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# Thermal based surface modification techniques for enhancing the corrosion and wear resistance of metallic implants: A review

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ABSTRACT

For successful implantation, biomaterials need excellent corrosion and wear resistance in the body environment, a combination of high strength and low modulus, appropriate ductility and non-cytotoxic. Due to their unique mechanical properties and durability, metallic biomaterials have been widely utilised in clinical applications, such as joint replacements, dental root implants, orthopaedic fixation devices, and cardiovascular stents. However, the wear and corrosion of metallic implants determine the service period of implantation owing to the release of incompatible metal ions into the body that may induce inflammation and allergic reactions. This review article focuses on the effect of corrosion and wear on the implant and the human body and mechanisms to enhance corrosion and wear resistance. Initially, metallic biomaterials and their properties are presented. Then, the reasons for implant failure are highlighted with a focus on details of wear and corrosion mechanisms. Finally, various thermal-based surface modification techniques and their applications in enhancing corrosion and wear resistance of Titanium-based biomaterials are presented. Surface modification techniques are currently discussed as the "best solution" to improve corrosion and wear resistance performance, providing superior tissue compatibility and encouraging osseointegration.

## 1. Introduction

The year 2019 saw the implantation of nearly 112,000 total hip and 118,000 total knee replacements in the UK, making hip and knee replacements the most commonly performed orthopaedic surgeries [1]. Such surgeries aim to reduce pain and improve the function of the joint by replacing the joint with a biomaterial implant [2]. The performance of biomaterials within biological structures is crucial for the success of biomedical implants and tissue engineering. Various metallic biomaterials can be used in the human body; however, Titanium and Titanium alloys are favoured owing to their superior fatigue and corrosion resistance, biocompatibility, and excellent mechanical properties, making them the most bone compatible metals [3].

Patients typically require joint replacements due to trauma or joint diseases, with osteoarthritis being common [4]. Osteoarthritis is a common joint disease in which the articular cartilage of synovial joints, such as the knee and hip, degenerates, affecting 10% of females and 18% of males [5]. The articular cartilage in synovial joints acts to absorb shock and evenly distribute weight across the bone, therefore, damaging this cartilage layer leaves the bone underneath vulnerable to frictional wear and injury. The degradation of this lubricating surface eventually allows the bones to rub against each other, creating friction and initiating an inflammatory response that causes pain and swelling. As cartilage is avascular, it has a minimal ability to repair itself, meaning that any damage is long term and eventually, the joint must be replaced by an implant [5].

Although the prevalence of osteoarthritis increases with age, lifestyle changes are now making the disease more and more common among younger people, with 35% of all hip and knee replacements performed in the UK by the NHS in 2013 being carried out in people below the age of 65 [6]. This change can be attributed mainly to increased obesity levels within the UK among younger people. The extra mechanical stress that the excess weight places on the joints accelerate the process of cartilage degradation resulting in early-onset osteoarthritis. People with a body mass index (BMI) greater than 30 kgm$^{-2}$ are seven times as likely to develop osteoarthritis than their peers of a healthy weight [6].

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Other lifestyle-based changes that have contributed to the rise in younger people developing osteoarthritis include increased participation in high-risk physical activities such as skiing [5,7]. These activities often result in injuries, stresses, and strains on the joints. The body responses to these by eliciting an inflammatory response as part of the healing process. During the inflammation stage, cytokines and growth factors are released, including Interleukin-1 (IL-1), Interlukin-6 (IL-6) and Tumour Necrosis Factor (TNF), which act to promote cartilage degradation or inhibit the already limited cartilage repair, therefore contributing to the early onset of osteoarthritis [5]. This inflammatory response is also a contributing factor to the prevalence of osteoarthritis among the elderly, with 28.9% of over 60-year olds suffering a significant fall each year [8].

Not only is demand for orthopaedic implants increasing due to an ageing population, with the percentage over 60 years old predicted to double by 2050 worldwide, but a rising life expectancy and an increase in early-onset osteoarthritis are also driving advances in orthopaedic implant technology [9]. With life expectancy increasing from 63.6 years in 1940, when the first orthopaedic implant was implanted, to 81.65 years in 2022, as well as 22% of children aged between 4 and 5 and 33% of children aged between 10 and 11 being overweight, implants that once out survived their recipient is now failing during life and needing replacement [10].

Biomaterials can be defined as those which create an interface with a biological system to support the function of or replace tissue or organ in the body [11]. The materials used for orthopaedic implants, particularly in load-bearing applications, should have i) bone cell compatibility, ii) corrosion resistance in the body, iii) a combination of high strength and low modulus, iv) good fatigue and wear resistance, v) high ductility and vi) be non-toxic in the joint environment [12]. The materials of choice are application-dependent and can be categorised as polymers, metals, ceramics, or composites. Metals tend to have high wear, and impact resistance and are used in applications such as staples, joint replacements and dental implants [13]. Compared to polymers and ceramics, metallic implants are routinely applied clinically due to their appropriate physical and mechanical characteristics. The global market size for biomaterials is estimated to be worth $35.5 billion and is set to increase to over $47.5 billion by 2025 with metallic biomaterials accounting for the largest segment of the market [14]. The metallic biomaterials used for these applications are 316L stainless steel, cobalt-chromium alloys, and titanium and titanium-based alloys. Despite their regular use, these biomaterials have shown tendencies to fail during long-term usage owing to numerous causes, including high modulus compared to that of bone, insufficient wear and corrosion resistance and lack of biocompatibility. Corrosion and wear of metallic implants lead to two main adverse effects: i) compromising the structural strength of the implant and ii) releasing metallic debris that often causes chronic inflammation, allergic reaction and granuloma (early wound tissue) formation [15].

Loss of implant mass due to corrosion results in reduced hardness and a lowered fatigue resistance. Joints such as the hip and knee are required to have high fatigue resistance because they are under several repeated load cycles a day, with the average person taking around 9000 steps a day [16]. The cracks that develop due to corrosion mechanisms create stress concentrations at the tip [17]. Stress concentrations create areas that will fail under applied loads of lesser magnitude than the rest of the implant, and this creates crack growth which leads to catastrophic failure of the implants due to fatigue [17].

The biological response to corrosion products is also a common reason that patients require revision surgeries regarding hip and knee replacements. Particulate and ion debris resulting from the corrosion process can initiate an immune reaction from the body, causing inflammation and swelling and pain [18]. If this inflammation persists, it is termed chronic inflammation and leads to long term pain and discomfort for the patient, and typically, the implant needs to be removed. In addition to this, over time, the adaptive immune response can cause granuloma formation, which disrupts the implant to the bone interface, causing implant loosening and pain, again resulting in the replacement of the implant [18]. Furthermore, the production of wear debris can result in osteolysis, again causing implant loosening. Wear debris generates an immune response in which macrophages are activated. These macrophages release cytokines, such as MCP-1, as they try to remove the wear debris; however, these cytokines initiate the recruitment of osteoclasts. Osteoclasts, which differentiate from macrophages, work to break down osteocytes around the implant, causing it to become loose [19].

For these reasons, a significant amount of work is being carried out in the area of new alloys development and surface modification of biomaterials to improve their corrosion and wear resistance and mechanical properties. Surface modification techniques remain the major field of study to improve the above-mentioned properties, and researchers worldwide are exploring different techniques to induce favourable surface modification of biomaterials resulting in an enhanced life span of the implants.

This paper aims to provide an overview of the fundamentals of metallic biomaterial failure and the mitigation methods based on surface modification using thermal energy mechanisms. Initially, the paper introduces the most common metals used for orthopaedic implant replacements. Then, the fundamentals of biomaterials wear and corrosion have been introduced to the readers and presented other common failure mechanisms of biomaterials. Later in the paper, some of the most recent research into thermal-based surface modification techniques to prevent the premature failure of Titanium alloys are outlined.

## 2. Metallic biomaterials

Successful biomaterials are often those that mimic the properties of the material they are replacing. For load-bearing, orthopaedic use, biomaterials require high strength, bone compatible Young's Modulus to avoid load shielding, low density, porosity and resistance to corrosion and wear [20]. Therefore, metals lend themselves well to this application, particularly Stainless Steel, Cobalt alloys, Titanium and Titanium alloys.

Commonly used metallic biomaterials and their advantages and disadvantages relating to their biocompatibility as an orthopaedic implant are listed in Table 1. Their typical ranges of mechanical properties in Table 2.

### 2.1. Stainless steel

Austenitic Stainless Steel 316L is used as a temporary biomaterial. Due to its chromium content, it offers good corrosion resistance in many corrosive environments; chromium forms an oxide layer with oxygen on the surface of the metal; this is a passivating layer [22]. Despite this, many studies, including Giordani et al. [23], found that Stainless Steel suffers from pitting, crevice, fretting and galvanic corrosion, and stress corrosion cracking under physiological conditions; therefore, it is used on a short timescale basis (less than 12 months). An investigation into the failure mechanism of a removed Stainless Steel femoral implant by Amel-Farzad et al. [24] determined that the implant had undergone crevice and pitting corrosion, as seen in Fig. 1, which weakened the implants fatigue resistance. However, it is essential to note that this study only looked at one implant, and failure mechanisms will vary due to the patient's lifestyle. The wear resistance of Stainless Steel is also poor, creating a large amount of wear debris [22]. In addition to poor corrosion and wear resistance, the use of Stainless Steel as a biomaterial has been seen to initiate allergic reactions in a significant number of patients requiring removal of the implants [25]. Furthermore, the Young's Modulus for Stainless Steel is 200 GPa [22], whereas that of bone is around ten times smaller. This leads to load shielding (bone is resorbed because it does not experience sufficient loading as all the load is transferred through the implant) which causes resorption of the bone,

**Table 1**
Evaluation of metallic biomaterials for orthopaedic use (Adapted from Refs. [2,21]).

| Metal | Advantages | Disadvantages | Applications | Primary uses |
|---|---|---|---|---|
| Stainless Steel<br>E.g. SS316L, | High corrosion and fatigue resistance. | Wear debris generated.<br>Initiates allergenic response.<br>Generates load shielding due to high Young's Modulus. | • Orthopaedic<br>• Orthodontic<br>• Cardiovascular | • Temporary devices (fracture plates, screws, hip nails, etc.) (Class II)<br>• Total hip replacements (Class II)<br>*(Routinely applied)* |
| Cobalt Alloys<br>E.g. CoCrMo, CoNiCrMo, CoCrWNi | High wear and corrosion resistance.<br>Corrosion-resistant in the presence of chloride.<br>Easy to cast. | Leaching of toxic elements.<br>Generates load shielding due to high Young's Modulus. | • Orthopaedic<br>• Orthodontic<br>• Cardiovascular | • Total joint replacements (wrought alloys) (Class II)<br>• Dentistry castings (Class II)<br>*(Routinely applied)* |
| Titanium and Titanium Alloys<br>E.g. Ti–6Al–4V, Ti–13Nb–13Zr, Cp-Ti | High corrosion resistance.<br>Relatively low Young's modulus which limits load shielding.<br>Low density.<br>Low electrical and thermal conductivities.<br>Good ossteointegration. | High friction coefficient.<br>Poor wear resistance. | • Orthopaedic<br>• Orthodontic<br>• Cardiovascular | • Stem and cup of total hip replacements with CoCrMo or ceramic femoral heads (Class II)<br>• Other permanent devices (nails, pacemakers) (Class III)<br>*(Routinely applied)* |

**Table 2**
Mechanical properties of metallic biomaterials and bone [16,17].

| material | Young's Modulus (GPa) | Elongation to failure (%) | Ultimate tensile stress (MPa) | Density ($kg/m^3$) |
|---|---|---|---|---|
| Bone | 20 | 1–2 | 90–140 | 1900 |
| Stainless steel | 200 | 45 | 465–950 | 7800 |
| colbalt alloys | 275–1585 | 5–30 | 600–1795 | 8500 |
| titanium | 105 | 15–24 | 785 | 4200 |
| ti-6al-4v | 110 | 10–15 | 960–970 | 4500 |

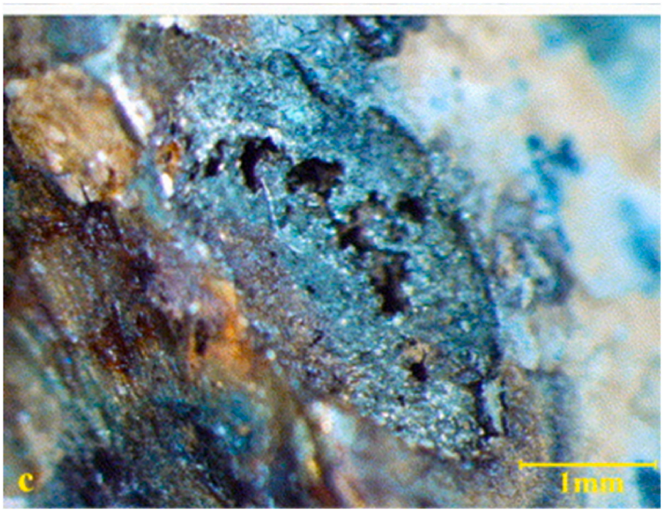


**Fig. 1.** Image of the crevice and pitting corrosion in the fracture zone of the Stainless-Steel femoral implant. Reprinted with permission from Elsevier [24].

which causes implant loosening [26].

### 2.2. *Cobalt alloys*

Among the Cobalt alloys, Co–Ni–Cr–Mo and Co–Cr–Mo are commonly employed for implantation applications [22]. The passive oxide layer that forms on these alloys under physiological conditions offers high resistance to corrosion, including when chloride is present, thus making them well suited as biomaterials. These alloys also offer high wear and fatigue resistance. However, like Stainless Steel, the alloys do not have Young's modulus compatible with bone, as Young's modulus for cobalt alloys is around 11 times that of bone [22]. In addition to this, the Ni, Cr and Co that leach out of the implants over time are highly toxic to the human body, with chromium being linked to skin ulcers and cancer of the central nervous system [11]. Most papers researching the area have investigated the prevalence of cobalt induced cancers in patients who had been fitted with a cobalt implant. However, there was no mention of the health implications the fitting of these implants had on the surgeons. Suh et al. [27] studied the carcinogenetic effects of inhalation of cobalt on rats and found that cancerous tumours in the lungs developed over time. Similarly, Czarnek et al. [28] and Lison et al. [29] found that cancerous tumours also developed in humans when cobalt is inhaled.

### 2.3. *Titanium and titanium alloys*

Titanium and its alloys have been widely used for implantation applications to restore damaged hard tissue since the 1970s, owing to their superior fatigue and corrosion resistance. The ability of these metals to form a thin oxide layer offers excellent corrosion resistance to Titanium alloys. Some applications include pacemakers, artificial hearts, bone plates, cornea, back plates, artificial hip/knee joints, screws for fracture fixation, cardiac valve prostheses, and dental and orthopaedic implants [30].

Titanium boasts a low density as well as low electrical and thermal conductivity when compared to other metals and good corrosion resistance due to the creation of a passive oxide surface layer [11]. The Young's modulus of commercially pure titanium or Ti–6Al–4V alloys is approximately 110 GPa [22]. In contrast, that of β-Ti alloys is reduced even further at around 50 GPa [31]. This makes these alloys the closest match in terms of mechanical properties to the bone when compared to the other metals discussed in this review. Another factor that makes the use of titanium well suited for use as an orthopaedic implant is its ability for osteointegration; this improves the long-term success of these implants [32].

The low modulus, excellent biocompatibility, and corrosion resistance of titanium alloys make them the first choice for orthopaedic applications compared to stainless steel and cobalt alloys. However, these alloys have the limitations of poor tribological properties, low abrasive resistance, and a lack of mechanical stability in the oxide layer. Therefore, the remainder of this review will focus on the surface modification techniques employed to improve such properties of titanium alloys [3].

## 3. Failure of metallic implants

The life expectancy of titanium orthopaedic implants is between 15 and 20 years [12], meaning that the implants are likely to fail within the patient's lifetime, thus requiring revision surgery and replacement implants. A study into the patterns and risk factors of orthopaedic implant failures completed by Onuoha et al. followed 535 patients for ten years following their implant surgery and found that 3% of these patients required total replacement of their implants in this period [33]. With each revision surgery costing the NHS anywhere between £6000 and £12000, these revision surgeries put patients through pain and discomfort [34]. They also place an enormous financial stain on the NHS. Poor osseointegration, development of biofilms, corrosion and wear, are the most common issues that lead to revision surgery.

### 3.1. Poor osseointegration

Osseointegration describes the direct structural and functional connections between bone and a biomaterial implant without the need for other (soft) connective tissue involvement [35]. The process involves osteoblasts reaching the surface of the biomaterial. These cells secrete collagen matrix followed by bone apatite onto the metals' surface, thus encouraging the integration of the implant with the bone, therefore, reducing the likelihood of loosening [36]. Without osseointegration, the implant cannot interface with the host tissue. This can damage the surrounding tissue causing pain to the patient and resulting in the need for revision or replacement surgeries [36]. Poor osseointegration is common among diabetic patients as these patients overproduce the advanced glycation end products (AGEs), which prevents the bone from attaching to the implant [37]. Studies have been conducted to enhance the osseointegration on titanium surfaces, including Anselme and Bigerelle, who showed that increasing surface roughness increases osseointegration and Petrie et al. [38], who investigated the effects of adding a hydroxyapatite coating to the metals surface, which increased the adhesion of osteoblasts. A study carried out by Jia et al. [39] looked at the use of 1α,25-dihydroxyvitamin D3 (1,25VD3) hormone therapy to improve osseointegration of titanium implants in diabetic rats. The results show that the use of 1,25VD3 hormone therapy improved the bone-implant contact by around 20% when compared to untreated, diabetic rodents. However, the long-term effects of this treatment cannot be determined as the rodents were killed after 12 weeks. In addition to this, 1,25VD3 works by downregulating the production of AGEs, therefore reducing the activation of osteoclasts [39]. Using a systemic hormone therapy that reduces the proliferation of osteoclasts could prevent the healthy turnover of bone and cause bone masses to develop.

### 3.2. Development of biofilms

The adhesion of bacteria onto implant surfaces can cause biofilm developments. Biofilms prevent the adhesion of host cells onto the surface of the metal, which prevents the integration of the device into the body, thus, leaving a space between implant and bone which allow movement [40]. Furthermore, biofilms can cause chronic inflammation that is difficult to treat and results in the need to remove the device [40]. Many studies have investigated methods to help mitigate this effect; one such study was carried out by Gu et al. [41]. They found that printing a micropattern containing biphasic calcium phosphate onto Ti-6AL-4V implant surfaces reduced the development of biofilms by accelerating osteoblast differentiation on the implant's surface, thus increasing the rate of osseointegration and inhibiting bacterial from accessing the surface. Beck et al. [42] virtually eliminated the formation of biofilms caused by *Staphylococcus epidermidis* on titanium and stainless steel implants. These results were obtained via an *in vitro* study of metals coated in sphingosine. Despite these promising results, this coating only targets one bacterial strain, and the results have not been verified through *in vivo* investigations.

### 3.3. Wear

The primary wear mechanism orthopaedic biomaterials suffer is oxidational wear. This mechanism involves the removal of the native oxide layer by a contacting asperity [43]. Titanium's native corrosion resistance is due to its high affinity for oxygen. An oxide layer develops on the surface of the metal, which helps prevent the transfer of ions between the metal beneath and the surrounding environment, thus preventing corrosion [44]. However, wear can cause damage to this passivating layer. Once this layer is damaged, the protection against corrosion is compromised, and the exposed metal may corrode. In atmospheric environments, the oxide layer gradually repassivates, so the extent of the corrosion is reduced. However, in physiological environments, the rate of repassivation is too slow to prevent advanced corrosion, resulting in the implant's failure [11]. This drastic variation in the repassivating rates can be attributed to variations in dissolved oxygen levels and partial pressures. In blood, the oxygen levels are much lower than in the atmosphere because, in blood, oxygen combines with haemoglobin. In addition to this, the partial pressure of blood is also up to 4 times lower than that of the atmosphere [11].

Moreover, this wear mechanism creates wear debris, as shown in Fig. 2. Such wear debris can initiate an immune response in which macrophages phagocytose the foreign matter. However, phagocytosing macrophages secrete TNF-α, which recruits osteoclasts and triggers osteolysis [45]. In severe cases, this osteolysis can cause the implant to become loose and thus require replacing.

Hardness, defined as the resistance of a material to indentation, permanent deformation and scratching, can be used to evaluate wear resistance [46]. Materials with higher surface hardness values require heavier loads to cause such effects to the surface layer; therefore, the higher the hardness, the greater the resistance to wear [47–49]. In addition to this, pin-on-disc wear testing is used readily within studies in the literature to obtain wear rate results. The wear rate is calculated by dividing the reduction in weight by the duration of the wear test.

### 3.4. Corrosion

About 42% of orthopaedic implant failures resulted from corrosion, making it the most common reason for patients to need revision surgeries [51]. Corrosion is defined as the chemical reaction of a metal with components of its environment to produce a product of a more stable form [11]. Once the oxide layer has been damaged (as described above), the metal beneath is exposed to a highly corrosive environment; body fluids contain corrosive components such as water, sodium, chlorine and proteins [44]. Corrosion occurs due to electrochemical reactions between the metal and the electrolyte in which the metal atoms are oxidised to become positive metallic ions. In contrast, components of the electrolyte (typically oxygen, sulphur or chlorine) are reduced. The two ions created are of opposite charge and so attract each other, creating a corrosion product. This corrosion product is in a lower energy state than the metal (as seen in Fig. 3); however, the corrosion product does not have the desirable properties that a biomaterial needs. Therefore, research is ongoing to identify effective ways to prevent or slow corrosion.

Conventional inert materials, such as base metals and alloys based on cobalt-chromium, titanium, and stainless steel, incline to provide electrons in solution and, as a result, are expected to corrode while exposed to fluids in the peri-implant environment, which is characteristically corrosive and rich in oxygen-containing chemical species. Metals dissolve because of these corrosion reactions, and metallic ions are created. The rate and chemistry of these reactions are determined by the material's chemistry and the environment's unique properties (see Table 3). For instance, when commercially pure titanium and Ti6Al4V alloy are subjected *in vitro* to fluoride $F^-$ ions at concentrations similar to those found in the oral cavity, the former experiences pitting corrosion, whilst the latter is affected by typical temperatures corrosion with distinctive surface micro-cracks [52].

Electrochemical analysis using potentiodynamic polarization methods is used to evaluate the rate of corrosion. From this, Tefal diagrams can be produced, and the corrosion potential and the corrosion current can be obtained via extrapolation, and a simple calculation


**Fig. 2.** A schematic diagram to show the creation of wear debris during oxidational wear [50].

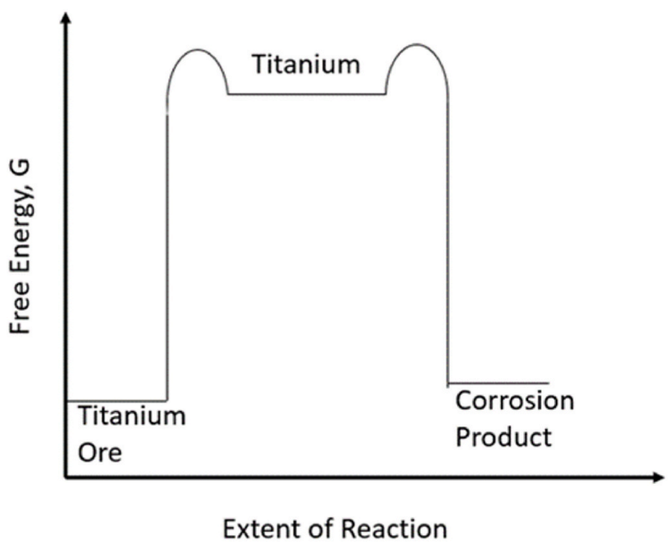


**Fig. 3.** The free energy changes associated with titanium and its corrosion products.

performed to get the rate of corrosion. To ensure the data is representative of *in vivo* conditions, the electrochemical analysis should involve an electrolyte that simulates human bodily fluids, such as simulated body fluid or Ringer's solution, with the test sample being the working electrode, the counter electrode of, for example graphite, and a reference electrode of for example gold. To mimic the physiological conditions, experiments will be performed at 37 °C. Before testing, immersion of the samples in the electrolyte will be required for 24 h to ensure stabilisation. To obtain reproducible and comparable results, the surface area of the test samples exposed to the electrolyte will need to remain consistent between all samples.

There are three main corrosion mechanisms discussed in the literature: crevice/pitting, fretting and galvanic [54].

### 3.4.1. *Crevice corrosion*

Crevice corrosion occurs when there is a restricted environment around part of the metal surface while the rest of the metal is exposed to a bulk electrolyte. In the shielded area, mass diffusion is restricted, causing a depletion in oxygen and a reduction in pH in this area [54]. These restricted environments can be created by scratches on the metal's surface. The rate of the surrounding cathodic/reduction reactions, where there are no restrictions on reactants, must be balanced by the anodic/oxidation reaction in the shielded area so the rate of corrosion in the crevice will increase.

Crevice corrosion is enhanced when chloride ions are present in the electrolyte [11], such as in blood and interstitial fluid, with chloride ion concentrations of 113 $mEqL^{-1}$ and 117 $mEqL^{-1}$, respectively [55]. In titanium, the anodic/oxidation and cathodic/reduction reactions produce $Ti^{4+}$ and $OH^-$. As titanium ions have a charge four times that of the hydroxide ions, $Cl^-$ are attracted towards the $Ti^{4+}$ and into the scratch to balance the charges. In the scratch, the available oxygen is used up over time, and so the $OH^-$ ions can no longer be formed; therefore, more and more $Cl^-$ ions are attracted in to balance the charges. This creates an acidic region within the scratch because the chloride ions are made from the dissolution of HCl, which means there is an increased production of $H^+$ ions. A lowered pH accelerates the rate of metal corrosion which causes more $Ti^{4+}$ to be produced; this then attracts more $Cl^-$ which lowers the pH. Therefore, this process can be described as autocatalytic [11]. Bhola et al. [56] studied the electrochemical corrosion behaviour of titanium and its alloys with *in vitro* testing under physiological conditions using the standard saline solution at 37 °C. The study measured the pH of the saline solution over time under a constant applied potential. They found that the pH of the saline solution increased from 6.6 to 8 after 7 days; using the Pourbaix diagram shown in Fig. 4, this change of pH indicated the formation of an oxide layer of $TiO_2$. However, it

**Table 3**
Physical and chemical elements in the body recognised to affect corrosion [53].

| Environmental condition | | Physical parameters | Concerns |
|---|---|---|---|
| *Body temperature* | | 36.1–37.2 °C | Enhanced chemical reactions |
| *pH* | Blood | 7.15–7.35 | Transient reduction in peri-implant space to ~5.2. Oxygen-containing chemical species drive corrosion. Transient rise in ROS in peri-implant milieu due to inflammation |
| | Intracellular | 7 | |
| | Matrix Cells | 6.8 | |
| *Dissolved oxygen* | Arterial blood | 100 mmHg | Oxygen levels affect formation of protective oxides |
| | Venous blood | 40 mmHg | |
| | Intracellular matrix | 2–40 mmHg | |
| *Chloride ion* | Serum | 113 mM | Monovalent chloride stabilises suspensoid sols preventing the formation of a protective corrosion product layer on metals |
| | Interstitial fluid | 117 mM | |
| | Cardiac muscle | 20–30 mM | |
| *Chemistry of body fluids (Interstitial, synovial, serum)* | $Na^+$ | 3127–3280 $mg\ l^{-1}$ | Affect formation of protective oxides and mechanism and rate of corrosion |
| | $K^+$ | 156 $mg\ l^{-1}$ | |
| | $Ca^{2+}$ | 60–100 $mg\ l^{-1}$ | |
| | $Mg^{2+}$ | – 24 $mg\ l^{-1}$ | |
| | $Cl^-$ | 3811–4042 $mg\ l^{-1}$ | |
| | $HCO_3^-$ | 1892 $mg\ l^{-1}$ | |
| | $HPO_4^{2-}$ | 96 $mg\ l^{-1}$ | |
| | $SO_4^{2-}$ | 48 $mg\ l^{-1}$ | |
| | Organic acids | 245 $mg\ l^{-1}$ | |
| | Protein | 15,000–4144 $mg\ l^{-1}$ | |

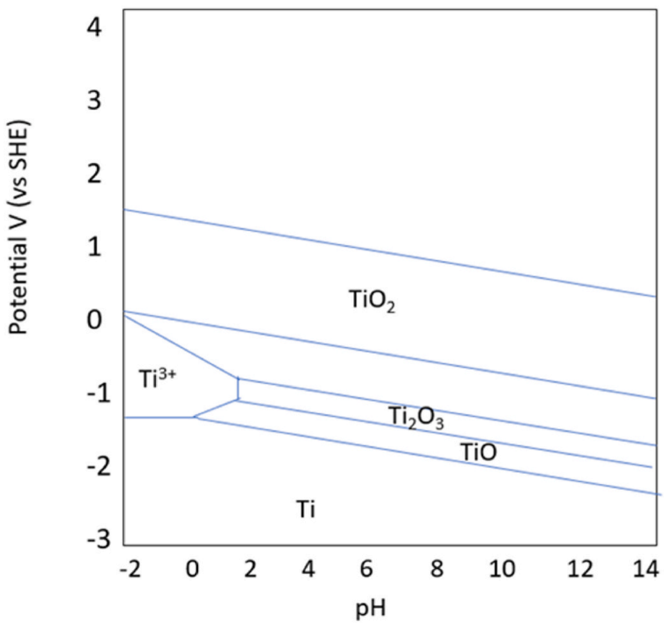


**Fig. 4.** Pourbaix diagram of titanium at 37 °C. Reprinted with permission from Elsevier [59].

should be noted this study may not fully represent the behaviour of titanium *in vivo* as the saline solution is missing components such as proteins and cells that are found within bodily fluids.

Many publications discuss surface defect production from wear that exposes the underlying metal and initiates crevice corrosion; however, few discuss the idea of protein adsorption on the metal surface. In the initial stages of biomaterials being introduced into the body, proteins adsorb to their surface (Fig. 5); the type of protein that adsorbs in a particular area depends on the metal's surface chemistry and topology. Therefore, across the surface of a biomaterial, there may be several different protein types adsorbed on the surface in different areas. Some of these proteins may act to facilitate or inhibit the transfer of ions across the titanium oxide layer, this creates restricted environments in some areas which can initiate crevice corrosion.

Pitting corrosion describes a form of crevice corrosion which results in the creation of cavities or holes on the metal's surface which increases the surface roughness. These cavities or holes create stress concentrations when under loading which can result in catastrophic failure of the implant- Stress Concentration Cracking (SCC) [57].

Hussey et al. [58] conducted a ten-year study of 1352 patients who had received a hip implant in 2002 to establish the prevalence of mechanically assisted crevice corrosion (MACC) within the implants. The

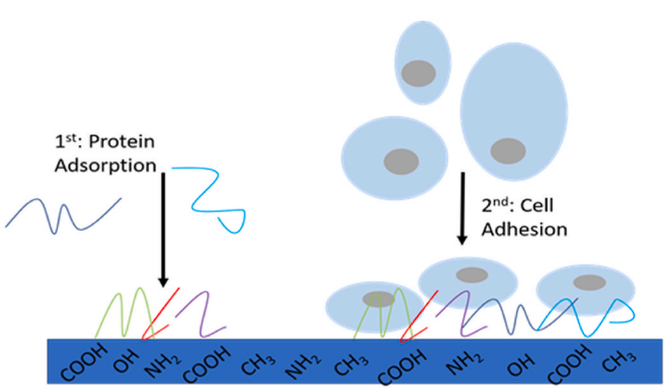


**Fig. 5.** Protein adsorption to a biomaterial surface depends on the exposed chemical groups. Reprinted with permission from Elsevier [60].

study found that 3.2% of the patients experienced symptoms of MACC within the ten-year study and of that 3.2%, 62.8% required revision surgery.

### 3.4.2. Fretting corrosion

Fretting Corrosion occurs when two different surfaces continuously rub against each other in an oscillating fashion. Of all the corrosion mechanisms discussed in this report, fretting corrosion creates the most debris due to its inclusion of both wear and corrosion. This produces weight loss of the implant, and it has been demonstrated that there is an inversely proportional relationship between the weight loss of an implant and hardness [54]. Reducing the surface hardness of a material increases its susceptibility to wear. Examples of fretting corrosion have been seen when cobalt alloys or ceramics are used in conjunction with titanium alloys due to the creation of intercomponent junctions [61].

Sivakumar et al. investigated the link between surface roughness of titanium metals and fretting corrosion using a ball-on-flat contact method. The study found that decreasing surface roughness reduced fretting corrosion effects as surface energy decreased with surface roughness. The optimum surface roughness to balance the need for osseointegration and corrosion resistance was 43 nm [62].

### 3.4.3. Galvanic corrosion

Galvanic corrosion, also known as dissimilar metal corrosion, occurs when two different metals are in physical contact in an ionic conductive medium, for example, interstitial fluid. This arrangement creates an electrochemical cell formation, resulting in one metal taking the role of an anode and the other as a cathode. Although modular orthopaedic implants predominantly are produced from a single metal type, thus mitigating the potential of galvanic corrosion, using titanium as a bone plate or bone screws has been seen to induce corrosion via this mechanism [54].

Zee et al. reported a case study of a 66-year-old male who suffered severe osteolysis (bone resorption) following the implantation of a cobalt-chromium alloy device to the knee to treat osteoarthritis; a titanium screw was used to secure the implant. The differences in electrochemical potential of the two metals caused galvanic corrosion resulting in the production of corrosion products and the initiation of an immune response [63]. This immune response activated the osteoclasts and caused degradation to the surrounding bone resulting in aseptic (no infection present) loosing of the implant.

Hydrogen Embrittlement is another corrosion mechanism; however, very few publications mention its role in the corrosion of biomaterial implants. Hydrogen embrittlement occurs when hydrogen from the surrounding environment diffuses into the metal. Diffusion of hydrogen occurs in metals of any crystal structure. However, it appears more readily in metals of a body-centred cubic (BCC) arrangement [64]. Where the hydrogen accumulates, it dilutes the metal structure, leading to severe cracking. Ti–6Al–4V, a commonly used Titanium alloy for biomaterials, is an alpha + beta phase alloy, and thus hydrogen embrittlement in the beta phase should be considered [65].

When a biomaterial is first introduced into the body, the pH in the surrounding area drops from around 7.4 to 3.5 [36]; the lower the pH, the greater the concentration of hydrogen ions. This high concentration of hydrogen ions in the area surrounding metallic biomaterials creates a steep concentration gradient for $H^+$ to diffuse into the biomaterial causing hydrogen embrittlement. It is possible that because the reduced pH in the local area only persists for between 10-15 days, the rate of diffusion is too slow to cause significant problems, and this is why many publications do not discuss this mechanism. Furthermore, although a pH of 7 at 25 °C refers to a neutral solution in which the concentration of hydrogen ions is equal to the concentration of hydroxide ions, due to pH's dependence on temperature, this neutrality is achieved at a pH of 6.81 when at the 37 °C, body temperature. Therefore, blood with a pH of 7.4 has a higher concentration of hydroxide ions than hydrogen ions and is alkaline in nature, thus creating another diffusion gradient for hydrogen ions to diffuse out of the biomaterial and back into the blood [11].

Corrosion and wear of metal implants lead to two main adverse effects: compromising the structural strength of the implant and releasing metallic debris that often causes chronic inflammation, allergic reaction and granuloma (early wound tissue) formation [15]. Loss of implant mass due to corrosion results in reduced hardness and a lowered fatigue resistance. Joints such as the hip and knee are required to have high fatigue resistance because they are under several repeated load cycles a day, with the average person taking around 9000 steps a day [16]. The cracks that develop due to corrosion mechanisms create stress concentrations at the tip. Stress concentrations develop areas that will fail under applied loads of lesser magnitude than the rest of the implant. This creates crack growth, leading to the implants' catastrophic failure due to fatigue [17].

The biological response to corrosion products is also a common reason patients require revision surgeries concerning hip and knee replacements. Particulate and ion debris resulting from the corrosion process can initiate an immune reaction from the body, causing inflammation and swelling and pain. If this inflammation persists, it is termed chronic inflammation and leads to long term pain and discomfort for the patient, and typically, the implant needs to be removed. In addition to this, over time, the adaptive immune response can cause granuloma formation, which disrupts the implant to the bone interface, causing implant loosening and pain, again resulting in the replacement of the implant [18]. Furthermore, the production of wear debris can result in osteolysis, again causing implant loosening. Wear debris generates an immune response in which macrophages are activated. These macrophages release cytokines, such as MCP-1, as they try to remove the wear debris. However, these cytokines initiate the recruitment of osteoclasts. Osteoclasts, which differentiate from macrophages, work to break down osteocytes around the implant, causing it to become loose [19].

For these reasons, it is critical that biomaterial implants are corrosion and wear-resistant.

## 4. Thermal based surface modification techniques to improve corrosion and wear resistance

Surface modification aims to alter the behaviour of the surface of metal without affecting its bulk properties. Such modifications can be used to tailor the host response, such as osseointegration, and improve bulk properties, such as corrosion resistance. The available surface modifications can be categorised into chemical, physical, thermal and coatings, as shown in Fig. 6. The global market size for medical device surface coatings and treatments is expected to reach $ 7.9 billion by 2021. Thermal surface treatment techniques make up the highest proportion of this in terms of value, therefore, they are of great interest [66]. This paper covers thermal-based surface treatment and coating techniques used for favourable surface modifications of the metallic biomaterials. Generally, thermal-based surface modification techniques are more suitable for enhancing corrosion and wear resistance and are typically the quickest to perform and give high-performance properties [67]. Thermal surface modification methods tend to possess more vital bonding forces between substrate and coating than physical methods, they are a cheaper alternative to chemical methods [68].

The literature review on thermal surface modification techniques is presented in the following sections. The keywords used to perform the literature search included, but were not limited to, titanium/titanium alloy followed by laser cladding, thermal spraying, thermal oxidation, friction stir processing, thermochemical salt bath treatments and electric discharge machining/coating. Within the area of interest, both original and review articles from journals available on Google Scholar and Scopus databases were used to compile the study. As this review aims to highlight modern surface modification methods, generally, only papers from the years 2014–2020 were used to collect the publication trend. The number of publications per year for each of the above stated vital search words is shown in Fig. 7.

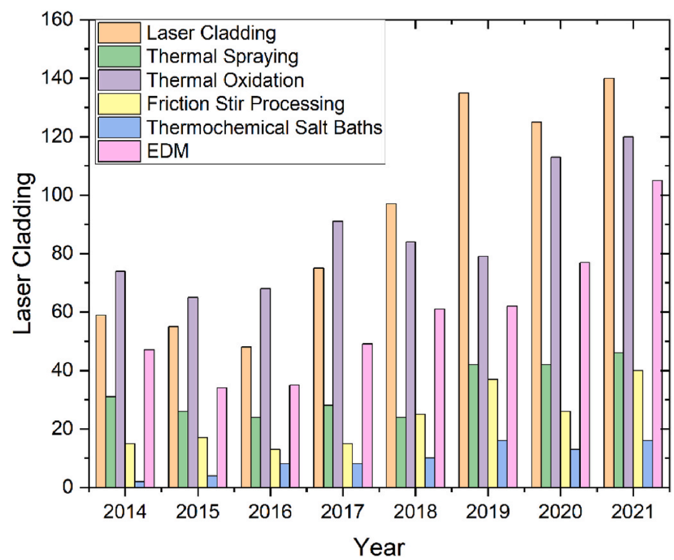


**Fig. 7.** Yearly publication of research articles in selected thermal based surface modification techniques.

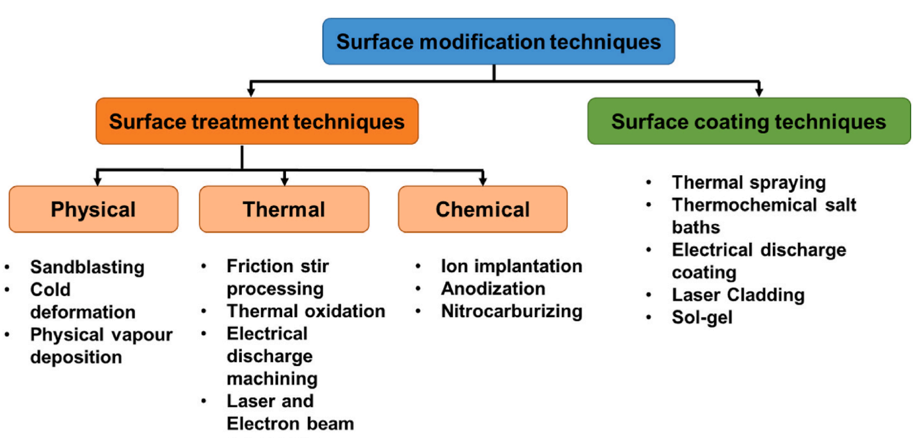


**Fig. 6.** A schematic diagram categorising some of the different surface modification techniques. Adapted from Ref. [69].

### 4.1. Laser cladding

Laser cladding is a thermal energy-based additive manufacturing technique used to coat metallic biomaterials to enhance wear and corrosion resistance. The technique uses a defocused laser beam in conjunction with either a preplaced or synchronous feed powder; generally, ceramic powders are used, such as TiC [70]. The high-density energy provided by the laser beam melts the powder and a thin portion of the underlying metal. The powder material and the metallic substrate form strong metallic bonds during resolidification. A schematic of the process can be found in Fig. 8. The quality of this coating layer is determined by three parameters, namely, the diameter of the laser beam, the power of the laser and the scanning velocity of the laser, each of these must remain constant to achieve a uniform coating. The laser cladding process increases wear and corrosion resistance via fine-grain strengthening. The choice of powder is limited due to the need for the powder to have a similar melting point, elastic modulus and thermal expansion coefficient to the metal substrate it is coating. Incompatible melting points lead to poor metallic bonds between the two materials. Incompatible thermal expansion coefficients and elastic moduli generate residual stresses, which cause cracking. In addition to issues with maintaining optimum parameters, two other problems limit the usefulness of laser cladding; pore formation due to gases that can't escape from the molten powder and crack formation due to the high residual stress caused by the heating and cooling cycle [70].

Furthermore, there is limited attention paid to the change in crystal structure from hexagonal close-packed (HCP) in the alpha phase of titanium to body-centred cubic (BCC), caused by the rapid heating and cooling, has on the effect of hydrogen embrittlement. As discussed previously, the diffusion of hydrogen from the surrounding area occurs more readily in BCC crystal structures; thus, this change to crystal structure could increase the titanium substrates' susceptibility to hydrogen embrittlement which would cause premature failure of the device. Research into the use of laser cladding to improve the corrosion resistance of titanium workpieces (implant surfaces) is ongoing. Table 4 summarises some of the recent literature in regards to this.

Liu et al. [49] investigated the impact of composite coatings applied via laser cladding on the microhardness of the substrate and phase composition of the cladding material. The titanium alloy, Ti–8Al–1Mo–1V, was used as the substrate material. Coatings were applied using a TruDisk 4002 disk laser operating continuously with a 1030 nm wavelength. In 5 samples, laser energy density was varied between 35 and 60 $Jmm^{-2}$, while in another five samples, the weight percent of $Ce_2O$ in the cladding material was varied. Liu et al. concluded that either increasing the laser energy or weight percent of $Ce_2O$ increased the coating thickness. With increased coating thickness, microhardness and wear resistance also increased. The friction coefficient of the uncoated surface ranged from 0.56 to 0.75, while the coated surface resulted in a friction coefficient of less than 0.45. The increase in anti-wear performance and microhardness would indicate a reduced likelihood of the coating layer being damaged, therefore maintaining adequate protection of the substrate beneath and preventing corrosion [67].

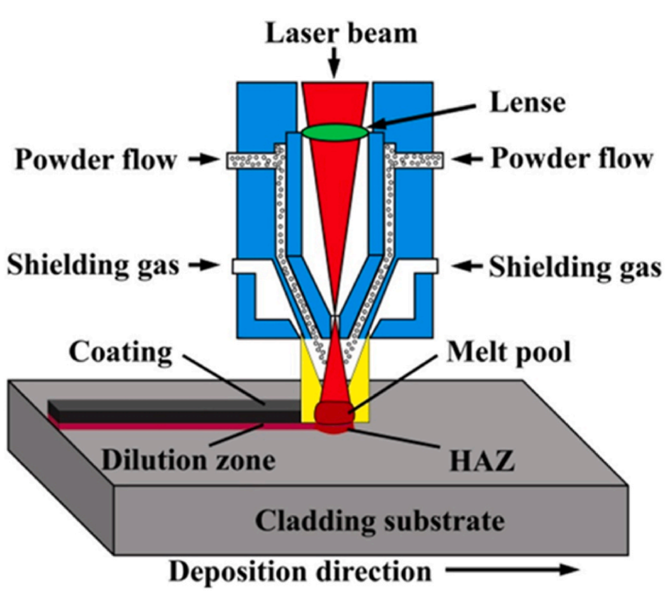


**Fig. 8.** A schematic of the laser cladding process. Reprinted with permission from Elsevier [67].

Adesina et al. [71] used potentiodynamic polarization techniques to study the corrosion behaviour of Ti–6Al–4V samples cladded with Ti–Co–Ni in 0.5 M sulphuric acid. The analysis utilised a three-electrode corrosion cell system with a counter electrode of graphite, a reference electrode of silver, the sample as the working electrode and an electrolyte of $H_2SO_4$. The Tafel extrapolation method was used to obtain the rate of corrosion of the system. The data indicates that the corrosion potential of the uncoated system is 0.36 V lower than for a TiCo–10Ni cladded sample and 0.41 V lower than a CoNi–10Ti cladded sample when applied at scanning speeds of 1.2 m/min. This corresponds to corrosion rates of 0.896$mmyr^{-1}$ in the uncladded sample, 0.0767 $mmyr^{-1}$ and 0.00000809 $mmyr^{-1}$ in the TiCo–10Ni and CoNi–10Ti cladded sample, respectively. XRD analysis of the samples before and after immersion in $H_2SO_4$ indicated that the density of the cladding layer for CoNi–10Ti was greater than for the TiCo–10Ni coating, thus resulting in a reduced ability for the sulphuric acid to diffuse through the coating and corrode the substrate.

### 4.2. Thermal spraying

Thermal spraying is a generic term describing a family of coating deposition techniques that involve the deposition, via spraying, of molten or semi-molten coating material onto a metallic substrate. The coating material is passed through a gun or torch that is heated via plasma, hot gases or flames to above their melting temperature. The resultant particles are accelerated through a gas stream onto the metallic substrate, forming a thin lamellar coating [74]. This process can be seen in Fig. 9. The coating material is usually harder and more wear-resistant than the substrate beneath [75]. Like laser cladding, the choice of material being sprayed onto the metallic substrate is limited due to the need for compatible properties and intermetallic bonding to occur at the interface of the materials [76].

Another limitation of this technique is pore formation; less precision in the distribution of coating material in this method means that pores can be created where areas are missed. Creating a non-uniform coating creates shielded environments in some areas and enhances crevice corrosion. The recent research into thermal spraying to improve the corrosion resistance of titanium alloys is summarised in Table 5.

Valente and Galliano [77] investigated the corrosion-resistant properties of commercially pure titanium substrates following the deposition of TiN coating using reactive plasma spraying. The samples were tested in both 0.5 M NaCl and 1 M HCl before being compared to results obtained in a neutral solution. Results concluded that the corrosion potential of the treated samples was lower than that of the commercially pure titanium when in both the acidic and the neutral solutions; therefore, coated samples were more susceptible to corrosion than untreated samples. This result can be attributed to the porosity in the coating. In the acidic solutions, interconnected pores within the coating enable the corrosive solution to disrupt the bonds between the coating layer and the substrate, thus causing the coating to become loose and dislodge, leaving the substrate exposed to the corrosive environment. In the neural solution, crevice corrosion due to the pores was the predominant corrosion mechanism observed. However, research conducted by Xu and Kong shows that some level of corrosion resistance can

**Table 4**
Summary of recent research on enhancement of corrosion resistance using laser cladding.

| Author(s) | Particulars of Process | Workpiece | Deposited Layer | Findings | Remarks |
|---|---|---|---|---|---|
| Liu et al. (2020) [49] | Scanning speed:300–500 mm/min<br>Beam Diameter: 3 mm<br>Powder feeding rate: 5 gm/min<br>Beam Power: 700–1100 W | Ti–8Al–1Mo–1V | $CeO_2$ | Improvement from around 500 $HV_{0.5}$ to 811.67$HV_{0.5}$ in microhardness and a reduction of 0.3 in the friction coefficient in treated samples. | The link between increased hardness and wear resistance and reduced corrosion resistance should not be assumed. Further testing is needed to comment on corrosion resistance. |
| Phume et al. (2018) [72] | Scanning speed: 0.3 m/min<br>Beam Diameter: 1 mm<br>Beam Power: 1000 W | Ti–6Al–4V | Nb | Cladded samples showed an 81.79% increase in corrosion resistance. | Used Hank's buffer salt solution as an electrolyte- it doesn't contain proteins that can act to increase corrosion (as discussed in the crevice corrosion section). |
| Nabhani et al. (2019) [73] | Scanning speed: 2 mm/s<br>Beam Diameter: 1 mm<br>Powder feeding rate: 500 mg/s<br>Beam Power: 150–250 W | Ti–6Al–4V | Ti–6Al–4V | Results from samples tested using potentiodynamic polarization in three different corrosive environments, including NaCl, $H_2SO_4$ and HCl. Show an increase in corrosion potential when in NaCl and $H_2SO_4$, but in HCl environments, the corrosion potential decreases. | HCL is present in the body, so the technique is not suitable for use on biomaterials. |
| Adesina et al. (2020) [71] | Scanning speed: 0.6 m/min- 1.2 m/min<br>Beam Diameter: 3 mm<br>Powder feeding rate: 1 g/min<br>Beam Power: 900 W | Ti–6Al–4V | Ti–Co–Ni | Untreated Ti–6Al–4V gave a corrosion potential of −0.18 V, which increased by 0.6 V in Ti–Co–Ni treated Ti–6Al–4V with scanning speeds of 0.6 m/min and by 0.36 V for 1.2 m/min, therefore reducing the corrosion rate. | Co and Ni are common allergens and carcinogenic. Tested 1 $cm^2$ samples- small area may not have been representative of full system. |

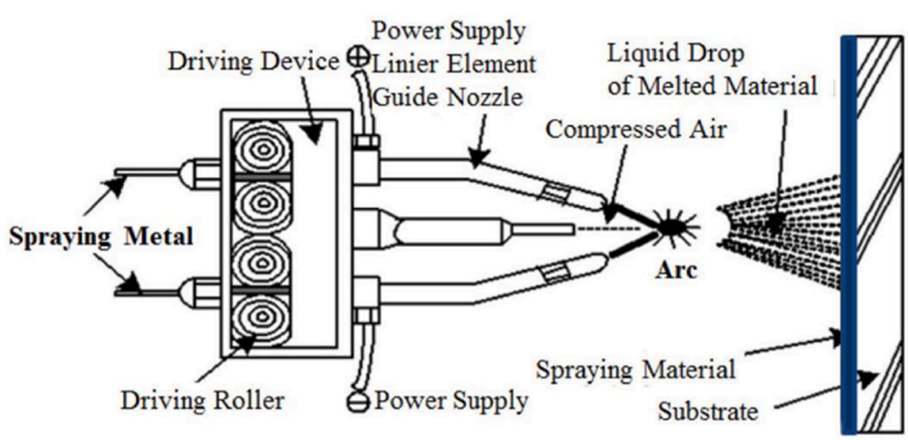


**Fig. 9.** A schematic of the thermal spraying process [75].

be obtained through the use of laser thermal spraying. Xu and Kong [78] applied a coating of $Co_{30}Cr_8W_{1.6}C_3Ni_{1.4}Si$ onto Ti–6Al–4V substrates before analysing the corrosion-wear behaviour of the samples in a 3.5% NaCl solution. This work concluded an increase in the corrosion potential of 0.4 V in coated samples compared to untreated samples. It can then be supposed that the corrosion resistance performance of this surface modification method is technique-dependent and does not give consistent results.

*4.3. Thermal oxidation*

Oxidation of titanium surfaces above 200 °C induces the thickening of the native titanium oxide layer. It also increases the dissolution of oxygen beneath the oxide layer (as seen in Fig. 10). The thicker the oxide layer, the less likely it is to become compromised and expose the metal beneath and thus, the better the corrosion resistance [81]. Thermal oxidation uses relatively low temperatures and uses no extra material. This reduces the cost compared to other thermal surface treatment methods [82]. The thermal oxidation process can be described in five steps (as shown in Fig. 10): oxygen absorption, oxygen dissolution, thin oxide film formation, oxide layer growth and thick oxide layer formation [83]. In addition to lower temperatures, the absence of a coating material mitigates the risk of poor intermetallic bonding and further reduces the costs. However, its use in enhancing corrosion resistance is limited, with some research indicating that corrosion resistance of thermally oxidised titanium is worse than that of non-treated titanium [84]. Investigation into the use of thermal oxidation to improve the corrosion resistance of titanium workpieces is ongoing. Table 6 summarises some of the recent literature in regards to this.

Maestro et al. [85] performed cyclic thermal oxidation on Ti–6Al–4V substrates with heating occurring over 24 h to a maximum temperature of 650 °C. Along with analysing the surface roughness and

**Table 5**
Summary of recent research on enhancement of corrosion resistance using thermal spraying.

| Author(s) | Particulars of Process | Workpiece | Deposited Layer | Findings | Remarks |
|---|---|---|---|---|---|
| Valente and Gallino's (2000) [77] | Reactive plasma spraying<br>Chamber pressure: 20–90 kPa<br>Plasma gases: Ar/ $H_2$<br>Power: 36–40.6 kW<br>Coating thickness: 300 μm<br>Powder feed rate: 5.5 g/min | Cp- Ti | TiN | No significant increase in the corrosion resistance after thermal spraying. Reductions in porosity increase the corrosion potential. | Nitrates in the body can reduce oxygen levels in the blood, thus preventing oxygen supply to organs. Therefore, TiN is not a suitable coating material for biomaterials. |
| Weitong and Dejun (2019) [79] | Laser thermal spraying<br>Powder Feed Rate: 10 g/min<br>Gas environment: Ar | Ti–6Al–4V | CoCrAlYTaSi | The friction coefficient was reduced in coated samples compared to non-treated samples. The corrosion resistance of treated samples was increased by 3.5% in NaCl. | NaCl was used as the electrolyte in the electrochemical tests performed- it doesn't contain components of bodily fluids and so is not an accurate representation of the behaviour within the human body. |
| Rocha et al. (2018) [80] | Plasma thermal spraying<br>Powder feed rate: 10 g/min<br>Gun to metal distance: 150 mm<br>Plasma gas: $H_2$ | Ti–6Al–4V | HAp-$TiO_2$ | Surface roughness was reduced by 0.4 μm, the porosity of the surface increased by 0.3%, hardness increased by 351$HV_{100}$, and adhesion increased by 13.4Mpa. | Increased surface roughness enables increased bacterial adhesion, which can form biofilms. Increased adhesion suggests increased friction between surfaces; however, this may be compensated for with increased hardness. |
| Xu and Kong (2020) [78] | Laser thermal spraying<br>Powder Feed Rate: 8 g/min<br>Laser Scanning Power: 1000–1200 W<br>Coating thickness: 200 μm | Ti–6Al–4V | $Co_{30}Cr_8W_{1.6}C_3Ni_{1.4}Si$ | The corrosion resistance decreased with increasing laser power. Wear rates of the treated samples were ~0.1 × $10^5$μm$^3$/Nm lower than in non-treated samples. | Cr, Co, Ni, W and Si have all been seen to have elicited adverse effects on the body, such as allergies and cancer. |

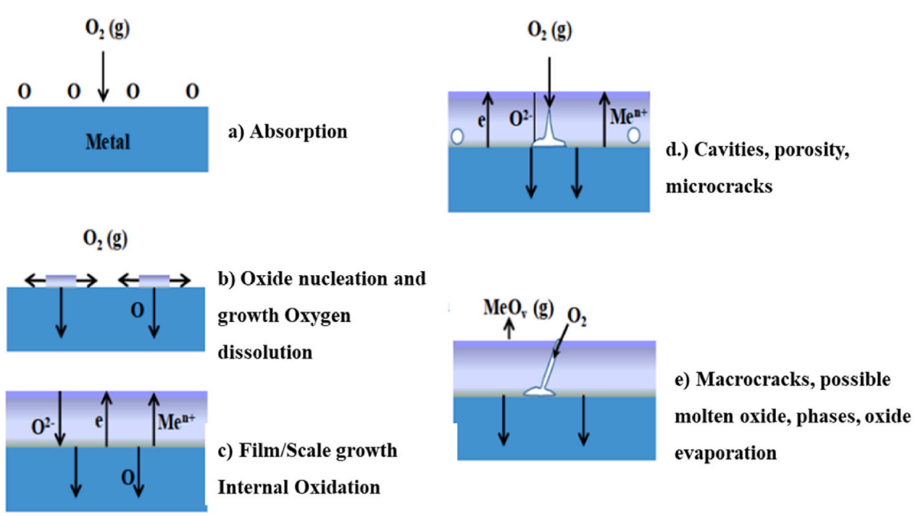


**Fig. 10.** A schematic of the thermal oxidation process [83].

microhardness of the heat-treated material, polarization corrosion testing was conducted under physiological conditions to assess the suitability of thermal oxidation as a surface modification treatment for increasing corrosion resistance in biomaterials. Loading of 0.2 kg for 20 s was used to determine the Vickers microhardness of the samples, for all samples treated by thermal oxidation, the microhardness had increased by almost double that of the untreated samples, meaning that the oxide layer is less likely to become compromised by asperities and thus prevents the substrate from becoming exposed. However, the polarization tests conducted using an electrolyte of simulated body fluid (SBF) showed evidence of pitting corrosion in treated samples. The treated samples offered comparable corrosion resistance to the untreated samples within the passive region (up to 1000 mV). However, above 1000 mV, the current density in the treated samples increased, which is indicative of pitting corrosion. Therefore, treated samples were more prone to corrosion than untreated samples.

Although the results obtained by Maestro et al. did not confirm the use of thermal oxidation to increase corrosion resistance on Ti–6Al–4V substrates, Bansal et al. [86] observed some improvement in corrosion resistance in commercially pure titanium samples after thermal

**Table 6**
Summary of recent research on enhancement of corrosion resistance using thermal oxidation.

| Author(s) | Particulars of Process | Workpiece | Findings | Remarks |
|---|---|---|---|---|
| Jamesh et al. (2013) [81] | Two processes were used: 14 h at 650 °C and 850 °C for 6 h. Furnace cooling, air cooling and water-cooling methods were also compared. | Cp- Ti | Samples heated at 850 °C for 6 h formed debris when cooled rapidly, and these samples performed worse in electrochemical studies than the samples heated for 14 h at 650 °C. Therefore, the corrosion resistance of thermally oxidised samples depends on the processing conditions. | 0.9% NaCl was used as the electrolyte in the electrochemical tests performed- it doesn't contain components of bodily fluids and so is not an accurate representation of the behaviour within the human body. |
| Bansal et al. (2017) [86] | Temperatures of between 200 °C and 900 °C. Heated for 1 h and cooled in the furnace at room temperature. | Cp-Ti | Maximum corrosion resistance was achieved at 500 °C, where corrosion potential decreased from ~-100 mV to ~ -500 mV. | Used a pH of 7.8 at 25 °C. The human body has a pH of ~7.4 and a temperature of 37 °C, so the results of this study do not represent the behaviour within the human body. |
| Aniołek (2017) [84] | Time varied between 6 and 72 h at 700 °C | Cp-Ti | The thickness of the titanium oxide layer increased by a factor of 6 when heated for 72 h when compared to samples heated for 6 h. Thicker oxide layers gave high microhardness values. | Thermal oxidation is said to use lower temperatures than other techniques; 700 °C is high, so this benefit is counteracted. |
| Maestro et al. (2019) [85] | Heated for 24 h to a maximum of 650 °C. Cooling method: 650 °C–400 °C or 650-200 °C in 48 cycles, then left to cool at room temperature. | Ti–6Al–4V | Potentiodynamic polarization testing was used with an SBF solution at 39 °C. Corrosion resistance was comparable in treated and untreated up to 1000 mV. Evidence of pitting corrosion in treated samples. | Experiments were done at 39 °C- body temperature is 37 °C, so they don't represent corrosion behaviour in the body. |

oxidation treatment. Similarly, Bansal et al. conducted polarization tests using SBF as the electrolyte. However, in Cp-Ti samples thermally oxidised at 500 °C, Bansal et al. observed a 1.7 mΩ increase in polarization resistance compared to untreated samples. Using XRD and Raman spectroscopy, this was attributed to the mix of $Ti_2O_3$ and rutile present on the surface. This highlights inconsistencies with thermal oxidation to improve corrosion resistance in titanium and its alloys.

### *4.4. Friction stir processing*

Friction Stir Processing (FSP) differs from friction stir welding in that it uses a stir tool made up of a pin and a shoulder. The friction created between the stir tool and the metal surface causes severe plastic deformation on the metal. The heat generated by the rotating stir tool locally melts the metal surface before solidifying when the stir tool progresses forward along a programmed route. The melted metal surface resolidifies with an ultrafine-grained structure, this strengthens the titanium, and the hardness of the surface layer is increased [67]. Increasing the hardness of the surface layer increases the wear resistance, which in turn prevents corrosion. The process involves producing contact between a non-consumable rotating tool and the work piece, as shown in Fig. 11 [87]. However, this technique is limited by a gradient in grain size created by the gradient of plastic deformation on the surface [88]. In addition to this, the tool material is restricted as it must be harder than the workpiece used. Therefore, in the case of titanium alloys, only tungsten-rhenium alloys can be used for the stir tool [89]. Although there is evidence that surface treating Ti–6Al–4V with FSP increases corrosion resistance, the low processing rate prevents it from being a scalable technique for biomaterial applications [67]. Recent research on the use of FSP to enhance corrosion resistance is summarised in Table 7.

Fattah-Alhosseini et al. [90] studied the effect of multi-pass FSP on the corrosion behaviour of Cp-Ti using a phosphate buffer solution. There was a notable reduction of corrosion density, from 0.09 μm/cm$^2$ in untreated Cp-Ti to 0.03 μm/cm$^2$ in samples treated with three passes of FSP, thus indicating an enhanced corrosion resistance after FSP has been performed. However, it must be noted that this experimental procedure was conducted in an essential electrolyte with a pH ~3 greater than that of blood and experiments was run for 3600 s. Therefore, this technique does not provide an accurate representation of the corrosion behaviour of the sample under physiological conditions.

FSP is thought to enhance the corrosion behaviour of metals by increasing the density of grain boundaries and producing other surface defects, which lower the energy required for the formation of the corrosion-resistant, passive layer [90]. A study by Vakili-Azghandi et al. [91] used scanning electron microscopy (SEM) and an electron back-scattered diffraction system (EBSD) to confirm that the number of grain

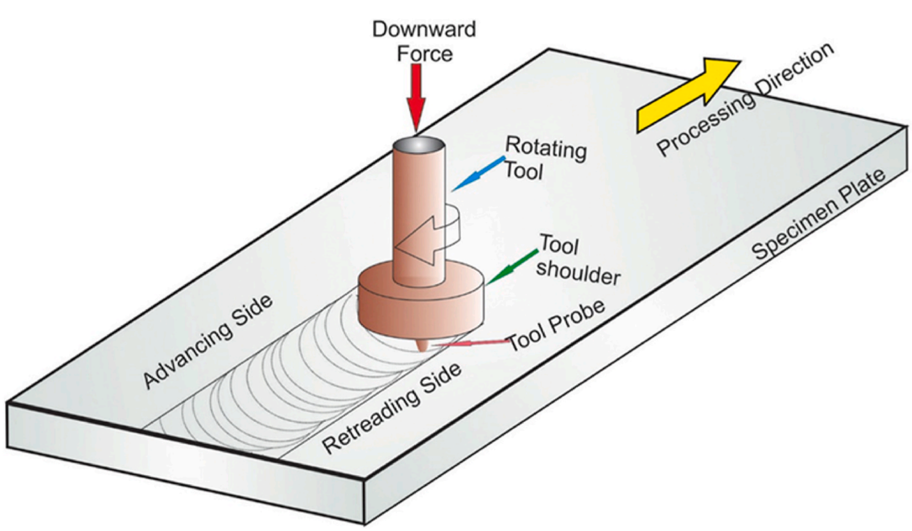


**Fig. 11.** The friction stir processing on a workpiece. Reprinted with permission from Elsevier [87].

**Table 7**
Summary of recent research on enhancement of corrosion resistance using friction stir processing.

| Author(s) | Particulars of process | Workpiece | Findings | Remarks |
|---|---|---|---|---|
| Farias et al. (2013) [93] | WC stir tool used with diameter of 4.8 mm. Rotational speed varied between 1000 and 1200 RPM. | Ti–6Al–4V | Increasing rotational speed of tool increased residual stress in workpiece after treatment-increase of 100 RPM increased residual stress by 120 MPa. Some workpiece adhesion seen on stir tool. | Imaging techniques of wear were used to obtained qualitative data but no quantitative data was produced. |
| Fattah-Alhosseini et al. (2017) [90] | CW tool. Penetration depth of 1.9 mm, rotational speed of 140 0RPM, traveling at 40 mm/min. | Cp-Ti | Corrosion potential of treated sample was −0.4 V while for untreated Ti it was −0.6 V. Therefore, treatment increased the corrosion resistance of the material. | Electrochemical testing done at pH of 10.69- this does not reflect physiological conditions. |
| Vakili- Azghandi et al. (2020) [91] | WC tool of diameter 6 mm. The rotational speed of 1400 RPM and traverse speed of 14 mm/min. | Cp-Ti | Beta Ti is present in some areas as FSP created local temperatures of 900 °C and the allotropic phase transformation temperature is 880 °C. Hardness increased by 36% in treated samples. The average grain size decreased by 1.4 μm after treatment. Friction coefficient reduced after treatment. | No direct measurement of corrosion rate and no mention that beta Ti may increase the diffusion rate of hydrogen into the metal causing hydrogen embrittlement. |
| Khodabakhshi et al. (2019) [94] | WC tool. Penetrating depth of 0.3–0.5 mm. The rotational speed of 900 RPM and traverse speed of 63 mm/min. | AA5083 with pure Ti coating | Reduces the porosity of coating materials. After FSP treatment, hardness increased by ~7 times. | The application of this alloy is very limited within the biomaterial industry. |
| Gu et al. (2019) [92] | Tungsten steel tool. Rotational speeds of 650 rpm and 850 rpm. Moved continuously at 50 mm/min. | Ti–35Nb–2Ta–3Zr | FSP was seen to reduce the rate of corrosion when tested in mimicked physiological conditions. Higher rotational speeds increased the corrosion resistance by a greater amount. | |
| Farias et al. (2013) [93] | WC stir tool used with diameter of 4.8 mm. Rotational speed varied between 1000 and 1200 RPM. | Ti–6Al–4V | Increasing rotational speed of tool increased residual stress in workpiece after treatment-increase of 100 RPM increased residual stress by 120 MPa. Some workpiece adhesion seen on stir tool. | Imaging techniques of wear were used to obtained qualitative data but no quantitative data was produced. |
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| Khodabakhshi et al. (2019) [94] | WC tool. Penetrating depth of 0.3–0.5 mm. The rotational speed of 900 RPM and traverse speed of 63 mm/min. | AA5083 with pure Ti coating | Reduces the porosity of coating materials. After FSP treatment, hardness increased by ~7 times. | The application of this alloy is very limited within the biomaterial industry. |

boundaries increased significantly after FSP. Using samples of Cp-Ti, allotropic phase transformations from α phase Ti to β phase Ti as a result of FSP caused the grain size to reduce by an average of 1.4 μm, therefore increasing the grain boundary density and helping to reduce the energy barrier associated with oxide layer formation.

Gu et al. [92] used FSP to incorporate TiO2 onto the surface of Ti–35Nb–2Ta–3Zr before evaluating its effectiveness at reducing the rate of corrosion when compared to the untreated substrate. A powder of 200 nm diameter TiO2 particles was distributed on the surface of the Ti–35Nb–2Ta–3Zr substrate before FSP was performed using a tungsten steel shoulder and pin. The probe moved continuously at a rate of 50 mm/min and rotation speeds of 650 rpm and 850 rpm. Potentiodynamic polarization was measured using a three-electrode cell in Hank's solution with a reference electrode of saturated calomel, a platinum counter electrode, and the test sample as the working electrode. The pH of the solution was maintained at 7.4 and a temperature of 37 °C. The corrosion potential of Ti–35Nb–2Ta–3Zr without FSP was higher than that of the treated sample. At the same time, the current density was reduced, thus indicating that the rate of corrosion is lower in the treated FSP treated samples. Moreover, the increase in corrosion resistance was greater in samples subjected to higher rotational speeds.

### 4.5. *Thermochemical salt bath treatments*

In thermochemical surface modification, thermal diffusion is employed by exposing the implant to high temperatures to incorporate non-metal or metal atoms into the implant surface to alter its chemistry and microstructure. Such treatment is carried out in a solid, liquid or gaseous medium with numerous active chemical elements. Typically, the surface modification mechanism comprises a decomposition of solid, liquid or gaseous elements, splitting gaseous molecules to form nascent atoms, absorption of atoms, their diffusion into a metallic lattice, and reactions within the substrate structure existing or developing new phases [95].

There are four main types of thermochemical treatments; carburizing, nitriding, nitrocarburizing and carbonitriding. All four of these techniques produce a surface layer on top of the workpiece. However, the composition of this surface layer varies; for example, in nitriding, the surface layer is made up of TiN. The process involves submerging the metal into a molten salt bath at temperatures between 950 and 1050 °C for 2–8 h before being quenched in water [96]. These baths create diffusion zones of ~5–7 μm thickness rich in carbon, nitrogen, and/or oxygen [97]. The single-phase nature of these surface layers typically offers increased hardness and wear resistance which contributes to an increased corrosion resistance [96]. However, the concentration of oxygen in the salt bath must be strictly controlled to prevent excess diffusion leading to a loss of titanium [98]. Some of the recent investigations using molten salt baths are summarised in Table 8.

Liu et al. [99] used a low temperature, 640 °C, salt bath to perform carburization of a Ti–6Al–4V substrate. The performance of the treated alloy was then assessed and compared to that of the untreated alloy concerning microhardness and frictional coefficients. Greater microhardness values can be correlated with greater corrosion resistance as the integrity of the coating or passivating layer is less likely to be compromised. Thus, the corrosion susceptible metal underneath is better protected from a corrosive environment. Furthermore, reductions in frictional coefficients indicate a reduction in wear of the alloy, again resulting in improved integrity of the coating or passivating layer and a reduction in corrosion. In this study, Liu et al. [100] used MH-3 microhardness meters to observe a 2.6 times increase in the microhardness of Ti–6Al–4V when treated in the salt bath compared to the untreated samples. Additionally, M2000 friction and wear test machining was used to measure a 56% decrease in the treated samples' frictional coefficient compared to untreated samples. Although this data does not directly conclude that treated samples are more corrosion resistant, it is a good indicator.

Despite the promising evidence shown by Liu et al. [100], treated implants can still fail prematurely. Lapaj and Rozwalka [101] studied the failure mechanisms responsible for the failure of 8 nitridated knee arthroplasties *in vivo* after 13–21 months. Defects such as pinholes and craters were detected under SEM on all eight failed implants, indicating that these defects rendered the metal susceptible to crevice corrosion. Furthermore, evidence of wear related to third bodies on the implant surface resulted in compromised coating integrity and a substrate exposed to corrosive bodily fluids. Therefore, the use of thermochemical salt bath treatment for *in vivo* applications is not advised.

### 4.6. Electric discharge machining

Electric discharge machining (EDM) is a material removal method used to shape difficult-to-cut materials. The technique erodes away conductive materials using thermoelectrical energy generated through repeated high-voltage sparks between the workpiece and the electrode [103]. An EDM setup mainly includes the tool and the workpiece (implant surface), power supply, controller, servo system, and dielectric supply system (Fig. 12).

Unlike other surface modification techniques, EDM does not require any surface preparation, and the electrode and workpiece are not in contact but separated by a small gap filled with dielectric fluid. The non-contact nature of the technique eliminates residual stress in the material, which can reduce the fatigue resistance [104]. The ionisation of the dielectric fluid occurs as a result of strong electric fields being established in the dielectric field when high voltages are applied. This creates plasma channels with variations in resistance between the electrode and the workpiece. With low resistance, electric discharges occur at high frequencies, making localised temperatures of 8000–12000 °C melt both the workpiece and the electrode to create small craters. Once the voltage is removed, the temperature drops and any debris formed during the process is released into the dielectric fluid [104]. On titanium alloy surfaces, the elevated temperatures result in titanium oxide formation on the surface, thus increasing the oxide layer thickness and improving corrosion resistance [105].

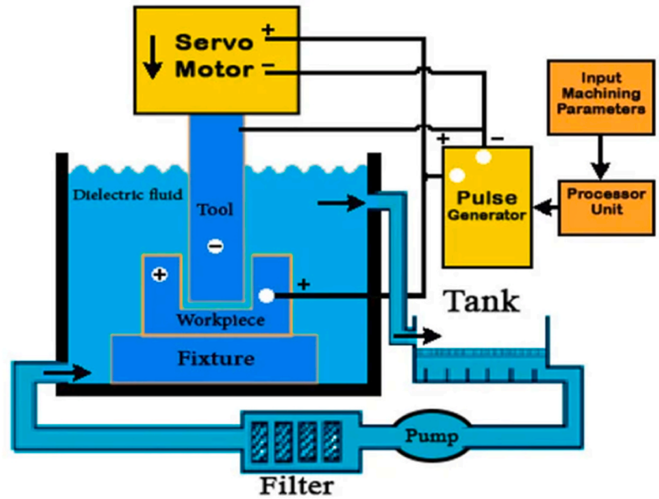


**Fig. 12.** A typical EDM set-up [105].

Both electrical and non-electrical parameters control EDM performance with surface roughness, metal removal rate (MRR), and tool wear rate (TWR) used as measurements of the process (Fig. 13) [106]. MRR measures the production rate and can be calculated by dividing the amount of workpiece material removed by the machining time. TWR measures the processing efficiency, calculated by dividing the amount of electrode or tool material eroded by the machining time. For optimum EDM, MRR is maximised, and TWR is reduced to a minimum. This prevents unnecessary increases in production costs as the tooling material can remain in use for longer [106].

Electric discharge coating (EDC) is a subset of EDM during which a coating material is deposited onto the workpiece. There are two ways to achieve this; adding powder of the coating material to the dielectric fluid and using a powder metallurgical electrode [107]. Depositing a protective layer onto a workpiece can improve the surface properties while

**Table 8**
Summary of recent research of enhanced corrosion resistance on metals treated with thermochemical salt baths.

| Author(s) | Particulars of Process | Workpiece | Findings | Remarks |
|---|---|---|---|---|
| Khater et al. (2020) [96] | Salt bath of 70% borax and 30% silicon carbide. The temperature varied between 850-1000 °C for 2–8 h. | Ti–6Al–4V | X-rays and SEM showed a single-phase coating. Coating thickness increased both time and temperature. Hardness increased from 8.6 GPa to 30–50 GPa after treatment. The friction coefficient lowered with increasing treatment time. | No direct measurements of corrosion were taken. |
| Deepak et al. [102] (2017) | Cyanate bath at 560–580 °C for 24 h. | Cp-Ti and Ti–6Al–4V | Nitride coating was observed to have a black colour. The hardness of treated samples was more significant than untreated. Surface roughness was reduced by up in Cp-Ti after treating but increased in treated Ti–6Al–4V samples. | The salt bath temperature fluctuated at 20 °C-reproducibility of the experimental technique is low if variables are not precise. |
| Liu et al. (2016) [100] | Carburizing in a salt bath of urea and carbonate at 640 °C for 3.5 h. | Ti–6Al–4V | Ti8C5 surface coating was produced on the workpiece—increased hardness by 2.57 times after treatment. The coefficient of friction was reduced by ~56% after treatment. | Urea used in the salt bath makes the process unsuitable for biomaterial use. |
| Lapaj and Rozwalka (2020) [101] | Analysing five failed knee replacements that had been nitrated in a salt bath before implantation. | – | Good coating adhesion was maintained after failure, but wear and surface roughness increased on the tibial bearing surface. Particulate defects acted as a third body causing increased wear. | Information on the production of examined implants was limited. All analysed samples failed after 13–21 months. This is not long enough to see much evidence of corrosion. |

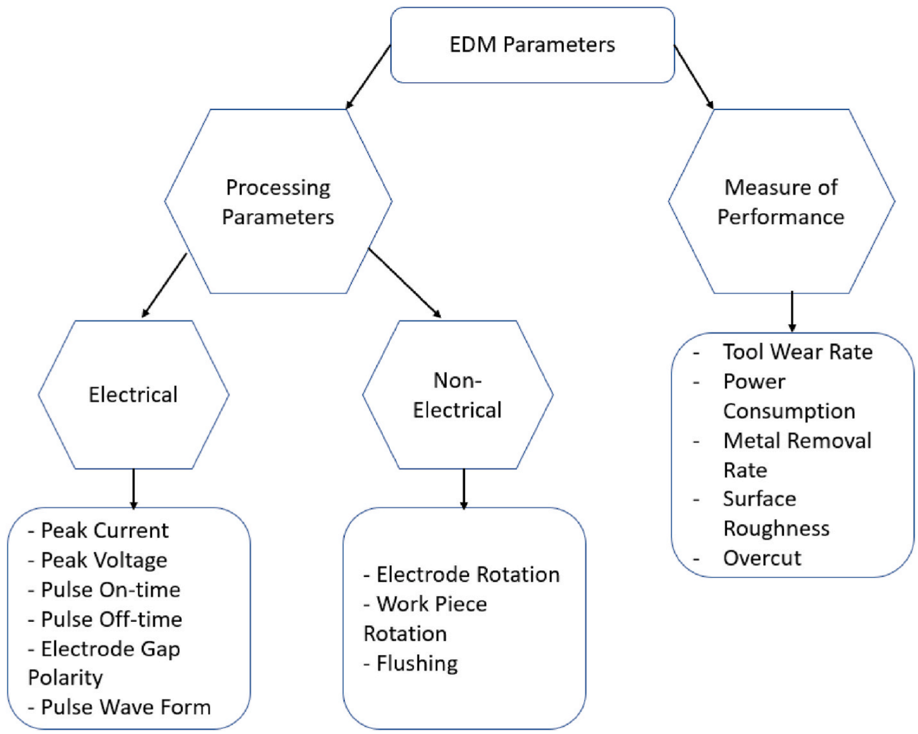


**Fig. 13.** The processing parameters affecting EDM and measurements of EDM performance. Adapted from Ref. [106].

maintaining bulk properties. The coating layer must be thick enough to act effectively as a protective layer but be thin enough that it does not affect the properties of the workpiece. This can be achieved by carefully tailoring the parameters described in Fig. 13.

Many researchers have investigated the use of EDM and EDC to improve corrosion resistance on metals. EDM/EDC is a promising alternative to laser cladding, thermal spraying and thermal oxidation. Table 9 summarises some of the recent work in area of application of EDM/EDC for surface modification of metallic biomaterials.

Das and Misra [109] explored the effect that varying the EDC parameters, such as peak current, pulse-on time, an electrode composition, have on the thickness of the deposited layer, TiC, on an aluminium workpiece. The experimental technique was based on the Box-Behnken design (BBD) of response surface methodology (RSM). Twenty-nine trials were conducted, including five controls, in which the variables were independently changed. Results were obtained through micrographs and were compared to the artificial neural network (ANN) and general algorithm (GA) prediction models to obtain an error. A peak current of 9.98 A, pulse-on time of 259.88 μs, 200.174 MPa compaction pressure and an electrode composition of 69.97% were the conditions required to obtain a maximum deposit layer thickness 69.42 μm.

Similarly, Mansor et al. [116] explored the effect of varying EDC parameters on nickel-titanium shape memory alloys. They conducted 38 trials with six controls, and, like Das and Misra, parameters varied with each run. SEM imaging was used to obtain porosity levels, crater size and coating thickness. The results indicate that changes in discharge duration had the most notable effects on coating properties. Tailoring the coating layer's thickness is vital as thicker coatings offer more excellent resistance to ion transfer and thus increase corrosion resistance. However, further validation of such experimental results is essential to consider.

Siddique et al. [115] investigated the effects of coating Ti–6Al–4V with $WS_2$ using EDC with a Brass electrode. Five coated samples were prepared with differing ratios of $WS_2$:Brass. The microhardness of samples was tested using Vickers Hardness at five different points along a sample length; the untreated samples had a hardness of 280 $HV_{0.5,}$ while the coated samples ranged between 402 and 578 $HV_{0.5}$. The wear behaviour of samples was also investigated using a pin-on-disc with a steel ball. The wear track diameter was 75 mm, loading conditions of 1 kgf, velocity 400 rpm and time 180 s were used. Coated samples had a lower wear rate than untreated Ti–6Al–4V, but the wear rate increased with increasing $WS_2$:Brass. Furthermore, Siddique et al. found that using coatings of $WS_2$ decreased the coefficient of friction; the more significant the $WS_2$:Brass, the greater the reduction in the coefficient. By increasing wear resistance, the risk of compromising the protective layer and exposing the reactive substrate is reduced, preventing corrosion.

In a recent study, Yu et al. [110] used nitrogen assisted EDC to generate a coating comprising TiO, $TiO_2$ and HA on titanium substrates. The hardness of the coated samples was 1082.8HV; 4.3 times greater than that of untreated titanium. Moreover, the corrosion testing results on the samples were plotted in potentiodynamic polarization curves and show that in coated samples, the corrosion resistance was higher than in untreated samples. For EDC-treated samples the corrosion potential was greater, and the corrosion current was lower, indicating that the movement of ions from the titanium workpiece into the surrounding environment was reduced. Although this coating has been shown to increase corrosion resistance, HA is brittle, so the thickness of the coating needs to be carefully controlled [117].

EDM/EDC are promising techniques that prevent time and money waste by mitigating the need for surface preparation. Scaling these cost savings by the high demand for implants would save vast amounts of money for the health service; other advantages and disadvantages are summarised in Table 10 [105].

## 5. Comparison of thermal surface modification techniques

Table 10 compares surface modification techniques applied to enhance corrosion and wear characteristics of Titanium alloys.

## 6. Challenges and future perspectives

Thermal based surface modification techniques have been applied for enhancing the wear and corrosion resistance through the surface modification of metallic biomaterials since more than last three decades.

**Table 9**
Summary of recent research of enhanced corrosion resistance on metals treated with EDM/EDC.

| Author(s) | Particulars of Process | Workpiece | Deposited Layer | Electrode | Remarks |
|---|---|---|---|---|---|
| Mussada and Patowari (2015) [107] | Pulse-on time: 25, 106, 463, 1010 µs<br>Peak Current: 6 and 8 A<br>Flushing Pressure: 5 $kgcm^{-2}$ | Al | 75% W– 25% Cu powder mix | W–Cu | Cracks of length 1–2 µm form on the top layer of the coating.<br>Grain size increased with increasing time (83 nm with $T_{on}$ is 463 µs and 51.75 nm when $T_{on}$ is 25 µs). Dislocation density decreased with increasing $T_{on}$ ($3.649 \times 10^{14}$ $m^{-2}$ for $T_{on}$ = 25 µs and $1.572 \times 10^{14}$ $m^{-2}$ for $T_{on}$ = 463 µs). |
| Prakash et al. (2019) [108] | Peak Current: 5, 10, 15, 20, 25 A<br>Pulse-on time: 50, 100, 200, 400, 800 µs<br>Dielectric medium: Hydrocarbon oil<br>Machining Time: 15 min | Ti–6Al–4V | Ti–Nb | Cp-Ti | Porosity in a deposited layer on ~25%, with pores between 5 and 15 µm in diameter. Microhardness increased with decreasing surface depth and was higher in EDC treated samples than in EDM. The critical adhesion failure of EDC treated samples was 36 N greater than that of EDM treated samples. |
| Das and Misra (2016) [109] | Peak Current: 4–10A<br>Pulse-on Time: 60–260 µs<br>Dielectric Fluid: Hydrocarbon Oil<br>Coating Time: 2 min | Al | 50%–70% TiC | 50%–70% TiC | Varying experimental parameters affect the properties of the EDC treated Al. The percentage contribution on the effect of the thickness of the deposited layer by varying parameters was found to be: 25.73% peak current, 32.9% pulse-on time, 33.19% electrode composition, 2.93% compaction pressure. |
| Yu et al. (2020) [110] | Electrode Rotary Speeds: 0, 300, 600 rpm<br>Coating Time: 10 min<br>Gas Flow Rate: 0, 0.02, 0.05 and 0.1 L/min | Ti | TiO, $TiO_2$ and HA | Ti allowing nitrogen gas flow | Increasing electrode rotary speeds and increasing gas flow increases the amounts of Ca and P in the coating, but increasing both in combination does not.<br>Corrosion resistance increased in EDC-treated samples compared to untreated. |
| Sharma et al. (2020) [111] | Voltage: 20, 40, 60 V<br>Powder Concentration: 6,8,10,12 g/L<br>Coating Time: 4 min | Ti–6Al–4V | BN, TiN–TiAlN | 63% Cu, 37% Zn | The corrosion rate of untreated samples was 5.92 µm per year; EDC reduced this to a rate of 2.83 µm per year.<br>Micro-hardness increased by a factor of between 2 and 5 in coated samples when compared to uncoated samples. |
| Bui et al. (2019) [112] | Polarity: Positive at tool electrode<br>Peak Current: 12A<br>Gap Voltage: 100 V | Ti–6Al–4V | Silver | WC-6wt% Co | Using high concentrations of Silver powder decreased the surface roughness slightly.<br>Silver coated samples reduced the adhesion of bacteria. |
| Prakash et al. (2017) [113] | Peak Current: 15 A<br>Pulse-on Time: 25 µs<br>Coating Time: 15 min | Ti–35Nb–7Ta–5Zr | HA | Cp-Ti | Corrosion potential of untreated samples was 150 mV greater than that of EDM- treated samples and 83 mV than EDC- treated samples with HA. Cell proliferation was significantly greater in EDC- treated samples. |
| Prakash et al. (2017) [114] | Pulse Duration: 5, 10, 20, 40, 80 µs<br>Pulse Current: 5, 10, 15, 20, 25 A<br>Polarity: Tool (+), Workpiece (−) | Ti–35Nb–7Ta–5Zr | Si | Cp-Ti | Surface roughness, MRR and TWR all increase with pulse current and pulse-on time. |
| Siddique et al. (2019) [115] | Voltage: 40, 60, 80 V<br>Coating Time: 5 min | Ti–6Al–4V | $WS_2$ | Brass | Micro-hardness increased by 298.55 HV in EDC-treated samples compared to untreated samples. The frictional coefficient was reduced from 0.4 in untreated samples to 0.07 in EDC-treated samples. |
| Mansor et al. (2020) [116] | Coating Time: 90 min<br>Gap Voltage: 80–260 V<br>Peak Current: 3–9 A<br>Pulse Interval: 6–8 ms | NiTi | TiN, TiC, TiCN, $Al_2O_3$, | Cp-Ti | When low operating parameters are used, voids are created on the surface due to gas bubbles.<br>Increased discharge duration increases the TWR by 39.39%, and the growing current increases by 15.52%. |

There is significant progress in related the individual techniques and lot of research and advancements have been already published in the literature. However, there are still few issues that need to be addressed. The challenges and future perspectives related to the various thermal based surface modification techniques, discussed in this paper, are presented below:

- **Laser cladding**: The application of the laser cladding technique for the preparation of wear and corrosion resistant coatings has attained increasing interest in the scientific community, and a large amount of work is focused on the enhancement of the wear resistance by refining the hardness and strength of the coating. In addition, the composite-reinforced phase structure and the use of nano-wear resistive coatings can considerably advance the wear-resistant of laser cladded surfaces, on the whole the bonding strength amongst the coating and substrate, hardness, and porosity. Hence, the exploration and progress of nano-wear-resistant coatings will enlarge the variety of cladding materials and benefit promoting the further development of the laser cladding technology of metallic biomaterials.

  The combination of ultraviolet, electromagnetic stirring, and laser cladding can alter the progression of grain model and considerably enhance the microstructure to accomplish coatings with superb performance without cracks and pores.
- **Thermal spraying**:
  While thermal spraying operation, the particles within the molten phase develop layered stacks when impact the substrate. A large number of pores form which influences the tribological behaviour of the coating. Thus, a reduction in coating porosity and anti-corrosive properties can be expected. Several studies pointed out that the pores or cracks in the coatings could be abridged by using post-processing practices such as laser remelting, annealing and sealing.
- **Thermal Oxidation**: Thermal oxidation is a comparatively simple and economical technique. It has been found to be favourable for surface treatment of artificial joints or in pre-processing of titanium alloys. The optimization of process parameters plays crucial role to attain the proper microstructure and researchers are working in this directions to optimize the process product oriented. The thermal oxidation temperature and time are the foremost parameters influences the characteristics of oxidised layer and specimen surface

**Table 10**
Comparison of thermal-based surface modification techniques.

| | Laser Cladding | Thermal Spraying | Thermal Oxidation | Friction Stir Processing | Thermochemical Salt Bath | Electric Discharge Machining/Coating |
|---|---|---|---|---|---|---|
| Function of Coating | Enhance corrosion and wear resistance. | Enhance corrosion and wear resistance. Improve osseointegration. | Enhance corrosion resistance. | Increase hardness and wear resistance. | Increase hardness and wear resistance. | Enhance corrosion and wear resistance. Improve osseointegration. |
| Hardness ($HV_{0.5}$) | 811.67 | 1231–1298 | 410–1220 | 1105->3000 | 600–1100 | 1149.03–1929 |
| Layer Thickness (μm) | 2–200 | 75–475 | 0.40–6.01 | >150 | >40 | 3–112 |
| Corrosion Potential (V) | 0.18–0.42 | −0.619–−0.71 | −500E-6 | −0.25–−0.4 | −0.423–−0.725 | −0.402–−2 |
| Coefficient of Friction | <0.45 | 0.2–0.31 | 0.56–0.88 | 0.21–0.52 | 0.15–0.56 | 0.2–0.55 |
| Coating Efficiency | High | High | High | High | Low | High |
| Issues associated with the technique | Safety issues associated with use of lasers. High residual stresses cause crack formation. Porous coating layer. Ceramic phases reduce the toughness and dutility. | High porosity levels in coating layer. Inherent high temperature causes oxide inclusions, affecting the hardness and abrasion resistance of the coating. | Time consuming process. Little effect on corrosion resistance compared to other techniques. High temperature and prolonged treatment duration result in larger stratification within the oxide scale, while insufficient temperature and duration lead to discontinuous oxides. | Slow. Gradient of grain sizes gives gradient in properties. Residual stresses reduce fatigue resistance. High surface roughness. | Prolonged high temperatures increase production costs. | Tool wear may affect the required accuracy of product. Higher sparking energy can induce the surface cracks on implant materials. Controlling layer thickness is difficult. Mechanism of layer formation is now well documented. |

roughness, cooling rate. Optimization of process parameters could achieve coatings without oxide scales.

- **Friction stir processing**: Friction stir processing can enhance metal's corrosion resistance by decreasing the grain size and improving the basal texture. Friction stir processing does the modifies of the microstructure and changes the corrosion behaviour of pure metal. The altered microstructure leads to the development of additional corrosion product layers that act as a protective barrier. The findings indicate that when compared to grained. Friction stir processing offers significant improvement of surface properties of biomaterials due to i) decreased grain size, ii) ability to control volume fraction of a specific phase, and iii) addition of reinforcement particles. However, several problems like enormous heat input result in severe plastic deformation. Further, the diffusion of reinforcement particles in not well studied. More importantly, elimination of rough surface after friction stir processing still remain a major challenge. To overcome these problems and ensure biocompatibility of metallic implants, novel methods like friction stir additive manufacturing, linear friction welding, rotary friction welding are being explored as possible better alternatives.
- **Electrical discharge machining:**
The application of EDM/EDC and allied process has found increased interest for enhacing wear and corrosion resistance as well as for improving the bioactivity and antibacterial properties of the metallic biomaterials since last decade. However, there are few issues related to the powder mixed dielectric medium, various electrode materials, and a composite electrode used in EDM/EDC could be addressed in future studies. It is challenging to regulate and evaluate the thickness of the layer deposited through EDM based processes. An extensive work in this direction will be help to establish suitable procedure to control the layer thickness. Determination of an optimum powder concentration for generation of coated layer size on the implant surface is difficult. Thus, ample amount of work is required defining relationship between the power concentration and layer thickness and also optimum values needed to be evaluated. The mechanism of material deposition during EDM/EDC is not well understood, due to the intricacy of the process. More work is required determine the material deposition mechanism and monitor it during the operation.

## 7. Summary

Metallic biomaterials, especially, Titanium and Titanium alloys, continue to be the most popular option for biomedical applications. Although these alloys have outstanding mechanical properties, biocompatibility and corrosion resistance, they can experience corrosion in the human body environment. In this review, the common reasons behind the failure of metal implants have been presented. Among the discussed reasons, the corrosion and wear of metallic implants typically lead to aseptic loosening of the implant and cause excessive metal ion releases, which could be toxic or dangerous to the body environment. To overcome poor corrosion and wear properties and enhance osseointegration and antibacterial capabilities of metallic biomaterials, various surface modification techniques play a crucial role. This paper reviews thermal-based surface modification techniques, including laser cladding, thermal spraying, thermal oxidation, friction stir processing, thermochemical salt bath treatments and electric discharge machining to improve the corrosion and wear enhancement of Titanium and Titanium alloys. Of the techniques covered, EDM shows the most significant potential to be a commercially viable surface treatment. Some of the reasons for this include i) no surface preparation of the metal is required before EDM is used, ii) the surface porosity and roughness can be controlled easily by selecting appropriate electrical parameters, iii) a corrosion-resistant Titanium oxide layer of controlled thickness can be produced. EDM's use as a surface treatment for Titanium/Titanium alloys implant surfaces is still in the early stages. While it has shown promise in recent studies, further research is required before the biomedical industry can accept it.

### CRediT authorship contribution statement

**Deepak Rajendra Unune:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Software, Methodology, Conceptualization. **Georgina R. Brown:** Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation. **Gwendolen C. Reilly:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

No data was used for the research described in the article.

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