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Surface modification of steel by metal plasma immersion ion implantation using vacuum arc plasma source

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Abstract

Employing an improved vacuum arc plasma source, metal plasma immersion ion implantation (PIII) is performed on 9Cr18 bearing steel. Titanium, tantalum, molybdenum and tungsten ions are implanted followed by nitrogen PIII to result in a modified surface layer with superior wear resistance. The surface properties of the 9Cr18 bearing steel samples are evaluated by measuring the microhardness, wear property, coefficient of friction, as well as elemental depth profiles and chemical composition of the modified layer. The results show that the wear resistance of the samples treated by metal plus nitrogen PIII is enhanced to a larger degree than that of the samples undergoing nitrogen PIII alone. The XPS results indicate that some nitride phases have been formed in the implanted layer. In this paper, we will also discuss the improvement on the metal vacuum arc plasma source and experimental protocols. Using metal and gas PIII, the surface properties of 9Cr18 bearing steel are enhanced significantly.

Keywords: Bearing steel; Plasma immersion ion implantation; Surface modification; Vacuum arc plasma source

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1. Introduction

9Cr18 martensitic stainless steel is widely used as a bearing material in the aerospace, nuclear and other special industries due to its good corrosion resistant properties. When a bearing fails, it will impact the machine and the reliability of the whole system. Hence, prolonging the working lifetime and reliability of bearings is a priority [1]. Previous studies have revealed that failure of bearings occurs mainly on the surface or in the near surface region [2]. Consequently, enhancing the surface properties by surface treatment is a good way to prolong the lifetime and working reliability of bearings.

Plasma immersion ion implantation (PIII) has no line-of-sight restriction and retained dose problem characteristic of conventional ion beam implantation [3–6]. It is therefore an excellent surface modification technique to treat complex-shaped industrial components such as precision bearings [7]. PIII also retains the advantages of beam-line ion implantation, for example, the ability to introduce multiple elements at concentrations exceeding the solubility limits of conventional alloys [8]. Thus, one can implant multiple species at high concentrations to create a special alloy in the near surface region.

Vacuum arc (or cathodic arc) plasma is a low voltage, high current plasma discharge that takes place between two metallic electrodes in vacuum and can be used to introduce metal ions [9,10]. There are some previous works on metal plasma immersion ion implantation and deposition (MePIIID) [9–11] or pure metal ion implantation [12,13] using vacuum arc plasma source. Contamination of the vacuum arc metal plasma by 'macroparticles' is a disadvantage, and several techniques have been developed to remove them from the metal plasma. The most common approach is the use of a curved magnetic field guide [14,15], but the plasma is transported through the curved duct with a large loss, thereby resulting in a low working efficiency of plasma source. The transmission efficiency of the filter can be enhanced by a positive wall bias [16], or a positively biased electrode like the one introduced by Bilek et al. [17] can achieve the same purpose when inserted into the filter duct along its outer major circumference. To increase the metal plasma density and plasma transport efficiency, we have recently made modifications of our

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vacuum arc plasma source [18,19]. Using the improved vacuum arc plasma source, pure titanium, tantalum, molybdenum and tungsten PIII can be performed with a long implantation voltage pulse to treat 9Cr18 steel samples. We have also combined metal PIII with nitrogen PIII without breaking the vacuum to attain superior tribological properties than by nitrogen PIII alone.

2. Experimental

In our vacuum arc plasma source, it is not straightforward to bias the duct wall because it is a part of the PIII equipment. Therefore a bias plate was inserted into the filter duct. An improvement of about a factor of four in the transport efficiency was attained at a bias of +15 V [18,19]. To further enhance the efficiency, an additional focusing coil was placed in the vacuum chamber at the plasma source to minimize scattering of the metal plasma.

Coupons of 9Cr18 bearing steel [composition (wt.%): Fe 79.655, Si 0.8, Mn 0.72, P 0.035, S 0.03, C 0.96, and Cr 17.8] were cut from an exterior race of an industrial bearing which is in the quenched-and-tempered state. The samples received a final polish to a surface roughness, R_a, of 0.04 μm, followed by an ultrasonic clean in acetone. The PIII experiment was carried out in a multipurpose plasma immersion ion implanter [20] equipped with several plasma generating tools, including RF discharge, hot filament discharge, and vacuum arc metal plasma source. Hence, we could perform metal PIII and nitrogen PIII consecutively without breaking the vacuum. The improved vacuum arc plasma source described in the previous section was used to implant Ti, Ta, Mo and W ions into the 9Cr18 samples. A glow discharge nitrogen plasma ignited by heated filaments was employed to implant nitrogen into the specimens. The PIII processing conditions are shown as follows.

1. Metal PIII: main arc peak current 300 A, arc pulse duration 230 μs, implantation voltage 25 kV, implantation pulse width 280 μs, pulse repetition rate 33 Hz, base pressure 3×10^{-3} Pa, and implantation time 80 min.
2. Nitrogen PIII: implantation voltage 35 kV, pulse width 30 μs, pulse repetition rate 300 Hz, discharge voltage 80 V, discharge current 1 A, and gas pressure 2×10^{-2} Pa.

Samples Ti1, Ti2, Ta1, Ta2, Mo1, Mo2, W1 and W2 were implanted using the corresponding metallic elements. An untreated 9Cr18 sample designated 0 constituted the control sample. Among the implanted samples, Ti1, Ta1, Mo1, W1 were first implanted with the respective metallic species followed by nitrogen PIII for 2 h, whereas Ti2, Ta2, Mo2, W2 underwent nitrogen PIII for 4 h after metal PIII. For comparison, only nitrogen PIII was performed on samples N1 (2 h) and N2 (4 h). We measured the substrate temperature using an in situ thermocouple [21]. The substrate temperature was lower than 200°C during both metal and nitrogen PIII treatment.

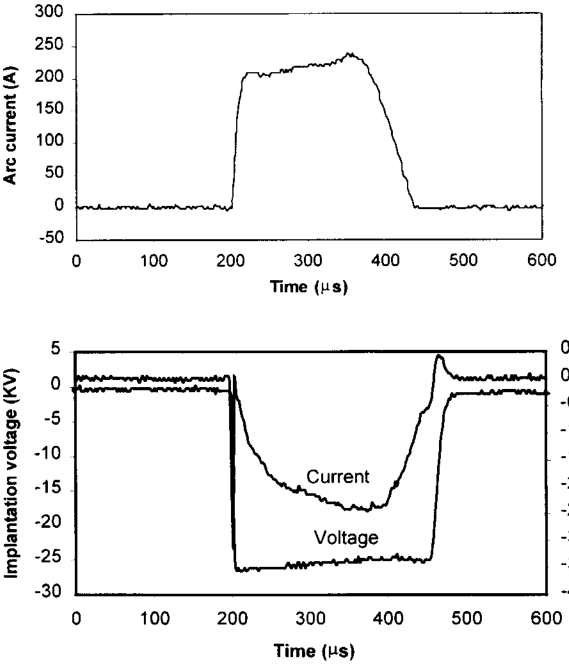

Fig. 1. Oscilloscope traces of (a) arc current, and (b) implantation voltage pulse and implantation current during metal plasma immersion ion implantation.

The arc current, target bias, and implantation current measured by an oscilloscope are exhibited in Fig. 1. Synchronization of the sample high voltage and arc pulses ensured pure metal plasma immersion ion implantation without significant metal deposition.

The coefficient of friction was measured from all samples using a pin-on-disk wear tester equipped with a ruby ball 3 mm in diameter. The tests were conducted using a load of 50 g and sliding speed of 1×10^{-3} m/s. An MXT-α7 digital microhardness tester was operated with a loading of 25 g to measure the microhardness of each sample. Chemical analysis of the implanted layers was carried out by X-ray photoelectron spectroscopy (XPS) and elemental depth profiles were acquired by Auger electron spectroscopy (AES) to derive the retained doses.

3. Results and discussion

Table 1 gives the microhardness of the 11 samples, including sample 0 that is the untreated control. Improvement after PIII treatment is quite evident. The samples implanted with metal plus nitrogen ions have higher microhardness than the samples treated by nitrogen PIII only. The samples implanted with (Mo+N)

Table 1
Microhardness and wear track width of the 11 samples

	Sample										
	0	Nl	N2	Til	Ti2	Tal	Ta2	Mol	Mo2	Wl	W2
Microhardness (HV)	551.4	680.4	765.2	814.3	845.2	792.6	832.6	912.3	988.7	813.9	831.5
Wear track width (μm)	250	115	87	53	40	60	45	54	40	52	45

show the largest enhancement effects, approaching 79%. It indicates that implanting metal ions into 9Cr18 steel yields a harder surface layer. Moreover, the samples implanted with a higher nitrogen dose have greater microhardness.

All the samples were subjected to a friction test of 3000 cycles. The coefficient of friction is measured during the test, and the wear tracks are inspected under an optical microscope to determine the track width after the test. A comparison of seven of the 9Cr18 samples is displayed in Fig. 2. The friction curves of sample Ti2, Ta2, Mo2, and W2 are almost the same as that of sample Til, that is, the friction coefficient maintaining lower value (0.1–0.3) during the whole test. The unimplanted sample has a relatively high coefficient of friction (0.7–0.8), and at the beginning of the test, the value is lower due to the existence of a small amount of water and adsorbates on the surface. As this layer is punched through during the test, the coefficient of friction increases rapidly after about 100 cycles. In comparison, for samples treated with PIII, the coefficient of fiction starts at a lower value (0.1–0.3) and maintains this level for a longer time as a result of the modified layer on the surface. With increasing rotating cycles, the coefficient of friction of four of the samples (N1, N2, Tal and W1) eventually reaches the same value (0.7–0.8) as the unimplanted sample. This is because the implanted layer is damaged and the underlying substrate is exposed. For samples Til, Ti2, Ta2, Mol, Mo2 and W2, the coefficient of friction remains small throughout the test. It implies that the implanted layers in these six samples have not been punched through even after 3000 rotating cycles, and they have a high wear resisting layer on the surface. It can be observed that the samples implanted with (Ti+N) and (Mo+N) have better tribological properties. Table 1 shows the wear track width of each sample after a pin-on-disk wear test of 3000 rotating cycles. A similar trend as the friction test is observed. The PIII samples have smaller track widths than the unimplanted sample. In addition, the samples treated by metal plus nitrogen PIII have smaller track widths than the samples treated by nitrogen PIII alone.

Fig. 3 depicts the elemental depth profiles acquired from sample Ti2 by Auger electron spectroscopy. The calculated retained doses of Ti and N are 2.92×10^{17} atoms/cm^2 and 5.7×10^{17} atoms/cm^2, respectively. Coupled with our tribological test results, it can be inferred that the co-existence of a metal ion and nitrogen plays a key role in the improvement of the surface properties of 9Cr18 steel. It can be observed that there is a fairly high amount of oxygen contamination in the modified layer due to oxygen species in the residual vacuum. The oxides formed in the surface layer are probably beneficial as they also contribute to the improvement of tribological properties of 9Cr18 steel.

Fig. 4 shows the XPS nitrogen 1s spectra acquired from samples Til and Tal at various depths. The sputtering rate was 4 nm/min and the energy spectra were acquired at three depths, surface, 20 nm and 60 nm. Sample Til shows only one salient peak at 400 eV on the surface. This peak corresponds to the α′ martensite containing nitrogen and α″ phase ($Fe_{16}N_2$). After sputtering for 5 min, i.e. at a depth of 20 nm, two peaks appear. The peak at 400 eV becomes smaller while the 396.5 eV peak becomes more dominant. The latter peak corresponds to the nitride state and is close to the

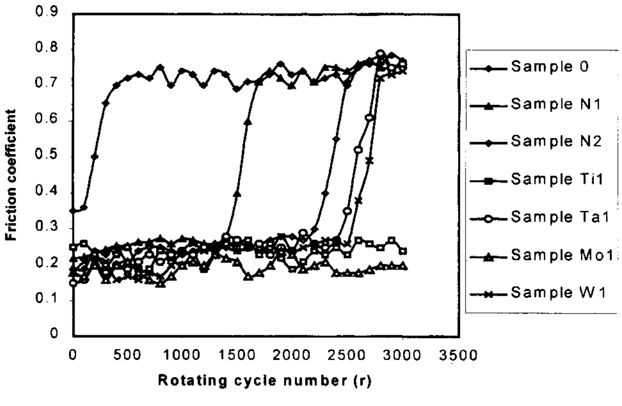

Fig. 2. Coefficient of friction curves of the 9Cr18 samples.

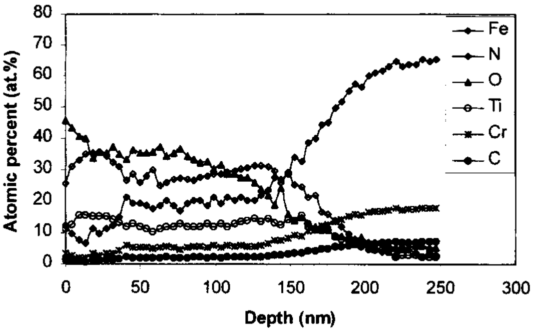

Fig. 3. Auger electron spectroscopy (AES) depth profile of sample Ti2.

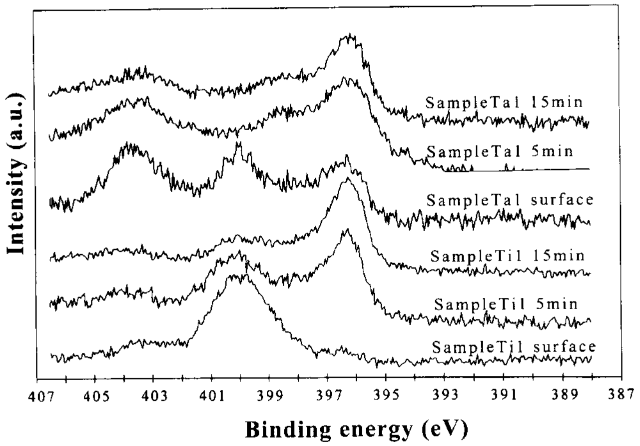

Fig. 4. X-ray photoelectron spectroscopy (XPS) nitrogen 1s spectra of samples Ti1 and Ta1 at three different depths: surface, 20 nm, and 60 nm.

binding energy of Cr_2N, CrN, and TiN. Therefore, nitride phases have formed at a depth of 20 nm. After sputtering for 15 min, that is, at a depth of 60 nm, the 400 eV peak almost vanishes, illustrating that at this depth, the implanted nitrogen atoms exist exclusively as nitrides. Nitride phases are known to have very high hardness and are believed to give rise to the superior microhardness and tribological properties reported in this work. It should be noted that some of the XPS peaks are not symmetrical, implying that the chemical states are not unique. The spectra acquired from sample Ta1 show a similar trend, except that the surface spectrum shows three peaks at 403 eV, 400 eV and 396.5 eV. The peak at 403 eV shows the formation of metallic nitric oxide (Me_3NO) stemming from minute oxygen contamination in the vacuum chamber. The peak at 396.5 eV indicates that nitride phases have formed on the surface of sample Ta1. The 403 eV peak diminishes with increasing sputtering depth. After sputtering for 15 min, this peak almost disappears as the amount of oxygen decreases. After sputtering for 5 min, the 400 eV peak no longer exists. The implanted nitrogen atoms mainly exist as nitrides, as demonstrated by the fact that the 396.5 eV peak is the dominant one. After sputtering for 15 min, there is only one peak corresponding to nitrides such as Cr_2N, CrN and TaN, implying that nitrides have become the dominant chemical state of nitrogen at this depth. These nitride phases with superior hardness exist in a dispersed state in the implanted layer and result in a dispersed phase hardening. They are believed to be responsible for the improvement in both the microhardness and wear properties.

4. Conclusion

The microhardness and wear properties of 9Cr18 bearing steel are significantly improved using plasma immersion ion implantation. Sequential metal and nitrogen PIII is an effective method to introduce multiple elements into steels. Our experimental results indicate that the tribological properties of the samples implanted with metal plus nitrogen plasma are enhanced to a larger degree than samples treated by nitrogen PIII alone. The XPS data show nitrides in the implanted layer and they are believed to play a key role in the improvement of the tribological properties of 9Cr18 steel. Our results confirm the efficiency of our improved metal arc source and show that metal and nitrogen PIII is an effective way to enhance the microhardness, wear properties, and lifetime of 9Cr18 bearing steel.

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