Materials and Design 32 (2011) 3287–3292

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

The wear and corrosion resistance of shot peened–nitrided 316L austenitic stainless steel

B. Hashemi *, M. Rezaee Yazdi, V. Azar

Department of Material Science and Engineering, School of Engineering, Zand Street, Shiraz, Iran

ARTICLE INFO

Article history:
Received 20 December 2010
Accepted 11 February 2011
Available online 17 February 2011

Keywords:
C. Surface treatments
E. Corrosion
E. Wear

ABSTRACT

316L austenitic stainless steel was gas nitrided at 570 °C with pre-shot peening. Shot peening and nitriding are surface treatments that enhance the mechanical properties of surface layers by inducing compressive residual stresses and formation of hard phases, respectively. The structural phases, micro-hardness, wear behavior and corrosion resistance of specimens were investigated by X-ray diffraction, Vickers micro-hardness, wear testing, scanning electron microscopy and cyclic polarization tests. The effects of shot peening on the nitride layer formation and corrosion resistance of specimens were studied. The results showed that shot peening enhanced the nitride layer formation. The shot peened–nitrided specimens had higher wear resistance and hardness than other specimens. On the other hand, although nitriding deteriorated the corrosion resistance of the specimens, cyclic polarization tests showed that shot peening before the nitriding treatment could alleviate this adverse effect.

1. Introduction

The 316L austenitic stainless steel is used for making implants according to FMTSA138 standard [1]. This is due to its excellent corrosion resistance as a biomaterial. The presence of molybdenum in the steel increases its resistance to pitting corrosion in a chlorine-containing environment. However, this steel does not show a suitable resistance to wear and fatigue [2]. Thus, there have been some attempts to improve these features in 316L stainless steel utilizing proper surface treatments such as shot peening and nitriding [3–8]. Surface properties depend on structure and chemical composition of the surface layers, so any change or modification of these features can change the surface properties [3].

Shot peening is a surface treatment method that increases the surface hardness by creating the residual compression stresses due to incidence of balls to surface [9]. Nitriding is another surface treatment that is used to introduce nitrogen into the surface layers and produces hard phases, which improves surface hardness as well as wear resistance [10]. An increase in wear resistance and hardness without considerable loss of corrosion resistance could broaden the application of austenitic stainless steels. In fact, the nitriding treatment is performed in many cases with the purpose of increasing the resistance to wear and corrosion [10–12].

However austenitic stainless steel is known as a material to be hardly nitrided because of low nitrogen diffusion, due to close packed structure of austenite. Therefore, surface mechanical treatments not only improve hardness and wear resistance but also change the surface condition, which is effective in nitrogen diffusion. Grain refinement and increasing non-equilibrium defects in surface layers increase the diffusion rate [13,14].

In the present research, the effects of shot peening followed by gas nitriding treatment, as simple surface treatment methods, on the hardness, wear and corrosion behavior of 316L stainless steel were investigated. Because of applications of 316L austenitic stainless steel in human body, the ringer's solution was used as the corrosive environment. Ringer's solution has a composition similar to the body fluid.

2. Experimental

2.1. Specimens preparation

The initial material used in this work was a 316L stainless steel sheet, 3 mm in thickness. The chemical composition of this steel was analyzed using a quantometer model Hilger CT9-4JL (Table 1).

Corrosion and wear test specimens were prepared in sizes of 1 cm × 1 cm and 2 cm × 6 cm respectively. The specimens were grinded up to 1000 mesh SiC paper to achieve a fine finished surface. Then the samples were cleaned by distilled water in an ultrasonic cleaner for 15 min. The shot peening treatment was performed on some of the samples for 15 min using a SBRT-ISO shot peening machine containing steel balls with mean hardness of 40–45 RC, diameter of 1–2 mm and shooting angle of 45° [4]. Afterwards, the shot peened and untreated specimens were

* Corresponding author. Tel.: +98 7116133399; fax: +98 7112307293.
E-mail address: hashemib@shirazu.ac.ir (B. Hashemi).

0261-3069/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.matdes.2011.02.037

Table 1
Chemical composition of 316L stainless steel.

Element	C	Ni	Cr	Mo	Si	Mn	P	S	Cu	Fe	Others
Wt.%	0.023	10.547	16.934	2.033	0.449	1.624	0.031	0.015	0.345	67.603	0.396

exposed to NH_3 gas in a furnace at 570 °C for 8 h, to obtain nitrided and shot peened–nitrided specimens.

2.2. Characterization

In order to characterize the new phases formed on the surface of specimens, X-ray diffraction analysis was carried out using a Bruker D8 diffractometer with Cu Kα radiation and scan rate of 5 deg/min. Scanning electron microscope (Oxford S360 model) was used to study the morphology of the wear surfaces and polished cross-sections of specimens etched in a solution, with the composition shown in Table 2.

2.3. Hardness, wear, and corrosion measurements

Wear tests were carried out using a rotating pin-on-disc wear testing machine with a speed of 2 cm s^{-1}. The diameter of wearing circumferential trajectory was adjusted to be 7 mm. These tests were performed against a 5 mm diameter SAE 52100 pin (ball) and repeated at least three times per specimen. The sliding distance was 250 m with normal loads of 5 and 10 N. The weight loss value of the specimens and the traversed distance were the criterion for comparison of the wear resistance.

The corrosion tests were performed utilizing direct current method by a potentiostat system, Autolab type III model, made by Ecochemie Company, and ringer's physiological solution as the corrosive environment (the chemical composition of which is presented in Table 3). After connecting a copper wire to one side of each specimen, they were cold mounted in an acrylic resin so that a two dimensional surface be in contact with the corrosive environment. The copper wire was brought out from the mount side using a glass pipe with outer diameter of 4 mm, as shown in Fig. 1.

The surface of each specimen was painted according to ASTM G1-90 standard [15] so that a 0.36 cm^2 surface was approached to the environment. The specimens were placed in the corrosive solution for 2 h to obtain a relatively stable potential. In order to measure the specimens' potential, an Ag/AgCl [3M KCl] as the reference electrode and a platinum rod as the working electrode were used. The cyclic polarization curve was started from the open circuit potential (which was previously measured) and scanned in the anodic direction (positive potential) with a rate of 5 mV/s. The direction of scan was reversed from a current density of 10 mA/cm^2 and continued in the cathodic direction to form a hysteresis loop. The values of the breakdown potential and corrosion current density for different specimens were measured using the GPES Manager software.

Table 2
Composition of the etching solution.

Compound	HCl	HNO_3	CH_3COOH
Volume (ml)	15	10	10

Table 3
The chemical composition of ringer's solution.

Compounds in the solution	NaCl	KCl	$CaCl_2 \cdot 2H_2O$	pH
Concentration (g/l)	8.6	0.3	0.33	7.4

Vickers micro-hardness tests were performed on the surfaces and cross-sections of specimens using a Leitz machine with a 10 g load. This test was done at least at 10 points of the surface for each specimen and the mean value was reported. The surface area of the prepared specimens for the micro-hardness test was 120 mm^2.

3. Results and discussion

3.1. Characterization of nitrided layer

Fig. 2 shows the cross-section microstructure of different specimens. A gray layer or nitrided layer is seen at the surface of nitrided specimen (Fig. 2c and d). The nitrided layer of shot peened–nitrided specimen was thicker than the nitrided specimen without shot peening. This could be due to the increase of dislocations density and grain refinement at the surface layers of specimen after shot peening (Fig. 2b). Since, nitriding is a diffusion-controlled process and dislocations and grain boundaries are suitable paths for diffusion, so it seems that the nitrogen diffusivity increases in the surface layers due to this treatment. This is consistent with other observations, in which a considerable enhancement of nitrogen diffusion has been demonstrated, after surface mechanical treatments [14,16]. On the other hand, severe plastic deformations due to shot peening may cause strain-induced martensite transformation in the surface layers [14]. Nitrogen has a higher diffusion coefficient in α'-martensite than in austenite. Therefore, more nitrogen atoms diffuse into the surface layers of shot peened specimen and the nitrided layer could be thicker.

The XRD patterns for nitrided and shot peened–nitrided specimens are shown in Fig. 3. As can be seen, the patterns show the presence of Fe_4N and CrN phases in the surface layers. Moreover, the XRD pattern of the shot peened–nitrided specimen shows an increase in the intensity of nitride phases. Chromium and iron nitrides precipitate along the grain boundaries and other defects, therefore their amounts increase in the shot peened specimens, which have higher density of defects and higher nitrogen density in surface layers.

3.2. Hardness measurements

The results of Vickers micro-hardness tests for the surface and cross-section of specimens are presented in Fig. 4. As shown, the shot peened–nitrided specimen has the maximum surface hardness as compared with other specimens. The hardness profile of cross-sections show that the hardness decreases from the surface towards the center of specimens. Therefore, the effect of these processes is limited to surface and subsurface layers and all of the specimens almost have same hardness in the core.

Shot peening has a more significant effect on the surface hardness in comparison with nitriding treatment. It can be attributed to the induced compressive residual stresses, work hardening, grain refinement and strain-induced martensitc transformation in the surface layers due to shot peening treatment [14,17]. In addition, the hardness of shot peened specimen increased after nitriding, because a thick nitrided layer with higher amounts of the nitride phases formed on the surface. It shows that shot peening–nitriding process is more effective than the only-nitriding process.

Fig. 1. A photograph of the electrode utilized in the corrosion test.

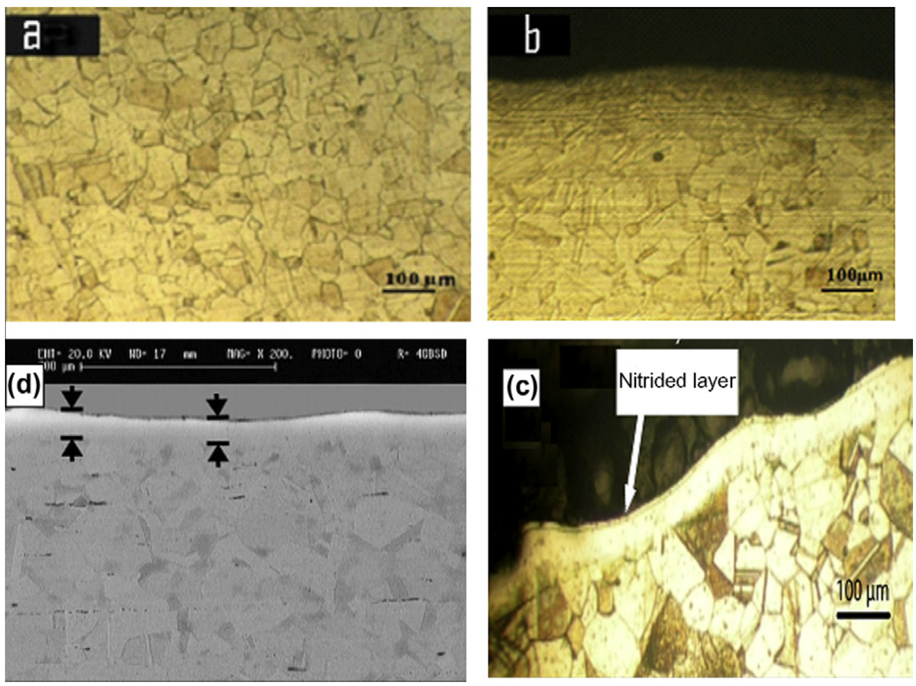

Fig. 2. Cross-section microstructure of untreated specimen (a) shot peened specimen (b), nitrided specimen (c) and SEM micrograph of nitrided specimen (d).

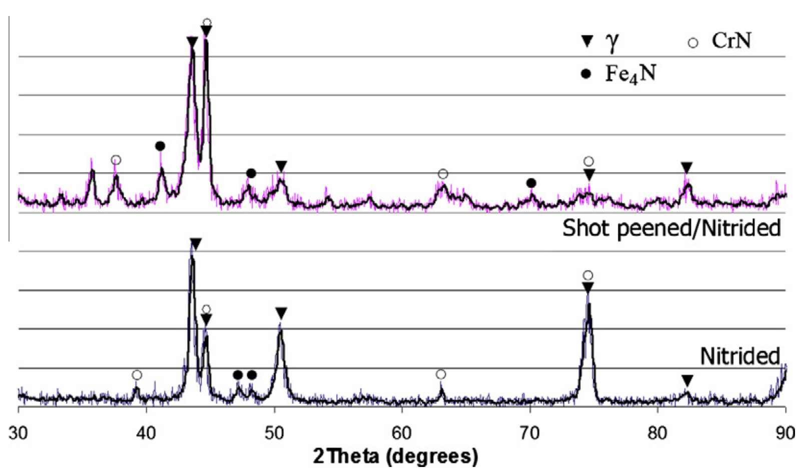

Fig. 3. The XRD patterns of nitrided and shot peened–nitrided specimens.

3.3. Wear behavior

The surface wear rate (K) was calculated based on K = weight loss/sliding distance ($\mu g\ m^{-1}$) relation, with two loads of 5 and 10 N (Fig. 5). As shown in the figure, the wear rate due to motion of pin on specimen's surface at a constant load, for the shot peened–nitrided specimen is less than this quantity for the nitrided specimen, which is itself less than that of the untreated specimen.

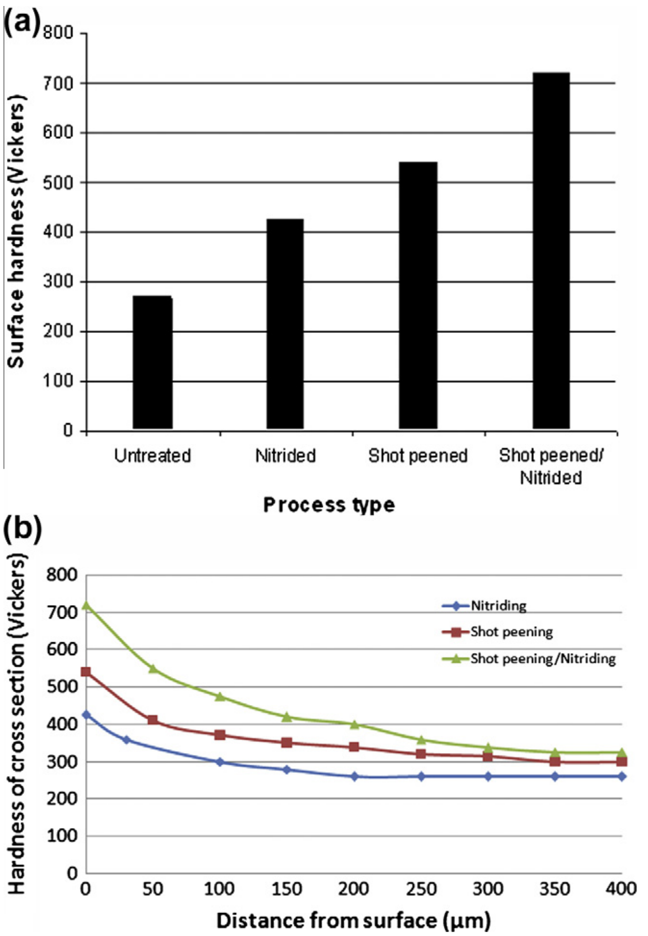

Fig. 4. Vickers hardness for (a) the surface (mean value), and (b) cross-section of the specimens.

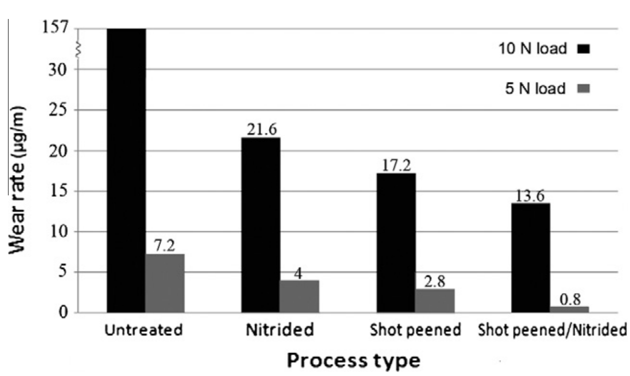

Fig. 5. A comparison between the wear rates of specimens under two different loads.

When 5 N load is exerted, the wear rate of specimens is eligible; however, exerting the 10 N load makes the wear rate of untreated specimens to increase intensely. While, the wear rate for the other specimens does not show a significant increase. Therefore, surface treatments played an important role in increasing the hardness and wear resistance of 316L stainless steel. Here, again according to surface hardness of specimens, shot peening–nitriding treatment has the highest effect in decreasing wear.

Fig. 6 shows the SEM images of the worn surfaces of specimens under a load of 10 N at room temperature. As seen in Fig. 6a, the signs of a mixture of adhesive (which is usually the predominant mechanism in wear of austenitic stainless steel) and abrasive wear mechanisms are observed on the surface of the untreated specimen. The crushed particles due to the high pressure of the pin are probably the reason of abrasive wear between the ball and the specimen. Fig. 6b shows the surface of nitrided specimen. The wear trace although is narrower, it is thoroughly white, smooth and homogeneous; therefore, the wear mechanism has been changed to complete abrasive [18–20]. For the shot peened specimen, in Fig. 6c, sequence of surface digging was observed. Therefore, it seems that the wear mechanism is abrasive again [21]. Fig. 6d which presents the surface of shot peened–nitrided specimen shows that there is relatively a very low wear value and no trace is visible. However, some inconsiderable wear traces become a bit visible on the surface of specimen at a higher magnification, as shown in Fig. 6e, and the abrasive mechanism is clearly observable.

According to the hardness values of the specimens (Fig. 4a), it seems that how much the surface hardness increases, the abrasive mechanism becomes more controlling. The controlling mechanism for the untreated specimen is adhesive–abrasive, according to its low hardness value. While, investigating the nitride, shot peened and shot peened–nitrided specimens showed that the controlling mechanism goes more and more to abrasive mechanism, because of the considerable increase in the surface hardness.

3.4. The corrosion behavior

In order to evaluate the resistance to corrosion, the cyclic polarization tests were performed on the specimens. The cyclic polarization diagrams of specimens (Fig. 7) show that the specimens can be susceptible to pitting corrosion in certain conditions. The tests were performed in a sweeping cycle and the results of breakdown potential of the oxide layer and corrosion current densities were obtained from it (Table 4). Considering Table 4 and cyclic polarization curves of specimens, untreated stainless steel AISI 316L has an excellent corrosion resistance shown by the existence of a wide passive region and the highest breakdown potential and lowest current density.

It was observed that the value of breakdown potential of the passive layer decreased and corrosion current density increased in the shot peened specimen in comparison with untreated ones. Since shot peening increases the surface roughness, therefore the preferred regions for the nucleation of voids are produced [4,22]. On the other hand, nitriding process shows the worst results, as the corrosion behavior is investigated. The conventional nitriding of stainless steels in such temperatures is generally characterized by the intense precipitation of chromium nitride (as the XRD pattern also showed), which deteriorates the corrosion resistance of steels due to the depletion of the chromium content in the steel matrix, as other researches have already shown [23].

The cyclic polarization curve obtained for the shot peened–nitrided specimen shows an improvement in the corrosion behavior in comparison with the only-nitrided specimen (higher breakdown potential and lower corrosion current density). This improvement as reported in another research [24] may be due to the formation of a thin-deposited layer (from nitride precipitates) on the surface of specimen (white thin layer in Fig. 2) which influences the corrosion behavior of steel. In shot peened–nitrided specimen, because of higher diffusion rate in the surface layers, nitride phases form easier than the nitrided specimen. Therefore corrosion resistivity of shot peened–nitrided specimen is higher than the nitrided specimen. However, more investigations is required to verify this behavior.

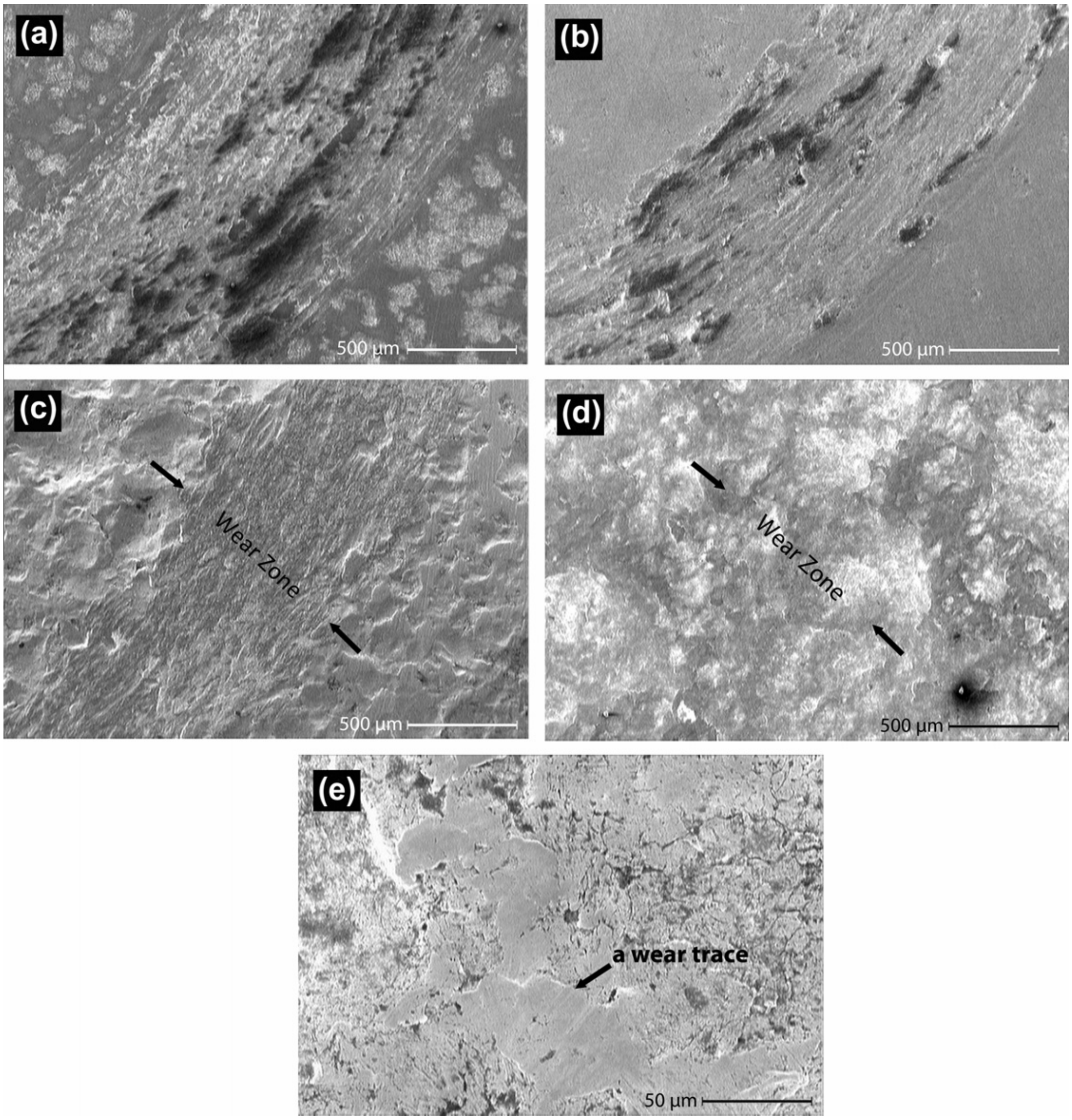

Fig. 6. SEM micrographs of the worn surfaces in wear test on (a) untreated, (b) nitrided, (c) shot peened, (d) shot peened–nitrided specimens in low magnification, and (e) shot peened–nitride specimen in a higher magnification.

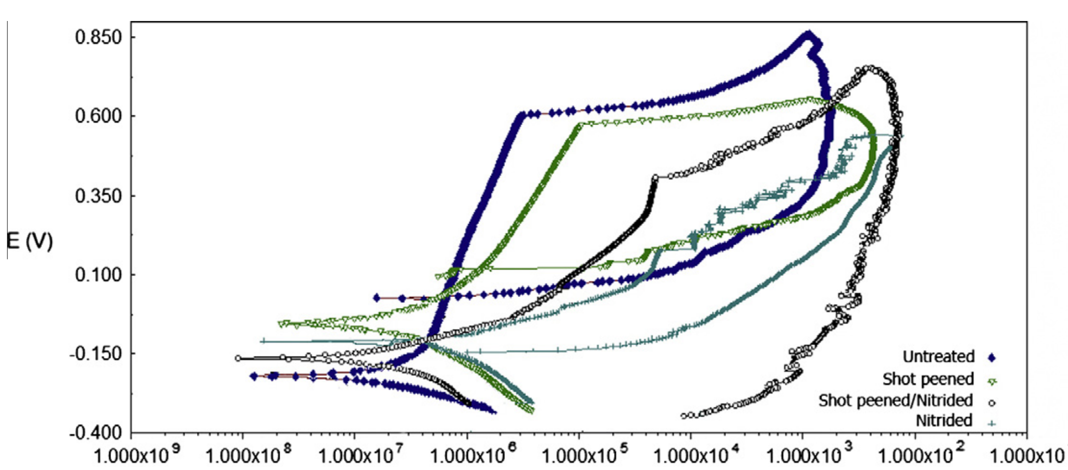

Fig. 7. Cyclic polarization curves of different specimens.

Table 4
Break down potential of the passive layer and corrosion current density of different specimens.

Specimen	Initial	Shot peened	Nitrided	Shot peened–nitrided
Break down potential of the passive layer (mV)	573	480	625	550
Corrosion current density (A/cm^2)	3.8×10^{-7}	13×10^{-7}	2.9×10^{-7}	5.7×10^{-7}

4. Conclusions

Hardness, wear resistance and corrosion behavior of shot peened, nitrided and shot peened–nitrided 316L stainless steel were investigated. Shot peened–nitrided specimen had highest hardness and wear resistance due to the formation of nitride phases, induction of compressive residual stresses and grain refinement in the surface layers. While corrosion resistance of the only-nitrided specimen in ringer's solution decreases tremendously in comparison with the untreated specimen, performing the shot peening surface treatment before nitriding, improves the corrosion resistance in comparison with the nitrided steel. This may be due to the formation of a thin-deposited layer at the surface of specimen. The obtained results in this research show the advantages of using shot peening–nitriding treatment as a low cost technique to improve the surface characteristics of 316L stainless steel. This treatment has characteristics of shot peening and nitriding in improving the surface mechanical properties of steel, while alleviating the adverse effects of nitriding treatment on the corrosion behavior.

References

[1] Standard specification for wrought 18 chromium–14 nickel–2.5 molybdenum stainless steel bar and wire for surgical implants. F138 Annual book of ASTM standards. American Society for Testing and Materials; 1999.
[2] Heras EDL, Egidi DA, Corengia P, Gonzalez-Santamaria D, Garcia-Luis A, Brizuela M, et al. Duplex surface treatment of an AISI 316L stainless steel; microstructure and tribological behavior. Surf Coat Technol 2008;202:2945–54.
[3] Yun-wei H, Bo D, Cheng Z, Yi-rning J, Jin L. Effect of surface mechanical attrition treatment on corrosion behavior of 316 stainless steel. J Iron Steel Res Int 2009;16:68–72.
[4] Azar V, Hashemi B, Rezaee Yazdi M. The effect of shot peening on fatigue and corrosion behavior of 316L stainless steel in Ringer's solution. Surf Coat Technol 2010;204:3546–51.
[5] Nakanishi T, Tsuchiyama T, Mitsuyasu H, Iwamoto Y, Takaki S. Effect of partial solution nitriding on mechanical properties and corrosion resistance in a type 316L austenitic stainless steel plate. Mater Sci Eng 2007;A 460–461:186–94.
[6] Dai K, Shaw L. Comparison between shot peening and surface nanocrystallization and hardening processes. Mater Sci Eng 2007;A 463: 46–53.
[7] Li KY, Xiang ZD. Increasing surface hardness of austenitic stainless steels by pack nitriding process. Surf Coat Technol 2010;204:2268–72.
[8] Souza SD de, Kapp M, Olzon-Dionysio M, Campos M. Influence of gas nitriding pressure on the surface properties of ASTM F138 stainless steel. Surf Coat Technol 2010;204(18–19):2976–80.
[9] Kastilnik T. Surface engineering, vol. 5. ASTM Handbook; 1994. p. 278–302.
[10] Wen DC. Plasma nitriding of plastic mold steel to increase wear- and corrosion properties. Surf Coat Technol 2009;204:511–9.
[11] Jellesen MS, Christiansen TL, Hilbert LR, Møller P. Erosion–corrosion and corrosion properties of DLC coated low temperature gas-nitrided austenitic stainless steel. Wear 2009;267:1709–14.
[12] Fernandes FAP, Heck SC, Pereira RG, Picon CA, Nascente PAP, Casteletti LC. Ion nitriding of a superaustenitic stainless steel: wear and corrosion characterization. Surf Coat Technol 2010;204:3087–90.
[13] Kikuchi S, Nakahara Y, Komotori J. Fatigue properties of gas nitrided austenitic stainless steel pre-treated with fine particle peening. Int J Fatigue 2010;32:403–10.
[14] Shen L, Wang L, Wang Y, Wang C. Plasma nitriding of AISI 304 austenitic stainless steel with pre-shot peening. Sur Coat Technol 2010;204:3222–7.
[15] Standard practice for preparing, cleaning, and evaluating corrosion test specimens. G1 Annual book of ASTM standards. American Society for Testing and Materials; 1999.
[16] Lin Y, Lu J, Xu T, Xue Q. Surface nanocrystallization by surface mechanical attrition treatment and its effect on structure and properties of plasma nitride AISI 321 stainless steel. Acta Mater 2006;54:55995605.
[17] Bagheri S, Guagliano M. Review of shot peening processes to obtain nanocrystalline surface in metal alloys. Surf Eng 2009;25:3–14.
[18] Li GJ, Peng Q, Li C, Wang Y, Gao J, Chen SY, et al. Effect of DC plasma nitriding temperature on microstructure and dry-sliding wear properties of 316L stainless steel. Surf Coat Technol 2008;202:2749–54.
[19] Liang W, Bin X, Zhiwei Y, Yaqin S. The wear and corrosion properties of stainless steel nitrided by low-pressure plasma-arc source ion nitriding at low temperatures. Surf Coat Technol 2000;130:304–8.
[20] Cheikh Larbi AB, Cherif A, Tarres MA. Improvement of the adhesive wear resistance of steel by nitriding quantified by the energy dissipated in friction. Wear 2005;258:712–8.
[21] Yan W, Fang L, Sun K, Xu Y. Effect of surface work hardening on wear behavior of Hadfield steel. Mater Sci Eng 2007;A 460–461:542–9.
[22] Wang XY, Li DY. Mechanical and electrochemical behavior of nanocrystalline surface of 304 stainless steel. Electrochim Acta 2002;47:3939–47.
[23] Nosei L, Farina S, Avalos M, Feugeas J. Corrosion behavior of ion nitrided AISI 316L stainless steel. Thin Solid Films 2008;516:1044–50.
[24] Li CX, Bell T. Corrosion properties of active screen plasma nitrided 316 austenitic stainless steel. Corros Sci 2004;46:1527–47.