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Wear and corrosion properties of PVD TiN coated Ti-6Al-4V materials

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Abstract

In recent years various coating techniques have been developed for the surface treatment of materials in metal industry. The application of coating techniques in mechanical engineering includes wear and corrosion properties. Physical vapor deposition (PVD) is one of the technique which have been used to coat the engineering materials and TiN hard coating is the most favorable one among the other PVD coating processes.

One application of TiN coating is to increase tribological properties of Ti-6Al-4V material. This alloy becomes popular in metal industry due to its high strength and low corrosion resistance at low specific weights. High friction coefficient, low wear resistance and a tendency to galling limits its widespread use in industry. Consequently, formation of TiN on the surface of this alloy is the most popular way to improve its tribological properties.

In the light of the above arguments, the present study examines, the PVD coating of Ti-6Al-4V substrate. Ion implantation technique was used to coat the substrate surface and with multi layer coating, the coat thickness of 4 μm was achieved. XRD and SEM microphotography techniques were used to identify the phases and structures in the nitrided layer. The wear resistance and friction coefficient of the resulting coats were measured. Corrosion resistance of the coat was achieved using potentiodynamic corrosion tests. It is found that TiN coating of Ti-6Al-4V substrate improves the wear resistance considerably and further improvement in corrosion resistance can be achieved. It was also demostrated that improvement in both wear and corrosion resistance depends upon the quality of the coat achieved in the process.

Introduction

Metal nitride coatings produced by physical vapor deposition (PVD) have been investigated intensively in the recent years [1,2]. It has been demonstrated that TiN has proved to have outstanding wear properties [3,4]. TiN is chemically inert in many environments and may be considered as electrochemically relatively noble material [5].

On the other hand, PVD coating results in microscopic defects on the substance surface. Pinholes may develop and extend through the coatings and act as pathways for rapid corrosion, which allows underneath metal to be corroded. This results the coating to flake away, i.e. a complete failure of the coating occurs. Consequently, preventing the pinhole defects may improve corrosion properties of the coated substance. Erdemir et.al. [6] studied the corrosion resistance of TiN coatings deposited by different PVD techniques. They showed that the morfology of the coating influences the corrosion resistance. Meletis [7] and his team investigated the corrosion resistance of TiN on an M50 steel substrate. They demonstrated that an adequately defect-free and dense structure of the TiN film can improve considerably the corrosion resistance.

In the light of the above discussions, the present study examines the corrosion behavior of both PVD TiN coated and untreated Ti-6Al-4V substrate. Ti-6Al-4V workpieces were PVD TiN coated to obtain 3-3.5 μm uniform coat thickness. Metallurgical study was carried out using SEM microscopy by taking micrographs of the workpiece cross-sections. Nuclear Reaction Analysis (NRA) technique was employed to measure the nitride compound depth profile. Corrosion testing was carried out using electrochemical technique employing potentiodynamic polarization measurements in deaerated 0.1N H_2SO_4 and 0.05M NaCl equeous solution at 25 °C

Experimental

The principle of the triode ion planting set up and the deposition process have been demonstrated previously [8]. The deposition parameters are given in table 1. In all coatings a thin transition layer on the surface occured. By controlling the amount of nitrogen flow, multilayer coatings consisting of successive nitride layers could be deposited.

Strips of Ti-6Al-4V samples were used as substrates. All the samples were polished and they were cleaned ultrasonically in a bath of ethanol before the deposition process. The samples were, then, sputter cleaned for one hour in the deposition chamber just before the coating.

Coating	TiN
Substrate bias voltage (V)	100
Nitrogen volume flow rate (cm^3/s)	50
Substrate current (A)	30
Coat thickness (μm)	2-4
Phases	TiN, ϵ-Ti_2N, Ti

Table 1: The deposition parameters.

Ti	Al	V	Cu	Cr	Fe	O
Balancing	6	4	0.03	0.01	0.32	0.2

Table 2: Elemental composition of Ti-6Al-4V (Typical analysis, %).

The specimens were cut 20 x 50 mm strips later modified to circular shapes for corrosion testing. The elemental composition of the samples is given in table 2.

SEM microscopy was carried out to obtain microphotographs of sample cross-section. The depth profile of TiN coat was obtained using NRA technique.

NRA using the $^{15}N(p,\alpha\gamma)^{12}C$ reaction offers a non distructive determination of nitrogen using the γ ray detection technique. This reaction has several sharp resonances at different proton energies. One of the resonances at 898 keV which has high cross section (800 mb) is very suitable to profile nitrogen in the TiN zone in the sample. Since the depth of the TiN zone is of the order of 2-4 μ it can be suitably scanned by using NRA.

A three electrode cell was used for the corrosion tests. The test cell accommodates inlet and outlet for an inert gas and a thermometer. A potentiostat maintaining the electrode potential within 1 mV of a preset value over a wide range of applied currents was used. A computer controlled scanning potentiostat (EG and G model 273) was used for potentiodynamic measurements. A record of the current and potential was plotted continuously using x-y recorder. During the measurements, standard methods were used and electrolyte was an aerated 0.1 N H_2SO_4 and 0.05 M NaCl held at a temperature of 25 ^oC. The test specimens were masked to expose a surface area of 1 cm^2.

TAFEL ANALYSIS		
	PVD coated	Untreated
E(I=0)	-280.94	-302.45
Cathodic Tafel	167.28	233.44
Anodic Tafel	100	488.46
I_{CORR} ($\mu A/cm^2$)	4.9	7.14
Corrosion rate (mpy)	2.23	3.25
POLARIZATION RESISTANCE		
	PVD coated	Untreated
E(I=0)	-321.2	-282.9
Polarization resistance	7.68	6.70
I_{CORR} ($\mu A/cm^2$)	2.83	3.24
Corrosion rate (mpy)	1.29	1.47

Table 3: Tafel analysis and polarization resistance results.

Discussions

Figure 1 shows the depth of nitride zone obtained from NRA tests for the Ti-6Al-4V plasma nitrided sample. It is evident that nitride layer extends upto 60 μm and after this distance the detector used in the measurement may not be able to measure any nitride compounds. This is due to the low nitride concentration, i.e. nitride concentration is less than 2%.

The potentiodynamic polarization curves for TiN coated and untreated Ti-6Al-4V samples in 0.1N H_2SO_4 and 0.05 M NaCl aqueous solution are shown in figure 2. It is evident that high corrosion current flows untreated samples. Saturation in corrosion current occurs at high applied potentials, since samples start to dissolve at high applied potentials. The linear polarization curve for TiN coated and untreated Ti-6Al-4V samples in 0.1N H_2SO_4 and 0.05M NaCl aqueous solution. is shown in figure 3. The corrosion corresponding to each specimen is calculated using this plots.

Table 3 gives the Tafel analysis and polarization resistance results. It can be seen clearly that TiN coated samples give minimum corrosion rate. The low corrosion rate of TiN coat may have less process defects such as pinholes or cracks, since the rate at which the substrate material reacts at the bottom of the pinholes obviously depends on the amount, size and length of these defects. In reality, there may be some defects exist on the surface of the coat, but these defects are long and narrow, therefore, they

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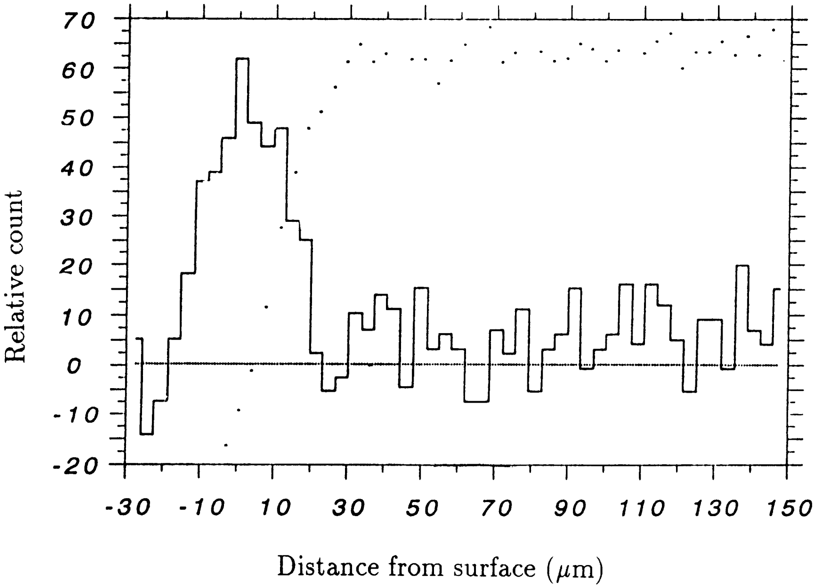

Figure 1: Depth of nitride zone obtained from NRA tests for the Ti-6Al-4V plasma nitrided sample.

actually decrease the reaction rates by reducing the mass transport between the bottom of the pinhole and corrosive environment, which in turn results in slow rate of corrosion reaction.

SEM photograph of cross-section of TiN coated samples are shown in figure 4. Homogeneously distributed coat was obtained. Coat thickness extends to 4 μm. Thin layer of oxide under the coat was developed locally. This is evident from figure 4. This oxide film may become chemically positive and sebsequently improves the corrosion resistance. It should be noted here that thin oxide layer developed on the surface of the untreated samples reduces the corrosion rate, but this reduction is not more than that obtained for the TiN coted samples.

Figure 5 shows the pits formed on the specimen surfaces after the corrosion tests. Locally shallow pits were developed for TiN coated samples.

Conclusions

From the SEM results it is evident that homogeneously distributed coat developed on the sample surface during TiN coating process. It was observed that very minor surface defects occur after the coating process. However,

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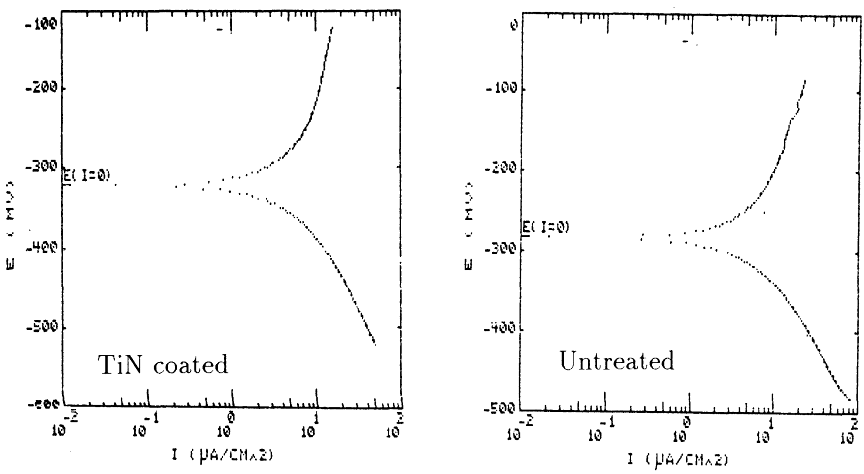

Figure 2: The potentiodynamic polarization curve for TiN coated and untreated Ti-6Al-4V samples in 0.1N H_2SO_4 and 0.05M NaCl aqueous solution.

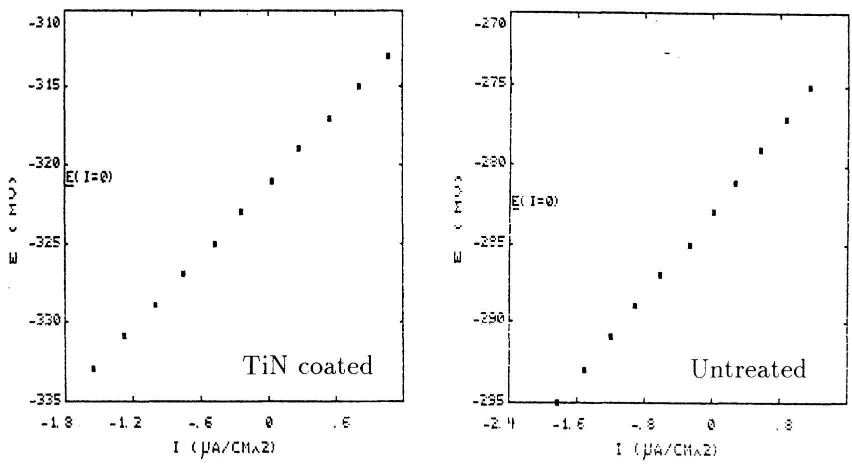

Figure 3: The linear polarization curve for TiN coated and untreated Ti-6Al-4V samples in 0.1N H_2SO_4 and 0.05M NaCl aqueous solution.

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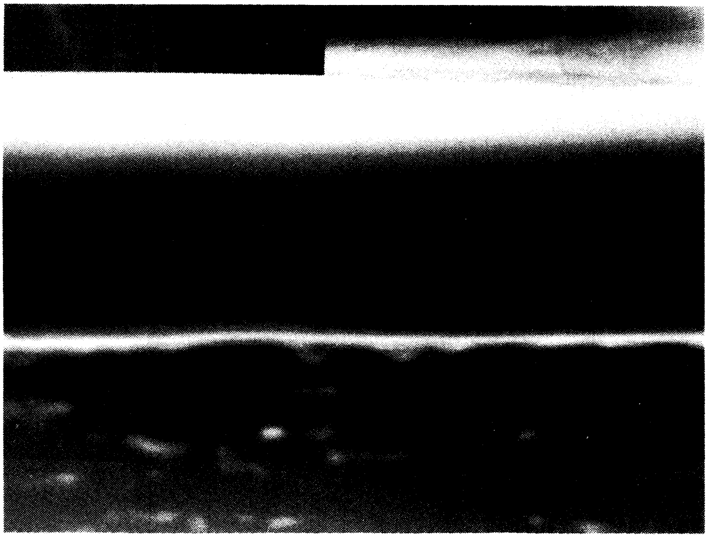

Figure 4: SEM photograph of cross-section of TiN coated samples.

Figure 5: Pits formed on the specimen surfaces after the corrosion tests.

some nano-layer oxide layer occurs locally between the specimen surface and the coat. This has a positive effect improving the corrosion resistance.

Layer properties effect the nature of the TiN resistance to corrosion. Corrosive attack due to pinhole defects and cracks are almost without exception the primary mechanism for coating failure. Homogeneously distributed coat obtained on the specimen surface improves the corrosion resistance. Pitting of the TiN coat surface occurs locally and smaller in size as compared to untreated Ti-6Al-4V samples.

Acknowledgment

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References

[1] Park, M.J., Leyland, A., and Matthews, A., *Surface and Coatings Technology*, 1990, **43/44**, 482-492.
[2] Molarius, J.M., Korhanen, A.S. and Ristolainer, E.O., *J. Vac. Sci. Technology, A*, 1985, **3**, 2419-2426.
[3] Korhanen, A.S., Molarius, J.M., and Harju, E., *Mater. Sci. Eng.*, 1988, **A105-A106**, 497-504.
[4] Raveh, A., *Materials Sci. and Eng.*, 1993, **A167**, 155-164.
[5] Elsener, B., Rota, A., Bohni, H., *Materials Sci. Forum*, 1987, **44-45**, 29-38.
[6] Erdemir, A., Carter, W.B., Hochman, R.F., Meletis, E.I., *Materials Sci. and Engineering*, 1985, **69**, 89-93.
[7] Meletis, E.I., Erdemir, A., and Hochman, R.F., *Ion Planting and Implantation Applications to Materials, ASM*, 173-177, 1986.
[8] Molarius, J., Korhanen, A., Harju, E., and Lappalainen, R., *Surf. Coat. Tech.*, 1988, **33**, 117-124.