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Progress in Synthesis and Applications of Zirconia

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Abstract:- Zirconia is one of the important ceramic which is used as a biomaterial that has a bright future because of its high mechanical strength and fracture toughness and has unique a characteristic called transformation toughening, which can give it higher strength and toughness compared with other ceramics. This paper reviews the synthesis methods and applications of Zirconia. It exhibits three well-established polymorphs, the monoclinic, tetragonal and cubic phases. Zirconia as biomaterial is useful for various applications and different methods are used for the synthesis of Zirconia. Zirconia based-ceramics has been increasingly used as implant biomaterials, which has some limitations. In this review an attempt has been made to elicit some of the applications as implants.

Keywords:- Biomaterials, Zirconia, Applications, Synthesis.

I. INTRODUCTION

Zirconia is one of the important ceramic which is used as a biomaterial that has a bright future because of its high mechanical strength and fracture toughness and has unique a characteristic called transformation toughening, which can give it higher strength and toughness compared with other ceramics. Zirconia is one of the ceramics which has unique properties such as electrical, mechanical, optical and thermal, which makes it a good choice for application such as: structural materials, thermal barrier coating, Solid oxide fuel cell electrolytes, and semiconductor materials. Its stable photochemical properties make it directly applicable to photonics. As reported in literature, Zirconia can be catalyst in various reactions such as isomerization of alkanes, dehydration of alchohols, decompotions of nitrous oxide [1]. Zirconia implants are becoming increasingly important in the field of dental medicine because of their good mechanical properties, biocompatibility, and for aesthetic reasons. However, zirconia is bioinert and this can lead to a poor fixation of the ceramic implant in the bone [2].The addition of "stabilising" oxides, like CaO, MgO, CeO_2, Y_2O_3 to pure Zirconia allows to generate multiphase materials known as Partially Stabilized Zirconia (PSZ). However, in later years, research efforts converged more upon the development of zirconia-yittria ceramics combinations commonly known as Tetragonal Zirconia Polycrystals (TZP). Excellent material physical properties, biocompatibility, and superior aesthetics make Y-TZP a popular material among the contemporary all-ceramic material [3]. Zirconia (ZrO_2) and Yttria stabilized Zirconia(Y-ZrO_2) have wider applications such as hip and knee prostheses, hip joint heads, temporary supports, tibial plates, and dental crowns. Zirconia exhibits three well-established polymorphs, the monoclinic, tetragonal and cubic phases. The structures of the tetragonal and the cubic phases of zirconia can however be stabilized at room temperature by the incorporation of many different metal cations. Zirconia ceramics have several advantages over other ceramic materials due to the transformation toughening mechanisms operating in their microstructure that can be manifested in components made out of them. Zirconia is in clinical use in total hip replacement (THR) but developments are in progress for application in other medical devices. Today's main application of zirconia ceramics is in THR ball heads. The biocompatibility of polarized partially stabilized zirconia(PSZ) ceramics were examined using osteoblastic cell cultivation [4]. Ultrafine zirconia (ZrO_2) particles have wide applications in the production of advanced ceramics, dense films, ultrafiltration membranes, catalysts, adsorbents, chromatography packing materials, pigments, cosmetics, *etc*. The potential use of nanosized zirconia in the fabrication of dense ceramics is based on its unique set of properties, such as high refractivity, corrosion resistance, mechanical strength, fracture toughness, and ion conduction. These properties are based on the high quality of nanoscaled zirconia powders with respect to chemical purity, crystallinity, homogeneity, controlled state of agglomeration and particle size distribution, as well as low production costs. Several methods have been reported for the production of ultrafine zirconia particles: sol–gel processing *via* hydrolysis and condensation of zirconium alkoxides, forced hydrolysis of zirconium inorganic salt solutions, forced hydrolysis *via* microwave heating, precipitation from solutions of inorganic salts or alkoxide complexes, hydrothermal and plasma decomposition methods, microemulsion and electrodispersion techniques combined with precipitation reactions, combustion synthesis and electric explosion and oxidation of zirconium metal wires [5].

II. APPLICATIONS OF ZIRCONIA

Ceramics are increasingly used for biomedical applications in recent years [6]. Zirconia is used as a biomaterial. It has advantages over other ceramics because of its high mechanical strength and fracture toughness. Biomaterials have been proposed as artificial bone fillers for repairing bone defects. Zirconia also finds other clinical applications such as: arthroplasty [7]. dental crowns [8].Though zirconia and Yttria stabilized Zirconia have orthopedic applications such as hip and knee prostheses, hip joint heads, temporary supports, tibial plates, dental crowns, not much literature reports are available on the studies of this oxide ceramics as drug carriers. etc. Zirconia toughened alumina ceramic foams can be used in potential bone graft applications [9]. Thin films of ZrO_2 (Zirconia) have beneficial ceramics properties that offers various possibilities for Technological application such as optical coating, thermal barrier, catalysis or catalytic supports [10]. Yttria-stabilized zirconia thin films by dip-coating for IT-SOFC application [11]. Solid oxide fuel cell (SOFC) ceria/yttria stabilized zirconia electrolytes for solid oxide fuel cell applications [12]. Zirconia is used as air-fuel ratio sensors for

automotive applications [13]. To combine the mechanical properties of a high strength inert ceramic with the specific properties of bioactive glasses, composite materials based on high-density zirconia substrates coated by bioactive glasses are reported to be used [14]. Zirconia ceramics can be used for functional as well as structural applications [15].

III. SYNTHESIS OF ZIRCONIA

Zirconia has been synthesis by using different methods, such as combustion synthesis, Ion exchange, solid-state reaction, sol-gel synthesis, glycothermal processing, pechini method, wet chemical method**.**

A. Combustion Synthesis

The synthesis of ZrO_2 involves two steps. In the first step the precursors were prepared by self sustaining combustion technique using urea as a fuel. In the second step the precursors were heated at elevated temperatures in order to get pure crystalline materials. The procedure for synthesis of the above mentioned materials are given below. The required amount of Zirconyl Nitrate was dissolved in minimum quantity of distilled water. To the solution appropriate amount of urea was added and mixed thoroughly. The mixture was heated using an electrical Bunsen burner. The clear solution was evaporated. The voluminous mass obtained was ground well. The precursor thus obtained was heated at 700°C for 3hrs. [16].The fine zirconium dioxide powder material is synthesized using zirconyl nitrate, $ZrO(NO_3)_2.2H_2O$, as pre- cursor salt and carbohydrazide, $N_2H_3CON_2H_3$, as fuel (Arul Dhas and Patil 1994) [17].

B. Ion Exchange

ZrO_2 white powder was obtained by means of ion exchange as follows. The first step was the Preparation of surfactant-exchanged hydrous zirconia. To an aqueous solution of zirconium oxychloride with a certain concentrate ion was added an aqueous solution of some surfactant at room temperature. The combined solution was stirred for 20 min for sufficiently mixing. Then stronger aqueous ammonia (28%) was slowly dropped in to the above mixed solution under continuous stirring to pH 11. Hydrous zirconia precipitated as a gelatinous solid half a moment after the addition of ammonia. The mixture was placed into a constant temperature water bath for a certain time under stirring at a high speed. Subsequently, the white precipitate was separated from the solution by centrifugal ion and repeatedly washed with distilled water until the surfactant and chloride ions were free. The white powder was dried at 80° in an oven for 12 hrs and calcined at different temperatures to form porous zirconia with a high surface area [18].

C. Solid-State Reaction

The nanocrystalline zirconia was prepared via a solid-state reaction using zirconyl chloride ($ZrOCl_2.8H_2O$) as the precursors. Several procedures were investigated to study the influence of Zr/NaOH ratios, calcination and crystallization temperature, and the role of surfactant. First, $ZrOCl_2.8H_2O$ and NaOH were milled in to fine powder and mixed at ambient temperature. The mixture were then transferred to an autoclave and kept at a desired temperature for certain period of time. Subsequently, the mixture was washed with deionized water until it was free of Cl^- ions, and then washed with ethanol twice to remove water contained in the solid. Finally, the samples were dried at 383 K overnight. The dried samples were calcined at temperatures of 523/773 K for 20 hrs [19].

D. Sol-Gel Synthesis

Zirconium nitrate ($Zr(NO_3)_4 \cdot 8H_2O$, Merck) and yttrium nitrate ($Y(NO_3)_3 \cdot 6H2O$, Merck) in a molar ratio of 83:17 were dissolved in distilled water. The solution was heated to 85–90 °C, while continuously stirring, to obtain a clear solution. It was then kept at 90 °C for 24 hrs to slowly evaporate the water. The dried gel was crushed into a powder using dry ball-mill, followed by calcination at 400 °C for 2 hrs to obtain the required YSZ powder [20].

E. Glycothermal Processing

Zirconia precursors were precipitated from 0.1 mol/L $ZrCl2O \cdot 8H2O$ solution by slowly adding NH_4OH water with rapid stirring, in which the pH of starting solutions varied between 7 and 11. The precipitated zirconia precursors were washed by respected cycles of centrifugation and re-dispersion in water. Washing was performed for a minimum of five times in ethanol. Excess solution was decanted after the final washing and the wet precursor was re-dispersed in 200 ml ethylene glycol under vigorous stirring. The resulting suspension was placed in a 1 L stainless steel pressure vessel. The vessel was then heated to 270°C at a rate of 10°C/min for 6 hrs. [21].

F. Pechini Method

To synthesize the liquid precursor containing $Zr4^+$ ions by the Pechini method, a solution of 80% in mass of zirconium but oxide in butanol (Aldrich) as the zirconium precursor source was used. The preparation involved the following steps: first, 28.64 g of the zirconium but oxide solution was added to a beaker containing 150 mL of deionized water. This solution was kept under constant stirring at a temperature of 80°C for 2 hrs to obtain a Zr(OH)4 suspension. Citric acid anhydride was then added to complex the metallic ion, establishing a citric acid: $Zr4^+$ metallic ion molar ratio of 3:1. The solution was kept under stirring at a temperature of 80°C for 48 hrs to trigger the complexation process, after which 51.72 g of ethyl glycol was added and the solution kept at 80°C to produce the esterification and polymerization reaction [22].

G. Template Based Synthesis Method Of Ceria–Zirconia

In order to prepare replicas of the mesostructures, silica templates were impregnated with nitrate salts of cerium ($Ce(NO_3)_3 \cdot 6H_2O$) and zirconium ($ZrO(NO_3)_2 \cdot 6H_2O$) as precursors. First, $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot 6H_2O$ solutions (0.1M) were prepared via dissolution of the precursors in water. Then, 1 mmol of total metal ions was prepared through

mixing proper ratios of above mentioned solutions. These were added to silica template as the first impregnation step. After calcinations at 350 ◦C for 4 h, a second impregnation step was performed using 0.5mmol of the ions ($[Zr^{4+}]$ + $[Ce^{3+}]$) followed by calcination at 800 ◦C. (The impregnation stage is performed in two steps in order to fill the porosities to the highest possible level.) Then, the template was removed using NaOH. The product is finally centrifuged, washed and dried [23].

H. Zro_2 Powder Preparation Using Natural Cellulosic Material.

Synthesis of Precursor: $ZrCl_4$ (9.83 gms) as precursor was reacted with isopropyl alcohol to produce zirconium isopropoxide ($Zr(i\text{-}C_3H_7O)_4$). The product then was dissolved in a mixture of 300ml ethanol and 300ml methanol along with stirring by a magnetic stirrer for 15 minutes. Then, 19.6 grams of Oryza Sativa pulp was put into the solution slowly along with stirring for 15 minutes. The weight ratio of precursor to pulp was 1: 2. Hereinafter, ammonia solution was poured slowly into the mixture until hydrolysis occurred by checking the pH, the process was carried out until the solution pH was equal to 6. Then an aging process was conducted for 48 hours. After that, the solution was filtered until a gel of zirconium hydroxide-pulp was obtained. The sample from the filtration was divided into three parts; the carbon content of each sample had to be removed by oxidizing it at a temperature of 400 °C for 3 hours in an oxidation furnace.

Precursor Calcination Process: After the oxidizing process, calcination was performed at the temperatures of 900 °C, 1000 °C, and 1100°C for 90 minutes. The samples were given labels based on the temperature calcination, namely ZrO2-900°C, ZrO2-1000°C, and ZrO2-1100°C [24].

IV. LIMITATION OF ZIRCONIA

Zirconia-based ceramics has been increasingly used as implant biomaterials. It is used as biomaterial has some limitation such as fatigue failure. It has been used to make crowns in dental restorations for decades. Thus, the orthopedic applications of ceramic hips/knees, and dental restoration implants must be designed against possible fatigue failure [25]. The yttria stabilized zirconia (YTZP) is a very attractive material for orthopedic applications. It has excellent biocompatibility, high fracture toughness; high strength and low wear rates. But case studies show that delayed failure can occur in vivo due to crack propagation. In order to improve the lifetime and the reliability of the prostheses, carbon nanotubes (CNT) are added. Zirconia-MWCNT nanocomposites are also proposed for biomedical applications [26]. Nanocrystalline materials are expected to show improved mechanical properties and the nanometric features in the surface of the prostheses seem to reduce the risk of rejection and to enhance the proliferation of osteoblasts (bone-forming cells) [26]. Due to metastability, zirconia is prone to ageing in the presence of water. In the development of new 'ageing free' zirconia ceramics are the key for gaining confidence in the future Mechanical property degradation in zirconia, known as 'ageing', is due to the progressive spontaneous transformation of the metastable tetragonal phase into the monoclinic phase[27].

V. CONCLUSIONS

Zirconia is an important biomaterial that is extensively used. The Zirconia, yttria stabilized zirconia and composites of Zirconia with polymers are widely used and the processing technologies have been standardized with the industry. Zirconia and its derivatives are synthesized using various starting materials like $ZrCl_4$, $Zr(i\text{-}C_3H_7O)_4$, $ZrO(NO_3)_2{\cdot}6H_2O$ and ZrO_2. The crucial aspect of the synthesis method is to obtain the tetragonal Zirconia at lower temperature and stabilization of this phase with the addition of stabilizing agents.

REFERENCES

[1]. Felora Heshmatpour, Reza Babadi Aghakhanpour, "Synthesis and Characterization Of Nanocrystalline Zirconia Powder by Simple Sol-Gel Method with Glucose and Fructose As Organic Additives", *Powder Technology, 205(2011), Pp193-200*.

[2]. Martin Stefanic, Kristoffer Krnel, Tomaz Kosmac, "Synthesis and Characterization of Calcium Phosphate Coatings on Zro2 Ceramics for Bone Implant Applications", *Engineering Ceramic Department, J.S.Institute, Ljubljana, Slovenia*.

[3]. Pilathadka S., Vahalová D., Vosáhlo T, "The Zirconia: A New Dental Ceramic Material. An Overview", *Prague Medical Report / Vol. 108 (2007) No. 1, Pp. 5–12.*

[4]. T. V. Thamaraiselvi and S. Rajeswari. "Biological Evaluation of Bioceramic Materials - A Review", *Trends Biomater, Artif Organs, Vol. 18 (1) (2004), Pp 9-17.*

[5]. Jelena P. Markovi, and Slobodan K. Milonji, "Synthesis of Zirconia Colloidal Dispersions By Forced Hydrolysis", J. *Serb. Chem. Soc. 71 (6) (2006), Pp.613–619*

[6]. M. Srinivas and G. Buvaneswari, "A Study of In Vitro Drug Release from Zirconia Ceramics", *Trends Biomater, Artif, Organs, Vol. 20(1) (2006), Pp.24-30.*

[7]. Olivier Roualdes , Marie-Eve Duclos , Dan Gutknecht , Lucien Frappart , Je´ Roˆ Me Chevalier and Daniel J. Hartmann, "In Vitro and In Vivo Evaluation of an Alumina–Zirconia Composite for Arthroplasty Applications", *Biomaterials, 31 (2010), Pp. 2043–2054.*

[8]. Christian Oetzel E Rolf Clase, "Preparation of Zirconia Dental Crowns via Electrophoretic Deposition", *J Mater Sci. (2006), 41:8130–8137.*

[9]. X. He, Y. Z. Zhang E.J. P. Mansell, E.B. Su, "Zirconia Toughened Alumina Ceramic Foams for Potential Bone Graft Applications: Fabrication, Bioactivation, and Cellular Responses", *J Mater Sci.: Mater Med (2008), 19:2743–2749*

[10]. E. Krumov, J. Dikova, K.Starbova, D. Popov, V. Blaskov, K. Kolev and L.D. Laude, "Thin Zro_2 Sol-Gel Films for Catalytic Application", *Journal of Materials Science: Materials in Electronics, 14 (2003)759-760.*

[11]. Yonglian Zhang, Jianfeng Gao, Guangyao Meng and Xingqin Liu, "Production of Dense Yttria-Stabilized Zirconia Thin Films by Dip-Coating for IT-SOFC Application", *Journal of Applied Electrochemistry, 34: 637–641, 2004*.

[12]. J. Luo, R. J. Ball, R. Stevens, "Gadolinia Doped Ceria/Yttria Stabilised Zirconia Electrolytes for Solid Oxide Fuel Cell Applications*", Journal of Materials Science 39 (2004), Pp. 235– 240.*

[13]. Jong-Heun Lee, "Review On Zirconia Air-Fuel Ratio Sensors for Automotive Applications", *Journal of Materials Science 38 (2003), 4247 – 4257.*

[14]. M.Bosetti, E.Verne, M.Ferraris, A.Ravaglioli, M.Cannas, "In Vitro Characterization of Zirconia Coated by Bioactive Glass", *Biomaterials, 22 (2001), 987-994.*

[15]. Shuigen Huang, Lin Li, Jef Vleugels, Peiling Wang, Omer Van Der Biest, "Thermodynamic Prediction Of The Nonstoichiometric Phase Zr1_Zcezo2_X in the Zro2–Ceo1.5–Ceo2 System*", Journal of The European Ceramic Society 23 (2003), Pp 99–106.*

[16]. M. Srinivas and G. Buvaneswari, "A Study Of In Vitro Drug Release from Zirconia Ceramics", *Trends Biomater. Artif. Organs, Vol 20(1), Pp 24-30, 2006.*

[17]. H Ranjan Sahu and G Ranga Rao, "Characterization of Combustion Synthesized Zirconia Powder UV-Vis, IR and Other Techniques." *Bull Mater. Sci., Vol. 23, No. 5, October 2000, Pp. 349-354. © Indian Academy of Sciences*.

[18]. Zhao Chun, Yan G Shao-Feng , Song Li-Zhu, Xu Hui-Fang, Yang Hua, Jiang Fu-Ming , Wang Zi-Chen And Niu Zhong-Guo, "Preparation of Porous Zro2 and Study on Its Properties." *Chem. Res. Chinese U. 2002, 18(3), Pp 337-340.*

[19]. Xinmei Liu, Gaoqing Lu, Zifeng Yan, "Preliminary Synthesis and Characterization of Mesoporous Nanocrystalline Zirconia", *Journal of Natural Gas Chemistry 12(2003), Pp161-166.*

[20]. N.Rajabbeigi, B.Elyassi, A.Khodadadi, S.S.Mohajerzadeh, M. Sahimi, "A Novel Miniaturized Oxygen Sensor with Solid-State Ceria–Zirconia Reference", *Sensors and Actuators B 100 (2004), Pp 139–142.*

[21]. Jun-Seop Kim, Dong-Hae Lee, Sung Kang, Dong-Sik Bae, Hoy-Yul Park, Moon-Kyeung Na, "Synthesis and Microstructure of Zirconia Nanopowders by Glycothermal Processing.", *Jun-Seop Kim, Et Al/Trans. Nonferrous Met. Soc. China 19(2009), Pp 88-91.*

[22]. Cleocir José Dalmaschio, Valmor R. Mastelaro, Pedro Nascente, Jefferson Bettini, José Luiz Zotin, Elson Longo, Edson Roberto Leite, "Oxide Surface Modification: Synthesis and Characterization of Zirconia-Coated Alumina" *Journal of Colloid and Interface Science, 343 (2010), Pp 256–262.*

[23]. S. Abdollahzadeh Ghom, C. Zamani, S. Nazarpour, T. Andreu, J.R. Morante, "Oxygen Sensing With Mesoporous Ceria Zirconia Solid Solutions", *Sensors and Actuators B 140 (2009), Pp 216–221.*

[24]. Rifki Septawendara, Bambang Sunendar Purwasasmitab, Suhandaa, Leanddas Nurdiwijayantob and Frank Edwin, "Nanocrystalline Zro_2 Powder Preparation Using Natural Cellulosic Material", *Journal of Ceramic Processing Research, Vol. 12, No. 1, Pp. 110-113 (2011).*

[25]. J. Zhou · J. Mah · P. Shrotriya · C. Mercer · W. O. Soboyejo, "Contact Damage in an Yttria Stabilized Zirconia:

[26]. Implications for Biomedical Applications", *J Mater Sci: Mater Med (2007)18:71–78.*[26] N. Garmendia, I. Santacruz, R. Moreno, I. Obieta, "Zirconia-MWCNT Nanocomposites for Biomedical Applications Obtained By Colloidal Processing", *J Mater Sci: Mater Med (2010) 21:1445–1451.*

[27]. Je´Roˆme Chevalier, "What Future for Zirconia as a Biomaterial?" *Biomaterials 27 (2006), Pp 535–543.*