Optimisation of surface characteristics of standard duplex stainless for bio-applications by using electrophoretic deposition: A brief review

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There are still some challenges and issues related to the long-term usage of the material, despite the apparent and successful expansion in metallic orthopaedic applications and bone replacement. The goal of the current study is to use 2205 duplex stainless steels instead of 316L stainless steels in medical applications (DSS). The 2205 DSS is characterised by a decreased nickel content, which offers a benefit in medical applications by lowering the release of nickel ions in the body. It is made up of two-phase (austenite and ferrite) microstructures. Additionally, this alloy finds employment in a range of media due to its excellent mechanical strength, hardness, toughness, and corrosion resistance at an affordable price. There is a pertinent issue to take into account with these constraints because of the poor osteoconductivity and the risk of surface contact, which leads to severe corrosion of metallic implants due to the presence of body fluid. This review demonstrates how to modify the surface of DSS-2205 by coating it with hydroxyapatite/multi-wall carbon nanotubes using electrophoretic deposition (EPD) to enhance corrosion resistance, biocompatibility, and osseointegration. It also discusses the impact of the two most crucial EPD variables (potential and time) on the characteristics of the deposited layer in order to determine the best EPD variable values.

INTRODUCTION

Recent advances in scientific understanding, notably in material science and biological research, have permitted tremendous progress in the development of new biomaterials [1]. Implants are now very effective and employed in a wide range of medical applications, increasing the quality of life for millions and saving countless lives. Today's triumphs, however, are the result of a long history of trial and error and scientific endeavour [2]. Because of their high strength, toughness, and low rate of *in vivo* corrosion, implant materials such as titanium, stainless steel, cobalt, and their alloys are frequently employed in orthopaedic and dental applications. Because of its high general corrosion resistance and cost-effectiveness, stainless steel (SS) has a wide range of applications [3]. Plasma spray, Sol-gel, pulsed laser deposition, and electrophoretic deposition are all utilised to modify the surface properties of metallic implants. Electrophoretic deposition (EPD) is becoming more popular as a way to process biomaterials, especially bioactive coatings and biomedical nanostructures [4].

The well-known advantages of EPD for the fabrication of a wide range of microstructures and nanostructures, as well as unique and complicated material combinations, are being utilised, beginning with highly dispersed suspensions of biomaterials in particulate form (micronized and nanoscale particles, nanotubes, and nanoplatelets). EPD of biological entities such as enzymes, bacteria, and cells is also being studied. EPD is commonly performed in a two-electrode cell [5].

The EPD process involves essentially three steps [6]:

- Formation of a stable particle suspension.
- Using an electric field, the particles migrate toward the depositing electrode.
- Particle deposition on the electrode surface.

A schematic of these steps in the EPD process is presented in Figure 1.

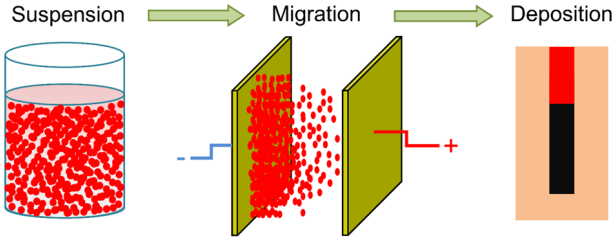


Fig. 1. The EPD steps are depicted schematically [6].

Although HA has excellent bioactivity, its weak mechanical qualities in comparison to bone have limited its usage in clinical applications. Dense HA has a compressive strength of four times that of cortical bone, but a much lower tensile strength and fracture toughness. The composition and crystal structure of HA, which are identical to those of the mineral component of bone, are the most critical determinants of its in vitro activity [7]. HA has been shown to improve metallic prosthesis osseointegration with bone tissue. Actually, HA's osteoconductive characteristics prevent the production of fibrous tissue around the implant. Bioactive materials, such as bioactive silicate glass coatings, have seen an increase in their application for this purpose in recent years, with encouraging results [8]. Hydroxyapatite (HA) coatings on metallic implants are one of the finest options for preventing corrosion and the resultant leakage of harmful metallic ions into surrounding tissues [9]. To overcome this constraint, scientists are developing manufacturing nanocomposites based on HA and carbon nanotubes (CNTs). Carbon nanotubes (CNTs) have got a lot of attention because of their unique structure and special properties, such as excellent mechanical properties, high corrosion resistance, unique structural properties, high specific surface area, low density, good biocompatibility, and low toxicity [10].

Because of their nano-size and high surface energy, carbon nanotubes have a significant tendency to agglomerate. However, the addition of chemical functionalities to the CNT surface, such as carboxyl groups, results in negative charges on the CNTs, which creates the electrostatic stability required for colloidal dispersion stability. This is validated by comparing the dispersion of pristine CNTs under functionalised and pristine circumstances [11]. Multi-walled carbon nanotubes can be created as biocompatible nanostructures of cylindrical buckytubes. Carbon nanotubes (CNTs) are an unusual allotrope of the carbon element due to their high aspect ratio, unique optical characteristic, and similarity to tiny molecules. The insolubility and difficulties of handling CNT in any solvent has severely limited its usage. The solution is to functionalise CNTs [12].

CNTs are becoming rising stars in several biological domains, including drug delivery, genetic editing, imaging, and bio-sensing, to treat and diagnose a variety of malignancies [13]. CNTs are becoming rising stars in various medicinal sectors, such as drug administration, genetic engineering, imaging, and bio-sensing, to treat and diagnose a range of cancers due to their increased water miscibility. Various compounds can be further linked to the surface of carboxylated CNTs (CNTs-COOH) for the intended uses. However, the effect of carboxylation on CNT cytotoxicity is far from clear [14].

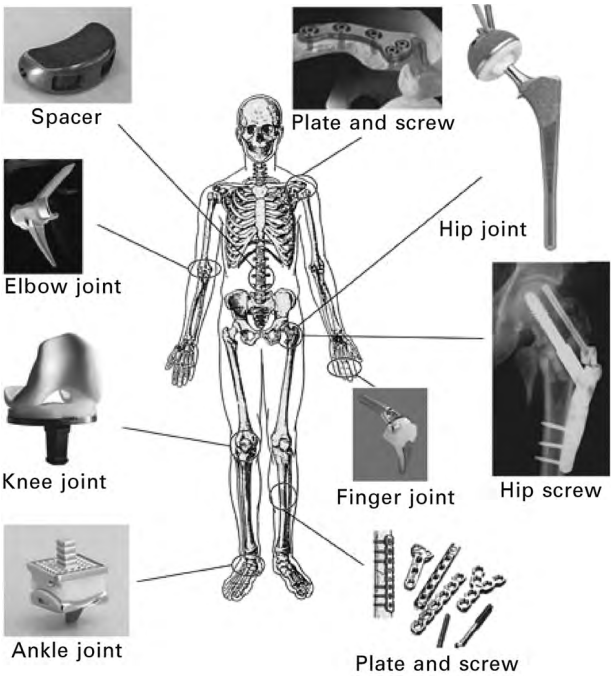


Fig. 2. Biomaterials for human application [18]

DUPLEX STAINLESS STEEL

Duplex stainless steels (DSSs) are a type of stainless steel that has a combined microstructure of austenite and ferrite phases. As a result, these stainless steels benefit from their individual ferritic and austenitic structures [15]. The high Cr, Mo, and N concentrations give the alloy very high strength while also providing good workability for extrusion into seamless tubes [16]. DSS has a chromium equivalent of approximately 28 mass percent and a nickel equivalent of approximately 6 mass percent. The components of the alloy are distributed unequally between austenite and ferrite. Austenite contains a larger concentration of nickel, carbon, and copper, while ferrite has a higher proportion of chromium and molybdenum [17]. With better diagnostic tools and more knowledge about materials and surgical procedures, implantology has become more important. Bioimplants are now commonly used in dentistry, orthopaedics, plastic and reconstructive surgery, ophthalmology, cardiovascular surgery, neurosurgery, immunology, histopathology, experimental surgery, and veterinary medicine (Fig. 2) [18].

SURFACE MODIFICATION TECHNOLOGIES

Surface alterations of biomaterials are critical to matching the intricacies of the biological system and increasing the efficacy of bioimplants. Surface alterations that are appropriately tailored can significantly improve the material's relationship to biocompatibility, bendability, and host cell interactions [19]. In biomaterials, coating the implant surface has been regarded as the

most promising method for increasing biocompatibility and introducing bioactivity to metallic materials. The material's performance is heavily dependent on the qualities of the material's surface [20]. The first and most important prerequisite for selecting a biomaterial is that it is accepted by the human body. The implanted material should not induce any adverse consequences such as allergy, inflammation, or toxicity, either immediately after surgery or in the post-operative period [21].

Coatings for biomedical applications

The primary purpose of surface design is to adjust the surface qualities of ingredients using a variety of classic and modern techniques. It can be separated into two broad groups: surfaces and coatings (Figs. 3 and 4). Surfacing procedures encompass all treatments that deal with bulk improvement without an obvious thickness increase. These may include changing the chemical composition of the bulk or not changing the chemical composition. Coating procedures, on the other hand, encompass all operations that introduce fresh, thick layers to the bulk. All of these techniques result in coating layers with completely different chemical compositions than the bulk materials [22, 23].

Plasma spraying, sol-gel deposition, dip coating, chemical solution deposition, sputter coating, biomimetic coating, and electrophoretic deposition are some of the coating processes utilised for surface modification of materials and coatings [24]. Surface treatments of

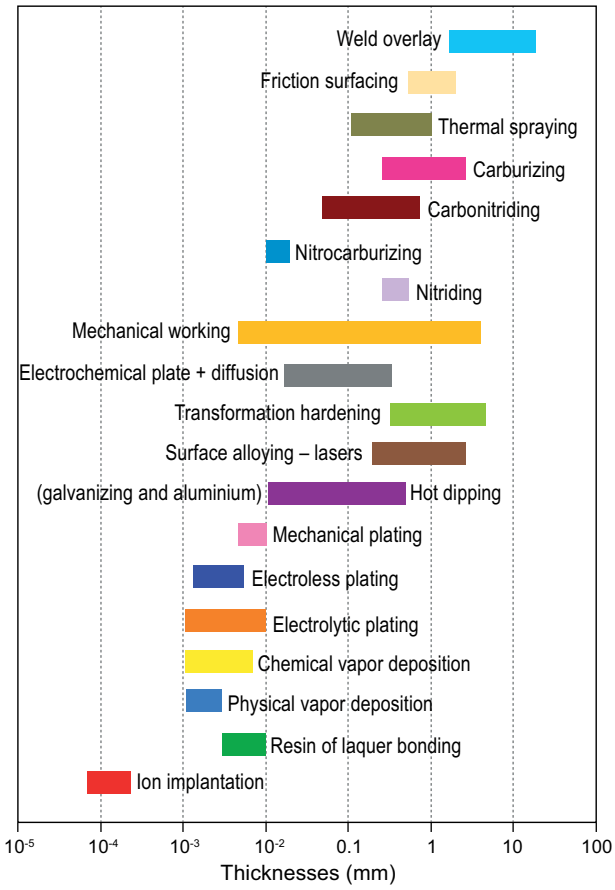


Fig. 4. Approximate thicknesses of various surface engineering modifications [23]

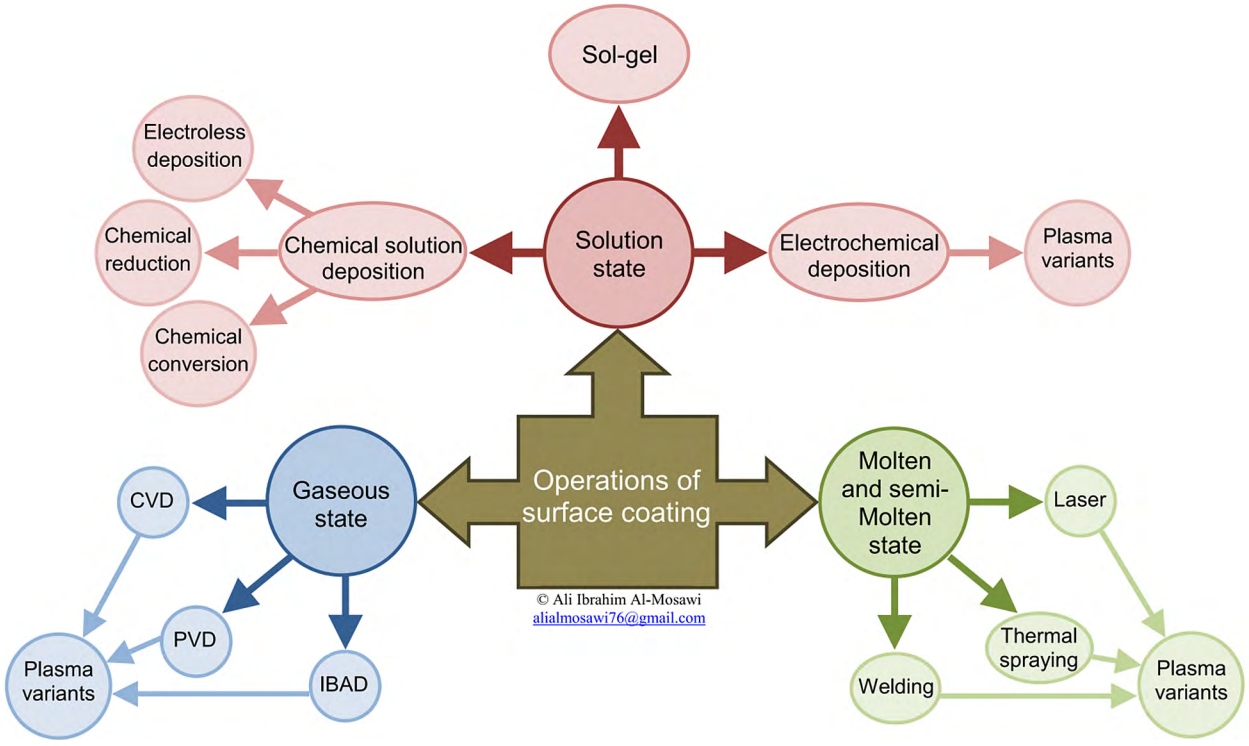


Fig. 3. A broad division of surface engineering methods

biomaterials demonstrate the ability to improve surface properties. They cause surface chemistry, energy, topography, and charge to alter [25]. At the same time, they retain the same engineering bulk qualities. Surface engineering can change the surface in the following ways [26]:

- Surface addition of materials with desirable functionality.
- Repurposing the current surface into more attractive compositions.
- Topographies and material removal from existing surfaces to create unique topographies.

Hydroxyapatite coating

Hydroxyapatite (HA) is a bioactive ceramic substance present in human teeth and bones. Bone is a structural component of our bodies that can be thought of as a natural biocomposite made up of biopolymers (collagen and noncollagenous proteins) and minerals (HA), as well as void spaces (porosity). Hydroxyapatite ($Ca_5(PO_4)_3(OH)$, although it is commonly written as $Ca_{10}(PO_4)_6(OH)_2$ to indicate that the crystal unit cell consists of two molecules, has a hexagonal crystal structure that stands in the hard tissues surrounded by collagen fibres as the organic phase of the bone (Fig. 5) [27, 28].

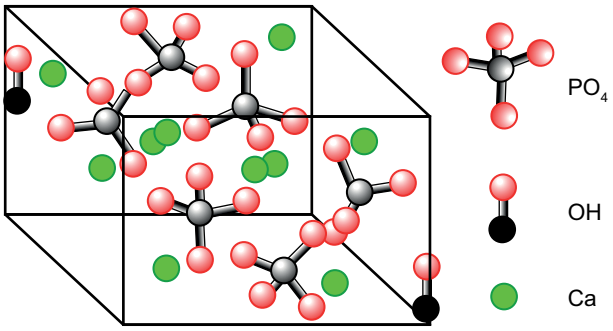


Fig. 5. Crystal structure of HA [29]

Because it can form and grow in the bone tissue around it, HA is a great material for covering metal implants. In order for posterior bone growth to occur, an intimate contact between the surface of the metallic implant and the neighbouring bone tissue is essential. The coating of the metallic implant with HA, on the other hand, results in a rapid bonding between them. The use of HA as a coating on a metallic implant combines the implant's hardness and durability with the bioactive qualities of the HA coating layer, which can encourage surrounding bone tissue growth and future chemical bonding forms. Furthermore, the presence of HA can improve the implant's corrosion resistance in the human body, limiting the release of metallic ions and boosting attachment via chemical bonding [30]. The main disadvantages of HA are its poor adhesion, low mechanical integrity, high brittleness, breakdown in acidic or basic conditions, and insufficient bone formation, which limits its use to non-load-bearing parts of the human body. So, people have tried to add carbon nanotube compounds to HA to make it better [31].

Multi wall carbon nanotube coating

MWCNTs are carbon-based, elongated, hollow, cylindrical nano objects. Their diameter ranges from 4 to 150 nm, and they can grow to be several centimetres long; therefore, their aspect ratio can range between 10 cm and 10 million. They differ from single-wall carbon nanotubes in their multi-wall structure and stiffness, and they differ from carbon nanofibers in their distinct wall structure, smaller outer diameter, and hollow interior [32]. Because of their exceptional properties, including an enormous surface area, high tensile strength, superior corrosion resistance, and good biocompatibility, MWCNs have recently gained a lot of attention in biomedical applications. The presence of such a robust substance in the mineral composite can greatly boost the strength of the tissue/bone junction and encourage new bone development in bone implants [33]. When CNTs and HA are combined, composites with greater mechanical strength than HA and greater biocompatibility than CNTs can be formed [34]. Recent research has shown that CNTs-HA composite coatings can be made using a number of different methods, such as plasma spraying, aerosol deposition, laser deposition, and electrophoretic deposition (EPD) [35].

Electrophoretic deposition

Electrophoretic deposition is an electrochemical technique for combining two fundamental processes: electrophoresis and deposition. In the first method, an electric field is set up between two electrodes, and charged particles in a suitable solution move toward the electrode with the opposite charge [36].

The EPD cell is made up of four parts: working electrodes (substrate and counter electrode), colloidal solution, and power supply (AC or DC). Despite the fact that several mechanisms have been postulated for EPD, there are certain unmistakable traits that separate EPD from other similar deposition-based approaches. As shown in Figure 6a, colloidal particles are well dispersed and able to move freely and independently in solvent suspension, 6b electrochemical equilibrium of the solvent is responsible for particle surface charge, 6c particles move electrophoretically in the bulk of the suspension to the oppositely charged electrode (substrate), and 6d the substrate is covered by a neutralised, firmly deposited layer of particles. As a result, EPD is a technique in which the moving species are solid particles, the liquid medium's required conductance is low, and organic liquids are preferred [37, 38].

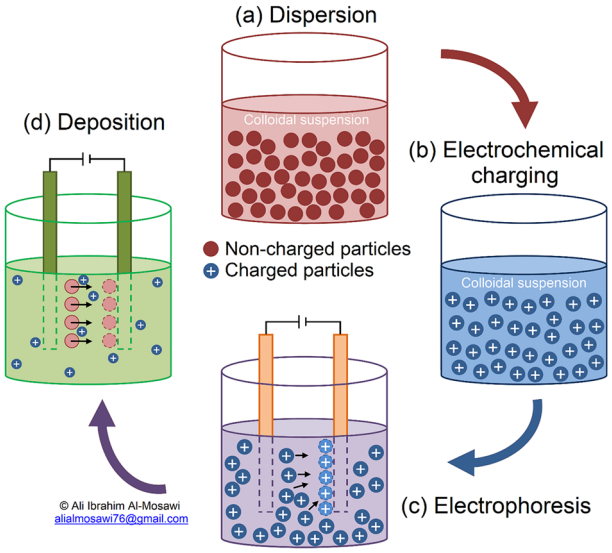


Fig. 6. EPD consists of four steps: a) dispersion, b) electrochemical charging, c) electrophoresis, and d) deposition [38]

This technology allows for the creation of one-of-a-kind microstructures and nanostructures, as well as novel and complicated material combinations in a wide range of macroscopic shapes, dimensions, and arrangements ranging from micron-sized to nano-sized particles. It's been used a lot to deposit CNT-ceramic composite layers on metallic substrates, especially HA-CNT nanocomposite coatings [39, 40].

Effect of an electrolyte composition

The concentrations of solids in the suspension are critical, especially for multi-component EPD. Although each particle species has the same sign of surface charge, they may deposit at various speeds depending on the quantities of solids in the suspension in specific instances. When there are a lot of solids in suspension, the deposition rates are even and uniform, but when there aren't many solids, the deposition rates are proportional to how mobile each particle is [41].

Effect of deposition potential

When the electric field is too strong, the quality of the deposits goes down, which makes the suspension turbulent. Electrophoresis is prevented when applied fields are too low. According to [42], the maximum deposit quality was obtained for the intermediate potential.

Effect of deposition time

The deposition time is the most important characteristic in the electrophoretic deposition process. In general, the thickness of the deposited coating grows with process time, but its mechanical qualities drop concurrently. In addition to electrical parameters, the main variable that impacts the morphology and mechanical properties of the generated structures is the time of the electrophoretic deposition process. Abdeltawab et al. [43] looked into the link between the thickness of the deposited coating and the time of the process. A voltage of 60 V was applied to a suspension of 1 g of HAP in 100 ml of dimethylformamide. Deposition times ranged from one to seven minutes. It is obvious that the thickness and mass of the formed coating increase solely during the initial deposition time, and that the deposition rate is a linear function of the deposition duration. However, over time, the deposition rate declines and reaches a plateau at very high deposition times. While the potential difference between the electrodes remains constant in a constant voltage EPD, the electric field diminishes with deposition time due to the development of an insulating layer of HAP on the electrode surface. This discovery is also consistent with Zhitomirsky's [44] research. During the initial period of EPD, there is a roughly linear connection between deposition mass and process time. This information, however, is insufficient to determine the appropriate duration of the process. Microscopic investigations are required to determine the morphology and homogeneity of the final structure. These findings reveal that a longer treatment time results in a less homogenous covering with more agglomerates and microscopic cracks.

The rate of deposition decreases as the time of deposition increases. This is attributed to a decrease in the electrical field, which affects electrophoresis, as a result of the creation of an isolating layer of ceramic particles on the electrode surface [45].

CONCLUSION

Surface modification of biomaterials is a vast issue with numerous considerations for increasing implant performance and service life in the human body. Electrophoretic deposition (EPD) is an appealing material-processing approach because of its versatility in terms of the wide range of materials (in particle form) to which it may be applied and the comparatively simple equipment required. Electrophoretic deposition is a low-cost and effective approach for depositing hydroxyapatite coatings, but it also necessitates the management of numerous parameters. In the electrophoretic deposition process, the composition of the electrolyte, the potential, and the time of deposition are all important parameters. Current review focuses on surface modification of standard duplex stainless steel by electrophoretic deposition with HA/MWCNT nanocomposite coating to prevent metal ion release (making it more corrosion resistant) and to make the metal surface bioactive.

CONFLICTS OF INTEREST

The authors certify that they have NO affiliations with or involvement in any organisation or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

Data availability statement

Statement for Data available on request from the authors: The data that support the findings of this study are available from the corresponding author upon reasonable request.

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