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# Polymer-derived sphene biocoating on cp-Ti substrates for orthopedic and dental implants

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## ABSTRACT

Sphene coatings were prepared by a novel process involving the use of a preceramic polymer containing nano-sized and micro-sized active fillers as precursors for the formation of the desired ceramic phase. A commercially available airbrush was used to cold-spray the suspension on the cpTi substrate, and the samples were heat treated to transform the precursor and fillers mixture into a ceramic coating. The processing conditions were optimized in order to obtain cracks free coatings, characterized by good adhesion to the substrate and a desired phase assemblage.

## 1. Introduction

Titanium and some of its alloys are widespread materials used for load bearing applications in metallic implants. Compared to hydroxyapatite (HAP) implants, the metallic counterpart offers more mechanical stability and absence of brittleness, even though they cause stress shielding due to stiffness mismatch between the metallic implant and the bone. In addition, they are often a source of infections in long-term applications because of their poor bioactivity.

In order to reduce the elastic modulus of the metallic prostheses, current research is directed toward development of porous structures [1]. In addition, to improve the bioactivity of the implant, its surface can be coated with a bioactive ceramic layer, such as HAP or bioglasses [2]. The major drawback of the HAP coating is that it cannot maintain long-term stability, and in certain situations, delamination of the HAP coating from the alloy occurs due to its limited adhesive bond strength and insufficient chemical durability [3] [4]. The high residual stress resulting from the mismatch of the coefficient of thermal expansion (CTE) between HAP ($13.3 \times 10^{-6}\ K^{-1}$) and Ti ($8.4–8.8 \times 10^{-6}\ K^{-1}$) is thought to be responsible for the higher tensile stress and microcracks at the interface, which decrease the bonding strength between the two materials and limit their long-term survival.

Sphene ($CaTiSiO_5$) ceramics have a CTE ($6 \times 10^{-6}\ K^{-1}$) similar to that of Ti, possess excellent chemical stability and have the ability to enhance the proliferation and differentiation of human primary osteoblast-like cells (HOBs) [5]. Sphene ceramics have been produced as coatings for Ti6Al4V substrates using the sol–gel method [6], a hybrid technique of microarc oxidation (MAO) coupled with heat treatment [7] and plasma-spraying [8]. In addition, an in vivo study demonstrated that Ti6Al4V implants coated with sphene modulated bone formation around the implants and enhanced osseointegration without any fibrous tissue responses, in a manner comparable to that of the hydroxyapatite coatings used as control [9].

Plasma-spraying is the main technique used for the deposition of ceramic HAP coatings on dental or orthopedic implants, even though it presents some disadvantages such as residual stress at the substrate/coating interface, as well as drastic changes in the composition and crystallinity of the initial calcium phosphate powder [10,11]. In order to avoid the drawbacks of plasma-sprayed coatings, scientists have developed new coating methods such as the electrodeposition of calcium phosphate by using a current, a titanium cathode and a platinum anode [12,13], biomimetic precipitation of calcium phosphate on titanium surfaces by immersion in simulated body fluids (SBF) [14,15,16].

Airbrush spraying is a low-cost and common coating technique, and recently it was proposed as an alternative to plasma-spraying, sol–gel deposition or cold-spraying for medical implants [15,16]. It offers the advantage of enabling thickness control, affording good adhesion strength with the substrate and the possibility to coat complex shapes.

The possibility of developing bioactive silicate-based ceramics and glass-ceramics starting from preceramic polymer containing fillers was already demonstrated in previous works [17]. The polymer-derived ceramics (PDCs) route showed favorable features in terms of the synthesis of bioactive ceramics at low processing temperatures

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**Table 1**
Samples definition, coating parameters. Samples sintered at 950 °C.

| Sample | Suspension composition | Coating Parameters<br>Spraying time, t [s]<br>Distance from substrate, D [mm] |
|---|---|---|
| Ti-Nano | MK + $TiO_2$ + nano$CaCO_3$ | t = 5<br>D = 100 |
| Ti-Micro | MK + $TiO_2$ + micro$CaCO_3$ | t = 5<br>D = 100 |
| Ti50/50-A | 50 wt.%[MK + $TiO_2$ + nano$CaCO_3$]<br>+ 50 wt.% Sphene* | t = 5<br>D = 100 |
| Ti50/50-B | 50 wt.%[MK + $TiO_2$ + nano$CaCO_3$]<br>+ 50 wt.% Sphene* | t = 1<br>D = 80 |

* Sphene was prepared starting from MK + $TiO_2$ + nano$CaCO_3$ suspension in isopropanol, and then the suspension was heat treated in static air at 1300 °C for 3 h.

with different compositions and high phase purity. In addition, the preceramic polymer technique permitted the shaping of these ceramics in different complex shapes, as bulk components and especially in the form of highly porous bioceramics obtained using unconventional direct foaming [18] as well as 3D printed scaffolds from additive manufacturing [19]. The present work focuses on the coating of commercially pure (cp) Ti substrates by sphene ($CaTiSiO_5$) based-ceramics synthesized via the PDC route, using the airbrush coating technique. The produced calcium titanate/titanium bioceramic composite possessed good adhesion of the bioactive ceramic coating to the underlying metal substrate, and could be a good candidate for orthopedic and dental implants.

## 2. Experimental procedure

### 2.1. Materials and methods

Sphene coatings on cpTi substrates were prepared by the preceramic polymer processing route. The preceramic polymer used in this work was SILRES® MK (polymethylsiloxane, Wacker-Chemie GmbH, München, Germany). The MK silicone resin, in powder form, was dissolved in isopropanol under magnetic stirring, then mixed with CaO and $TiO_2$ precursors as active fillers, in the molar ratio resulting in sphene ($CaTiSiO_3$) as a final product after ceramization. The ceramic yield of MK after heating in air at 1000 °C is ~84 wt.% [20], CaO was provided by $CaCO_3$, in the form of micro-sized particles (~10 μm, Industrie Bitossi, Vinci, Italy) and nano-sized particles (PlasmaChem, Berlin, Germany, 90 nm), while $TiO_2$ was introduced in the form of nano-sized particles (21 nm, Evonik Degussa GmbH, Germany). Three different suspensions were developed, as reported in Table 1: samples labeled as Ti-Nano were prepared using nano-sized $CaCO_3$, Ti-Micro were prepared using micro-sized $CaCO_3$, samples labeled as Ti50/50 A and B were both prepared using 50 wt.% of MK, $TiO_2$ and nano-sized $CaCO_3$ suspension in isopropanol and 50 wt.% of already synthesized sphene using the preceramic polymer approach described above, heated at 1300 °C for 3 h in air and finely ground in a mortar. In these last two kinds of sample, which differed only by the coating parameters, the silicone mixture containing the fillers was homogenized by adding a dispersing agent (DISPERBYK-180, BYK-Chemie GmbH, Germany, 2.5 wt.%) followed by sonication for 15 min. The homogenous dispersions were transferred into a commercially available airbrush (professional airbrush gun type 138, WilTec Wildanger Technik GmbH, Eschweiler-Germany) and used as a coating material on cp Ti substrates (Fig. 1).

**Table 2**
Chemical composition of the cpTi substrate, as given by the producer (wt.%).

| Fe | O | N | H | C | Ti |
|---|---|---|---|---|---|
| 0.060 | 0.140 | 0.004 | 0.003 | 0.016 | 99.78 |

Commercially pure grade II titanium rectangular plates of size 25 × 20 × 3 $mm^3$ were used as substrate (Torresin Titanio s.r.l., Padova, Italy). The substrate composition is reported in Table 2, as specified by the producer. Plates were cleaned in an ultrasound bath of acetone, deionized water and alcohol for 10 min, respectively, and then dried by compressed air.

The suspension was maintained under magnetic stirring during the coating process. The air inlet was set at 2 bars and the airbrush nozzle was maintained at a specific distance from the substrate. Substrates were preheated at 60 °C before the deposition of the suspension by a hot air gun.

The distance between the nozzle and the substrate, and the deposition time were the parameters that varied in this study, as reported in Table 1. These parameters were chosen after preliminary optimization tests. After coating, the samples were then heat treated in air (5 °C/min, 3 h) at 950 °C as reported in Table 1.

Coatings were visually analyzed by optical stereo-microscopy (Carl Zeiss Stemi 2000-C). The phase assemblage of the coating after thermal treatment was investigated by X-Ray Diffractometry (XRD Bruker D8 Advance, Milano, Italy) equipped with Cu-Kα radiation and operating at 40 mA and 40 mV. The morphology of the coatings was analyzed by Field Emission Gun Scanning Electron Microscopy (FEG-SEM, Quanta 250 Fei, Eindhoven, The Netherlands) and Energy Dispersive Spectroscopy (EDS, EDAX); investigations were performed both on the cross-section and the surface of the coated samples. The sections of the samples were prepared by embedding the samples into a resin and by finishing the surfaces using up to 2100 SiC grit paper followed by polishing with 3 μm diamond paper and a $SiO_2$ colloidal dispersion in demineralized water and $H_2O_2$. The embedded and polished samples were cleaned in ultrasound for 15 min in acetone, rinsed in demineralized water and then dried by compressed air.

EDS line scan (section) and EDS maps (surface) were carried out in order to detect the diffusion of elements from the substrate to the coating and to verify the homogeneity of the coatings, respectively. The coating thickness was determined from FEG-SEM images of the samples sections; at least ten measurements were performed in different zones of the samples and averaged.

The average surface roughness (Ra) of both uncoated and coated substrates was measured by a Surtronic $3^+$ profilometer (Taylor Hobson Precision instruments, Milano, Italy).

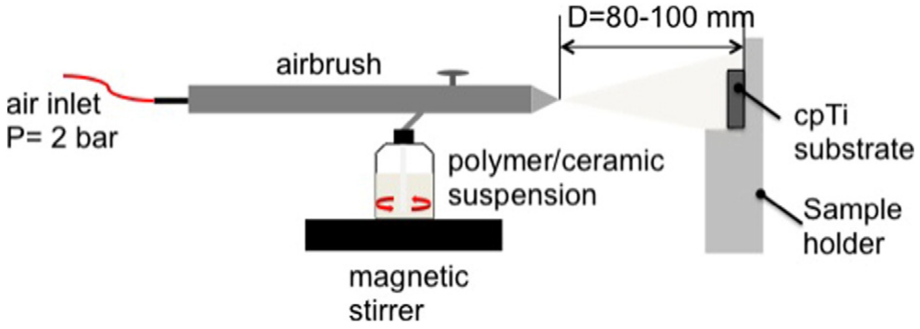

**Fig. 1.** Schematic drawing of the experimental set-up used for coating the cpTi substrates.