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Review

Phosphate chemical conversion coatings on metallic substrates for biomedical application: A review

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ABSTRACT

Phosphate chemical conversion (PCC) technology has been investigated for improving the surface performance of metallic implants in the biomedical field over the last decade. The metallic materials, such as magnesium and its alloys, titanium, pure iron and stainless steel are widely used as orthopedic devices for immobilization of bone fractures in clinic. They were previously studied as metal substrates for PCC coating aiming to modify their biocompatibility and osteoconductivity. Zinc, calcium and zinc-calcium PCC coatings are frequently utilized considering their nature and the end-use. Although PCC coating has been confirmed to potentially improve the bioperformance of metallic implants in vitro and in vivo by many researchers, there are no unified standards or regulations to give quantitative appraisal of its quality and property. As such, an overview of several main phosphate phases together with their properties and behaviors in vitro and in vivo was conducted. The mechanism of phosphating was also briefly discussed. Critical qualities of PCC coating used for biomedical application including corrosion resistance, wettability and bonding strength were analyzed separately. Biological response including in vitro cell investigations and in vivo tissue response were discussed in terms of the cytocompatibility and bioactivity of PCC coating. Further investigations are proposed to develop appropriate performance evaluation measurements by combining conventional technologies and biomedical procedures.

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1. Introduction

Metallic materials with appropriate surface modifications have been suggested for biomedical applications to accelerate bone healing at early implantation stages [1–4]. Stainless steel, magnesium, titanium, cobalt-chromium and their alloys are traditional orthopedic device materials [5,6]. Although these metals have performed the advantage of load-bearing properties, the long-term implantation stability in the inner environment like corrosion [7,8], toxic ions releasing [9,10] and degradation [11] limit their clinical applications. Biocompatible protective coatings are an optimum option for metallic implants [12,13]. Coatings can provide a barrier between the metal substrate and its environment and improve the bioactivity of the metal surface. To achieve a desired coating, various surface modification treatments have been explored such as physical deposition techniques (physical vapor deposition (PVD) [14], thermal spraying [15,16] and pulsed laser deposition [17,18]), wet-chemical methods (sol–gel [19,20], alkali-heat treatment [21] and biomimetic methods [22]), and electrochemical techniques (electrophoresis [23] and electrodeposition [24,25]). Though so many methods have been used in clinic, many limitations still exist. These include the high-cost, toxic reactants, high temperature and long coating duration during the procedure of a coating fabrication, as well as the interfacial separation under repeated loading condition [2,25,26].

In the last decade, phosphate chemical conversion (PCC) technology has been introduced as a new surface modification method to improve the surface performance of metallic implants in the biomedical field. As a traditional mature technology for metal pretreating, PCC has been widely used in industry. It was also investigated as an effective means to be applied to biomedical metallic implants due to many advantages such as low-cost, easy operation, rapid coating formation, and usage for treatment of irregular surface [27]. PCC coating not only offers corrosion protection to the metallic subsurface but also enhances the biocompatibility and osteoconductivity of different metallic devices.

As an insoluble phosphate layer formed on the substrate surface, PCC coating ranges in thickness from 1–50 μm [27] and shows various chemical compositions and phases from different phosphate baths. These phases are closely related to the entire coating performances. In industry, PCC coating is basically classified as six types based on the nature of the metal ion constituting the major component of the phosphating solution: zinc, zinc-calcium, zinc-manganese, manganese, iron and alkali [27]. Although such a wide variety of phosphating compositions are available, the right choice should be made in consideration of the nature of the metal and its end-use. Recent studies have investigated the behaviors of various phases in both in vivo and in vitro testing to determine the biocompatibility, osteoinduction and osteoconduction of the different phosphate phases [28]. Combining the coating performance and metal nature, PCC coating for biomedical usage has covered zinc, calcium, zinc-calcium, and others which contain the essential elements of a human body in the research of recent years. The purpose of these researches on PCC coating mainly focused on the promotion of cell growth and tissue formation.

2. Pretreatment process prior to PCC

The original metal materials are usually inappropriate for the immediate operation of PCC. In general, a metallic sample must experience the pretreatment process that includes degreasing, rinsing, pickling and activation in turn prior to PCC [27,29]. The operations of degreasing, pickling and rinsing are designed to guarantee a clean surface of the substrate free from contaminants such as oils, waxes and corrosion products. Activation treatment plays an important role for nucleation and formation of coating regarding crystal density and size [30].

In the laboratory, the operation of PCC is usually carried out by immersion of the metal samples into the phosphating baths. The coating fabrication can be affected by many factors. The concentration of reactants, especially accelerators used in the phosphating bath, affects the crystal size and morphology of the coating to some extent [27]. The pH of phosphating bath has a strong affect on characteristics of the coating, too [31]. It is vital in determining the rate and the amount of coating formed [32]. Phosphating must be operated at a specific temperature so that an equilibrium can be maintained during the reaction. Increasing the solution temperature and time favors an easy precipitation of the coating [33]. However, it delays the precipitation when the baths are overheated above the recommended operating temperature [27]. In some cases, solution temperatures may even affect the phase compositions of the coating [34]. Likewise, a fixed treatment time based on the kinetics of the phosphating process has been assigned, any attempt of increasing and/or reducing the operating time will result in unsatisfying performance of PCC coating [27,33]. In a word, it is for sure that only in the case of appropriate pretreatment process and reactive condition, a desired PCC coating with optimum properties and phase constitutions can be achieved.

3. Phase constitutions of PCC coating

Different phosphate phases of PCC coating on various metallic substrates present distinct properties such as solubility, stability, suitability to the substrates and biocompatibility to the cell and blood. Furthermore, some phosphate phases can be transformed into other more stable phases by certain chemical treatment or in the environmental conditions. For example, calcium phosphate dihydrate (DCPD) can be converted to a more stable phase hydroxyapatite (HA) [35–37]. Table 1 summarizes the key phosphate phases that were reported to be successfully fabricated on metallic substrates by PCC technology for biomedical application in the present studies.

3.1. Zinc phosphate tetrahydrate — hopeite

Zinc phosphate tetrahydrate is known as hopeite. It is reported that hopeite is considered as a potential versatile biomedical material. In nature, it exists in two structures, orthorhombic Hopeite and ParaHopeite [38,39]. Hopeite is an important phase in hardened zinc phosphate bone cement. It has been used in previous investigations as a joint material at the tooth interface between tooth root and crown [40,41]. As for PCC techniques, zinc PCC coating has been successfully used as a primer coating on steels and aluminum alloys for automotive industries for many years [29,42,43]. As for biomedical application, zinc phosphate tetrahydrate as a main phase composition of PCC coating was successfully deposited onto magnesium alloys [34], stainless steel [44] (Fig. 1a) and titanium [45] (Fig. 2b) substrates, as illustrated in Table 2. Due to the existence of PO_4^{3-} species, zinc phosphate coatings can facilitate the adsorption of Ca^{2+} from the electrolytic solution. In fact, hopeite can be transformed into HA by chemical treatment in calcium nitrate solution. The zinc PCC coating containing mainly hopeite also facilitates HA growth from simulated body fluid (SBF) [44].

3.2. Dicalcium phosphate dihydrate — brushite (DCPD)

Dicalcium phosphate dihydrate (DCPD) crystals are monoclinic with relatively greater solubility than the other calcium phosphate phases [46]. DCPD has been demonstrated with remarkable biocompatibility because of the chemical similarity with biological calcified tissues.

Table 1
The key phosphate phases used for PCC coating in biomedical application.

Name	Chemical formula
Zinc phosphate tetrahydrate (hopeite)	$Zn_3(PO_4)_2 \cdot 4H_2O$
Dicalcium phosphate dihydrate (brushite)	$CaHPO_4 \cdot 2H_2O$
Zinc calcium phosphate dihydrate (scholzite)	$CaZn_2(PO_4)_2 \cdot 2H_2O$
Hydroxyapatite (HA)	$Ca_{10}(PO_4)_6(OH)_2$