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Structural and mechanical properties of polymer additive based zirconia thin films prepared sol-gel

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ABSTRACT

In the present study sol–gel method has been employed using polymers additives to deposit zirconia thin films. Effect of reaction temperature (50, 100 and 150°C) have been investigated on structural and mechanical properties of zirconia thin films. Addition of polymers has prominent effect on structural and mechanical properties of zirconia. Phase analysis was executed by X-Ray diffractrometer (XRD). Formation of tetragonal zirconia (t-ZrO_2) along with monoclinic content has been observed at relatively higher reaction temperatures (100 and 150°C). A sharp decrease in crystallite has observed at reaction temperature 100°C. Higher reaction temperatures cause volume shrinkage due to removal of hydroxyl (OH) ions since OH ions are responsible for monoclinic content. Removal of OH ions at relatively higher reaction temperatures leads to presence of tetragonal zirconia at room temperature. Hardness of the polymer additive zirconia has obtained up to 850HV confirmed by Micro Vickers hardness indenter. These as deposited thin films with presence of tetragonal content can be successfully employed for teeth coatings.

1. INTRODUCTION

Now-a-days, thin films are used in many applications for example in protective and thermal barriers, thin film capacitor, biomaterials and teeth coatings etc. (Shyjua et al. 2012). Among all these applications, protective coatings with a suitable thickness and homogeneity are important for biomedical field (Hu et al. 2012). Hence metal oxides are widely used for biological protective coatings. Among metal oxides, zirconium oxide (zirconia, ZrO_2) represents one of the most studied oxide material because of its unique physical and structural properties (Rathod et al. 2010). These unique properties are high value of hardness, higher melting point (~2600°C), high corrosion resistance and biocompatibility (Balakrishnan et al. 2013). While, it has been widely used, researchers are still looking forward for the applications of ZrO_2 especially in biomedical. Among biomedical applications most important ones are bio implants, bio sensors, and teeth coatings (Heiroth et al. 2010).

ZrO_2 exhibits in three crystal structure monoclinic, tetragonal and cubic. Monoclinic phase (m-phase) exists in room temperature. Tetragonal phase (t-phase) form at temperature ~1170°C and cubic phase (c-phase) is stable at higher temperature (~2300°C) (Kohorst et al. 2012). Among these phases, the most biocompatible and tougher is t-phase (Davar et al. 2013). Stabilized t-phase can be achieved by addition

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of some polymers (Shukla et al. 2003). However reaction temperature and initial synthesis conditions have dominant effect on the transformation of low temperature m-phase to high temperature stable t-phase (Li et al. 2013). The transformation from m-phase to t-phase could lead to 3-5% volume decrease and consequently increase in density (Denry and Kelly 2008) which is one of the requirements for the implants in biomedical applications.

Recently, materials for coatings, specifically zirconia (ZrO_2) coatings, have gained a lot of potential since they meet with bio implants and coatings requirements (Zawawi et al. 2013). Polymers additive zirconia coatings have been prepared by using different experimental techniques such as co precipitation (Maheswari et al. 2013), ball milling (Adam et al. 2008) and sol gel (Bashir et al. 2014a) etc.

In this research article we have synthesized polymer additive ZrO_2 nanoparticles at different reaction temperatures and their structural and mechanical properties are investigated.

2. EXPERIMENTAL DETAILS

$ZrOCl_2.8H_2O$ (Sigma–Aldrich, 99.99% pure), and NH_3 anhydrous (Sigma–Aldrich, 99.99% pure) were used without further purification. DI water was used as solvent.

2.1 Synthesis of Nanoparticles

Zirconium oxychloride octahydrate ($ZrOCl_2.8H_2O$) was mixed in DI water to form 0.1M solution. Meanwhile, NH_3 was added into 0.1M solution of zirconium oxychloride which results in formation of milky sol of pH 5.5. This synthesized sol was stirred and heated at different temperature ranges 50-150°C for 5 minutes. After that transparent and shiny sols were obtained. These sols were deposited on glass substrates. Before deposition of sols substrates were cleaned in acetone and then isopropanol alcohol for 10 minutes respectively (Riaz et al. 2011, Asghar et al. 2006a, Asghar et al. 2006b).

2.2 Characterizations

X-ray diffractometer (Bruker D8 Advance) was used to study the crystalline structure of the deposited thin films. The Cu K-alpha radiation source was used. Mechanical properties were studied by using Shimadzu HMV-2 Micro Vickers hardness indenter.

3. RESULTS AND DISCUSSION

Recently different polymers have been employed for biocompatible zirconia (Suciu et al. 2008, Suciu et al. 2006 and Suciu et al. 2003). However, polymer additive zirconia for teeth coatings, pH 5.5 has two important aspects. (1) At pH 5.5 polymer does not oxidize readily (2) Teeth do not demineralize and re-mineralize (Piangprach et al. 2009). Fig. 1 shows the XRD patterns of as deposited polymer additive zirconia thin films at different reaction temperatures. At reaction temperatures 50°C to 150°C peaks at approximately 23. 0º, 31.8º, 41.2º and 46.2° correspond to the (011), (111) (021) and (-202) planes of monoclinic zirconia (m-ZrO_2) [JCPDS 13-307]. However, peaks correspond to 47.9°, 53.5º, 59.0º, 68.8º, 73.5° and 78.1º correspond to the (221), (113) (123) (004) and (330) planes of tetragonal zirconia (t-ZrO_2) [JCPDS 17-923]. As the reaction temperature precedes monoclinic content decreases and intensity of monoclinic peak along (011) plane decreases. In Fig. 1c relatively increased in intensity with increasing reaction temperature of the sol, indicating that the phase became more oriented. No peaks relating to a crystalline phase of polymer were detected.

The presence of high temperature stable tetragonal phase in as synthesized samples is due to presence of polymer. The reduction in monoclinic content with temperature is due to removal of hydroxyl ions. Actually these hydroxyl ions are responsible for monoclinic content of zirconia (Chevalier and Gremillard 2009). Moreover, presence of amorphous behavior along with polycrystalline nature is due to presence of carbon chains (come from polymer addition).

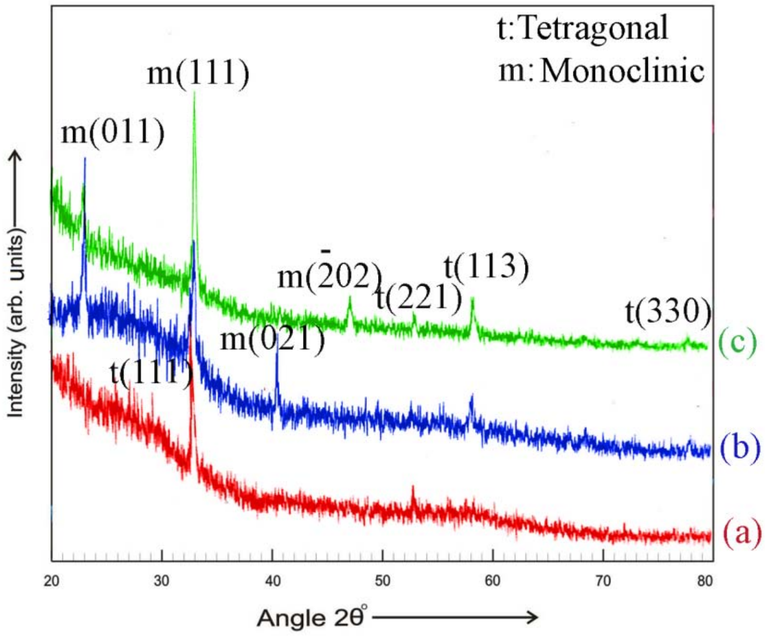

Fig. 1 XRD patterns of Polymer additive zirconia thin films at different reaction temperatures a) 50, b) 100 and c) 150°C

Monoclinic content fraction (V_m) at different reaction temperature was calculated by using Eq. (1) and (2); (Sahu and Rao 2000);

$$X_m = \frac{I_m(111) + I_m(011)}{I_t(113) + I_m(111) + I_m(011)} \tag{1}$$

$$V_m = \frac{(1.311X_m)}{1 + (0.311X_m)} \tag{2}$$

Where, I_m and I_t denote to the intensities of monoclinic and tetragonal peaks respectively. Whereas, volume fraction of tetragonal phase was calculated by using Eq. 3;

$$V_t = 1 - V_m \tag{3}$$

Volume content of monoclinic zirconia phase decreases with the increase in reaction temperature. The volume fraction ratio of monoclinic and tetragonal powders is calculated by Eq. 2. The results are summarized in Table 1.

Table 1. Tetragonal to monoclinic ratio (t:m) as a function of reaction temperature

Reaction Temperature (°C)	t:m
50	9:91
100	14:86
150	27:73

Crystallite size of polymer additive zirconia thin films was calculated by using Debye Scherer's formula is given in Eq. 4 (Cullity 1956).

$$D = \frac{0.9\lambda}{\beta Cos\theta} \tag{4}$$

Crystallite size of polymer additive zirconia thin film for highest peak along (111) plane calculated and plotted in Fig. 2. It is evident from Fig. 2. The mean crystallite size of polymer additive zirconia thin films is ~23nm. It is evident from mean crystallite size less than 30nm, which is critical size effect for occurrence of tetragonal zirconia at room temperature (Garvie 1965).

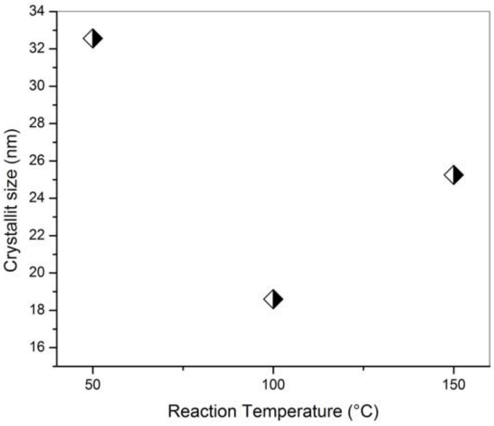

Fig. 2 Crystallite size of polymer additive zirconia thin films at different reaction temperatures

Dislocation lines/m^2 (dislocation density) was calculated by 1/D^2, where D is the crystallite size (m). Relatively lower dislocation lines/m^2 was calculated for polymer additives zirconia thin films at different reaction temperatures are shown in Fig. 3. Reduced value of dislocation density causes less cracks and larger size of grain boundary. This larger size of grain boundary leads to formation of strong bonding between atoms. Strong bonding is preferable for biological implants ad coating applications (Bashir et al. 2014a).

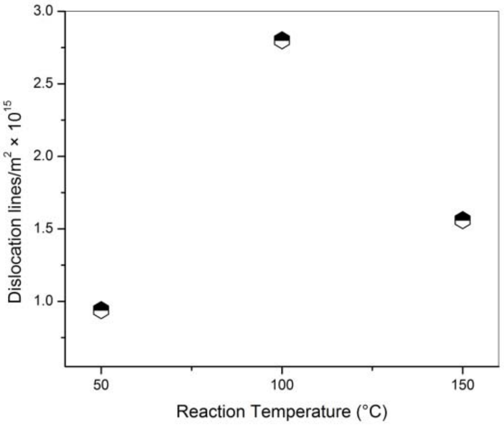

Fig. 3 Dislocation lines/m^2 (Dislocation density) of polymer additive zirconia thin films at different reaction temperatures

As reported earlier 3 to 5 % shrinkage in volume results in martensitic transformations (Denry and Kelly 2008). It can be evident from JCPDS cards of monoclinic [13-307] and tetragonal zirconia [17-923], accompanied different unit cell volume and monoclinic has slight larger volume than tetragonal. Unit cell volume and density of m-ZrO_2 and t-ZrO_2 is calculated by using Eqs. 5 - 7.

$$V_{Monoclinic} = abcSin\beta \tag{5}$$

$$V_{Tetragonal} = a^2b \tag{6}$$

$$\rho = \frac{1.66042\sum A}{V} \tag{7}$$

Where a, b, and c are lattice parameters and ΣA is sum of atomic weights of all the atoms present in unit cell (Cullity 1956).

Volume variations in zirconia strongly influence the crystal structure. As reaction temperature precedes Oh ions removes from the samples. As mentioned earlier OH ions are responsible for monoclinic content and consequently, larger volume. Whereas, shrinkage in volume leads to transformation of monoclinic phase to tetragonal.

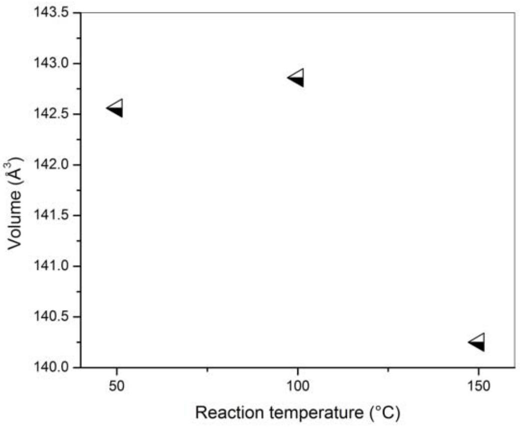

Fig. 4 Unit cell volume of polymer additive zirconia thin films as a function of reaction temperatures

For biological coatings a material should be dense enough to protect the surface. Temperature has significant effect on density and porosity of materials. It can be seen from Fig. 5 coatings become dense as the reaction temperature increases. At 150°C relatively high value of density (~5.75g/cm^3) has obtained with presence of tetragonal content [Fig. 1]. Along with high density films has low value of porosity as depicted in Fig. 6. Whereas, porosity was calculated by using density relation given in Eq. 8 (Cuilty 1956);

$$Porosity(\%) = \frac{\rho_{Experimental}}{\rho_{Standard}} \times 100 \tag{8}$$

Where, ρ experimental is calculated density of value from the XRD data obtained and ρ standard is the density of obtained from standard data.

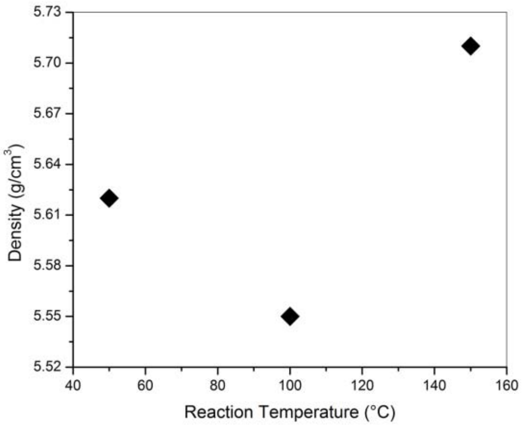

Fig. 5 Density of polymer additive zirconia thin films as a function of reaction temperatures

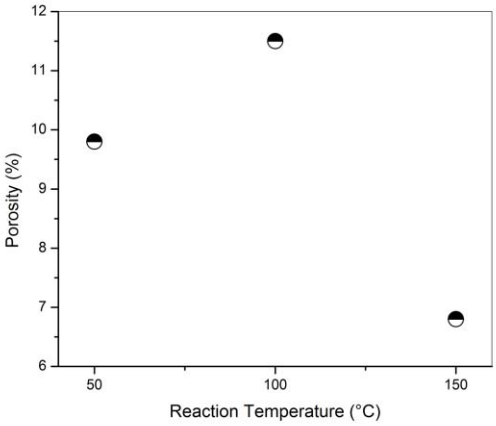

Fig. 6 Porosity of polymer additive zirconia thin films as a function of reaction temperatures

For biological implants, mechanical properties along with structural properties play a vital role. As discussed earlier among all phases of ZrO_2, t-phase has relatively higher value of hardness and presence of mix phases degrades the mechanical properties of samples. Moreover, presence of water molecules produces shear strain and consequently leads to cracks formations (Piconi and Maccauro 1999). For hardness measurements indentation tests was performed using the Micro Vickers test. The dwell time at 1.961N load was equal to 10s. Hardness of the samples is in the range of 682 to 853HV. As reaction temperature increases, an increase in hardness values has observed. Hardness of the samples is in consistent with XRD data where monoclinic phase content decreases and density of the samples increase with reaction temperature. Table 2 summarizes the values of hardness obtained at different reaction temperatures.

Table 2: Hardness of samples with Reaction temperature

Reaction Temperature (°C)	Hardness (HV)
50	682
100	669
150	853

3. CONCLUSIONS

In this research article we deposited polymer additive zirconia thin films on glass substrates. Effect of different reaction temperature on structural and mechanical properties was investigated. XRD patters revealed the presence of tetragonal content along with even at low reaction temperature. As the reaction temperature increases, an increase in volume fraction of tetragonal content was observed. As reaction temperature precedes, reduction in volume and increase in density was investigated due to removal of OH ions. Relative higher density and low porosity of thin films caused relative high value of hardness up to 850HV.

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