

## **Stabilization of Zirconia Ceramics for Dental Coatings - Effect of Aging Conditions**

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### **ABSTRACT**

Zirconia has excellent properties for restoration and implantation in dentistry and orthopedics. Among three phases of zirconia (monoclinic, tetragonal and cubic) tetragonal zirconia is most widely used in stress bearing applications due to its high mechanical strength but its transition towards monoclinic (low strength phase) upon penetration of water. Present study's aim is to compare the low temperature degradation (LTD) process in zirconia implants in hydrothermal environment. The time-dependent evolution of tetragonal-to-monoclinic transformation and the related residual stresses are nondestructively monitored by XRD and micro Vickers hardness indenter. It is suggested that if a hydrophobic material is coated on zirconia surface, it will reduce the effect of LTD in hydrothermal environment and results in long term in vivo application of implants. For this purpose, polyethylene glycol is added during synthesis since biocompatibility of polyethylene glycol has already been proven. Aging time is varied from 1 to 5 hours. One-hour exposure under the selected aging condition is estimated to correspond to in vivo exposures of 4 and 2 years according to ISO and ASTM criteria, respectively. X-ray diffractometer (XRD) results reveal the retention of tetragonal zirconia with crystallite size consistent with literature for occurrence of tetragonal zirconia. The morphology, mechanical flexural strength and hardness do not show considerable decrease with aging time due to retention of phase purity. SEM results reveal the formation of well dispersed and well defined nanoparticles with spherical shape and size in the range of 30-35nm. These synthesized nanoparticles with high durability and hardness are well suited for implants.

### **1. INTRODUCTION**

Use of zirconia based systems as a dental coating has gained significant attention among medical community. Since 1970s, many researchers have done a lot of work from the discovery of phase transformable  $ZrO_2$ . Zirconia impedes strongest mechanical properties among other ceramics. Due to this property it is widely used in dentistry (Bassilio et al. 2016). Restorative implants and coatings on a tooth required

most precise esthetic locations and properties. Best implant results depend upon the correct osseointegration, optimum implant positioning, durability and acceptable esthetic outcomes. Although titanium implants are used but they have negative effects such as dark shade and soft tissues. Therefore, titanium implants have been replaced by zirconia. Zirconia ivory color and esthetic properties make it suitable for dental coatings and implants (Park et al. 2007).

Zirconia ( $ZrO_2$ ) is a significant functional material, and the transition among its different phases has great effect on the mechanical and physicochemical properties (Kelly and Rose 2002). Among three phases of zirconia (monoclinic, tetragonal and cubic), the monoclinic phase (m-phase) is the most stable at room temperature, while tetragonal phase (t-phase) and cubic phase (c-phase) become more stable at elevated temperatures (Bashir et al. 2014). The transition between phases, in particular, is widely used in toughening mechanism (Jin 2005) and in heterogeneous catalysis for modification of surface activity (Wang et al. 2007) due to rapid and reversible transformation around  $\sim 1000$  °C. Transitions from t-phase to m-phase leads to significant increase in volume ( $\sim 4\%$ ), while coordination number of Zr decreases from 8 to 7 (Bhattacharya et al. 2004). Zirconia has applications in high-performance, wear applications and thermal barrier coatings (TBCs) to biological implants. Nonetheless, in spite of the achievements of zirconia, it has been reported that zirconia degrades in hydrated environment known as low-temperature degradation (LTD). LTD is a dynamic phenomenon in which tetragonal zirconia gradually transforms to m-phase. It is suggested that if a hydrophobic material is coated on zirconia surface, it will reduce the effect of LTD in hydrothermal environment and would result in long term in vivo application of implants (Chevalier 2006).

Few researches have done some work to investigate the aging effects in complex metal oxide structures. Now a days, absence of connection exists between aging and clinical failures. The main reason behind this failure is because of the absence of any authentic scientific approach. Therefore, investigating aging in-vivo and in-vitro may produce more significant effects on materials to be used as implants and coatings (Chevalier et al. 2011).

The present study deals with the deposition of stable, dense zirconia coatings using sol-gel approach. In order to confer good properties to the final product, ethylene glycol has been used as organic additive.

## **2. Experimental Details**

### *2.1 Materials*

Zirconyl chloride octahydrate ( $ZrOCl_2 \cdot 8H_2O$ , BDH, 99.99% pure) was obtained from Sigma Aldrich. Ethylene glycol and ammonia (32%) were obtained from Merck. Deionized (DI) water was used as solvent.

### *2.2 Method*

Zirconyl chloride octahydrate was dissolved in DI water to form 0.1M solution. This stock solution was stirred at room temperature. Ammonia was added as gelation agent. 5ml of ethylene glycol was added in pre-synthesized zirconia sol and stirred for 5 hours. These stirred sols were dried at 60-70°C for powder formation. The powder was subjected to hydrated environments by varying the time from 1 to 5 hours. One-hour exposure under the selected aging condition is estimated to correspond to in vivo

exposures of 4 and 2 years according to ISO and ASTM criteria, respectively (Arita et al. 2015).

### 2.3 Characterizations

Structure of ethylene glycol added zirconia was obtained by X-ray diffractometer (Bruker D8 advance) using Cu  $\alpha$  radiation ( $\lambda=0.1540598$  nm). Mechanical properties were studied by Shimadzu HVM-2 micro vickers hardness indenter. Morphological characteristics were studied by Hitachi S-3400N Scanning Electron Microscopy (SEM).

## 3. Results and Discussion

Fig. 1 depicts XRD patterns of  $ZrO_2$  powders at different aging times. XRD patterns of as-synthesized zirconia show polycrystalline structure. Samples exposed to 1 to 5 hours to hydrated environment after ethylene glycol coatings did not show any significant structural changes. However, shifting in peaks has been observed with increase in exposure time. Along with phase purity amorphous content has also been observed in samples.  $Zr(OH)_4$  is responsible for amorphous nature and has been considered as short range structure of isomorphous to tetragonal zirconia. In short range isomorphous tetragonal atoms are arranged for emerging crystallization to t- $ZrO_2$ . Presence of amorphous phase along with slight shifting in peaks due to water absorption has been explained by Gou et al. (2004). They revealed that it consists of following steps 1) water is absorbed on the surface; 2)  $OH^-$  is formed by reaction of water with  $O^-$  on the zirconia surface, 3) diffusion of  $OH^-$ , 4) formation of proton defects by filling of oxygen vacancies by OH ions.

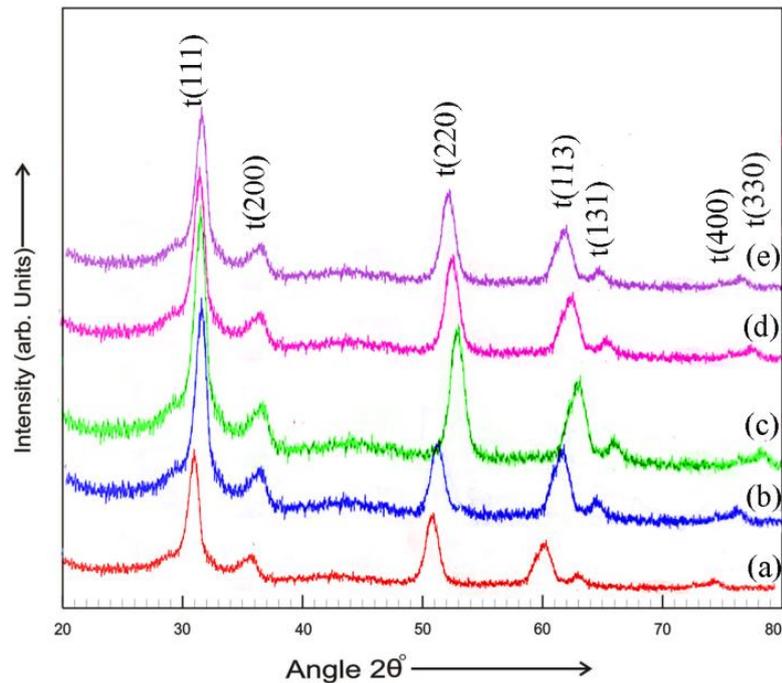


Fig. 1 XRD patterns at aging time (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5hrs

Crystallite size and dislocation density of ethylene glycol coated zirconia was estimated by using Eqs. 1 and 2 (Cullity 1956). With the increase in exposure time crystallite size decreases and broadening of the peaks has been observed due to incorporation of amorphous content. It has also been discussed earlier that stable phase of zirconia at room temperature is monoclinic. So, it is very important to control zirconia crystallite size to obtain tetragonal structure at room temperature. One of the effective methods is ethylene glycol-based process, which has been established for the preparation of fine ceramic oxide powders. In this technique, a uniform particle size powder is produced by means of a homogeneous distribution of metal ions in the polymeric gel.

Crystallite size of t-phase [Fig. 2] is less than 30nm, which is consistent with literature that says that tetragonal phase is stable around 30 nm (Garvie 1965). Relatively lower dislocation density was calculated for ethylene glycol added zirconia as shown in Fig. 3.

$$D = 0.9\lambda / B \cos \theta \quad (1)$$

$$\delta = 1 / D^2 \quad (2)$$

Where  $D$  is crystallite size,  $\lambda$  is wavelength of X-rays used ( $1.5406\text{\AA}$ ),  $B$  is full width at half maximum and  $\theta$  is diffraction angle.

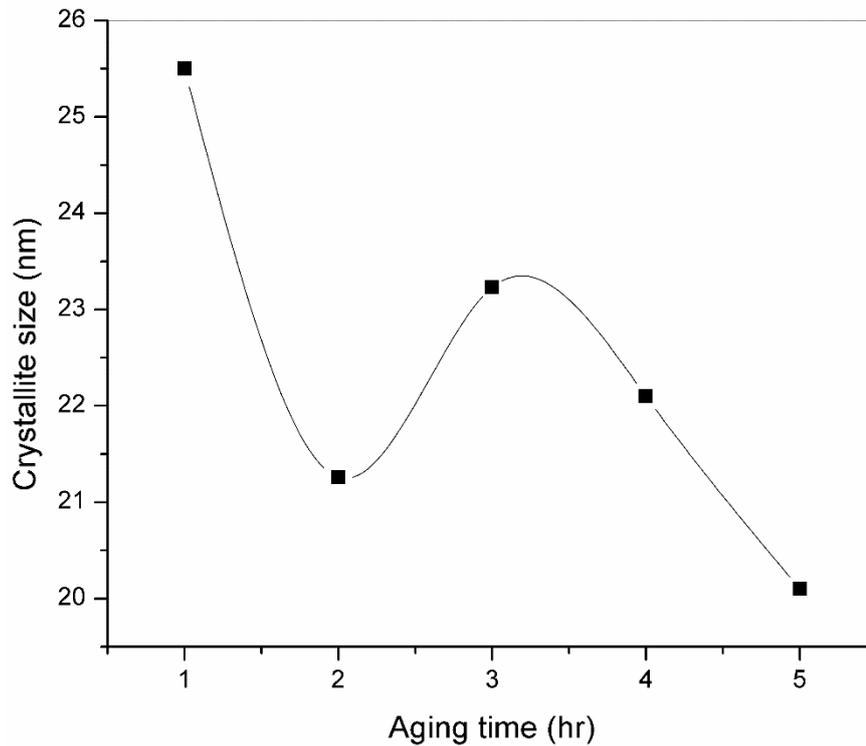


Fig. 2 Crystallite size of ethylene glycol added zirconia at various aging time

Unit cell volume calculations [Fig. 4] revealed the increasing behavior with aging time. Adsorption of water in  $ZrO_2$  increases with aging time. This adsorption causes stresses and forms t-phase with higher volume. With increase in exposure time Zr-OH formation occurs which lead to expansion in unit cell volume. Increase in volume leads to decrease in density especially for sample exposed for 5hrs in hydrated environment [Fig. 4] with phase purity. For biological applications relatively higher densities are required because more dense the material, more compact the powder and higher the hardness values

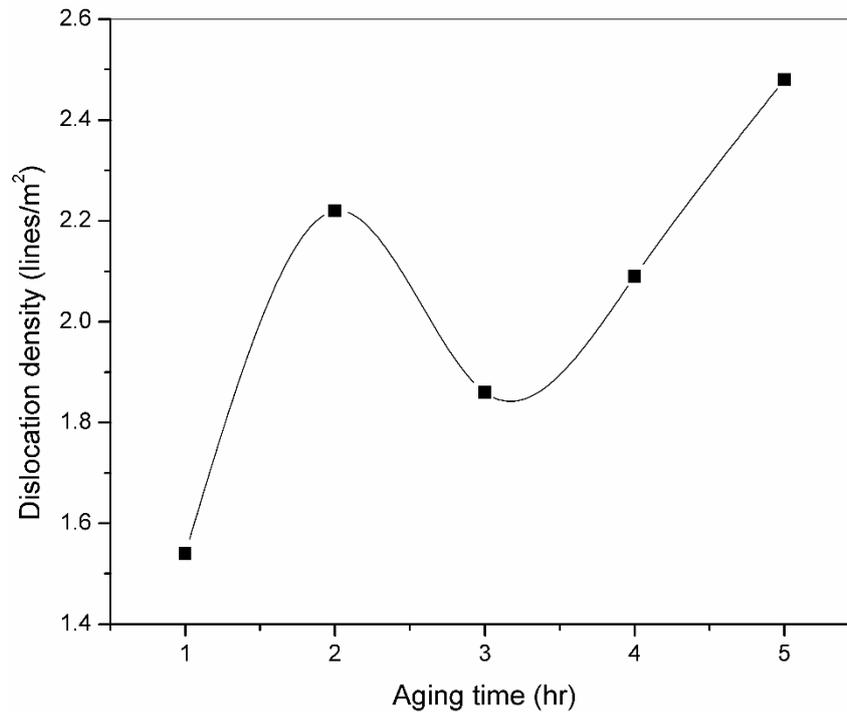


Fig. 3 Dislocation density of ethylene glycol added zirconia at various aging time

For hardness measurement Vickers indentation under 4.9N load for 15 seconds dwell time was performed according to American standard testing machine (ASTM C-1327-99). From Fig. 4, higher x-ray density was observed. Higher density leads to high value of hardness which is confirmed by Micro Vickers Hardness test. Hardness of the samples is in the range of 1380HV to 1520HV [Table 1].

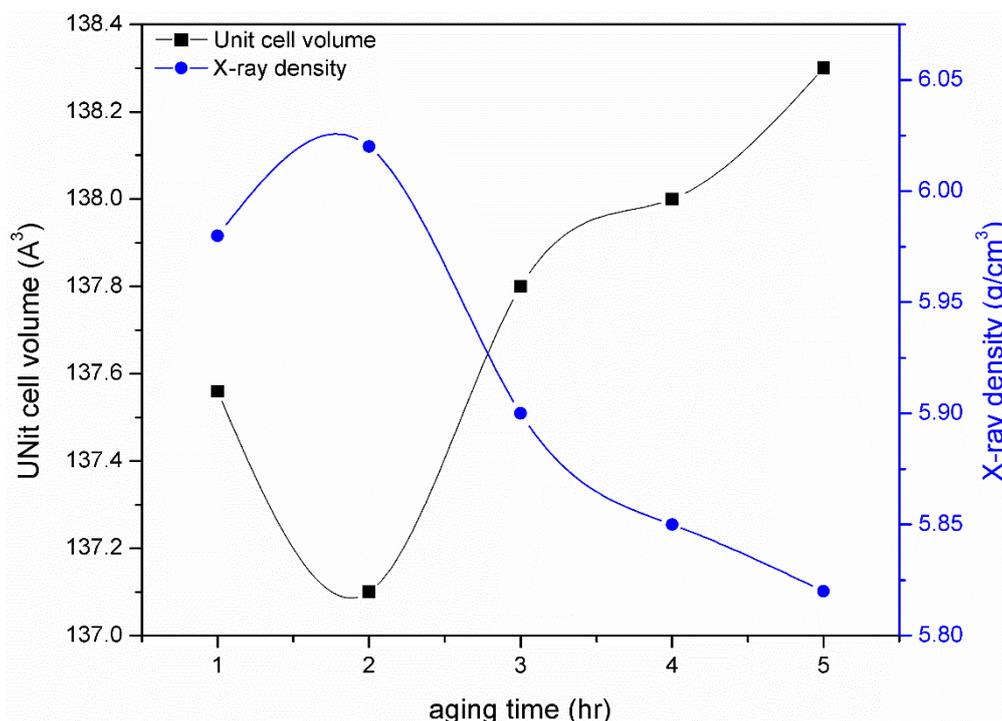


Fig. 4 Unit cell volume and x-ray density of ethylene glycol added zirconia at various aging time

Along with structural properties microstructural properties of zirconia has strong impact on phase transformation and consequently to the hardness of the material. Effect of aging time on morphological properties of zirconia has been observed through SEM images. Surface morphology of ethylene glycol added zirconia results in nanoparticles with large surface area growth. Well dispersed and spherical shape nanoparticles of size is in the range of 30-35nm were observed (results will be presented elsewhere). Samples did not agglomerate with aging which means ethylene glycol has been fully coated on these nanoparticles and acts as hydrophobic end as discussed earlier.

**Table 1** Hardness of ethylene glycol added zirconia as a function of aging time

<b>Aging time (hr/hrs)</b>	<b>Hardness (HV) at constant load and time ASTM C- 1327-99</b>
1	1520
2	1503
3	1419
4	1389
5	1380

### 3. CONCLUSIONS

(1) In this research article effect of LTD has observed on zirconia samples. Ethylene glycol was used as additive to coat these samples. These synthesized powders were subjected to hydrated environment in order to study the effect of moisture absorption. Exposure time was varied from 1 to 5hrs. (2) Tetragonal zirconia retained its phase purity after 5hrs of exposure. (3) Crystallite size of the samples was consistent with literature for occurrence of tetragonal zirconia. (4) Maximum hardness of the samples was observed as 1520HV.

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