



Zirconia in Dental and Other Biomedical Applications: An Overview

Firas H. Alwade^{1*}, Intisar J. Ismail² and Farah J. Ibrahim³

¹ Department of Basic Science, College of Dentistry, Mustansiriyah University, Baghdad, Iraq

² Department of Dentistry, Al-Israa University, Baghdad, Iraq

³ Ministry of Higher Education and Scientific Research, Baghdad, Iraq

*Corresponding e-mail: firasalwadephysics@uomustansiriyah.edu.iq

ABSTRACT

An extensive range of biocompatible materials has been used in patients. Diverse biomedical applications demand different properties of materials, implicating mechanical, physical, chemical, and biochemical properties. Amongst biocompatible ceramics, zirconia-based biomaterials are considered as a biomaterial for retexture of hard tissues related to their excellent mechanical properties and good biological and chemical compatibilities. Zirconia is used in dentistry and in orthopedics, specifically in the area of femoral heads for total hip replacements.

Keywords: Zirconia, Yttrium oxide, Staining, Tetragonal, Toughening phenomenon, Biocompatibility

INTRODUCTION

Zirconia, officially known as zirconium dioxide (ZrO_2), is a white crystalline oxide of zirconium [1]. Zircon has been known as a jewel since past times. In 1987, a German chemist isolated the oxide of zirconium from zircon (which is zirconium silicate, $ZrSiO_4$) [2].

Zirconia microstructure consists of about 2.5% to 3.5% Yttrium oxide (Y_2O_3) and is formed mostly by particles of micrometric ZrO_2 after sintering form a metastable tetragonal structure at room temperature [3,4]. The standard density of zirconia is 6 g/cm^3 , while its theoretical density is 6.51 g/cm^3 . The surface strength of the material increases when the particle area is small to approximate the theoretical and practical value of the density [5].

Zirconia Processing

The first and essential step in the fabrication process of zirconia is a blank fabrication. Next factors may effect in the final zirconia property:

Chemical powder purity: It has been noticed that the more impurities inserted to zirconia powder will lead to increase in grain size and increments more yttria transfer, exhausting the tetragonal grains performance more cubic phase formulation, which results in more transformation susceptible and less stable zirconia.

Grain qualities and pressing type: In zirconia powder, the ideal crystallite size is around 30 nm to 40 nm, from which coalesce of 20 μm to 80 μm are produced. While the handling is uniaxial compression and owing to the intense reduction in compaction compared to the isostatic compression, where at the grain boundaries the coarse agglomerates leave microspores, which can make the zirconia more susceptible to low-temperature degradation (LTD) by water diffusion [6]. At this stage, the pre-sintered zirconia blanks can influence the machinability of the zirconia, the form that chippings can take, and the final sharpness of zirconia [7].

Sintering Process

Temperature and sintering times have a lineal impact on zirconia's grain size, yttrium distribution and amount of cubic phase that in turn has an effect on zirconia's mechanical and optical properties. It has been well-scripted that by increasing the temperature of sintering the grain size will increase. Fewer boundaries in larger grains that can increase the translucency of the zirconia but made them more susceptible to transformation, thus it may improve the optical properties but affect its stability [8]. At least, sintering consists of two heat-activated processes, densification and grain

growth. The most common method for sintering zirconia would be the use of conventional furnaces at temperatures between 1350°C to 1600°C and holding times ranging from 2-4 hrs. For sintering zirconia, multiple alternative methods have been introduced such as spark plasma sintering, microwave sintering and use of vacuum furnaces, all purposing to progress the esthetic and mechanical of zirconia, and to some scope save on sintering time and energy. In a vacuum furnace, the lack of air or other gases prohibit heat transfer with the product through convection and ejects a source of contamination. As yet, some manufacturers demand that use of vacuum furnaces can increase mechanical properties and enhance the translucency of the zirconia. As many characteristics of zirconia are thus far to be clinically definite, information concerning the effects of LTD on the clinical performance of dental zirconia has never been reported in the clinical experiments. Many factors can activate LTD as high sintering temperatures, low-grade powders and hydrous environments [9].

Zirconia Staining (coloring)

Zirconia, and its inveterate opacity and whether it will ever mimic the translucency and color of the natural dentition, is possibly one of the biggest challenges facing the clinical admittance of monolithic zirconia. An estimation from a ceramic-engineering, the coloring oxides would be best to add to the powders before it is pressed. Powder color-doping is another possibility. The great number of shades required makes these techniques rather expensive and challenging. The nomination of metal salts at low concentration has been used to color zirconia [10]. In this technique, some setbacks have been reported likes non-uniform colors and limited diffusion depth [11]. In a survey determining the effect of coloring zirconia framework in its pre-sintered stage with different colors on its surface microhardness mechanical properties the authors concluded that there was an immaterial reduction in the microhardness and strength of zirconia after coloring, and the staining of zirconia produced some dimensional changes which can influence on the suitable accuracy of the final restoration [12].

MATERIAL AND METHODS

Material Properties

Transmutation toughening phenomenon: Zirconia, a polymorph, at room temperature exists in its monoclinic (m) form (pure zirconia). When the temperature rises to 1170°C it transforms into its tetragonal (t) form and then to its cubic (c) form at temperatures reaching around 2370°C, with a melting point at temperatures more than 2716°C [13]. The transformation of pure zirconia upon cooling (t-m) is accompanied by an approximately 3% volume expansion which can produce cracks in the bulk of the material and eventually catastrophic failure [14]. The ceramic engineering community has been researching the possibilities of adding different oxides as MgO, La₂O₃, and Y₂O₃ to stabilize t and c phases of zirconia at room temperatures. Partial stabilization by 2-5 Mol% of Yttrium oxide, formally known as Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP), is commonly used in the dental field and will be referred to as (partially stabilized zirconia, PSZ) in this concatenation of studies. On the other hand, full stabilization by <8 Mol% Yttrium oxide is known as fully stabilized zirconia (FSZ) [15]. Figure 1 illustrated 3 crystal structures to zirconium [16].

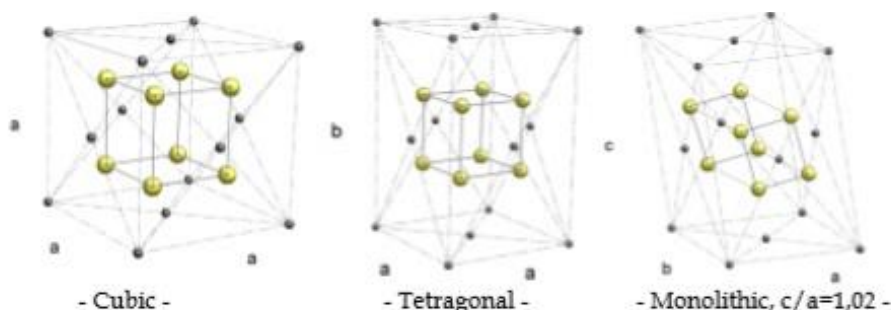


Figure 1 Cubic, tetragonal and monolithic zirconia [16]

Generally, fractures and cracks are observed through changeable phases because of the 8% volume variance when the transition to tetragonal structure from the monolithic structure. To prevent this and make zirconia stable in the cubic structure at room temperature, alkaline earth elements such as CaO (calcium oxide), MgO (magnesia), Y₂O₃ (Yttria) and oxides of rare elements are inserted to zirconia. Zirconia-based ceramic materials stabilized with yttria have preferable properties comparing with zirconia-based ceramic materials which are stabilized by magnesia and calcium

oxide [17,18]. Mechanical properties of cubic structure zirconia are weak. The transition from tetragonal zirconia to monolithic zirconia take place at lower temperatures between 850-1000°C and this transition has some properties similar to martensitic transition properties which are noted in tempered steels. In practice, partially stabilized cubic zirconia (PSZ) which consists of monolithic and tetragonal phases as sediments, is surpassed owing to its improved mechanical properties and importance of martensitic transition [16].

The metastable tetragonal phase that results from the addition of yttria oxides to zirconia is the most desired and toughest form. As a crack propagates towards the core of the material, tensile stresses develop around the tip of the crack, transforming the tetragonal particles to monoclinic. Monoclinic particles are larger in size, and that is accompanied by compressive stress that opposes the crack tip and prevents its propagation, thus increases its localized fracture toughness as in Figure 2. The transformation toughening phenomena increases the zirconia’s flexural and tensile fracture resistance. However, excessive grinding, temperature changes, and stresses may exceed the compressive strengths around the crack tip, and the crack will propagate towards the core of the material leading to complete failure of the zirconia. Therefore, the transformation toughening phenomena may be beneficial to the strength of zirconia at first, but as the fatiguing forces and stresses in moist environments increase, the challenges of zirconia strength become questionable. Yet the definitive answer awaits quantitative clinical assessment [19].

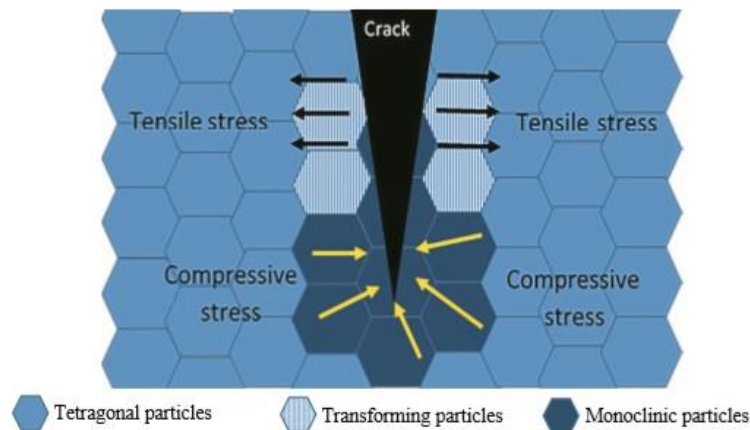


Figure 2 Schematic illustration of the transformation toughening phenomenon

Unfortunately, because of the metastability of the tetragonal phase, TZP ceramics are prone to aging [20].

Physical Properties

Owing to the transmutation toughening phenomenon, zirconia ceramics are rated the toughest and strongest among other the present dental ceramics. Table 1 compares some properties of the generality ceramic materials used in fixed prosthodontics. The flexural strength of zirconia can range from 800-1500 MPa in its partially stabilized form, as the fully stabilized form has been adduced to have lower flexural strengths of around 600 MPa. The fracture toughness of zirconia has also been adduced to be high ranging from 6.3-11.5 MPa m^{1/2} [21,22]. As for other properties like chemical solubility, zirconia has been adduced to be very stable [1], which is counted important to withstand the different environmental changes in the oral cavity. Zirconia is also counted to have low thermal conductivity and protecting the pulp from temperature changes in the mouth.

Table 1 Properties of zirconia in comparison to other ceramic materials used in fixed prosthetic dentistry

Material	Flexural Strength (MPa)	Elastic modulus (GPa)	Hardness (VHN)	References
Feld spathic porcelain (Vita VMK 68)	83	57	703	[21]
Letucite reinforced glass ceramics (Empress2)	283	96	550	[23]
Alumina (Al ₂ O ₃)	500	380	2200	[1]
Zirconia (Y-TZP)	800-1500	210	1200	[1]

Zirconia Thermal Degradation

The irritation of the physical aforesaid properties of zirconia comes with a possible threat to the duration of this

material [24]. This unfavorable phenomenon was low-temperature degradation (LTD) [25]. The effects of this aging process have defined the degradation of the zirconia surface with the grain pullout and then microcracking of the structure. This phenomenon represents strength degradation as illustrative in Figures 3 and 4 [26].

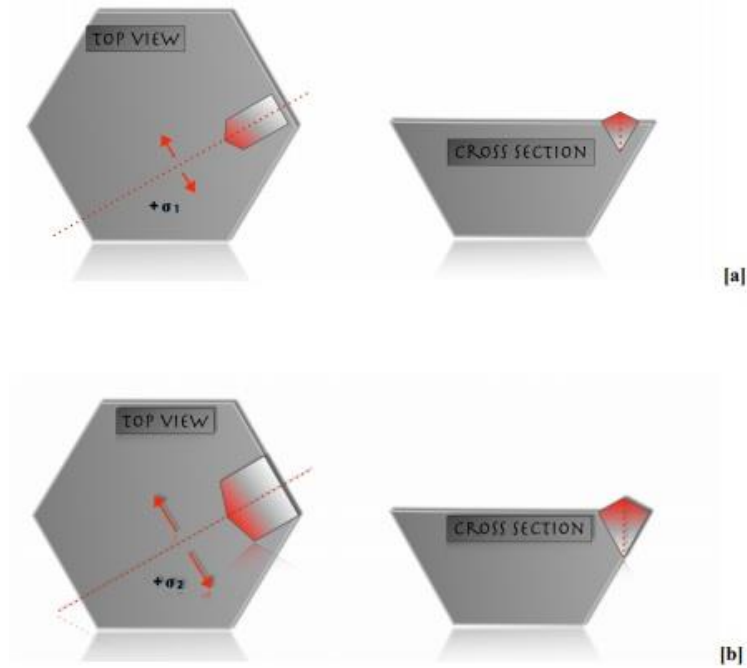


Figure 3 The t-m transformation starts (a) from the surface of the sample and (b) then proceed inside

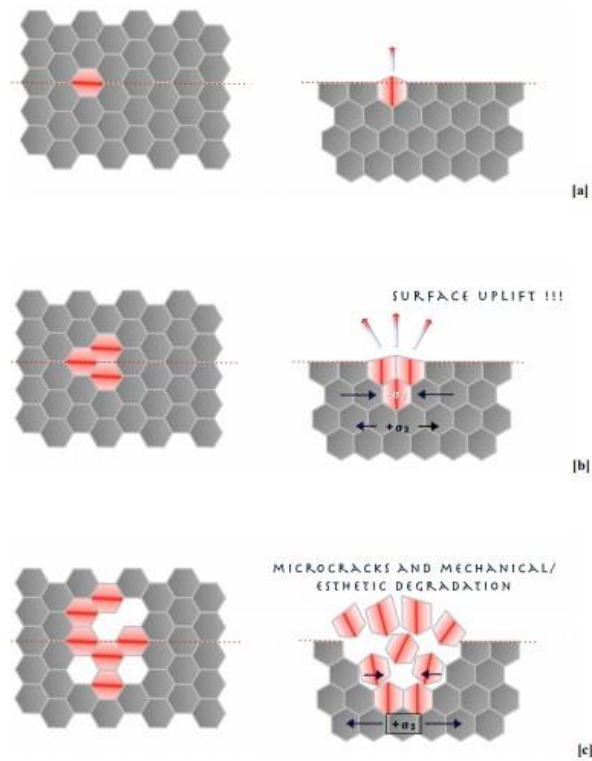


Figure 4 The phase transformation determines (a) the increase of the grain volume with the subsequent uplift of the surface, (b) the presence of the water rapidly causes micro cracks and (c) esthetic degradation of the zirconia surface [26,27]

There are hypotheses of low-temperature degradation. The first estimate that there is the diffusion of water species (here OH-) into the lattice via oxygen vacancies and second resulting in a change of lattice parameters [28], it is illustrative in Figure 5.

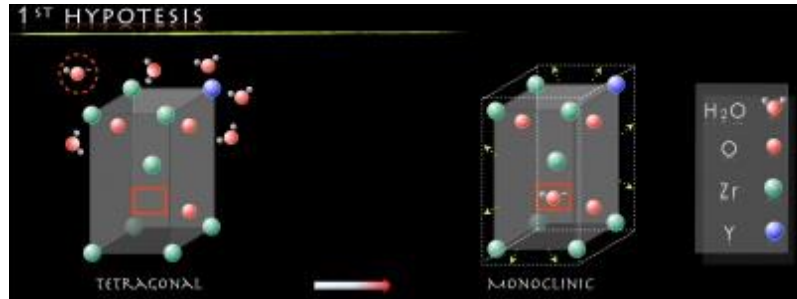


Figure 5 Diffusion of the OH- into the regular lattice arrangement of the particles (molecule of the water in the dashed circle that migrate in the red rectangle) [26]

Second hypothesis demand that H_2O reacts with Y_2O_3 to compose clusters rich in $Y(OH)_3$ [29] illustrative in Figure 6.

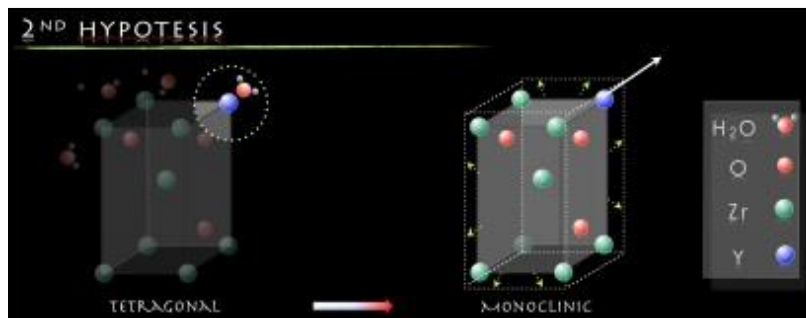


Figure 6 Y_2O_3 and H_2O reacts together [26]

The last hypothesis enhances that the water vapor attacks the Zr-O bond, breaking it and leading to a stress accumulation due to the movement of -OH. This, in turn, generates lattice defects acting as nucleating agents for the subsequent T-M transformation [30] illustrative in Figure 7.

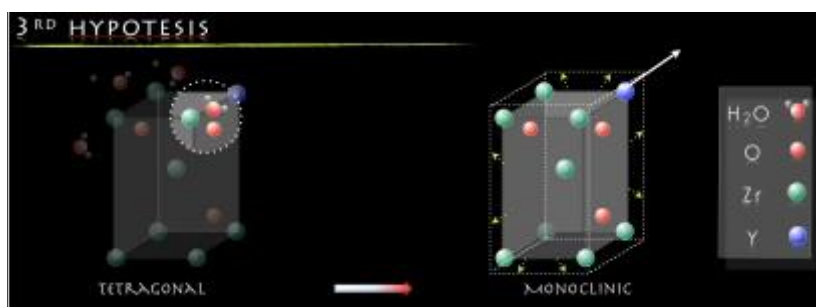


Figure 7 Rupture of the Zr-O bond due to the water vapor

The transformation mainly passes between temperatures of 200-300°C and is time dependent.

- The transformation is enhanced by water or water vapor
- The transformation starts from the surface and proceeds towards the core of the material
- The resistance to LTD is enhanced by smaller grain size and more stabilizing (Ytria) content [25]

Biocompatibility of Zirconia

Any materials before placed in the human body must be tested for their biocompatibility [31]. Biocompatibility indicates to the ability of a biomaterial to proceed its coveted function with respect to a medical therapy, without

reducing any inflammatory, allergic, immune, toxic, mutagen, or carcinogenic effects in the recipient or beneficiary of that therapy, but generating the most appropriate beneficial cellular or tissue response in that specific situation, and optimizing the clinically relevant performance of that therapy [32].

Zirconia was induced in orthopedics to overcome the trouble of alumina brittleness, alumina being the generality used oxide bioceramic. The fabulous, mechanical properties of zirconia are principally due to the tetragonal to monoclinic phase transformation. This transformation, which can be induced by external stresses, results in a 4% increase of volume. That causes localized compressive stresses to develop about the crack tip and for a crack to propagate this clamping constraint must be overcome. This property explains the increased fracture toughness of zirconia compared with other ceramics [33]. This phase transformation from tetragonal to monoclinic can only occur above a critical grain size; this critical grain size was reported to be 18 nm [34].

Zirconia Biomedical Applications

Zirconia biomaterials have been submitted as artificial bone fillers for repairing bone defects [35]. Zirconia also finds other clinical applications such as arthroplasty. Though zirconia and Yttria stabilized zirconia have orthopedic applications such as hip and knee prostheses, hip joint heads temporary supports, tibial plates, and dental crowns [36].

Only 3 types of zirconia systems are used in dentistry although currently there are many systems of zirconia available on the market. The first is Yttrium cation-doped tetragonal zirconia polycrystals (3Y-TZP), the second is magnesium cation-doped partially stabilized zirconia (Mg-PSZ) and finally the zirconia-toughened alumina (ZTA) [37].

Zirconia toughened ceramics (ZTC) symbolized a wide class of materials and microstructures [38]. In addition to TZP and PSZ, another ceramic appears promising in biomedical application, Zirconia toughened alumina (ZTA) in dies or prosthetic components.

ZTA structures can be formed by a fine and uniform dispersion of T-phase zirconia in the alumina matrix [39]. The energy of the advancing crack encourages a phase transformation of the dispersed zirconia grains that due to the volume expansion in the T-M transition stresses the brittle alumina matrix, creating a microcrack network around the transformed particle. The fracture energy is dissipated in the phase transformation and in the increase of the crack surface into many microcracks, enhancing toughness. ZTA structures can also be obtained by introducing metastable zirconia polycrystals agglomerates in the alumina matrix [40]. Toughening is due to the cracks that will preferentially cross in their progress the zirconia particles with their Young's modulus lower than the one of the matrix. Stress-induced phase transformation of the agglomerates will stop the advancing crack [41].

CONCLUSION

Briefly, zirconia has been proved to be biocompatible *in vitro* and *in vivo*; it has very interesting microstructural properties, and it is Osseo conductive, only TZP has found wide use as a biomaterial. Around 300000 TZP ball heads were implanted in Total hip replacement (THR). Penetrations can be expected in the future in (THR) joints and in Total knee replacement (TKR) femoral components. Perfections in the predecessor to increase material stability in processing to lowering flaws due to forming techniques and tooling of components to obtain near-to-net shape parts are fostering the expectations of future developments in biomedical applications of zirconia ceramics. The use of zirconia as a ceramic biomaterial can be summarized to:

- No domestic or systemic counter reactions correlatable to the material were detected, neither were cytotoxic effects directly correlatable to the turnout of zirconia ceramics or precursors noticed in spite of the diversity of the materials tested and test methods
- Mechanical characteristics of TZP authorize the manufacture of 022.22 mm ball heads convenient for clinical applications. TZP properties authorize a high safety factor in terms of low sensitivity to the stress risers in the cavity, allowing more flexibility in modular design
- Mechanical properties are dependent on the process and precursors selected for the manufacture of components
- The manufacture of TZP ceramic biomaterials request the use of high chemical and radiochemical purity precursors, as high purity materials can only react with the levels of hydrothermal stability requested to TZP in the specific application

REFERENCES

- [1] Piconi C., Maccauro G, "Review Zirconia as a ceramic biomaterial", *Biomaterials*, Vol. 20, 1999, pp. 1-25.
- [2] Živko-Babić, Jasenka, Andreja Carek, and Marko Jakovac. "Zirconium oxide ceramics in prosthodontics", *Acta Stomatologica Croatica*, Vol. 39, No. 1, 2005, pp. 25-28.
- [3] Denry, Isabelle, and J. Robert Kelly. "State of the art of zirconia for dental applications." *Dental Material*, Vol. 24, No. 3, 2008, pp. 299-307.
- [4] Vagkopoulou T, Koutayas SO, Koidis P and Strub, JR, "Zirconia in Dentistry: Part 1. Discovering the nature of an upcoming bioceramic." *The European Journal of Esthetic Dentistry*, Vol. 4, No. 2, 2009, pp. 130-51.
- [5] Duran, P., and C. Moure. "Sintering at near theoretical density and properties of PZT ceramics chemically prepared." *Journal of Materials Science*, Vol. 20, No. 3, 1984, pp. 827-33.
- [6] Sulaiman, T. "Monolithic zirconium dioxide as a full contour restorative material." *With special emphasis on the optical and mechanical properties. Turun yliopisto. Turku: Turun Yliopiston julkaisuja, Painosalama Oy*, 2015.
- [7] Filser, Frank, P. Kocher, and L. J. Gauckler. "Net-shaping of ceramic components by direct ceramic machining." *Assembly Automation*, Vol. 23, 2003, pp. 382-90.
- [8] Denry, I., and J. R. Kelly. "Emerging ceramic-based materials for dentistry." *Journal of Dental Research*, Vol. 93, No. 12, 2014, pp. 1235-42.
- [9] Keuper, M., et al. "Direct evidence for continuous linear kinetics in the low-temperature degradation of Y-TZP." *Acta Biomaterialia*, Vol. 9, 2013, pp. 4826-35.
- [10] Suttor, Daniel, et al. "Coloring ceramics by way of ionic or complex-containing solutions." U.S. Patent, 2004, p. 709.
- [11] Oh, Gye-Jeong, et al. "Effect of metal chloride solutions on coloration and biaxial flexural strength of yttria-stabilized zirconia." *Metals and Materials International*, Vol. 18, 2012, pp. 805-12.
- [12] Hjerpe, Jenni, et al. "Effect of shading the zirconia framework on biaxial strength and surface microhardness." *Acta Odontologica Scandinavica*, Vol. 66, No. 5, 2008, pp. 262-67.
- [13] Subbarao, E. C. "Zirconia- An Overview." 'Science and Technology of Zirconia'. Proc. 1 st. Int. Conf. held at Cleveland, Ohio, June 16-18, 1980. *Advances in Ceramics*, 1981, pp. 1-24.
- [14] Garvie RC, Hannink RH, and Pascoe RT., "Ceramic steel? Nature", Vol. 258, 1975, pp. 703-04.
- [15] Goff, J. P., et al. "Defect structure of Yttria-stabilized zirconia and its influence on the ionic conductivity at elevated temperatures." *Physical Review B*, 59, Vol. 59, No. 22, 1999, p. 14202.
- [16] Shi, Feng. *Ceramic Coatings-Applications in Engineering*. InTech, 2012, p. 198.
- [17] Yaşar, H. *Effects of Thermal Barrier Coating to Performance of a Turbocharged Diesel Engine*. Diss. Ph.D. Thesis, Istanbul Technical University, Turkey (in Turkish), 1997.
- [18] Geçkinli, A. "Advanced Technology Materials." *Teknik Üniversite Matbaası Publishing House, Istanbul, Turkey*, 1992.
- [19] Lawson, Simon. "Environmental degradation of zirconia ceramics." *Journal of the European ceramic society*, Vol. 15, 1995, pp. 485-502.
- [20] Chevalier, Jérôme, Laurent Gremillard, and Sylvain Deville. "Low-temperature degradation of zirconia and implications for biomedical implants." *Annual Review of Material Research*, Vol. 37, 2007, pp. 1-32.
- [21] Tinschert, J., et al. "Structural reliability of alumina-, feldspar-, leucite-, mica- and zirconia-based ceramics." *Journal of Dentistry*, Vol. 28, No. 7, 2000, pp. 529-35.
- [22] Aboushelib, Moustafa N., Cornelis J. Kleverlaan, and Albert J. Feilzer. "Evaluation of a high fracture toughness composite ceramic for dental applications." *Journal of Prosthodontics: Implant, Esthetic and Reconstructive Dentistry*, Vol. 17, No. 7, 2008, pp. 538-44.
- [23] Aboushelib, Moustafa N., et al. "Effect of loading method on the fracture mechanics of two-layered all-ceramic restorative systems." *Dental Materials*, Vol. 23, No. 8, 2007, pp. 952-59.

- [24] Kobayashi, K., H. Kuwajima, and T. Masaki. "Phase change and mechanical properties of ZrO_2 - Y_2O_3 solid electrolyte after aging." *Solid State Ionics*, Vol. 3, 1981, pp. 489-95.
- [25] Chevalier, Jérôme, Bernard Cales, and Jean Michel Drouin. "Low-temperature aging of $Y-TZP$ ceramics." *Journal of the American Ceramic Society*, Vol. 82, 1999, pp. 2150-54.
- [26] Monaco, Carlo. *Zirconia in dentistry*. Diss. alma, 2013, pp. 14- 17.
- [27] Chevalier, Jerome. "What future for zirconia as a biomaterial?" *Biomaterials*, Vol. 27, 2006, pp. 535-43.
- [28] Kollar, Andrea, et al. "Zirconia for teeth and implants: a case series." *International Journal of Periodontics and Restorative Dentistry*, Vol. 28, 2008, pp. 479-87.
- [29] Çehreli, Murat Cavit, Ali Murat Kökat, and Kivanç Akça. "CAD/CAM Zirconia vs. slip-cast glass-infiltrated Alumina/Zirconia all-ceramic crowns: 2-year results of a randomized controlled clinical trial." *Journal of Applied Oral Science*, Vol. 17, No. 1, 2009, pp. 49-55.
- [30] Örtorp, Anders, Maria Lind Kihl, and Gunnar E. Carlsson. "A 3-year retrospective and clinical follow-up study of zirconia single crowns performed in private practice." *Journal of Dentistry*, Vol. 37, No. 9, 2009, pp. 731-36.
- [31] Williams, David F. "On the mechanisms of biocompatibility." *Biomaterials*, Vol. 29. No. 20, 2008, pp. 2941-53.
- [32] Williams, David. "Revisiting the definition of biocompatibility." *Medical Device Technology*, Vol. 14, No. 8, 2003, pp. 10-13.
- [33] Vythilingum, Vijay. *Zirconia nanocomposites for biomedical applications*. Diss. 2013.
- [34] Chraska Tomas, Alexander H King and Christopher C Berndt, "On the size-dependent phase transformation in nanoparticulate zirconia." *Materials Science and Engineering A*, Vol. 286, No. 1, 2000, pp. 169-78.
- [35] Afzal, Adeel. "Implantable zirconia bioceramics for bone repair and replacement: A chronological review." *Materials Express*, Vol. 4, No. 1, 2014, pp. 1-12.
- [36] Thakare, Vaishali. "Progress in synthesis and applications of Zirconia." *International Journal of Engineering Research and Development*, Vol. 5, No. 1, 2012, pp. 25-28.
- [37] Salomoni, A, et al. "Forming and sintering of multiphase bioceramics." *Journal of Materials Science: Materials in Medicine*, 1994, Vol. 5, No. 9-10, pp. 651-53.
- [38] Claussen, Nils. "Microstructural design of zirconia-toughened ceramics (ZTC)." *Science and Technology of Zirconia II*, 1983.
- [39] Szutkowska, M, "Fracture toughness of advanced alumina ceramics and alumina matrix composites used for cutting tool edges." *Journal of Achievements in Materials and Manufacturing Engineering*, Vol. 54, No. 2, 2012, pp. 201-10.
- [40] Stevens, R, "Transformation toughening by dispersed polycrystalline zirconia." *British Ceramics Transactions*, Vol. 83, 1984, pp. 23-31.
- [41] Nordlund, A., L. Zetterqvist, and A. Oden. "A comparative experimental investigation in monkeys between three different implant materials." *International Journal of Oral and Maxillofacial Surgery*, Vol. 18, 1989, pp. 373-77.