Effect of nitrogen ion implantation on corrosion resistance of Ti films deposited on steel 304 by ion beam sputtering

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Abstract:

In this paper effect of N^+ implantation on Ti film coated on steel 304 by ion sputtering has been studied. Samples of steel and the samples were coated with Ti and then implanted nitrogen ions at energy 30 keV in the range of 9×10^{16} to 1×10^{18} ions/cm^2 has been prepared. The surface and morphology characterization of the implanted samples was carried out by means of X-ray diffraction (XRD) and atomic force microscopy (AFM). The corrosion resistance tests were performed by a the electrochemical method in 1 M H_2SO_4 solution at temperature of 37°C and the effect of corrosion tests was analyzed using scanning electron microscopy (SEM). Saturation in corrosion improvement was noticed at higher doses.

Key words: ion implantation, corrosion, sputtering and TiN

1. Introduction

Titanium and its alloys have attracted attention from industry for their favorite physical and mechanical characteristic such as good corrosion resistance and high strength to weight ratio, but their low surface characteristic have limited their usage in some cases. Therefore, regarding their usage, different covering methods and surface procedures have been carried out to modify their surface characteristics [7,3]. One of these methods is ion implantation which improves and corrects the surface characteristics of semiconductors by inserting certain type of impurity into them. Also, formation of compounds of some types of implantation such as compound of (O, N, C) and host material [1-3]. For example, nitrogen ion implantation into Ti in molded tools is very efficient in the way that their average longevity becomes 10 times more. TiN is primarily used in plastic mold and aerospace industries, medical engineering, industrial knives, punches and cleaners [2-6].

Investigations performed on nitrogen ion implantation into Ti alloy at different doses prove that nitrogen dose increase delays surface layer erosion and corrosion [10, 5].

Aim of this article is to investigate TiN corrosion accompanied with implanted nitrogen into deposited Ti [5-9].

2. Experiment

Several steel 304 samples of 1cm × 1cm with thickness of 1mm are provided . The samples are polished by means of sandpaper. The coarseness of sandpapers is from 800 p to 3000 p . Also 1 micron diamond paste has been used to polish up the samples. Furthermore, the prepared samples were inserted into ultrasonic bath of alcohol and acetone for complete cleanliness.

Next step was to insert the polished samples into ion sputtering facility to create Ti layer. In this system, Ar gas with the energy of 4.5 keV strikes Ti target for 4 hours. The produced titanium particles, whose angle difference to samples surface is 45°, reach steel surface and Ti surface is formed on steel surface. After creation of Ti layer, samples were exposed to nitrogen ion, radiation of energy of 30 keV in ion implantation facility. The dose rate of implanted nitrogen ions is in the range of 9×10^{16} to 10^{18} ions/cm^2.

Nitrogen ion implantation characteristics are shown in Table.1.

Table. 1 Nitrogen ion implantation characteristics

Sample	1	2	3	4	5	6	7
Energy(keV)	-	-	29	29	29	29	29
Ion current(μA/cm2)	-	-	5	6	5	8	8
Dose(ions/cm2)	S.S	Ti	9×10^{16}	1×10^{17}	3×10^{17}	7.5×10^{17}	1×10^{18}
Time(s)	-	-	140	160	480	1200	1600
Temperature(°C)	-	-	110	152	300	350	364

To ensure the creation of TiN layer and to investigate the created compounds, XRD (Xpert,PHILIPS) was utilized. XRD is performed with X-ray of Cu(Kα) in time interval of 1s and location interval of 0.02°.

AFM is utilized to show two-dimensional and three-dimensional structures of surface which indicates roughness yielded from implantation.

For all samples, AFM was done in tangential mode with

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scanning range of 1 μm^2.
Corrosion test was performed using Potentiostate / Galvanostate (Model 273A) by potentiodynamic method with scan rate of 1 mV /s in 1M sulfuric acid.

A PHILIPS-XL30 was utilized for scanning electron microscopy (SEM) to scan sample surfaces which indicates corrosion rate and corrosion type of TiN surface yielded from sulfuric acid.

3. Results and discussion

XRD analysis results are shown in Fig. 1. As it can be seen in Fig. 1, there is no change in XRD analysis for unimplanted samples comparing to that of implanted ones up to dose of 3×10^{17} ions/cm^2, but a new peak (TiN) is observed at dose of 7.5×10^{17} ions/cm^2 and this peak increases when dose reaches to 1×10^{18} ions/cm^2.

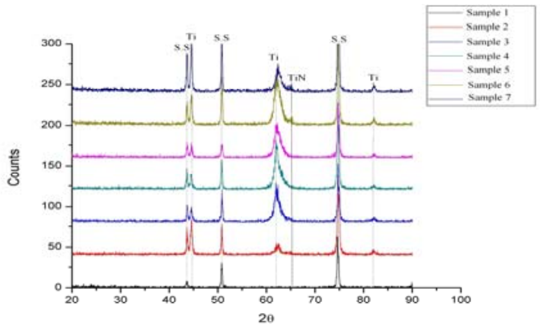

Fig. 1. X-Ray diffraction pattern of non-implanted and implanted samples

Regarding the constancy of all the conditions during ion implantation, creation of this new phase (TiN) can only be justified with nitrogen ion dose increase and an increase in the probability of formation of binds between nitrogen and titanium inside the crystalline structure.

One of the characteristics which undergoes a substantial change is roughness of sample surfaces exposed to radiation. AFM was utilized to investigate surface morphology (such as roughness etc). AFM results in Fig. 2 show that surface roughness initially increases with increase of nitrogen ion rates and then decreases.

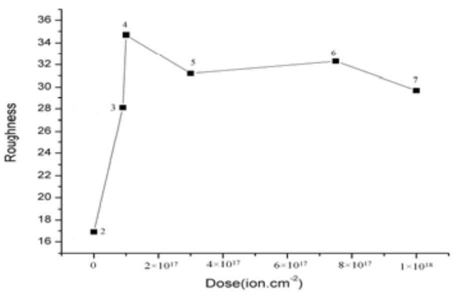

Fig. 2. variation of roughness with dose

Justification of ion sputtering process is that Ti created on steel is a multi crystalline metal, and crystalline surfaces are affected by nitrogen ion radiation, and physical erosion in different surfaces creates a serrated surface leading to surface roughness.

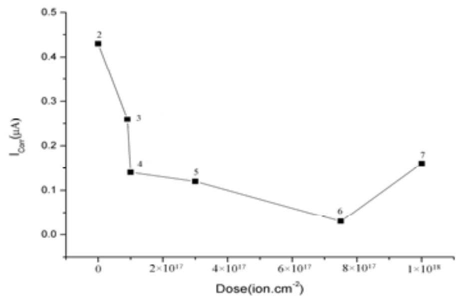

Fig. 3. variation of corrosion current with dose

As the nitrogen ion rate increases, after a while, surface (miniscule protrusions) hights prohibit ion reaching to lower points of the surface. This, in turn, creates shadow on the surface. It can be predicted that physical erosion by the ions continues in these heights and nothing occurs in low points. Therefore, erosion of atoms from heights consequently leads to a decrease in surface roughness.

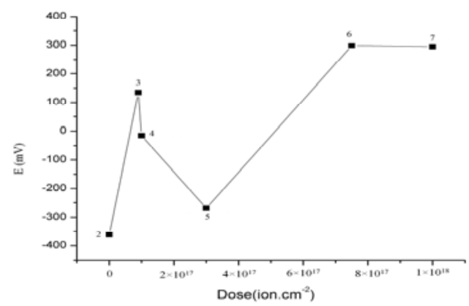

Fig. 4. variation of corrosion potential with dose

As it can be observed in Fig. 5, potentiodynamic polarization curve behavior of Ti sample is very similar to that of pure titanium.

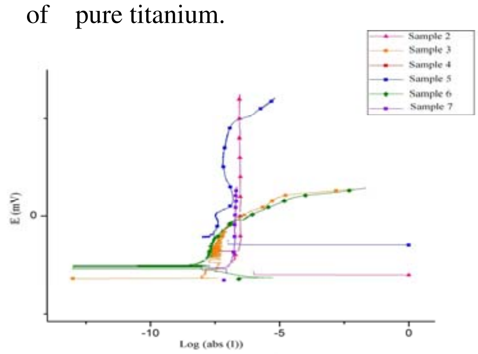

Fig. 5.Potentiodaynamic polarization curves of TiN / Ti

Creation of protective titanium layer on stainless steel can be indicated by referring to and comparing the yielded corrosion current and corrosion potentials. The SEM images of sample surface show no sign of creation of hole erosion caused by defects in deposited layer Fig. 7. This sample keeps its resistance to corrosion even in high potentials close to oxygen exponential potential.

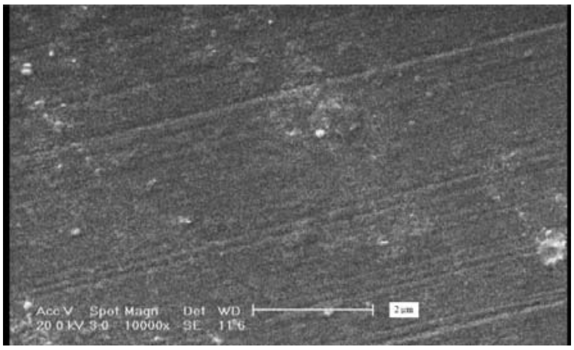

Fig. 6 SEM observed of surface morphology of the Ti

According Fig. 4, results show that corrosion rate decreases with increase of nitrogen ion rate and reaches its minimum at dose of 7.5×10^{17} ions/cm^2.

At higher dose of 1×10^{18} ions/cm^2, it seems that increase of effective surface by high incidence rate of ions on the surface causes an increase in corrosion rate. This created rough surface can also be verified by electron microscopy image Fig. 7.

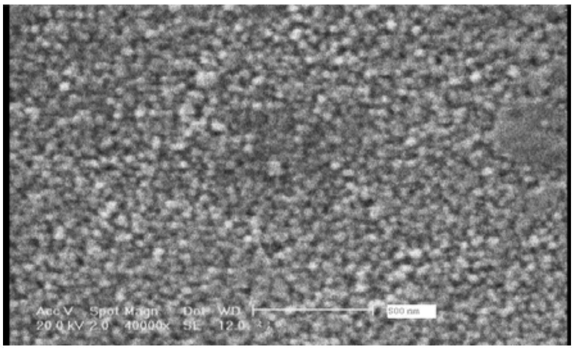

Fig. 7 SEM observed of surface morphology of the S#7

4. Conclusion

In summary, results of nitrogen implantation on titanium deposited by ion sputtering can be justified as :

1. According to Fig. 1 minimum nitrogen rate for creation of the new TiN phase on Ti layer has been 7.5×10^{17} ions/cm^2.
2. According to Fig. 2 surface roughness variations caused by ion implantation have a returning point which can be justified by shadow effects.
3. According to Fig. 3 corrosion current variations after nitrogen ion implantation into Ti have increased to 14 times that can be observed at dose of 7.5×10^{17} ions/cm^2 .
4. According to Fig. 4 corrosion potential variations after nitrogen ion implantation into Ti have been substantial and almost 2.2 times more and its maximum is at 7.5×10^{17} ions/cm^2.
5. According to SEM images of Fig. 3, and Fig. 7 verify this conclusion. We observe a corrosion current increase with increase of nitrogen ion dose to 1×10^{18} ions/cm^2 which is caused by surface roughness increase and consequently an increase in effective surface area.
6. According to Fig. 6 deposited titanium on steel 304 corresponds to pure titanium

5. References:

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