Effect of Element Diffusion Through Metallic Networks During Oxidation of Type 321 Stainless Steel

Z. Zeng, K. Natesan, Z. Cai, D. Gosztola, R. Cook, and J. Hiller

(Submitted December 22, 2013; in revised form January 25, 2014; published online February 20, 2014)

A detailed study was conducted on localized oxidation on Type 321 stainless steel (321ss) using synchrotron x-ray nanobeam analysis along with Raman microscopy. The results showed the presence of metallic nanonetworks in the oxide scales, which plays an important role in the continued oxidation of the alloy at 750 °C. A mechanism is proposed to explain the rapid oxidation of 321ss in complex gaseous environments at elevated temperature. Neutral metal atoms could diffuse outward, and carbon atoms could diffuse inward through the metallic nanonetworks in oxide layers. Alternately, diffusion tunnels can dramatically affect the phase composition of the oxide scales. Since the diffusion rate of neutral metal and carbon atoms through the metallic nanonetworks can be much faster than the diffusion of cations through Cr_2O_3 , the metallic nanonetwork provides a path through the protective Cr_2O_3 layer for the rapid outward diffusion of metallic chromium and iron atoms to the nonprotective spinel layer. This diffusion process affects the solid-state reaction near the alloy-oxide boundary, and a dense Cr_2O_3 protective layer does not form. The classic stable structure of the oxide scales, with a dense Cr_2O_3 layer at the bottom, is damaged by the rapid diffusion through the tunnel at the reaction front, resulting in locally accelerated oxidation. This process can subsequently lead to “breakaway” oxidation and catastrophic failure of the alloy.

Keywords advanced characterization, corrosion testing, electron microscopy

1. Introduction

Oxidation and carburization of alloy materials at high temperatures is a long-standing problem that leads to huge economic and energy losses (Ref 1–4). Such degradation retards the improvement of energy conversion efficiency that requires higher operating temperatures in process systems (Ref 1–4). If the efficiency of coal-fired power plants can be improved from the current $\approx 30\%$ to 50%, then 4.6 billion tons of CO_2 emissions could be reduced annually. Meanwhile, 1.6 billion tons of coal and fuel costs of 200 billion dollars would be saved annually. To improve the oxidation resistance of metallic materials at elevated temperatures, it is important to further understand the potential oxidation mechanisms of alloys exposed to high-temperature complex gaseous environments.

In general, alloys are protected from continuous oxidation by the oxide scales that develop on their surface at high temperatures when exposed to complex gaseous environments (Ref 5). Phase composition of the oxide scales dramatically affects the capability of the scales to protect the alloy from oxidation at high temperatures. Typically, Cr_2O_3 scales are protective, but spinel is not.

With advances in surface analysis techniques, it is currently possible to analyze the oxidized surfaces to a much higher resolution in characterizing the phases, compositions, composition gradients, and other factors in alloys that develop reaction layers when exposed to complex gas environments at elevated temperatures. x-ray diffraction (XRD) is the best method to evaluate the composition of phases in the oxide scales, but the sizes of regular x-ray beams means they generally cannot be focused on the oxide scales that are normally fairly thin with the size range on the order of nanometers-to-micrometer scale.

The 2ID-D beamline of the APS at Argonne National Laboratory produces a monochromatic x-ray beam size of 200×300 nm. The advantage of the synchrotron x-ray nanobeam is that the technique can be used to determine both the chemical composition by x-ray fluorescence and phase identification by XRD, within the nanosize area. Our recent study using nanobeam x-ray analysis indicated that the surface scales on alloys could be a mixture of oxides and metallic particles. These metallic nanoparticles can self-assemble into nanonetworks and act as channels for the transportation of certain constituent elements that exhibit high diffusion rates in metals (Ref 6). Although metallic particles have been observed in the oxide scales on alloys after exposure to steam at elevated temperatures since 1970 (Ref 7, 8), the effects of metallic nanonetworks on elemental transport and oxidation have not been evaluated in traditional oxidation/corrosion experiments.

Diffusion of alloy constituents and gas-phase constituents play an important role in the development of the oxide scales and in their microstructural characteristics. Since the proposal of the theory of oxidation by Carl Wagner in 1933 (Ref 5), diffusion of charged species such as cations, anions, and electrons has been considered as the avenue for transport through oxide scales because the scales are usually considered to consist of only oxide phases. However, if there are metallic

Z. Zeng, K. Natesan, Z. Cai, D. Gosztola, R. Cook, and J. Hiller, Argonne National Laboratory, Argonne, IL 60439. Contact e-mail: zeng@anl.gov.

nanonetworks in the oxide scales, then an additional diffusion route emerges since neutral metal atoms like Cr and Fe can diffuse outward, and carbon atoms can diffuse inward along the metallic nanonetworks.

In this paper, we present a novel transport route for breakaway oxidation that can lead to catastrophic degradation of metallic components exposed to elevated temperatures.

2. Experimental Procedures

2.1 Oxidation Experiments

Type 321 stainless steel (321ss) with a composition (in wt.%) of 70.35Fe-17.3Cr-10.3Ni-1.2Mn-0.4Si-0.4Ti-0.04C-0.01N was selected for the experiments. Oxidation experiments were conducted in an experimental system that consists of a horizontal, tubular, high-temperature furnace capable of operating up to 1000 °C. The reaction chamber consisted of a quartz tube (74-cm length, 5-cm OD, 0.32-cm thick), which was centered in a 30-cm-diameter resistive heating furnace. Type 316ss flange caps with an O-ring seal were used to close the ends of the quartz tube. The flange caps provided port fittings for the gas flow and steam/vapor preheater. A Barber-Coleman Model 560 three-mode controller was used to control the furnace temperature. A chromel-alumel thermocouple, inserted from one end of the reaction chamber, was used to monitor the specimen temperature. Specimens were suspended from quartz rods held on the top of a high-purity alumina boat. The specimens and the boat were positioned in the constant-temperature section of the reaction chamber. The specimens were exposed to pure CO₂, 0.1% O₂-99.9% CO₂, 3.97% O₂-96.03% CO₂, and 21% O₂-79% CO₂ with a gas flow rate of 300 ml/min at 750 °C. Specimens were weighed after exposure, and the mass gain was measured to evaluate the oxidation resistance.

2.2 Characterization of the Oxide Scales

After exposure at elevated temperatures, the specimens were cut and metallographic mounts were prepared for cross-sectional analysis. The microstructure of each specimen was examined using a Hitachi S4700-II scanning electron microscope (SEM). Nanobeam x-ray analysis was performed at the 2ID-D beamline of the APS at Argonne National Laboratory. The x-ray nanobeam (beam size of 200 × 300 nm) was scanned across the cross sections at both the breakaway and protective regions from the surface to the interior of the alloy specimens (Ref 6). Using a Si(001) double-crystal monochromator and zone plate optics, the x-ray nanoprobe in the experimental station produced a monochromatic x-ray beam of size of 200 × 300 nm and a photon flux of 5 × 10⁹ photons/s with an x-ray energy bandwidth (dE/E) of 0.01 %. The focal plane of the zone plate optics was adjusted to obtain a minimum spot size at the surface of the specimen. The beam was incident upon the region of interest on the specimen, and scattering intensity in a section of reciprocal space was captured by a flat, two-dimensional detector (CCD camera). Specimens for synchrotron radiation experiments were prepared in a similar manner as those for the cross-sectional analysis in SEM. The beam energy was 8.5 KeV for the XRD experiment. The position of the oxide-metal interface was determined by monitoring the Fe-fluorescence counts as the sample was translated across the beam.

Raman spectra were recorded using a Raman microscope (Renishaw, Inc.) typically using 5 mW of 514.5-nm excitation,

10 s/point, and 2-μm steps between map points. The microscope was equipped with a 50× 0.75 na objective (Leica) and a computer controlled X-Y sample stage (Prior), which was used for automated mapping.

Electron energy loss spectra (EELS) and energy-dispersive x-ray spectra (EDX) were acquired with a FEI Tecnai F20ST transmission electron microscope (TEM). The sample for the TEM experiment was cut by a Zeiss 1540XB focused ion beam (FIB) microscope from a cross section of 321ss after exposure in pure CO₂ at 750 °C.

3. Results and Discussion

3.1 Observation of Metallic Networks in Oxide Layer on Alloy After Breakaway Oxidation

The cross sections of 321ss after 24-h exposure in pure CO₂, 0.1% O₂-99.9% CO₂, and 3.97% O₂-96.03% CO₂ at 750 °C were examined by using a SEM. Although most of the areas on the alloy surface were covered by protective scale, locally enhanced oxidation was observed on the surface of all specimens (Fig. 1). The number of local corrosion points and the corrosion depth decreased with the increasing oxygen partial pressure. Breakaway oxidation was initiated from a localized attack on the surface of 321ss, and subsequently propagated over the entire surface after prolonged exposure. However, such breakaway oxidation did not occur when the stainless steel was exposed to 21% O₂-79% CO₂ for 320 h at the same temperature.

Two oxide layers were observed in the breakaway region. The nanobeam XRD analysis indicates that the outer layer of the breakaway region consists of Fe₃O₄, whereas (Mn,Fe)-Cr₂O₄ spinel is observed at the middle and inner scale regions (Fig. 2a). Fe₂O₃ was also observed on some areas of the oxide-gas interface. Cr₂O₃ and FeO were not observed in the scales of the breakaway area within the detection limit. In the protective region, Cr₂O₃ was the primary phase in the oxide scales near the alloy-oxide boundary, whereas spinel was the primary phase at the oxide scales near the surface. Diffraction peaks from Ni-Fe metal phases were observed in the oxide scales of the protective areas (Fig. 2b). These metallic nanoparticles can form in the thermal growth process of the oxide scales (Ref 6, 9). Both ferritic and austenitic phases occur in these Ni-Fe nanoparticles. The intensity of the ferritic diffraction peak at 42.1° (d -space at 2.03 Å) is much higher than the austenitic diffraction peak at 41.1°, which indicates that the primary phase in these Ni-Fe nanoparticles in the oxide scales is ferritic. In contrast, 321ss has an austenitic structure with the 111 diffraction peak at 41.1° (d -space at 2.08 Å) when an x-ray beam energy of 8.5 keV is applied. The intensity of the diffraction peak at 47.6° from the austenitic Ni-Fe phase near the surface is higher than that near the alloy-oxide boundary, which indicates an increase in the content of austenitic phase in metallic particles. Part of the metallic phase changes to austenitic structure, which may be due to the decrease in iron content in metallic particles near the surface, because iron is more readily oxidized than nickel at high p_{O_2} near the surface.

Nano-XANES (x-ray absorption near-edge structure) indicate that the chemical shift of Ni at the oxide scales of the protective area is close to that of Ni metal (Fig. 3a). The nickel particles in the oxide scales of the protective area are in their

Fig. 1 SEM images of 321ss upon exposure at 750 °C for 24 h to: 3.97% O₂-96.03% CO₂, 0.1% O₂-99.9% CO₂, and pure CO₂

Fig. 2 Synchrotron nanobeam XRD of 321ss after exposure to pure CO₂ at 750 °C for 284 h: (a) At the breakaway region; (b) at the protective region. A: austenitic Ni-Fe phase; F: Ferritic Ni-Fe phase

metallic state. Therefore, both nano-XANES and nano-XRD confirm that metallic particles with a primary phase different from the alloy substrate are present in the oxide scales of the protective region. In the breakaway region, the chemical shift of nickel in the inner oxide layer is almost the same as the chemical shift of pure nickel and nickel inside the alloy substrate (Fig. 3b), but it is far away from the +2 nickel in the NiCr₂O₄ and NiO standards. Therefore, the primary oxidation state of nickel in the inner oxide layer is determined to be zero. A feature of nanonetworks throughout the inner layer of the nonprotective region was observed (Fig. 4a). SEM shows a two-dimensional network, but both oxide and metallic nanonetworks are probably continuous in three dimensions. Metallic phases were also observed at the inner oxide layer of the breakaway region by nanobeam XRD. The intensity of the ferritic Ni-Fe diffraction is higher than that of the austenitic phase, which indicates that the ferritic Ni-Fe is the primary phase.

These observations indicate that metallic nanoparticles are present in the oxide scales at both the breakaway region and the protective region. The elemental distribution in the oxide scales in the protective region on 321ss is different from that observed in the breakaway region. The nickel content is low in the oxide scales of the protective area, whereas the nickel content in the inner oxide layer of the breakaway region is higher than that in the alloy (Fig. 5a and b). These metallic nanoparticles in the oxide layer connect to form networks in the breakaway region, but such networks do not form in the oxide scales of the protective region because the nickel meal particle density is not as high as in the oxide layer of the breakaway region.

The pre-edge feature in the K-edge XANES spectra of transition metals is associated with quadrupole transitions from the 1s to 3d orbital (Ref 10, 11), and has been shown to increase in strength with the increasing Fe valence (or *d*-hole population). The oxidation state of iron in Fe₃O₄ is higher than that in

Fig. 3 The normalized absorption coefficients of K edge of 321ss after exposure to pure CO_2 at 750 °C for 284 h: (a) Ni K edge at the protective region; (b) Ni K edge at the breakaway region; (c) Fe K edges at the outer and inner positions in oxide scale at protective region; (d) Fe pre-K edges at the outer and inner positions in oxide scale at protective region; (e) Fe K edges at the positions from gas-oxide surface at the breakaway region; (f) Fe pre-K edges at the positions from gas-oxide surface at the breakaway region

$\text{Fe}^{2+}\text{Cr}_2\text{O}_4$. Therefore, the intensity of the pre-edge in Fe_3O_4 is higher than that in FeCr_2O_4 , and the peak position of the pre-edge of iron in Fe_3O_4 is also shifted to higher energy. The peak position and intensity of the Fe pre-edge at the outer oxide layer (5 μm from surface) in the breakaway region is between those of Fe_3O_4 and FeCr_2O_4 (Fig. 3e). Therefore, the Fe oxidation state at the outer oxide layer is between 2 and 2.66. Near the boundary of outer and inner oxide scales, the intensity of Fe pre-edge decreases, and the peak position moves to lower energy, which indicates that the oxidation state of iron decreases. Figure 3(f) shows that the chemical shift of Fe systematically moves to lower energy when the scan position moves toward the metal-oxide boundary. The chemical shift of Fe at the inner oxide layer is at a lower energy than that of the

Fe^{2+} standard of FeCr_2O_4 . This indicates that there is a mixture of iron metal and iron oxides in the inner scale layer of the breakaway region. The systematic shift indicates that the metallic iron content increases with the decreasing distance from the alloy-oxide boundary. In the protective region, the oxidation state of iron near the gas side is between 2 and 2.66, and the metallic iron is also observed near the oxide-metal boundary (Fig. 3c and d). Since metallic nickel was also observed in the oxide layers in both the breakaway and the protective region, the metallic nanoparticles or networks consist of both metallic nickel and iron.

Metallic nanonetworks will be oxidized if the p_{O_2} is too high at location near surface. The above results indicate that the outer layer primarily consists of Fe_3O_4 , where p_{O_2} is high

Fig. 4 SEM images of breakaway region of 321ss after 284-h exposure to pure CO₂ at 750 °C: (a) Oxide layer grows out at the localized attack region. Oxidation propagates along the red arrow. The green arrow indicates that the oxidation process cannot propagate across discontinuities in the metallic network across the grain boundary. (b) Oxidation propagates from a point and forms arc lines in grain α and ϵ . (c) High-magnification images from the blue square region of a, EDX analysis indicates that there is more nickel and less oxygen in the bright network than in the dark region. (d) Schematic diagram of metallic nanonetworks in an oxide layer. The bright areas are the Ni-Fe metallic nanonetworks that connect to the alloy substrate and the dark area is oxides. Although some locations within the network are discontinuities in the two-dimensional image, the network is considered to be continuous to allow for the outward diffusion of Cr and iron atoms because the network is three dimensional. The oxides also form a continuous network to allow oxygen inward diffusion. The network is observed in the entire inner oxide layer (Color figure online)

enough to oxidize nickel metal. The inner layer consists of FeCr₂O₄ and Fe-Ni metallic nanonetworks. The metallic nanonetworks extends to 20 μ m (a typical metal grain size), and is about 13 μ m away from surface in the gaseous environment of pure CO₂ at 750 °C.

A FIB microscope was used to cut a small specimen from the breakaway region of the same sample for TEM analysis. The sample was oriented in the TEM so that the different phases had differing contrast in the TEM image of the breakaway region (Fig. 6). The diffraction spots for spinel oxide are observed at location A. Electron diffraction is also observed from the metallic phase in the oxide layer. The chemical compositions of these phases were determined by EDX analysis (Table 1). The analysis (ESVision software, standardless analysis) shows that the phase at location A of Fig. 6 contains 56 at.% oxygen (57 at.% oxygen in spinel). The oxygen content in the other phase at location B of Fig. 6 is small, which indicates that there is a metallic (non-oxide) phase in the oxide layer of the breakaway region. The nickel content in the oxide phase is low, whereas, its content in the metallic phase is about 25 at.%, which is consistent with the nano-XANES analysis. The Cr content in the metallic particle dramatically drops to 1.6 from 18.3 at.% in the alloy substrate

(nominal composition, Table 1). Iron is found in both the oxide phase and the metallic phase (72 at.%). The oxidation state of iron can be determined by electron energy loss spectra (Ref 12). The peak ratio of Fe_{L3} to Fe_{L2} is 3.4 for metallic iron, but the ratio increases to 5.5 for FeO. The EELS at location B is similar than the EELS of the iron at the alloy substrate (Fig. 7). The measured peak ratio of Fe_{L3} to Fe_{L2} is 3.7, which is close to the ratio at the alloy substrate and that for metallic iron as measured by Leapman et al. (Ref 12). These results confirm that iron is in metallic form at location B.

EDX analysis using SEM indicated that the bright spots in Fig. 4(a) are rich in iron and nickel but contained less oxygen and chromium than those in the dark region. Based on the previous analysis (Ref 6), which has now been confirmed by the present TEM analysis, these bright spots in the SEM image in Fig. 4(a) are Ni-Fe metal particles. The contrast reversal between the SEM and TEM images is due to different imaging methods. It seems that oxidation stops at the grain boundary as indicated by the green arrow on Fig. 4(a). Oxidation cannot directly propagate down if the network is terminated by the grain boundary, whereas the red arrow indicates that oxidation continued if the network is connected to the alloy substrate. Figure 4(b) shows the oxidation at grain α and ϵ initiating from

Fig. 5 Nanobeam x-ray fluorescence and diffraction of protective (left) and breakaway (right) regions of 321ss after exposure to pure CO₂ at 750 °C for 284 h, as a function of scale depth. (a) The nickel concentration in the oxide scale of the protective region is lower than that in the alloy substrate. (b) The nickel concentration in the inner oxide layer of the breakaway region is higher than in the alloy substrate. (c) The relative content of Cr vs. Fe is high in the oxide scale of protective region. (d) The relative content of Cr vs. Fe is low in the oxide scale of breakaway region. (e) The relative content of the Cr₂O₃ phase vs. spinel phase is high in the protective region. (f) The relative content of the Cr₂O₃ phase vs. spinel phase is low in the breakaway region

a point and propagating with an arc frontline. Although metallic nanoparticles were observed in oxide scale in the protective region, the metallic nanonetworks were only observed in situations where breakaway oxidation occurred. The results indicate that the metallic nanonetworks play an important role in leading to and in continuation of breakaway oxidation. In contrast, no such metallic network feature was observed when 321ss was oxidized in 21% O₂-79% CO₂ at 750 °C for 200 h. Therefore, metallic nanonetworks are easy to form in the low *p*O₂ environment.

3.2 Stabilities of Spinel and Cr₂O₃

The relative amount of Cr in the oxide scales is much higher than that in the alloy, and it forms a sharp peak in the oxide scales of the protective region (Fig. 5c). In contrast, Cr distributes uniformly in most of the inner oxide layer in the breakaway region, and the concentration ratio of Cr/Fe is much

lower (Fig. 5d). This ratio affects the phase composition in the oxide scales because the formation of the spinel needs both iron and chromium. In the protective region, both spinel and Cr₂O₃ are observed. The content of spinel is high in the outer layer, but it is low in the inner layer of the oxide scales of the protective region (Fig. 5e). In contrast, only spinel is observed in the inner oxide layer of the breakaway region (Fig. 5f). Micro-Raman mapping also confirms a similar phase distribution pattern (Fig. 8). Raman spectra were collected using a 50× microscope objective with a 5-mW, 514.5-nm laser excitation. The Raman shift at 553 corresponds to Cr₂O₃, and the Raman shift at ~680 corresponds to spinel (Ref 13, 14). The breakaway area of 321ss consists of spinel only and shows the complete absence of Cr₂O₃. However, both Cr₂O₃ and spinel were observed in the protective region, with spinel in the outer layer and Cr₂O₃ in the inner.

In general, Cr₂O₃ is thermodynamically more stable than FeCr₂O₄ spinel. The question is why a highly stable Cr₂O₃

Fig. 6 Left: TEM image (diffraction contrast) at the oxide layer near the alloy substrate in the breakaway region of 321ss after 284-h exposure to pure CO₂ at 750 °C. Right: the electron diffraction patterns from oxide and metal were taken at locations A and B, respectively. Both the oxide and metal are cubic with lattice parameter of 8.35 and 3.51 Å, respectively

Table 1 EDX analysis results of the metallic network and oxide layer in Fig. 6

Elements	Concentration in oxide layer (at.%)	Concentration in metallic network (at.%)
Cr	27.4	1.6
O	55.9	See caption
Fe	13.1	71.7
Ni	0.2	25.3
Mn	1.8	0.4
Other	1.6	0.9

The carbon K_α signal was ignored in both cases. The small oxygen K_α signal from metallic network (<8 at.%) was ignored in the analysis because it was assumed to have originated from post-preparation surface oxidation of the TEM specimen

layer does not exist near the oxide-metal boundary interface. Hansson et al. attribute the primary reason for this phenomenon to the low contact energy between the oxide grain and the metal grain(Ref 15). However, we believe the chemical equilibrium can be affected by the activity of Cr in the metallic phase in the metallic phase.

The standard change of reaction in Gibbs free energy (ΔG°) for the following three competitive reactions were obtained from references (Ref 16, 17).

Fig. 7 The electron energy loss spectra that are taken at the metallic particle in oxide layer and at the alloy substrate (used as an iron “standard”)

At the equilibrium, the equilibrium constant (K) for each reaction can be calculated from the following equation:

$$\ln (K) = -\frac{\Delta G^\circ}{RT}, \quad (\text{Eq 4})$$

where R is the gas constant, and T is the absolute temperature.

Fig. 8 (a) Micro-Raman area map of a cross section of 321ss following 284-hour exposure to pure CO₂ at 750 °C. Red areas are primarily Cr₂O₃, green is primarily spinel. (b) Optical image of the surface of 321ss following 24-hour exposure to pure CO₂ at 750 °C. (c) Micro-Raman area map of (b). Degraded spot consists of spinel (Color figure online)

In a nanomixture system, if we assume that the chemical activity of chromium (a_{Cr}) in alloy equals the mole fraction of chromium in the alloy, then the equilibrium constant can be written as

$$\text{For reaction 1, } K_1 = \frac{a_{Cr_2O_3}}{a_{Cr}^2 a_{O_2}^{3/2}}$$

$$\log a_{O_2} = \frac{2(\log a_{Cr_2O_3} - 2\log a_{Cr} - \log K_1)}{3} \quad (\text{Eq 5})$$

$$\text{For reaction 2, } K_2 = \frac{a_{FeCr_2O_4}}{a_{Cr}^2 a_{Fe} a_{O_2}^2}$$

$$\log a_{O_2} = \frac{\log a_{FeCr_2O_4} - 2\log a_{Cr} - \log a_{Fe} - \log K_2}{2} \quad (\text{Eq 6})$$

$$\text{For reaction 3, } K_3 = \frac{a_{NiCr_2O_4}}{a_{Cr}^2 a_{Ni} a_{O_2}^2}$$

$$\log a_{O_2} = \frac{\log a_{NiCr_2O_4} - 2\log a_{Cr} - \log a_{Ni} - \log K_3}{2} \quad (\text{Eq 7})$$

If we assume the chemical activities of Cr₂O₃, FeCr₂O₄, and NiCr₂O₄ as 1, then Eq 5, 6, and 7 become

$$\text{For reaction 1, } \log a_{O_2} = \frac{2(-2\log a_{Cr} - \log K_1)}{3} \quad (\text{Eq 8})$$

$$\text{For reaction 2, } \log a_{O_2} = \frac{-2\log a_{Cr} - \log a_{Fe} - \log K_2}{2} \quad (\text{Eq 9})$$

$$\text{For reaction 3, } \log a_{O_2} = \frac{-2\log a_{Cr} - \log a_{Ni} - \log K_3}{2} \quad (\text{Eq 10})$$

The thermochemical calculation results are shown in Fig. 9(a), with the assumption that the activity of iron in the scale as 0.72 and that of nickel in the scales as 0.25.

In the protective region where the metallic networks are absent, Cr₂O₃ is the stable phase on the oxide-metal boundary interface for 321ss (which contains 17.4 wt.% Cr). A protective layer of Cr₂O₃ can form after Cr is oxidized and accumulate near the oxide-metal boundary. However, when the metallic networks exist, Cr can diffuse through the nickel-iron metallic network because the diffusion rate of Cr in metal is higher than its diffusion rate in oxides (Ref 18, 19). In the breakaway region, metallic networks become channels for Cr transport. Some of the Cr can be consumed by oxidation during transport,

Fig. 9 (a) Thermochemical stability of oxides as a function of chromium activity at 750 °C. ΔG for Reactions 1-3 are -870.018 , -1104.3 , and -1039.622 kJ/mol, respectively, at 750 °C. The activities of Fe, Ni, and Mn in metallic nanonetworks are assumed to be 0.72, 0.25, and 0.01 respectively. (b) Thermochemical stability of oxides as a function of temperature

and its concentration at the end of the metallic networks can be much lower than that in the alloy. As the Cr concentration drops to less than 3.4×10^{-3} at.% in metal, $FeCr_2O_4$ can become more stable, which can prevent protective Cr_2O_3 from forming.

The metallic nanonetworks or nanoparticles can be formed in the thermal growth process of the oxide scales (Ref 6), or may remain in the scale during continued oxidation. However, the critical issue is that the presence of metallic phase can, in turn, affect the diffusion process and the distribution of Cr in the oxide scales. If the oxidation process does not form such metallic nanonetworks, then Cr accumulates at the flat alloy-oxide boundary, and a protective Cr_2O_3 layer will form by regular diffusion process. If oxidation process results in the formation of metallic nanonetworks, then Cr will be diffused out and diluted into the oxide layer, and may not accumulate at the alloy-oxide boundary to form a dense Cr_2O_3 layer. This process can lead to accelerated oxidation and can subsequently lead to breakaway oxidation.

The order of decreasing chemical stability of spinel phases is $MnCr_2O_4 > FeCr_2O_4 > NiCr_2O_4$ (Fig. 9b). $MnCr_2O_4$ is more stable than Cr_2O_3 even though the activity of Cr is 1 (Ref 16, 17). Since the increasing Cr concentration will enhance the formation of stable Cr_2O_3 , the maximum chromium concentration (MC_{Cr}) in metals in which spinel can remain in a stable phase also increases in the same order. Our calculations show MC_{Cr} values of 3.4×10^{-3} at.% for $FeCr_2O_4$ and 5.1×10^{-11} at.% for $NiCr_2O_4$ (Fig. 9a). The spinel in the oxide scales on 321ss actually is the solid solution of $(Mn,Fe)Cr_2O_4$. The stability of solid solution of $(Mn,Fe)Cr_2O_4$ is between those of $FeCr_2O_4$ and $MnCr_2O_4$. Therefore, the critical concentration of Cr in the metal phase to make spinel stabler than Cr_2O_3 is between 3.4×10^{-3} at.% and near 100 at.%, which depends on the content of Mn in spinel. An increase in the Mn content would increase the stability of the solid solution. It is possible that when Mn is concentrated enough, the alloy would develop a spinel phase in the scales without a protective Cr_2O_3 layer. TEM-EDX analysis indicates that the ratio of Fe/Mn is 13.1/1.8 in the oxide phase (see Table 1). The value for x in the spinel of $Fe_{1-x}Mn_xCr_2O_4$ is ≈ 0.12 , whereas the content of Cr in metallic nanonetwork is 1.6 at.%. The Mn concentration in oxide and Cr concentration in metal may not be accurately determined because of the overlaps of Mn- K_α and Cr- K_β and their low concentrations. However, the results indicate that the critical C_{Cr} in metallic nanonetwork can be

> 1 at.%, if there is enough Mn in the oxide layer. Type 321ss contains manganese, and the formation of an oxide scale without Cr_2O_3 layer is observed in the breakaway region. This result confirms that the manganese in alloy can diffuse to oxide layer and increase the stability of the spinel phase, which leads to the formation of a nonprotective oxide layer without Cr_2O_3 when the Cr concentration in metallic nanonetworks decreases.

Since oxygen diffusion in spinel is much faster than in Cr_2O_3 (see Table 2), the oxidation rate in this region is also greater than that in the region with a protective Cr_2O_3 layer. Our analysis suggests that breakaway oxidation is initiated upon the formation of a continuous metallic network within the scales.

Carburization of alloys was often observed at high temperature in a gas environment with CO_2 (Ref 1, 20). The diffusion rate of carbon in the oxide scales is negligible (Ref 21). Diffusion of carbon through oxide is very difficult. However, carbon can dissolve and diffuse through metals (Ref 6). If there is a metallic nanonetwork through the oxide layer, then carbon can rapidly diffuse through these nanonetworks in the oxide layer. Figure 10(a) shows that carbides were observed at the grain boundary. Small crystals are also evident in grains under the nonprotective region (Fig. 10b). In contrast, no such small crystals are observed in grains under the protective region (Fig. 10c). EDX analysis indicated that the concentrations of carbon and chromium are high in these small crystals. Weak diffraction peaks from $Cr_{23}C_6$ are observed in the nonprotective region by synchrotron nanobeam XRD analysis. Although the thickness of the oxide scale at the protective region is much smaller than that at the nonprotective region, these carbide crystals could not be observed either by the SEM or the nanobeam XRD analysis. Therefore, it can be concluded that metallic nanonetwork provides a path for fast transport of carbon through oxide layer. The diffused carbon reacts with chromium in 321ss and affects the mobility of chromium, which can further increase the corrosion rate.

3.3 Effect of Metallic Nanonetworks on the Diffusion Mechanism

High-temperature oxidation can be affected by many factors, such as grain boundary diffusion and chromia evaporation. Several mechanisms were proposed to explain the breakaway

Table 2 Diffusion data for metallic elements and oxygen in oxides and in metals

Solvents	Diffusing element	Q (kJ/mol)	D_0 (cm ² /s)	T (°C)	D (cm ² /s)	Ref.
α -Fe-Cr	Cr	230.48	1.29	750	5.6×10^{-12}	44
α -Fe	Fe	238.61	1.9390	750	1.3×10^{-12}	45
α -Fe	O	92.1	0.00378	750	7.5×10^{-8}	46
γ -Fe-Cr	Cr	180.00	0.0005	750	3.2×10^{-13}	45
γ -Fe-Cr-Ni	Fe	209.30	0.003	750	6.2×10^{-14}	45
γ -Fe	O	166	1.3	750	4.34×10^{-9}	48
Ni metal	Cr	171	0.03	750	5.7×10^{-11}	50
Ni metal	Fe	133	7.3×10^{-4}	750	1.2×10^{-10}	44
Ni metal	O	164	0.049	750	2.07×10^{-10}	49
Ni Metal	C	138	0.08	750	7.19×10^{-9}	19
Cr ₂ O ₃	Cr	280	5.84×10^{-9}	1300	3.1×10^{-18}	51
Cr ₂ O ₃	Fe	237	4.4×10^{-7}	720	1.2×10^{-19}	52
Cr ₂ O ₃	O	422	15.9	750	4.4×10^{-21}	53
Cr ₂ O ₃	H	70.3	1.78×10^{-5}	750	4.57×10^{-9}	54
Spinel oxide scale	O			800	3.1×10^{-12}	55
CoCr ₂ O ₄	Cr	292	2	750	2.5×10^{-15}	56
NiCr ₂ O ₄	Cr	303	0.74	750	2.6×10^{-16}	57
Spinel oxide scale	Cr			750	1×10^{-19}	58
MnCr ₂ O ₄	Cr			800	9.7×10^{-13}	18
MnCr ₂ O ₄	Mn			800	1.7×10^{-12}	18
MnCr ₂ O ₄	Fe			800	1.2×10^{-12}	18

$D = D_0 \exp(-\frac{Q}{RT})$, Q is activation energy, and D_0 is pre-exponential factor

Fig. 10 SEM images of cross section of 321ss after 24-h exposure to pure CO₂ at 750 °C: (a) At breakaway region (b) High-magnification images from the blue square region of a, EDX analysis indicating that there is more Cr and C at the bright particles than in the dark region; (c) At protective region, a nice oxide scale was observed. The bright particles (chromium carbides) are not observed here (Color figure online)

oxidation (Ref 22-25). However, these mechanisms may not explain all the observations from this experiment. The aforementioned phase-stability analysis indicates that the primary phase at the nonprotective region is spinel. Thick spinel layer of over hundred micrometers obviously cannot protect the alloy from continued oxidation at the nonprotected region, since oxygen can rapidly diffuse through spinel. In contrast, the alloys can be protected by a Cr₂O₃ layer with a thickness of only ~1 μm when 321ss is oxidized in 21% O₂-79% CO₂. Therefore, the key issue to understand the breakaway oxidation is what happens at the reaction front of the alloy-oxide boundary to suppress the formation of a protective Cr₂O₃. Figure 2(c) shows the reaction front processes in a grain. Regular grain boundary diffusion obviously does not play a significant role in the front reaction in these grains. Typically, grain boundary diffusion increases alloy oxidation. However, Figure 2(c) indicates that fast oxidation is terminated at grain boundary and that such a fast oxidation phenomenon cannot be explained by classic grain boundary diffusion. Cr₂O₃

evaporation typically occurs in an environment with steam. However, when an experiment is conducted in pure CO₂ without steam, the effect of Cr₂O₃ evaporation can also be ignored. These factors that affect the oxidation process cannot be used to explain the observations in our experiments. We will focus our discussion on whether the breakaway oxidation is led by internal oxidation or a new mechanism of metallic nanonetwork-assisted oxidation.

Since diffusion plays an important role in alloy oxidation, it is important to understand the diffusion mechanism involved in high-temperature oxidation. Figure 11 shows three types of diffusion mechanisms that we plan to discuss in this paper. In general, it is considered that cations such as Fe²⁺, Mn²⁺, and Cr³⁺ diffuse outward to form the oxide scales. Figure 5(e) shows that there are two layers in the oxide scales in the protective region. The outer scale consists primarily of spinel (Fe,Mn)Cr₂O₄, and the primary phase of the inner layer is Cr₂O₃. The Cr concentration near the alloy-oxide boundary is close to the Cr concentration at the center of the alloy

Fig. 11 Diffusion models. Type A: protective model, Fe^{2+} and Cr^{3+} cations diffuse out, and O^{2-} inward diffuses through oxide scales. Type B: internal oxidation model, O^{2-} inward diffuses through oxide scales and enter alloys. Type C: metallic nanonetwork-assisted oxidation, neutral Fe, and Cr outwardly diffuse and carbon diffuses inward through metallic nanonetworks. O^{2-} inward diffuses through oxide networks

(18.3 at.%), which indicates that the Cr depletion near the boundary is limited. Since the p_{O_2} in the inner layer near the alloy-oxide boundary is much lower, the FeCr_2O_4 spinel does not form. Although MnCr_2O_4 spinel can form in the inner layer, the low concentration of Mn in alloy indicates that the concentration of MnCr_2O_4 spinel is not high enough to form a continuous tunnel for the outward diffusion of Fe^{2+} . Fe^{2+} has to diffuse through the Cr_2O_3 to the outer layer where the p_{O_2} is high enough to form stable FeCr_2O_4 . Since the Fe^{2+} diffusion rate through Cr_2O_3 is very low (see Table 2), the growth rate of the scale is also low, and the scale is protective. The diffusion mechanism for the protective region corresponds to Type A, as shown in Fig. 11(a).

Internal oxidation has been studied for several decades (Ref 8, 26-40). The mechanism is extensively discussed in the literature. The inward diffusion and precipitation of oxygen in metal were considered to have caused the alloy oxidation (shown in Fig. 11b). When the concentration of an active alloying component is increased above a critical concentration, the oxidation process results in the formation of a protective oxide scale, and the alloy is minimally oxidized internally.

Originally, the application of the concept of internal oxidation was limited to low concentration of an active element in a relatively inert substrate (Ref 26-36). However, the concept has been widely used for analyzing oxidation in concentrated alloys in many Fe- and Ni-based alloy systems with high concentrations of active elements (Ref 7, 39, 41-45). Although internal oxidation is always possible during high-temperature oxidation, the question is whether internal oxidation is the primary cause for breakaway oxidation. In general, if the oxygen inward diffusion flux is larger than the chromium outward diffusion flux, internal oxidation plays a major role in oxidation. Therefore, the required condition for the internal oxidation mechanism in Cr containing alloy is as follows (Ref 40):

$$N_{\text{O}}D_{\text{O}} > N_{\text{Cr}}D_{\text{Cr}}, \quad (\text{Eq 11})$$

where N_{O} is the concentration of oxygen in metal (in mole fraction), D_{O} is the diffusion coefficient of oxygen in the metal, N_{Cr} is the concentration of Cr in metal (in mole fraction), and D_{Cr} is the diffusion coefficient of Cr in the metal.

If there is no Mn, $N_{\text{Cr}} < 3.4 \times 10^{-5}$ to stabilize FeCr_2O_4 . However, the above TEM-EDX analysis indicates that N_{Cr} can be 0.016, if the spinel phase of the oxide layer contains Mn with $x \approx 0.12$ in $\text{Fe}_{1-x}\text{Mn}_x\text{Cr}_2\text{O}_4$. At the inner oxide layer, the inward diffusion of oxygen is retarded by the external oxide layer. The partial pressure of the oxygen is very low, and so the iron content in the metallic nanonetwork can be as high as 72 at.%. Synchrotron nanobeam XRD result indicates the presence of both ferritic and austenitic iron in the metallic phase. Table 2 shows the diffusion coefficients for various elements (Ref 46-60). The diffusion coefficients of Cr and Fe in α -Fe are $5.6 \times 10^{-12} \text{ cm}^2/\text{s}$ (Ref 46) and $1.3 \times 10^{-12} \text{ cm}^2/\text{s}$ (Ref 47), respectively, at 750 °C. Therefore, the $N_{\text{Cr}}D_{\text{Cr}}$ is $\approx 1 \times 10^{-13} \text{ mol cm}^2/\text{s}$, and the $N_{\text{Fe}}D_{\text{Fe}}$ is $\approx 9.4 \times 10^{-13} \text{ mol cm}^2/\text{s}$ at 750 °C. The recent experiment indicated that the diffusion coefficient of oxygen in α -iron is $7.5 \times 10^{-8} \text{ cm}^2/\text{s}$ (Ref 48), and the solubility of oxygen in α -Fe under the equilibrium of Fe-FeO is 3.8×10^{-7} (Ref 49). Therefore, the value for $N_{\text{O}}D_{\text{O}}$ in α -Fe is $\approx 2.8 \times 10^{-14} \text{ mol cm}^2/\text{s}$ at 750 °C.

The diffusion rates of both metallic elements iron and chromium and oxygen in γ -iron are smaller than those in α -Fe. The diffusion coefficient of Cr and Fe in γ -iron is $3.2 \times 10^{-13} \text{ cm}^2/\text{s}$ (Ref 47) and $6.2 \times 10^{-14} \text{ cm}^2/\text{s}$ (Ref 47), respectively, at 750 °C. Therefore, the $N_{\text{Cr}}D_{\text{Cr}}$ is $\approx 5.8 \times 10^{-15} \text{ mol cm}^2/\text{s}$, and the $N_{\text{Fe}}D_{\text{Fe}}$ is $\approx 4.6 \times 10^{-14} \text{ mol cm}^2/\text{s}$ at 750 °C. The recent experiment indicated that the diffusion coefficient of oxygen in γ -iron is $4.3 \times 10^{-9} \text{ cm}^2/\text{s}$ (Ref 50). The solubility of oxygen in γ -iron under the Fe-FeO equilibrium is $4.6 \times 10^{-7} \text{ cm}^2/\text{s}$ (Ref 49). Therefore, the $N_{\text{O}}D_{\text{O}}$ in γ -iron is $\approx 2 \times 10^{-16} \text{ mol cm}^2/\text{s}$ at 750 °C.

It seems that the oxygen inward diffusion flux rate is comparable to the chromium outward diffusion flux under the equilibrium of Fe-FeO. However, the nanobeam XRD analysis indicates that FeO does not form in the oxide layer on the surface of 321ss. FeO reacts with Cr_2O_3 and forms stable FeCr_2O_4 . The p_{O_2} of the FeCr_2O_4 is approximately five orders of magnitude lower than FeO at 750 °C (Fig. 9). The solubility of oxygen in α -Fe under the equilibrium of Fe- FeCr_2O_4 should be much lower than the solubility of oxygen in α -Fe under the Fe-FeO equilibrium, since oxygen can react with chromium in metallic nanonetwork to form FeCr_2O_4 . Therefore, the $N_{\text{O}}D_{\text{O}}$

$< N_{Cr}D_{Cr} < N_{Fe}D_{Fe}$ in the metallic nanonetwork in the oxide layer of the nonprotective region on the surface of 321ss. The actual oxygen inward diffusion flux should be much lower than $N_{Cr}D_{Cr}$ after oxygen diffusion is further retarded by the outer layer of the oxide scales. The oxygen concentration in the metallic nanonetwork may not reach the saturated concentration. In contrast, the concentration of Cr and Fe can be much higher than that of oxygen, when the metallic networks connect to the alloy substrate. This leads to a faster outward diffusion of Cr and Fe than the inward diffusion of oxygen through metallic nanonetworks. If $N_O D_O < N_{Cr} D_{Cr}$, internal oxidation may not play a major role for alloy oxidation, although internal oxidation can still occur.

Internal oxidation mechanism cannot fully explain our experimental observations either. In general, there are three types of oxidation: (i) exclusive internal oxidation without external scales; (ii) both internal oxidation and scale formation; and (iii) exclusive external scales. Type (i) obviously is not applicable to 321ss because external scales have been observed after exposure to CO_2 at 750 °C. According to the theory of internal oxidation, the required chromium concentration to form an exclusive external scale is calculated by the following equation:

$$N_{Cr}^O = \left(\frac{\pi g^*}{3} \frac{V_m}{V_{CrO_{1.5}}} \frac{N_O^{(s)} D_O}{D_{Cr}} \right)^{1/2}, \quad (\text{Eq 12})$$

where the factor g^* is generally approximated as 0.3 (Ref 36). V_m and $V_{CrO_{1.5}}$ are the molar volumes of alloy and oxide, respectively, which were assumed as 7 and 14.6 cm³/mole, respectively. N is oxygen solubility in the metal, D_O is diffusivity of oxygen in the metal, and D_{Cr} is the diffusion coefficient of Cr in the metal.

For an austenitic alloy, the diffusivity of oxygen and chromium are available in the literature. D_{Cr} is 3.2×10^{-13} cm²/s, and D_O is 4.3×10^{-9} cm²/s at 750 °C. The oxygen solubility is 4.6×10^{-7} at 750 °C in γ -Fe under the equilibrium of Fe-FeO. The critical concentration N should be ≈ 3 at.% at 750 °C, based on the oxygen solubility in γ -Fe under the equilibrium of Fe-FeO. However, it should be noted that application of Eq 12 is limited to diluted alloys with concentration of active element (B) < 1 at.%. Equation 12 was also derived from a simple assumption that only simple oxides of AO_x and BO_y form in the oxidation process. For the Fe-Cr alloys, the nanobeam XRD results indicate an absence of simple oxides such as FeO and Cr_2O_3 in the inner layer of the nonprotective region. The only oxide in the nonprotective layer on 321ss is AB_2O_4 ((Fe,Mn) Cr_2O_4). FeO was also not observed in the oxide scales of the protective region. The oxygen solubility in either γ -Fe and α -Fe under the equilibrium of Fe- $FeCr_2O_4$ is currently not available, and its value will be much lower than that under the equilibrium of Fe-FeO. Therefore, the critical concentration of Cr in steel for the formation of an exclusive external scale should be less than 3 at.%. The concentration of Cr in 321ss is 18.3 at.%. An exclusive external scale should form on 321ss, theoretically. SEM cross-sectional images also indicate that an external scale was observed initially when 321ss was exposed to pure CO_2 at 750 °C, and the surface of 321ss was still protected by the external scales after exposure to 21% O_2 -79% CO_2 at 750 °C for 320 h. Therefore, both theoretical and experimental results have proven that an exclusive external scale can form on 321ss with Cr content of 17.3 wt.% initially. If an exclusive external

scale can form, the Type (ii) internal oxidation with external scale should not occur. Although the scale broke away late, internal oxidation mechanism cannot really explain why the external scale broke away after it was initially formed.

Results from Rapp's experiment indicates that less-active alloying element is needed for the transition of internal oxidation to external oxidation at low p_{O_2} than that at high p_{O_2} (Ref 35, 36). In the breakaway region of 321ss, the p_{O_2} in the inner oxide layer is low since the oxygen inward diffusion is retarded by the relatively thick oxide layer. According to Rapp's results, less Cr content would be required to prevent internal oxidation. When an alloy can form a protective external oxide scale at the gas-oxide surface, it is not reasonable to consider the observation in Fig. 4(a) to be "internal oxidation zone" where p_{O_2} at the inner-layer is lower than that at the outer layer at the gas-oxide surface.

The theoretical density of $FeCr_2O_4$ spinel is 4.7 g/cm³. The density of 321ss is 7.92 g/cm³. If oxygen inward diffusion is the dominant mechanism, then the mass increase and the density decrease during the oxidation of 321ss to $FeCr_2O_4$ should lead to a large volume expansion and deformation of the alloy grains. However, the straight grain boundary at the interface of oxide-metal in Fig. 2(c) (indicated by the green arrow) shows that the former grains do not deform after oxidation, which also indicates that the oxygen inward diffusion through metallic networks is not the predominant mechanism. The iron content in the metallic nanonetwork in the oxide layer is 72 at.%. However, the Cr content in the metallic nanonetwork near the alloy substrate has dropped to 1.5 at.%, which is too low to form a Cr_2O_3 protective layer. Therefore, the oxidation of the major component of the alloy, Fe, occurs in the metallic nanonetwork region, instead of the interior of the alloy.

Therefore, the classical internal oxidation mechanism (developed for dilute alloys) may not be the best mechanism to explain the breakaway oxidation of 321ss. We believe that the rapid oxidation phenomenon can be better explained if we carefully consider the other possible diffusion mechanism shown in Fig. 10(c). For internal oxidation mechanism, the volume of oxide is less than the volume of metal. In the case of Ag-In alloys, Rapp found that the volume fraction was less than 0.3 for internal oxidation. For the opposite case, in which the volume of oxide is more than the volume of metal, the effect of the metal in the oxide layer on the oxidation has not been studied yet. If these metallic particles in the oxide layer are isolated, diffusion mechanism may not be affected. However, if these metallic particles connect together to form a nanowire in the oxide layer, as shown in Fig. 11(c), the diffusion mechanism at the reaction front will be dramatically changed.

The difference in the distributions of Fe between breakaway and protective regions indicates that the metallic networks play an important role in the transport of Fe. Rapid transport of Fe outward through the Ni-enriched metallic networks in the breakaway region results in high Fe content in the outer layer. Such a process does not occur in the protective region. Typically, Cr, Fe, and Mn diffuse outward through the oxide scales as cations. If there are no metallic nanonetworks, then their outward diffusion rates will be slow because the cation diffusion rates through Cr_2O_3 are very low (see Table 2). However, the diffusion rates of these neutral metal atoms through metallic nanonetworks are much higher than in the Cr_2O_3 layers. For example, D_{Fe} in Ni metal is 1×10^9 larger than in Cr_2O_3 . The diffusions of Cr, Fe, and Mn in Ni metal are

also faster than those in spinel. The metallic nanonetworks act as rapid diffusion tunnels to break through the diffusion barrier of the Cr_2O_3 layers that can protect the alloy from continued high-temperature oxidation. Thus, the transportation mechanism is fundamentally changed.

The diffusion data for oxygen in the oxide scales are not available at 750 °C. It was reported that D_{O} in the oxide scales is $3.1 \times 10^{-12} \text{ cm}^2/\text{s}$ at 800 °C (Ref 57). Nanobeam XRD analysis indicated that spinel is the only oxide phase in the scale layer at the nonprotective region. Oxygen concentration in spinel (FeCr_2O_4) is 0.57, which is much higher than that in both $\alpha\text{-Fe}$ and $\gamma\text{-Fe}$. $N_{\text{O}}D_{\text{O}}$ in the oxide layer is $1.8 \times 10^{-12} \text{ mole cm}^2/\text{s}$ at 800 °C. D_{O} in $\alpha\text{-Fe}$ and $\gamma\text{-Fe}$ are 1.2×10^{-7} and $1.1 \times 10^{-8} \text{ cm}^2/\text{s}$, respectively, at 800 °C. N_{O} in $\alpha\text{-Fe}$ and $\gamma\text{-Fe}$ are 7.2×10^{-7} and 7.8×10^{-7} , respectively, under the equilibrium of Fe-FeO at 800 °C. $N_{\text{O}}D_{\text{O}}$ in $\alpha\text{-Fe}$ and $\gamma\text{-Fe}$ are 8.6×10^{-14} and $8.6 \times 10^{-15} \text{ mol cm}^2/\text{s}$, respectively, under the equilibrium of Fe-FeO at 800 °C. Therefore, the oxygen flux through spinel is one or two orders of magnitude higher than that in metallic nanonetwork, if the oxygen solubility can reach the saturated concentration under the equilibrium of Fe-FeO at 800 °C. However, since FeO has reacted with Cr_2O_3 to form FeCr_2O_4 , the actual equilibrium should be with FeCr_2O_4 . The solubility of oxygen under the equilibrium of Fe- FeCr_2O_4 should be much smaller than that under the equilibrium of Fe-FeO since the p_{O_2} under the equilibrium of Fe- FeCr_2O_4 is five orders of magnitude smaller than that under the equilibrium of Fe-FeO. $N_{\text{O}}D_{\text{O}}$ in $\alpha\text{-Fe}$ and $\gamma\text{-Fe}$ under the equilibrium of Fe- FeCr_2O_4 should also be much smaller than that under the equilibrium of Fe-FeO at 800 °C. $N_{\text{O}}D_{\text{O}}$ in spinel will be much larger than that in metallic nanonetwork at 800 °C. At 750 °C, this order will not change. Therefore, the rapid oxygen inward diffusion at the nonprotective region on 321ss should be through spinel, instead of through metallic nanonetworks.

A transportation mechanism that leads to breakaway oxidation can be proposed as the following: Cr, Fe, and Mn transport outward, and carbon diffuses inward through the metallic networks, while oxygen diffuses inward through the spinel phase. Since both the metallic elements and oxygen transport through the fastest routes, the oxidation rate at the location adjacent to the metallic networks would be higher than that at the region without the metallic networks, leading to localized oxidation (see Fig. 1). Figure 4(b) shows that oxidation of α and ϵ grains seem to initiate from the upper left corner of the grain. The oxide-alloy boundary forms an arc line with the center at the corner of the grain. The presence of the large dark region at the corner of the grain is due to the accumulation of oxides of Cr, Fe, and Mn transported via the metallic networks from the alloy. EDX analysis confirms high concentrations of Cr, Fe, Mn, and O in the dark regions. The accumulation of the oxides, which forms the dark and thicker grain boundaries in the oxidized region, is evidence of outward diffusion of metallic elements. Meanwhile, the grain boundaries of the upper grains are not as straight as those near the oxide-metal boundary, most likely due to the insertion of Cr, Fe, and Mn oxides. For the grain β , the accumulation of the oxides of Cr, Fe, and Mn also leads to thicker upper boundaries. For the grain δ , the oxidation initiates from two active sites, namely the upper corner and upper grain boundary. However, the thickness of the grain boundary with active sites is much greater than that without the active sites. These observations can be explained by the outward diffusion of metal atoms through the metallic network, but they cannot be explained by the inward diffusion

of oxygen. Cr and Fe outward diffusions through metallic nanonetworks are explained as the mechanism responsible for the rapid oxidation when metallic networks connect to the alloy substrate. This metallic nanonetwork-assisted oxidation mechanism (MNAO) with different diffusion routes (see Fig. 11c) can clearly explain the experimental observation. Internal oxidation is due to the oxygen inward diffusion. In contrast, MNAO is due to the metallic elements' outward diffusion through metallic nanonetworks in a system with oxide multilayers. Since the proposal of the theory of oxidation by Wagner in 1933 (Ref 5), diffusions of charged species such as cations, anions, and electrons have been considered as the only avenue for transport in the oxide scales because the scales are usually considered to consist of only oxide phases. However, the formation of metallic nanonetworks in the oxide layers fundamentally changes the transport mechanism.

3.4 Effect of Metallic Nanonetworks on the Phase Formation in Oxide Layers

If there are no metallic nanonetworks, then the dual layer structure with Cr_2O_3 at the bottom is a stable structure because a thin layer of Cr_2O_3 of 1 μm is good enough to protect the alloy from breakaway oxidation. Fe^{2+} has to diffuse through the dense Cr_2O_3 layer if there are no the metallic nanonetworks. However, the diffusion rate of Fe^{2+} in Cr_2O_3 is very low. D_{Fe} is only $1.2 \times 10^{-19} \text{ cm}^2/\text{s}$ at 750 °C (see Table 2) and is smaller than D_{Cr} ($3.1 \times 10^{-18} \text{ cm}^2/\text{s}$). Meanwhile, iron is difficult to be oxidized to Fe^{2+} in the inner oxide layer because oxygen is difficult to diffuse into Cr_2O_3 and p_{O_2} in a dense Cr_2O_3 layer is also very low. Therefore, the concentration of Fe^{2+} in Cr_2O_3 layer is low. The Fe^{2+} outward diffusion flux ($N_{\text{Fe}}D_{\text{Fe}}$) is much smaller than the Cr^{3+} outward diffusion flux. A dense continuous Cr_2O_3 layer will form to protect the alloy from further oxidation.

However, if there are metallic nanonetworks, then metallic iron can be directly delivered to the spinel layer, where both p_{O_2} and the diffusion rate of Fe^{2+} are high. Iron is rapidly oxidized, and high concentration Fe^{2+} can diffuse back to react with Cr_2O_3 to form spinel:

Cr_2O_3 was quickly consumed by reacting with a large amount of Fe^{2+} . Finally, the amount of Cr_2O_3 remaining in the oxide layer is not enough to form a continuous layer. The protective layer and the phase structure with a dense Cr_2O_3 layer at the bottom are totally damaged because spinel is not as protective as Cr_2O_3 . The formation of spinel provides a path for fast oxygen inward diffusion to increase p_{O_2} at the inner layer, thus, in turn, increasing the stability of FeCr_2O_4 . This effect combined with the stabilizing effect of Mn^{2+} to form spinel. The protective Cr_2O_3 layer was almost totally removed in the nonprotective region of the 321ss. The nanobeam XRD analysis on the inner layer of the nonprotective region confirmed the effect of metallic nanonetworks on the phase formation and the phase structure in the oxide layer after breakaway oxidation occurred (see Fig. 3a).

3.5 Effect of Oxygen Partial Pressure on the Formation of Metallic Nanonetworks and Oxidation

Breakaway oxidation was observed in 321ss after exposure in pure CO_2 . Figure 1 shows that the development of local

Fig. 12 Schematic of the effect of oxygen partial pressure on metallic nanonetwork-assisted oxidation. Oxygen diffuses fast in spinel, but slowly in Cr_2O_3 . A metallic nanowire can directly deliver chromium metal to the nonprotective spinel layer when the low gradient of the oxygen partial pressure allows the metallic nanowire to grow sufficiently long

Fig. 13 SEM images of breakaway region of 321ss after 284-h exposure to pure CO_2 at 750 °C. (a) Green arrows indicate that oxidation was terminated at grain boundaries. Red arrows indicate that oxidation continued to propagate. (b) Oxidation was terminated at grain boundary. (c) Oxidation was terminated at grain boundary, and then restarted at the edge of another grain (indicated by yellow arrow) (Color figure online)

oxidation is slower in 3.97% O_2 -96.03% CO_2 than in 0.1% O_2 -99.9% CO_2 . Breakaway oxidation has not occurred on the same alloy within 320 h, when the alloy was exposed to 21% O_2 -79% CO_2 with higher p_{O_2} than that in pure CO_2 . The proposed MNAO mechanism can explain why the oxide scales are easy to break away at low p_{O_2} environment.

Since Cr is a strongly reducing element, the oxygen partial pressure at the alloy-oxide boundary is very low. If a_{Cr} is assumed to be 0.183 (the mole fraction of Cr of 321ss with 17.3 wt.% Cr), the calculated p_{O_2} at the alloy-oxide boundary from Eq 8 is 7.9×10^{-30} atm at 750 °C. The oxygen partial pressures of CO_2 is $\approx 10^{-6}$ in the system (1ppm O_2 impurity in the CO_2 gas, 1.8×10^{-7} atm O_2 at 750 °C from the equilibrium) are lower than that in 21% O_2 -79% CO_2 . Therefore, the oxygen partial pressure gradient in the oxide scales for specimens exposed to CO_2 or steam would be several orders of magnitude smaller than that exposed to 21% O_2 -79% CO_2 , assuming a constant oxide scale thickness. The oxygen partial pressure gradient in the oxide scales can play two roles with respect to the formation and growth of metallic nanonetworks.

First, metallic nanoparticles cannot survive in high p_{O_2} environment as iron and nickel can be oxidized. The region of

the oxide scales in which p_{O_2} is low enough for the formation of these metallic nanoparticles is small at a high oxygen partial pressure gradient and little, if any, metallic nanoparticles can form. The probability of these metallic nanoparticles connecting together to form metallic nanowires is therefore also low. Second, even if a metallic nanowire has formed in an oxide scale, it cannot grow long enough at a high gradient of oxygen partial pressure. In contrast, it is possible to grow a long metallic nanowire in an environment with a low oxygen partial pressure. After long distance diffusion, the chromium concentration at the end of the metallic nanowire drops below the minimum required to form stable Cr_2O_3 . Cr is delivered to the nonprotective spinel layer (see Fig. 12). This can be the cause of the enhanced oxidation rate seen in CO_2 in which oxygen partial pressures are lower than in 21% O_2 -79% CO_2 .

The oxide scales, in general, are mixtures of Cr_2O_3 and spinel phases. Oxygen diffuses fast in spinel but much slower in Cr_2O_3 . Figure 5(e) shows the Cr_2O_3 /spinel ratio for the protective region on 321ss. The content of Cr_2O_3 phase in the oxide scales generally increases with the decreasing distance from the alloy-oxide boundary. It is reasonable to assume that the scale is protective only if the Cr_2O_3 contents are larger than a critical value $C_{\text{Cr}_2\text{O}_3}$. Higher than this value, spinel

particles are isolated, and the contact of spinel particles is totally blocked by Cr_2O_3 , so that the fast oxygen diffusion path is blocked. We define this layer with Cr_2O_3 contents $> C_p$ as the protective layer. The oxygen activity in the mixture will be a function of external p_{O_2} . If the external p_{O_2} is large, then the oxygen partial pressure gradient is also large, which can lead to the p_{O_2} in the protective layer to be larger than that required p_{O_2} to oxidize nickel. The metallic nanonetwork cannot extend out of the protective layer. A sufficient amount of Cr can diffuse through the short metallic wire to form Cr_2O_3 . In contrast, if the external p_{O_2} is low, then the oxygen partial pressure gradient is also low, which can cause the p_{O_2} in the protective layer to be lower than the p_{O_2} required to oxidize nickel. The metallic nanonetwork can grow long enough to extend out of the protective layer. Chromium will be continuously delivered to the nonprotective layer through the long metallic wire but cannot form Cr_2O_3 since the concentration of Cr is not large enough after long-distance diffusion. The outward diffused Cr is consumed by gradual carburization in the inner oxide layer to allow the outward diffusion process to continue. These metallic nanonetworks cannot be considered only as the results of internal oxidation. These nanonetworks in oxide layers fundamentally change the transport mechanism. Cr, Fe, and Mn diffuse outward and carbon diffuses inward through the networks, while oxygen diffuses inward through the spinel phase. Since transports of both the metallic elements and oxygen occur through the fastest routes, the oxidation rate greatly increases and leads to breakaway oxidation.

Figure 13(a) shows that oxidation stopped at the grain boundary because the metallic nanonetworks could not be extended across the grain boundary. The p_{O_2} in the grain will gradually increase when oxygen continues inward diffusion through the oxides, and metals are gradually oxidized. The dark spots indicate the regions where metals were totally oxidized. The oxidation process will stop when the entire grain was oxidized. Figure 13(b) shows the termination of the MNAO. Figure 13(c) shows that the MNAO has restarted at the corner of another grain. Therefore, the MNAO is not a continuous process under microscale. It is a virus-like propagation process. The rapid oxidization starts at a weak point of an infected grain. If time is not sufficient to develop such a metallic nanonetwork structure in the next grain, then the oxidation process will be terminated. Fast inward diffusion of oxygen in a high p_{O_2} gas environment can lead to easier termination of MNAO in a high p_{O_2} gas environment than in a low p_{O_2} gas environment. This is another reason why breakaway oxidation of 321ss is easy to propagate in a low p_{O_2} environment.

4. Conclusions

The present study shows that metal nanoparticles could form in the oxide scales that develop on alloy surfaces upon exposure to elevated temperatures. Metallic nanonetworks were observed in the breakaway region. In contrast, metallic nanoparticles have not connected to metallic nanonetworks at the protective region. The phase structures at the protective region are totally different from those at the nonprotective region. Cr_2O_3 is the major phase at the protective region, but Cr_2O_3 is almost absent in the breakaway region where metallic nanoparticles exist. The oxidation rate of an alloy is much faster when these metallic nanonetworks appeared. A model is

proposed to explain the accelerated/breakaway oxidation using the metallic nanonetworks.

Metallic nanonetworks can act as important channels in the mass transport during the oxidation process. In contrast to diffusion of charged species such as cations, anions, and electrons as the only avenue for transport in the oxide scales, neutral metal atoms can transport through the metallic nanonetworks when these nanonetworks exist in the oxide layers. The change of the diffusion mechanism dramatically affects the solid reactions at the important reaction front at the alloy-oxide boundary. More iron atoms can be released into the oxides though the fast diffusion tunnels of metallic nanonetworks. Meanwhile, chromium is also diluted after diffusing out through metallic nanonetworks. This process results in more spinel phase and less Cr_2O_3 in the oxide layer on the alloy surface. A dense protective Cr_2O_3 does not form and, as a consequence, leads to rapid breakaway oxidation. MNAO is a type of rapid oxidation. Virus-like propagation of MNAO from grain to grain was observed. To minimize rapid MNAO, alloys should not contain elements that can lead to the formation of highly stable spinel phases in the oxide scales, which would lead to the formation of an oxide layer without Cr_2O_3 .

Acknowledgments

The authors thank D. L. Rink for conducting the oxidation experiments, and Jianguo Wen for consultation on EELS analysis of iron. This study is supported by the U.S. Department of Energy, Office of Fossil Energy, Advanced Research Materials Program. The authors gratefully acknowledge the use of these following U.S. Department of Energy Office of Science User Facilities: the Advanced Photon Source, the Center for Nanoscale Materials; and the Electron Microscopy Center at Argonne National Laboratory, a U.S. Department of Energy Office of Science Laboratory operated under Contract No. DE-AC02-06CH11357 by UChicago Argonne, LLC.

References

1. G. Cao, V. Firouzdor, K. Sridharan, M. Anderson, and T.R. Allen, Corrosion of Austenitic Alloys in High Temperature Supercritical Carbon Dioxide, *Corros. Sci.*, 2012, **60**, p 246–255
2. N.J. Simms, J. Sumner, T. Hussain, and J.E. Oakey, Fireside Issues in Advanced Power Generation Systems, *Mater. Sci. Technol.*, 2013, **29**, p 804–812
3. S.K. Varma, Refractory Metals—An Exploration of High-Temperature Materials, *JOM*, 2010, **62**, p 12
4. B. Bordenet, Influence of Novel Cycle Concepts on the High-Temperature Corrosion of Power Plants, *Mater. Corros.*, 2008, **59**, p 361–366
5. C. Wagner, Theory of the Tarnishing Process, *Z. Phys. Chem. B.*, 1933, **21**, p 25–41
6. Z. Zeng, K. Natesan, Z. Cai, and S.B. Darling, The Role of Metal Nanoparticles and Nanonetworks in Alloy Degradation, *Nat. Mater.*, 2008, **7**, p 641–646
7. E. Essuman, G.H. Meier, J. Zurek, M. Hansel, L. Singheiser, and W.J. Quadakkers, Enhanced Internal Oxidation as Trigger for Breakaway Oxidation of Fe-Cr Alloys in Gases Containing Water Vapor, *Scr. Mater.*, 2007, **57**, p 845–848
8. N.K. Othman, J. Zhang, and D.J. Yong, Water Vapor Effects on Fe-Cr Alloy Oxidation, *Oxid. Met.*, 2010, **73**, p 337–352
9. E. Sommer, S.G. Terry, W. Sigle, C. Mennicke, T. Gemming, G.H. Meier, C.G. Levi, and M. Rühle, Metallic Precipitate Formation During Alumina Growth in a FeCrAl-Based Thermal Barrier Coating Model System, *Mater. Sci. Forum*, 2001, **369-372**, p 671–678

10. Z. Zeng, M. Greenblatt, M.A. Subramanian, and M. Croft, Large Low-Field Magnetoresistance in $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ Without Double Exchange, *Phys. Rev. Lett.*, 1999, **82**, p 3163–3167
11. P.E. Petita, F. Fargesb, M. Wilkeb, and V.A. Solé, Determination of the Iron Oxidation State in Earth Materials Using XANES Pre-Edge Information, *J. Synchrotron Radiat.*, 2001, **8**, p 952–954
12. R.D. Leapman, L.A. Grunes, and P.L. Fejes, Study of the L23 Edges in the 3D Transition-Metals and Their Oxides by Electron-Energy-Loss Spectroscopy with Comparisons to Theory, *Phys. Rev. B*, 1982, **26**, p 614–635
13. R.L. Farrow, R.E. Benner, A.S. Nagelberg, and P.L. Mattern, Characterization of Surface Oxides by Raman-Spectroscopy, *Thin Solid Films*, 1980, **73**, p 353–358
14. R.J. Thibau, C.W. Brown, and R.H. Heidersbach, Raman Spectra of Possible Corrosion Products of Iron, *Appl. Spectrosc.*, 1978, **32**, p 532–535
15. A.N. Hansson, H. Danielsen, F.B. Grumsen, and M. Montgomery, Microstructural Investigation of the Oxide Formed on TP 347HFG During Long-Term Steam Oxidation, *Mater. Corros.*, 2010, **61**, p 657–665
16. F. Muller and O.J. Kleppa, Thermodynamics of Formation of Chromite Spinel, *J. Inorg. Nucl. Chem.*, 1973, **35**, p 2673–2678
17. I.-H. Jung, Critical Evaluation and Thermodynamic Modeling of the Mn-Cr-O System for the Oxidation of SOFC Interconnect, *Solid State Ionics*, 2006, **177**, p 765–777
18. J. Gilewicz-Wolter, Z. Zurek, J. Dudala, J. Lis, M. Homa, and M. Wolter, Diffusion of chromium, Manganese, and Iron in MnCr_2O_4 Spinel, *J. Phase Equilib. Diffus.*, 2005, **26**, p 561–564
19. S.P. Zholobov and M.D. Malev, The Diffusion of Oxygen in Metals on Electron Bombardment of the Surface, *Zh. Tekh. Fiz.*, 1971, **41**, p 627–635
20. H.E. McCoy, Type 304 Stainless Steel vs Flowing CO_2 at Atmospheric Pressure and 1100–1800F, *Corrosion* 1965, **21**, p 84–94
21. I. Wolf and H.J. Grabke, A Study on the Solubility and Distribution of Carbon in Oxides, *Solid State Commun.*, 1985, **54**, p 5–10
22. C. Pettersson, T. Jonsson, C. Proff, M. Halvarsson, J.-E. Svensson, and L.G. Johansson, High Temperature Oxidation of the Austenitic (35Fe27Cr31Ni) Alloy Sanicro 28 in $\text{O}_2 + \text{H}_2\text{O}$ Environment, *Oxid. Met.*, 2010, **74**, p 93–111
23. H. Asteman, J.E. Svensson, L.G. Johansson, and M. Norell, Influence of Water Vapor and Flow Rate on the High-Temperature Oxidation of 304L, Effect of Chromium Oxide Hydroxide Evaporation, *Oxid. Met.*, 2000, **54**, p 11–26
24. J. Shen, L. Zhou, and T. Li, High-Temperature Oxidation of Fe-Cr Alloys in Wet Oxygen, *Oxid. Met.*, 1997, **48**, p 347–356
25. D.J. Young, *High Temperature Oxidation and Corrosion of Metals*, Elsevier, Amsterdam, 2008
26. C. Wagner, *Z. Elektrochem.*, 1959, **63**, p 772–782
27. S. Wood, D. Adamonis, A. Guha, W.A. Soffa, and G.H. Meier, Internal Oxidation of Dilute Cu-Ti Alloys, *Met. Trans.*, 1975, **6A**, p 1780–1793
28. J. Megusar and G.H. Meier, Internal Oxidation of Dilute Co-Ti Alloys, *Met. Trans.*, 1975, **7A**, p 1133–1140
29. J. Kapteijn, S.A. Couperus, and J.L. Meijering, High-Temperature Oxidation of Copper with up to 4.1 wt.% Si, *Acta Metall.*, 1969, **17**, p 1311–1315
30. P. Bolsaitis and M. Kahlweit, The Internal Oxidation of Cu-Si Alloys, *Acta Metall.*, 1967, **15**, p 765–772
31. A. Atkinson, A Theoretical Analysis of the Oxidation of Fe-Si Alloys, *Corros. Sci.*, 1982, **22**, p 87–102
32. D.L. Douglass, A Critique of Internal oxidation in Alloys During the Post-Wagner Era, *Oxid. Met.*, 1995, **44**, p 81–111
33. G.R. Laflamme and J.E. Morral, Limiting Cases of Subscale Formation, *Acta Metall.*, 1978, **26**, p 1791–1794
34. J.L. Meijering, Internal Oxidation in Alloys, *Advances in Materials Research*, Vol 5, H. Herman, Ed., Wiley-Interscience, New York, 1971, p 1–81
35. R.A. Rapp, Kinetics, Microstructures and Mechanism of Internal Oxidation—Its Effect and Prevention in High Temperature Alloy Oxidation, *Corrosion*, 1965, **21**, p 382
36. R.A. Rapp, The Transition from Internal to External Oxidation and the Formation of Interruption Bands in Silver-Indium Alloys, *Acta Metall.*, 1961, **9**, p 730–741
37. F. Gesmundo and F. Viani, Transition from Internal to External Oxidation for Binary Alloys in the Presence of an Outer Scale, *Oxid. Met.*, 1986, **25**, p 269
38. J.L. Meijering, On the Diffusion of Oxygen Through Solid Iron, *Acta Metall.*, 1955, **3**, p 157–162
39. E. Essuman, G.H. Meier, J. Zurek, L. Hansel, and W.J. Quadakkers, The Effect of Water Vapor on Selective Oxidation of Fe-Cr Alloys, *Oxid. Met.*, 2008, **69**, p 143
40. A.S. Khanna, *Introduction to High Temperature Oxidation and Corrosion*, Materials Park, OH, ASM International, 2002, p 118
41. J. Zurek, D.J. Young, E. Essuman, G.H. Meier, M. Hansel, H.J. Penkalla, L. Niewolak, and W.J. Quadakkers, Growth and Adherence of Chromia Based Surface Scales on Ni-Base Alloys in High- and Low- $p\text{O}_2$ Gases, *Mater. Sci. Eng. A*, 2008, **477**, p 259–270
42. E. Essuman, G.H. Meier, J. Zurek, M. Hansel, L. Singheiser, and W.J. Quadakkers, Enhanced Internal Oxidation as Trigger for Breakaway Oxidation of Fe-Cr Alloys in Gases Containing Water Vapor, *Scr. Mater.*, 2007, **57**, p 845–848
43. N.K. Othman, J. Zhang, and D.J. Yong, Water Vapor Effects on Fe-Cr Alloy Oxidation, *Oxid. Met.*, 2010, **73**, p 337–352
44. A.N. Hansson, H. Danielsen, F.B. Grumsen, and M.A.J. Somers, Microstructure Evolution During Steam Oxidation of a Nb Stabilized Austenitic Stainless Steel, *Oxid. Met.*, 2010, **73**, p 289–309
45. G.H. Meier, K. Jung, N. Ma, N.M. Yanar, F.S. Pettit, J.P. Abellan, T. Olszewski, L.N. Hierro, W.J. Quadakkers, and G.R. Holcomb, Effect of Alloy Compositions on the Selective Oxidation Behavior of Ferritic Fe-Cr and FeO-Cr-X Alloys, *Oxid. Met.*, 2010, **74**, p 319–340
46. J. Askill, *Tracer Diffusion Data for Metals, Alloys, and Simple Oxides*, IFI/Plenum Data Corporation, New York, 1970, p 48
47. J. Kucera and K. Stransky, Diffusion in Iron, Iron Solid-Solution and Steel, *Mater. Sci. Eng.*, 1982, **52**, p 1–38
48. J. Takada, S. Yamamoto, and M. Adachi, Diffusion-Coefficient of Oxygen in Alpha-Iron Determined by Internal Oxidation Technique, *Z. Metallkd.*, 1986, **77**, p 6–11
49. J.H. Swisher and E.T. Turdogan, Solubility, Permeability and Diffusivity of Oxygen in Solid Iron, *Trans. Met. Soc. AIME*, 1967, **239**, p 426–431
50. J. Takada, S. Yamamoto, S. Kikuchi, and M. Adachi, Determination of Diffusion Coefficient of Oxygen in γ -Iron from Measurements of Internal Oxidation in Fe-Al Alloys, *Met. Trans.*, 1986, **A17**, p 221–229
51. J.W. Park and C.J. Altstetter, The Diffusion and Solubility of Oxygen in Solid Nickel, *Met. Trans.*, 1987, **A18**, p 43–50
52. S.P. Murarka, M.S. Anand, and R.P. Agarwala, Diffusion of Chromium in Nickel, *J. Appl. Phys.*, 1964, **35**, p 1339–1341
53. A.C.S. Sabioni, B. Lesage, A.M. Huntz, J.C. Pivin, and C. Monty, Self-Diffusion in Cr_2O_3 . 1. Chromium Diffusion in Single-Crystals, *Philos. Mag. A*, 1992, **66**, p 333–350
54. A.C.S. Sabioni, A.M. Huntz, F. Silva, and F. Jomard, Diffusion of Iron in Cr_2O_3 : Polycrystals and Thin Films, *Mater. Sci. Eng. A*, 2005, **392**, p 254–261
55. W.C. Hagel, Anion Diffusion in $\alpha\text{-Cr}_2\text{O}_3$, *J. Am. Cer. Soc.*, 1965, **48**, p 70–75
56. R. Hempelmann and C.H. Karmonik, Proton Diffusion in Proton Conducting Oxides, *Phase Trans.*, 1996, **58**, p 175–184
57. T. Horita, K. Yamaji, Y.P. Xiong, H. Kishimoto, N. Sakai, and H. Yokokawa, Oxide Scale Formation of Fe-Cr Alloys and Oxygen Diffusion in the Scale, *Solid State Ionics*, 2004, **175**, p 157–163
58. R. Sun, Diffusion of Cobalt and Chromium in Chromite Spine, *J. Chem. Phys.*, 1958, **28**, p 290–293
59. R. Lindner and A. Akerstrom, *Z. Phys. Chem.*, 1956, **6**, p 162–177
60. A.C.S. Sabioni, R.P.B. Ramos, V. Ji, F. Jomard, W.A.D. Macedo, P.L. Gastelois, and V.B. Trindade, About the Role of Chromium and Oxygen Ion Diffusion on the Growth Mechanism of Oxidation Films of the AISI, 304 Austenitic Stainless Steel, *Oxid. Met.*, 2012, **78**, p 211–220