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Research progress in preparation of hydroxyapatite coatings by electrophoretic deposition

Lisha Ma[1,2,a], Jiyuan Liu[1,2,b], Huiyu He[1,2,*]

[1]*Department of Prosthodontics and Dental Implantology, The First Affiliated Hospital of Xinjiang Medical University (Affiliated Stomatological Hospital), Urumqi, Xinjiang, 830054, China*
[2]*Xinjiang Uygur Autonomous Region Institute of Stomatology, Urumqi, Xinjiang, 830054, China*
[a]*1055128717@qq.com*, [b]*2165464056@qq.com*
[*]*Corresponding author: hehuiyu01@163.com*

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Abstract: The composition of hydroxyapatite (HA) is similar to human bone and teeth. After implantation into human body, its hydroxyl (OH) forms chemical bond with bone cells, and has good biological activity and biocompatibility. It is considered to be the best biomedical material for replacing human hard tissue. Electrophoretic deposition (electrophoretic deposition, EPD) is a new kind of coating preparation method, it can solve the traditional biological ceramic coating preparation technology on the various deficiencies, the paper introduced the domestic and foreign studies of hydroxyapatite coating of electrophoretic deposition. In this paper, the process flow of electrophoretic deposition method and the possible failure reasons are summarized, and various influencing factors are discussed in detail, and the corresponding ideas and prospects are put forward.

1. Introduction

Since the 1970s, the preparation of hydroxyapatite (HA) bioceramic coating has aroused the interest of researchers. It has good biocompatibility and biological activity, and has similar material composition to the inorganic substance of human hard tissue bone and teeth. After it is implanted into human body, it can form a close combination with the soft tissue of human body in a short time. However, its brittleness, low strength, flexural strength and fracture toughness indexes are lower than artificial dense bone, which limits its application in the weight-bearing parts of the human body, so people seek a composite method with other materials to prepare high-strength HA bioceramics. In recent years, various technical researches and applications have been able to coat HA on the surface of bioinert metal materials with good mechanical properties to obtain HA bioceramic coatings that can not only take advantage of the strength and toughness of metal matrix, but also have biological activity [1-3].

Bioceramic coatings are mainly divided into two categories [4]: bioinert ceramic coatings and bioactive ceramic coatings.The bioinert ceramic coating has relatively stable chemical properties and forms a layer of fiber tissue between the human body and the human tissue after implantation, so that the human tissue grows to the surface of the implant to form a bond. However, its inertness is not conducive to promoting the binding and growth of bone tissue, and its clinical application is limited.

Bioactive ceramic coatings mainly include hydroxyapatite (HA), bioactive glass and calcium-silicon-based bioactive ceramic coatings. HA is similar to human bone and teeth and contains calcium, phosphorus and other elements required for human bone metabolism. After implantation into human body, its hydroxyl group (-OH) is chemically bonded with bone cells, so it has become a research hotspot. This paper mainly introduces the preparation method of electrochemical deposition HA coating, and briefly analyzes the reasons of coating failure in its implant.

Currently, mature coating methods for preparing HA bioceramic coatings include plasma spraying, laser cladding, sol-gel method, electrochemical deposition method, dip coating method, etc. [5].(1) Plasma spraying method Under the action of plasma or plasma jet, the metal or non-metal powder is heated to a molten or semi-molten state. Under the action of working gas, these particles accelerate and impact on the surface of the pretreated matrix material, where the surface of the matrix is dispersed, deformed and solidified, and the molten particles behind are then layered on the previously solidified particles. Forming the coating is relatively expensive [6-8]. The coating has some disadvantages: HA powder is easy to decompose under high temperature conditions. The bonding type between coating and substrate is mechanical bonding, so the bonding strength is low. The coating can show good performance in the body in the short term, but from the long-term point of view, the coating is easy to degrade in body fluids. (2) Laser cladding method The process of preparing HA coating by laser cladding is to hit a high-power laser beam on the matrix, and melt it quickly on the surface of the matrix in the way of preset powder or synchronous powder feeding, thus forming a cladding layer. The strengthening mechanism of laser cladding coating can be summarized as [9]: (1) fine grain strengthening. Thanks to rapid heating and cooling, the microstructure of the laser cladding coating is refined. (2) Dispersion reinforcement. The reinforced phases are either cladding materials or synthesized during the in-situ laser cladding process and are uniformly dispersed in the matrix. The prepared coating has the following advantages: high wear resistance, good corrosion resistance and good biocompatibility [10], but there are also some defects in the laser cladding HA coating. In the process of laser cladding, HA decomposes at high temperature and reacts to generate impurity phase, resulting in low HA content [11]. (3) Sol-gel method is to uniformly cover the surface of the substrate after HA is made into sol, and the coating is formed due to the rapid volatilization of the solvent and the subsequent polycondensation reaction. This method is not easy to change the pore size and other parameters of crystallization [12]. (4) Biomimetic method In this method, HA coating is grown on the surface of metal matrix under biomimetic environment, but the obtained coating has a low binding force with the matrix [13]. (5) electrophoretic deposition (electrophoreticdeposition, EPD) is charged in the suspension of solid particles in the electric field under the action of directional movement, on the electrode surface and the formation of sedimentary process, is applied in the preparation of HA coatings in recent years, a new method has many remarkable advantages.

EPD can avoid the phase change and brittle fracture layer caused by traditional high temperature coating, and the binding force between metal matrix and HA coating is further improved after subsequent treatment. Secondly, EPD can form a uniform HA bioceramics layer on the surface of metal substrate with complex shape or porous surface, and can accurately control the thickness and porosity of coating components. In addition, EPD is a directional movement of charged particles that will not affect the binding force between coating and metal matrix due to a large amount of gas generated during the electrolysis of water solvent. In addition, EPD has the advantages of simple equipment, low cost, convenient operation and easy control of deposition process [14,15].Therefore, EPD in the preparation of HA metal matrix bioceramic coating has attracted the attention of scholars at home and abroad, and has broad research and development application prospects.

2. EPD-HA coating process

At present, domestic and foreign scholars are quite active in the study of EPD-HA coating. From the perspective of the process, the EPD-HA coating generally includes four main process stages: (1) preparation of the suspension (2) pretreatment of the base material (3) EPD-HA coating (4) follow-up treatment of the EPD-HA coating.

2.1 Preparation of HA suspension

The preparation of HA suspension with stable properties is the key to the success of EPD-HA coating. It is difficult for bioceramic particles to form stable colloid in aqueous solution, so non-aqueous system is generally selected as the dispersion medium of EPD-HA coating, such as ethanol and other organic solvents. At present, most researchers use ultrasonic oscillation to disperse the particles in the medium as much as possible, so as to produce a stable suspension. As suspension is a thermodynamically unstable system, bioceramic particles tend to coalesce with each other and reduce their surface area. Therefore, in order to obtain stable suspension, the surface charge of bioceramic particles must be uniform. This period during which the suspension forms stable colloids is called critical aging time [16].Only after the critical aging time can bioceramic coatings be deposited on the surface of the substrate material by electrophoretic method.

2.2 Pretreatment of substrate materials

In the preparation of bioceramic coatings, the surface of the metal substrate must be pretreated. Methods such as polishing or chemical etching are generally adopted, and then further processed in a natural air drying or drying oven environment. After pretreatment, the surface of the substrate material is conducive to deposition, so that chemical bonds can be formed between the surface of the substrate material and the EPD coating, and the interface bonding strength between the substrate material and the coating can be more effectively improved.

2.3 EPD-HA Coating

EPD is a combination of electrophoresis and deposition processes, and EPD can be used to deposit suspended particles on cermet organic materials. EPD-HA coating is divided into two working modes: constant potential and constant current. The deposition rate of EPD-HA coating is determined by the current density. In constant current mode, if the concentration of suspended particles remains unchanged or no other side reactions occur on the electrode, the deposition rate of particles during the entire deposition process is the same, and there is a linear relationship between the amount of ceramic deposition and the deposition time. The EPD process is more complex than that of pure electrophoresis. With the increase of the deposition layer, the resistance of the deposition layer also increases. The deposition velocity of most particles in the suspension applied on the bioceramic deposition layer gradually decreases with time, and the deposition current gradually decreases until the deposition velocity of the particles drops to zero. In fact, the reason why the solid particles in the suspension deposit on the electrode is that the charged solid particles undergo REDOX reaction on the electrode surface, so the uniform dense continuous coating can be made on the surface of the metal substrate material by using EPD.

2.4 Follow-up treatment of EPD-HA coating

The relative density of EPD-HA coating before sintering is generally relatively low, regardless of the thickness of the powder used, the density of EPD layer is very small. For example, the relative density of the deposited layer of EPD nano-scale biocerceramic powder is only direct sintering, which will produce a large dry shrinkage rate, which is the characteristic of the electrophoresis method for biocerceramic preparation. In order to densify the deposited layer, hot pressing sintering can be used to densify the EPD layer so that it can fully shrink freely during high temperature sintering.

3. Research progress on failure of HA bioceramic coatings

In recent years, the number of orthopedic implants has risen sharply, and the total annual demand for orthopedic implants in China exceeds 1.3 million [17]. The main failure forms of orthopedic implants are fracture, allergy, sterile inflammation, non-union, pain, bending, loosening, infection, rejection and so on. The above failure phenomena were analyzed, including the manifestations caused by coating failure mainly include: allergy, aseptic inflammation, non-healing, pain, loose.

3.1 Mechanical Properties of coating

In human body, the lack of mechanical properties of HA coating will lead to falling off, which is mainly caused by two aspects [18] : (1) Due to the mismatch of linear expansion coefficient, the binding strength of titanium-based coating and matrix is low;(2) The solubility of the coating is relatively high, because the plasma spraying is carried out at high temperature, and HA crystals are easily decomposed into amorphous tricalcium phosphate, tetralcium phosphate, CaO and other heterophase [4], and the high solubility of these substances accelerates the dissolution of the coating, resulting in a decline in the internal bonding strength of the coating, thus accelerating the coating falling off. The bond strength between the coating and the implant substrate is a very critical factor, which greatly affects the long-term performance of HA-coated implants. The bonding strength between coating and substrate depends on interfacial chemical bonding and mechanical interlocking [19].Mechanical interlocking can be achieved by increasing the surface roughness of the coating. When the coating is sintered, the incorporation and diffusion of elements lead to a stronger chemical bond between the coating/substrate, increasing interlock, reducing porosity and becoming denser. The addition of CaF2 and F elements in the HA coating is conducive to the formation of hydrogen bonds, and the formation of complex Ti-P-O-F-Ca chemical bonds in the transition region. In addition, the thermal expansion coefficient of the fluorine-containing HA coating is reduced from 15×10^{6}/°C to 9.1×10^{6}/°C, which helps to improve the bond strength [20]. In terms of corrosion performance, corrosion usually occurs in places where the surface damage is serious, and cracks increase the contact area of the corrosion liquid, forming local corrosion. Water and CL- enter the coating through micropores and cause an electrochemical reaction between the substrate/coating. Hydrogen ions (H+) generated at the coating/substrate interface reduce the local ph value and accelerate the dissolution of HA [21]. Adding Si or ZrO_2[22,23], which are essential biocompatible elements in osteoblasts, to the coating can form a dense and uniform coating with smaller cracks.

Polarization experiment results show that the composite coating has better electrochemical behavior in SBF than pure hydroxyapatite coating. The coated implant is in a state of friction and wear for a long time during human service. Due to the low hardness of the coating, surface cracks and other reasons, the coating wears quickly and produces a large number of wear particles. The passivation film produced by corrosion has low stability, and the abrasive particles damage and peel the rapidly formed film, so cracks and pores are formed. At the wear marks, corrosion film formation and destruction occur alternately, thus increasing the amount of coating wear. Corrosion and wear show a synergistic effect [24]. Under the complex residual stress and applied stress caused by the bending of the crack front, the coating crack can spread through possible defects such as internal micropores and micro-cracks or unbonded flat particles, resulting in the coating fracture. Since a large number of defects are in the coating rather than at the interface, the fracture energy of the coating/matrix interface is higher than that of the HA coating, and the bending fracture mainly occurs near the HA coating/matrix interface [25].

3.2 In terms of coating biological activity

The causes of pain caused by implants in human body are as follows [26] : implant loosening, infection, fracture, inflammation, metal hypersensitivity, etc. The main reasons for implant loosening are as follows [27] : The growth of surrounding bone tissues is inhibited by fretting between the implant and bone interface, and the implant lacks effective support from these tissues. Interstitial fluid flow and resulting changing pressure. The broken down particles of the coating cause inflammation that leads to osteolysis. After implantation, the competition between host tissue cells and bacteria and microorganisms on the surface of the implant is called surface competition [27].Bacterial infection is the result of bacterial adhesion and subsequent colonization of the biofilm layer that forms with it. Post-operative complications caused by peri-implant infections can reduce the success rate of traumatic orthopedic surgery. HA coating on the surface of metal prosthesis can promote the bony connection of implant-bone interface, obtain bone stability, and produce a sealing effect, which can effectively prevent the flow of interstitial fluid and the migration of wear particles. Therefore, HA coating can prevent the occurrence of aseptic loosening of implants. But the HA coating also has the risk of falling off, being absorbed and disintegrating. In the absorbed area, new bone of sufficient quality cannot be formed, which affects the stability of the implant and the sealing performance of the HA coating [28].In long-term patient follow-up, some HA coatings have been reported to have worn, loosened, unstable, or infected bone surfaces. The particles generated by HA decomposition are embedded on the surface of polyethylene to form trisomic wear, resulting in the production of more polyethylene particles, causing polyethylene diseases such as osteolysis [29].

During implant surgery, implant-associated infections often occur despite aggressive antibiotic therapy [27], and studies have also reported a higher risk of infection around implants with calcium and phosphorus coatings than with uncoated implants. Silver is a powerful antibacterial agent, and bioactive silver ions ($Ag+$) have a lethal effect on pathogens and have a broad spectrum of activity [30]. The silver ion release system in the prepared HA coating can be used to prevent post-operative infection and aid bone integration [27].In some in vitro studies, the kinetic release of diclofenguidine, vancomycin, tobramycin and other antibiotics by HA coating has good antibacterial effect [31]. In clinical cases over the past several decades, the incidence of implant loosening with or without HA coating and the postoperative Harris score have no significant difference, and the debate on the assumed advantages of HA coating is still ongoing [26].

4. Conclusion

The development of HA composite coating is a key means to solve the bonding problem between HA coating and metal matrix. Successful HA composite coating is expected to be widely used in bone replacement materials in the future, so it has important significance. With the in-depth study of HA composite coating, the basic goal of HA composite coating preparation is to solve the problem of thermal expansion coefficient mismatch between coating and base material. So far, people have carried out a lot of research, in improving the bonding between the coating and the substrate, through the combination of various processes, the formation of complementary advantages, effectively reduce the thermal stress, and at the same time improve the HA crystallinity of the composite coating surface and the biological activity of the coating.

In order to further solve the problem of the difference of the expansion coefficient between the materials and the film falling off caused by the dissolution of the coating after implantation, it is not only necessary to explore some new technology, but more importantly, it is necessary to combine with the design of the surface components of the HA composite coating to make up for the shortcomings in the process. It is not realistic to prepare HA coatings with good comprehensive properties and meet the requirements of clinical application by using a single method. The preparation of high performance HA bioactive coatings by combining two or even multiple methods will be the main direction of future research. In addition, the choice of coating materials is also gradually diversified, and will be developed from a single coating material to a composite material, in order to achieve a smooth transition between the HA linear expansion coefficient and the expansion coefficient of the metal matrix material.

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