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Experimental Evaluation of Corrosion and Hardness on AISI 316l Stainless Steel Implanted with Nitrogen and Argon Ions

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ABSTRACT
In this work the AISI 316L SS was implanted with two different ions namely nitrogen and argon separately at 100 KeV with fluence of 1x1017ions/cm^2 at room temperature. The crystallographic orientation and surface morphology were studied using X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The effects of ion implantation, on the corrosion performance of AISI316L stainless steel were evaluated. Microhardness was also measured by Vickers method by varying the loads. The results of the studies indicated that there was a significant improvement in both corrosion and hardness in the case of implanted samples.

INTRODUCTION
AISI316L stainless steel is being widely used in artificial knee and hip joints as well as internal fixation devices in bio-medical applications. More specifically, AISI316L SS is used in the medical field as an implant material due its unique property of good corrosion resistance and biocompatibility. The success of implants in the human body depends on many factors such as bio safety, biocompatibility and biofunctionality in the environment wherein the implants are placed. But if the body environment is rigorous, this might result in corrosion of implants [1]. Although AISI316L stainless steel shows extremely good corrosion resistance, it is nevertheless prone to pitting. Vivo pitting corrosion has been observed in those cases of implants. Surface modification techniques have been applied to improve the corrosion resistance of AISI 316L stainless steel [2-7]. In the recent years, the application of coatings for implants has been attracting considerable attention of the researchers [1]. Lon implantation is a high end technology adopted specifically for modifying surface properties of materials. Though it is similar to the coating process, it does not involve the addition of a layer on the surface. Importantly ion implantation serves as a powerful tool of surface engineering of biomaterials. The main advantages of this technique are the possibility of introducing any element into any solid target and the low temperature of the process [8].

The past literatures show that various ions were implanted in bio materials and studies have been conducted. The extensive study on nitrogen implantation was done. Nitrogen was implanted in polymers and various biomaterials for different applications [8-13]. Nitrogen was implanted in Titanium, NiTi [8, 14, 15], and SS316L as well [12,16]. Implantation of helium also attracts considerable attention of the researchers. Helium ions were implanted in polymers [8, 10, 11, 17] and metals [18]. Kripton was implanted in Ti-6Al-4V alloy [19]. Argon, nitrogen, and oxygen were implanted in titanium modified SS316L [20]. Argon was implanted in ceramics [8] and polymers [18]. In stainless steel, nitrogen and oxygen implantations were studied [21]. Mixer of ions implantation was also studied with nitrogen and argon [22], nitrogen and carbon [23] and calcium and phosphorus [24].

In the present study nitrogen and argon ions were selected which were tried earlier with other bio material substrate [8, 25]. The implanted AISI 316L stainless was characterized. The effect of the implantation on the corrosion performance of the AISI3l6L stainless steel was then evaluated. In order to simulate the natural tissue environment, the electrochemical test such as cyclic polarization was done in a 0,9% sodium chloride solution at a pH value of 6,3 and temperature at 37 °C. This was carried out on both virgin and implanted AISI316L stainless steel for the purpose of comparison of the performances. In addition to this, the hardness of the virgin and implanted samples was also studied using Vickers micro hardness tester by varying the loads. Besides, the surface morphologies of the implanted samples and the corroded samples were studied with XRD and SEM respectively.

EXPERIMENTAL PROCEDURES

SAMPLE PREPARATION AND ION IMPLANTATION

The AISI316L SS was used as the metal substrate and the elemental composition is given in Tab. 1. The AISI316L SS alloy in as-received mill annealed condition was cut into 8 mm diameter and length of 5 mm and 15 mm size pieces. Prior to the study, the AISI316L SS samples were polished using silicon carbide emery papers of 120, 220, 320, 400, 500, 600 and 800 grit. Final polishing was done using coarse (5μm) and fine (1μm) diamond pastes in order to produce scratch-free mirror-finish surface. The polished specimens were examined under optical microscope for the presence of pits or scratches on the surface. The polished specimens were washed with detergent solution, degreased with acetone and thoroughly washed with distilled water. They were further subject to ultrasonic cleaning in acetone for 10 min. Finally the sample was rinsed in de ionized water, dried and used for further studies.

The ion implantation of both the nitrogen and argon ions was accomplished with a 150 KeV accelerator. AISI316L SS had undergone an implantation of selected ions at an energy level of 100 keV, dose 1x1017 ions/cm^2 at normal room temperature. Ions were accelerated in a linear accelerator. This implantation process is a line-of-sight process.

CORROSION TEST (ELECTROCHEMICAL TEST)

The anodic polarization tests were carried out using the conventional three-electrode cell of 250 ml capacity. This cell was fitted with the work electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum sheet as the counter electrode. The ion implanted and virgin samples were placed as work electrode one by one. The standard cyclic anode polarization test was performed in an electrolyte solution of NaCl (9 g/l of H_20) at pH=6,3 at the temperature of 37°C. This solution simulates the natural tissue environment [26]. After 3600 seconds of immersion in NaCl solution, when a fairly stable potential could be achieved, the potentiodynamic polarization test was carried out at a scan rate of 100 mV/s.

The electrode potential or scanning potential was raised from -1000mV to 1000mV. It is to remind that the experiment was carried out in such a way that the electrolyte was in contact with the implanted surface. The contact area in all cases was 0,1956cm^2. The scan was started in the anode direction with a scanning rate of 100 mV/s. After the completion of corrosion tests for both the treated and virgin materials of AISI316L SS, the corrosion current density

Seel	C	Mn	Si	Cr	Ni	Mo	P	S	Fe
316L SS	0,020	1,10	0,469	16,49	10,02	2,01	0,015	0,013	Bal

Tab.1 *Composition of the AISI316L Stainless steel (wt.%)*

(icorr), corrosion potentials (E corr) and pitting potential (Epit) were estimated by linear fit and Tafel extrapolation to the cathodic part of the polarization curve.

HARDNESS TEST

The hardness test was carried out to measure the microhardness of both the virgin and implanted specimens. The Ever One, Model no MH-3 (Germany) microhardness testing machine was used to carry out the test. The hardness profile of the surface layers was measured with varying loads ranging from 10 gms to 100 gms. The Vickers hardness of AISI 316L stainless steel is found to be 195 Hv and it is in good agreement with the hardness values measured by the other authors [7, 23].

RESULT AND DISCUSSION

CORROSION BEHAVIOR

Tafel analysis is a well-established electrochemical technique [27], in which a typical potential scan of ±25mV around the open circuit voltage is imposed on a metal sample and the current value obtained was recorded. It can be seen that linear relationship exists between current and voltage in this voltage range, and the slope is the polarization resistance.

Fig. 1. shows the potentiodynamic polarization curves of both the implanted and virgin AISI 316L SS samples in an aerated solution of NaCl 9 g/l of H_2O (physiological serum) at a pH value of 6,3 at a temperature of 37°C. The relevant parameters are listed in Tab. 2. The anodic polarization curves can be divided into two regions. In the first region, the dissolution of the implanted AISI316L SS was kinetically limited and the anodic current was increased slowly with potential, showing a "passive-like" behavior. Finally there is a transpassive second region beginning at a critical potential (Epit), where the rapid increase in the current value occurs due to breakdown of the passive film. This phenomenon is commonly known as pitting corrosion [26] and the potential at which a rapid increase of the current density occurs is usually termed as the "pitting potential" or "breakdown potential" (Epit or Ebrk). The anodic potentiodynamic polarization curve of virgin AISI316L SS obtained in the present investigation was similar to that previously obtained for the virgin AISI316L stainless steel [26]. From Fig.1, it is observed that the corrosion potential Ecorr value for virgin AISI316L SS is - 435 mV and with tafel analysis, it is found that the corrosion current density icorr and the Epit as 1,2187 mA/cm² and 92 mV respectively. The other curves of this family provide better values of Ecorr and icorr. From Tab. 2. it can be observed that the Ecorr of nitrogen implanted (- 430 mV) was shifted towards a slightly higher value, which is very much in agreement with values found in literature [26]. In the case of argon implanted samples, it can be observed that the Ecorr is - 301 mV, which is an appreciable value.

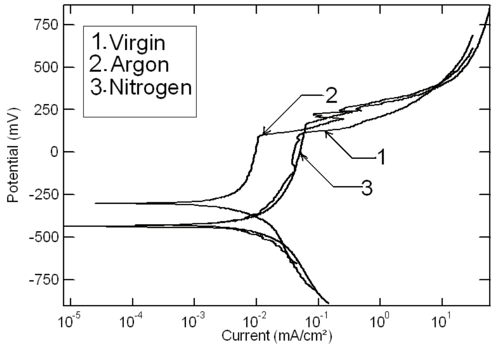

Fig. 1 *Potentiodynamic polarization curves of the virgin and implanted AISI316L SS in aerated 0,9 wt % NaCl solution*

Sample	E_{corr} (mV)	i_{corr} (mA/cm²)	E_{pit} (mV)
Nitrogen implanted	- 430	1,1183	170
Argon implanted	- 301	1,05	96
Virgin material (AISI316LSS)	- 435	1,2187	92

Tab. 2 *Electrochemical Parameters estimated from the polarization tests in an aerated 0,9 wt % NaCl solution*

The corrosion current density (icorr) was estimated by linear fit and tafel extrapolation to the cathodic part of the polarization curve. From these polarization curves, it is observed that the corrosion current density icorr is inversely proportional to the corrosion potential Ecorr and implies same pattern of corrosion tendency. While the icorr of virgin AISI316L SS is observed as 1,2187 mA/cm², in the case of nitrogen implanted samples it is reduced to a smaller val-

ue of 1,1183 mA/cm^2. Likewise, for argon implanted specimens, it is moved to 1,05 mA/cm^2, which is an appreciable value. Since the icorr values are directly proportional to the corrosion rate, the argon implanted samples can be said to poses a good corrosion resistance. Thus it can be concluded that argon implanted AISI 316L SS has high resistance to corrosion. The nitrogen implanted specimens tend to show a less resistance to corrosion when compared to argon implanted specimens.
An analysis of the pitting potential or breakdown potential (E_{pit} or E_{brk}) values reveals that the virgin sample poses a very low value of 92 mV compared to the nitrogen implanted samples, which provide a good pitting potential of 170 mV. The argon implanted samples provide a smaller improvement in pitting potential with the value of 96 mV. The pitting corrosion and general corrosion relationship between virgin and nitrogen was found to be in good agreement with the literature [26].

HARDNESS BEHAVIOR

The Vickers microhardness for various ions implanted specimens are shown in Fig. 2. The microhardness for all the implanted samples at 10 g load is greater than that of virgin samples. The microhardness increases at 10 g load and decreases to zero (ie microhardness equal to the substrate material) at about 50 g load, because at higher loads the indenter is basically probing the substrate.

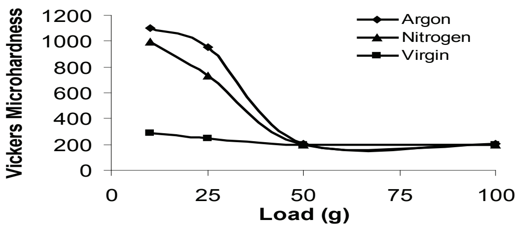

Fig. 2 *Microhardness of virgin and implanted with argon and nitrogen ions*

From this family of hardness graphs, it can be observed that the hardness of the virgin AISI 316 l is 195 Hv and the argon ion implanted sample shows the highest hardness value of 1100 Hv. When compared with virgin specimens, this increase is about 550%. Nitrogen implanted samples were found to show a hardness of 998 Hv. When compared with the virgin specimens the increase is about 500%. It can be seen that the virgin AISI316L SS hardness increases near the surface where it reaches 289 Hv. This could be attributed to work hardening caused by mechanical polishing [28]. In summary this is in agreement with the previous work reporting the increase in microhardness with ion implantation in AISI316L SS [28].

SURFACE MORPHOLOGY ANALYSIS

The ion implanted samples were analyzed by X-ray diffraction (XRD) using Shimadzu - Model XRD 6000 machine with 2θ range 30˚- 110˚. Fig. 3 (a-c) represents the X-ray diffraction pattern of the virgin, nitrogen and argon implanted AISI316l SS samples. The X-ray diffraction pattern of virgin material shows peaks at 43,6˚ and 50,6˚. This is due to Fe-γ (austenite) [22]. The XRD pattern of materials implanted with nitrogen and argon ions exhibits an extra peak at 44,8˚ in addition to the Fe-γ (austenite). This peak could be the result of the presence of a metastable single phase [22]. The corrosion resistance studies indicate that these samples are found to show fairly good resistance to corrosion. This indicates that the formation of metastable single phase could be the instrumental in protecting the substrate material from corrosion. The peak intensity of extra peak at 44,8˚ for materials implanted with argon ions is more than that of nitrogen implanted. This is in accordance with the result of our earlier studies related to corrosion resistance.

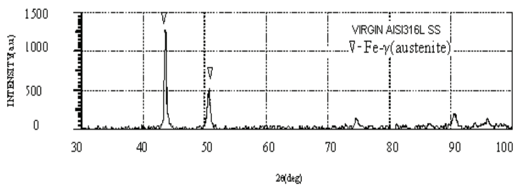

Fig. 3 (a) *XRD Pattern of virgin AISI316L SS*

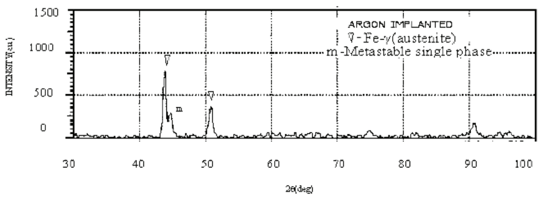

Fig. 3 (b) *XRD Pattern of argon implanted AISI316L SS*

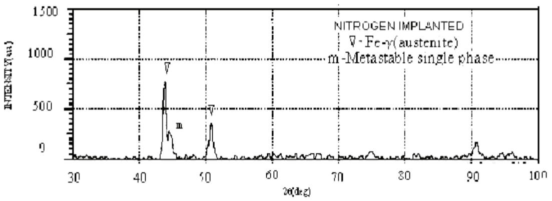

Fig.3 (c) *XRD Pattern of nitrogen implanted AISI316L SS*

The surfaces of corroded samples were analyzed by JEOL-MODEL 6390 scanning electron microscope (SEM). The morphological analysis carried out in the surface of the corroded samples shows the pits in the surface. Fig. 4 (a-f) shows the typical corrosion morphology of the implanted and virgin samples. For each of the ion implanted samples, two images, as non-zoomed and zoomed were plotted. The analysis of the morphological images of corroded samples is in agreement with the electrochemical test results of pitting potential values. Those samples implanted with the nitrogen ions show considerably less damage, where as the virgin sample display greater extent of damage. Also, those samples implanted with argon show a greater extend of damage and the size of the pits were observed to be larger. The general view in Fig. 4 (a&c) shows the presence of multiple round shaped small pits growing underneath a very thin glassy layer. The zoomed images of the pits can be seen clearly in Fig. 4 (b&d). The general view suggests that the imposed potential leads to pit initiation. In parallel, the dissolution of the passive film underneath the glassy film was also found to progress. At this stage, the dissolution of the passive film appears to be hindered. The coating with the implanted ions formed on the top of the implanted surface was found to completely modify the corrosion properties of the material. Further, since the reaction is controlled by the film coating done with the substrate material, resistance to corrosion was found to be improved.

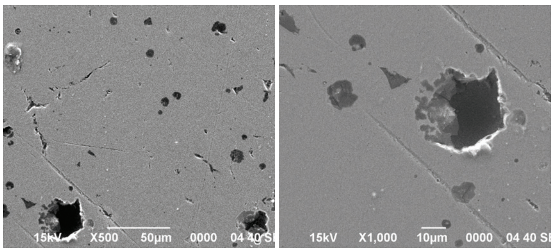

Fig. 4 (a) *Nitrogen implanted corrosion morphology* (b) *Nitrogen implanted pit morphology*

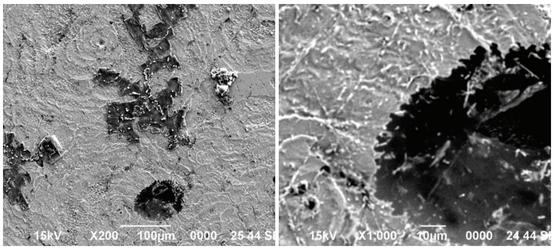

Fig. 4 (c) *Argon implanted corrosion morphology* (d) *Argon implanted pit morphology*

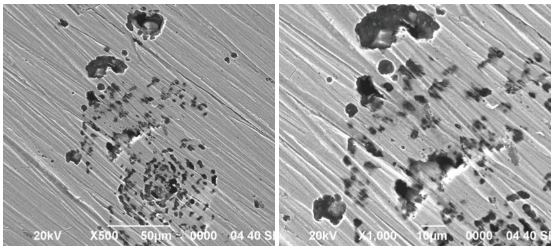

Fig. 4 (e) *Virgin material corrosion morphology* (f) *Virgin specimen pit morphology*

CONCLUSION

The implantation of nitrogen and argon ions was done on AISI316L SS at an energy level of 100 KeV at a dose of 1x1017ions/cm^2, at room temperature. Polarization test was carried out to evaluate the corrosion behavior of the implanted samples in the simulated natural tissue environment. Hardness test was also carried out to evaluate the hardness behavior of the implanted specimens. The XRD test and SEM images were used to analyze the surface morphology. The following conclusions were emerged from the analysis.

- *The XRD and SEM results were found to be in accordance with the corrosion test results.*
- *The general corrosion behavior showed a significant improvement in the case of both argon implanted (i_{corr} = 1,05 mA/cm^2) and nitrogen implanted (i_{coor} = 1,1183 mA/cm^2), when compared to the virgin AISI 316L SS (i_{coor} = 1,2187 mA/cm^2).*
- *The pitting corrosion showed a significant improvement for nitrogen implanted (E_{pit} = 710 mV) when compared to virgin material (E_{pit} = 92 mV). The argon implanted showed a smaller improvement (E_{pit} = 96 mV) when compared to the virgin material.*
- *The surface hardness is found to be1100 Hv for argon implanted and 998 Hv for nitrogen implanted, while it is found to be 195 Hv for the virgin material. The hardness of the argon and nitrogen implanted samples is found to be increased by about 550%*

and 500% respectively, when compared to the virgin samples.

- *Argon implanted samples show better performance in terms of corrosion resistance and hardness when compared to those of the nitrogen implanted samples, and the nitrogen implanted show better performance in pitting corrosion.*

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