



Review on Surface Modification of Zirconium Based Alloys for Bio Application by Micro-Arc Oxidation Process

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Abstract

Because of their excellent mechanical properties, metal implants are the best option in the long replacement of hard tissues such as the hip and knee joints. Zr and its alloys are widely accepted as biocompatible metal implants because the self-regulating oxide layer to prevent the surface from corrosion and minimizes ion release. Surface modification is essential to promote the Osseointegration of these vital materials. MAO is being used to modify the surface of metal implants. The purpose of this paper is to provide an overview of recent MAO research on zirconium and its alloys in bio mineral implants.

Keywords: Micro-arc oxidation (MAO), Zirconium based alloy (Zr), Oxide coating

1- Introduction

1-1 Bone structure, composition and properties

Age, like other parts of the body, accidents, and disease, causes bones to weaken and be damaged. Bone fractures, low back pain, osteoporosis, scoliosis, and other musculoskeletal problems are common in the elderly, but not always. Implants and other biomaterials are used to treat injured bones, cartilage, ligaments, and tendons [1]. Basic bone composition, according to Weiner and Wagner [2], is mostly fibrous protein collagen, carbonated apatite ($\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3(\text{OH})$), and water. Over time, the crystal size and proportions of these components change. As a result, younger bones gradually take the place of older ones. [3] Uddin and his colleagues. Bone-forming cells, such as osteoblasts, are responsible for the synthesis and deposition of calcium phosphate crystals, that are required for bio mineralization's hardness and strength. Fig.1 shows the schematic representation of the hierarchical structure of cortical bone. It can be seen that cortical bone provides a variety of structures that can be noticed on a surface levels of scale starting from sub-nanostructures. Mour et al. [4]. Bone is a visco elastic material due to these pores, which are filled with fluid and cells: osteoblasts, osteoclasts, osteocytes and bone-lining cells that are regenerative shown in Fig.2 [5].

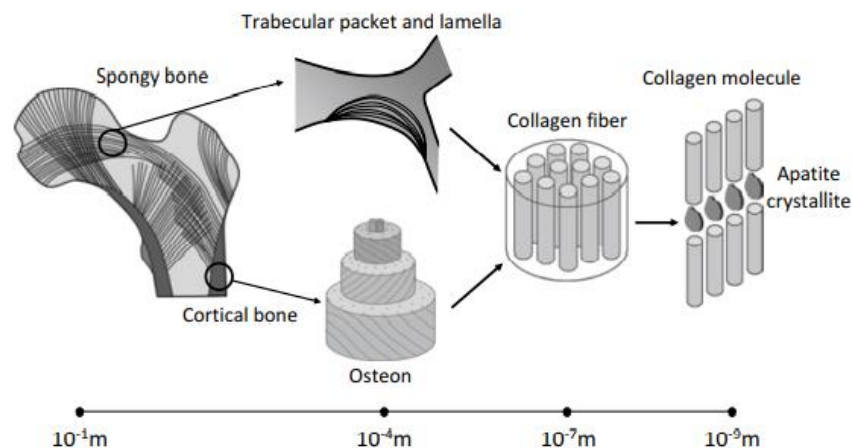


Fig. 1 Schematic illustration of hierarchical structure of bone[5]

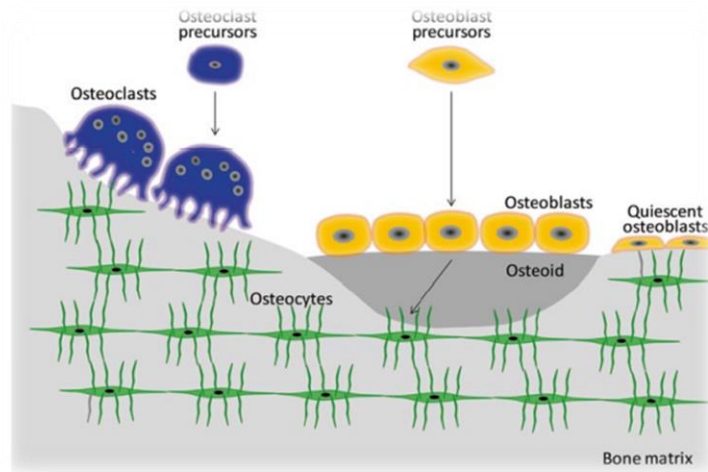


Fig. 2 Bone cells[5]

1-2 Zirconium as Orthopedic Applications

The medical application plays a big role in deciding which metal to use as an implant. These metals should have a few essential properties such as excellent biocompatibility, high corrosion and wear resistance, suitable mechanical properties, Osseo integration, ductility, and high hardness to serve safely and retainable for a longer period without rejection. [6]

Zr is used for biomedical applications to total knee replacement (TKR) and total hip replacement (THR) (THR). The femoral knee surface and the head of the hip joints are made of a Zr-2.5 alloy called Oxinium, which was developed by Smith and Nephew in 1997 for TKR and in 2002 for THR. When the Zr-2.5Nb alloy is heat-treated at approximately 773 K in air, thin zirconium oxides (ca. 5 m) form, because of Zr's low wear resistance due to its low hardness [7].

Zr and its alloys have excellent corrosion resistance, but their use in surgical and dental applications has been limited due to their low bioactivity. The design of a biocompatible layer at the surface of Zr-based materials could provide a solution to this problem [8]. A wide range of surface treatment technologies (sol-gel, thermal oxidation, anodizes, MAO) are available.[9]

Due to their low young modulus, high fracture resistance, high flexural strength, high corrosion resistance, low cytotoxicity, and biocompatibility, Zr and its alloys have sparked considerable interest for dental and orthopedic implant applications. Zr-based surfaces are coated with ZrO₂ to improve bioactivity[10].

MAO coatings on zirconium alloys are often made of zirconium oxide, which is known for its chemical and thermal stability, wear resistance, and mechanical strength[11]. The coatings' efficiency is closely associated with the phase composition of current zirconia, which can be influenced by MAO processing conditions such as electrolyte composition, electrical regime, and so on. Silicate-,

aluminate-, and phosphate-based electrolytes have been commonly used among the various electrolytes suitable for MAO. [12]

1.3 zirconium and zirconium alloy

In 1789, when Klaproth studied the precious stone jargon, he discovered it contained an element he couldn't identify; in 1797, Vauquelin researched the new compounds known as zirconia; in 1824, Berzelius succeeded in isolating impure zirconium; in 1925, van Arkel and de Boer invented the iodide decomposition process for metal purification; and in 1947, Kroll developed the method to produce zirconium [7].

Pure Zirconium, Zr-2.5Nb alloy (UNS R60901) is given for surgical implant applications and is regulated in ASTM F2384-10. Zirconium 705 is zirconium combined with niobium to increase its strength and enhance formability, and is regulated in ASTM F2384-10[7,10].

Physical and Chemical Properties

Zr's atomic number is (40) The atomic mass is (91.22) Pure Zr has a density of 6.52 g/cm³. Structure (hcp; alpha phase) exists in Zr (bcc; beta phase) The addition of tin (Sn) and oxygen (O) helps to stabilize the process (nickel and niobium). To increase the strength and corrosion resistance, the sum of these elements added can be changed. [7,13].

Mechanical Properties

Pure Zr has excellent deformability. It is one of the active metals, and it highly reacts with oxygen to form dense and continuous zirconium oxide at the surface. For the initial stage, the black oxide layer forms in steam at temperatures ranging from 533 to 673 K. As the reaction time is extended, the oxide color changes to ash gray [7,13,14].

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

2- Advance surface modification\ Micro-arc oxidation

In body fluids, zirconium implants are subjected to wear-accelerated corrosion. When the corrosive environment differs from what was predicted, when process temperature excursions occur, or when some impurities are incorporated into the chemical environment during chemical processing, zirconium corrosion can occur [15,16]. Severe operating conditions demand an improvement in zirconium and its alloys' wear and corrosion resistance. To increase the corrosion and wear resistance of zirconium alloys, various surface treatments such as thermal oxidation, physical vapour deposition, ion implantation, thermal spray, and Micro-arc oxidation are used [17].

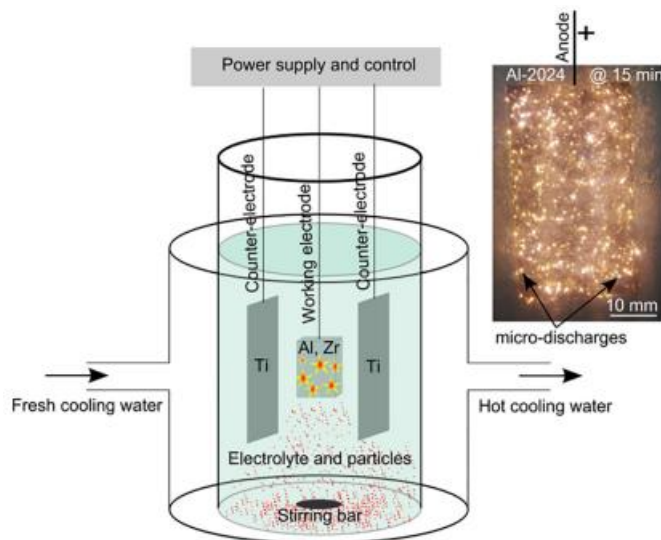


Fig 3 Schematic view of the experimental using the MAO process (picture of a 2024 aluminium alloy during MAO at 15 min processing time)[18]

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 [19,20]. In the alkaline electrolyte, a pulsed alternating current 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.

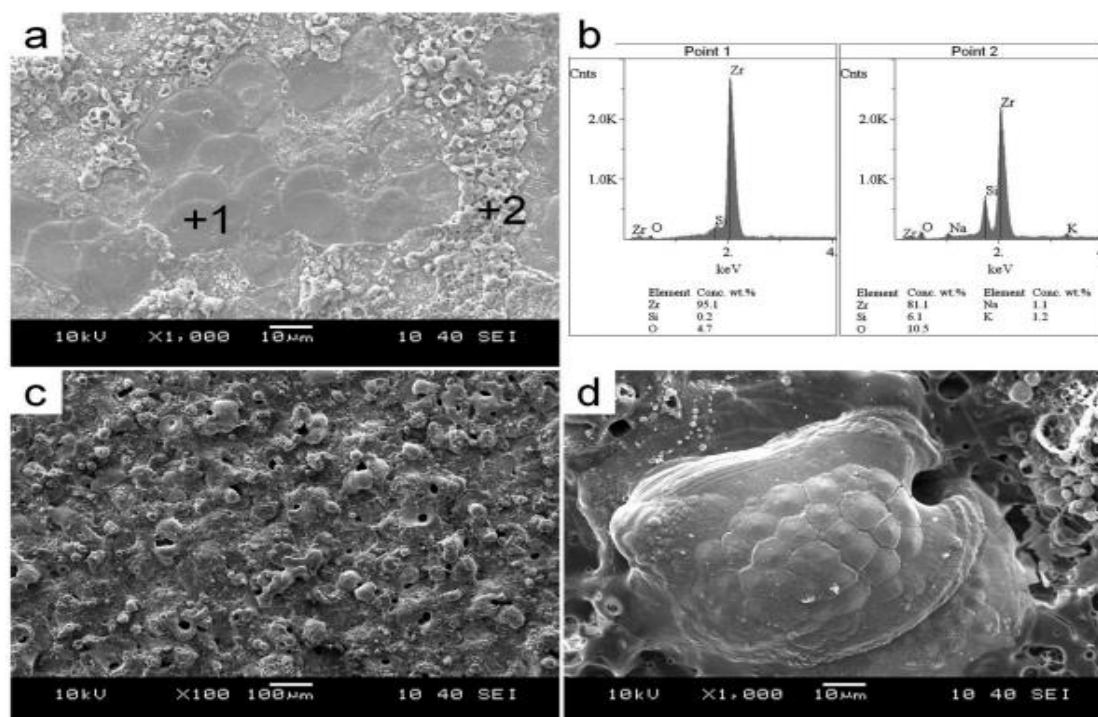


Figure 4 The surface image of the coating produced in different two time for Zr 702 [17].

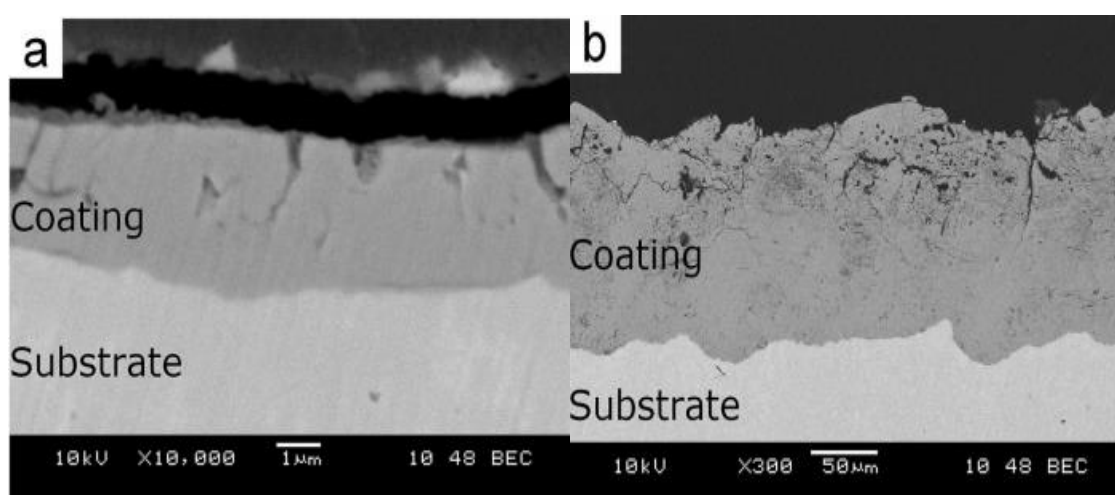


Figure 5 Cross-sections of as-produced coatings Zr 702 (a) 3.5 min and (b) 90 min[17]

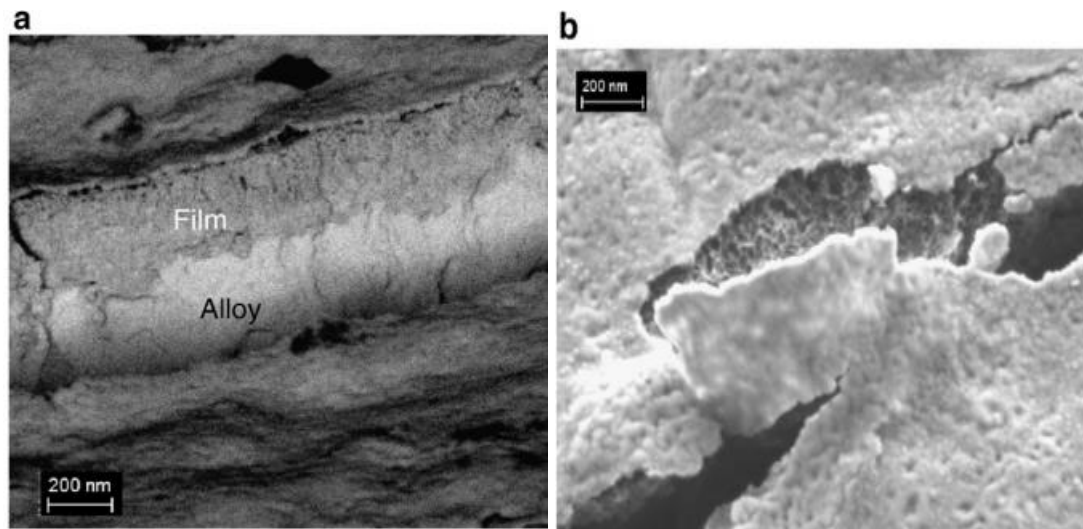


Fig.6 Scanning electron micrographs of the coating formed to 100 V on Zirlo (a) Backscattered electron image of a fractured region of coating. (b) Secondary electron image of the coated surface.[22]

Summary

The osteoclasts must accept the implant because the bone is alive. When inserted near a bone, it must be able to attach to and grow on it to avoid loosening and inflammation. Zr and its alloys are well known for being more biocompatible than other metal implants, with the lowest Young's modulus and the highest biocompatibility. Metal oxide that can be controlled in an electrolyte thanks to MAO. ZrO_2 is affected by electrochemical oxidation conditions such as the electrolyte type, concentration, and pH, as well as the applied potential and time. If the pH value remains constant, can be increased by increasing the applied potential; and pH independent if the applied potential remains constant. If an electrolyte is used instead of an aqueous electrolyte, a higher applied potential is required to achieve the same coating. The length or thickness of the layer increases as MAO progresses, but there is always a point where the thickness remains constant as time progresses. It's worth noting that in an alkaline electrolyte with a pH of over 12, implant material surfaces have a lot of potential for cell adhesion, proliferation, and differentiation. Antibacterial agents can be loaded into the layer to control bacterial infection.

References:

- [1] Navarro M, Michiardi A, Castaño 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., Yalcin, E., Cavusoglu, 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. Muddle, 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., Ntomproukidis, 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] Aktuğ, 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.