td>
<td>18.2 kJ/L</td>
</tr>
<tr>
<td>Enthalpy (kJ/L)</td>
<td>3.8*</td>
<td>3.8*</td>
<td>3.8*</td>
<td>3.8*</td>
</tr>
</tbody>
</table>

*Current per electrode set—3 electrode sets in the torch.

**The standard deviation corresponds to the sample distribution, and not the experimental error.

***Approximation; velocity higher than the standardized range.
Example 3

Microstructure

Mirostructures of the coatings were obtained with a JSM-6100 SEM from JEOL or the FE-SEM Hitachi S4700, under back scattered electron (BSE) mode. EDS analyses were performed using JEOL JSM-840 SEM. Coatings were sectioned with a coolant-assisted diamond wheel and then cold vacuum mounted in an epoxy resin. Grinding and polishing were done using standard metallographic preparation procedures.

Microhardness, Toughness and Shear Strength

Microhardness and toughness values were measured for TiO$_2$-Cr$_2$O$_3$ coatings D1 to D4, and shown in Table 3 below. It was found that coating D3 exhibited the best microhardness and toughness properties and was then further compared to coatings A, B and C.

Table 3

<table>
<thead>
<tr>
<th>Coating</th>
<th>Microhardness (HV-300 gf, n = 10)</th>
<th>Toughness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>829 ± 52</td>
<td>222 ± 27</td>
</tr>
<tr>
<td>D2</td>
<td>902 ± 28</td>
<td>176 ± 13</td>
</tr>
<tr>
<td>D3</td>
<td>1200 ± 49</td>
<td>132 ± 10</td>
</tr>
<tr>
<td>D4</td>
<td>798 ± 18</td>
<td>254 ± 22</td>
</tr>
</tbody>
</table>

Coatings D1, D2, D3 and D4 are shown in Table 4 below. As expected, the highest microhardness is achieved when the hardest phase, Cr$_2$O$_3$, is primary used for the coating. The second highest coating in microhardness is the n-TiO$_2$-Cr$_2$O$_3$ coating D3.

Table 4

<table>
<thead>
<tr>
<th>Coating</th>
<th>Cr$_2$O$_3$</th>
<th>TiO$_2$-Cr$_2$O$_3$</th>
<th>n-TiO$_2$</th>
<th>n-TiO$_2$-Cr$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1423 ± 62</td>
<td>912 ± 42</td>
<td>729 ± 46</td>
<td>1200 ± 49</td>
</tr>
<tr>
<td>B</td>
<td>42 ± 7$^a$</td>
<td>46 ± 2$^b$</td>
<td>36 ± 2$^a$</td>
<td>38 ± 5$^a$</td>
</tr>
<tr>
<td>C</td>
<td>42 ± 7$^a$</td>
<td>46 ± 2$^b$</td>
<td>36 ± 2$^a$</td>
<td>38 ± 5$^a$</td>
</tr>
<tr>
<td>D3</td>
<td>42 ± 7$^a$</td>
<td>46 ± 2$^b$</td>
<td>36 ± 2$^a$</td>
<td>38 ± 5$^a$</td>
</tr>
</tbody>
</table>

*Adhesive failure (occurs at bond line with substrate)
$^a$Epoxy failure (glue)
$^b$Cohesive failure (failure within the coating)
$^c$Mix mode of all or partial of the above

Example 4

Energy Dispersive X-ray Spectroscopy (EDS)

EDS spectra acquired from the four coatings A, B, C and D3 are shown in Fig. 6. The chemical composition of each coating is confirmed.

Example 5

Mechanical Properties

Microhardness and shear strength were measured using respectively microhardness indentation testers and universal tensile testing equipment.

Microhardness measurements were performed on coating polished cross-sections with a Buehler Micromet II Tester (Vickers Tip) under 300 gf load. For each specimen, a minimum of 12 indentations was performed (straight line pattern, at the center of the coating cross-section), and the highest and lowest values removed from the dataset.

Coating adhesion on titanium substrates was assessed through shear tests (ASTM F1044). An Instron 5582 universal testing machine was used to determine the maximum shear loads required to obtain sample separation.

Toughness was measured by indenting the cross-section of the coatings using a Vickers tip and a load of 1 kgf, and then measuring the length of the cracks formed at the tip of the indentation. The shorter were the cracks, the tougher was the coating.

All coatings produced were found to provide good bonding to the substrate. The best coating adhesion in shear is achieved with TiO$_2$-Cr$_2$O$_3$ (coating B). Even though the variation in coating adhesion is relatively low, it can also be seen that n-TiO$_2$ and n-TiO$_2$-Cr$_2$O$_3$ (coatings C and D3) display lower adhesion. This is believed to be due to the higher thickness of those coatings. Thicker thermal sprayed coatings typically display lower adhesion due to the buildup of residual stresses.
Example 6

[0098] Tribo-Mechanical Properties

[0099] Wear resistance of coatings A, B, C and D3 under different conditions such as sliding wear and abrasion were measured by standard pin-on-disc tests and abrasion tests. Galling resistance was also measured for coatings A, B, C and D3 using a custom-designed and automated galling tester.

[0100] Sliding Wear Resistance

[0101] A custom-made pin-on-disc tribometer was employed to evaluate the sliding wear behavior of the coatings. A normal load of 25 N was applied to a tungsten carbide ball (4.75 mm diameter) used as a counterpart material. A new ball was used for each test. The diameter of the wear track ring (d), was 7 mm and the rotation speed was 546 revolutions per minute (rpm). This result in a linear speed of 20 cm/s (7.9 in/s). The coefficient of friction, COF, was recorded every second during the tests. The wear rate (K), was evaluated using the formula K = V/(F.S), where V is the worn volume, F is the normal load, and S is the sliding distance. Pin-on-disc wear track profiles were evaluated by the Sloan Dektak II profilometer, and the wear track morphology was examined by optical microscopy (Nikon Epiphoto 200).

[0102] The coefficient of friction, COF, as a function of the sliding distance is shown in FIG. 7. In the first 500 m sliding distance, the COFs of different coatings exhibited a value in the range of 0.6 to 0.7. After the accommodation period (resulting in the high COF value of about 0.65 at the beginning of the wear test for Cr2O3), the COF of Cr2O3 (coating A) progressively decreased and reached a stable value of about 0.5. The COF of n-TiO2-Cr2O3 coating D3 exhibited fluctuations ranging from about 0.6 to about 0.7 during its relatively long accommodation period, and it eventually reached a value of about 0.6. In comparison, coatings TiO2-Cr2O3 (coating B) and n-TiO2 (coating C) show a trend of progressively increasing COFs from about 0.6 to about 0.7 and from about 0.7 to about 0.8, respectively.

[0103] Frictional behavior of various coatings correlates with their different wear resistance as shown in FIG. 8. The Cr2O3 coating A has a substantially enhanced wear resistance, showing a wear rate of about 5.5x10−8 mm³/(N.m). The n-TiO2-Cr2O3 coating D3 exhibits a low wear rate of about 1.3x10−6 mm³/(N.m). In contrast, coatings TiO2-Cr2O3 (coating B) and n-TiO2 (coating C) show wear rates of about 3.7x10−6 and about 7.6x10−5 mm³/(N.m), respectively, approximately three orders of magnitude higher compared to the Cr2O3 coating A. This is in agreement with the microscopic observation of the wear tracks after pin-on-disc tests as shown in FIG. 9: Coatings TiO2-Cr2O3 and n-TiO2 (coatings B and C) had wide and deep wear tracks. On the contrary, Cr2O3 and n-TiO2-Cr2O3 (coatings A and D3) showed small wear scars on the shallow surface, reflecting a mild abrasive wear process for these two coatings.

[0104] Dry Sand Abrasion Resistance

[0105] Coating dry abrasion resistance was tested through dry sand/rubber wheel abrasion test (ASTM G65/procedure D-modified, 45 N, 2000 wheel revolutions, Durometer A-60 wheel). Two samples were tested for each coating type. Prior testing, the sample surfaces were ground with diamond wheel to produce a surface finish of about 0.2-0.3 µm. Evaluation of the sample volume loss due to the test was performed with a optical profilometer.

[0106] Dry abrasion volume loss was measured for coatings A, B, C and D3. The results are shown in Table 5 below. It can be seen that the best dry abrasion wear performance is achieved with the n-TiO2-Cr2O3 coating D3. On the opposite, the poorest wear performance was achieved with the n-TiO2 coating C, which is the coating displaying the lowest hardness. Despite the much higher hardness of the Cr2O3 coating A displayed average wear performance. This deceptive performance is attributed to Cr2O3 brittleness. The wear tracks are shown in FIG. 10.

<table>
<thead>
<tr>
<th>Table 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>D3</td>
</tr>
<tr>
<td>Dry abrasion volume loss with method</td>
</tr>
<tr>
<td>D-mod (mm²/ n = 2)</td>
</tr>
</tbody>
</table>

[0107] Wet Sand Abrasion Resistance

[0108] Coating wet abrasion resistance by means of wet sand/rubber wheel was measured following ASTM G105-2 modified procedure guidelines using a Falex™ sand abrasion test machine and controlled slurry. For each coating type, one rectangular shape specimen (1"x3"x0.5") was submitted to 1000 and 5000 cycles runs with 22N normal load using a 7" diameter and Durometer A-60 neoprene rubber wheel at a nominal speed of 245 rpm. The slurry mixture was composed of rounded quartz grain sand APS 50/70 and deionized water with respect to the ratio of 0.940 kg water/1.500 kg sand. Prior to testing, the sample surfaces were ground with diamond wheel to produce a surface finish of about 0.2-0.3 µm. The 1000 cycles run allowed ranking for the coating wet abrasion rate. Evaluation of the sample volume loss due to the test was performed with an optical profilometer. The 5000 cycles run allowed for ranking coatings that resist penetration to its substrate while wet abrasion rate was reported as mass loss (accuracy ±0.1 mg) of the specimen.

[0109] Wet sand abrasion after 1000 cycles was observed for coatings A, B, C and D3. As it can be seen in Table 6 below, the best performance was obtained with the n-TiO2-Cr2O3 coating D3. On the opposite, and similarly to dry abrasion testing, the poorest wet abrasion performance was achieved with the n-TiO2 coating C.

<table>
<thead>
<tr>
<th>Table 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>D3</td>
</tr>
<tr>
<td>Wet abrasion volume loss according to modified ASTM G105-2 (mm²/ n = 2)</td>
</tr>
</tbody>
</table>

[0110] Wet sand abrasion after 5000 cycles was observed for coatings A, B, C and D3. As can be seen in FIG. 11 and in accordance with the 1000 cycles wet abrasion run and the dry abrasion results, n-TiO2-Cr2O3 (coating D3) presented the best wet abrasion wear performance and was the only coating that resisted substrate penetration. At the end of the test, n-TiO2-Cr2O3 mass loss was equal to 122.9 mg. Cr2O3 coat-
ing A showed a slight penetration of the substrate while both n-TiO₂ (coating C) and TiO₂-CrO₃ (coating B) displayed the poorest performance and the largest penetrations.

[0111] Variable Temperature Galling Resistance

Galling resistance was measured using a custom-designed and automated galling tester (see FIG. 12). The tester consisted in quarter-turn rotating an annular coated specimen (dia. 1.25"x1.5" thickness, 1 in² coated surface) against a second annular coated and fixed specimen under controlled contact pressure, stroke motion and temperature conditions. Contact load and stroke motions were respectively applied with a pneumatic thrust actuator (Samson 3277) and a quarter-turn actuator (Metso BICU6/20L) while the temperature was adjusted with a radiation-type furnace (Lindberg Blue M Tube Furnace) coupled with a K-Type thermocouple probe tack-welded on one specimen. All test parameters were controlled from a centralized panel. Coated surface of each specimen was successively prepared and inspected before being tested. The coated surface preparation consisted in manually polishing with several grades of polishing clothes (from P320 to P1200 grit) using a thin buffer of commercial machinery oil. The specimen inspection allowed for selecting specimens presenting a surface roughness Ra below 10 µm with a flatness below 0.005 inch in addition to measuring the specimen mass (+/-0.5 mg). For each coating type, one set of two self-mated specimens was tested according to the procedure detailed in Table 7 (see below). The test procedure was stopped as soon as one coated specimen displayed significant wear pattern (ex.: micro-welding, scoring). Repeating this test procedure for each coating type allowed material ranking based on galling resistance and total mass loss over a given period.

TABLE 7

<table>
<thead>
<tr>
<th>Step</th>
<th>Duration (nb. cycles)</th>
<th>Specimen temperature, °C.</th>
<th>Nominal contact pressure, MPa (psi)</th>
<th>Nb. cycles per minute</th>
<th>0°-90° and 90°-0° stroke times (s)</th>
<th>Temporization at 0° and 90° position (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>R.T.</td>
<td>6.9 MPa +/- 0.3 (1,000 +/- 50)</td>
<td>0.2</td>
<td>10 +/- 0.5</td>
<td>140</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>220 +/- 7° (428 +/- 12°)</td>
<td>6.9 MPa +/- 0.3 (1,000 +/- 50)</td>
<td></td>
<td>10 +/- 0.5</td>
<td>140</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>220 +/- 7° (428 +/- 12°)</td>
<td>16.3 MPa +/- 0.3 (1,500 +/- 50)</td>
<td></td>
<td>10 +/- 0.5</td>
<td>140</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>220 +/- 7° (428 +/- 12°)</td>
<td>13.8 MPa +/- 0.3 (2,000 +/- 50)</td>
<td></td>
<td>10 +/- 0.5</td>
<td>140</td>
</tr>
</tbody>
</table>

* Heating rates are adjusted to 204° C. (400° F) per hour.

[0112] FIG. 13 shows the number of steps prior significant wear patterns observation and the total mass loss of the different self-mated specimens (rotating*fixed specimens). Total mass loss is measured between 0° and 100 cycles (i.e. after step 2). FIG. 14 provides macro-scale pictures of the specimens after the variable temperature galling test. It is demonstrated that Cr₂O₃ (14-a and 14-b) and n-TiO₂-Cr₂O₃ (14-g and 14-h) present the best galling resistance with apparition of light material pick-up and scoring during step #4 (200 cycles run/220° C./13.8 MPa). However, Cr₂O₃ mass loss after 100 cycles (77 mg) is approximately four times higher than n-TiO₂-Cr₂O₃ (20 mg). In comparison, both n-TiO₂ (14-e and 14-f) and TiO₂-Cr₂O₃ (14-c and 14-d) combine intermediate galling resistance with low mass loss. They respectively show galling, microwelding and material pick-up at step #2 (100 cycles run/220° C./6.9 MPa) and step #3 (150 cycles run/220° C./10.3 MPa) while their mass loss stay below 22 mg after 100 cycles. It is assumed that Cr₂O₃ high mass loss in comparison to other specimens is mainly due to its brittleness. By achieving the highest number of steps prior significant wear patterns observation and by exhibiting a low mass loss, n-TiO₂-Cr₂O₃ (coating D3) ranks 1st. Cr₂O₃, TiO₂-Cr₂O₃, n-TiO₂ are respectively ranked 2nd, 3rd and 4th.

[0113] Several alternative implementations and examples have been described and illustrated herein. The implementations of the invention described above are intended to be exemplary only. A person of ordinary skill in the art would appreciate the features of the individual implementations, and the possible combinations and variations of the components. A person of ordinary skill in the art would further appreciate that any of the implementations could be provided in any combination with other implementations disclosed herein. It is understood that the invention may be embodied in other specific forms without departing from the spirit or central characteristics thereof. The present examples and implementations, therefore, are to be considered in all respects as illustrative and not restrictive, and the invention is not to be limited to the details given herein. Accordingly, while the specific embodiments have been illustrated and described, numerous modifications come to mind without significantly departing from the spirit of the invention. The scope of the invention is therefore intended to be limited solely by the scope of the appended claims.

1. A method for depositing a ceramic coating on a substrate, the method comprising:

[0112] FIG. 13 shows the number of steps prior significant wear patterns observation and the total mass loss of the different self-mated specimens (rotating*fixed specimens). Total mass loss is measured between 0° and 100 cycles (i.e. after step 2). FIG. 14 provides macro-scale pictures of the specimens after the variable temperature galling test. It is demonstrated that Cr₂O₃ (14-a and 14-b) and n-TiO₂-Cr₂O₃ (14-g and 14-h) present the best galling resistance with apparition of light material pick-up and scoring during step #4 (200 cycles run/220° C./13.8 MPa). However, Cr₂O₃ mass loss after 100 cycles (77 mg) is approximately four times higher than n-TiO₂-Cr₂O₃ (20 mg). In comparison, both n-TiO₂ (14-e and 14-f) and TiO₂-Cr₂O₃ (14-c and 14-d) combine intermediate galling resistance with low mass loss. They respectively show galling, microwelding and material pick-up at step #2 (100 cycles run/220° C./6.9 MPa) and step #3 (150 cycles run/220° C./10.3 MPa) while their mass loss stay below 22 mg after 100 cycles. It is assumed that Cr₂O₃ high mass loss in comparison to other specimens is mainly due to its brittleness. By achieving the highest number of steps prior significant wear patterns observation and by exhibiting a low mass loss, n-TiO₂-Cr₂O₃ (coating D3) ranks 1st. Cr₂O₃, TiO₂-Cr₂O₃, n-TiO₂ are respectively ranked 2nd, 3rd and 4th.

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1. A method for depositing a ceramic coating on a substrate, the method comprising:
4. The method of claim 1, wherein the powder of sprayable n-TiO₂ comprises nanosized constituents agglomerated and/or sintered in microsized n-TiO₂ particles.

5. The method of claim 4, wherein the nanosized constituents have a size ranging from 50 nm to 500 nm.

6. The method of claim 4, wherein the microsized n-TiO₂ particles have a diameter distribution ranging from 4 μm to 100 μm.

7. The method of claim 1, wherein the n-TiO₂-Cr₂O₃ powder blend comprises 40 wt % to 70 wt % of n-TiO₂ and 30 wt % to 60 wt % of Cr₂O₃.

8. The method of claim 7, wherein the n-TiO₂-Cr₂O₃ blend comprises 53 wt % to 57 wt % of n-TiO₂ and 43 wt % to 47 wt % of Cr₂O₃.

9. The method of claim 1, wherein the average in-flight particle temperature is 2400°C to 2800°C.

10. The method of claim 1, wherein the average in-flight particle temperature is 2500°C to 2800°C.

11. The method of claim 1, wherein the average particle in-flight velocity is greater than 400 m/s.

12. The method of claim 1, wherein the average particle in-flight velocity is greater than 450 m/s.

13. A mechanical part coated with a nanostructured titanium(IV) oxide-chromium(III) oxide (n-TiO₂-Cr₂O₃) coating, the coating having a microhardness of at least 1000 HV and a dry abrasion volume loss of less than 15 mm³.

14. The mechanical part of claim 13, wherein the dry abrasion loss is less than 8.4 mm³.

15. The mechanical part of claim 13, wherein the n-TiO₂-Cr₂O₃ coating comprises 40 wt % to 70 wt % of n-TiO₂ and 30 wt % to 60 wt % of Cr₂O₃.

16. The mechanical part of claim 13, wherein the n-TiO₂-Cr₂O₃ coating comprises 53 wt % to 57 wt % of n-TiO₂ and 43 wt % to 47 wt % of Cr₂O₃.

17. The mechanical part of claim 13, wherein the mechanical part is a ball-valve.

18. A mechanical part coated with a ceramic coating, wherein the ceramic coating is deposited using the method of claim 1.

19. A powder blend for use in thermal spraying for coating a substrate, the powder blend comprising 40 wt % to 70 wt % of sprayable n-TiO₂ and 30 wt % to 60 wt % of Cr₂O₃.

20. The powder blend of claim 19, comprising 53 wt % to 57 wt % of n-TiO₂ and 43 wt % to 47 wt % of Cr₂O₃.

* * * * *