Review: The Surface Modification of Pure Titanium by Micro-Arc Oxidation (MAO) Process

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Abstract. Titanium and titanium alloys are broadly used in biomedical applications, particularly orthopaedic and dental implants, due to their suitable properties, such as low modulus, high specific strength to weight, high machining, high corrosion resistance, and biocompatibility. Micro-arc oxidation (MAO) is one in every of many surface modification processes that can provide porous, adhesive, and bioactivity for implantation, resulting in better and more improved osseointegration. Furthermore, antimicrobial surface coatings hold a lot of promise for reducing infection-related errors. This study provides a summary of the biological evaluation of bioactive coatings. It primarily focuses on ways for enhancing the biological characteristics of MAO-coated titanium and related alloys. The overview is to discuss the MAO process of the titanium implant to enhance bone/implant interaction.

1. Introduction
Metallic orthopaedic implants are regularly used as additives of restorative prostheses or bone stability merchandise with internal the human skeletal system (e.g. slabs, bolts, and rivets). The anatomy and frame structure of the human body skeletal structure decide and restrict the layout of those implants [1]. The mechanical and chemical balance of biomedical implants, similarly to their biocompatibility with tissues and body fluids, are critical for effective bone fracture and replacement treatment [2]. If an orthopaedic implant wishes to be eliminated from the frame prematurely, it's far acknowledged to have failed [1]. This might result in local or systemic irritations, prompting implant removal in certain cases [3]. In addition, allergenic reactions do arise from time to time. The fundamental difficulty affecting the carrier lifestyles of orthopaedic implants is corrosion [3]. Titanium is a powerful biocompatible cloth that is extensively utilized in biomaterials programs, specifically for bone anchoring structures like dental and orthopaedic implants, similar to osteosynthesis [4].

A range of techniques for creating HA coatings on Ti substrates was published, mostly for the motive of enhancing the osteoconductivity of bone-interface implantation. thermal spraying, electroplating methods, sol-gel, laser cladding, ion implantation processes, and micro-arc oxidation are examples of those processes [5]. Because of the intermediate layer between coatings and metal, such coatings have excellent adhesion with the surface of the treated metal. Depending on future and intent operating conditions of components, this method could create coatings with thicknesses ranging from fractions to several micrometers that obtain many features, Because of the high dissipating potential of the electrolyte, it is also possible to...
handle challenging parts and shape several coatings on Ti substance [6]. Surface changes of titanium surfaces to increase corrosion resistance, wear resistance, surface roughness, and biocompatibility have resulted as a consequence. Apart from increasing other desirable attributes, all redesigned surfaces should be checked for behaviour of corrosion at all times [7]. This paper introduce review the MAO process of pure titanium used in biomedical applications to increased biological properties.

1.1. Titanium and titanium alloys implant:

Due to their greater power to weight ratio, Ti alloys outperform the competition and also the reliability and overall performance are of maximum importance critical so that Ti and its alloys are utilized in several stressful programs [8 and 9]. they are gaining popularity in each science and dental fields because of their high biocompatibility, exquisite corrosion resistance, and light weight[10].

pure titanium (Cp-Ti) and its alloys are often employed, in a variety of biomedical uses, including dental and orthopedic surgical implants; implant devices, such as joint replacement joint replacements; osseointegration gadgets, such as broken bones clamps, and spinal surgery procedure devices; prosthetic cancer and heart valves, synthetic lungs, pacemakers, and artery stent additives in the cardiac and circulatory system; and spine hearing aids in hearing services [11]. According to both oxygen and iron concentration, there are four classes of Ti alloys also known as Ti6-4 and Ti-5 [12].

Ti alloys are primarily well-suited for implant packages because to their superior corrosion resistance as compared other biomedical materials[13]. Table 1 shows the mechanical properties of some biomedical materials[14]. Each Ti6Al4V and Cp-Ti is protected by a passive oxide film. This thick and adhesive oxide layer film prevents Ti alloys from pitting, intergranular, and crevice corrosion, and in big element responsible for Ti alloys' high biocompatibility[14]. Despite the fact that titanium-implant completely readily laid low with the environment and might create difficulties. As a result, improving the durability of Ti implants is important to lowering biomechanical and organic characteristic failure[13 and 14].

To avoid bodily injury, titanium alloy should be surface tuned to pass science application specifications. Both CP-Ti and Ti-64 offer various benefits that have already been noted; however, they do have some drawbacks in terms of implant applications, in that low resistance of wear qualities, and cytotoxic of the Ti-64 alloy because found of vanadium this means that this alloy is restricted to sure applications, and elastic modulus that's taken into consideration to be high while as in comparison to the bone These factors, therefore, restrict the software of the Ti and alloys [15]. A low modulus of elasticity is desired in implants leading bone resorption as a result of stress shielding , which can shorten the implant's service life. This difficulty can be solved to a significant extent by using an appropriate surface modification method[16].
1.2 Micro-Arc Oxidation (MAO) Process

MAO, which forms an excellent hardened ceramic film on implant surfaces and is dependent on anodic oxidation, is a comparatively successful surface treatment technique with inside the biomedical application [17, 18 and 19]. As proven in Figure 1 [20]. Because of the benefits of low cost, excessive-performance, excessive bonding the energy among the MAO technique is no restrict at the surface form of the painting's material, MAO has been considerably studied in a range of fields, consisting of biomedical applications [21, 22 and 23]. The interaction between implants and surrounding host tissues determines the microstructure and mechanical features of the micro-arc oxide layer, which may be precisely regulated by electrolyte form, matrix composition, and process parameters [24 and 25].

| Material       | Young E(GPa) | Modules Yield strength (MPa) | Tensile Strength (MPa) | Fatigue Limit (MPa) |
|----------------|--------------|-----------------------------|------------------------|---------------------|
| Stainless steel| 190          | 221-1213                    | 586-1351               | 241—820             |
| Co-Cr alloys   | 210-253      | 448-1606                    | 655-1896               | 207-950             |
| Titanium (Ti)  | 110          | 485                         | 760                    | 300                 |
| Ti-6Al-4V      | 116          | 896-1034                    | 965-1103               | 620                 |
| Cortical bone  | 15-30        | 30-70                       | 70-150                 |                     |

Table 1 suggests the mechanical properties of several bioactive materials [14].

Fig 1. The micro-arc oxidation (MAO) mechanism is depicted in this diagram [20].
During MAO treatment, the implant increases molecular adhesive, transport, proliferation, differentiation and biocompatibility is determined by electrolyte and biological element composition in addition to oxidation time [26, 27 and 28]. Alloying parameters impact the microstructure, morphology, and mechanical properties of the micro-arc oxidation coating [28]. The MAO mechanism is influenced by several factors. Substrates structure, electrolytes composition, and additives are the first two. Process temperature, oxidation time, and electrical parameters[29].

The MAO is a process for forming ceramic coatings on sequence classification that involves applying an excessive potential (at the order of loads of volts) to electrolytic cells, with the substrate content, usually, a barrier like Ti, serving as the anode as the voltage is increased anodization occurs, which motivates the formation of an anodic oxide film [30]. Regardless, layer thickness does not increase evenly above a set potential, and dielectric breakdown occurs, with the initial barrier film breaking down in the form of multiple freely moving sparks. The deposition of material and localized repair at one point in the coatings are connected to the action of sparks, with subsequent flickering at other sites[30]. The voltage required to purpose dielectric breakdown differs depending on the anode materials, electrolyte compositions, and temperature [30]. The temperature of the electrolytes is lowered by using a cooler, while plasma formation raises the temperature of the electrolyte[31].

1.3 MAO of Pure Titanium

MAO is a difficult method that combines several fractional oxide layer processing methods (pre-existing layer disintegration, anodic fuel online evolution, and dielectric collapse) In addition to the modern-day density, the color of the metal, its elements, and the electrolytic solution's attention, are all factors to consider. all influenced the probability of hegemony with all of these fractional methods. So, in the micro-arc discharge canals, micro-arc oxidation is a method of energy consumption that is always followed by chemical, physical, plasma chemical, and electrochemical reactions [6].

A variety of studies have stated that a complete MAO method of metals has been proposed, taking in to account the dynamics and growth of the oxide film during MAO treatment, according to a number of investigations. The first process includes the melting of substrates and the subsequent loss of melted debris inside the electrolyte, where the melted debris is oxidized and settles as thin plates on the substrate which expand repetitively [25].

Z.Q. Yao et.al [32] enhanced the bioactivity of Ti surfaces utilized in scientific implants, on ultrafine-grained and coarse-grained Ti, MAO was employed to organize Ca/P-containing porous titanium coatings. The segment description, form, morphology, and microstructure of ultrafine-grained Ti coatings, as well as their thermal equilibrium duration of MAO, have been investigated subsequently. Figure 2 SEM of MAO coating formed at various reaction times[32].

Fig.2 SEM cross-sections of MAO coatings formed at various reaction times [32].
Su Cheng et.al [33] investigated pure Ti through The effects of MAO on microstructures and factor distribution on the inside coating surface. The results revealed that the coating floor, which consists of Ti, O, Si, Ca, and Na, increases as the MAO period increases. When the MAO time approaches ten minutes, the rate at which factors information material grows slows. As the MAO time approaches five minutes, the rate of pore length growth and pore quantity reduction slows.

Wang Ping et.al [34] The deposition of TiO$_2$ on a pure titanium by using MAO technique in the solution of NaAlO$_2$ concentrations become examined. voltage have to upward thrust because the attention of NaAlO$_2$ will increase, selling the increased charge of MAO on herbal titanium. MAO coatings, in particular, were found to include TiO$_2$, rutile, and anatase, according to X-ray diffraction (XRD) results. As shown in Figure 3 MAO coatings at various concentrations of NaAlO$_2$ [34].

Lin Xu et.al [35] To improve blood compatibility and wettability of ultrafine-grained natural titanium, researchers examined the synthesis of TiO$_2$ by the MAO technique on an ultrafine-grained pure titanium surface. The MAO coating exhibited a rougher surface, lower distilled water contact angles, and higher surface energy. The MAO modification effectively lowered hemolysis rate, extended dynamic coagulation time, prothrombin time (PT), and activated partial thromboplastin time (APTT), decreased platelet adhesion and deformation degree, and improved blood compatibility. The sample with a 9-minute oxidation time had the highest surface energy, the highest PT and APTT values, the lowest hemolysis rate, much less platelet adhesion, a lower degree of deformation, and more favorable blood compatibility. Figure 4 suggests version of thickness coating by MAO voltage and times.
Yada Li et al. [36] studied the coating with a macro/micro/nano triple hierarchical form have become organized on titanium surface with the useful resource of using a step micro-arc oxidation (MAO) remedy which includes macropores (100-103) μm, micro slots (3-10) μm, and submicron/nanopores (80-200) nm. Macropores have been original with the aid of using MAO remedy forming a “cortex-like” shape, in a 2nd MAO. The outcomes advocate that NaOH complements the corrosion resistance and has a notable effect on the size and uniformity of macropores. The coating hydrophilicity and the formation of hydroxyapatite of the coating had been decided with the beneficial aid of the usage of the second one-step remedy, i.e. the “cortex-like” form as shown in Figure 5. This novel triple hierarchical form can be promising to beautify the adhesion of osteoblasts to implants similarly to the fixation of implants.

S. Stojadinović [37] investigated the formation of TiO$_2$ coatings by PEO of titanium. Diffraction types of coatings show well-pronounced reflections inherent to the anatase phase of TiO$_2$. The trivalent oxidation state of included Tb is inferred from photoluminescence measurements. Overlapping regions are normal of photoluminescence emission spectra. The first location is related to the TiO$_2$ host band, even as the second area, which’s successful of a couple of emission bands, is related to Tb$^{3+}$ f-f transitions from excited diploma lower degrees as proven in Figure 6 [38]. The photodegradation of methyl orange beneath synthetic daylight conditions is used to research the photocatalytic behavior (PA) of Tb$^{3+}$ doped TiO$_2$ coatings, implying that the number one element influencing PA is the popularity of Tb$^{3+}$ ions integrated into coatings. Tb$^{3+}$ doped TiO$_2$ coatings fabricated in a quick length have a better PA than pure TiO$_2$ coatings fabricated beneath the equal conditions; the coating fabricated after 1 minute of PEO operation has the best PA.
A.R. Ribeiro et.al [38] investigated the formation of MAO was used to explore the growth of calcium and phosphorus-doped oxide coatings on titanium surfaces. As a result, at the top surface of the oxide film, a nanometric-thick calcium-rich amorphous layer emerges, which is the essential pressure supporting quick osteoblast adhesion and spreading, as well as increased degrees of IFN-cytokine production, rearrangement, and cell spreading, which is assumed to govern inflammatory responses and bone microarchitecture (stopping osteoporosis) in addition to cytoskeleton reorganization and cell spreading.
Shu-Chuan Liao et al. [39] investigate the creation of a ceramic coating on the surface of pure Ti. Then, to immobilize biodegradable polymer at the floor, HMDSZ/O₂ plasma therapy and an energetic natural layer were applied to the natural silicon film through. had been implemented onto the natural silicon movie to immobilize biodegradable polymer on the floor. the biocompatibility and corrosion resistance of the surface were tested using the capacity polarization dynamic check and the Alamar blue molecular viability assay. The experimental results show that improves surface of Cp-Ti substrate's resistance of corrosion, and biocompatibility as shown in Fig. 7 [39].

1.4. Conclusions
This research aims to provide an overview of MAO methods for improving the chemical and organic properties of pure titanium for biomedical applications. Scientific studies should be included in future MAO research to further our knowledge of bone reactions to implant surfaces with various coating and properties. to achieve the necessary composition, thickness, and uniformity of floor oxide layers, which play an essential position in modifying the resistance of corrosion and biocompatibility of pure Ti and Ti alloys. As a result, the classified literature supplied in this research is predicted to help the layout and management of surface modification approaches utilized for improving biomedical Ti materials corrosion conduct.

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