

Structure and Composition of Scales Formed on AISI 316 L Steel Alloyed with Ce/La Using High Intensity Plasma Pulses after Oxidation in 1000 °C

B. SARTOWSKA^{a,*}, J. PIEKOSZEWSKI^{a,b}, L. WALIS^a, M. BARLAK^{a,b}, W. STAROSTA^a,
C. POCHRYBNIAK^b AND K. BOCHEŃSKA^b

^aInstitute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland

^bThe Andrzej Sołtan Institute for Nuclear Studies, 05-400 Otwock/Świerk, Poland

It is well documented that the high oxygen affinity elements such as Y, Ce, La, Er and other rare earth elements added to steel in small amounts can improve their high temperature oxidation resistance. Rare earth elements can be either alloyed during the steel making process or introduced through surface treatment techniques. Improvement of high temperature oxidation resistance of AISI 316 L steel by incorporation Ce and La elements into its near surface region using high intensity pulsed plasma beams in so-called deposition by the pulse erosion mode was investigated in the present work. The samples were irradiated with 3 short (μs scale) intense (energy density 3 J/cm²) plasma pulses. Heating and cooling processes occur under non-equilibrium conditions. In all samples the near surface layer of the thickness in μm range was melted and simultaneously doped with cerium and lanthanum. The modified samples were oxidized at 1000 °C for 100 h in air. The obtained effects were: oxide scales formed on the treated samples were more fine-grained, compact and adhering better than those formed on the un-treated samples.

PACS: 52.77.-j, 72.15.Eb, 81.65.Mq

1. Introduction

Austenitic stainless steels are used in numerous industrial applications, mainly due to their excellent corrosion resistance. However, engineering components made of these steels are in many applications operating under such extreme conditions that improvement of their already excellent high-temperature oxidation resistance is desirable. It is well known that high oxygen affinity elements such as Y, Ce, La, Er and other rare earth elements (REE) added to steels in small amounts can improve their corrosion and high temperature oxidation resistance. The beneficial effect of active elements with high oxygen affinity on high temperature oxidation resistance and corrosion resistance against the aggressive media has already been studied [1, 2].

REE added to the bulk alloys or to their surfaces significantly improve the oxide scale adherence [3]. Scales growing at the metal surface tend to spall upon thermal cycling as a result of excessive mechanical stresses in the oxide layer. It is generally believed that reduced spallation at a given temperature is caused by a slower scale growth in the REE implanted substrates and its tougher structure [4].

REE can be alloyed during the steel making process and then technical elements are produced from the obtained material, for example tubes, wires or machine details [5]. REE can be added to the surface region of materials using different surface modification techniques. The incorporation via surface treatment acts in favour of REE concentration at the surface where the oxide will form [2]. Different methods of surface treatment can be applied for REE incorporation to the surface layer of steels: conventional ion implantation [1, 4], plasma immersion ion implantation [6], metal organic chemical vapour deposition [7], sol-gel coating [4], pack cementation [2].

In the present work incorporation of REE into steel was performed using high-intensity pulsed plasma beams in the deposition by pulsed erosion (DPE) mode. One of the characteristic features of this technique is that both energy sufficient to melt the near-surface region of the substrate and the ions/atoms eroded from electrodes are deposited on the substrate by the same plasma pulse. The deposited elements diffuse rapidly within the molten phase. After resolidification the layer is modified in comparison to the initial material. The results of investigations of the structure and composition of scales formed on austenitic stainless steel alloyed with REE (Ce+La) using high intensity plasma pulses after oxidation in 1000 °C/100 h are reported in this paper.

* corresponding author; e-mail: b.sartowska@ichtj.waw.pl

2. Experiment

Austenitic stainless steel AISI 316 L grade with the main elements concentration (in wt%) Cr — 16.29, Ni — 11.47, Mo — 2.03, Mn — 1.27, Cu — 0.31, Fe-balance was used as the substrate. As a REE source the mishmetal of the composition (in wt%): Ce — 65.3, La — 34.0 and balance of Fe, Mg, Pr was used. REE were incorporated into one surface of steel samples using high intensity pulsed plasma beams generated in a rod plasma injector (RPI) operated in the DPE mode described elsewhere [8, 9]. In this mode of operation the plasma contains ions of the working gas and also ions/atoms eroded from the electrode tips. In the DPE process the transient melting of the near-surface occurs. The melt duration lasts in the μs range and the rapid solidification takes place. The cooling rate was estimated in the range $10^7\text{--}10^8\text{ K s}^{-1}$.

The present experiment was carried out as follows: titanium rods coated with mishmetal tips as electrodes, nitrogen as the working gas and 3 pulses with the energy density 3.0 J/cm^2 . The modified samples were oxidized at 1000°C for 100 h in air. The samples were characterized by: scanning electron microscopy (SEM) with DSM 942 (Zeiss, Germany) for initial, modified and oxidized surface morphology observations; energy dispersive X-ray spectrometry (EDX) with Quantax 400 (Bruker, Germany) for surface and cross-section elemental concentrations determination; Rutherford backscattered spectroscopy (RBS) measurements for the analysis of elemental depth distribution.

3. Results and discussion

At the surfaces of initial steels the grains in different sizes are visible as a result of steel making process. After pulse modifications the initial grains disappeared and different morphological details were observed. Atomic concentrations of REE (Ce+La) incorporated into the specimens were in the range 0.3–6.0 at.%.

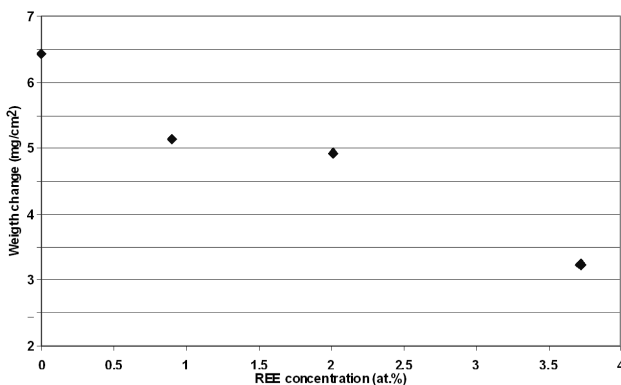


Fig. 1. Normalized weight changes of modified surface as the high temperature oxidation process $1000^\circ\text{C}/100\text{ h}/\text{air}$.

Increase of the weight after the oxidation process was observed for all oxidized samples (Fig. 1). It was assumed that changes of non-modified and lateral surfaces of the samples were the same for all samples. For the REE concentration equal to or higher than 0.9 at.%, the mass increase was smaller than for initial material. It means that the surfaces enriched for REE have greater resistance to high temperature oxidation. The decreased weight gain of AISI 316 L samples may be attributed to the reduction in internal oxidation [2].

Observations of specimens' surface containing different amounts of REE after the oxidation process were carried out. The surface of untreated sample is covered with pittings and regions of detached scales. Even small REE concentration (0.3 at.%) remarkably reduced the number of surface failures. Figure 2 shows the examples of surface images of the initial and REE enriched surfaces after the oxidation process, where the above mentioned features are visible.

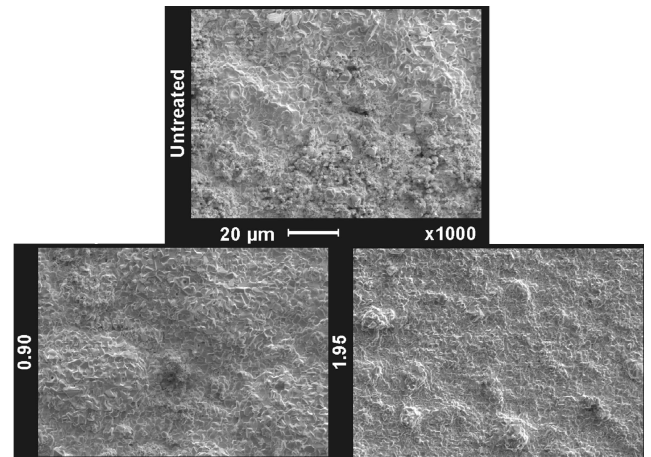


Fig. 2. SEM images of scales surface morphology after the oxidation process $1000^\circ\text{C}/100\text{ h}$: untreated, 0.9 at.% REE treated samples and 1.95 at.% REE treated samples.

The granular morphology of the untreated and treated samples can be seen in Fig. 3. In both cases the particles with rounded shape and those with sharp-edged shape can be distinguished. On the average, the sizes of particles are larger in the case of untreated samples as compared to those of treated. The observed grains diminished with the increasing REE concentration.

The results of point elemental analysis of single grains of unmodified and modified samples show that the observed grains are the oxide particles like in work [10] and allowed us to determine the grains structure. The ratio of metal atoms concentration to oxygen atoms concentration was: 0.88 and 0.98 for the initial material and 316L + 3.75 REE at.%, respectively. These results are in agreement with those obtained by [5, 10].

Point analysis in different positions of the oxidised layer observed at metallographic cross-section show dif-

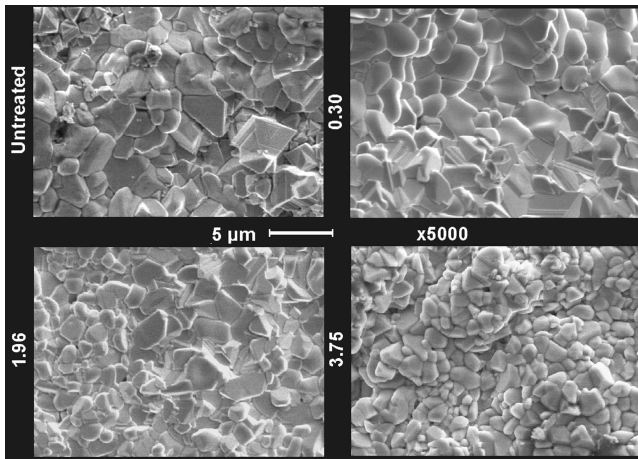


Fig. 3. SEM images of scales surface morphology after the oxidation process 1000 °C/100 h: untreated and treated samples enriched with REE to 0.3 at.%, 1.95 at.%, 3.75 at.%.

ferences in the scale elemental composition in the case of unmodified and high intensity plasma pulses (HIPP) modified materials. Some results of elemental concentration are presented below (in at.%):

— upper part of the scale: untreated+oxidised: Fe — 33.69, Cr — 16.46, Ni — 0.71, O — 45.09; and treated+oxidised: Fe — 25.58, Cr — 14.09, Ni — 0.84, O — 54.13, REE — 0.66;

— middle part of the scale: untreated+oxidised: Fe — 30.96, Cr — 13.84, Ni — 2.11, O — 49.37; and treated+oxidised: Fe — 27.49, Cr — 13.11, Ni — 0.48, O — 54.59, REE — 0.41;

— bottom part of the scale: untreated+oxidised: Fe — 35.34, Cr — 8.35, Ni — 0.51, O — 43.39 and treated+oxidised: Fe — 39.81, Cr — 8.31, Ni — 0.54, O — 48.68, REE — 0.21.

As can be noticed the chromium concentration is the highest in the upper part of the scale. It confirms the theory of chromium diffusion from the bulk to the surface of material [5, 10]. The chromium concentration in the upper part of the scale at the REE enriched sample was about 12.5% as small as that compared with the untreated material after oxidation. These results are with agreement with those obtained by [2]. The detailed interpretation taking into account the changes of concentrations of the present and added elements in the investigated material is planned.

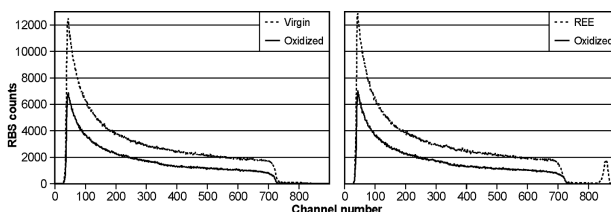


Fig. 4. RBS results of initial, enriched in 2.0 at.% REE and oxidised surface of AISI 316 L steel.

The spectra of RBS measurements of the unmodified and HIPP with REE modified samples as well as the unoxidised and oxidised material are presented in Fig. 4. The main part of the spectra of initial and REE enriched material is similar. The peak visible at 850 channel confirms the presence of REE in the surface layer of the modified sample. After the oxidation process in both cases (initial and alloyed with REE material), the lower level of the spectra of the oxidized samples was observed. This result is connected with the scale presence on the surface.

4. Conclusions

The main observation of this study is that alloying of AISI 316 L stainless steel with REE using high intensity pulsed plasma beams in the DPE mode leads to changes of the surface layer properties, especially the high temperature resistance.

1. Oxide scales formed on the DPE treated samples are more fine-grained, compact and adhere better than those formed on the untreated ones.
2. Structure of grains observed at the oxide layer in the case of initial and modified materials was determined as the spinel type.
3. Chromium concentration is the highest in the upper part of the scale which confirms the theory of chromium diffusion from the bulk to the surface of material during the oxidation process of chromium alloys.

We plan to extend the experiments to different oxidation temperatures and other types of stainless steel.

Acknowledgments

This work has been partially supported by the EU — “Research Infrastructures Transnational Access” program AIM “Centre for Application of Ion Beams in Materials Research” under EC contract no. 025646.

This work has been partially supported by the Polish Ministry of Science and Higher Education under the project with decision: 1197/6.PRUE/2009/7.

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