Improvement of the slurry erosion resistance of an austenitic stainless steel with combinations of surface treatments: Nitriding and TiN coating

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Abstract

The combination of different surface treatments for improving the erosion resistance of an AISI 304 stainless steel was studied. Six kinds of sample conditions were tested in a slurry composed of distilled water and SiC particles: High temperature gas nitriding (HTGN), low temperature plasma nitriding (expanded austenite), high temperature gas nitriding followed by a PVD-TiN coating, low temperature plasma nitriding followed by a PVD-TiN coating as well as PVD-TiN coated and uncoated samples in the solubilized condition. The erosion tests were performed during 6 h in a jet-like device with a normal angle of incidence and an impact velocity of 8.0 m/s.

Wear rates were assessed by accumulated mass loss measurements and through analysis of scanning electron microscopy images of the worn surfaces. The results were related to the microstructure and hardness of the surface to establish a ranking of the different surface treatments. After the first few minutes of testing cutting of the surface occurred in the solubilized, in the HTGN and in the low plasma nitrided AISI 304 samples, whereas TiN coated samples did not show any cutting marks, although some indentation marks could be observed. The TiN coated samples showed wear resistances one order of magnitude greater than the solubilized, HTGN and low plasma nitrided samples.

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Keywords: Slurry erosion; TiN coatings; High temperature gas nitriding; Low temperature plasma nitriding; Expanded austenite

1. Introduction

Austenitic stainless steels have been used in a lot of industrial applications owing to their good corrosion resistance. However this steel suffers from poor wear resistance in comparison to other stainless steels, leading to premature failure of engineering parts. Many of these failures in marine, food, chemical, and energy industries are related with erosion wear, due to impact of high velocity particles entrained in fluid streams. During the last years, different surface treatments using nitrogen have been developed for improving the wear resistance of this material without loss of its corrosion resistance. These treatments include high temperature gas nitriding HTGN [1] low temperature plasma nitriding [2,6], and TiN coatings deposition [4]. In this work the potential of these surface treatments for reducing erosive wear behavior of an AISI 304 stainless steel is assessed.

During a HTGN process, a sample is annealed in a nitrogen rich atmosphere, between 1273 and 1473 K. In this range of temperatures, nitrogen diffuses through the surface forming a layer with nitrogen in solid solution. HTGN has been successfully used to improve the erosion resistance of different stainless steels [1,5]. On the other hand, low temperature plasma nitriding forms a layer of a metastable fcc solid solution supersaturated in nitrogen, sometimes called ‘expanded austenite’. This phase is very hard and improves the load bearing capacity and the wear resistance while maintaining the corrosion resistance of austenitic stainless steels [2,3,7]. The formation of this layer may not be enough to avoid wear under severe testing conditions. The deposition of an additional hard coating on a nitrided substrate improves the adherence of the layer to the substrate and avoids the abrupt change of mechanical properties between the TiN layer and the substrate. An abrupt variation of hardness and elastic modulus leads to failure of the coating due to a low load bearing capacity of the substrate [3]. When the duplex treatment is composed by a pulsed plasma nitriding treatment followed by a PVD-TiN
coating and both processes are carried out in the same chamber the treatment is called a hybrid treatment.

In this work, the combination of different surface treatments using nitrogen, for improving the erosion resistance of an AISI 304 stainless steel, was studied.

2. Experimental procedure

2.1. Specimens and treatments

Solubilized (solution annealed) samples of AISI 304 stainless steel were used as base material for the different treatments. The surface of the samples was manually polished with diamond paste until 1.0 μm, washed in acetone and hot dried. The chemical analysis of the concentrations of the elements gave in wt.% Cr 18.9, Ni 7.2, Mn 1.5, Mo 0.22, C 0.04, S 0.004, Fe bal.

Six kinds of specimens were analyzed: solubilized, high temperature gas nitrided (HTGN), pulsed plasma nitrided (expanded austenite), solubilized with a PVD-TiN layer deposition, HTGN with a PVD-TiN layer deposition and pulsed plasma nitrided plus PVD-TiN layer deposition.

The solubilizing treatments were performed with the aim of dissolving carbides present in the microstructure, and were carried out in an Ar atmosphere inside a tubular furnace described elsewhere [1]; the samples were heated up to 1373 K for 1 h and quenched in water. High temperature gas nitriding was carried out in the same equipment at 1473 K for 6 h under 0.15 MPa N₂ pressure. After nitriding the samples were directly quenched in water.

The pulsed plasma nitriding and the PVD-TiN layer deposition were carried out in a hybrid reactor. The TiN layer was deposited by Triode Cathode Magnetron Sputtering [4]. The hybrid process allows coating the pre-nitrided sample with a TiN layer without exposing the specimen to atmospheric pressure, avoiding cleaning operations of the surface between depositions. Table 1 shows the parameters used in both treatments.

2.2. Test conditions

Slurry erosion wear tests were performed in a jet-like device described elsewhere [8]. The test was carried out with slurry composed by 900 ml of distilled water and 100 g of angular-shaped silicon carbide particles. The size of the particles was between 212 and 300 μm. The SiC abrasive particles with 26 GPa hardness are shown in Fig. 1. The impact angle was fixed in 90° and the velocity of the jet was 8.0 m/s.

The samples were cleaned with distilled water for 10 min, dried in hot air, and weighed in a Shimadzu AUW 220D scale with a precision of 0.01 mg. Thereafter, the samples were eroded and then weighed again.

**Table 1**

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Pressure (Torr)</th>
<th>H₂:N₂ Ratio</th>
<th>Time (min)</th>
<th>Ar:N₂ Ratio</th>
<th>Current (A)</th>
<th>Potential (V)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion nitriding</td>
<td>6.0</td>
<td>1:3</td>
<td>1200.0</td>
<td>–</td>
<td>0.75</td>
<td>550</td>
<td>400</td>
</tr>
<tr>
<td>TiN layer deposition</td>
<td>3.0</td>
<td>–</td>
<td>140.0</td>
<td>20:3</td>
<td>3.0</td>
<td>330</td>
<td>320</td>
</tr>
</tbody>
</table>

Fig. 1. Morphology of SiC particles used in slurry tests.

Fig. 2. XRD patterns for TiN and expanded austenite.

Fig. 3. Cross section of a duplex treated sample: TiN plus expanded austenite.
2.3. Surface characterization

The topography of the eroded surface, the thickness of the TiN coatings and the thickness of the expanded austenite layer were observed using a Philips XL30 scanning electron microscope (SEM). Hardness of the surface samples was measured in a FischerScope H100V instrumented indentation testing equipment, using a 50 mN load. The expanded austenite and TiN coating layers were characterized by XRD in a Rigaku diffractometer.

3. Results and discussion

3.1. Microstructure and hardness

The specimen submitted to HTGN treatment showed a 1.2 mm hardened case with 0.55 wt.% N at the surface, all the nitrogen being in solid solution in austenite [1]. On the other hand, the low temperature plasma nitrided specimen presented an expanded austenite layer 3.5 μm in thickness showing a structure of grains and twins grown epitaxially on top of the austenite grains of the substrate.

X-ray diffraction patterns of the expanded austenite and TiN coatings are shown in Fig. 2. The spectrum of expanded austenite revealed peaks which cannot be matched in any standard X-ray index and appeared as lower angle austenite peaks reflecting the expanded lattice of the expanded austenite. The lattice parameters measured elsewhere [9] show that the expanded austenite can be described by a special triclinic \((t)\) crystalline structure, with a distortion \(\varepsilon\) of the lattice angles due to the presence of nitrogen in solid solution.

The microstructure of the duplex treated specimens – low temperature pulsed plasma nitriding plus PVD-TiN coating – is presented in Fig. 3 where one can see an expanded austenite layer followed by the TiN coating. Hardness values \((H)\) measured on top of the samples for the six different conditions are shown in Table 2, together with the Young Modules \((E)\) values and the \(H_{SiC}/H_{Surface}\) ratios.

3.2. Erosion rates

Accumulated mass losses as a function of time are presented in Fig. 4 for the six surface treatment conditions. The calculated wear rates are shown in the Table 3. They are calculated through the slopes of the mass loss curves shown in Fig. 4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Erosion rate ((\mu g/min))</th>
<th>Interval of time ((min))</th>
<th>Correlation coefficient (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubilized</td>
<td>88.0</td>
<td>240.0</td>
<td>0.999</td>
</tr>
<tr>
<td>HTGN</td>
<td>57.0</td>
<td>240.0</td>
<td>0.996</td>
</tr>
<tr>
<td>Expanded austenite</td>
<td>43.0</td>
<td>240.0</td>
<td>0.992</td>
</tr>
<tr>
<td>Solubilized+TiN</td>
<td>4.3</td>
<td>60.0a*</td>
<td>0.961</td>
</tr>
<tr>
<td>HTGN+TiN</td>
<td>5.2</td>
<td>60.0a*</td>
<td>0.956</td>
</tr>
<tr>
<td>Expanded austenite+TiN</td>
<td>5.2</td>
<td>60.0a*</td>
<td>0.975</td>
</tr>
</tbody>
</table>

\(a\)At this time, the coating started to be removed from the surface of the sample.

---

Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic module ((GPa))</th>
<th>Hardness ((GPa))</th>
<th>(H_{SiC}/H_{Surface})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubilized</td>
<td>200±10.0</td>
<td>1.85±0.21</td>
<td>14.0</td>
</tr>
<tr>
<td>HTGN</td>
<td>200±10.0</td>
<td>3.17±0.35</td>
<td>8.2</td>
</tr>
<tr>
<td>Expanded austenite</td>
<td>200±10.0</td>
<td>15.0±0.9</td>
<td>1.7</td>
</tr>
<tr>
<td>Solubilized+TiN</td>
<td>430±25.6</td>
<td>21.86±2.14</td>
<td>1.2</td>
</tr>
<tr>
<td>Expanded austenite+TiN</td>
<td>425±23.4</td>
<td>22.50±1.81</td>
<td>1.2</td>
</tr>
<tr>
<td>HTGN+TiN</td>
<td>435±19.5</td>
<td>21.54±2.21</td>
<td>1.2</td>
</tr>
</tbody>
</table>

---

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Erosion rate ((\mu g/min))</th>
<th>Interval of time ((min))</th>
<th>Correlation coefficient (R)</th>
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<td>0.975</td>
</tr>
</tbody>
</table>

\(a\)At this time, the coating started to be removed from the surface of the sample.

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Fig. 4. Accumulated erosion as a function of exposure time.
losses 1.5 times lower than those observed for the solubilized condition, whereas the plasma nitrided specimens showed mass losses 2 times lower.

On the other hand, TiN coated samples showed a substantial reduction in mass loss during the first testing hour, the mass loss being approximately 20 times lower than the one observed for the solubilized condition. From this time on, the erosion rate increases, indicating the beginning of the coating removal process and a change in the mass loss mechanism (Fig. 6).

Using the values shown in Table 2 it is possible to rank the severity of the wear rate in terms of the ratio $H_{\text{SiC}}/H_{\text{Surface}}$. The TiN coated samples with $H_{\text{SiC}}/H_{\text{TiN}}$ near 1, show a moderate wear regime, whereas the other samples where $H_{\text{SiC}}/H_{\text{surface}}$ is greater than 2.2, a severe wear regime showed up.

Figs. 5 and 6 show the scanning electron micrographs of the worn surfaces at the first seconds of testing and after one hour testing, respectively. The solubilized specimen shows considerable amounts of cutting marks since the beginning of the test. The worn surface reveals lips and craters and allows observing the way the particles cut the surface. A similar topography is observed for the HTGN sample (Fig. 5a and c). The surface of the plasma nitrided specimen is shown in Fig. 5e. The number of cutting marks decreases and some indentation marks can be observed.

The samples coated with the TiN layer showed a considerably reduced number of cutting and indentation marks on the surface (Fig. 5b, d and f).

The mass removal mechanism observed in the solubilized and HTGN samples was cutting, in spite of the normal...
incidence of the particles. This behavior is due to a combined
effect of the fluid streamlines, and the sharpness of the SiC
particles. When the fluid jet impacts the surface, there is a
spreading effect that makes that particles rotate. On the other
hand, the deformation caused by an angular particle depends on
the orientation of the particle as it strikes the surface, and on
whether the particle rolls during contact [10].

After 1 h, the surface of the solubilized sample shows
extensive indentations and cutting marks. One can observe
plates that were displaced from impact sites and were detached
by plastic rupture. For all the coated samples the TiN film
started to be removed, exposing the substrate surface to the hard
SiC particles, as shown in Fig. 6. After that, the coating was
progressively removed in all the coated samples. It is worth
noting that the coatings failed by the action of the SiC particles
and not due to a poor adherence.

For the testing conditions used in this work, all the coated
samples showed the same wear rates during the first hour of test,
independent of the substrate properties. It has been widely
reported that in spite of having a very high hardness, a TiN thin
film does not guarantee a wear resistance as good as the one
obtained after a duplex treatment. This is due to a higher ad-
herence of the film to the substrate, immediately beneath the TiN
film, provided by the higher hardness of the substrate, a better
mechanical support and a more gradual transition of hardness and
elastic modulus across the coating/substrate interface [5].

Nevertheless, it was not possible to distinguish the effect of
the substrate properties on the wear resistance of the coating. In
this case, the particles velocity was not high enough so the
influence of the load carrying capacity of the substrate did not
show up. In testing conditions, such as cavitation-erosion,
where greater amounts of kinetic energy and momentum are
transferred to the specimen a greater loading support capacity of
the substrate should play an important role on the adherence of
the TiN coating to the substrate.

Once the TiN coating was removed, the effect of the
substrate hardness differences was observed and the intense
cutting processes observed in the uncoated samples appeared.
From that point of view, the consequence of the coating ap-
application was to delay the beginning of mass losses.

4. Conclusions

After testing an AISI 304 austenitic stainless steel submitted
to high temperature gas nitriding, low temperature pulsed plasma
nitriding, and PVD-TiN coating, in slurry made of water con-
taining SiC particles, it is possible to conclude:

1. High temperature gas nitriding reduced 1.5 times the wear
rate of the austenitic stainless steel.
2. Low temperature pulsed plasma nitriding reduced 2 times the
wear rate of the austenitic stainless steel.
3. PVD-TiN coatings deposited over different surface treat-
ments of the austenitic stainless steel reduced the wear rate
by 20 times.
4. The mechanical properties of the substrate did not affect the
erosion rate of the TiN coated specimens.
5. When the TiN coating is removed, the effect of the substrate
hardness differences is observed and intense cutting of the
samples is observed.

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