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Oxidation behavior of 316L austenitic stainless steel in high temperature air with long-term exposure

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Abstract
The oxidation behavior of 316L stainless steel exposed at 400, 600 and 800 °C air for 100, 500 and 1000 h was investigated using different characterization techniques. Weight gain obeys a parabolic law, but the degree of deviation of n index is increasingly larger with the increase of temperature. A double oxide film, including Cr2O3 and Fe2O3 oxide particles in outer and FeCr2O4 oxides in inner, is observed at 400 °C. As regards to samples at 600 °C, a critical exposure period around 100 h exists in the oxidation process, at which a compact oxide film decorated with oxide particles transforms to a loose oxide layer with a pore-structure. In addition, an oxide film containing Fe-rich outer oxide layer and Cr-rich inner oxide layer is observed at 600 °C for 500 and 1000 h. Spallation of oxide scale is observed for all samples at 800 °C regardless of exposure periods, resulting in different oxidation morphologies, and the degree of spallation behavior is getting worse. A double oxide film with the same chemical composition as 600 °C is observed, and the thickness increases over exposure periods.

Introduction

As very important structural materials, austenitic stainless steels are widely used in industries, such as in nuclear power plants for pump materials and core structural materials, and in fossil fuel power stations for tubes and pipes and other fields due to their excellent mechanical properties and corrosion resistance at high temperature [1–3]. Currently, austenitic stainless steels used in nuclear power plants are mainly 316L and 304 stainless steels [4]. The mechanical properties and corrosion resistance of 316L stainless steel (316LSS) are further improved by the addition of 2%–3%Mo in comparison of 304 stainless steel [5], which makes 316LSS as a candidate material for fuel cladding or other components in advanced nuclear power reactors [6, 7].

Currently, a lot of research work was conducted on the mechanical properties and corrosion behavior of 316LSS at high temperature [8–16]. At present, the main work in respect to mechanical properties is to further improve it by using different technologies or methods, such as surface mechanical attrition treatment [8], selective laser melting treatment [9], and optimizing of alloying elements [10, 11]. Meanwhile, the corrosion behavior of 316LSS at high temperature was extensively studied, especially for the high temperature and high pressure water [12–16], revealing that it has excellent corrosion resistance under these conditions. However, few investigations on the oxidation behavior of 316LSS in high temperature air are conducted even if it is selected as a candidate material for high temperature nuclear reactor, which requires alloys to perform well at temperatures around 727 and 1127 °C [17–21]. Besides, different thicknesses and chemical compositions of oxide films are detected for 316LSS exposed to high temperature air with different exposure periods. A. Bautista et al investigated the oxidation behavior of 316L at 600, 700 and 800 °C air for 240 h, indicating that compared with other stainless steels, including 434L, 304L and 304L + Yttria, 316L has the worst oxidation resistance at these temperatures, and the main oxides are (Fe0.9Cr0.4)2O3, Fe2O3 and NiCr2O4 [17]. Meanwhile, W. Zieliński et al
found that a double-structure oxide film, including a Fe-rich oxide in the outer layer and a Cr-rich oxide in the inner layer, is formed on the surface of 316L exposed at 600 °C air for 1 h [18]. However, electron backscatter diffraction (EBSD) results of M. Jepson et al showed that the scales on the 316 stainless steel at 1200 °C air consist of three oxide films in which the lowest one is a fine equiaxed region with a uniform distribution of chromium, the middle one is a larger equiaxed layer with very low chromium but high iron content, and the highest one is a columnar layer with very high nickel [19]. Besides, Tanabe et al investigated the oxidation behavior of 316 austenitic stainless steel at 600°C–800 °C air with and without mechanical polishing, and found that the as received samples showed the growth of Fe-rich surface oxides while mechanically polished specimens generated Cr-rich oxides on the surface [20]. The results briefly summarized above suggest that all investigations are focused on short-term oxidation, such as 240 h for [1, 17 h for [18], 1 to 4 h for [19] and 2 to 60 h for [20], which means that the results obtained from these conditions do not represent the oxidation behavior of 316LSS through the whole service periods. Therefore, we need to seek the oxidation mechanism of 316LSS exposed to high temperature air for long-term in order to predict the oxidation behavior during long-term service. Additionally, most studies on the oxidation behavior of 316LSS are conducted in high temperature, ranging from 600 to 1200 °C [17–20], rather than low temperature, while oxidation behavior under low temperature also plays an important role in understanding the oxidation mechanism of 316LSS at high temperature. The primary purpose of this paper is to investigate the oxidation behavior and mechanisms of 316LSS in air at 400, 600 and 800 °C for 100, 500 and 1000 h.

### Material and methods

The material used in present study is an 316LSS, and the major chemical compositions (in wt.%) are listed in table 1. Austenitic steel 316LSS specimens of approximate dimensions 20 × 10 × 3 mm³, purchased from Taiyuan Iron and Steel Co., Ltd, were polished on SiC papers up to 2000 polishing grade, then washed with acetone and finally dried under a drying box before isothermal oxidation at different temperatures. The 316LSS samples were put into quartz crucibles during high temperature oxidation process in order to ensure the accuracy of weight data. Oxidation temperatures are 400, 600 and 800 °C in air, held for 100, 500 and 1000 h, and then cooled to room temperature at a rate of 40 °C min⁻¹.

| Alloy | Cr    | Ni    | Mo | Si  | Mn  | Cu  | C   | S    | P    |
|-------|-------|-------|----|-----|-----|-----|-----|------|------|
| 316L  | 16.68 | 12.63 | 2.09 | 0.59 | 1.57 | 0.13 | 0.023 | 0.003 | 0.024 |

All the samples were weighed using a METTLER TOLEDO ME104T/02 milligram balance with an accuracy of 0.1 mg prior to and after exposure to high temperature air. A FEI Nova Nano 450 scanning electron microscope (SEM), equipped with energy dispersive X-ray spectroscopy (EDS), was used to investigate the oxide thickness, chemical composition and oxide morphology. D8 ADVANCE x-ray diffraction (XRD) with Cu Kα (λ = 0.154 051 nm) was used for analyzing the crystal structure of oxides. The diffracted x-ray signal was collected over an angle theta from 5 to 45. Phase stability of the Fe-Cr-Ni-O2 system in 316LSS samples was considered using the software FactSage 7.1. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250Xi X-ray photoelectron spectrometer using a monochromatic Al Kα source operated at 150 W with initial photo energy 1486.6 eV. The Cls peak from adventitious carbon at 285 eV was used as a reference to correct the charging shifts.

### Results

**Weight gain**

The weight gain of 316LSS exposed to high temperature air for various exposure periods is shown in figure 1(a). The results show that exposure temperature has a significant effect on the weight gain of 316LSS. With an increase in temperature, weight gain gradually increases. Weight gain at 800 °C for 1000 h is about 32.46 times greater than that of samples at 400 °C, and about 2.83 times for samples exposed at 600 °C. In addition, weight gain obeys a parabolic law, while the degree of deviation of index n, which normally is 0.5 [22], is increasingly larger with the increase of temperature, which are 0.488 for 400 °C, 0.599 for 600 °C and 0.231 for 800 °C. The relationship between weight gain of samples exposed at 800 °C air and exposure periods after subtracting spalled oxide films is shown in figure 1(b). Weight gain gradually increases after less than 150 h of exposure, while weight loss appears when exposure tests extend to more than 150 h. Moreover, the weight loss gradually
increases with increasing exposure periods from 150 h to 1000 h, and the maximum value is $-12.04 \text{ mg cm}^{-2}$ at 1000 h.

**Phase composition of oxide layer**

The structures of oxide phases of 316LSS after exposure to air at 400, 600 and 800 °C for 100, 500 and 1000 h are identified by XRD in $\theta-2\theta$ mode, as shown in figure 2. The results of oxidized samples at 400 °C show that no significant differences in the phase composition of oxide films are detected regardless of exposure periods. The diffraction peaks appear at 42.641, 43.728, 49.723 and 73.613 degree two-theta, in line with the diffraction patterns of $\gamma$-Fe (JCPDS 52-0513) and chromic oxide Cr$_2$O$_3$ (JCPDS 01-1294), implying the formation of a thin oxide film on the surface of samples. In order to further identify the surface oxides of samples exposed at 400 °C, the spectra of Cr 2p$_{3/2}$, Fe 2p$_{3/2}$, Ni 2p$_{3/2}$ and O 1s in oxide films from free surface to the deeper site of 316LSS exposure for 1000 h is obtained by XPS, as shown in figure 3. Sputtering time is 10 and 70 s, corresponding to a depth of oxide layer of 3 and 21 nm. The results show that Cr$_2$O$_3$ and Fe$_2$O$_3$ are formed on the surface of sample, while FeCr$_2$O$_4$ and Ni-rich oxides appear at the depth of 21 nm.

The results obtained from figure 2(b) reveal that in addition to $\gamma$-Fe and chromic oxide Cr$_2$O$_3$, a new diffraction peak appeared at 24.826 degree two-theta, which belongs to chromic oxide Cr$_2$O$_3$ (JCPDS 01-1294), is observed for samples exposed at 600 °C for 100 h. In addition, two new oxides, one located at 22.859, 31.717, 34.282, 39.685, 42.336, 48.150, 49.620, 52.767, 61.129, 62.702 and 70.670 corresponding to hematite $\alpha$-Fe$_2$O$_3$ (JCPDS 24-0072) and another located at 34.761, 42.644, 53.057, 56.615, 61.436 and 74.022 corresponding to Fe-Cr mixed oxide FeCr$_2$O$_4$ (JCPDS 24-0511), are identified with increasing exposure periods from 500 h to 1000 h, suggesting the occurrence of a change in the chemical composition of oxide films. For samples exposed at 800 °C for different exposure periods, noting that no significant differences in the phase composition of oxide films is detected in comparison of samples exposed at 600 °C, as shown in figure 2(c), while the intensity of chromic oxide Cr$_2$O$_3$ significantly increases because of the higher oxidation kinetics and the spallation of oxide films.

**Surface oxide morphologies**

Figure 4 shows the surface oxide morphologies of 316LSS exposed to air at 400 °C for 100, 500 and 1000 h. Oxide particles rather than oxide films are observed along the scratches, and the number of oxide particles gradually increase with increasing exposure periods. According to the chemical composition of EDS, as shown in table 2, and the results of XPS and XRD, it can be inferred that the oxides marked in A and B are Fe-rich M$_2$O$_3$.

The oxidation scale morphologies of 316LSS exposed to air at 600 °C for different exposure periods are shown in figure 5. A similar oxide morphology at 400 °C is observed for samples exposed to 100 h, while a porous structure decorated with rod-like oxides are detected for samples exposed for 500 and 1000 h. The number of rod-like oxides gradually increases with the increase of exposure periods, as shown in figures 5(e) and (f). Besides, the results of EDS of oxides with different structures, as shown in table 2, reveal that find particle (marked C) and rod-like oxide (marked D) are Fe-rich (Fe,Cr)$_3$O$_4$, and porous structure oxide (marked E) is Fe-rich M$_2$O$_3$.

Figure 6 shows the oxidation morphologies of 316LSS exposed at 800 °C air for different exposure periods. It is worth noting that spalling behavior appears for all samples regardless of exposure periods, and the range of spalled area increases with increasing exposure periods, as shown in figures 6(a) to (c), resulting in different oxidation morphologies. For samples oxidized for 100 h, a great number of isolated oxide islands present in the
spalled area, as shown in figure 6(d), while an Fe-rich M₂O₃ (marked F) with irregular granular structure appears in the unspalled area, as shown in figure 6(g). The same oxide morphology is also observed in the unspalled area of samples oxidized for 500 h, while a Cr-rich spiral structure without obvious oxide films appears in the spalled areas, as shown in figure 6(h). As regards the samples oxidized for 1000 h, a great number of Fe-rich fine particle oxides (marked G) are observed in the area without spalling, as shown in figure 6(i), while granular oxides of Fe-rich M₂O₃ present in the spalled area (marked H), as shown in figure 6(f).

**Cross-sectional analysis**

Figure 7 shows the SEM images of cross-sectional structures and the depth profiles of chemical composition of 316LSS samples exposed at 600 and 800 °C for 100, 500 and 1000 h. The depth profiles of chemical composition across the thickness of oxide layers are shown under the images. Only a Fe₂O₃ oxide particle rather than an oxide film is detected for samples exposed at 600 °C for 100 h, as shown in figure 7(a). For samples exposed at 600 °C for 500 and 1000 h, a double structure oxide film, of which the outer is composed of Fe₃O₄ and the inner is composed of NiFe₂O₄ and NiCr₂O₄, is observed, as shown in figures 7(b) and (c). The thicknesses of the outer and inner oxide layer increase with the increasing of exposure periods, from 1.94 μm for 500 h to 5.89 μm for 1000 h for outer oxide layer, and 2.52 μm and 2.72 μm for inner oxide layer.

The SEM images of cross section of oxide films of 316LSS exposed at 800 °C for different exposure periods are shown in figures 7(d) to (h). Similar to samples exposed to air at 600 °C for 500 and 1000 h, a duplex-structure oxide film with outer and inner oxide layer is observed, while it has a poor uniformity with respect to the thickness of oxide films due to the spalling of oxide layers. The thickness of oxide film of samples after 100 h of exposure shows the thickest oxide film of 22.71 μm consisting of the outer oxide layer of 14.14 μm and the inner of 8.57 μm in figure 7(d) and the thinnest oxide film of 11.51 μm, including the outer of 5.28 μm and the

![Image of XRD patterns](image-url)
inner of 6.23 μm in figure 7(e). The thickness of oxide films of samples of 500 h exposure is ranging from 13.52 μm to 18.45 μm, while the range for 1000 h is from 18.95 μm to 41.69 μm, as shown from figures 7(f) to (h). Besides, some big cracks are observed on the cross sections of samples exposure for 100, 500 and 1000 h.

Figures 8 to 10 show the thermodynamic stability diagrams of the system Fe–Cr–Ni–O2 at 400, 600 and 800 °C, respectively. Noting that an oxide film including an outer layer consisting of M2O3 and spinel and an inner layer of spinel is formed on the surface of samples regardless of exposure temperature, corresponding to the results obtained from XPS, XRD and EDS of different exposure temperatures, which show a Cr-rich/Fe-rich M2O3 outer oxide layer and a spinel inner oxide layer. In addition, the partial pressure of oxygen forming the surface oxide films gradually decreases as the exposure temperature increases, suggesting that it is easier to form an oxide film at high temperature, which is confirmed by the chemical composition and thickness of oxide films.

Figure 3. The XPS spectra of Cr 2p3/2, Fe 2p3/2, Ni 2p3/2 and O1s in oxide films from the free surface to the deeper site of 316LSS after exposure at 400 °C air for 1000 h.
of samples exposed at 400, 600 and 800 °C. It also should be noted from figure 10 that M₂O₃ structure oxides will be formed under the spinel oxide layer at 800 °C, which may be the Cr-rich Cr₂O₃ oxide particles formed by the inward diffusion of oxygen. Currently, although no Cr-rich Cr₂O₃ oxide particles are observed in our results, however, it was observed in previous investigations on the oxidation behavior of 316L in high temperature air using transmission electron microscopy [18].

### Discussion

#### The deviation of parabolic law

In the case of 316LSS exposed at 400, 600 and 800 °C air for different exposure periods, it appears from the results of figure 1 that the mass gain curves of samples follow a parabolic law given by [23],

| Positions | Fe  | Cr  | Ni  | Mn  | Cu  | O   | Inferred oxides composition |
|-----------|-----|-----|-----|-----|-----|-----|----------------------------|
| A         | 73.43 | 17.83 | —   | —   | —   | 8.74 | M₂O₃                      |
| B         | 73.30 | 16.78 | —   | —   | —   | 9.91 |                           |
| C         | 45.96 | 14.66 | 6.86 | —   | —   | 32.52 | M₃O₄                      |
| D         | 65.72 | 5.72  | —   | —   | —   | 28.52 |                           |
| E         | 25.30 | 4.46  | —   | 5.07 | 6.03 | 59.14 | M₂O₃                      |
| F         | 39.51 | 8.16  | —   | —   | —   | 52.34 | M₃O₃                      |
| G         | 35.76 | —     | —   | —   | —   | 64.24 | M₂O₃                      |
| H         | 28.21 | 5.67  | 4.73 | —   | —   | 53.71 | M₃O₃                      |

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Figure 4. The oxidation morphologies of 316LSS exposed to air at 400 °C for different exposure periods: (a) 100 h; (b) 500 h; (c) 1000 h.

Figure 5. The oxidation morphologies of 316LSS exposed to air at 600 °C for different exposure periods: (a) and (d) for 100 h; (b) and (e) for 500 h; (c) and (f) for 1000 h.
Figure 6. The oxidation morphologies of 316LSS exposed at 800 °C for different exposure periods: (a), (d) and (g) for 100 h; (b), (c) and (h) for 500 h; (c), (f) and (i) for 1000 h.

Figure 7. The SEM images of cross sectional structures and the depth profiles of the chemical composition of 316LSS samples exposed at 600 and 800 °C for different exposure periods: (a) 100 h for 600 °C; (b) 500 h for 600 °C; (c) 1000 h for 600 °C; (d) and (e) 100 h for 800 °C; (f) 500 h for 800 °C; (g) and (h) 1000 h for 1000 °C.
Figure 8. The thermodynamic stability diagram of the system Fe–Cr–Ni–O₂ calculated by means of the software FactSage at 400 °C.

Figure 9. The thermodynamic stability diagram of the system Fe–Cr–Ni–O₂ calculated by means of the software FactSage at 600 °C.
where $\Delta M$ is the weight change of the samples before and after oxidation in mg, $S$ is the surface area of the samples in cm$^2$, $A$ is constant, $t$ is exposure time in h and $k_p$ is parabolic rate constant in g$^2$ cm$^{-4}$ s$^{-1}$. The $n$ value, which normally is 0.5 [22], of our experiments fitted from figure 1 is 0.488 for 400 $^\circ$C and 0.599 for 600 $^\circ$C, but it is 0.231 for 800 $^\circ$C, which seriously deviates from a parabolic law. Chen and Yuen reviewed the high temperature oxidation of iron and carbon steels in air or oxygen, and agreed among those investigations that isothermal oxidation kinetics follows a parabolic law in the range of 570 to 700 $^\circ$C [22]. Meanwhile, they also pointed out that the oxidation behavior of iron in this temperature range is more variable, resulting in less consistent for the results of previous research [22]. For the oxidation kinetics of different austenitic stainless steels exposed at more than 800 $^\circ$C air, different researchers present different results [24–27]. In a study carried out by Wang et al [25], it was reported that isothermal oxidation kinetics curves of bulk nanocrystalline 304 stainless steel at 900 $^\circ$C obey an approximately parabolic law. N. Karimi et al’s results revealed that the oxidation kinetics of AISI 304 steel obeys a parabolic law during exposure in air at 800 and 1000 $^\circ$C, but oxidation kinetics curves present a linear regime during the first 10 h of oxidation test, and then turn to a parabolic regime at 900 $^\circ$C [26]. The same results also are observed by Huntz et al, Li et al, and Wood, who investigated the oxidation behavior of Fe–Cr alloys and stainless steels in high temperature air [27–29], but Li et al’s results revealed that for super-austenitic stainless steel S32654, oxidation kinetics follows a linear law at 1000 and 1200 $^\circ$C [28]. Li et al believed that molten MnMoO$_4$–MoO$_3$ molybdate electrochemical reaction and oxide layer cracking are the main reason for the linear law of oxidation kinetics of S32654 steel [28]. Pérez et al found that adding some other elements in AISI 304 stainless steel, such as Si, Mo and Ce, can significantly influence the oxidation kinetics of this material at 900 $^\circ$C [24]. Besides, Wood and Chen et al summarized the previous results, and found that the oxygen partial pressure and temperature also have a significant influence on the oxidation kinetics of iron, Fe–Cr alloys and stainless steels when they are exposed to high temperature air [23, 27]. Compared with previous investigations on the oxidation kinetics of iron, Fe–Cr alloys and stainless steels, weight gain at 400 $^\circ$C follows a parabolic law in our experiments, while it deviates from a parabolic law at 600 and 800 $^\circ$C. The main reason for different oxidation kinetics at 400 and 600 $^\circ$C is the different diffusion coefficient of O, Cr, Fe and Ni through the oxide films at different oxidation temperatures. The thinner oxide film at 400 $^\circ$C causes the elements to diffuse out more easily, resulting in the appearance of a parabolic law for oxidation kinetics. The rate of diffusion gradually decreases as the thickness of oxide films rises, causing a deviation from the parabolic law at 600 $^\circ$C. As regards to samples exposed at 800 $^\circ$C, the oxidation kinetic dependents on the spalling of oxides and diffusion.

$$\left(\frac{\Delta M}{S}\right)^2 = A + k_p \cdot t$$

(1)
coefficient of different elements. The spalling of the oxides will create a new surface to form new oxides, which will lead to an increase in the rate of oxidation, and improve the diffusion rate of metal ions and oxygen during the oxidation process [30]. Besides, the appearance of cracks and porous structures will also promote the diffusion rate of Cr, Fe and O. Therefore, oxidation kinetics deviates from the parabolic law at 800 °C.

Oxidation mechanism

Currently, a great number of oxidation mechanisms of austenitic stainless steels exposed to high temperature air were proposed [20, 26, 31], while all data used to establish the oxidation mechanisms are obtained from short-term oxidation instead of long-term. It is well known that the thermodynamics of chemical reactions determines the formation of different types of oxides, and oxidation kinetics determines the nucleation and growth of the oxides [32, 33]. Both the thermodynamics and kinetics of the formation of oxides are determined by temperatures, exposure periods, oxygen partial pressure and chemical composition [34]. According to the thermodynamics of chemical reactions, it should be noted that Cr-rich and Ni-rich oxides are nucleated on the surface of 316LSS at the beginning due to the lower Gibbs free energy, and then for Fe-rich oxides, which is confirmed by Riffard et al who investigated the oxidation behavior of 304 steel at 1000 °C in air using in situ XRD and revealed that Mn1.5Cr1.5O4 and Cr2O3 are nucleated at the beginning of the oxidation process [35]. The same results are also observed by Karimi et al who investigated the oxidation behavior of AISI 304 stainless steel at 1000 °C air by XRD and infrared spectroscopy [26]. However, nucleation rate for different oxides is different. Birks et al proposed that the nucleation rate of oxides is proportional to the initial concentration of elements in materials [34], which means that the rate of nucleation for elements having a higher concentration is faster than that of elements with a lowe concentration, indicating that Fe-rich oxides are more easily formed as the increasing of exposure periods. Such predictions are in complete agreement with our experimental results, revealing that the main oxides formed on the surface of samples is Fe2O3. Besides, the same results are also observed from the thermodynamic stability diagrams of the system Fe–Cr–Ni–O2 at different temperatures, as shown in figures 9–11, in which the oxides formed on the surface of samples at 400, 600 and 800 °C is spinel and corundum M2O3.

For samples exposed to air at 400 °C, Fe-rich, Cr-rich and Ni-rich oxides will be nucleated at the beginning of oxidation, while the number of Cr-rich oxides is significantly more than that of Fe-rich and Ni-rich oxides due to the lower Gibbs free energy to form Cr-rich oxides than that of Fe-rich oxides and higher concentration in matrix in comparison of Ni element. Meanwhile, the size of nucleated oxide particles gradually grows with increasing exposure periods at different temperatures, and then reacts with each other to form new oxides, such as FeCr2O4, NiFe2O4 and NiCr2O4, forming an oxide film on the surface of samples and hindering the outward diffusion of metal ions [26, 36]. After that, a great number of Fe-rich oxide particles will be formed on the surface of Cr-rich oxide films due to the high diffusion coefficient for Fe than Cr and Ni in this oxide layer [32], as shown in figure 4. It is well known that oxidation temperature determines the diffusion coefficient of different elements during the oxidation process [37], and therefore the rate of diffusion for Fe at 400 °C is significantly lower than at 600 and 800 °C, resulting in the formation of oxide particles rather than obvious oxide films, as shown in figures 4–6. Furthermore, an increase in the number of oxide particles is observed at 400 °C even though the exposure periods extend to 1000 h, while no significant differences in the size of oxides appears, further confirming the lower diffusion rate and Gibbs free energy at this temperature. For samples exposed at 800 °C, owing to the high rate of diffusion and the lower Gibbs free energy of chemical reactions, the oxides will be formed and grew quickly, and therefore an oxide film is observed for samples exposed for 100 h rather than oxide particles.

In addition, oxygen will diffuse into the matrix along the defects of 316LSS, such as dislocations and grain boundaries [26], even though a Cr-rich oxide film is formed on the surface of samples, resulting in the formation of an outer oxide layer composed of Fe2O3 and FeCr2O4 and an inner oxide layer composed of NiFe2O4 and NiCr2O4. Since the higher nucleation and reaction energy of oxides at 400 °C, only a thinner oxide film decorated with a large number of oxides is formed on the surface of 316LSS. With the increasing of exposure periods, the inward diffusion rate for oxygen and outer diffusion rate for Fe will get equilibrium when exposure periods extend to a long term [38], causing no significant variations in the thickness and chemical composition of oxide layer. In the case of samples oxidized at 600 °C, a critical point, around 100 h of exposure, exists in the oxidation process, at which a compact oxide film decorated with oxide particles transforms to a loose oxide film with a porous structure, as shown in figure 5, suggesting that two oxidation states, nucleation and gestation stage before 100 h and growth stage after 100 h, occur at this temperature. After transformation, a duplex-structure oxide film is formed, and the thickness of oxide film increases with extending exposure periods. However, for samples exposed at 800 °C, the spalling behavior becomes more and more serious as the exposure periods increases due to the mismatch of thermal expansion between oxides and substrate alloys during the cooling process [39]. The appearance of new surface will hinder the further oxidation of 316LSS due to the high concentration of Cr under the outer oxide layer, as shown in figure 7, while the thickness of oxide films in...
unsplalled area will continue to increase, resulting in the poor uniformity of oxide films. Besides, a great number of small and large cracks present as the increasing of exposure periods, which means that new area will be further oxidized, resulting the deviation of parabolic law, as shown in figure 1.

**Conclusion**

The oxidation behavior of 316LSS exposed at 400, 600 and 800 °C for long-term exposure was investigated by XPS, SEM, EDS and XRD. The main results are summarized as follows:

1. Weight gain obeys a parabolic law, but the degree of deviation of n index, which normally is 0.5, is increasingly larger with the increase of temperatures, which are 0.488 for 400 °C, 0.599 for 600 °C and 0.231 for 800 °C. Equilibrium state will never be reached even though samples are exposed at 800 °C for 1000 h due to the appearance of cracks and the spallation of oxide films.

2. An outer oxide layer consisting of Cr2O3 and Fe2O3 oxide particles and an inner oxide layer containing FeCr2O4 are observed for samples exposed at 400 °C for different exposure periods. As regards to samples at 600 °C, a critical point, around 100 h of exposure, exists in the oxidation process, at which a compact oxide film decorated with oxide particles transforms to a loose oxide film with a porous structure. Besides, an oxide film containing Fe-rich outer oxide layer and Cr-rich inner oxide layer is observed when exposure periods extend to 500 and 1000 h at 600 °C.

3. The spallation of oxide films appears for samples exposed at 800 °C regardless of exposure periods, resulting in different oxidation morphologies, and the degree of spallation becomes more and more serious with increasing exposure periods. Meanwhile, a double oxide film with the same chemical composition as 600 °C is observed regardless of exposure temperature, and the thickness of oxide films increases over exposure periods.

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