Surface Nanocrystallization of 310S Stainless Steel and Its Effect on Oxidation Behavior

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Two techniques, unbalanced magnetron sputter deposition and high-energy short-pulsed plasma discharge, have been used to produce a nanocrystalline surface on AISI 310S stainless steel specimens. The average grain size after surface modification was estimated as ~100 nm by using atomic force microscopy. Cyclic oxidation was performed at 1000 °C with treated and untreated 310S stainless steel specimens. The oxide products formed on the specimens consisted of an outer spinel layer that was rich in chromium, iron, manganese, and nickel, and an inner chromium-rich layer. It was found that the concentrations of iron and manganese in the outer layer of treated specimens were higher, and adherence of the scale was better in the treated specimens. The observed oxidation behavior can be explained by the increase of the creep diffusion rate in the fine oxide scale formed on the nanocrystalline surfaces.

1. Introduction

AISI 310S stainless steel is an important commercial alloy that is widely used in applications associated with high temperatures. Its high-temperature oxidation resistance is one of the most important properties. Previous research (Ref 1), however, showed in some environments that the oxide spallation resistance at 1000 °C was not satisfactory, although the alloy contains a high chromium content (~25 wt% Cr).

A number of researchers have reported that surface microcrystallization is an effective way to improve the oxidation resistance of alloys (Ref 2, 3). It is believed that the beneficial effects of surface microcrystallization on the oxidation behavior of stainless steels can be attributed to: (a) the enhancement of chromium diffusion to the surface along grain boundaries, (b) the release of the stresses stored in the oxides, and (c) the mechanical “keying” effects of oxides to the high concentration of grain boundaries of the substrate metal.

A variety of techniques have been developed to produce surface micro- and nanocrystallization. Among them, unbalanced magnetron sputter deposition (UMSD) is a popular method. The UMSD method and a newly developed method, high-energy short-pulsed plasma discharge (HESPPD), were used to produce nanocrystalline surfaces on 310S stainless steel specimens. The average grain size in the treated surface layers was less than 100 nm. Cyclic oxidation testing was conducted with the treated and untreated specimens at 1000 °C. Both the oxidation and spallation kinetics were measured. In order to study the effects of nanocrystallization on the oxidation behaviors, the samples did not undergo separate vacuum annealing before oxidation testing.

Table 1 Chemical composition of 310S stainless steel (wt%)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.04</td>
<td>0.61</td>
<td>0.97</td>
<td>0.016</td>
<td>0.001</td>
<td>19.5</td>
<td>25.0</td>
<td>bal</td>
</tr>
</tbody>
</table>

2. Experimental Procedure

The chemical composition of the stainless steel used in this work is shown in Table 1. Specimens were prepared to the dimensions of 3.0 by 10.0 by 15.0 mm.

In the UMSD method, a single target of 310S stainless steel was used. The predeposition procedure consisted of 90 min of radio frequency (RF) plasma substrate cleaning and 5 min of target cleaning. The deposition time was 120 min. The argon pressure during deposition was 0.066 Pa (0.5 mTorr). The distance between the substrate and target was ~125 mm. During deposition, substrates were rotated in front of the target at a rate of 4.2 rpm.

The HESPPD method has been developed for surface treatment. Figure 1 shows a schematic drawing of the technique. The treated specimen was used as one electrode, and a pure aluminum was used as another electrode. The discharging pulse width was ~60 µs with the voltage of ~10,000 V, the discharging interval time was ~3 s, and the distance between the two discharging points was 1 mm. When electrons were discharged between the specimen and the aluminum rod, extremely high...
Energy was released as a spark in a very short period of time. The local temperature can be raised to ~20,000 °C. The high energy means that the surface can be melted and resolidified within a very short time. The surface micro- or nanocrystalline structures were formed due to the extremely high cooling and solidification rates.

Oxidation testing was performed in a horizontal furnace at 1000 °C for up to 200 h in ambient atmosphere. Temperature accuracy in the hot zone of the furnace was within ±1 K. Each specimen was held in a quartz crucible so that the spalled oxides could be collected and measured. After the required period of time, the crucibles were removed from the furnace and cooled to room temperature. The total weight change of a specimen plus crucible and the net weight change of the specimen were measured and recorded. The specimens were then placed back in the hot zone of the furnace for the next thermal cycle.

An atomic force microscope (AFM) was used to observe the morphologies of the specimens before and after treatments. Scanning electron microscopy (SEM) was used to study the cross sections of oxide scales. Energy dispersive spectroscopy (EDS) was used to determine the chemical compositions of the oxide scales. X-ray diffraction (XRD) with Co-Kα radiation was used to study the changes in crystal structures before and after treatments, and in the oxide scales.

![AFM images](image1)

**Fig. 2** AFM images of the (a) untreated, (b) UMSD, and (c) HESPPD 310S stainless steel samples

![XRD spectrum](image2)

**Fig. 3** The XRD spectrum of the treated and untreated specimens

![Oxidation and spallation kinetics](image3)

**Fig. 4** The oxidation and spallation kinetics of UMSD, HESPPD, and untreated 310S specimens (at 1000 °C)