

Bioinert nano yttria stabilized zirconia coatings on 316L SS for dental applications

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The optimization of applied voltage for deposition of yttria-stabilized zirconia (YSZ) on metal substrate and its electrochemical behavioural studies have become major concern for the preparation of nanostructured zirconia suitable for the realization of dental devices. In the present work, we report YSZ coating on 316L SS by electrophoretic deposition (EPD) process. Optimum coatings were obtained in the coating range of 60V-70V and a coating time of 5 minutes. The YSZ coated 316L SS samples were sintered under vacuum at 800 °C for 1 hr. Cubic phase of YSZ coated samples was observed by X-ray diffraction. FE-SEM analysis confirms that the YSZ particles were roughly spherical and distributed uniformly on 316LSS. The anti-corrosion properties of the YSZ coated 316L SS samples were characterized in artificial saliva solution by electrochemical techniques. The electrochemical results confirm the coating of YSZ on the surface of 316L SS and it resist vigorous ions attack from artificial saliva.

Key words: EPD, YSZ, 316L SS, Artificial saliva, Corrosion studies.

Introduction

Biocompatibility of the implants and its associated structure is important for proper function of the prosthesis in the mouth. Noble alloys such as gold, silver, and platinum are used in dentistry are so stable chemically that they do not undergo significant corrosion in the oral environment [1]. The noble alloys based crowns are expensive and it is not easily available for many people. On the other hand economically affordable dental implants which are based titanium and stainless steel have been used widely as an alternative to noble alloys based dental implants. The major concern about dental implants are corrosion, because a large amount of metal ions and debris are generated in this process, of which accumulation may lead to adverse tissue reactions in the oral environment. A several studies have reported cases of severe corrosion of titanium and stainless steel dental implants as being the cause for implantation failure, because of saliva with salt, acts as a weak electrolyte. The electrochemical properties of saliva depend on the concentration of its components, pH, surface tension, and buffering capacity. Each of these factors may influence the strength of any electrolyte. In acidic medium, the active dissolution of metal ions can occur upon exposure to the bulk metal [2]. Corrosion can severely limit the fatigue life and

ultimate strength of the material leading to mechanical failure of the dental materials [2, 3]. High biocompatibility, chemical stability, good aesthetic characteristics, flexural strength and fracture toughness are essential for dental materials in order to allow an efficient restoration of the tooth appearance and functionality. Biomedical grade yttria stabilized zirconia (YSZ), has been intensely investigated for this purpose. YSZ possess high flexural strength, high toughness, chemical inertness, and corrosion resistance with biocompatibility in the oral cavity. They are chemically inert materials, allowing good cell adhesion compared to other dental ceramics [4–8]. There have been several methods (electrodeposition [9], metal-organic chemical vapour deposition [10], Plasma spraying [11], Micro-arc oxidation [12], electrochemical [13] and electrophoretic deposition (EPD) [14], etc.) are available for deposition of YSZ material for various applications. But, these methods required highly sophisticated equipment for depositing the ceramic materials. Moreover, uniformity of the coatings remain challenging. On the other hand, electrophoretic deposition (EPD) process required simple equipment and provides highly packed uniform coating from the alcoholic suspension [15]. The advantages of EPD process includes rate of deposition can be controlled by varying applied voltage, low cost and coating process can be completed in a few minutes [16].

Optimization of applied voltage for the deposition of nano YSZ and its electrochemical behavioural studies are rarely reported. Hence, in this paper we report the deposition of nano YSZ material on metal substrate by EPD process and its electrochemical studies in artificial saliva for dental applications.

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Materials and Methods

Nano YSZ (99.99%) (Particle size < 100 nm) obtained from Saint Gobain, China. All other chemicals and solvents used in the following experiments were of analytical grade.

Substrate preparation

316L stainless steel metallic substrates were grounded and polished according to the ASTM F-89 standard [17]. The substrates were gently washed in dil. HCl, soap oil, and ultrasonically cleaned in acetone. The cleaned substrates were stored in desiccators before EPD process.

Suspension preparation

To prepare 1% nano YSZ suspension, the nano YSZ powder was finely grounded in mortar and pestle then accurately weighed 2 grams of nano YSZ and then mixed with 50 ml of isopropyl alcohol in a 100 ml beaker. The obtained suspension were placed in ultrasonicator for 10min to get agglomerate free suspension. The 1.2 cm² of 316 L SS were used as cathode and 314 stainless steel used as anode.

YSZ deposition on metal substrate by EPD process

The 316L SS specimens were encapsulated in Teflon and electrodes were totally immersed in the 2% YSZ suspension so that only the uncovered substrate face in front of the anode can be coated. A magnetic stirrer was used in order to avoid particle sedimentation. A power source was used to apply the desired current density to the suspension for a fixed time. The coatings were deposited from 30 to 90 V to study the effect of deposition at a constant time of 5 minutes. The YSZ coated 316L SS samples are removed from the bath and dried at room temperature then the dried samples were sintered at 800 °C at vacuum furnace.

Characterization

The crystalline phase of the YSZ deposited samples were investigated by X-ray diffractometer (Bruker model D8) using Cu K_α radiation $\lambda = 1.5406 \text{ \AA}$. Raman spectra were analysed on a JEOL-JRS-S1 spectrophotometer (double grating monochromator and photon counting system). The uniformity and microstructure of the YSZ deposits on metal substrate was observed by Optical microscopy using Leica microscope (Leica, model DM 2700 M). The morphology of the YSZ deposited samples were taken by field emission scanning electron microscopy (FESEM) (Model Carl Zeis Supra 55) and the elemental analysis was carried out using energy dispersive X-ray analysis (EDAX) system attached to FESEM.

The electrochemical behavior of both uncoated and YSZ coated 316L SS samples were analyzed in artificial saliva. Electrochemical studies were operated by a

conventional three electrode system at room temperature ($25 \pm 1^\circ\text{C}$). A saturated calomel electrode (SCE) and graphite electrode were used as reference electrode and counter electrode respectively. The electrochemical studies such as an open circuit potential (OCP)-time measurements, Cyclic potentiodynamic anodic polarisation (CPP) and electrochemical impedance spectroscopic studies (EIS) were carried out using Biologic-SP240 for both bare and YSZ coated 316 L SS samples. The flat corrosion cell were used for electrochemical measurements, where the area of the sample dipped in solution was 1.0 cm². The current density (I_{corr}) and corrosion potential (E_{corr}) for both YSZ coated 316 L SS and uncoated samples were calculated from the polarisation curve by means of Tafel fit. Potentiodynamic anodic polarisation was originated after the samples touched a constant potential. The potential was increased from 0.250 V below the E_{corr} and the passivation region was reached at a scan rate of 1.67 mVsec⁻¹. EIS studies were carried out at OCP condition with the frequency range from 10 kHz down to 10 mHz.

Result and Discussion

The coating weight of YSZ on 316L SS is shown in Fig. 1. From the Fig. 1(a) we can observe that the coating weight is increased from 30 to 70 V and it starts decreases at 80 V. As the coating potential increases the particles moves rapidly and there would not be proper packing of the particles owing to develop on the metallic substrate [18]. At higher potentials there exists significant hydrogen gas evolution at the working electrode which results in more pores on the surface of coatings. There would not be proper cohesion of the particles on the substrate which leads to very thin coatings with more porous and crack formation on the coatings [19]. The change in coating thickness of YSZ with change in applied potential is given in Fig. 1. The coating thickness can be calculated from the following equation [20].

$$\text{Coating thickness} = \text{weight gain (g/m}^2\text{)} / \text{surface area (cm}^2\text{)} \times \text{density (g/cm}^3\text{)} \quad (1)$$

The theoretical density of YSZ is found to be 5.6 g/cm³. The coating thickness was increased from 30 to 70 V and gradually decreased from 80 V onwards. It is observed that the above 80 V, particles distribution on the substrate is not uniform. Macroporous and as well as crack formation on the coatings were observed at above 80 V. The maximum weight gain was observed at 70 V and 5 minutes with coating thickness varies from 23 to 24 μm . YSZ coatings on stainless steel at this coating potential showed uniform distribution of the particles on the whole substrate. The coating thickness of YSZ at 30 V to 50 V varies from 15 to 18 μm . The movement of the particles towards the electrode

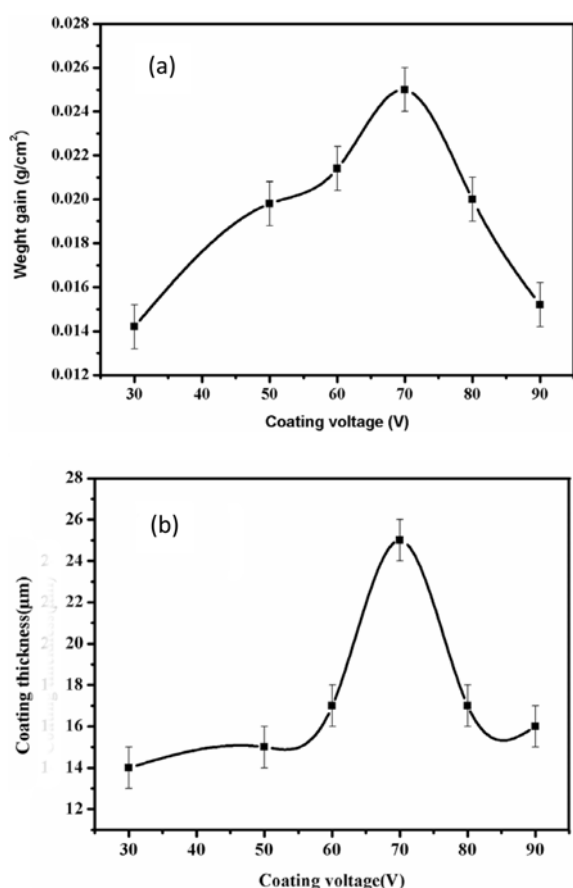


Fig. 1. (a) Weight gain and (b) coating thickness of nano YSZ deposits on 316L SS with respect to applied voltage.

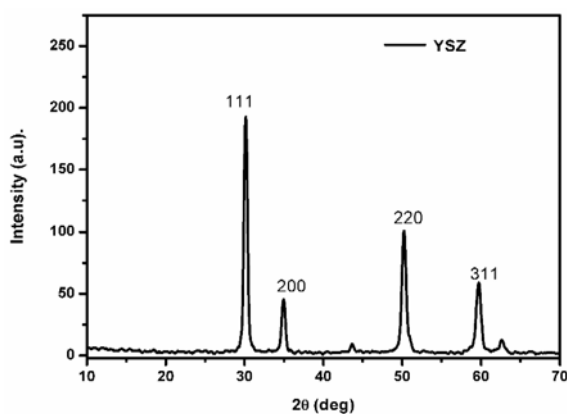


Fig. 2. X-ray diffraction of nano YSZ coated on 316L SS sample.

depends up on the given applied field [18]. Thus, at low coating potential lesser number of particles gets deposited on the substrate and hence we observed thin coatings on the metallic substrate. The coating thickness calculated at 80 to 90 V varies from 17 to 15 μm. The decrease in coating thickness above a coating potential of 80 V is due to the improper collision of the particles because of its rapid movement at higher potentials. Also, hydrogen evolution exist at higher potentials near cathode reduce the formation of

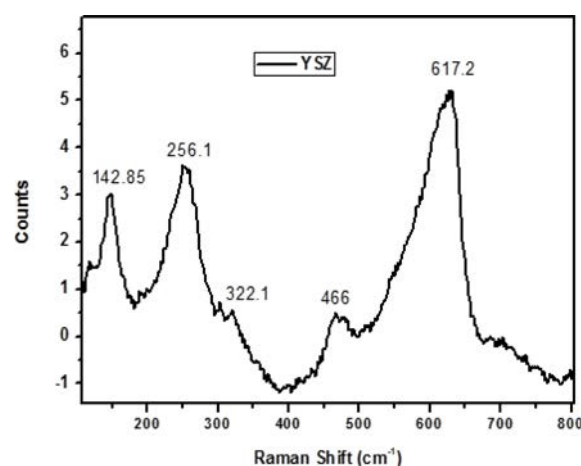


Fig. 3. Raman spectra of nano YSZ deposits on 316L SS.

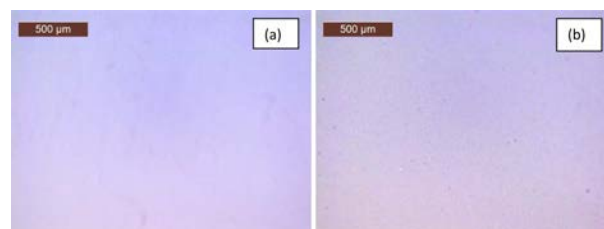


Fig. 4. Optical microscopic images of YSZ coated on 316L SS (a) before sintering (b) after sintering.

thick and uniform layer on the metallic substrate. Thus, from the above results we observed that the maximum weight gain with desired thickness was observed at 70 V and 5 minutes.

The XRD pattern of the nano YSZ deposited on 316LSS after vacuum sintering is given in Fig. 2. The sharp peaks reveal that the coatings are highly crystalline in nature and confirm the presence of YSZ on 316L SS. The peaks are indexed with standard JCPDS file No. 82-1246 confirming the presence of YSZ. No peaks of impurities are observed thus indicating that pure nano YSZ phase binding on 316L SS.

The phase composition of the coatings was investigated with Raman spectroscopy, which is very sensitive to the zirconia polymorphs. Typical spectra of the deposited films are shown in Fig. 3. As can be seen in this figure, the films show only the cubic phase with no evidence of residual tetragonal or monoclinic zirconia and are in agreement with the XRD investigation.

Optical microscopic images of YSZ coated 316L SS samples (70 V for 5 minute), (a) before sintering and (b) after sintering and are given in Fig. 4. It is observed that the obtained coating shows uniform deposition, crack free and non-porous. The pit and porosities are not observed in both before and after sintered samples.

Fig. 5 shows the FESEM of the optimized sample (70V for 5 minute) before and after sintering. The spherical shape of the YSZ particles were observed

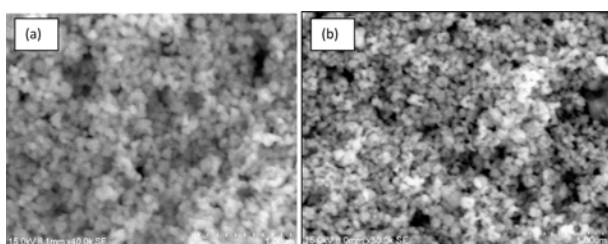


Fig. 5. FESEM images of nano YSZ coated sample: (a) before sintering (b) after sintering.

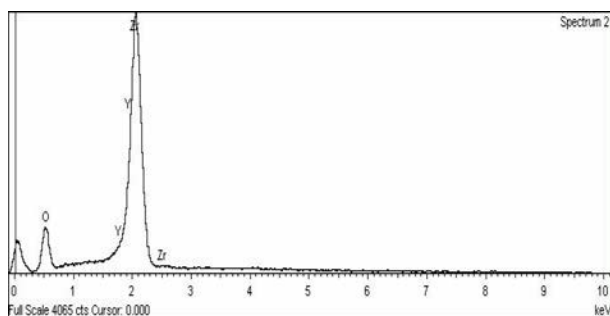


Fig. 6. EDAX spectrum of nano YSZ coated on 316L SS sample obtained after Sintering.

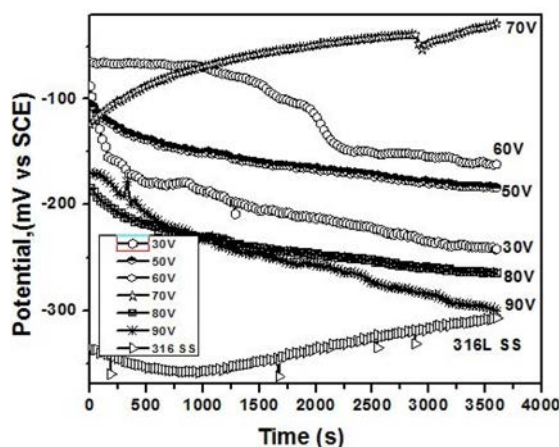


Fig. 7. Open circuit potential time measurement for nano YSZ coated on 316L SS at coating potentials ranging from 30-90 V in comparison with uncoated 316LSS.

with the particle size ranges between 40-80 nm and distributed uniformly on the metal substrate. It can be seen that the sintered sample shows shrinkage in the coating when compared to un-sintered sample surface, but the uniformity of the coating was unaffected. This indicates the particles are closely packed on the metal surface.

The EDAX analysis of YSZ deposited on 316L SS (70 V for 5 minutes, after sintering) given in Fig. 6. It confirms the presence of oxygen, Zr, along with Y peaks. This further confirms the absence of impurities from the base metal and decomposition of zirconia and formation of new products on the surface.

The OCP time measurements carried out in equilibrium condition between reference electrode and the working

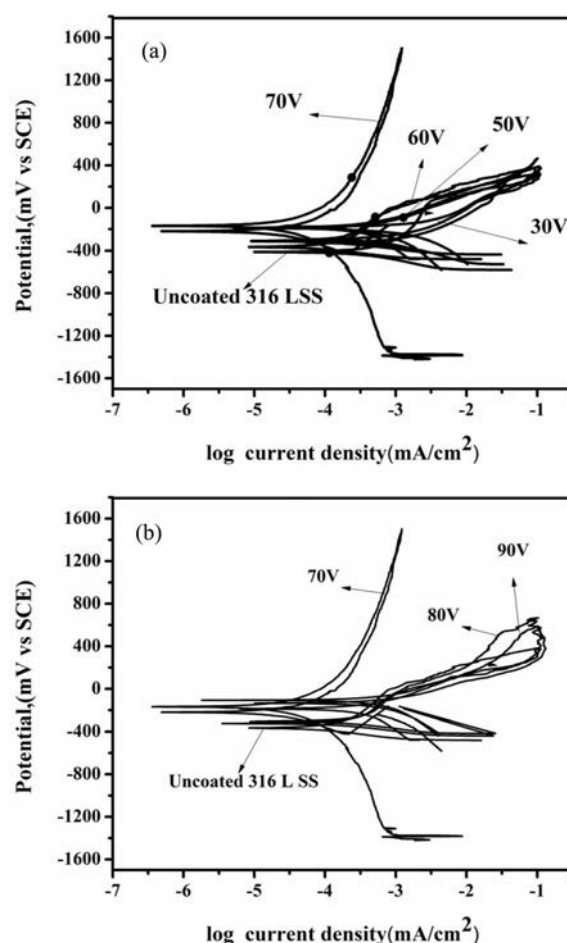


Fig. 8. Potentiodynamic cyclic polarization curves for nano YSZ coated on 316L SS at coating potentials ranging from 30-90 V in comparison with uncoated 316LSS.

electrode [21]. OCP for both uncoated and nano YSZ coated 316L SS (30 to 90 V) after sintering in artificial saliva is shown in Fig. 7. We can observe that the uncoated samples shift towards more active direction. The OCP potential of uncoated sample after 60 minutes was found to be -307 mV. The more negative potential is due to the presence of single oxide layer on the surface which gets affected on immersing in the solution. This initiates the release of electrons from the surface and as well as interaction of ions towards the metals surface. Thus there is a chance of corrosion process involves on the metal surface. Nano YSZ coated 316L SS samples shift towards nobler direction when compared to uncoated sample. This is due to the protective nano YSZ coatings on the metal surface. The OCP of nano YSZ coated sample at 70V and 5 minutes shift towards more positive direction when compared to uncoated sample. The OCP potential reached after 60 minutes was found to be -28.2 mV. The less negative potential is due to uniform crack free coatings formation at 70 V for 5 minutes. Thus nano YSZ coated stainless steel at 70 V and 5 minutes showed better performance in artificial saliva when compared to uncoated sample.

Cyclic potentiodynamic polarization study is a destruction method which is used to check the stability of the coatings on the metal surface. It is carried out with the help of three electrodes immersed in artificial saliva. The current flow inside the cell can be measured with the help of counter electrode and the corrosion property of metal can be evaluated from the relation between current density per unit surface area and potential scanned.

The cathodic and anodic polarization curves of uncoated metal and nano YSZ coated 316L SS (30 to 90V) after sintering in vacuum at 800 °C is shown in Fig. 8. The corrosion parameters such as E_{corr} and I_{corr} values was calculated from Tafel fit analysis on the polarization curves. E_{corr} and I_{corr} values for uncoated and coated samples is shown in Table 1 Higher the corrosion potential and lower the corrosion current density leads to more protective nature of coatings for the metal surface from the corrosion process. It means high potential is required for the penetration of ions in to the metal surface and the current density is low because of the reduced movement of ions in to the solution. From Table 1 we can observe that all the nano YSZ coated samples has high E_{corr} and low I_{corr} values when compared to uncoated sample. The E_{corr} and I_{corr} values for uncoated sample were found to be -425 mV and 2.308 $\mu\text{A}/\text{cm}^2$ respectively. The decrease in E_{corr} and increase in I_{corr} value is due to the ions in solution can easily try to penetrate in to the passive layer of the metal surface. The E_{corr} and I_{corr} values for nano YSZ coated sample at 70 V and 5 minutes were found to be -230 mV and 0.018 $\mu\text{A}/\text{cm}^2$ respectively. The increase in E_{corr} and decrease in I_{corr} value for this coating potential is due to the uniform coatings with desired thickness, microporous and no crack formation were observed on the whole substrate. This prevents the release of ions from the metal surface in to the solution. The coating potential of 30, 50, 60, 80, and 90 V have high E_{corr} and low I_{corr} values when compared to

uncoated metal. These results show that the optimized potential for nano YSZ coatings was found to be 70V and 5 minutes. Nano YSZ coatings with microporous and crack free coatings exhibits high corrosion resistant to the metal surface and hence extends its metal surface.

Electrochemical impedance study is a non-destructive method which is carried out in equilibrium condition and it is used to understand the protection efficiency of the coatings in terms of its impedance value. Both Nyquist and Bode plots were analysed to evaluate the corrosion behaviour of uncoated and nano YSZ coated 316L SS in artificial saliva. Fig. 9 shows the Nyquist plot for both uncoated and YSZ coated 316L SS at 30 to 90 V. We can observe that all the coated samples show maximum impedance when compared to uncoated stainless steel. nano YSZ coated sample at 70 V and 5 minutes showed maximum impedance when compared to other coated sample and as well as uncoated sample. An equivalent circuit is shown in the inset of Fig. 9. The circuit is obtained by fitting the Nyquist and Bode impedance spectra on the curves using Biologic SP-240 instrument (EC-Lab V10.37 software). The most suitable spectra are selected on the basis of best fitting with small chisquare values. The fitted EIS results for all coated and as well as uncoated sample were tabulated in Table 1. The EIS spectra were fitted with model $[R_s(R_2C_2)]$ and $[R_s(R_1Q_1)(R_2Q_2)(R_3C)]$ to characterize the uncoated and nano YSZ coated 316L SS respectively as shown in inset of Figure. The components present in the circuit for uncoated sample is represented as follows: R_s represents the solution resistance, R_2 and C indicates polarisation resistance and capacitance of metal surface respectively. The components present in the circuit for nano YSZ coated sample is represented as follows: R_s represents the solution resistance, R_1 and Q_1 represents polarization resistance and constant phase element (CPE) of coated layer respectively. R_2 and Q_2 represent polarization resistance and constant phase element of passivation layer on the metal surface. R_3 and C indicates polarization resistance and capacitance of metal surface respectively. CPE is introduced in the EIS fitting results of nano YSZ coated 316L SS. Generally CPE does not act as pure capacitor [23]. CPE is introduced in the coated and passivation layer where we observed high polarization resistant values. It means nano YSZ coatings on the metal surface were tightly packed with uniform coatings on the whole substrate. The impedance of CPE can be defined by the equation [22, 23].

$$Z_{\text{CPE}} = 1 / [(j\omega)^n Q] \quad (2)$$

Q is the constant phase element, ω is the angular frequency and n is the exponent of CPE which is associated with non-uniform distribution of current and due to surface roughness with values between -1 and 1

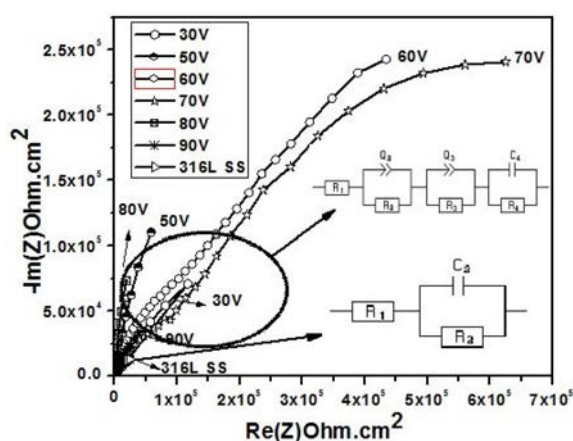


Fig. 9. Nyquist impedance for nano YSZ coated on 316L SS at coating potentials ranging from 30-90 V in comparison with uncoated 316LSS.

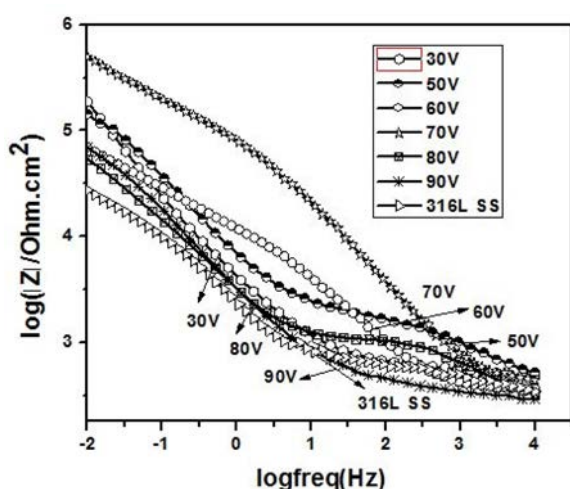


Fig. 10. Bode impedance for nano YSZ coated on 316L SS at coating potentials ranging from 30-90 V in comparison with uncoated 316LSS.

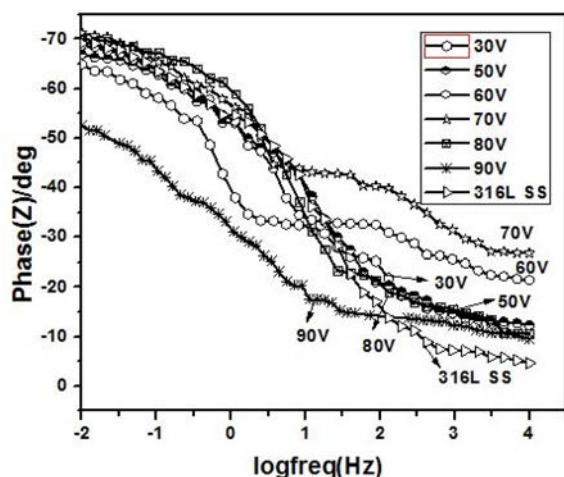


Fig. 11. Bode phase for nano YSZ coated on 316L SS at coating potentials ranging from 30-90 V in comparison with uncoated 316LSS.

($0 < n < 1$). If n is equal to 1 it behaves as an ideal capacitor and if n is equal to 0 it represents a pure resistor. From the Table 1 we can observe that n value for uncoated sample is 0.81 which is nearly equal to one. This is due to the presence of single passive layer on the metal surface which has direct contact to the ions

present in the solution. But the n value for nano YSZ coated layer on the metal surface was in the range of 0.58 to 0.67. This reduced value is due to tightly packed nano YSZ coatings on metal surface. The passivation layer present in between the coated layer and the metal surface which is free of ions and has reduced n value in the range of 0.51-0.65. Out of these n values for YSZ coated samples, the coating potential at 70 V and 5 minutes showed very low CPE with least n value. This shows more protective nature of nano YSZ coatings with uniform and no crack formation at 70 V and 5 minutes.

From the Table 1 we can observe that polarization resistance of coated layer (R_1) value is very high than polarization resistance of passivation layer and metal surface. The polarization resistance value were increased from 30 to 70 V and decreased at 80 and 90 V. Also the capacitance values were decreased from 30 to 70 V and increased at 80 and 90 V. These results were obtained due to crack free coatings on the substrate from 30 to 70 V and cracks formed with macro pores on the coated surface at 80 and 90 V. Nano YSZ coated sample at 70 V and 5 minutes showed high polarization resistance and very low capacitance value than other coating potential and uncoated sample. This is due to uniform coatings with crack free and desired thickness obtained at this coating potential. This helps in protecting the metal surface from the penetration ions present in the solution for the corrosion process.

Bode impedance plot and Bode phase plots are shown in Figs. 10 and 11, respectively. From the Bode impedance plot (Fig. 10), we can observe that from the low frequency to high frequency all the coated samples has maximum impedance when compared to uncoated sample. Nano YSZ coated sample at 70 V and 5 minutes showed maximum impedance value when compared to other coating potential and uncoated sample. From the Bode phase plot (Fig. 11), we can observe that the phase angle shift for uncoated sample is around -70° and is constant from low frequency to high frequency region (10^{-2} to 10^2 Hz). This is due to the presence of single passive layer on the metal surface [24]. The maximum phase angle was observed for nano YSZ coated sample at 70V and 5 minutes when compared to other coating potential and uncoated sample. In the mid frequency region there is more shift in phase angle for

Table 1. Electrochemical impedance parameters for nano YSZ coated on 316L SS at coating potentials ranging from 30-90 V in comparison with uncoated 316LSS.

Coating potential	$ Z \Omega \text{ cm}^2$	$R_s \Omega \text{ cm}^2$	$Q_{\text{coat}} (\text{F cm}^{-2} \text{ s}^n)$	n_{coat}	$R_1 (\text{coat})$	$Q_b (\text{F cm}^{-2} \text{ s}^n)$	n_b	$R_2 \Omega \text{ cm}^2$	$C_{dl} \text{ F cm}^{-2}$	$R_3 \Omega \text{ cm}^2$
Uncoated	38547.2	388	----	0.81	190.5	----	----	----	3.933×10^{-5}	534.5
30V	83790.6	354	0.140×10^{-3}	0.67	52375	28.42×10^{-6}	0.65	55219	0.866×10^{-7}	4836
50V	109919.3	168	5.948×10^{-6}	0.64	109798	0.1974×10^{-3}	0.61	179237	32.12×10^{-8}	19549
60V	204135.1	58	0.624×10^{-3}	0.62	179237	78.29×10^{-6}	0.60	331939	72.05×10^{-8}	22846
70V	265641.5	33	6.431×10^{-6}	0.58	443688	0.34×10^{-6}	0.51	357895	0.161×10^{-9}	75894
80V	72258.1	106	0.350×10^{-3}	0.71	41094	0.4872×10^{-3}	0.69	53752	84.82×10^{-6}	2249
90V	61876.3	102	4.145×10^{-6}	0.75	6071	48.43×10^{-6}	0.72	5839	12.56×10^{-6}	1953

this coating potential. It means the interaction of ions in to the metal surface is high, because of tightly packed nano YSZ coatings on the metal surface. Thus nano YSZ coatings at 70V and 5 minutes with uniform and crack free coatings showed maximum impedance and phase angle value and thus it could improve the corrosion resistant behaviour of the metal surface.

Conclusions

Bio inert nano YSZ deposits were developed on 316L SS by simple and inexpensive EPD technique. Crack free uniform nano YSZ coatings on 316L SS were obtained at 70 V and 5 minutes by EPD followed by sintering at 800 °C in vacuum. XRD and FESEM analysis confirmed that the deposited YSZ on metal substrate to be that of the nanometric YSZ. The micrographs proved that the particles were roughly spherical with an average size of nano YSZ in the range of 40-80 nm. Raman spectra confirm the coating is in cubic nature which is good agreement with XRD pattern. The average grain size calculated from XRD was 23.8 nm. The electrochemical studies in artificial saliva revealed that the nano YSZ coated samples exhibit higher corrosion resistance than bare 316L SS sample. The OCP shifted towards the nobler direction for the nano YSZ coated samples along with better polarization resistance and lower capacitance values from EIS measurements. The electrochemical studies confirm that the better stable nano YSZ coating obtained only 70 V at 5 minutes time. Nano YSZ coated 316L SS at 70 V could be active as a good barrier against corrosive ions and resist ions penetration from artificial saliva to the metal surface. Hence, the optimized (70 V for 5 min) nano YSZ coated 316L SS samples would open up a new way to fabricate dental implants.

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References

1. J.J. Jacobs, J.L. Gilbert, R.M. Urbani, J. Bone Joint Surg Am. 80 (1988) 268-82.
2. K.J. Anusavice editors. Phillips's science of dental materials. 11th ed. Saunders-Elsevier; (2003) 56-70.
3. K. Yokoyama, T. Ichikawa, H. Murakami, Y. Miyamoto, K. Asaoka, Biomaterials 23 (2002) 2459-2465.
4. M. Cortada, L. Giner, S. Costa, F.J. Gil, D. Rodriguez, J.A. Planell, J. Mater. Sci. Mater. Med. 11 (2000) 287-93.
5. P.F. Manicone et al., Journal of Dentistry 35 (2007) 819-826.
6. I. Denry et al. Dental Materials Journal 24 (2008) 299-307.
7. R.J. Kohal, W. Att, M. Bächle, F. Butz, Periodontol. 47 (2008) 224-243.
8. I. Denry, J.R. Kelly, Dent. Mater. 24 (2008) 299-307.
9. F. Daftary, T. Donovan, Journal of Prosthetic Dentistry 57 (1987) 41-46.
10. K.L. Choy, Progress in Materials Science 48 (2003) 57-170.
11. Y. Zeng, S.W. Lee, L. Gao, C.X. Ding, Journal of the European Ceramic Society 22 (2002) 347-351.
12. X. Nie, A. Leyland, A. Matthews, Surface and Coatings Technology, 125 (2000) 407-414.
13. O. Jude, W.S. Iroh, Electrochimica Acta 46 (2000) 15-24.
14. O. van der Biest, J.V. Joos, B. Baufeld, Journal of Materials Science 41 (2006) 8086-8092.
15. T.M. Sridhar, N. Eliaz, U.K. Mudali, B. Raj, Corros. Rev. 20 (2002) 255-293.
16. J.-H. Yum, S.-S. Kim, D.-Y. Kim, Y.-E. Sung, Journal of Photochemistry and Photobiology 173 (2005) 1-6.
17. F. George, V. Voort, and ASM Handbook Vol. 9: Metallography and Microstructures, ISBN: 978-0-87170-706-2.
18. L. Besra, M. Liu, Progress in Materials Science 52 (2007) 1-61.
19. K.D. Harris, D. Vick, E.J. Gonzalez, T. Smy, K. Robbie, M.J. Brett, Surface and Coatings Technology 138 (2001) 185-191.
20. I. Zhitomirsky et.al, J. Mater. Sci.: Mater. Med. 8 (1997) 213-219.
21. S.K. Tiwari, J. Adhikary, T.B. Singh, R. Singh, Thin Solid Films 517 (2009), 4502-4508.
22. G.J. Brug, A.L.G. van den Eeden, M. Sluyters-Rehbach, J.H. Sluyters, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry 176 (1984) 275-295.
23. S.P. Vinodhini, B. Venkatachalapathy, T.M. Sridhar, Journal of Ceramic Processing Research 17 (2016) 947-955.
24. Q. Mohsen, A. Sahar, Fadl-allah, S. Nahla. El-Shenawy, Int. J. Electrochem. Sci. 7 (2012) 4510-4527.