Hierarchical structures of anodised cold gas sprayed titanium coatings
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ABSTRACT
Cold gas spray (CGS) titanium coatings have been produced to obtain porous and rough coatings with enhanced mechanical performance. The coatings from optimal spraying conditions reached tensile strength values up to 40 MPa, shear strength up to 39 MPa and a loss mass of 37 mg/100 cycles in abrasive testing, values in accordance with the ASTM standards to be applied for orthopaedic joint prostheses. An innovative hierarchical structure (micro-nano) consisted of a TiO2 nanotubes top layer obtained by anodisation onto a CGS Ti coating. The present paper focuses on the characterisation of both surfaces, as-sprayed CGS Ti layer and double Ti-TiO2 layer, in terms of mechanical properties, surface topography and wettability (contact angle). There were not significant changes in micro-roughness, Ra∼40 µm and Ra∼30 µm, but a significant decrease in contact angle, from ≈26° up to 0°, was observed between these two structures. This behaviour indicates that the combination of the CGS + anodising results in promising high roughness superhydrophilic surfaces, ideal for biomedical applications.

1. Introduction
Titanium, like a number of other metals, has been quite extensively studied for its deposition by the solid-state coating process, cold gas spray (CGS), due to its potential in aeronautical and aerospace industry1 as well as anodic protection in corrosive environments2 and in dimensional restoration and repair fields. These applications mainly require the formation of dense coatings. Regarding the use of the CGS technology, this has been quite easy for ideal materials, i.e. those with relatively low melting points, high densities, low mechanical strength and low heat capacities such as Zn and Cu; for others, more expertise and development has been needed. In the titanium case, it has been influenced by (i) its high strength to weight ratio but relative low deformability due to its hexagonal close-packed crystal structure, (ii) the noticeable flow stress rate sensitivity and strain hardening at high strain rates; (iii) low thermal softening sensitivity and (iv) the disruption of oxide layers to promote metallurgical contacts.3 Dense coatings could be achieved with small sized particles (16 µm) using helium gas.4 Nevertheless, this is still quite a challenge when using nitrogen, whatever the particle size is, as lower particle velocities are reached in comparison with helium gas. Actually, what has been mostly observed is the formation of a gradual increasing porosity from the inner part of the coatings to the outer part due to the lower tamping effect of the top layer.5

However, a porous titanium coating could be quite useful in biomedical applications. In this case, the final application would have a demand for a different microstructure. The strategy in this case used for such a purpose has been employing large sized irregular particles. Van Steenkiste et al.,6 used a new nozzle configuration to be able to successfully deposit aluminium particles in the range between 63 and 106 µm, but, in their case, to obtain dense coatings. Using coarse particles to produce porous coatings is easier than using small particles due to their lower velocities and wider gaps to be filled between the deposited particles during spraying. In addition, large dimensions involve lower cooling rates as well as lower strain rates and thus lower strain rate hardening. To a certain extent, all these points, considering also the low thermal diffusivity of titanium which facilitates the local retention of interfacial heating, may favour the occurrence of shear instabilities and, therefore, better bonding at the contact points; the formation of adiabatic shear instabilities has been reported to be the mostly accepted bonding mechanism in CGS.7

Commercial joint prosthesis currently uses the vacuum plasma spray (VPS) technology to produce porous coatings in total hip and knee arthroplasty.8–10 VPS is an extended technology that enables the spraying of oxygen and high-temperature sensitive metals; this is why it has been used for spraying titanium, avoiding oxidation and enabling its use for biomedical applications. As an alternative, some studies have recently approached the CGS technology, which is a process where there is no heat source from combustion or electrical arc discharge. Rather, the high kinetic energy of the particles given by a heated accelerated gas, causes them to plastically deform and typically create a metallurgical bond at the contact interfaces. Since the bonding mechanisms are different, with the biomedical application in mind, the specific mechanical requirements need to be accomplished in order to make sure that the minimum values are surpassed for that industry.

Hierarchical structures consisting of micro- and nanostructured surfaces have been investigated for their effects on cell activities.11 Surface microstructures mainly contribute to the mechanical fixation as well as long-term stability of the implant. The surface roughness and open porosity play a key role in the in vivo interaction. The achievement of porous surfaces by thermal spraying is a versatile system that offers an off-the-shelf solution for various problems, including aseptic loosening, infections, periprosthetic

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fractures and instability. It has been well demonstrated that cells show a high sensitivity to surface roughness at the micro- and nanoscale level.\textsuperscript{12–16} Surface nanofeatures have been demonstrated to improve protein and cell adhesion, thus enhancing osseointegration and promoting bone ingrowth.\textsuperscript{17} One of the treatments to improve the bioactivity of the prosthesis is by performing an anodising treatment, which has been actually mostly applied to dental implants.\textsuperscript{18} Several studies have revealed considerable impact of TiO\textsubscript{2} nanotubes (NTs) surfaces on osteoblast differentiation\textsuperscript{19,20} as well as on proliferation and subsequent mineralisation of extracellular matrix,\textsuperscript{21} which makes such surfaces ideal for their use in orthopaedic applications.

The present paper suggests the combination of the two strategies CGS + anodising in order to produce hierarchical structures with different surface topographies. Xie et al.\textsuperscript{17} performed anodisation of VPS-Ti coatings deposited on Ti-6Al-4 V alloy substrates, and found higher cell adhesion quantity (about 30% more) on the hierarchical structure than that on the as-sprayed VPS coatings. The anodising on titanium surfaces can also have other influences which have been investigated in the biomedical field in terms of their antibacterial properties,\textsuperscript{22,23} drug delivery\textsuperscript{24,25} systems and cell viability,\textsuperscript{19,21} due to their simple fabrication and also their appropriate biological response.

In view of the overall above considerations, the aim of the present work is twofold: (i) perform the mechanical characterisation of the as-sprayed porous CGS-Ti coatings in order to verify it as an alternative to VPS and (ii) perform an evaluation of the surface topography and wettability compared to the double process CGS + anodising in order to elucidate the micro/nanofeatures that might influence the cell attachment.

2. Materials and methods

Irregular coarse commercially pure Ti (CP-Ti) powder was used to obtain rough surfaces by CGS. Grade 5 Ti6Al4 V alloy (20 × 50 × 5 mm) from Technoalloy (Spain). Previous to spraying, Ti6Al4 V alloy substrates were ground with #240 grade SiC paper and cleaned with ethanol in an ultrasonic bath. The CGT KINETICS\textsuperscript{®} 4000 (Cold Gas Technology, Ampfing, Germany) equipment was used in order to produce the rough titanium coatings, with a maximum operating gas pressure of 40 bars and gas temperature of 800°C; nitrogen was used as the propellant gas. The cross section sample was prepared by grinding and polishing down to 1 μm size diamond suspension.

The spraying conditions were optimised under the criteria to obtain a high roughness and high coating adhesion.\textsuperscript{26} The cross-sectional area was prepared by grinding and polishing samples down to 1 μm size diamond suspension. Thickness values were measured according to ASTM F1854 with Optical Microscopy (Leica DMI5000 M) and surface topography with Confocal Microscopy (Leica DCM3D).

The optimal CGS CP-Ti coating was characterised according to standard specifications ASTM F-2068 (2015), ASTM F-2083 (2012), ASTM F-1378 (2012) (Femoral, total knee and shoulder prostheses, respectively). The standard test method for the evaluation of tensile strength of the rough CGS CP-Ti coatings was applied following ASTM F-1147 using a Servosis ME-402/10 model equipment with a strain rate of 0.02 mm s\textsuperscript{−1} which was controlled by position until failure occurred. The test consists of gluing a cylindrical coated specimen with a resin to an uncoated sand-blasted specimen. Shear testing was applied following ASTM F-1044, by using a Shimadzu AG-IS 50 KN model equipment with a constant speed of 0.25 cm min\textsuperscript{−1} until failure. This test also consists of gluing a cylindrical coated specimen with a resin to an uncoated sand-blasted specimen. Free and fracture surfaces were examined by scanning electron microscopy (SEM); using a JEOL 5510 operated at 20 kV.

Abrasion measurements were performed by using a S135 model Taber rotary platform abrasion tester following the standard specification ASTM F-1978, with H-22 Calibrade\textsuperscript{™} Vitrified Clay and Abrasive grain wheel and 250 g mass of the abrading head without added weight during 100 cycles. The specimens were weighed before and after being tested in order to measure the mass loss.

The anodisation step was performed on the as-sprayed CGS CP-Ti coatings and 99.7% titanium foils of 0.25 or 2 mm thick (Sigma-Aldrich) in a two electrode configuration cell using a DELTA ELEKTRONIKA SM 400-AR-4 power supply, controlled by LabVIEW. An AA304 stainless steel foil was used as auxiliary electrode. An ethylene glycol bath with 2.5/5 wt-% H\textsubscript{2}O and 0.25/0.5 wt-% NH\textsubscript{4}F was used. In the anodisation process, 30 to 60 V were applied at different anodising times.

Coating morphology was analysed with a JEOL JSM 5310 SEM or a field emission-scanning electron microscope (FE-SEM) JEOL JSM-7100F. The CP-Ti powder and the coating were analysed by X-ray diffraction (XRD) using a X’Pert PRO MPD diffractometer (PANalytical). The surface composition of the CGS CP-Ti coating was investigated by X-ray photoelectron spectroscopy (XPS) using a PHI 5500 Multitechnique System (from Physical Electronics) with a monochromatic X-ray source (aluminium Kα line of 1486.6 eV energy and 350 W), placed perpendicular to the analyser axis and calibrated using the 3d5/2 line of Ag with a full width at half maximum (FWHM) of 0.8 eV. A home-made water contact angle goniometer with ImageJ software program has been used for the measurement of the contact angles, performing static measurements after 10 s in sessile drop mode with 2 μL volume Milli-Q H\textsubscript{2}O droplet.

3. Results

3.1. Cold gas sprayed coating

Figure 1 shows a schematic illustration of the parts that can be coated by porous titanium on femur prosthesis (general view of a typical commercial prosthesis with a titanium porous coating), together with the top surface morphology and the cross section of the proposed CP-Ti coatings obtained by CGS. A quite abrupt topography can be observed providing an enhancement of specific surface with a coating thickness of 294 ± 75 μm. Moreover, a good bonding interface could be observed between coating and substrate in which delamination was not perceived.

To check that no bulk oxidation was produced during spraying, XRD from the CP-Ti powder and coatings were obtained (Figure 2(a)), as well as the XPS spectra of the as-sprayed surface, and after 2 min of Ar sputter-cleaning (Figure 2(b)).
XRD spectra from the Ti powder and the CGS CP-Ti coatings show the same pure titanium pattern (Figure 2(a)). In addition, high-resolution XPS Ti (Ti 2p1/2 and Ti 2p3/2) spectra of CGS CP-Ti coatings show TiO2 peaks at 464.16 and 458.42 for the as-sprayed coating (native TiO2 layer), and Ti (0) peaks at 459.53 and 453.4 eV after 2 min of Ar sputtering (Figure 2(b)). These results show that bulk oxidation was not produced during spraying and only a thin (2–10 nm) spontaneously formed oxide layer appears on the CGS CP-Ti coating after the process.

### 3.2. Mechanical characterisation of CGS CP-Ti coatings

The standard test method for adhesion following ASTM C-633 was applied for the evaluation of coating adherence. The strength value obtained from CP-Ti coatings by CGS is 40 ± 4 MPa. In accordance with the ASTM C-633 standard specifications, the coating should overcome the 20 MPa requirement (ASTM F-2068 and ASTM F-2083). The coating failure mode was mainly cohesive.

Figure 3(a) shows a general view of the surface fracture section of the coating. It appears that the coating has mainly failed at particle-particle interfaces through de-cohesion. Further magnification reveals the presence of particles that have been deposited with plastic deformation (Figure 3(b,c)). The features such as those in Figure 3(b) reveal the high level of material flow at interfaces when shear stresses take place upon impact.

In addition, shear testing was performed. From the five specimens tested, a mean value of 39 ± 2 MPa was obtained, overcoming the 20 MPa required from ASTM F-1044. A low scattering of the values was found due to the good bonding strength between the coating and the substrate. The fracture type was cohesive.

For the abrasive test, six specimens were tested according to ASTM F-1978 resulting in a mean loss mass of 37 ± 4 mg/100 cycles. Figure 4 shows SEM micrographs of the wear track after the Taber abrasion test. They reveal abrasive wear mechanism as observed with the scratch wear scars on the top asperities of the coating.

### 3.3. Functionalisation by anodising

Taking into account the relevance of the surface structure and composition on the properties and performance of Ti
materials, nano-structures were obtained on the CGS CP-Ti coatings by anodising in ethylene glycol-based electrolytes. Using this approach, new hierarchical coatings with a top TiO$_2$ NTs layer with controlled diameter were obtained. However, it is well known that it is difficult to obtain useful clean NTs surfaces in the anodising process of Ti due to the remaining compact oxide layer formed in the initial steps of the process. Figure 5(a) shows the typical structure obtained without an accurate control of anodising conditions on smooth Ti surfaces. A double anodising process on smooth foils has been usually applied to minimise the presence of such compact oxide layer (Figure 5(b)). However, the difficulty in etching the first anodic layer on the CGS CP-Ti surface prevents the application of this approach. Therefore, the conditions needed to obtain the cleanest surfaces in single anodising processes were obtained on controlled smooth Ti and CGS CP-Ti substrates. 30V-2700s or 40V-1800s are experimental conditions that allow us to optimise the surface morphology, on both smooth Ti foil and CGS CP-Ti surface: a NTs layer with 30–100 nm pore diameter was obtained (Figure 5(c)) in a single anodising step.

### 3.4. Roughness

Table 1 and Figures 6 and 7 show the 2D and 3D roughness and micro-roughness values of different analysed samples, including functionalised smooth Ti foil samples as a reference. Figure 6 includes the 3D profile of the analysed samples and Figure 7 the 2D profile of the CGS CP-Ti coatings and after their anodisation at 30V-2700s, showing the contribution of the filtered waviness and micro-roughness profile. It is interesting to remark that the anodising process of the Ti surface increases slightly the 2D and 3D roughness of the smooth Ti foil but decreases the 2D of the CGS CP-Ti surface.

### 3.5. Wettability behaviour intended for biomedical applications

Table 2 shows the contact angles measured for the as-sprayed coating and the smooth Ti foil samples. As-prepared, anodised (CGS CP-Ti coating and smooth Ti foil) and double anodised (smooth Ti foil) samples were analysed. The smooth Ti sample showed a hydrophobic behaviour with a contact angle near to 70° but, as can be expected...
According to the roughness values, the as-sprayed sample reduces the contact angle to 50°. In addition, in any case, the simple anodised samples increase the hydrophilic behaviour with respect to the non-anodised ones. However, while the contact angle is reduced to less than 20° for the anodised smooth Ti foil, super-hydrophilicity (contact angle 0°) was observed for the anodised CGS samples (Figure 8). These results show that the rough surface with the presence of NTs increased wettability to the maximum level. Many authors have actually observed the reduction of the contact angle in Ti-treated surfaces, which leads to high surface energy and affects cell adhesion, spreading and growth. It is noteworthy also that double anodised samples show an increase in hydrophobicity, directly related to the double structure of the cells observed in the surface of the porous structure (Figure 5(e)). This structure is fixed by the geometry defined in the first anodising step.

4. Discussion

VPS is the current most established commercial technology to produce porous and rough metallic titanium coatings for biomedical purposes, although other options have also been investigated. CGS CP-Ti provides low-cost free oxide coatings with good mechanical properties with values to the requirements of ASTM Standards, as well as better control of the composition of the sprayed structure and surface topography. Large irregular sized Ti particles were used in the current CGS deposition processes to achieve porous rough coatings (up to Ra ≈ 40 µm) with controlled mechanical performance. This is more feasible than using small particles due to their lower velocities and wider gaps to be filled between the deposited particles during spraying. The use of coarse particles in CGS has been used, however, in very few occasions in the past. Actually, to produce controlled porosity in titanium coatings by CGS, some porogen elements have been reported in the literature, such as magnesium, reaching porosities of ~48% and pore sizes in the range of 70 to 150 µm or aluminium with pore percentage between 48–66% and pore size 74–91 µm. Thus, rough CP-Ti coatings by CGS did not show the presence of oxide after the spraying (Figure 2(a)). However, the detection of a spontaneous thin TiO2 layer by XPS was attributed to surface passivation due to its thickness of 2–10 nm (Figure 2(b)).

The optimal porous and rough coating achieved here, reaches a mean tensile strength of 40 ± 4 MPa and shear strength of 39 ± 2 MPa with an adhesive failure. Compared to other thermal spray techniques, VPS reaches tensile and shear strength values of 40 MPa with porosities between 20% and 60%, but, in certain conditions, 60 MPa can be achieved by CGS for titanium coatings. The increasing of particle size leads to a decrease in mechanical properties but an increase in roughness. The fracture surface of CGS CP-Ti coatings shows extended plastic deformation of the particles before fracture. The failure appears to be through decohesion at the few contact points at particle boundaries.

Table 1. Global profile, 2D and 3D roughness filtered (µm) of analysed samples.

| Identification                          | Global profile | 2D roughness (filtered) | 3D roughness |
|----------------------------------------|----------------|-------------------------|--------------|
|                                        | Rg, Rz         | µRg, µRz                | Sz, Sz       |
| Smooth Ti foil                         | 0.4 ± 0.1, 2.9 ± 0.5 | 0.3 ± 0.1, 1.7 ± 0.4 | 23 ± 2, 52 ± 6 |
| Smooth Ti foil + Anodisation (30V-1200s)| 0.4 ± 0.2, 3.3 ± 0.6 | 0.2 ± 0.1, 1.1 ± 0.2 | 33 ± 6, 80 ± 7 |
| Smooth Ti foil + Double-Anodisation (first step: 60V-900s; second step: 40V-900s)| 0.6 ± 0.2, 4.3 ± 0.7 | 0.4 ± 0.1, 2.2 ± 0.4 | 21 ± 2, 80 ± 8 |
| CGS CP-Ti coating                      | 40 ± 1, 236 ± 5 | 12 ± 1, 68 ± 8 | 49 ± 7, 350 ± 13 |
| CGS CP-Ti coating + Anodisation (30V-2700s)| 30 ± 1, 143 ± 9 | 12.7 ± 1, 57 ± 6 | 50 ± 8, 348 ± 15 |

Figure 5. FE-SEM images of the optimisation of a TiO2 NTs layer: (a) non-accurate single-anodised process at 30V-1200s; (b) double anodised process onto smooth Ti foil: first step: 60V-900s, second step: 40V-900s with magnification (inset) and (c) single-anodised process onto CGS CP-Ti coating at 30V-2700s with magnification (inset).
The fibrous appearance of the surface showed the extensive plastic deformation of the particles upon impact. The material ‘pulled apart’ leaving a rough surface, thus a slow crack propagation and absorption of a large amount of energy before the fracture (Figure 3). In addition, Taber abrasion testing shows similar results of CGS CP-Ti coatings and VPS-Ti coatings, resulting in 37 ± 4 mg and 31 ± 12 mg tensile and shear strength, respectively. The wear track surface reveals an abrasive wear mechanism. Two-body abrasion occurs when the asperity of the wheel contacts the CP-Ti coating surface. Non-particle detachment between both surfaces is strongly observed in this work, scratching is produced on the top of the asperities and would progressively promote levelling of those asperities reducing the surface roughness, although in view of the obtained results this would occur at very slow rates (Figure 4).

The anodising approach has been mainly applied to rough surfaces to improve the surface wettability with the aim of facilitating cell attachment in biomedical applications. Table 2 and Figure 8 reflect that phenomenon. The anodisation of smooth Ti foils leads to higher wettability, as well as on CGS CP-Ti coatings; although the micro-roughness is slightly decreased after anodic oxidation treatment onto CGS CP-Ti coatings, it is maintained at a high level (Ra ≈ 30 µm) with high free surface area due to the nanotexturing of the TiO2 NTs layer (Table 1): a high surface energy and high topography of titanium modified surfaces, by treatments such as acid-etching, show that both micron scale and submicron scale structural features are necessary. The production of hierarchical structures is promising, but the exact role played by the micro- or nano-topographies needs further study.

Figure 6. 3D micro-roughness patterns of the (a) smooth Ti foil, (b) anodised Ti foil (30V-2700s) and (c) double-anodised Ti foil (first step: 60V-900s; second step: 40V-900); (d) as-sprayed CGS CP-Ti coating and (e) after anodisation at 30V-2700s.
Xie et al. \textsuperscript{17} performed an anodisation of VPS-Ti coatings deposited on Ti-6Al-4 V alloy substrates, and found higher cell adhesion quantity (about 30\% more) on the hierarchical structure than that on the as-sprayed VPS coatings. Also, Hall et al. \textsuperscript{40} anodised Ti6Al4 V beads sintered to a Ti6Al4 V hip stem substrate; it was clinically proved that when the femoral implants were inserted into dogs, they improved bone in growth and implant integration, and, as well, a decrease in fibrous tissue was achieved.

The current anodising conditions lead to an NT diameter of 30–100 nm (Figure 5(c)); these are values in accordance with the ones described in previous analysis of cell integration.\textsuperscript{41} Minagar et al.\textsuperscript{42} listed the different studies reporting cell responses to various TiO$_2$ NTs on Ti ranging from 15–30 nm to 70–100 nm. It should be pointed out here that anodising such an irregular surface makes it more difficult to avoid the presence of the compact oxide layer than when compared to a titanium smooth foil.

In terms of biological properties, CGS CP-Ti coatings provide a higher free surface area, but also surface wettability due to their topography, both ideal for cell deposition and cell response. However, the performance of TiO$_2$ NTs onto CGS CP-Ti coatings acts as a barrier against metal ion release and provides superhydrophilic behaviour due partly to the surface nanofeatures but also the coating’s composition of titanium oxide.\textsuperscript{43} TiO$_2$ NTs have been demonstrated to promote cell adhesion thus cell proliferation and differentiation, and decrease bacterial adhesion.\textsuperscript{44}

To sum up then, the present use of the CGS technology with superimposed anodising results in good mechanical performance and superhydrophilic surfaces; this can be foreseen as a new route to produce micro-/nano hierarchical surfaces that need to be revised under \textit{in vitro} and \textit{in vivo} conditions.

\begin{table}[h]
\centering
\begin{tabular}{|l|c|}
\hline
Identification & Contact angle (°) \\
\hline
Smooth Ti foil & 73 ± 2 \\
Smooth Ti foil + Anodisation (30V-2700s) & 20 ± 4 \\
Smooth Ti foil + Double-Anodisation: (first step: 60V-900s; second step: 40V-900s) & 67 ± 6 \\
CGS CP-Ti coating & 26 ± 10 \\
CGS CP-Ti coating + Anodisation (30-2700s) & 0 \\
\hline
\end{tabular}
\caption{Values of the contact angles of as-prepared and anodised samples with and without NTs presence.}
\end{table}

Figure 7. 2D Global profile divided into waviness and roughness patterns of as-sprayed CGS CP-Ti coatings (left) and after anodic oxidation treatment 30V-2700s (right).

Figure 8. Contact angle images Milli-Q H$_2$O droplet of: (a) smooth Ti foil, (b) anodised Ti foil (30V-2700s) and (c) double-anodised Ti foil (first step: 60V-900s; second step:40V-900); (d) as-sprayed CGS CP-Ti coating and (e) after anodisation at 30V-2700s.
5. Conclusions

- CGS has been demonstrated to be a suitable technique to produce porous pure titanium coatings for medical purposes in prosthetic applications. The evaluation of such coatings indicates that the process can become competitive to the currently established VPS method with cost-effective characteristics.

- According to ASTM standard specifications for hip, knee and shoulder joint prostheses applications, the selected CGS CP-Ti coatings more than match all mechanical requirements with 40 ± 4 MPa of tensile strength, 39 ± 2 MPa of shear strength and 37 ± 4 mg/100 cycles of weight loss in abrasive testing. The hydrophilicity of the CGS CP-Ti surface coating is noticeably increased compared to a smooth foil. Controlled anodising was successfully applied to functionalise such coating surfaces to obtain a layer of anatase TiO2 nanotubes. The increase in hydrophilicity favours cell attachment, thus cell response. Thus, nanostructured surfaces enhance biological properties such as cell proliferation and differentiation.

Disclosure statement

No potential conflict of interest was reported by the authors.

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