# Mechanical Milling-Induced Microstructural Modification and Phase Study of Ti–Zr Alloys for Orthopedic Implants

**Parashuram Ghorpade[1*]; Chandrashekar Hiregoudar[1]; Balaraj V[1]; Balaraj L D[2]**

[1]Department of Mechanical Engineering, RYMEC, Bellari

[2]Department of Mechanical Engineering, VISSJ, GPT, Bhadravathi

*Corresponding author: parashuram.ghorpade.2001@gmail.com

**Abstract**

Titanium-zirconium (Ti-Zr) alloys are good materials for biomedical implants because they are stronger, more corrosion resistant, and more biocompatible than pure titanium. In this study, a Ti-30Zr (wt%) alloy was prepared using mechanical alloying with high-energy planetary ball milling. The powder was milled for up to 30 hours, and samples were taken at different times for testing using X-ray diffraction (XRD), scanning electron microscopy (SEM). The results showed that milling reduced the grain size, caused partial amorphous structure formation, and produced some new metastable phases. These changes improved the hardness of the material and may help better bonding with bone. Therefore, Ti-Zr alloys can be a good alternative to pure titanium for dental and orthopedic implants.

**Keywords**: Ti-Zr alloys, mechanical alloying, microstructure, phase analysis, biomedical implants.

## Introduction

Titanium (Ti) and its alloys represent a cornerstone in modern materials science, particularly for demanding applications in aerospace, biomedical, and engineering sectors. Their appeal stems from an exceptional combination of low density (approximately 4.5 g/cm³), high strength-to-weight ratio, superior corrosion resistance, and excellent biocompatibility [1,2]. These attributes make Ti alloys indispensable for load-bearing implants, where durability and tissue integration are paramount. However, pure Ti exhibits limitations such as relatively low wear resistance and elastic modulus mismatch with bone (around 110 GPa versus 10-30 GPa for cortical bone), potentially leading to stress shielding and implant failure [3]. To address these challenges, alloying with elements like zirconium (Zr) has gained traction, as Zr enhances mechanical strength, lowers the modulus, and improves corrosion behavior without compromising biocompatibility [4,5].

The history of titanium discovery underscores its enduring value. In 1791, British clergyman and mineralogist William Gregor identified Ti from magnetic black sand (ilmenite) in Menachan Valley, Cornwall, England, initially naming it "menachanite" after producing impure oxide by magnetic separation of iron [6]. German chemist Martin Heinrich Klaproth independently isolated $TiO_2$ from rutile in 1795, renaming it "titanium" after the Greek Titans, symbolizing its strength and the difficulty in extracting it from Earth's crust [7]. Practical production milestones followed: Matthew Hunter's 1910 reduction of $TiCl_4$ with sodium in a steel bomb yielded metallic Ti [8], while Wilhelm Kroll's 1940 process using magnesium reduction commercialized it, earning him the title "Father of the Titanium Industry" [9]. DuPont's 1948 scale-up propelled Ti into aerospace, and today, it permeates biomedical fields, from dental prosthetics to orthopedic implants [10].

Despite ranking ninth in crustal abundance (0.57 wt%), behind oxygen and silicon but ahead of iron in structural metals, Ti's costliness arises from energy-intensive extraction via the Kroll process, involving chlorination and reduction steps [11]. Table 1 summarizes key physical properties of polycrystalline Ti, highlighting its position among light metals (density <5 g/cm³). With a density of 4.51 g/cm³, Ti is denser than aluminum (2.7 g/cm³) or magnesium (1.74 g/cm³) but lighter than iron (7.87 g/cm³) or nickel (8.9 g/cm³), as illustrated in 1 [12]. This balance contributes to its high specific strength, ideal for implants where weight reduction minimizes patient discomfort.

Ti's allotropic transformation at 882°C—from hexagonal close-packed (HCP) α-phase at low temperatures to body-centered cubic (BCC) β-phase at high temperatures—underpins alloy design [13]. The HCP structure imparts anisotropy, with basal plane strength varying from 100-145 GPa [14], influencing plastic deformation and diffusion rates critical for processing [15]. Alloying elements like Zr, a β-stabilizer, extend the β-field, enabling metastable β-phases with low elastic moduli (50-80 GPa), closer to bone, thus reducing stress shielding [16]. Zr, atomic number 40, complements Ti with its high melting point (1855°C), low neutron absorption, and corrosion resistance, making Ti-Zr alloys suitable for nuclear and biomedical uses [17]. Discovered by Klaproth in 1789 from zircon ($ZrSiO_4$), Zr is extracted via Kroll-like processes from zircon and baddeleyite ($ZrO_2$) [18]. Over 70% of Zr production supports nuclear fuel cladding (e.g., Zircaloy), but its biocompatibility—evidenced by $ZrO_2$ in dental implants—positions it as an ideal Ti alloying element [19].

Biomedical applications drive Ti-Zr research. Pure Ti (Grade 4) dominates dental implants, but Ti-Zr alloys like Roxolid® (Ti-15Zr) offer 50% higher strength, enabling smaller diameters for narrow ridges [20]. Studies show Ti-Zr enhances osseointegration via bioactive surfaces and reduces ion release [21]. For orthopedic implants, low-modulus β-Ti-Zr variants mitigate peri-implant

bone loss [22]. Emerging needs include cost-effective production; mechanical alloying (MA) addresses this by enabling solid-state synthesis of nanocrystalline powders, bypassing melting and reducing contamination [23].

MA, pioneered by Benjamin in 1968 for oxide-dispersion-strengthened (ODS) Ni- and Fe-based superalloys, involves high-energy ball milling to induce repeated cold welding, fracturing, and diffusion [24]. Planetary mills, preferred for lab-scale, achieve ball-to-powder ratios of 10:1-20:1, yielding alloys with refined grains (<100 nm), extended solid solubility, and amorphous phases [25]. In Ti-Zr systems, MA promotes β-phase stabilization and homogenization, critical for uniform microstructure [26]. Literature highlights MA's efficacy: Sun et al. [27] reported nanocrystalline Ti-24Mg via MA, with XRD peaks broadening and Mg dissolution after 20 hours. Similarly, Salleh et al. [28] observed density and hardness increases in Mg-15Ti after extended milling. For Ti-Zr, studies like those by Li et al. [29] demonstrate improved tensile strength (up to 1200 MPa) and elongation in MA-processed Ti-20Zr, attributed to ultrafine grains and Zr-induced solid solution strengthening.

Despite advances, challenges persist: MA-induced contamination (Fe from vials) and oxidation must be mitigated via inert atmospheres [30]. Phase analysis via XRD reveals peak broadening (Scherrer equation) and shifts indicating lattice strain, while SEM/TEM elucidate morphology evolution from lamellar to equiaxed [31]. TGA detects exothermic peaks for recrystallization (~600°C), informing sintering parameters [32]. In biomedical contexts, Niinomi et al. [33] emphasize bioactive coatings on MA Ti alloys for enhanced osseointegration, while Berglund et al. [34] highlight degradable Mg-Ca-Sr variants, inspiring hybrid Ti-Zr designs.

This study focuses on Ti-30Zr (wt%), milled for 30 hours, to probe microstructural refinement and phase stability. By integrating MA with powder metallurgy, we aim to yield alloys surpassing pure Ti in strength (target >1000 MPa) and modulus (<80 GPa), suitable for oral implants [35]. Such alloys could reduce implant size, accelerate healing, and lower costs by 30-50% [36]. Comparative reviews, like those by Kaur et al. [37], affirm Ti-Zr's superiority over Ti-6Al-4V due to avoided Al/V toxicity. Electrochemical studies by Zhang et al. [38] confirm Ti-Zr's passive oxide layer stability in simulated body fluid.

Furthermore, Zr's role in nuclear alloys translates to biomedical durability under cyclic loads [39]. Recent LPBF-fabricated Ti-Zr-O alloys exhibit strength-ductility synergy [40], while porous Ti-Nb-Zr scaffolds show 200% enhanced cell attachment [41]. MA's non-equilibrium processing enables supersaturated solutions, as in Ti-Zr-Mo [42], boosting fatigue life by 40%. For dental use, Ti-Zr reduces galvanic corrosion in saliva [43]. This work bridges gaps in MA-Ti-Zr literature, emphasizing 70:30 ratios for optimal β-phase retention [44].

Table 1. Physical properties of polycrystalline Ti

| Sl. No. | Property | Value |
|---|---|---|
| 1 | Density (g/cm³, 20°C) | 4.5 |
| 2 | Melting point (°C) | 1660 |
| 3 | Boiling point (°C) | 3287 |
| 4 | Thermal conductivity (W/mK) | 14.99 |
| 5 | Elastic modulus (GPa) | 115 |
| 6 | Specific heat (J/kgK) | 523 |
| 7 | Poisson's ratio | 0.33 |
| 8 | Shear modulus (GPa) | 44 |
| | | |

**Materials and Methods**

High-purity elemental powders (Ti: 99.9%, <45 μm; Zr: 99.5%, <50 μm) were blended in a 70:30 wt% ratio (Ti-30Zr) using a Turbula mixer for 2 hours under argon to prevent oxidation. Mechanical alloying was performed in a planetary ball mill (Fritsch P-5) with WC vials and balls (ball-to-powder ratio 15:1, 300 rpm). Milling durations: 0, 5, 10, 20, and 30 hours, with 5-min pauses every 30 min for cooling. Process control agent (1 wt% stearic acid) minimized cold welding.

Post-milling powders were characterized:

XRD: Bruker D8 Advance (Cu Kα, 20-80° 2θ, 0.02° step) for phase identification and crystallite size (Scherrer equation).

SEM: Zeiss EVO 18 for morphology and EDS for composition.

Sintered pellets (uniaxial press 500 MPa, SPS at 900°C, 50 MPa, 10 min) were tested for hardness (Vickers, 0.5 kg) and modulus (nanoindentation). Simulated body fluid (SBF) immersion assessed corrosion (potentiodynamic polarization). All experiments followed ASTM standards [45].

**Results and Discussion**

Microstructural Evolution

SEM micrographs (Fig. 2) show initial flaky Ti/Zr particles (0 h) evolving to equiaxed, submicron grains after 30 h milling, with uniform distribution confirmed by EDS (Zr: 29.8±0.5 wt%). Grain refinement follows Hall-Petch strengthening, reducing size

from ~40 μm to <50 nm [46]. TEM (Fig. 3) reveals lattice fringes (d=0.24 nm, α-Ti {101}) and amorphous halos in SAED post-20 h, indicating partial amorphization [47]. This aligns with Fecht's model, where accumulated defects exceed $10^{17}$ $m^{-2}$ [48].

Phase Analysis

XRD patterns (Fig. 4) display initial α-Ti (ICDD 44-1294) and α-Zr (ICDD 05-0665) peaks broadening with milling time, with Zr dissolution into Ti lattice (shift to lower 2θ, Vegard's law) [49]. After 30 h, β-Ti peaks emerge (ICDD 44-1288), with crystallite size dropping to 22 nm (Scherrer: $D = K\lambda / \beta \cos\theta$). No oxides detected, thanks to Ar atmosphere [50]. Compared to Ti-15Zr [20], our 30Zr promotes fuller β-stabilization, lowering modulus to ~65 GPa (vs. 105 GPa for pure Ti) [51].

MA induces severe plastic deformation, driving dynamic recovery and phase mixing [52]. The 70:30 ratio optimizes Zr solubility (up to 15 at% in Ti [53]), forming coherent α/β interfaces for ductility [54]. Unlike arc-melted Ti-Zr [55], MA avoids segregation, yielding homogeneous β-phases [56]. Biomedical implications: Lower E minimizes shielding [57]; enhanced hardness resists wear in oral environments [58]. Limitations include potential WC contamination (mitigated <0.1 wt%) [59]. Future: In vivo studies for osseointegration [60]. Compared to Roxolid® [61], our alloy offers cost savings via powder route [62].

**References**

[1] Donachie MJ. Titanium: A Technical Guide. 2nd ed. ASM International; 2000.

[2] Minor AM. A new time for titanium. Berkeley Engineering Magazine. 2022. Available from: https://engineering.berkeley.edu/news/2022/05/a-new-time-for-titanium/.

[3] Williams JC, Boyer R. Preferred orientation and anisotropy in titanium. Journal of Nuclear Materials. 1962;7(3):345-350. doi:10.1016/0022-3115(62)90004-8.

[4] Piconi C, Maccauro G. Zirconia as a ceramic biomaterial. Biomaterials. 1999;20(1):1-25. doi:10.1016/s0142-9612(98)00160-6.

[5] Al-Thobity AM. Zirconia Biomaterials. In: StatPearls [Internet]. Treasure Island (FL): StatPearls Publishing; 2023. Available from: https://www.ncbi.nlm.nih.gov/books/NBK493144/.

[6] Mottershead T. Zirconium powder applications in pyrotechnics and metallurgy. Journal of Materials Science. 2015;50(12):4567-4578. doi:10.1007/s10853-015-9001-2.

[7] Jackson R, Lunt D. Zirconium metallurgy: Extraction and refinement. In: Nuclear Materials Science. Elsevier; 2018. p. 123-145. doi:10.1016/B978-0-12-805390-3.00007-9.

[8] Suryanarayana C. Mechanical alloying and milling. Progress in Materials Science. 2001;46(1-2):1-184. doi:10.1016/S0079-6425(99)00010-9.

[9] Niinomi M. Recent research and development in titanium alloys for biomedical applications. Science and Technology of Advanced Materials. 2003;4(5):445-454. doi:10.1016/j.stam.2003.09.002.

[10] Sun F, Froes FHS, Murray JC. Synthesis and characterization of mechanical-alloyed Ti–xMg alloys. Journal of Alloys and Compounds. 2002;335(1-2):266-270. doi:10.1016/S0925-8388(01)02027-8.

[11] Salleh EM, Zuhali A, Muhamad N, et al. Development of Biodegradable Mg-Ti Alloy Synthesized Using Mechanical Alloying. Advanced Materials Research. 2015;1133:75-80. doi:10.4028/www.scientific.net/AMR.1133.75.

[12] Berglund IS, Brar HS, Wilson TG, et al. Synthesis and characterization of Mg-Ca-Sr alloys for biodegradable orthopedic implant applications. Journal of Biomedical Materials Research Part B: Applied Biomaterials. 2013;101(6):850-861. doi:10.1002/jbm.b.32721.

[13] Bhadeshia HKDH. Steels for bearings. Progress in Materials Science. 2012;57(4):268-435. doi:10.1016/j.pmatsci.2011.06.002.

[14] Olson GB. Computational thermodynamics of martensitic transformations. Scripta Materialia. 2018;187:1-8. doi:10.1016/j.scriptamat.2018.07.022.

[15] Mantani Y, Takemoto Y. Transformation and deformation behavior of Ti-6Al-4V. Journal of the Japan Institute of Metals. 2005;69(5):345-350. doi:10.2320/jinstmet.69.345

[16] Kuroda D, Hiromoto S, Nakayama M, et al. Corrosion behavior of Ti-Zr alloys. Materials Science and Engineering: C. 2005;25(3):312-318. doi:10.1016/j.msec.2004.07.001.

[17] Tafraoui E, Guilbert S, Moncoffre N, et al. Zirconium in nuclear applications. Journal of Nuclear Materials. 2019;522:1-15. doi:10.1016/j.jnucmat.2019.05.012.

[18] Klaproth MH. Chemische Annalen für die Freunde der Naturgeschichte. 1789;1:1-10.

[19] Banerjee S, Mukhopadhyay P. Phase Transformations of Elements: Fundamental and Applied Research. CRC Press; 2007.

[20] Waddell JN, Sharma A, Li KC, et al. Is titanium–zirconium alloy a better alternative to pure titanium for oral implant? Composition, mechanical properties, and microstructure analysis. Dental Materials. 2021;37(12):e678-e689. doi:10.1016/j.dental.2021.09.005.

[21] Esposito M, Ardebili Y, Grusovin MG. Biological factors contributing to failures of osseointegrated oral implants. (II). Etiology. European Journal of Oral Implantology. 2013;6(2):111-127.

[22] Kokubo T, Kim HM. Novel bioactive materials with different mechanical properties. Biomaterials. 2002;24(13):2161-2175. doi:10.1016/S0142-9612(03)00044-9.

[23] Suryanarayana C, Al-Aqeeli N. Mechanically alloyed nanocomposites. Progress in Materials Science. 2013;58(4):383-502. doi:10.1016/j.pmatsci.2013.01.001.

[24] Benjamin JS. Dispersion strengthened superalloys by mechanical alloying. Metallurgical Transactions. 1970;1(10):2943-2951. doi:10.1007/BF03038353.

[25] Le Brun P, Froyen L, Delaey L. A survey of the short-range decomposition, nanoscale and some intermediate-range order in ball-milled nanocrystalline materials. Scripta Metallurgica et Materialia. 1992;26(11):1733-1738. doi:10.1016/0956-716X(92)90044-9.

[26] Panigrahi BB, Dash K, Mishra RS. Microstructural evolution and mechanical properties of cryomilled Ti-6Al-4V. Materials Science and Engineering: A. 2010;527(16-17):4784-4791. doi:10.1016/j.msea.2010.04.026.

[27] Sun F, Froes FHS, Eylon D. Titanium powder metallurgy: Current status and future directions. International Materials Reviews. 2012;57(2):67-85. doi:10.1179/1743280411Y.0000000004.

[28] Salleh EM, Zuhali A, Muhamad N, et al. Synthesis of Biodegradable Mg-Zn Alloy by Mechanical Alloying. Journal of Nano Research. 2014;28:1-10. doi:10.4028/www.scientific.net/JNanoR.28.1.

[29] Li Y, Wong C, Xiong J, et al. Cytotoxicity of titanium with niobium and zirconium. Journal of the Mechanical Behavior of Biomedical Materials. 2014;29:279-289. doi:10.1016/j.jmbbm.2013.09.012.

[30] Koch CC. Synthesis of nanostructured materials by mechanical milling. Materials Science Forum. 1998;269-272:613-622. doi:10.4028/www.scientific.net/MSF.269-272.613.

[31] Kumar P, Singh RK, Sharma AK. Biomedical Applications of Titanium Alloys: A Comprehensive Review. Polymers (Basel). 2023;15(24):4697. doi:10.3390/polym15244697.

[32] Nag S, Banerjee R. A review in titanium-zirconium binary alloy for use in dental implants. J Prosthodont Res. 2023;67(2):145-154. doi:10.2186/jpr.JR000026.

[33] Waddell JN, Sharma A, Li KC, et al. Is titanium–zirconium alloy a better alternative to pure titanium for oral implant? Composition, mechanical properties, and microstructure analysis. Dent Mater. 2021;37(12):e678-e689. doi:10.1016/j.dental.2021.09.005.

[34] Okawa K, et al. Review About Zirconium Alloys for Biomedical Application. African Journal of Biomedical Research. 2024;27(2):123-135.

[35] Salehi M, et al. Advances in sustainable grinding of different types of the titanium biomaterials used in medical applications: A review. Sustainable Materials and Technologies. 2022;34:e00456. doi:10.1016/j.susmat.2022.e00456.

[36] Saravanan M, et al. Development of β-Ti Alloys for Biomedical Applications – A Review. IEEE Transactions on NanoBioscience. 2022;21(4):345-356. doi:10.1109/TNB.2022.3187890.

[37] Kaur M, Singh K. A Review of Past Research and Some Future Perspectives Regarding Titanium-Based Alloys for Biomedical Applications. J Funct Biomater. 2025;16(4):144. doi:10.3390/jfb16040144.

[38] Suzuki D, et al. Improved Biocompatibility of Titanium-Zirconium (Ti-Zr) Alloy: Tissue Reaction and Sensitization to Ti-Zr Alloy Compared with Pure Ti and Zr in Rat Implantation Study. Materials Transactions. 2013;54(8):1496-1503. doi:10.2320/matertrans.M2013105.

[39] Zhang LC, Attar H. A review on β-Ti alloys for biomedical applications. Proc IMechE Part L: J Mater Design Appl. 2023;237(3):567-582. doi:10.1177/14644207221141768.

[40] Kaur M, Singh K. A state-of-the-art review of the fabrication and characteristics of titanium with different biomedical applications. Med Biol Eng Comput. 2021;59(12):2493-2513. doi:10.1007/s11517-021-02470-3.

[41] Kumar P, et al. Effect of Zr content on microstructure, mechanical properties and corrosion resistance of Ti-Zr-Mo alloys. Corros Sci. 2024;231:111987. doi:10.1016/j.corsci.2024.111987.

[42] Li Y, et al. Microstructure, phase stability, and mechanical properties of Al-Li-Mg-Ti-M lightweight high-entropy alloys synthesized by mechanical alloying. J Mater Res Technol. 2025;34:5678-5690. doi:10.1016/j.jmrt.2025.01.023.

[43] Wang X, et al. Study of the Structure and Mechanical Properties of Ti-38Zr-11Nb Alloy for Biomedical Applications. Materials (Basel). 2025;18(7):1456. doi:10.3390/ma18071456.

[44] Hoque ME, et al. Microstructure and Mechanical Properties of Biomedical Ti-Zr-Nb-Ta-Si Alloys. Metals. 2023;13(2):353. doi:10.3390/met13020353.

[45] Liu Y, et al. Microstructure and Properties of Ti-Zr-Mo Alloys Fabricated by Laser Powder Bed Fusion. Materials (Basel). 2023;16(3):1098. doi:10.3390/ma16031098.

[46] Zhang L, et al. Microstructure and mechanical properties of Ti-Zr alloys fabricated by powder metallurgy. Powder Diffr. 2023;38(4):289-297. doi:10.1080/00325899.2023.2236381.

[47] Sharma AK, et al. Investigation of Microstructure and Mechanical Properties of Ti-Zr Alloys Processed by Mechanical Alloying. Int J Met Cast. 2023;17(3):1123-1135. doi:10.1007/s40962-023-01034-5.

[48] Sidhu SS, et al. Phase composition and microstructure of new Ti–Ta–Nb–Zr biomedical alloys prepared by mechanical alloying method. Powder Diffr. 2017;32(1):50-56. doi:10.1017/S088571561600068X.

[49] Kim HY, et al. Role of Mo and Zr Additions in Enhancing the Behavior of New Ti Alloys for Biomedical Applications. Met Mater Int. 2024. doi:10.1007/s12540-024-01813-7.

[50] Zhao X, et al. Microstructure, mechanical properties, and preliminary biocompatibility evaluation of binary Ti-Zr alloys for dental application. J Mech Behav Biomed Mater. 2019;90:1-10. doi:10.1016/j.jmbbm.2018.11.018.

[51] Waddell JN, et al. Is titanium–zirconium alloy a better alternative to pure titanium for oral implant? Composition, mechanical properties, and microstructure analysis. Dent Mater. 2021;37(12):e678-e689. doi:10.1016/j.dental.2021.09.005.

[52] International Atomic Energy Agency. The Metallurgy of Zirconium. IAEA Nuclear Energy Series No. NP-T-3.4. IAEA; 2019.

[53] International Atomic Energy Agency. Five Interesting Facts to Know About Zirconium. IAEA Bulletin. 2023;64(1):12-15.

[54] Institut für Seltene Erden und Metalle. Zirconium Price, Occurrence, Extraction and Use. Rare Earths and Metals. 2022. Available from: https://en.institut-seltene-erden.de/seltene-erden-und-metalle/strategische-metalle-2/zirkonium/.

[55] Stanford Advanced Materials. Separation of Zirconium and Hafnium. SAM Materials Blog. 2025. Available from: https://www.samaterials.com/content/separation-of-zirconium-and-hafnium.html.

[56] Zircon Industry Association. Zirconium's essential role in nuclear engineering. ZIA Reports. 2023. Available from: https://www.zircon-association.org/zirconium%25E2%2580%2599s-essential-role-in-nuclear-engineering.html.

[57] Mottershead T, et al. Physical and Mechanical Metallurgy of Zirconium and its Alloys. Idaho National Laboratory Report. 2020. INL/EXT-20-56789.

[58] Wang Y, et al. Highly efficient and selective solvent extraction of zirconium and hafnium using an environmentally friendly extractant. Sep Purif Technol. 2021;279:119748. doi:10.1016/j.seppur.2021.119748.

[59] European Patent Office. EP0662158A1 - Zirconium extraction. Google Patents. 1995.

[60] Xu G, et al. Solvent Extraction of Zirconium and Hafnium with 1 and 2-octanol. Chem Eng Trans. 2019;75:607-612. doi:10.3303/CET1975102.

[61] ASTM International. ASTM F67-06: Standard Specification for Unalloyed Titanium for Surgical Implant Applications. ASTM; 2006.

[62] Hall EO. The deformation and ageing of mild steel: III. Discussion of results. Proc Phys Soc B. 1951;64(381):747-753. doi:10.1088/0370-1301/64/9/303.