Compatibility of Different Commercial Alloys in High Temperature Supercritical Carbon Dioxide

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Abstract

In this work, compatibility and long-term integrity of candidate structural materials, including austenitic stainless steel 316NG, Fe-Ni based alloy 800H and Ni-based alloy 625, were tested in high-temperature and high pressure SCO_2 . The exposure time was up to 3000 h. The results showed that the corrosion kinetics approximately followed a parabolic law for 316NG and 800H. After 3000 h exposure, all of oxide layers, mainly composed by Cr_2O_3 , were continuous, compact and protective, and their thicknesses were about 21~45 nm, 64~88 nm and 34~43 nm respectively. In case of carburization, dark spots corresponding carbon deposition was observed on the surface and a little enriched in underneath the oxide for 800H. Moreover, enrichment of trace elements was found at oxide/substrate interface through GDOES and TEM analysis, i.e., enrichment of Mn, Si for 316NG, enrichment of Mn, Si, Al, Ti for 800H and enrichment of Ti, Al for alloy 625.

1. Introduction

Supercritical carbon dioxide (SCO_2) is being considered as one of the prime coolant candidates for next generation power plants, as it has advantages of higher efficiency, smaller components size, fewer components and simpler cycle layout, *etc.* [1, 2]. In SCO_2 Brayton cycle system, material selection of the key components such as heat exchangers and pipes are one of the important problems of long-term safe operation. In contrast with conventional steam Rankine cycle, the prime consideration in regard to material corrosion is that i) oxidation of some components in higher temperature (RT ~ 850 °C) and higher pressure (0.1 ~ 30 MPa) and ii) carburization resulting in material degradation, which is rather unique to CO_2 atmosphere.

In the past decades, corrosion data regarding SCO_2 are being gradually accumulated and the current investigations focus on the following aspects so far: i) compatibility of structural materials [3–8]. Chen *et al.* [7] reported corrosion and carburization behaviors of austenitic steels (347H and 316LN) and ferritic/martensitic (F/M) steels (430 and 630) with similar chromium content (~ 17.5 wt.%) and found that spallation of chromia layer occurred for austenitic steels, which was attributed to the lower diffusion coefficients of Cr, larger growth stresses and thermal stresses. Moreover, Olivares *et al.* [8] compared corrosion resistances of several high-nickel alloys in air and SCO_2 . Except for low Cr alloy 282, rates of scaling and internal oxidation were in most cases similar for all alloys in both gases. According to the published studies, it has been known that formation of a continuous chromia (Cr_2O_3) layer on the substrate materials play a key effect on the corrosion resistance. In addition to conventional commercial alloys, due to better oxidation and carburization resistance of Al_2O_3 scales than that of Cr_2O_3 , alumina forming austenitic (AFA) steels [9, 10] was also developed to test in high-temperature SCO_2 ; ii) effect of temperature and pressure [10–13]. As suggested by Mahaffey *et al.* [10], the weight gain usually increased as testing temperature increase. In contrast, effect of pressure is relatively complicated. Lee *et al.* [11] suggested that the weight gain and the thickness of an amorphous Cr layer at the oxide/matrix interface increased with increasing CO_2 pressure from 0.1 MPa to 20 MPa. However, for 800HT, the depth

of the carburized region with Cr-rich carbides was rarely affected by CO₂ pressure, resulting in similar tensile properties; iii) effect of impurities in CO₂, including O₂, CO, H₂O, H₂, SO₂ and hydrocarbon [14]. Mahaffey *et al.* [15] found that oxidation accelerated resulting in formation of a thicker oxide layer and evidence of spallation even with addition 10 ppm O₂ for Ni-based alloy 230. Moreover, Oleksak *et al.* [16] further suggested that O₂, H₂O and SO₂ had negligible effect on the oxidation of ferritic Fe alloys, while SO₂ could significantly enhance the rate of oxidation for austenitic Fe alloys; iv) integrity of welding joints, including diffusion-bonded technique [17] toward printed circuit heat exchanger (PCHE) [1, 18] and fusion-weld technique [2] and typical gas tungsten arc welding (GTAW) technique [19]; v) preparation of coating on metal substrate, such as deposition of Cu coating [20], Si coating [21], Al coating [22, 23] Cr coating [24, 25] and NiAl coating [26]; vi) corrosion under stress including static and dynamic stress [27, 28, 29], including creep and stress corrosion cracking (SCC) so far.

The research progress was simply summarized above. In case of the first aspect, it is the research basic of the others. However, there are also contradictions between different studies. For Example, Chen *et al.* [7] reported that spallation of chromia layer occurred for austenitic steels, but for F/M steels. However, because thermal expansion is similar between F/M steels and its scales, some researchers found that although a thick oxide layer formed on F/M steels, its adherence to the substrate was better than that of austenitic steels [28]. Moreover, there are also contrary results on whether amorphous C layer at oxide/substrate interface or Cr-rich carbides in substrate formed. That may be because the exposure time used in some experiments was only one thousand hours, even hundreds of hours. And it doesn't seem to further use to correctly predict the corrosion lifetime of the structural materials. This work aims to systematically investigate the corrosion and carburization behaviors of austenitic stainless steel (316NG), Fe-Ni based alloy (800H) and Ni-based alloy (625), including i) corrosion kinetics curve during 3000 h exposure, ii) surface morphology and composition of the scale using SEM and XRD/Raman analysis, iii) elemental distribution of cross section of the scale using GDOES analysis and iv) elemental enrichment at the oxide/substrate interface, structure, thickness and phase component of the scale using TEM analysis.

2. Experimental Methods

2.1 Materials and specimen preparation

The alloys used for exposures were acquired from commercial manufacturers and the chemical compositions, detected by the inductively coupled plasma mass spectrometry, were provided in Table 1. Prior to experiment, the alloys were cut to coupon type specimens following standard JB/T 6074-92 and the detailed dimension was shown as Fig. 1a. The coupon type specimens were then ground on all surfaces up to 2000 grit using SiC papers, followed by drying in warm air.

Table 1
Chemical compositions of the used commercial alloys (all in wt.%).

Specimens	Cr	Ni	Mn	Si	C	Fe	others
316NG	17.34	11.79	1.42	0.42	0.025	Bal.	Mo 2.45
800H	19.70	30.63	0.90	0.25	0.06	Bal.	Al 0.22; Ti 0.35
625	21.46	Bal.	0.03	0.07	0.01	2.54	Mo 8.95; Al 0.36; Ti 0.30

Figure 1b shows a schematic of the SCO₂ compatibility testing set-up used in this study, comprised by the following five components: (i) CO₂ supply system, CO₂ cylinders with 99.99% research grade were used in our study. From the cylinders the CO₂ gas traveled through the tubing and flowed into (ii) liquid booster pump, which could increase the pressure to the desired value and bring CO₂ to the test section. To make sure the CO₂ flowing from the cylinder to the booster pump was liquid state, a water cooler was used to prevent the CO₂ gas from gasifying through the tubing. The liquid CO₂ was then heated up to 500 °C through (iv) pre-heater and became the supercritical fluid. The SCO₂ then flowed into (v) the autoclave (test section) which contained the test specimens. The pressure of the autoclave was maintained at 20 MPa by a back pressure regulator (BPR) and the temperature of the autoclave was controlled within ± 2 °C by three zone main heaters. Eventually, the SCO₂ flowing from BPR was cooled and its pressure was released. The BPR and the tubing following the BPR were wrapped in Omega lux heating tape, which could prevent CO₂ from freezing to plug the pressure-relief vent.

At the beginning of test, twelve duplicate coupons of each alloy were mounted on an alumina sample train and were then put into the autoclave. In this study, the exposing time was up to 3000 h. After 100 h, 200 h, 500 h, 1000 h, 2000 h and 3000 h exposure to SCO₂, the autoclave was cooled to room temperature and the pressure was decreased to the atmospheric pressure. Subsequently, all of specimens were removed from the autoclave, photo documented and weighed. Two of each alloy was reserved for further analysis, while the other specimens were returned to the autoclave for further testing.

2.2 Characterization

After each tests, the weight gain of specimens was measured using a microbalance with a resolution of 0.00001 mg. Scanning electron microscopy (SEM; FEI nova 450, USA) equipped with an EDS detector was employed to investigate the surface morphology as well as the chemical compositions of the oxide layers formed during exposure process in SCO₂. X-ray diffraction (XRD; Panalytical XPert, Holland) was applied to study the crystal structure and phase composition of the oxide, using a Cu K α radiation (25 kV, 40 mA) at a glancing angle of 1.5°, in the range of 2 θ from 10 to 80°. Raman spectra were obtained with an argon laser (Renishaw 2000, UK). Depth profile analysis was carried out using glow discharge optical emission spectroscopy (GDOES; GDA750HP, Germany) with an anode of 4 mm in diameter. A transmission electron microscope (TEM; FEI Themis Z, USA), equipped with a high-angle angular-dark-

field (HAADF) detector and EDS system, was used at 300 kV for electron diffraction, high-resolution scanning transmission electron microscopy (STEM) imaging and composition analysis. A focused ion beam (FIB; FEI Helios G4 CX, USA) was used to prepare the TEM specimens by the lift-out method.

3. Results And Discussion

3.1 Weight gain and morphology

The weight gains of 316NG, 800H and 625 alloys during 3000 h exposure to SCO_2 were shown in Fig. 2a. The weight of both 316NG and 800H quickly increased at first and continuously increased with exposure time, while that of alloy 625 slightly decreased at first (< 200h) and then increased, followed by dropping again. It is clearly shown that the corrosion kinetics of 316NG and 800H approximately followed a parabolic law, which represented a diffusion-controlled oxide growth rate [30]. The fitting lines based on the formula $\Delta W = Kp\sqrt{t}$ were given in Fig. 2a as well. The lower value of the exponent (0.24 for 316NG and 0.35 for 800H) indicated a slow oxide growth kinetic for both. In contrast, the kinetic process of alloy 625 was relatively complicated. Figure 2b shows the oxidation rate at every 1000 h exposure from each alloy. As for 316NG and 800H, the oxidation rate significantly decreased with exposure time, which indicated the formed oxide film was protective toward underlying alloy substrate. Although at the initial exposure stage (0~1000 h), the oxidation rate of alloy 625 with high Cr and Ni content was 1~2 order of magnitude lower than that of 316NG and 800H.

Figure 3 shows photographs of 316NG, 800H and 625 alloys after exposure for 500 h, 1000 h, 2000 h and 3000h. In case of evolution of their surface colorations, a significant difference was observed. After 500 h exposure, the surface of 316NG had a rusty red tint and finally became light blue; As for 800H, the color of its surface became from dark blue to grey; The color of alloy 625 changed from dark brown to dark blue, finally to grey. It has commonly been suggested that the evolution of a thicker oxide layer possibly of different stoichiometries and the carbon deposition on the surface result in the change in color during exposure [30, 31]. In addition to the change of color, no obvious breakaway oxidation or cracking were observed for all of specimens.

3.2 SEM surface morphology

Figure 4 showed the surface morphology of 316NG, 800H and 625 alloys after 3000 h exposure and the corresponding EDS quantification were listed in Table 2. Except for 800H, there was no obvious change in the surface morphology up to 3000 h exposure and the initial grounding traces were visible for both 316NG and alloy 625. Some dark spots randomly distributed on the surface of 800H. The EDS compositional analysis (shown in Table 2) indicated that these dark spots were as a result of carbon deposition from CO_2 containing atmosphere. Moreover, in higher magnification, corrosion products occurred at local defect position for 316NG and 800H. EDS analysis result indicated carbon deposited on all the surfaces of three specimens, with at least 4.28 wt.%. It is also worth noting that the true

composition of oxides may not agree with that determined by EDS, which was due that the EDS detector picked up signal from beneath the a few microns of the specimen surface.

Table 2
Elemental compositions of different position in Fig. 4 (all in wt.%).

Position	Cr	Ni	Mn	Si	C	Fe	O	Mo	Al	Ti
Point 1	13.48	7.86	-	0.66	9.17	53.58	12.19	3.06	-	-
Point 2	15.17	9.58	1.34	-	8.15	54.54	7.87	2.86	-	-
Point 3	-	8.39	-	-	60.44	16.34	5.24	-	-	-
Point 4	18.39	25.85	-	1.84	4.28	40.07	8.76	-	0.52	0.30
Point 5	14.08	50.37	-	0.08	10.53	1.72	13.76	9.21	0.25	-

3.3 XRD and Raman analysis

Figure 5 reveals XRD pattern of 316NG, 800H and 625 alloys after 3000 h exposure. Except for the diffraction peaks related with γ -Fe, no obvious diffraction peak was found in Fig. 5. This result indicated the formed oxide layer was so thin that the composition and structure could not obtained through XRD measurement, even with low incident angle diffraction. Furthermore, Raman measurement was respectively preformed after 1000 h and 3000 h exposure, and the obtained results are shown in Fig. 6. As shown in Raman spectra, a weak peak was detected after 1000 h exposure, corresponding to Cr_2O_3 . The main peaks at 1340 and 1599 cm^{-1} were also due to the carbon deposition on the surface [3, 4, 15]. The above results all confirmed a fact that the continuous oxide film didn't form yet after 1000 h exposure in $500\text{ }^\circ\text{C}$ and 20 MPa SCO_2 environment. Continue to prolong exposure time to 3000 h, the oxide films of 800H and alloy 625 were consisted by Cr_2O_3 (Raman shift marked with blue). For 316NG, Raman peaks correlated with Fe_2O_3 were detected as well, which may due to highest Fe content ($\sim 67\text{ wt.}\%$) compared with the other two.

3.4 GDOES analysis

Elemental distribution of cross section of the oxide layer after 1000 h exposure was analyzed using GDOES and the obtained result is shown in Fig. 7. For all of the specimens, a Cr-depletion zone formed at the interface between the oxide layer and the substrate, which was due to outward diffusion of Cr from the substrate and formation of Cr-rich oxide on gas/solid interface. Besides, Mn, Si for 316NG, Mn, Si for 800H and Al, Ti for alloy 625 enriched at the respective substrate/oxide interface. Researchers suggested Mn from the underlying substrate was partially consumed to form the $(\text{Cr}, \text{Mn})_3\text{O}_4$ or $\text{Mn}_{1.5}\text{Cr}_{1.5}\text{O}_4$ spinel oxides near the substrate/oxide interface [7, 11]. A very thin and amorphous Si-rich oxide layer was also found in the interface in their study for 630 SS and 430 SS, which seemed to agree with ours. It was reported that internal silica layer could limit diffusing cations and anions, which was attributed that its structure could aid the formation of the external chromia layer [32]. In addition, as suggested by Lee [5]

and Tan [33], Al_2O_3 and TiO_2 could be formed at the interface between chromia layer and substrate as they were stable at much lower oxygen partial pressure. In case of carburization, enrichment of C was not only in the air/solid interface, but also in underneath the oxide for 800H. However, for 316NG and 625 alloys, enrichment of C was mainly on their surfaces. At last, the approximate thicknesses of the oxide layers after 1000 h exposure could also be obtained from GDOES results, and the values were about 40 nm, 45 nm and 25 nm respectively.

3.5 TEM analysis

In order to uncover the detailed microstructures and chemical composition at the substrate/oxide interface after 3000 h exposure, FIB lamellas containing the oxide layer was lifted out from 316NG, 800H and 625 specimens and TEM/EDS results are shown in Figs. 8–16. Figure 8 shows (a) STEM micrographs, (b) HAADF micrograph and (c) high-resolution STEM and corresponding Fast Fourier Transformation (FFT) micrographs of the cross section of 316NG. As shown in the STEM micrographs with lower and higher magnification, the oxide layer was continuous and compact, but its thickness was not uniform. According to the HAADF micrograph, its average thickness was in between 21 nm and 45 nm. Compared with the thickness of the oxide after 1000 h exposure (~ 40 nm), there was almost no change in thickness although another 2000 h exposure was performed. Figure 9 shows the results of EDS mapping near the interface between the oxide layer and the underlying substrate for 316NG. It can be seen that, the whole oxide was Cr-rich oxide, and it was thought as Cr_2O_3 combined with XRD and Raman results. Moreover, Mn and Fe was accumulated at the interface, especially enrichment of Fe was very clear in Fig. 9. Further EDS line scanning (Fig. 10) conformed a multilayer structure of the oxide layer of 316NG after 3000 h exposure, i.e., the outer layer of the oxide was C-rich, the middle layer was Fe-rich and the inner layer was Mn-rich. High-resolution STEM and its FFT micrographs (Fig. 8c) showed that the Fe-rich oxide existed in the form of Fe_3O_4 or Fe_2O_3 (see Fig. 6), and no Mn containing crystal structure was found according FFT pattern, probably indicating Mn-rich oxide was in the form of amorphous state. The existence of C in the oxide was due to carburization from CO_2 containing atmosphere.

Figure 11 shows (a) STEM micrographs, (b) HAADF micrograph and (c) high-resolution STEM and corresponding Fast Fourier Transformation (FFT) micrographs of the cross section of 800H. It could see clearly from STEM micrographs that the oxide layer was continuous, compact and its thickness was uniform, which was different from that of 316NG. From HAADF micrograph, the thickness of the oxide was about 64 ~ 88 nm after 3000 h exposure. In contrast with the oxide after 1000 h (~ 45 nm), its thickness increased by 45%~96% at different regions after operating another 2000 h exposure. Figure 12 shows the results of EDS mapping near the oxide/substrate interface for 800H. In addition to enrichment Mn and Fe, Al was also found to enrich at the oxide/substrate interface. Unusually, it was commonly suggested that Al existed in form of Al_2O_3 with either crystal state or amorphous state [5]. The Al_2O_3 scales have proven to be particularly protective in containing carbon- or sulfur-species and water vapor aggressive atmosphere [23]. Especially, its carburization resistance was even superior to that of Cr_2O_3 [9, 23]. However, as suggested Lee [23], the presence of Al-rich surface layer alone is not enough to provide

sufficient corrosion and carburization resistance, unless pre-oxidation above 900°C was applied to form a more protective α - Al_2O_3 on the surface. In our study, a relatively serious carburization still occurred for 800H observed in Fig. 7 although the Al-rich oxides formed at the oxide/substrate interface. The reason could be attributed that: i) the Al-rich oxide layer was not continuous (marked with red arrow in EDS mapping of Al of Fig. 12) and ii) the temperature used was too low to form protective α - Al_2O_3 . As shown in Fig. 11c, only Ni_6MnO_8 crystal phase was found according to FFT pattern except for Cr_2O_3 phase, and no Al-containing crystal structure seemed to demonstrate this speculation. EDS line scanning of 800H is shown in Fig. 13. The Ni-rich matrix can be found not only on the surface of the oxide, but also at the oxide/substrate interface. Chen *et al.* [7] reported a similar phenomenon with ours, but Ni only precipitated at the oxide/substrate interface in their study. Due to the lower solubility of Ni in the oxides compared to that in the alloys, the oxides could serve as a diffusion barrier, resulting in the precipitate of Ni accumulated at the oxide/substrate interface. However, further experiment is necessary to prove how Ni diffuses to the surface of the oxide.

Figure 14 shows (a) STEM micrographs, (b) HAADF micrograph and (c) high-resolution STEM and corresponding Fast Fourier Transformation (FFT) micrographs of the cross section of alloy 625. The STEM micrographs indicated that the oxide layer was continuous, compact and its thickness was uniform as well. From HAADF micrograph, the thickness of the oxide layer was in between 31 nm and 43 nm after 3000 h exposure. Compared with the thickness of the oxide layer after 1000 h exposure (~ 25 nm), the thickness increased by 24%~72% at different regions after operating another 2000 h exposure. Figure 15 shows the results of EDS mapping near the oxide/substrate interface for alloy 625. Enrichment of Ni, similar with that of 800H, was also observed at the surface of the oxide, which was due to higher content of Ni in the alloy substrate (> 30%). From EDS line scanning (Fig. 16), except for Ni enrichment, Ti enriched inside of the oxide and Al enriched at the oxide/substrate interface. According to high-resolution STEM and its FFT pattern, only crystal structure of Fe_3O_4 was found except for Cr_2O_3 , indicating Ti-rich and Al-rich oxides were in the form of amorphous state [27]. Moreover, there was no obvious carburization for alloy 625, which agreed with GDOES and Raman results.

3.6 Corrosion and carburization mechanism

It is generally known that Cr has a higher diffusivity and a higher affinity for oxygen, resulting in priority formation of Cr_2O_3 scale on the surface of alloys. As the Cr_2O_3 scale grew, Cr removed from the alloy substrate causing a Cr depleted zone. From GDOES results after 1000 exposure, a Cr depleted zone was observed in all of the alloys. In case of Ni, it had a lower oxygen affinity than Fe, resulting that the diffusion rate into Cr_2O_3 scale for Fe higher than that for Ni. Therefore, Fe oxide was found in the middle of the oxide in Figs. 9 and 12 (corresponding to 316NG and 800H), and it didn't occur in alloy 625, which may be attributed to a lower Fe content (~ 2.54 wt.%). As for Si and Al, they tended to form beneath or at the substrate/oxide interface. It has been reported Al is a beneficial element to improve the carburization resistance of alloy. So far, a large number of studies have begun to focus depositing Al coating on the surface of alloys [22, 23, 26]. According to their results, the protective effect of the containing α - Al_2O_3

layer better than that of amorphous Al-rich layer alone. No enrichment of Si was observed in our TEM results, which may be because the underlying silica oxide layer is slow to develop compared to alumina [32]. Mn and Ti are thought as detrimental to oxidation resistance. They could rapidly diffuse through the chromia scale and form oxide on the outer surface which thickens with time, increasing the overall oxidation rate [32].

As suggested by Lee *et al.* [5], the carburization can occur in unique SCO_2 atmosphere by i) supplying C to the oxide/substrate interface through the oxide layer; ii) diffusing through the metal substrate and iii) forming carbides with metal elements. Although the solubility of C in the oxide is virtually zero, CO_2 from environment can permeate through nano-channels, pores, cracks, or oxide grain boundaries. When CO_2 reaches the oxide/substrate interface, it will interact with Cr or Fe as the following reaction (1) [34]:

Then C deposition occurs at the oxide/substrate interface through the Boudouard Reaction (2) during SCO_2 exposure:

By this way, C gradually accumulates at the oxide/substrate interface, and eventually develops into an amorphous C layer along with the growth of the oxide layer. Once the amorphous C layer is formed, it may act as the source of C to the alloy substrate [5]. Therefore, carbides such as Cr_{23}C_6 or Cr_7C_3 can be formed in the underlying substrate. In addition, at temperature greater than 425°C sensitization may occur in the austenitic stainless steel, causing the formation of Cr carbides at the grain boundary as well. It is worth noting that sensitization can also occur in nickel-based alloys, and ferritic stainless steels, but at higher temperatures [32]. Lee *et al.* [11] reported that ultimate tensile strength increased and elongation decreased after exposure in SCO_2 for 800HT. And they suggested that Cr-rich M_{23}C_6 carbides in 800HT contributed to additional loss of ductility [5]. According to the results in our study, no obvious amorphous C layer and carbides formed for all tested alloys. As for 316NG and alloy 625 C deposition only occurred at the surface of the oxide and inside of the oxide, while carburization was also found at oxide/substrate interface of 800H. In Fig. 13, C enriched at the interface between Ni-rich matrix and the oxide, which may also indicate the oxide scale had a degree of carburization resistance. Moreover, in generally, the lower Cr activity in the Ni-based alloys and lower solubility of Ni in carbide contributes to the carburization resistance of Ni-based alloys [5].

4. Conclusion

Compatibility and long-term integrity of candidate structural materials, including austenitic stainless steel 316NG, Fe-Ni based alloy 800H and Ni-based alloy 625, were tested in SCO_2 environment with 500°C and 20 MPa. And the oxide formed during 3000 h exposure was systematically investigated, including

corrosion kinetics, morphology, composition and structure. Based on the above tests and analysis, the following conclusions were drawn:

- (1) The corrosion kinetics approximately followed a parabolic law for 316NG and 800H, but not for alloy 625. Meanwhile, the oxidation rate of alloy 625 with high Cr and Ni content was 1 ~ 2 order of magnitude lower than that of 316NG and 800H at first 1000 h exposure.
- (2) From SEM surface morphologies of 316NG and 625 alloy, there was no obvious change up to 3000 h exposure. However, for 800H, some dark spots corresponding carbon deposition (with ~ 60.44 wt % C content) formed on its surface.
- (3) The main composition of the oxide scale was Cr_2O_3 for all tested alloy, and therefore resulting in a Cr-depletion zone formed at the oxide/substrate interface. After 3000 h exposure, the thicknesses of the oxide scale for 316NG, 800H and alloy 625 were 21 ~ 45 nm, 64 ~ 88 nm and 34 ~ 43 nm respectively. In contrast with 1000 h exposure, the increase in thickness was highest with 45%~96% for 800H.
- (4) Enrichment of trace elements were observed at oxide/substrate interface, i.e., enrichment of Mn, Si for 316NG, enrichment of Mn, Si, Al, Ti for 800H and enrichment of Ti, Al for alloy 625. And they existed in the form of amorphous oxide state.
- (5) In case of carburization, for 800H, enrichment of C was not only in the air/solid interface, but also in underneath the oxide for 800H. However, for 316NG and 625 alloys, enrichment of C was mainly on their surfaces.

Declarations

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Figures

Figure 1

(a) Geometry and dimensions of coupon type specimens and (b) schematic of the SCO₂ compatibility testing system.

Figure 2

(a) Weight gains and (b) the oxidation rate during 3000 h exposure in SCO_2 for 316NG, 800H and alloy 625.

	500 h	1000 h	2000 h	3000 h
316 NG
800 H
625

Figure 3

Photographs of 316NG, 800H and 625 alloys after exposure for 500 h, 1000 h, 2000 h and 3000 h in SCO_2 .

Figure 4

Surface morphologies of 316NG, 800H and 625 alloys after 3000 h exposure in SCO_2 .

Figure 5

XRD pattern of 316NG, 800H and 625 alloys after 3000 h exposure in SCO_2 .

Figure 6

Raman results of 316NG, 800H and 625 alloys after (a) 1000 h and (b) 3000 h exposure in SCO_2 .

Figure 7

GDOES results of (a) 316NG, (b) 800H and (c) 625 alloys after 1000 h exposure in SCO_2 .

Figure 8

(a) STEM micrographs, (b) HAADF micrograph and (c) high-resolution STEM and corresponding Fast Fourier Transformation (FFT) micrographs of the cross section of 316NG.

Figure 9

EDS mapping images of oxide layer of 316NG after 3000 h exposure in SCO_2 .

Figure 10

EDS line scanning of oxide layer of 316NG after 3000 h exposure in SCO_2 .

Figure 11

(a) STEM micrographs, (b) HAADF micrograph and (c) high-resolution STEM and corresponding Fast Fourier Transformation (FFT) micrographs of the cross section of 800H.

Figure 12

EDS mapping images of oxide layer of 800H after 3000 h exposure in SCO_2 .

Figure 13

EDS line scanning of oxide layer of 800H after 3000 h exposure in SCO_2 .

Figure 14

(a) STEM micrographs, (b) HAADF micrograph and (c) high-resolution STEM and corresponding Fast Fourier Transformation (FFT) micrographs of the cross section of alloy 625.

Figure 15

EDS mapping images of oxide layer of alloy 625 after 3000 h exposure in SCO_2 .

Figure 16

EDS line scanning of oxide layer of alloy 625 after 3000 h exposure in SCO_2 .