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SURFACE MODIFICATION OF METALS USING HIGH-FREQUENCY LOW-VOLTAGE PLASMA IMMERSION ION IMPLANTATION

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Abstract

Plasma immersion ion implantation (PIII) is a burgeoning surface modification technique and not restricted by the line-of-sight limitation plaguing conventional beam-line ion implantation. It is therefore an excellent technique to treat interior surfaces as well as components of a complex shape. To enhance the implant uniformity, we are utilizing a high-frequency, low-voltage process. The high dose rate and diffusion depth can be accomplished at a high pulsing frequency whereas the thinner sheath is more favorable to conformal implantation. In this paper, we will describe our hardware and experimental results. This high-frequency, low-voltage process increases the hardness of SS304 by nearly 65% and the wear track width is half of that of the unimplanted sample.

Plasma immersion ion implantation (PIII) is a fledgling technique to modify the surface of materials and industrial components [1-2]. It has a number of advantages over conventional beam-line ion implantation (IBII) such as high throughput and no line-of-sight restriction. The surface properties of many low-alloyed and micro-alloyed steels, stainless steel, tool steel, and so on have been successfully improved using PIII [3].

One of the biggest advantages of PIII over IBII is the ability to implant objects of irregular shape without either beam rastering or target manipulation. However, the dose uniformity may not be adequate especially on interior surfaces [4-6]. Theoretically, conformal implantation can be achieved when the ion sheath is completely conformal around the target, but in practice, it is very difficult due to the irregular shape of real objects. In addition, the corners and edges represent a special challenge since the local sheath is especially nonuniform [7]. Hence, the ion impact angle near a corner is oblique and the flux, which is enhanced above its planar value, peaks close to, but not at the corner [8]. Consequently, dose non-uniformity and sputtering which affects the retained dose is quite severe. It has been shown that samples with edges may exhibit considerable lateral dose variation. For samples with a wedge shape, the variation in the concentration of implanted argon can be as high as a factor of six depending on the process parameters [9-10].

Owing to the limited energy range of PIII, it is difficult to achieve a thick modified layer suitable for engineering applications. PIII is not practical over 100kV due to expensive instrumentation and arcing [11]. Alternatively, PIII can be carried out at an elevated temperature to increase dopant diffusion. Previous research has demonstrated that elevated temperature PIII (ET-PIII) works well for ferrous materials. Enhanced nitrogen diffusion increases the thickness of the modified materials, and the surface hardness and wear resistance improvements are greater than those achieved by conventional IBII [12-13]. For instance, ET-PIII of 34CrAlNi7 steel at 300°C - 500°C reduces the wear rate against ruby pin [14]. ET-PIII at 500°C gives rise to a 8µm - 10µm diffusion depth. ET-PIII is, however, different from conventional plasma nitriding. ET-PIII offers the possibility of producing surface structures typical of ion implantation, plasma nitriding, or a combination of the two, depending on the treatment temperature.

Recently, it has been pointed out that high-energy ion bombardment is not always essential, albeit desirable, to achieve satisfactory enhancement [15]. The hardness-load relation using 5kV PIII is close to that using 40kV PIII. Therefore, there are technical reasons favoring the use of a lower voltage, although high-energy bombardment have advantages in removing oxide layers which prevent nitrogen uptake as well as implantation through a surface layer. Meanwhile, it has also been shown that a higher dose rate is more favorable in conjunction with employing a lower implantation voltage [16]. A high frequency process increases the dose rate and raises the sample temperature during implantation. This can be coupled with using a low implantation voltage that reduces the sheath thickness and improves the lateral implant uniformity in samples possessing a complex shape. The potential of low-voltage PIII is not as well explored [17,18]. In this work, we concentrate on high frequency pulsing and an implantation voltage less than 5 kV. We will describe our newly developed power supply and present experimental results obtained using the high-frequency, low-voltage PIII technology.

Apparatus

The vacuum chamber and plasma sources of our PIII equipment has been described in detail elsewhere [19,20]. There are different means to generate the required voltage pulses and the

most desirable method is to use solid state switching [21]. To meet the requirement of high-frequency, low-energy plasma immersion ion implantation and nitriding, a semiconductor-based pulsing source utilizing solid state switching device has been developed in our laboratory. Fig.1 shows the schematic of our modulator. The pulsing circuit is based on the inverse transformation technology. When the drive signal is switched to the IGBT, the current will pass by the primary coil through IGBT1 and IGBT2. The primary DC voltage will be transformed into a square wave voltage on the secondary side of the transformer due to the digital nature of the IGBT, that is, on and off states only. This voltage is then delivered to the target in the vacuum chamber. The voltage transformation is achieved using four transformers (with a ratio of 1:4 each). They work in two modes and in a synchronous manner. The first mode is that the primary coils operate in parallel and the secondary windings are connected in series. Thus, a 310V DC input can produce a 4960V pulsed AC output to the plasma load. In the second mode, the secondary coils work in parallel to increase the capacity. However, the transformation ratio is limited to 1:4 to reduce the distributed capacitance because it is proportional to the square of the ratio. The pulsing frequency is designed to operate from 5kHz to 35kHz. The output voltage is adjustable with an upper ceiling of 5000V that is deliberately chosen to be our lower voltage limit for the present experiments. Fig. 2 displays the voltage waveform under a real plasma load. The instrumental conditions are: pure nitrogen, pressure= 2.0×10^{-2} Pa, glow discharge voltage = 90V, discharge current = 1.2A, filament voltage = 25V, filament current = 45A, and the exposed surface of the target is nearly 140cm².

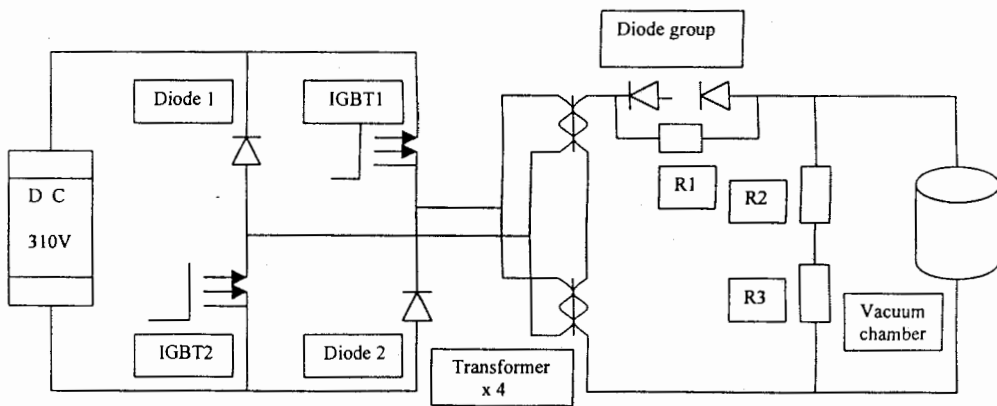


Figure 1: Schematic of the high-frequency, low-voltage generator

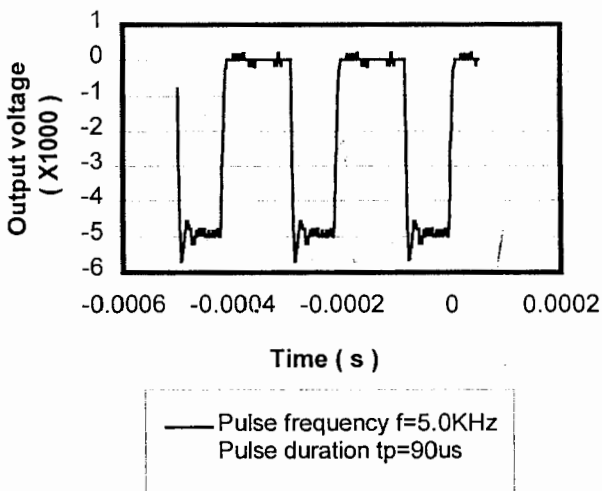


Figure 2: Output voltage of spell out generator

Results and Discussion

Samples 30 mm in diameter and 5 mm in thickness were cut from a bar of SS304. Each sample was polished progressively (800 grit silicon carbide abrasive paper was used at the end). The samples were implanted in our PIIH equipment using the conditions exhibited in Table 1.

Table 1: Experimental conditions

Sample	Implant voltage (KV)	Pulse frequency (KHz)	Pulse duration (μ s)	Implant time (min)
1	Unimplanted			
2	1.5	8.5	30	200
3	2.0	8.5	30	200
4	3.5	5.0	50	200
5	5.2	1.0	35	200

The hardness measurement of the treated and unimplanted samples was carried out on an HX-1000 microhardness tester. The results are depicted in Figs. 3 and 4. There is a discernible improvement in all the treated samples and the maximum improvement is observed to be more than 60% with a load of 25 g (comparing samples 4 and 1 in Fig. 3).

Fig. 3 shows the relationship between the surface microhardness and applied load. It is evident that the greater the applied load, the smaller is the hardness value. This characteristic has been observed in previous plasma immersion ion implantation and nitriding experiments. The results indicate a significant increase in surface hardness of all the treated samples. In particular, the sample treated at 3.5 kV (sample 4) demonstrates the most dramatic hardness improvement, and

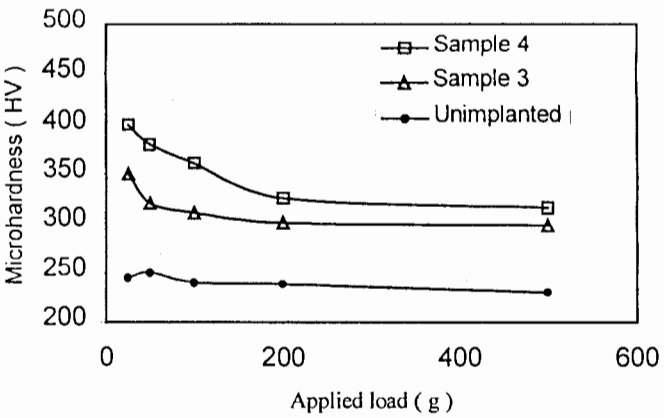


Figure 3: Effect of treatment conditions on surface microhardness

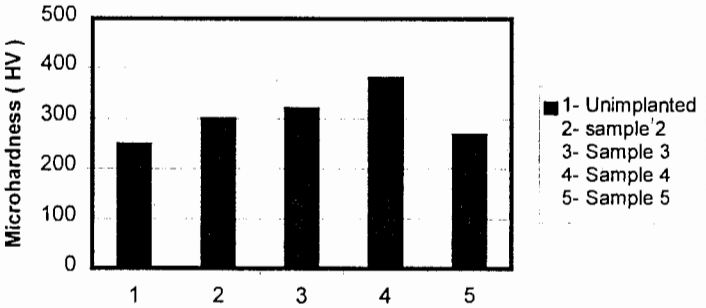


Fig. 4 The microhardness of different samples at a load of 50g

the microhardness with a test load of 500 g is higher by 30% than that of the unimplanted sample. This implies that the modified zone using the high-frequency, low-voltage process is much thicker than the implanted layer. It can also be inferred that substantial diffusion has taken place during the PIII step due to the high ion flux, higher sample temperature (>300°C), and radiation induced diffusion. The wear test conducted using pin-on-disk also shows that our process dramatically increases the wear resistance of SS304. The width of the wear tracks with 5000 passes is displayed in Fig. 5. The unimplanted sample produces a wear track width of about 120 μm at a load of 25 g. In comparison, the track width of the 3500V-treated sample is less than 60 μm and is half of that of the unimplanted sample.

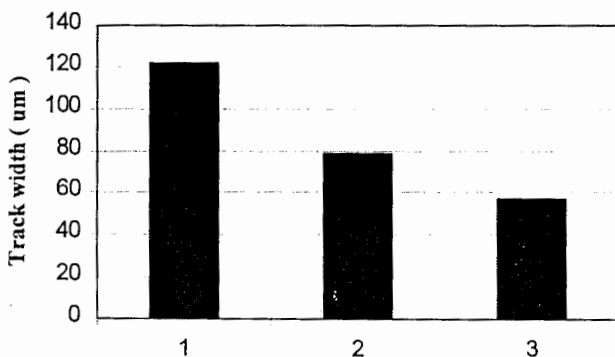


Figure 5: Wear track width of the samples against a 9Cr18 pin (pin radius=1.5mm) at a load of 25g, at a linear speed of 1.2cm/s after 5000 passes

The improvement in the surface hardness and wear resistance can be attributed to a deeper diffusion zone using our high-frequency, low-voltage experimental protocols, in spite of sputter etching of the surface at 5 kV. The enhancement in the surface properties is the result of the competition between implantation / dopant diffusion and surface sputtering. Further optimization of the treatment parameters, including the pulse frequency, implantation voltage, pulse duration, temperature, will produce better surface properties.

Conclusion

A new approach involving nitrogen plasma immersion ion implantation and nitriding is proposed for improving the surface properties of stainless steel materials. Using our newly designed high-frequency modulator, we have conducted high-frequency, low-voltage experiments to demonstrate the benefits and viability of this unique process. Because of the smaller plasma sheath, the process is more suitable to specimens of an irregular shape.

Acknowledgments

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