Shot peening effects on corrosion behavior of Hydroxyapatite coated AISI 316L Stainless steel alloy for medical implant application

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Abstract:

The effect of several Almen intensities of shot peening on the corrosion behavior, surface roughness, micro hardness profiles, and residual stresses of stainless steel AISI 316 L were investigated. Hydroxyapatite coating (HA) were applied to shot peened materials to improve their corrosion resistance. The corrosion behaviour were studied using potentiodynamic polarization. The electrochemical tests were performed in HANK solution. The results show that shot peening can be enhancement the mechanical properties (microhardness and residual stresses) and increasing the pitting corrosion on stainless steel 316L. Shot peening generates a rough surface, which is possible one of the causes of decreasing the corrosion resistance of AISI 316L. The deposition of hydroxyapatite over shot peened surface proved the excellent results for stainless steel corrosion.

Keywords: shot peening, corrosion, hydroxyapatite coated, stainless steel

Introduction

Austenitic stainless steel (especially medical grade of 316L stainless steel) is utilized as an implant material to make devices like artificial joints, bone plates, stents and prosthesis, because it has good mechanical properties , high corrosion resistance and relatively low cost compared with other metallic biomaterials [1]. Corrosion is one of the most significant phenomena which happens for the alloys or metals used as implants in the body [2]. Because of the high concentration of chloride ions (Cl^-) and temperature range of the body (36.7–37.2 °C), the human body fluid is considered as a severely corrosive environment. Studies on retrieved implants show that more than 90 % of the failure of implants of AISI 316L SS is due to localized electrochemical cells resulting in pitting attack, or crevice corrosion at the interface between a plate and a locking screw [3]. Despite these problems, stainless steel implants are still currently used due to a combination of corrosion resistance, mechanical strength, ductility, toughness and easy fabrication at low cost [4]. Failures of these materials such as corrosion, fatigue fracture and wear are initiated from their surface layer. Improvements of metals performance are therefore often done through the optimization of surface microstructure and properties [5]. Coatings [6], deep rolling [7] and surface mechanical treatments [8] are among the techniques, which are used for this purpose. The surface condition of an alloy has the most effect on these phenomena and a very limited number of surface modification techniques can be applied to austenitic stainless steels without causing any loss of their advantageous properties [9]. Sandblasting and shot peening [10-11] are among the examples of this treatment. Sandblasting and shot peening are principally performed by affecting the particles onto the sample surface by means of pressurized airflow. The corrosion studies of metallic materials after particle or shot blasting treatments have been reported in literatures. Refs. [10,11] indicates a reduction in corrosion resistance after sandblasting, shot peening and surface mechanical attrition treatment (SMAT). The reduction in corrosion resistance is related to the formation of a rough surface of the treated samples. Surface modifications produced by the shot peening treatment are increase roughening of the surface. Topographical modifications to implants have shown that rougher surfaces obtained by shot peening on implants presented a better osseous integration compared to smooth surfaces. This is due to the increased bone implant contact [12]. Hydroxyapatite (HA) coatings are also widely employed to enhance the osseous integration of orthopaedic and dental implants [13]. These coatings [$Ca_5(PO_4)_3OH$] consists 39.9 % Ca, 18.5 % P, 41.4 % O and 3.4 % OH (values in percent by weight) and the Ca/P molar ratio is 1.67. This chemical composition resembles the mineral component of human bones and hard tissues [14]. In this paper, the shot peening were used with different Almen intensity as a surface mechanical treatment onto the surface of AISI 316L stainless steel. Effects of this treatment on microhardness, surface structure, roughness evolution and corrosion resistance of the stainless steel are investigated. Corrosion tests were carried out in Hank solution as a simulated body fluid. In addition, hydroxyapatite coating (HA) will be applied to shot peened samples to enhance their corrosion resistance and biocompatibility.

Experimental Work

Simple disk specimens of AISI 316L stainless steel with a diameter of 25 mm were used for all investigations. The samples chemical compositions (wt%) are 0.03 C, 24.30 Cr, 11.96 Ni, 1.75 Mo, 1.24 Mn, 0.44 Si, 0.86 Cu, and balanced Fe. Shot peening was performed on Injektoranlage model 1000 shot peening machine utilizing different Almen intensities of 0.17, 0.24 and 0.28 mmA respectively. Mixture of SiO2 and ZrO2 ceramic balls with the diameter of 850 µm was used as a peening medium. The phase transformation after shot peening was recorded by X-ray diffraction (XRD) spectra. Microhardness was determined by using a Struers Duramin tester with a force of 100 ponds (HV0.1) and a loading time of 10 s. Residual stresses were evaluated with the incremental hole drilling technique using an oscillating drill with a 1.9 mm diameter driven by an air turbine with a rotational speed of 200,000 rpm. The as-received material were ground to 600 grit using silicon carbide (SiC) papers. As received and shot peened samples then ultrasonically cleaned in ethanol bath. The samples were coated by hydroxyapatite (HA) coating using chemical method. The surface morphology and composition of CaP coatings were identified by SEM and EDX. After applying the various surface treatments, the surface roughness was determined by a profilometer from Perthen Company. The electrochemical polarization measurements were carried out in a round bottom polarization cell using VersaSTAT3 potentiostat from the Princeton Applied Research company, interfaced to a computer. The electrolyte used for simulating human body fluid conditions was Hank solution, prepared using laboratory grade chemicals and distilled water. Freshly prepared solution was used for each experiment. The composition of the Hanks solution used was (in gm/l) 8.6 NaCl, 0.3 KCl, and 0.48 $CaCl_2$. A conventional three-electrode cell was used, the counter electrode was a platinum sheet and all the potential values were reported relative to saturated calomel electrode (SCE). Haber Luggin capillary was placed close to the working electrode. A constant electrolyte temperature of 37±1°C was maintained using a heating jacket. All the potentiodynamic polarization studies were conducted after stabilization of the free corrosion potential. The scan rate used was 1 mV/s. The corrosion rate was determined using the Tafel extrapolation method. The surfaces of the corroded samples were examined by SEM.

Results and Discussion

3.1 Surface structure

Metallographic examination of the cross-section of shot peening specimen at high Almen intensity (0.28 mmA) exhibited large numbers of severe plastic deformation near the surface and large difference in the grain size of modified surface layer and the unaffected substrate beneath it. The grain size in the modified layer registered an increase with distance from the surface as shown in Fig. 1. Liu et al. reported significant grain refinement and severe plastic deformation in the top 30 nm thick surface layer in type 316L SS because of ultrasonic shot peening [15]. In order to study phase transformation taking place during shot peening surface treatment of 316 stainless steel specimens were subjected to XRD. Fig. 2 shows the XRD patterns of the surface layer of as-received sample and 0.28 mmA shot peened sample. It can be seen from Fig. 2 there is no significant effect of shot peening on the austenite transformation. D. Kirk and N.J. Payne reported that no martensite transformation occur even with gross surface plastic deformation in the AISI 316 stainless steel whilst martensite formation was easily induced by plastic deformation in the

AISI 304 stainless steel. The reason for this is attributed to the higher nickel content in the AISI 316 stainless steel that made the austenite phase more stable [16]. The big difference between the intensities of XRD patterns of as-received and shot peened samples refers to high roughness and defects of shot peened comparison with as-received sample. Microhardness distributions across the samples sectional areas with various almen intensity shot peening process (0.17, 0.24 and 0.28 mmA) are shown in Fig. 3. The shot peening treatment increases the microhardness of samples surface and subsurface. The microhardness of the shot peened samples decreases gradually and approaches the values of the control (230 HV 0.1) as the increasing distance from the surface. The increase in the almen intensity enhances the surface microhardness and the thickness of the hard layer, however, the effect of shot peening is limited to a very small depth of deformed layer. Fig. 4 shows the residual stress-depth distribution in 316 L stainless steel after shot peening treatment with 0.28 mmA Almen intensity. Shot peening surface treatments resulted in residual compressive stresses with pronounced maxima below the surface.

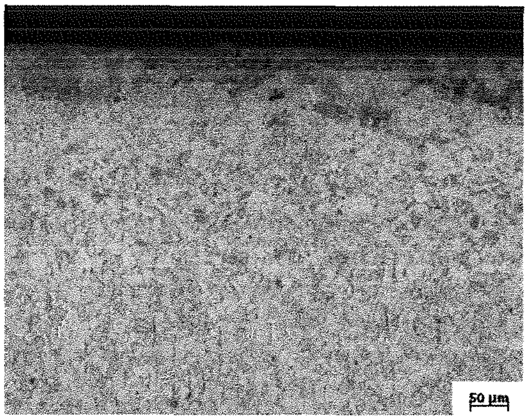

Fig. 1 Cross-section of 0.28mmA SP specimen showing modified surface layer

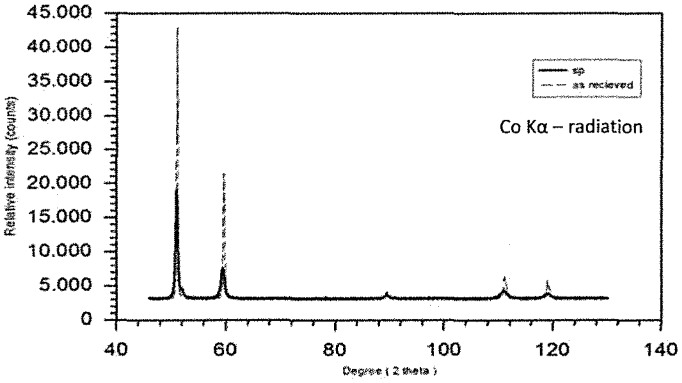

Fig. 2 XRD spectra of the as received and 0.28mmA SP 316L stainless steel

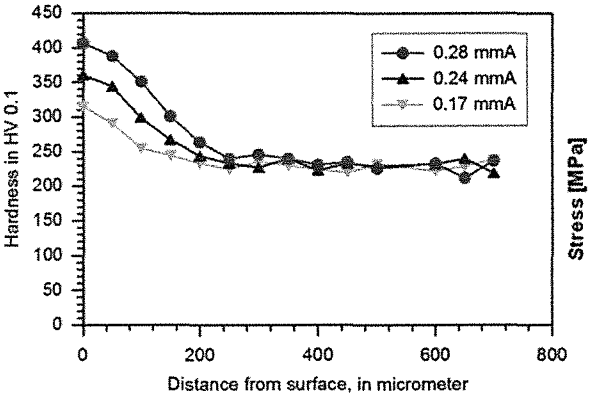

Fig.3 Microhardness-depth distribution after different Almen intensity shot peening.

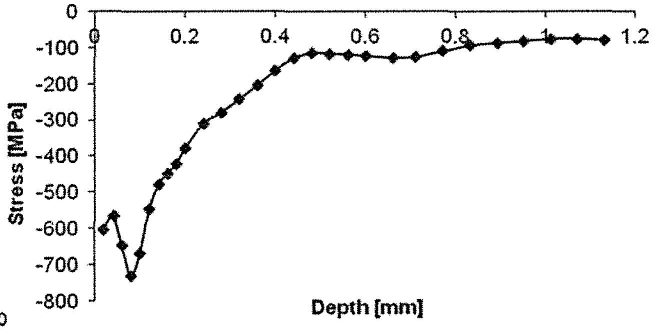

Fig. 4 Residual stress-depth distribution after 0.28 mmA shot peening.

Figure 5 shows a SEM micrograph of the formed HA coating on a shot peened sample with intensity 0.28 mmA. The HA coatings exhibit a acicular morphology. The obtained coatings were homogeneous, dense, crack-free and completely covered the substrate material. The coating shows a rough topography. The results of EDX analysis have the atomic % are: 60.2 O, 0.31 Na, 11.9 P, 1.0 K, 21.0 Ca, 1.1 Cr and 4.3 Fe shown that HA coating has an average Ca/P ratio of 1.76, which is close to the Ca/P ratio (1.67) of stoichiometric HA [$Ca_{10}(PO_4)_6(OH)_2$]. Table 1 shows surface roughness parameters (Rmax and Ra) of the samples during the shot peening treatment. Surface roughening is measured after shots peening as shown in table 2. The sample roughness increases from *Ra* = 0.55 to 0.77 µm during the Almen intensity 0.17 – 0.28 mmA of the treatment. The roughness markedly increases to reached *Ra* = 1.34 µm after coating by hydroxyapatite on the 0.28 mmA shot peened sample. The HA coated surface revealed markedly higher roughness values compared to the uncoated shot peened samples surface. Surface roughness has been reported as very important factors for implant tissue interaction and to affect the biocompatibility in clinical use [17]. The potentiodynamic polarization curves of shot peened and as received samples are shown in Fig. 7. According to table 2 and the polarization curves of specimens, at high shot peening intensity treatment, the corrosion potential (E_{corr}) of the passive layer and corrosion current density (i_{corr}) increases with respect to shot peened and un-shot peened specimens. It shows a decrease in resistance to pitting corrosion after shot peening treatment. Metallographic observations of samples surface after electrochemical tests showed numerous corrosion pits (Figure 8). It can be seen that the number, size and depth of corrosion pits on high intensity shot peened surface are more than that on the surface of lower shot peening intensity and as-received samples. Therefore, it can be concluded that high intensity shot peening treatment causes a reduction in the corrosion rate of the specimens. The corrosion studies of metallic materials after shot peening treatments have been reported in literatures. Refs. [18,19]

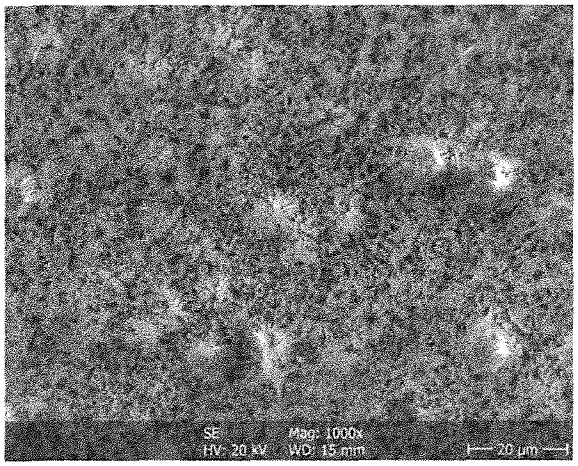

Figure (5) SEM micrographs of HA coating

Table 1 Roughness values

Shot peening conditions	Rmax/ µm	Ra/ µm
As received	0.55	0.05
0.17 mmA	4.54	0.55
0.24 mmA	4.72	0.67
0.28 mmA	5.13	0.77
0.28 mmA + HA coating	8.33	1.34

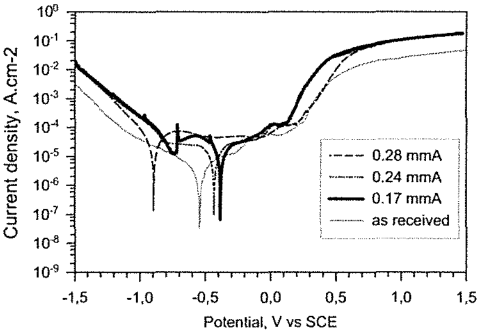

Fig. 7 Results of potentiodynamic corrosion

Table 2: Results of electrochemical corrosion of AISI 316L

Surface condition	current density, i_{corr}/ µA/cm^{-2}	potential E_{corr}/ mV	Corrosion rate/ mpy
As received	4.2	- 541	0.89
0.17 mmA	15.66	- 383	1.83
0.24 mmA	16.51	- 432	1.95
0.28 mmA	30.54	- 894	3.32
0.28 mmA+ HA coating	0.43	-330	0.18

indicates a reduction in corrosion resistance after shot peening. The reduction in corrosion resistance is related to the formation of a rough surface of the treated samples. the surface roughness and heterogeneity in the surface increase with intensity of shot peening. Therefore with increasing roughness and heterogeneity of the surface the preferred locations for initiation of pits increase. The large number of defects on the rough samples increases the practical area for corrosion per unit area [18]. The defects at the rough surface may also act as the pit initiation sites, which subsequently result in the destruction of passive region at the sample surface [19]. Ref. [20] reported that sandblasting increases the dislocation density of the microstructure, which is subsequently able to weakening bonding between the passive film and material surface. The reduction in corrosion resistance of metals by sandblasting is related to such impaired bonding of the passive film with the material surface. Other studies reveal the presence of surface compressive stress instead of roughness that influences the corrosion behavior of metals after sandblasting. The change in the internal parameters of the crystal lattice because of sandblasting causes a more reactive surface, which subsequently decreases the corrosion resistance of metals [11]. The effect of HA coating on the corrosion behaviour, in terms of potentiodynamic polarization, is represented in Fig. 9 and table 2. The figure shows the potentiodynamic polarization curves of the uncoated and shot peened 0.28 mmA + HA coating samples. It is clear that HA coating results in significant reduction of the corrosion current density. The corrosion potential E_{corr} shows a relative shift to the positive direction. The formation of the passive film is found to occur with wider potential range for HA coated materials in comparison with the un-coated materials. This indicates that the passivation through the HA coating significantly leads to the enhancement of the passive properties of the surface oxide film [21]. This passive film prevents the dissolution of the substrate into the electrolyte. The progressive enhancement of the corrosion resistance after coating is related to the good protection provided by the HA barrier between the substrate and the environment.

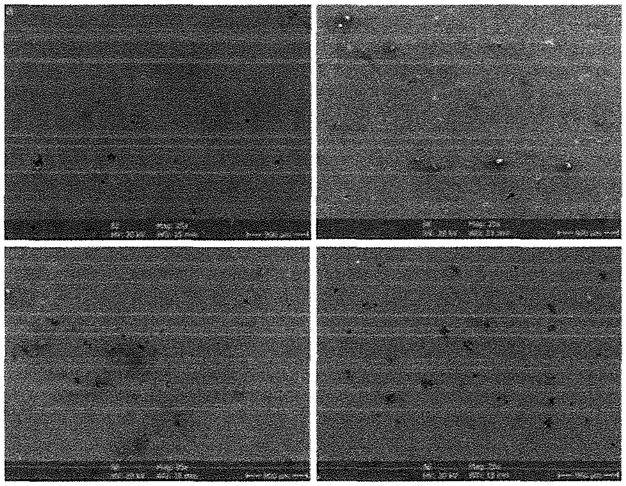

Fig. 8 SEM of surface morphologies of a) asreceived b) 0.17 mmA c) 0.24 mmA and d) 0.28 mmA

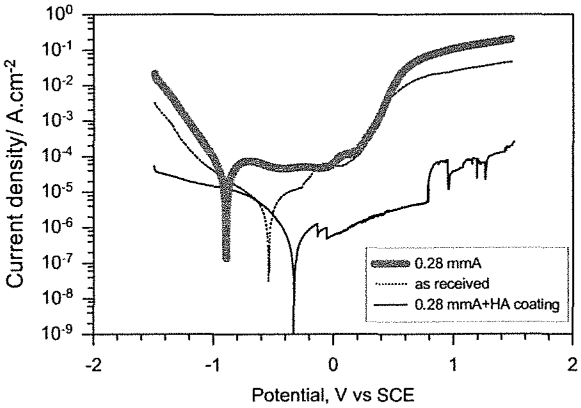

Fig. 9 Corrosion results of HA

Conclusions

The conclusions of this study can summarized with these points :

- The effect of the shot peening on microstructure , microhardness, surface roughness , and corrosion resistance of AISI 316L stainless steel was studied.
- Shot peening increases the surface microhardness and surface roughness of the steel by applied different Almen intensities

- The shot peening treatment decreases the pitting and corrosion resistance.
- Shot peening generates a rough surface, which is possible one of the causes of decreasing the corrosion resistance of AISI 316L.
- HA coating was homogeneous, dense, and completely covered the underlying substrate material.
- The HA coated surface revealed markedly higher roughness values compared to the shot peened samples surface.
- HA coating resulted in significant reduction of the corrosion current density and the corrosion rate.
- HA coating on the shot peened 316L SS material possesses a combination of good mechanical properties and an excellent corrosion resistance, and hence act as a promising implant material for biomedical applications.

References:

1. J. A. Disegil and L. Eschbachz, Stainless steel in bone surgery, Injured 31 (2000) p,D2
2. J.B. Park, R.S. Lakes, Biomaterials, 1992 An Introduction, Plenum Publishing.
3. M. Sivakumar and S. Rajeswari, J., Mater. Sci. Lett.,1992, 11, 1039 .
4. M. Terada, A. F. Padilha, A. M. P. Simo˜es, H. G. de Melo and Costa, Materials and Corrosion 2009, 60, No. 11
5. Tao NR, Wang ZB, Tong WP, Sui ML, Lu J, Lu K, J., Acta Mater. 2002; 50(18):4603-4616.
6. Berrios JA, Teer DG, Puchi-Cabrera ES, Surf. Coat. Technol. 2001; 148(2-3):179-190.
7. Nikitin I, Altenberger I, Maier HJ, Scholtes B, Mater. Sci. Eng. A. 2005; 403(1-2):318-327.
8. Lu K, Lu J, Mater. Sci. Eng. A. 2004; 375-377:38-45.
9. T. Kastilink, Surface Engineering, ASM Handbook, Vol 5, 1994, p 278
10. Azar V, Hashemi B, Yazdi MR, Surf. Coat. Technol. 2010; 204(21-22):3546-3551.
11. C. Aparicio, F.J. Gil, C. Fonseca, M. Barbosa, and J.A. Planell, Biomaterials, 24(2003), p. 263.
12. Lincks J, Boyan BD, Blanchard CR, Lohmann CH, Liu Y, Cochran DL, Dean DD, Schwartz Z. Biomaterials, 1998;19:2219–32
13. J. Dumbleton, M.T. Manley, J Bone Joint Surg Am. 86 (2004) 2526.
14. R. Gadow, A. Killinger, N. Stiegler, Surface & Coatings Technology 205 (2010) 1157–1164
15. G. Liu, J. Lu, and K. Lu, Mater. Sci. Eng., A, 2000, 286, p 91–95
16. D. Kirk and N.J. Payne, The 7th International conference on shot peening, 1999.
17. D.D. Deligianni, N. Katsala, S. Ladas, D. Sotiropoulou, J. Amedee, Y.F. Missirlis, Biomaterials 22 (2001) 1241}1251
18. Lee H, Kim D, Jung J, Pyoun Y, Shin K, Corr. Sci. 2009; 51(12):2826-2830.
19. Hao Y, Deng B, Zhong C, Jiang Y, Li J, J., Iron Steel Res., Int. 2009; 16(2):68-72.
20. Jiang XP, Wang XY, Li JX, Li DY, Man CS, Shepard MJ, Zhai T, Mater. Sci. Eng. A 2006; 429(1-2):30-35.
21. D. Gopi J. Indira L. Kavitha J. M. F. Ferreira, J Appl Electrochem, 2013, 43:331-345