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High-temperature oxidation inducing strain for the 2205 duplex stainless steels

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Abstract

The results from Raman spectra and XRD demonstrated that the surface oxides were mainly composed of iron oxides enriched with chromium and spinel type oxide for high temperature oxidized 2205 duplex stainless steels. The EBSD analysis indicated that the austenitic phase showed more excellent antioxidant ability than the ferritic one. The relative higher IQ value could improve high temperature antioxidant ability of the 2205 duplex stainless steel. The KAM maps showed a relative high value near the grain boundaries and near the interface. In addition, the high temperature oxidation inducing deformation could occur based EBSD analysis.

1. Introduction

The duplex stainless steels are increasingly used due to its outstanding mechanical strength [1] and excellent corrosion resistance [2]. The creep strength and oxidation resistance of the duplex stainless steel are very important for application in high temperature environment. It was found that the inner layer and outer layer contained mainly chromium oxide and iron oxide during initial oxidation process of duplex stainless steel [3]. A duplex-layer of oxides were found for duplex stainless steels S32304 at 1050 °C in under different high-temperature oxidation conditions [4]. It was found that the amount of Fe3O4 and Fe2O3 increased with the increasing of temperature for UNS 1.4462 duplex stainless steel [5]. Austenitic phase and ferritic phase have complicate oxidation characteristics due to different chemical compositions and crystal structures [6]. Previous investigations showed that high-temperature oxide formed on ferritic phase was relative uniform, while many oxide nodules were observed on the austenitic phase [7, 8]. Since the duplex stainless steels are treated at elevated temperatures in an oxidizing atmosphere for an extended duration, moreover, the properties of the oxides also play important roles in the corrosion process [9], therefore, the investigation of the oxidation characteristic of the duplex stainless steels is very significant. It was found that the α′-martensite was formed for austenitic stainless steel during the cooling part after cyclic high temperature oxidation in humidified air due to local depletion of Cr [10]. This indicated that the high temperature oxidation could induce strain. The strain induced high density dislocations could facilitate diffusion of chromium element, which promoted to form a denser protective oxidation film and enhanced high temperature antioxidant ability [11]. The effect of high temperature oxidation on the deformation of the matrix and microstructures is worth studying. The effects of high temperature oxidation on two-phase and grain boundaries of 2205 duplex stainless steels are evaluated by the Electron Back scatter diffraction (EBSD). The x-ray diffractometry (XRD) and Raman spectroscopy analysis also are used in the present study.

2. Experimental

The 2205 duplex stainless steel with chemical compositions (wt.%) of C 0.05, S 0.0008, Mn 1.05, P 0.022, Si 0.75, Cr 21.85, Ni 5.36, Mo 3.18, Cu 0.18, V 0.13, W 0.054, N 0.155, Ti 0.015 and Fe balance was investigated in the
study. Energy spectrum analysis showed that the Cr, Mo and Si are enriched in ferrite, while Ni and Mn are enriched in austenite. The sample was oxidized at 1000 °C in air for 2 h. The EBSD technique was used to characterize the microstructure of 2205 duplex stainless steel. The crystallinity of grain boundaries can be evaluated by image quality (IQ) value in EBSD. The IQ value during EBSD analysis is defined as follow equation (1).

\[ \text{IQ} = \frac{1}{N} \sum_{i=1}^{N} H(\rho_i, \theta_i) \]  

Figure 1. (a) SEM cross-section and EDX element mapping of oxidized 2205 duplex stainless steel for (b) Cr, (c) Fe, (d) Ni and (e) O, (f) Raman spectra and (g) the x-ray diffraction patterns of two 2205 duplex stainless steels.
where, $H(\rho_i, \theta_i)$ stands for the Hough Transform [12]. $\rho_i$ and $\theta_i$ define the position of measured Kikuchi lines. $N$ is the total number of measured Kikuchi lines.

The phase analyses of the duplex stainless steel and surface high-temperature oxides were performed by using XRD (Rigaku Ultima IV x-ray diffractometer with monochromatized Cu K$_\alpha$ (0.154056 nm) and radiation at 40 kV and 40 mA). The Raman spectroscopy (Renishaw InVia Raman Microscope System) with 633-nm excitation wavelength was also used to analyze phases.

3. Results and discussion

The longitudinal cracks are observed within the nodule at the interface between stainless steel and oxide in figure 1(a). Depending on the activity and diffusion coefficient of these elements in metal and the solubility and
diffusion of oxygen, these oxides could precipitate internally or form an underlying layer at the metal/scale interface. The oxidation process may also induce high residual stresses in the matrix. Figures 1(b)–(e) present cross-section energy dispersive spectroscopy maps of 2205 duplex stainless steels after high temperature oxidation. Obviously, high temperature oxides on the surface of 2205 duplex stainless steels were enriched with chromium. The results from Raman spectra indicate that oxides are mainly composed of iron oxides, iron oxide enriched with chromium and spinel type oxide in figure 1(f). Figure 1(g) shows that the characteristic peaks are spinel, magnetite and hematite type oxides. The oxides enriched chromium could be formed during the initial stage of oxidation, and then the oxygen partial pressure at the metal/oxide interface strongly decreased [13]. More stable oxides Fe$_2$$_x$Cr$_x$O$_3$ and NiFe$_2$O$_4$ should be formed. The diffusion coefficient of chromium in austenitic and the ferritic phases is different, resulting in inhomogeneous oxide distribution [14]. These oxides also could precipitate internally or along the grain boundaries, which could induce the strain of the substrate in the area near the interface. This will be evaluated through the following the EBSD experiment.
The EBSD scanning maps of high temperature oxidized 2205 duplex stainless steel is shown in figure 2(a). Oxides are unindexed due to rough. Some of the small non calibrated points could be attributed to precipitated carbides. Corresponding phase map is also showed in figure 2(b). The local breakaway regions in the ferritic phase facilitate element diffusion and act as the origins of high temperature internal oxidation. The ratio of the two phases is also shown below. Xu et al[15] found that the diffusion of manganese ions from substrate to oxides could induce phase transformation from austenitic phase to ferritic phase during oxidation process. Obviously, austenitic phase shows more excellent antioxidant ability than the ferritic one.

Figure 3(a) shows IQ value distribution near interface area. The relative higher IQ value could improve high temperature antioxidant ability of the 2205 duplex stainless steel. High IQ value in 2205 duplex stainless steel demonstrates that the region has a high degree of recrystallization, more ordered atomic arrangement undoubtedly improve the oxidation resistance of stainless steel near the surface in the high temperature environment. Moreover, the lattice constant of the oxides is larger than that of the stainless steel matrix, the mismatch could induce compressive stress. The vacancies in the chromium depleted region results in lattice distortion, which induces residual stress and strain. The accumulation of vacancies leads to voids and even cracks. Twin boundaries also show good oxidation resistance in figure 3(b). The high fraction of twin boundary also effectively break the percolation in the random high angle grain boundaries network during high
temperature corrosion [16]. The chromium oxidation at random grain boundaries could lead to formation of thick Cr₂O₃ layer on the surface and chromium depletion underneath, while twin boundary could effectively inhibit element diffusion during high temperature oxidation.

The IQ value change along A red line and B red line in figure 3(a) is shown in figure 3(c). The IQ value decreases at grain boundary, which should be attributed to the low recrystallization characteristic of grain boundary. The IQ value decreases rapidly in interface position due to oxidation induced deformation. Low IQ value, i.e., low recrystallization level decreases antioxidant ability of 2205 duplex stainless steel, conversely, oxidation induced strain also decreases IQ value. In addition, (111) densely packed plane showed excellent IQ value. From the matrix to the oxide the IQ value continuously decreases, especially for B line. The continuous oxidation induced strain also decreases IQ value. In addition, low IQ value, i.e., low recrystallization level decreases antioxidant ability of 2205 duplex stainless steel, conversely, oxidation induced strain also decreases IQ value. In addition, low IQ value, i.e., low recrystallization level decreases antioxidant ability of 2205 duplex stainless steel.

The Kernel Average Misorientation (KAM) value distribution in the EBSD data represents the average misorientation between a given point and its nearest neighbors in the same grain (and thus associated with a misorientation less than 5°) [17]. Then resultant misorientations provide a measurable signature of the strain [18]. The KAM mapping was then used to evaluate local plastic strain in figure 4(a). Obviously, the KAM maps show a relative high value, especially near the grain boundaries and near the interface, as shown in figures 4(b) and (c). This demonstrates that high temperature oxidation have induced plastic strain or stress for 2205 duplex stainless steel. The higher KAM value indicates more dislocations due to plastic strain [19].

4. Conclusions

The effect of high temperature oxidation on the microstructure of the 2205 duplex stainless steel is evaluated by the EBSD, XRD and Raman spectroscopy. The main conclusions are as follows:

1. The EBSD analysis showed that austenitic phase exhibited more excellent antioxidant ability than ferritic one.

2. High temperature internal oxidation decreased the IQ value of the 2205 duplex stainless steel near interface position.

3. The KAM value analysis demonstrated that high temperature oxidation could induce plastic strain or stress for 2205 duplex stainless steel.

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