Hybrid elevated-temperature, low/high-voltage plasma immersion ion implantation of AISI304 stainless steel


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Abstract

Elevated-temperature plasma immersion ion implantation (PIII) is an effective non-line-of-sight technique to harden austenitic stainless steel by producing expanded austenitic phases in the near surface region. We report here a hybrid elevated-temperature, low/high voltage approach, which improves the efficiency while retaining the non-line-of-sight advantages of PIII. A low-voltage (4 kV), elevated-temperature (355°C) PIII process is first used to produce the modified layer, but the nitrogen concentration in this layer is typically relatively low and the thickness may not be adequate. This is followed by high-voltage (25 kV) PIII at a lower temperature to increase the nitrogen concentration and to achieve the desirable surface enhancement effects. To assess the efficacy of the technique, the samples are characterized using X-ray diffraction (XRD), nanohardness measurements, and secondary ion mass spectrometry (SIMS) depth profiling. The experimental results show that the nitrogen concentration increases by nearly 75% and the nitrogen penetration depth nearly doubles that of the low-voltage sample. The surface microhardness also improves by 150% and our data suggest that it is due to the formation of expanded austenites.

Keywords: Plasma immersion ion implantation; 304 Stainless steel; Microhardness; Nitriding

1. Introduction

The use of ion implantation to improve the mechanical and corrosion properties of austenitic stainless steels is quite common in industry [1–3]. Austenitic stainless steels are widely used in the chemical and food industries due to their excellent corrosion resistance, but the relatively poor wear resistance and low hardness of the materials are drawbacks precluding many would-be industrial applications. Austenitic stainless steels are difficult to nitride directly unless a high treatment temperature is employed, but high temperature can cause precipitation of CrN thus removing Cr from the solid solution and degrading the corrosion resistance of the materials. Implantation at a lower temperature can produce semi-satisfactory surface properties, but the nitriding efficiency is compromised. Recently, several treatment techniques have been proposed, for example, plasma immersion ion implantation (PIII) [4,5], low-voltage, high-current-density ion implantation [6,7], and high-frequency, low-voltage PIII [8,9]. These previous results have shown that thick expanded austenites several to tens of micrometers thick can be generated in the surface region at or near 400°C, and the metastable expanded austenite phase accounts for the improvement of the wear and corrosion resistance.

Unfortunately, for processes employing a high treatment temperature, the nitrogen concentration in the near surface region is not high on account of rapid thermal diffusion. This is particularly true for low-voltage PIII [10] required for samples possessing an irregu-
lar shape. This may be overcome by subsequent high-voltage PIII at a lower temperature to efficiently introduce a high concentration of nitrogen into the materials to take advantage of its low diffusivity at low temperature [11,12]. In this paper, we present this hybrid elevated-temperature, low/high voltage process on AISI304 in an immersion configuration. The process combines the benefits of low-voltage and high-voltage treatment while retaining the non-line-of-sight advantage necessary for odd-shaped and large industrial components.

2. Experimental apparatus and procedures

AISI304 stainless steel samples, 25 mm in diameter and 3 mm thick, were used in our experiments. One side of each specimen was ground and polished to an average surface roughness, $R_a$, of less than 0.01 μm. The samples were ultrasonically cleaned in alcohol and acetone before loading onto a custom-designed sample platen installed in a multi-purpose plasma immersion ion implanter [13]. The equipment was originally designed for low-temperature PIII and the sample chuck was sealed with F-rubber and cooled by recycling oil. In order to conduct ion implantation at high temperature, we designed and installed a sample extension as shown in Fig. 1. The ‘secondary’ sample platen was erected from the permanent or ‘primary’ chuck by means of a thin stainless steel tube. Owing to the relatively poor heat conduction along this thin tube, the samples placed on the secondary platen were easily heated by the incident ions even in the absence of external heating. In addition, this configuration made the installation of an in situ temperature-monitoring device relatively straightforward. In our improved thermocouple device, the read-out meter was electrically floated to alleviate problems associated with arcing and a large potential difference on the meter [14]. Therefore this system can work reliability even in the presence of electrical discharge between the target and vacuum chamber wall.

When performing low-voltage, elevated-temperature PIII, the samples were laid on the secondary platen, but for high-voltage PIII, the samples were put on the primary platen directly. This was necessary because during high-voltage PIII, the implanted ions excessively heated the samples unless there was efficient cooling.

The instrumental and experimental parameters are summarized in Tables 1 and 2. Sample #0 was the untreated sample serving as the control. Sample #1 was treated only with the low-voltage process, whereas samples #2–#4 underwent both low-voltage and high-voltage processing. The low-voltage experiments were conducted using a DTI semiconductor-based pulse modulator (HVPM 100–300) whereas the high-voltage treatment used a vacuum-electron-tube-based power supply [13]. The ion flux was calculated from the rate of the temperature rise as measured by the thermocouple for the low-voltage process or the implantation current for the high-voltage process. In the latter case, the displacement and secondary electron currents were subtracted to derive the ion density [16].

Table 1

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Sample platen temperature (°C)</th>
<th>Pulse voltage (keV)</th>
<th>Pulsing frequency (Hz)</th>
<th>Pulse duration (μs)</th>
<th>Implantation time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>355 a</td>
<td>4</td>
<td>2000 b</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>2 c</td>
<td>&lt; 100</td>
<td>25</td>
<td>500</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>3 c</td>
<td>&lt; 100</td>
<td>25</td>
<td>500</td>
<td>30</td>
<td>120</td>
</tr>
<tr>
<td>4 c</td>
<td>&lt; 100</td>
<td>25</td>
<td>500</td>
<td>30</td>
<td>180</td>
</tr>
</tbody>
</table>

aThe processing temperature is 355°C and it took 40 min to reach 355°C using nitrogen ion implantation and then further processed at that temperature for 30 min.

bEquilibrium pulsing frequency (4 kHz during the temperature rise).

cSubsequent high-voltage PIII after low-voltage PIII similar to sample #1.
Table 2

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Average ion current density (mA/cm²)</th>
<th>Implant dose (×10¹⁷ ions/cm²)</th>
<th>Information source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.03016⁶ + 0.01508⁶</td>
<td>4.75⁴ + 1.25⁴</td>
<td>Temperature rising rate at low temperature</td>
</tr>
<tr>
<td>2</td>
<td>0.0155⁵</td>
<td>3.5</td>
<td>Total current</td>
</tr>
<tr>
<td>3</td>
<td>0.0155⁵</td>
<td>7.0</td>
<td>Total current</td>
</tr>
<tr>
<td>4</td>
<td>0.0155⁵</td>
<td>10.4</td>
<td>Total current</td>
</tr>
</tbody>
</table>

a Current and implant dose during temperature rise.
b Current and implant dose at processing temperature of 355°C.
c Secondary electron coefficient assumed to be 4.7 [15].

3. Results

3.1. SIMS depth profiling

Elemental depth profiles of the four treated samples acquired by secondary ion mass spectrometry (SIMS) are exhibited in Fig. 2. Although the SIMS data have not been quantified due to the lack of a reference standard, direct comparison among the samples is valid. To facilitate comparison, only the nitrogen profiles are shown here even though iron and nickel were co-monitored during the analysis to check for matrix effects. As shown in Fig. 2, there are considerable differences between the two sets of samples. Samples #3 and #4 display much higher nitrogen concentration and deeper nitrogen penetration into the substrate.

3.2. X-Ray diffraction

The glancing angle X-ray diffraction patterns are depicted in Fig. 3. The angle (2θ) was scanned from 35 to 55° to disclose the phase change in the modified layer since the primary austenite peaks (γ(220), γ(311)) located near 75° and 90° are quite small. Compared to the untreated sample (sample #0), the low-voltage PIII specimen (sample #1) shows an inappreciable phase change. This suggests a relatively small nitrogen concentration in the modified layer or a thin layer. After subsequent high-voltage PIII, the diffraction spectra change more dramatically. New peaks appear next to the primary austenite peaks indicating the formation of new phases, and the diffraction patterns in the high-voltage PIII samples depend on the implant dose. The spectra acquired at 5–20° from the high-voltage samples show the formation of an fcc phase whose peak broadens and shifts to a lower Bragg angle than the austenite peaks. The peak shift becomes larger as the implant dose increases. These peaks can be attributed to an expanded austenite phase (γN). The lower Bragg angles reflect the volume expansion of the lattice to accommodate the excess nitrogen [18]. At all incident
Fig. 3. X-Ray diffraction spectra of the samples ($\alpha = 20^\circ$).

angles, the austenite peaks of sample #3 have a low intensity in comparison with the expanded austenite peaks. This indicates that expanded austenite has formed to a considerable depth.

3.3. Surface hardness

The nanohardness and elastic modulus of the untreated and implanted samples are depicted in Fig. 4. Nitrogen PIII increases the surface hardness of all the treated samples. The best improvement is attained when the hybrid low-voltage/high-voltage process is adopted. For practical comparison, Si has a hardness value of 10 GPa, fully hardened M2 tool steel has a hardness of $\sim 12$ GPa, and TiC has a hardness of $\sim 18$ GPa [19], indicating that our hybrid approach is quite effective. A closer look at our data reveal that samples #1 and #2 have similar surface hardness, and the same is true for samples #3 and #4. Among the four treated specimens, sample #3 exhibits the most dramatic hardness improvement, approximately 150% better than that of the untreated sample (sample #0). The elastic modulus data also displayed in Fig. 4 indicate that the implant dose has a negligible influence on the elastic modulus.

4. Discussion

The nitrogen profiles in general are characteristic of thermal diffusion in stainless steel. The nitrogen concentration diminishes rapidly at the diffusion front and the peak of the nitrogen profile occurs just below the surface. The lower nitrogen concentration at the top surface region is due to surface oxidation upon exposure to air. Previous SIMS results on nitrogen-implanted AISI304 demonstrate that the nitrogen peak location corresponds to the thickness of the oxide layer [20]. In low-voltage PIII, the ion current is typically lower than in that low-voltage, high-ion-current-density ion implantation [6,7], and the pulsing frequency or duty cycle is also low in order to maintain a reasonable sample temperature. In addition, sputtering is quite severe in this voltage range and the net retained dose of nitrogen is thus not high enough to yield the desirable surface properties. It is speculated that a lower implantation voltage, higher target temperature or long treatment time will produce a thicker modified layer.

As shown in Fig. 5, subsequent high-voltage PIII increases nitrogen incorporation as well as the modified layer thickness substantially. Compared to sample #1 (low energy), the nitrogen peak concentration of sample #3 increases by nearly 75% and the nitrogen penetration depth nearly doubles. In contrast, sample #2 shows very little change in the nitrogen concentration, even though the thickness of the modified layer does increase. Our findings suggest that high-voltage PIII enhances nitrogen diffusion by radiation and local heating effects. The biggest advantage of this proposed hybrid process is that a high nitrogen dose as well as a thick modified layer can be generated at relatively low temperature and in a reasonable period of time, and this technique is therefore desirable for materials such as AISI304. Our results also suggest that there is a certain process window that yields optimal enhancement effects, particularly with regard to the high-voltage implant dose. It appears that a proper implant dose is critical to the improvement of the surface properties, and an excessively high implantation dose does not yield further improvement. This may be related to the effects of the maximum retained dose in low-temperature ion implantation.

The treated samples reveal a shift of the austenite peaks (Fig. 3). This shift that has been observed previously [4–7,10,21–23] is associated with the expanded austenite caused by the nitrogen remaining in solid solution in the fcc lattice. The peak shift and intensity in samples #1 and #2 are small compared to those in
samples #3 and #4. This indicates that the latter two samples possess more nitrogen in the surface layer that can be verified by the space constant. That is to say, as the nitrogen content increases with the treatment time, the expansion also increases, for example, \( d = 0.207 \text{ nm} (\gamma_{(111)}), d = 0.210 \text{ nm} (\gamma_{N(111)}), \) and \( d = 0.213 \text{ nm} (\gamma_{N(111)}) \) for the untreated sample, sample #2, and sample #4, respectively. In our case (\( \leq 355^\circ \text{C} \)), diffusion of interstitial nitrogen is enhanced relative to that of chromium. Therefore, only the expanded austenite, depending on the thickness of the modified layer and substrate austenite peaks, are detected. This is very important to ensure that the corrosion resistance does not degrade. In fact, similar surface structures have been observed in austenitic stainless steel by other nitrogen-adding methods, for instance, plasma nitriding [22,24], ion implantation [6,7,25], and PIII [4,5,23].

It can be observed that the formation of expanded austenite is the principle microstructural change in the treated samples. This phase has a high hardness and good wear resistance due to the compressive nature of the substrate. Moreover, the hardness increases with the treatment time since the hardness of the expanded austenite increases with nitrogen supersaturation [23]. In fact, enhancing the surface properties of iron-based materials by nitrogen ion implantation has been applied for many years and it has been demonstrated that many mechanisms are responsible for the strengthening effects for different materials [26,27]. In this hybrid treatment process of AISI304, solid solution strengthening is the most likely mechanism due to materials involved and processing temperature. The hardness improvement stems from not only the penetration depth of nitrogen but also the nitrogen concentration. According to calculation based on the parameters provided with the instrument, \( \text{HV} = 15 \text{ GPa} \) corresponds to an indentation depth \( h \) of approximately 0.07 \text{ m}, which is within the nitrogen-modified zone but larger than the thickness of the surface oxidation layer. In summary, the nitrogen profiling results and X-ray diffraction spectra are consistent. Samples #1 and #2 show only a small increase in hardness whereas samples #3 and #4 show improved hardness.

In this work, we present the experimental results demonstrating the efficacy of our hybrid treatment process on AISI304 stainless steel in a plasma immersion configuration. Low-voltage implantation/nitriding and subsequent high-voltage implantation increase both the nitrogen concentration and penetration. However, the process must be further optimized to achieve the more ideal situation with a higher surface nitrogen and thicker underlying expanded austenite zone (with nitrogen concentration of approx. 20 at.\%). In addition, more work must be done to comprehend the enhancement mechanism which we speculate to be a synergistic effect of the low-voltage and high-voltage processes.

5. Conclusion

Low-voltage plasma immersion ion implantation introduces some nitrogen into AISI304 materials at a low temperature, but a relatively thin modified layer and low nitrogen concentration result. Subsequent high-voltage PIII process improves the hardness significantly. Our results indicate that it is due to expanded austenite phases and deeper in-diffusion of the implanted nitrogen. The proposed technique is better than a one-step low (or high)-voltage, elevated-temperature PIII process. The hybrid process increases not only the nitrogen concentration but also the retained implant dose. Throughout the hybrid process, the sample temperature remains relatively low thereby precluding the formation of CrN phases and the loss of Cr from the solid solution, which may lower the corrosion resistance. Our methodology can be further simplified by installing a sample platen allowing control of the sample temperature over a wide range, so that the two steps can be performed consecutively without breaking vacuum. Our results suggest an interesting and practically important phenomenon in that the implant dose in the high-voltage process is critical to achieve the optimal results. Further work is needed to reveal the statistical variations as well as detailed mechanisms.

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References