Oxygen-induced nickel segregation in nitrogen plasma implanted AISI 304 stainless steel

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Abstract

Austenite stainless steel is widely used commercially due to its superior corrosion resistance. Plasma surface treatment has been shown to improve the wear resistance of the materials without degrading the corrosion resistance. Plasma immersion ion implantation (PIII) is a special form of plasma treatment in which the ion energy can be adjusted easily and its non-line-of-sight characteristic makes it suitable for large industrial components possessing an irregular geometry. We observe nickel segregation beneath the top surface in nitrogen plasma immersion ion implanted AISI 304 stainless steel. The amount of segregated nickel and the location depend on the implantation conditions. The phenomenon can be attributed to oxygen-induced surface segregation despite the use of high-purity (99.999%) nitrogen in our experiments. The Auger results indicate that the sample surface has been unexpectedly oxidized in spite of a very small amount of oxygen in the residual vacuum. This is due to the non-UHV (ultra-high vacuum) nature of PIII instruments and the reactive plasma environment. It is believed that the movement of the nickel atoms away from the surface is due to the higher affinity of oxygen to Cr or Fe than Ni. Our investigation also shows that the phenomenon is not related to nitrogen incorporation. As the properties of the treated sample depend on many factors, nickel segregation must be considered in designing PIII experiments. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Plasma implantation; Surface oxidation; Segregation; Stainless steel

1. Introduction

Nitrogen ion implantation has been shown to enhance the wear resistance of austenitic stainless steel which is widely used in the industry due to its good corrosion characteristics [1]. Plasma immersion ion implantation (PIII) combining the abilities to treat, implant, and deposit coatings offers increased process flexibility such as larger implantation energy range and the non-line-of-sight advantage for the treatment of large and irregularly-shaped industrial components [2,3]. Our previous experiments have demonstrated that nitrogen PIII can effectively enhance the surface properties at either low or elevated temperature [4–7]. At low temperature, the implanted layer tends to be quite thin, and some nitrogen atoms remain in solid solution while the rest may bond to chromium and iron atoms to form nitrides. In general, the chromium oxide film is quite dense and thus very effective as a corrosion resistant layer, although it does not contribute significantly to the tribological properties [4,8]. At elevated temperature (generally <450°C), if enough nitrogen is present at the surface, the nitrogen will diffuse into the bulk and form expanded austenite [9]. The thickness of the modified layer can be much larger than the projected range of the nitrogen ions under the right conditions. The expanded austenite is responsible for the improvement of the wear and corrosion resistance despite its metastable nature, and so elevated temperature PIII has recently received much attention.

Unlike conventional beam-line ion implantation, processes such as ion implantation, ion bombardment assisted deposition and plasma adsorption take place simultaneously in pulsed mode PIII. Thus, the impurity incorporation mechanism is different from that of beam-line ion implantation. At elevated temperature or in a reactive gas ambient, impurity adsorption onto the surface of the sample is quite prevalent thereby altering
the surface structure and properties of the materials together with high-energy ion implantation. Therefore, it is important to note that during PIII, surface reactions including surface adsorption and implantation as well as diffusion take place simultaneously. The movement of atoms is not strictly simple diffusion. Our previous experiments reveal nickel accumulation beneath the surface after low temperature PIII [4]. This phenomenon has seldom been explored even though several groups have applied PIII processing to austenite stainless steel [4–7]. It may be related to surface oxidation, and in this work, we investigate the nickel segregation phenomenon by studying the effects of surface oxidation and nitriding.

2. Experimental

The test samples were made of commercial AISI304 stainless steel. They were polished to attain a good surface finish before the PIII experiments. To investigate the effects of oxygen and nitrogen on nickel segregation, three different experiments were conducted in our multi-purpose plasma immersion ion implanter [10]:

1. Low-temperature, high-voltage (LTHV) plasma immersion ion implantation for a thin modified layer and low oxygen incorporation due to low temperature and low diffusivity.
2. Elevated-temperature, low-voltage (ETLV) plasma immersion ion implantation for a thick modified layer with low oxygen incorporation due to severe sputtering of surface oxide.
3. Elevated-temperature, medium-voltage (ETMV) plasma immersion ion implantation for a thick layer with high oxygen incorporation due to thermal diffusion and less sputtering.

The instrumental parameters are summarized in Table 1.

<table>
<thead>
<tr>
<th>Processing conditions</th>
<th>Temperature (°C)</th>
<th>Voltage (kV)</th>
<th>Pulse frequency (Hz)</th>
<th>Expected oxygen content</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTHV</td>
<td>&lt;100</td>
<td>30</td>
<td>500</td>
<td>Less</td>
</tr>
<tr>
<td>ETLV</td>
<td>300</td>
<td>2.5</td>
<td>5000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>8</td>
<td>320</td>
<td></td>
</tr>
<tr>
<td>ETMV</td>
<td>360</td>
<td>16</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>25</td>
<td>150</td>
<td>More</td>
</tr>
</tbody>
</table>

In the low-temperature experiments, the samples were laid on the oil-cooled target holder and the sample temperature was <100°C. In the elevated-temperature experiments, the samples were put on a secondary platen without cooling. The sample temperature was monitored in-situ employing an electrically floating thermocouple. The nitrogen plasma was sustained by hot filament glow discharge at a working gas pressure < 0.05 Pa. The high-voltage experiments at low-temperature or elevated temperature were carried out using a hard-tube-base modulator [10] and the low-voltage PIII was performed using a high-frequency, low-voltage pulse modulator [11].

3. Results

The elemental depth profiles of the treated samples were obtained by Auger electron spectroscopy (AES) with argon ion sputtering. As shown in Fig. 1, the low-voltage, elevated-temperature sample has a thick modified layer rich in nitrogen. The nitrogen concentration is ~ 18 at.% and similar to the atomic concentration of chromium. On the very surface, the iron atomic fraction is low on account of severe surface oxidation and carburizing effects. The chromium concentration is higher near the surface and there is a slight pileup of nickel beneath the surface oxide. Fig. 2 shows the depth profile acquired from the high-voltage, low-temperature sample. The modified layer is thinner compared to that displayed in Fig. 1, and the nitrogen distribution resembles a Gaussian distribution. The surface is also abundant in oxygen but has lower carbon. The chromium concentration is higher in the near surface region.

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Fig. 1. Elemental depth profile acquired from the sample treated by the elevated-temperature, low-voltage (ETLV) process by sputtering Auger electron spectroscopy.
reaching a maximum of 32 at.% that is 1.8 times higher than that in the bulk. The oxygen profile shows a surface peak. The ratio of oxygen to chromium indicates that iron oxide and chromium oxide exist in the top layer because of a surplus of oxygen. The elevated-temperature, medium-voltage sample shows very different results. As shown in Fig. 3, the oxygen-enriched layer is thick and the nitrogen concentration is low. There is an apparent pileup of nickel atoms underneath the oxide. Fig. 4 compares the oxygen and nickel depth profiles of the samples treated at elevated temperature (360°C) and different implantation voltages. A higher implantation voltage leads to a higher oxygen concentration and deeper nickel pileup. Therefore, the experimental conditions have a large influence on the redistribution of nickel.

4. Discussion

The AES results indicate high surface oxygen after nitrogen PIII. Oxygen atoms can be recoiled from the original oxide film on the sample surface into the substrate by energetic ion bombardment. At the same time, ion bombardment introduces sputtering and some of the sputtered species can be deposited or implanted back onto the sample at a later stage. There also exists a small amount of oxygen contamination in the residual vacuum of our instrument due to out-gassing and minor leaks. Oxygen containing gaseous species can react with the surface. They can also be ionized in the plasma and co-implanted into the substrate together with nitrogen ions. In fact, oxygen contamination is inevitable as PIII instruments are usually not designed for ultra-high vacuum (UHV) operation, and surface oxidation has been reported by several groups using different machines [12–14].

Our results disclose nickel segregation under all our three PIII conditions even though the extent of it depends on the individual process. A segregation process is characterized by a driving force and diffusion. In vacuum, if the temperature is high enough, certain atoms will re-distribute to reduce the surface free energy. If the solid surface is in direct contact with a gas, the chemical reaction between the gas molecules and the solid atoms will play a dominant role in surface segregation. In our experiments, the AISI304 stainless steel sample surface should react with nitrogen. However, the more energetically favored oxidation reaction causes the surface to be severely oxidized. This occurs even in the presence of a relative small partial pressure of oxygen in the vacuum chamber. Oxygen is activated and ionized in the plasma and there is enhanced oxygen adsorption onto the irradiated sample surface in concert with implantation. As shown in Fig. 5, the location of the maximum nickel concentration appears beneath
the oxygen-enriched surface zone. This oxygen-induced segregation behavior can be explained in terms of chemisorption induced surface segregation [15, 16]. The oxygen affinity to different elements is key to this phenomenon. Oxygen chemisorption provides a driving force to enrich the surface with the element forming stronger chemical bonds. This phenomenon has been reported for the oxidation of binary alloys such as Ni–Mg [17] and Ni–Nb [18] as well as semiconductors like SiGe [19, 20]. In the SiGe experiments, Ge is depleted from the silicon oxide layer and piles up at the oxide/substrate interface forming a Ge-rich layer. This phenomenon is sometimes desirable and useful. For example, Ge nanoparticles produced this way exhibit interesting optical properties [21]. It should be noted that the previous work has demonstrated direct oxidation of binary alloys, but the oxygen-induced segregation theory may also apply to Fe–Cr–Ni ternary alloys and nitrogen implantation described here.

During PIII, oxygen reacts with the sample surface. The heat of formation of nickel oxide is $-58.1 \text{ kcal mol}^{-1}$ while the heat of formation is $-63.64 \text{ kcal mol}^{-1}$ for FeO, $-197.0 \text{ kcal mol}^{-1}$ for Fe$_2$O$_3$, and $-252.9 \text{ kcal mol}^{-1}$ for Cr$_2$O$_3$ [22, 23]. Therefore, Cr and Fe are preferentially oxidized. Similar to the behavior of Ge in the SiGe system, nickel is depleted from the iron and chromium oxide region during oxidation. The final depth profile shows the outward movement of chromium and iron and inward migration of nickel. The investigation on the oxidation behavior of Ni$_{30}$Zr$_{64}$ [24] has demonstrated that oxidation of nickel appears to occur only after all surrounding Zr atoms have been completely oxidized (the heat of formation of Zr is $-249.5 \text{ kcal mol}^{-1}$ and similar to that of chromium). As a consequence, a higher concentration of Zr will result in a lower oxidation efficiency of nickel under the same oxidation conditions. In our samples, chromium and iron are more abundant than nickel and the oxygen partial pressure is low. Therefore, it is difficult to oxidize nickel in this environment and nickel is preferentially segregated towards the oxide interface.

As it is practically impossible to get rid of oxygen in PIII instruments, the efficacy of nitrogen PIII will be impacted by oxygen adsorption and implantation. Consequently, the surface properties of the treated samples will be affected by the incorporated elements and segregation effects induced by them. In conjunction with the presence of oxides and nitrides, the depletion of nickel from the surface will affect the surface properties of the treated AISI 304 stainless steel samples. This behavior is not observed in conventional nitriding experiments at high temperature. Our low-voltage, elevated-temperature (ETLV) experiments suggest that nickel segregation is not related to nitrogen incorporation. The formation of a thick layer rich in nitrogen is revealed, but the nickel distribution is not modified significantly, as shown in Fig. 2. If the nickel movement was influenced by nitriding, the nickel concentration in the nitrogen-enriched zone would change. From the viewpoint of chemical bonding, oxygen-induced nickel segregation is related to the change of the chemical bond or structure. The elements are redistributed in the layer to attain a lower energy. Oxidation of chromium or iron is energetically preferred over nitriding. This is confirmed by our X-ray diffraction (XRD) experiments that no new nitride phases are detected after PIII treatment of austenite stainless steel when the treatment temperature is not high (but $<400^\circ\text{C}$). Consequently, nitrogen incorporation does not substantially change the metallic bonds between the elements. Our results are consistent with those shown by Garke et al. who show that there is only a small amount of nickel in the oxygen-implanted region, whereas there is no change in the nickel concentration and nickel is elemental in the nitrogen-implanted zone [13].

The presence of different alloying or impurity elements leads to different properties of the stainless steel materials. For example, chromium is responsible for its corrosion-resistance, nitrogen can increase the strength, and nickel acts as a stabilizer of austenite. It has also been suggested that nickel influences the adhesion and mechanical properties, reduces the rate of euton diffusion in Cr$_2$O$_3$ scales, and retards the transformation of Cr$_2$O$_3$ to FeCr$_2$O$_4$ + Fe$_2$O$_3$ [25]. As there is nickel redistribution in nitrogen PIII samples, there is a corresponding change in the equivalent nickel content ($\delta$) on the surface [26]:

$$
\delta = 1.0(\text{wt.}%\text{Ni}) + 30(\text{wt.}%\text{C}) + 30(\text{wt.}%\text{N})
+ 1.0(\text{wt.}%\text{Co}) + 0.5(\text{wt.}%\text{Mn}) + 0.3(\text{wt.}%\text{Cu})
$$

(1)

$$
\text{wt.}\%\text{Element}_i = \frac{\text{at.}\%\text{Element}_i \times M_i}{\sum_{j=1}^{L} \text{at.}\%\text{Element}_j M_j}
$$

(2)
Fig. 6. Depth profile of equivalent nickel content ($\delta_i$) for the three PIII processes. $\delta_i$ is normalized by its maximum value ($\delta_{i\text{max}}$).

where Element$_i$ represents the $i$th element, $M_i$ or $M_j$ is the $i$th or $j$th atom mass, and $L$ is the total number in the bulk.

As shown in Fig. 6, different degree of nickel segregation is observed under different PIII conditions and the equivalent nickel content in the near-surface region differs. Nickel re-distribution may lead to non-uniform $\delta$ and different material properties (e.g. crevice corrosion) along the depth. As a result, different corrosion characteristics due to the different composition and non-uniformity may be expected at different depths in the near surface region [4]. This phenomenon must therefore be considered in the design of PIII experiments.

5. Conclusion

We observe nickel segregation in AISI 304 stainless steel samples treated by nitrogen plasma immersion ion implantation. Even though PIII-treatment of AISI 304 has been investigated before, our results show that the phenomenon is not due to nitrogen implantation or nitriding but rather because of surface oxidation. As PIII instruments are typically designed for non-UHV operation, there is a small amount of oxygen and oxygen-containing species in the residual vacuum even though the purity of the nitrogen gas used is 99.999%. Due to the highly reactive solid surface in the plasma environment and the presence of excited oxygen species in the plasma, there is significant surface oxidation together with oxygen co-implantation. Chromium and iron have a higher affinity to oxygen than nitrogen, and so the surface is preferentially oxidized and not nitrided. Similar to the behavior of Ge in the oxidation of SiGe, nickel is preferentially snow plowed into the substrate as confirmed by our three PIII experiments. Since the surface properties of the treated samples depend on many factors, the oxidation effects and change in the nickel concentration must be considered when designing PIII experiments.

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