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The challenge and promise of low-temperature bioceramic coatings: An editorial

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ABSTRACT

Low-temperature coating deposition is carried out at or near ambient temperature temperatures, much below the incongruent melting point of hydroxyapatite. However, frequently post-depositional heat treatment must be applied to either crystallise amorphous calcium phosphate (ACP), transform (dehydrated/dehydroxylated) precursor phases such as octacalcium phosphate to hydroxyapatite, and/or to remove organic compounds used in coating preparation, for example during sol–gel, dip coating, electrochemical, and electrophoretic deposition. The contributions to this Special Issue deal predominately with low-temperature deposition of hydroxyapatite coatings applied by electrochemical deposition (ECD), plasma electrolytic oxidation (PEO), electrophoretic deposition (EPD), and ion-beam assisted deposition (IBAD) to the surfaces of Ti6Al4V, cp-Ti, CoCrMo, Mg, as well as Zr and PEEK substrates.

1. Socioeconomic background

Presently, research into and development of biomaterials *sensu lato* are at the forefront of health-related issues in many countries worldwide. Arguably, this research effort has reached levels of involvement and sophistication second only to electronic ceramics [1]. The reason for this is obvious as large proportions of an ageing population, predominately in developed countries, rely on repair or replacement of body parts, or restoration of lost body functions ranging from dental roots to alveolar ridge and iliac crest augmentation to artificial skin grafts to hip and knee endoprostheses. A particular important segment, preferentially caused by osteoporosis, is in this context the repair of hip degeneration eventually leading to fracture, a typical ailment of elderly people. Indeed, in 2002 the World Health Organization (WHO) has put osteoporosis on the list of the ten most frequent diseases worldwide.

The number of patients receiving large-joint reconstructive hip and knee implants to repair the ambulatory knee–hip kinematic as well as dental and other small-joint implants aimed at correcting skeletal defects and healing diseases is constantly on the rise. A rough estimate of the amount of metallic, ceramic, and polymeric implants of all kinds delivered worldwide to patients is in the range of 10 million annually. Consequently, the global number of orthopaedic surgeries increases by 10–12% per year. Currently, in the United States and in the European Union in excess of 1,200,000 hip and knee arthroplasties are being performed annually, and this number is expected to double by the year 2025 [2]. In terms of health care costs, in 2012 this figure amounted to worldwide sales of hip and knee endoprosthetic implants as high as US$ 14 billion, and is estimated to grow by 5% annually up to 2016 [3].

1.1. Function of bioceramic coatings

Total hip replacement (THR) is known to be among the most successful surgical procedures today, combining a safe and well-controlled operation technique and reliable pain reduction with little limitations during daily activities, acceptable longevity of the implant up to 20 years, and a high overall success rate topping 95%. In cementless prostheses, a biocompatible calcium phosphate coating applied to the stem of hip endoprostheses or the dental root implant serves to support osseointegration. Since the composition of the coating is close to that of the inorganic component of natural bone, this will result in a strong and lasting bond between living tissue and biomaterial. Porous hydroxyapatite (HAp) coatings appear to promote bone ingrowth even in the presence of metallic and polymer wear debris, in particular in acetabular components [4]. Clinical studies strongly suggest that HAp-coated hip implants show exceptionally high survival rates exceeding 95% at 10 years observation time [5]. Similarly, HAp-coated dental implants showed survival rates between 79 and 96% at 8 years observation time [6]. Consequently, at present HAp-coated implants are considered the 'gold standard' in hip arthroplasty and dental restoration.

However, despite this impressive clinical success, a sizeable need for revision surgery exists and has to be dealt with aggressively. Among several THR revision causes that include osteonecrosis, fractures, and hip dysplasia, a major antagonistic issue is periprosthetic wear debris-mediated inflammatory osteolysis, frequently resulting in aseptic loosening of acetabular and femoral components of hip endoprosthetic implants [7]. As one of the key determinants of aseptic loosening is an insufficient degree of osseointegration, proper design and application

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of bioceramic coatings [8] are important intervention to prevent premature implant failure.

It is not surprising then that research is ongoing worldwide into various methods to deposit bioceramic coatings on the metallic parts of medical implants. Such coatings are known to support the ingrowth of bone cells and thus serve to anchor the implant solidly to the surrounding cortical bone bed by a multi-stage mechanism of osseointegration [9]. The interaction mechanism of a bioceramic coating with living bone tissue is closely controlled by both necessary and sufficient osseoconduction and osseoinduction. On the one hand, osseoconduction refers to the ability of a biomaterial to foster the ingrowth of bone cells, blood capillaries, and perivascular tissue into the gap between implant and existing bone bed. On the other hand, osseoinduction relates to the transformation by mitosis of undifferentiated mesenchymal precursor stem cells into osteoprogenitor and finally osteoblast cells, eventually resulting in intermembranous ossification without intervening soft tissue such as cartilage.

In addition, the coatings must have sufficient mechanical stability when under physiological stresses associated with locomotion as to not detach prematurely from the implant surface. Finally, the implant coating should have antimicrobial properties to minimise the risk of post-implantation periprosthetic osteomyelitis, for example by *Staphylococcus aureus*. As it turns out, currently none of the commercially available types of coating is able to satisfy fully all of the above criteria, further emphasising the need for research and development of new and improved biomedical coatings for orthopaedic implants.

1.2. Coating technologies at high temperature: state-of-the-art

Most often, the bioceramic materials selected for implant coatings are calcium phosphates [10], in particular hydroxyapatite, a compound very similar in chemical composition and crystallographic structure to the inorganic constituent of the natural composite bone. This similarity will guarantee biocompatibility, meaning that the presence of the coating will not trigger significant immune or foreign-body responses. Despite a plethora of techniques employed to deposit hydroxyapatite coatings [9] that are to be optimised in terms of biocompatibility, cohesion, adhesion, surface roughness, porosity, *in vivo* solubility and thermodynamic stability, state-of-the-art is still deposition by thermal spraying, most notably atmospheric plasma spraying (APS) [11]. Notwithstanding acknowledged shortcomings including thermal decomposition of hydroxyapatite in the hot plasma plume, line-of-sight limitation, the inability to deposit coatings of less than about 10 μm thickness, and undesirable heating of the metallic implant that may affect its microstructure, today thermal spraying is still the method of choice to provide coatings to the metallic parts of commercially supplied hip- and knee endoprostheses as well as dental root implants [12]. Currently, plasma spraying of hydroxylapatite powder particles with diameters of tens to hundreds micrometres is the most popular and the only Food and Drug Administration (FDA)-approved method to coat implant surfaces for clinical use.

In the recent past, other high-temperature techniques have been added to the toolbox of biomedical engineers. These novel techniques include suspension plasma spraying (SPS), solution precursor plasma spraying (SPPS), low-energy plasma spraying (LEPS), and high velocity suspension flame spraying (HVSFS) [9]. They offer a fast, well controlled, economically advantageous, and in its processing technology mature way to coat almost any substrate with those materials that possess a defined congruent melting point. However, hydroxyapatite clearly does not abide by the latter requirement in that it melts incongruently, *i.e.*, melting is accompanied by dehydroxylation into oxyhydroxy- and oxyapatite [13] and, subsequently, decomposition into tri- and tetracalcium phosphates, or even highly cytotoxic calcium oxide. Consequently, the coatings deposited by thermal spray technology will have properties differing in chemical and phase composition, crystallinity, crystallite size, and defect density from the natural bone-like apatite they are supposed to mimic. Furthermore, line-of-sight limitation prevents coating of geometrically complex substrate shapes. Hence, as one of several alternatives, low-temperature electrochemical methods have been widely studied to deposit calcium phosphates the composition of which can be closely controlled and adjusted to the intended application. This method, however, requires an electrically conducting substrate as well as post-depositional heat treatment. Although it is not well suited to coat non-conducting ceramics and heat sensitive polymers, it offers promising advantages for coating metallic implant parts. Consequently, several contributions in this collection of recent research deal with electrochemical deposition (ECD) of bioceramic coatings on metallic substrates [14–19].

1.3. Coating technologies at low temperature: novel developments

To alleviate the above-mentioned disadvantages of thermally sprayed coatings, the search is on to research, develop, and eventually clinically apply low-temperature coating methods. Hence, there is a strong impetus to move away from high-temperature deposition techniques and their shortcomings towards developing low-temperature coatings. Non-thermal deposition methods are defined as being carried out at temperatures much below the incongruent melting point of hydroxyapatite at 1570 °C, ideally at or near ambient temperature. However, frequently post-depositional heat treatment must still be applied to either crystallise amorphous calcium phosphate (ACP), transform non-apatitic precursor phases such as octacalcium phosphate (OCP) or dicalcium phosphate dihydrate (DCPD, brushite) to hydroxyapatite, and/or to remove organic compounds used in coating preparation, for example during sol–gel, dip coating, electrochemical, and electrophoretic deposition processes. It ought to be mentioned that lacking sufficient adhesive and cohesive strengths of low-temperature deposited coatings remains an issue. However, insufficient coating adhesion can be remedied somewhat by applying appropriate bond coats, unreliable coating cohesion by reinforcing polymeric additives. In addition, deposition of dense, stoichiometric, and well-crystallised hydroxyapatite coating layers is frequently ineffective, as those coatings tend to be bioinert. Indeed, to behave in a bioactive, *i.e.*, osseoconductive mode, hydroxyapatite ought to have some degree of non-stoichiometry, expressed by both Ca deficiency caused by substitution of metabolic elements such as Mg, Sr, Na, K and others for Ca, and substitution of carbonate ions for orthophosphate (type-B defect) or hydroxyl (type-A defect) ions. Such non-stoichiometric, disordered, nanocrystalline carbonated hydroxyapatite (CHAp) resembles so-called 'bone-like apatite'.

Low-temperature deposition techniques [9] include but are not limited to

- biomimetic precipitation from simulated body fluids,
- wet chemical processing *via* sol–gel routes including dip, spray and spin coating,
- thermal substrate deposition,
- hydrothermal deposition,
- radio-frequency magnetron sputtering,
- ion beam-assisted deposition (IBAD),
- electron beam-assisted deposition (EBAD)
- electrochemical deposition (ECD),
- electrophoretic deposition (EPD),
- cold gas dynamic spraying (CGDS),
- plasma electrolytic oxidation (PEO), and
- pulsed laser deposition (PLD).

The three latter techniques involve localised high peak temperatures, either at the substrate interface in case of cold gas dynamic spraying [20], at the electrode-electrolyte interface in case of plasma electrolytic oxidation [21,22] or at the target surface during laser irradiation in case of pulsed laser deposition [23]. Hence, these techniques