Surface modification of Zirconium based alloys for bio application by Micro-arc oxidation process: A Review

Maysam Abbood Salman¹*, Ali Hubi Haleem², Samir Hamid Awad³

¹,²Department of Metallurgical Engineering, College of Materials Engineering, University of Babylon, Babylon, Iraq
³Department of Ceramic Engineering, College of Materials Engineering, University of Babylon, Babylon, Iraq

maysam.salman@student.uobabylon.edu.iq

Abstract. Because of their superior mechanical properties, metal implants are the ideal choice for long-term reconstruction of hard tissues like the hip and knee joints. Zr and its alloys are widely recognized as biocompatible metal implants because of the self-regulating oxide coating that prevents the surface from corrosion and restricts ion release. The Osseo incorporation of these critical elements requires surface modification. The surface of metal implants is modified via micro-arc oxidation (MAO). The goal of this study is to give a summary of contemporary Micro-arc oxidation (MAO) research on zirconium and related alloys in biometal implants.

1. Introduction

1.1. Structure, composition, and characteristics of bones
Bones weaken and are injured as a result of aging, accidents, and disease, much like other parts of the body. Bone fractures, low back pains, osteoporosis, scoliosis, and other musculoskeletal problems are common in the elderly, but not all. To heal broken bones, cartilage, ligaments, and tendons, implants and other biomaterials are employed [1]. According to Weiner and Wagner [2], the basic bone composition is primarily fibrous protein collagen, carbonated apatite (Ca5(PO4, CO3)3(OH), and water. The size and proportions of these components alter throughout time. As a consequence, older bones progressively give way to younger ones. [3] Uddin and his associates The synthesis and deposition of calcium phosphate crystals, which are essential for bio metal’s hardness and strength, is carried out by bone-forming cells such as osteoblasts. The hierarchical organization of cortical bone is seen schematically in Figure 1. It can be recognized that cortical bone has a range of structures visible on a surface scale, starting with sub-nanostructures [4]. Because of these holes, which are filled with fluid and regenerating cells such as osteoblasts, osteoclasts, osteocytes, and bone-lining cells, bone is a visco elastic substance its shown in Figure 2 [5].
1.2 Zirconium as Orthopedic Applications

The medical application plays a big role in deciding which metal to use as an implant. To service safely and retainable for a longer duration without rejection, these metals should have a few vital features such as outstanding biocompatibility, high corrosion and wear resistance, acceptable mechanical characteristics, Osseo integration, ductility, and high hardness. [6] Zr is employed in total hip replacement (THR) and total knee replacement (TKR) biomedical applications (THR). Smith and Nephew developed a Zr-2.5 alloy (UNS R60901) named Oxinium for the femoral knee surface and the head of the hip joints in 1997 for TKR and in 2002 for THR. Because of Zr's low wear resistance due to the Zr-2.5Nb alloy is heat treated in air at 773 K, thin zirconium oxides (about 5 m) form due to its low hardness. Chemical compositions and tensile strength characteristics of Zr alloys are shown in Table 1. The content of hafnium (Hf) is the evident distinction between the classes. Industrial grades allow (Hf) concentration of up to (4.5) percent, whereas nuclear grade (Hf) concentration is limited to less than 0.01 percent due to the greater thermal neutron cross section [7].
Table 1: Compositions and tensile properties of Zr alloys[7].

| Element        | (Mass%)    |
|----------------|------------|
|                 | R60702     | R60704     | R60705     | R60901     |
| Zr+Hf, min     | 99.2       | 97.5       | 95.5       | Balance    |
| Hf, max        | 4.5        | 4.5        | 4.5        | 0.010      |
| Fe+Cr          | 0.2, max   | 0.2–0.4    | 0.2, max   | Fe:0.15, Cr:0.020 |
| Sn             | ...        | 1.0–2.0    | ...        | 0.0050     |
| H, max         | 0.005      | 0.005      | 0.005      | 0.0025     |
| N, max         | 0.025      | 0.025      | 0.025      | 0.0080     |
| C, max         | 0.05       | 0.05       | 0.05       | 0.027      |
| Nb             | ...        | 2.0–3.0    | 2.40–2.80  |
| O, max         | 0.16       | 0.18       | 0.18       | 0.13       |
| Tensile properties | R60702 | R60704     | R60705     | R60901     |
| UTS, min (MPa) | 379        | 413        | 552        | 450        |
| Yield strength, min (MPa) | 207    | 241        | 379        | 310        |
| Elongation, min (%) | 16     | 14         | 16         | 15         |

Zr and its alloys have good corrosion resistance, but because to their poor bioactivity, their usage in surgical and dental applications has been limited. This difficulty might be solved by creating a biocompatible layer on the surface of Zr-based materials [8]. Surface treatment processes like as sol-gel, thermal oxidation, anodizes, and MAO are all accessible[9]. Zr and its alloys have aroused substantial interest for dental and orthopedic implant applications due to its low young modulus, strong fracture resistance, high flexural strength, good corrosion resistance, low cytotoxicity, and biocompatibility. ZrO2 is applied to Zr-based surfaces to increase bioactivity[10]. Zirconium oxide is commonly used for MAO coatings on zirconium alloys because of its chemical and thermal stability, wear resistance, and mechanical strength[11]. The effectiveness of the coatings is highly linked to the phase composition of current zirconia, which is determined by MAO processing variables including electrolyte composition, electrical regime, and so on. Among the different electrolytes suited for MAO, silicate, aluminate, and phosphate-based electrolytes have been widely employed [12].

1.3 zirconium and zirconium alloy

When Klaproth investigated precious stone jargon in 1789, he discovered an element he couldn't name; in 1797, Vauquelin analyzed the new zirconium compounds; and in 1824, Berzelius succeeded in isolating impure zirconium. The iodide decomposition procedure for metal purification was created by van Arkel and de Boer in 1925, and Kroll developed the procedure to produce zirconium in 1947 [7]. ASTM F2384-10 regulates the use of pure zirconium, Zr-2.5Nb alloy for surgical implant applications. Zirconium 705 is a zirconium alloy that has been mixed with niobium to improve strength and formability. It is governed by ASTM F2384-10 [7 and 10].
• Chemical and Physical Characteristics

Zr has an atomic number of 40. An atom's mass is equal to 91.22. Pure Zr has a density of (6.52) g/cm³. Structure exists in Zr (hcp; alpha phase) (bcc; beta phase). To help stabilize the operation, tin and oxygen are added (nickel and niobium). The quantity of these components added the strength and corrosion resistance of the material can be increased by adjusting it. [7 and 13].

• Mechanical Characteristics

The deformability of pure Zr is outstanding. It is an active metal that forms thick and continuous zirconium oxide at the surface when it combines with oxygen. The black oxide layer formed in steam at temperatures ranging from (533 – 673) K in the first stage. The oxide color changes to ash gray when the reaction time is increased [13 and 14].

The review's aim

Because the bone is living, it must accept the implant. It should be able to stick to and grow on the bone when implanted near to it to minimize loosening and irritation. With a lower Young's modulus and the maximum biocompatibility, Zr and its alloys are recognized to be more biocompatible than other metals implants. However, because their hardness is reduced, we use a current surface modification to create a layer with a higher hardness surface and greater potential for cell adhesion, proliferation, and differentiation. Antibacterial medicines may also be placed into the layer to limit bacterial infection.

2. Advance surface modification \ Micro-arc oxidation

Zirconium implants are prone to wear-accelerated corrosion in bodily fluids. Zirconium corrosion can occur when the corrosive environment is different than expected, when there are process temperature excursions or when such chemicals are introduced into the chemical system during chemical manufacturing [15 and 16]. Extreme working conditions necessitate an increase in zirconium and its alloys' wear and corrosion resistance. Thermal oxidation, physical vapor injection, ion implantation, thermal mist, and Micro-arc oxidation are some of the surface treatments used to improve zirconium alloy corrosion and wear resistance. [17]. Diluted in deionized water after being treated with MAO in a flask containing a basic solution (potassium hydroxide). In order to protect the electrolyte from contamination and to avoid particle diffusion in the cooling circuit, A double wall method was used to chill the electrolyte. As seen in Figure 3. MAO [17] is a metal oxide that may be regulated in an electrolyte. Electrochemical_oxidation parameters electrolyte form, concentration and pH, to name a few, as well as applied voltage and duration, have an impact on ZrO₂. If the applied potential remains constant, the pH value can be raised; if the applied potential maintains constant, the pH value is pH independent. Instead of an aqueous electrolyte, an electrolyte is employed. To produce the same coating, a larger applied potential is necessary. As MAO continues, the length or thickness of the layer rises, but there is always a point when the thickness remains constant. It's worth mentioning that in an alkaline electrolyte with a pH higher than 12, the pH is higher.
MAO is a promising surface treatment with excellent adhesion properties. Environmentally friendly Alkaline electrolytes with ceramic oxide coating on light alloys [17]. There have been some investigations into MAO treatment of zirconium alloys with testing. Microstructural characteristics corrosion protection [18], biocompatibility [21], as well as friction and corrosion properties [19 and 20]. In the alkaline electrolyte, a pulsed alternating current system was used. Quite slim Various processes are used to make thick coatings. When it comes to electrochemical corrosion and corrosion properties, now is the time to look into it.

The smooth substance area is determined by the EDX analysis is adjacent to Zirconium and oxygen are abundant in the core pores. (Figure 4(b)) indicates that the structures are similar to the pancake they are mainly formed due to the strong discharging which starts at the coating / substrate The pie-like forms vanished as the MAO process advanced, and the amount of material deposited increased. A coarse coating surface forms around the discharge channels (Figure 4(c)). Unlike the paint made in 3.5 minutes, the coating made in 90 minutes had an even granule on the surface (Figure 4(d))[17]. As shown in Figure 5 (a,b) The coatings are made up of two layers: a thick base and a thin porous top layer with a thermal shrinkage age. [17]. Figure 6 is a Scanning Electron Microscopy (SEM) of coats on Zirlo by an MAO process where coating formed in 100 V [22].
Figure 4. EDX examination of the surface picture of the coating formed at two separate times for Zr 702: a) A 3.5-minute surface view of the coating, and b) EDX findings for the regions 1 and 2 shown on the image. c) The surface morphology of the 90-minute coating, and d) a detailed surface picture revealing the characteristic solidification structure [17].

Figure 5. Cross-sections of as-produced coatings Zr 702 a) 3.5 minutes; b) 90 minutes [17].
Figure 6. Scanning electron micrographs (a) A backscattered electron picture of a coating broken field. (b) Coated surface secondary electron picture.[22]

Acknowledgments
I'd like to express my gratitude to my colleagues and professors for their help and guidance in completing this project.

References
[1] Navarro M, Michiardi A, Castañó O, Planell JA. Biomaterials in orthopaedics. J R Soc Interface 2008;5:1137–58.
[2] Weiner S, Wagner HD. The material bone: structure–mechanical function relations. Annu Rev Mater Sci 1998;28:271–98.
[3] Uddin MH, Matsumoto T, Okazaki M, Nakahira A, T S. Biomimetic fabrication of apatite related biomaterials. In: Mukherjee A, editor. Biomimetics, Learning from Nature. Vukovar: In-Teh; 2010. p. 289–303.
[4] Mour M, Das D, Winkler T, Hoenig E, Mielke G, Morlock MM, et al. Advances in porous biomaterials for dental and orthopaedic applications. Materials 2010;3:2947–74.
[5] Minagar, S., Berndt, C. C., Wang, J., Ivanova, E., & Wen, C. (2012). A review of the application of anodization for the fabrication of nanotubes on metal implant surfaces. Acta biomaterialia, 8(8), 2875-2888
[6] M. Tarakci, Plasma electrolytic oxidation coating of synthetic Al-Mg binary alloys, Mater. Charact. 62 (2011) 1214–1221.
[7] Niinomi, M., Narushima, T., & Nakai, M. (2015). Advances in metallic biomaterials. Heidelberg, DE: Springer.
[8] Y.T. Liu, T.M. Lee, T.S. Lui, Enhanced osteoblastic cell response on zirconia by bioinspired surface modification, Colloid Surface B 106 (2013) 3
[9] Cengiz, S., Azakli, Y., Tarakci, M., Stanciu, L., & Gencer, Y. (2017). Microarc oxidation discharge types and bio properties of the coating synthesized on zirconium. Materials Science and Engineering: C, 77, 374-383.
[10] Durdu, S., Aktug, S. L., Aktas, S., Yalçın, E., Cavuşoğlu, K., Altinkok, A., & Usta, M. (2017). Characterization and in vitro properties of anti-bacterial Ag-based bioceramic coatings formed on zirconium by micro arc oxidation and thermal evaporation. Surface and Coatings Technology, 331, 107-115.
[11] R.H. Hannink, P.M. Kelly, B.C. Muddles, Transformation toughening in zirconia-containing ceramics, J. Am. Ceram. Soc. 83 (3) (2000) 461–487
[12] Li, N., Yuan, K., Song, Y., Cao, J., & Xu, J. (2020). Plasma electrolytic oxidation of Zircaloy-2 alloy in potassium hydroxide/sodium silicate electrolytes: The effect of silicate concentration. Boletín de la Sociedad Española de Cerámica y Vidrio.
[13] Kashkarov, E. B., Nikitenkov, N. N., Syrtanov, M. S., Sutygina, A. N., Shulepov, I. A., & Lider, A. M. (2016). Influence of plasma immersion titanium implantation on hydrogenation and mechanical properties of Zr–2.5 Nb. Applied Surface Science, 370, 142-148.
[14] Wadekar, S. L., Raman, V. V., Banerjee, S., & Asundi, M. K. (1988). Structure-property correlation of Zr-base alloys. Journal of Nuclear Materials, 151(2), 162-171.
[15] Moniz, B. J. (1984, January). Corrosion resistance of zirconium in chemical processing equipment. In Industrial Applications of Titanium and Zirconium: Third Conference. ASTM International.
[16] Yau, T. L., & Annamalai, V. E. (2016). Corrosion of zirconium and its alloys.
[17] Malayoğlu, U., Tekin, K. C., Malayoğlu, U., & Belevi, M. (2020). Mechanical and electrochemical properties of PEO coatings on zirconium alloy. Surface Engineering, 36(8), 800-808.
[18] Martin, J., Haraux, P., Ntomprougkidis, V., Migot, S., Bruyère, S., & Henrion, G. (2020). Characterization of metal oxide micro/nanoparticles elaborated by plasma electrolytic oxidation of aluminium and zirconium alloys. Surface and Coatings Technology, 397, 125987.
[19] Matykina, E., Arrabal, R., Skeldon, P., Thompson, G. E., Wang, P., & Wood, P. (2010). Plasma electrolytic oxidation of a zirconium alloy under AC conditions. Surface and Coatings Technology, 204(14), 2142-2151.
[20] Cheng, Y., Cao, J., Peng, Z., Wang, Q., Matykina, E., Skeldon, P., & Thompson, G. E. (2014). Wear-resistant coatings formed on Zircaloy-2 by plasma electrolytic oxidation in sodium aluminate electrolytes. Electrochimica Acta, 116, 453-466.
[21] Aktaş, S. L., Durdu, S., Yalçın, E., Çavuşoğlu, K., & Usta, M. (2017). In vitro properties of bioceramic coatings produced on zirconium by plasma electrolytic oxidation. Surface and Coatings Technology, 324, 129-139.
[22] Cheng, Y., Wu, F., Dong, J., Wu, X., Xue, Z., Matykina, E., ... & Thompson, G. E. (2012). Comparison of plasma electrolytic oxidation of zirconium alloy in silicate-and aluminate-based electrolytes and wear properties of the resulting coatings. Electrochimica acta, 85, 25-32.