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# Surface modification of 9Cr18 bearing steels by a metal and carbon co-plasma immersion ion implantation

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## Abstract

In the aerospace industry, 9Cr18 martensitic stainless steel (AISI 440) is commonly used as a bearing material. Because of its ability to rapidly treat irregular industrial components, plasma immersion ion implantation (PIII) is an effective method to improve the wear resistance of 9Cr18 precision bearings and prolong their working lifetime. Vacuum arc plasma sources provide a good means of introducing metal ions into the bearing steel to create a special surface to enhance its surface properties. In this work, tungsten and titanium PIII was performed on 9Cr18 bearing steel using a vacuum arc plasma source, followed by carbon PIII using acetylene ( $C_2H_2$ ) plasma, without breaking the vacuum. The surface properties were evaluated by measuring the microhardness, wear properties and friction coefficient, as well as the elemental depth profiles and chemical composition of the modified layer. It was found that the microhardness of the treated samples was much higher. The tribological characteristics were also significantly improved, as demonstrated by the reduced friction coefficient and wear track width. This improvement can be attributed to the diamond-like-carbon (DLC) surface layer, as well as favorable ion mixing caused by the implanted metal ions. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Plasma immersion ion implantation; Bearing steel; Surface modification; Metal ion implantation; Carbon ion implantation

## 1. Introduction

Plasma immersion ion implantation (PIII) is a burgeoning non-line-of-sight technique for the surface modification of industrial components, offering several inherent advantages over conventional beam-line ion implantation [1–5]. One of these advantages is the capability to efficiently treat irregular-shaped samples without complex sample or ion beam manipulation. It is, therefore, an excellent surface modification technique to prolong the lifetime of machine parts and tools. Because of its good corrosion resistant properties, 9Cr18 martensitic stainless steel is widely used as a bearing material in aerospace, nuclear, and other special industries. Previous studies have revealed that fail-

ure of bearings occurs mainly on the surface, or in the near surface region [6]. Thus, surface modification techniques play an important role in the improvement of industrial bearings. In this work, metal and carbon ion implantation is performed on 9Cr18 bearing steel in a plasma immersion configuration. Our results show that the microhardness and tribological properties are significantly improved after the treatment.

## 2. Experimental

Coupons of 9Cr18 bearing steel (composition in wt. %: Si-0.8, Mn-0.72, P-0.035, S-0.03, C-0.96; and Cr-17.8, Fe-79.655) were cut from a real bearing ring in a quenched-and-tempered state. The samples were grounded and mechanically polished to a surface roughness,  $R_a$ , of 0.05  $\mu\text{m}$ . They were then cleaned with acetone before PIII. Implantation was carried out

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in a multi-purpose plasma immersion ion implanter [7], equipped with several plasma generating tools, including RF discharge, hot filament discharge and vacuum arc metal plasma sources. Hence, metal PIII and gas PIII could be conducted consecutively in the same instrument without breaking the vacuum. The base pressure in the vacuum chamber was  $3 \times 10^{-4}$  Pa. Titanium or tungsten plasma was created by a vacuum arc discharge, and was introduced into the chamber through a curved magnetic field guide duct to remove deleterious macroparticles [8,9]. Pure titanium or tungsten PIII was carried out using the following conditions: main arc average current  $I_a = 1$  A; arc pulse duration  $t_a = 230$   $\mu$ s; target bias  $V_i = -25$  kV; voltage pulse width  $t_p = 350$   $\mu$ s; and the pulse repetition rate  $f = 33$  Hz.

The untreated or control sample was designated sample 0. Samples Ti1, Ti2 and Ti3 were implanted with titanium for 0.5, 1 and 2 h, and samples W1, W2 and W3 by tungsten for 0.5, 1 and 2 h, respectively. Synchronization of the target bias and vacuum arc pulses ensured pure metal plasma immersion ion implantation, without a significant metal deposition. After metal PIII,  $C_2H_2$  was introduced into the vacuum chamber, and a 200-W RF was applied to the antenna inside the vacuum chamber to ignite the plasma. In this mode,  $C_2H_2$  PIII was carried out directly after Ti or W PIII in the same instrument without breaking the vacuum, thereby eliminating potential contamination from venting.  $C_2H_2$  PIII was conducted at a constant pulse repetition rate of 100 Hz and a pulse width of 30  $\mu$ s. The target bias was  $-30$  kV and the processing time was 2 h.

The coefficient of friction was measured using a ball-on-disk wear tester equipped with a  $Si_3N_4$  ball, 6 mm in diameter. The tests were conducted using a load of 50 g and a sliding speed of  $1.5 \times 10^{-3}$  m/s. An MXT- $\alpha$ 7 digital microhardness tester was operated at a loading from 10 to 200 g, to measure the microhardness of each sample. The surface structure of the implanted sample was analyzed by Raman spectroscopy. Auger electron spectroscopy (AES) was employed to acquire elemental depth profiles.

### 3. Results and discussion

The microhardness values measured at different loads are shown in Fig. 1. The improvement is higher as the load is reduced. The samples that were implanted with tungsten and carbon (W + C) exhibit larger enhancement effects than those implanted with titanium and carbon (Ti + C). At the lowest load (10 g), the untreated sample shows a value of HV690, whereas the maximum microhardness value of the treated sample is HV1170. The samples that were implanted with a

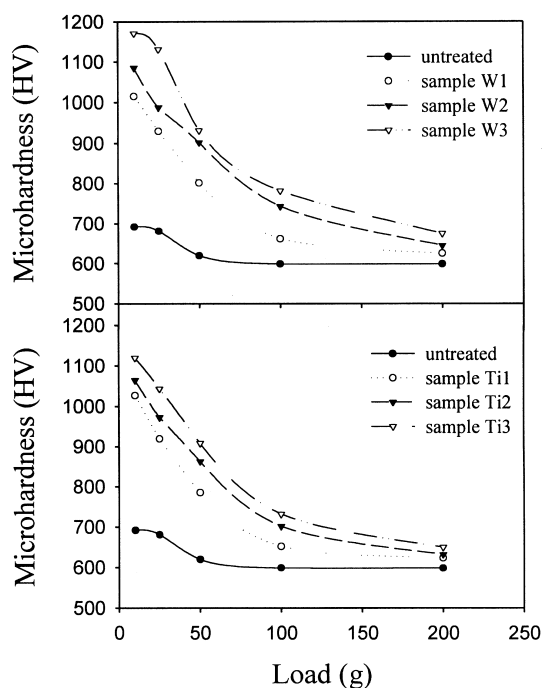


Fig. 1. Measured microhardness of the seven 9Cr18 samples at different loads.

higher metal ion dose have larger microhardness, indicating that the amount of implanted metal affects these properties.

The tribological characteristics were assessed using a ball-on-disk wear tester. The coefficient of friction was measured during the test, and the resulting wear tracks were inspected under an optical microscope to determine the track width. Fig. 2a,b, plots the friction coefficients as a function of the rotating cycles. The friction coefficient of the control sample quickly reaches a relatively high value of 0.8–1.0. On the other hand, the friction coefficient of the treated samples remains low (about 0.2) throughout the test. Fig. 3 shows the wear track width of each sample after being wear tested for 3000 cycles. The PIII samples have smaller track widths than the control. In addition, the samples implanted with (Ti + C) have smaller track widths than those implanted with (W + C). Therefore, better wear resistance is observed for the samples implanted with (Ti + C), although their microhardness is lower than that of the specimens implanted with (W + C). Fig. 4 depicts the SEM image of the wear tracks of the control and treated sample Ti1. The wear track is very evident on the control sample, displaying a severe and adhesion wear mode. On the contrary, the wear track is almost undetectable on the treated sample Ti1.

Fig. 5 shows the elemental depth profile acquired from sample Ti2 by Auger electron spectroscopy. A 400-nm thick carbon film was formed on the surface. The titanium profile manifests an 'implant-like' Gauss-

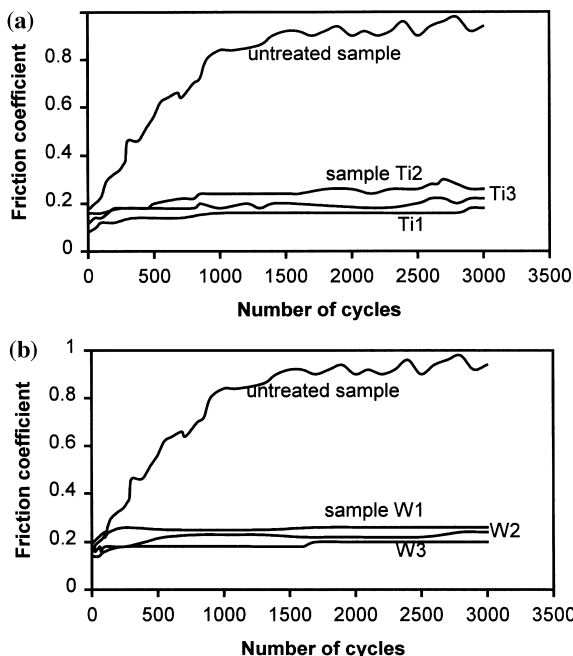


Fig. 2. Coefficient of friction vs. number of cycles: (a) Ti + C implanted samples; and (b) W + C implanted samples.

ian distribution, implying that pure titanium ion implantation has been achieved. Moreover, carbon atoms have penetrated into the substrate and an approximately 250-nm thick interfacial region, in which carbon, titanium, and substrate elements have been mixed, is delineated. In the Auger depth profile, since an average sputtering rate is used for the depth scale calibration, and different materials are known to sputter at different rates, the indicated film thickness is only an estimate. Fig. 6 shows the Raman spectrum of the surface carbon film of sample Ti2. The spectrum exhibits a broad Raman intensity distribution in the range 1400–1700  $\text{cm}^{-1}$ , centered at 1550  $\text{cm}^{-1}$ , which is in agreement with the results reported by other researchers [10–12]. This confirms that the film is amorphous, and that a carbon film with diamond-like-carbon (DLC) structure has been formed on the surface of 9Cr18 steel after  $\text{C}_2\text{H}_2$  PIII. The superior

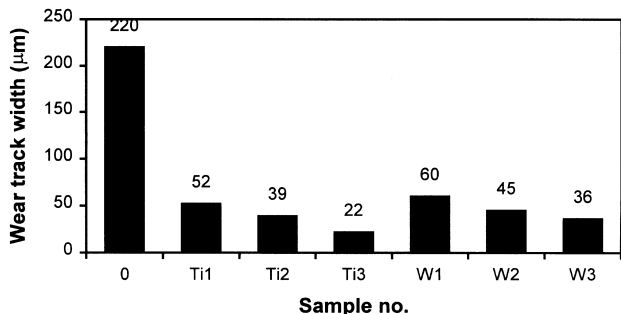


Fig. 3. Measured wear track widths of the control and treated samples.

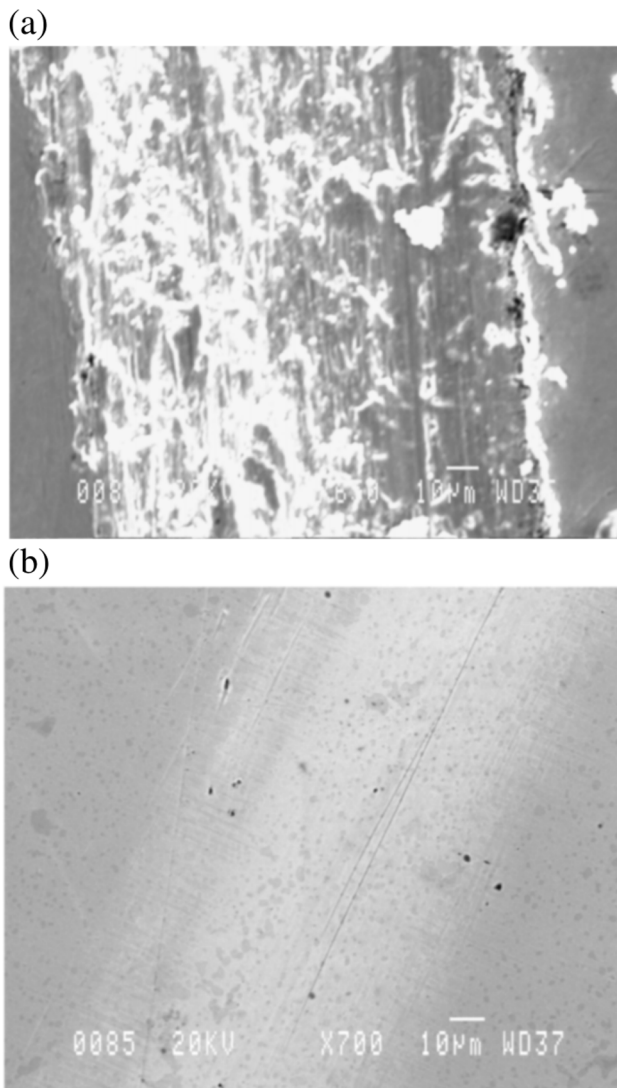


Fig. 4. SEM photographs showing the wear tracks on the 9Cr18 bearing steel samples after wear test on (a) the control sample; and (b) PIII sample Ti1.

properties of DLC as a coating material are well known, but good bonding of DLC films to the substrate may be difficult to accomplish. We have discovered a novel

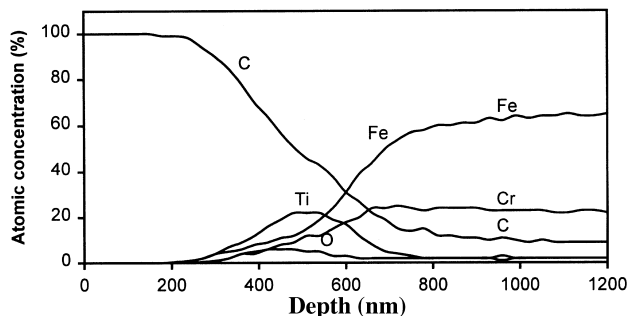


Fig. 5. Auger depth profile acquired from sample Ti2. The depth scale is estimated based on an average sputtering rate.

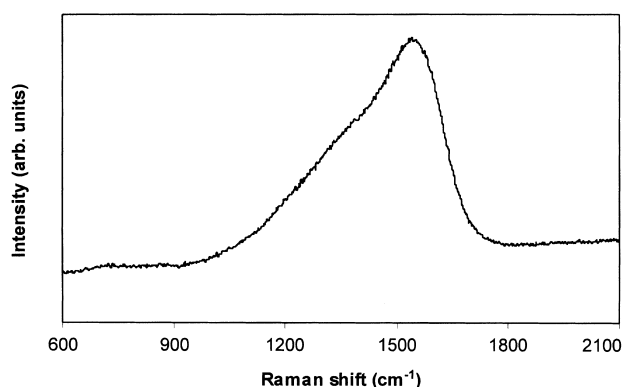


Fig. 6. Raman spectrum acquired from sample Ti2 indicating a surface diamond-like-carbon structure.

method to deposit DLC films with excellent properties. Due to its heavy mass, the implanted metal ions introduce significant sub-surface ion mixing, in addition to strengthening the materials. The synergistic effects of the surface DLC film and a well-mixed interface are believed to be responsible for the observed improvement in the surface properties of treated 9Cr18 steel samples.

#### 4. Conclusion

A method combining metal and acetylene plasma immersion ion implantation (PIII) has been shown to improve the microhardness, wear, and friction properties of 9Cr18 bearing steel. In this treatment process, Ti or W PIII was followed by  $C_2H_2$  PIII in the same chamber without breaking the vacuum, thus eliminating potential atmospheric species contamination. The Auger depth profiling data show a surface carbon film and a well-mixed interfacial layer. Raman spectroscopy indicates that the surface film is composed of diamond like carbon. The superior tribological properties of the

treated samples are believed to result from the DLC film and the well-mixed interface caused by metal PIII. Being a plasma immersion technique, this method is also applicable to machine parts with irregular geometries.

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