The role of metal nanoparticles and nanonetworks in alloy degradation

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Oxide scale, which is essential to protect structural alloys from high-temperature degradation such as oxidation, carburization and metal dusting, is usually considered to consist simply of oxide phases. Here, we report on a nanobeam X-ray and magnetic force microscopy investigation that reveals that the oxide scale actually consists of a mixture of oxide materials and metal nanoparticles. The metal nanoparticles self-assemble into nanonetworks, forming continuous channels for carbon transport through the oxide scales. To avoid the formation of these metallic particles in the oxide scale, alloys must develop a scale without spinel phase. We have designed a novel alloy that has been tested in a high-carbon-activity environment. Our results show that the incubation time for carbon transport through the oxide scale of the new alloy is more than an order of magnitude longer compared with commercial alloys with similar chromium content.

The United States loses 4% of the gross national product annually owing to alloy corrosion1. Among the corrosion reactions, carburization and metal dusting, a high-temperature corrosion in strongly carburizing gas atmospheres at carbon activities (ac) > 1, are long-standing problems in energy conversion and production systems such as ethylene furnaces and hydrogen reformer plants2–5. It is estimated that 137 quadrillion joules of energy is lost annually owing to high-temperature corrosion problems5. All alloys are generally protected from continued corrosion by oxide scales that develop on the alloy surface at high temperatures. To minimize the corrosion problem, oxide scales on alloy surfaces need to be carefully analysed and their composition and phases have to be optimized to achieve high resistance in various corrosive environments6–8. The diffusion rate of carbon in oxide scales is negligible6. However, it is often seen that carbon diffuses into alloys and leads to brittleness and even pitting corrosion (a form of extremely localized corrosion that leads to the creation of small craters in the alloy)9–20. Carbon transport through oxide scale is traditionally considered to involve the diffusion of carbon-bearing molecules such as CO and CO2 through pores or cracks9,21. However, if carbon-bearing molecules can diffuse through these defects, oxygen can also diffuse through and react with alloy elements to form a new oxide scale, which will self-heal the oxide and stop the further intrusion of carbon-bearing molecules. According to the diffusion mechanism of oxidation proposed by Wagner22, it is possible to form a layer comprising a mixture of oxides and metal particles for a binary alloy23. However, formation of metal particles in oxide scale has been largely ignored9,21. It is well known that carbon can diffuse through nickel and iron metals24. Therefore, if metal particles are present in oxide scale in low pO2 environments, a new path for carbon atom transport is available that does not involve oxide defects. Our current study of oxide scales using nanobeam X-ray analysis, magnetic force microscopy (MFM) and scanning electron microscopy (SEM) has led us to believe that metal nanoparticles are indeed present in the scale. These metal nanoparticles join to form continuous channels for carbon transfer. This finding may have broad influence on not only metal dusting and carburization, but also in other research areas such as alloy development and surface coatings. For example, solid-oxide fuel cells require low resistivity for oxide scales that develop in service on metallic interconnects25. If we can control the formation of clusters of metal particles in oxide scale, we may be able to greatly reduce the area resistance of metallic interconnects, even if the alloy develops an oxide in service. On the other hand, if we can prevent the formation of metal particles in oxide scale, the carburization and metal-dusting problem can be greatly retarded by minimizing the carbon transfer channels.

Areas attacked by metal-dusting corrosion usually form pits10–21. Corrosion pits on the surface of Alloy 321 (composition: Fe-17.3%Cr–10.3%Ni–0.3%Mn–0.4%Si–0.4%Ti–0.04%C) were observed after 1,130 h exposure to a metal-dusting gas mixture consisting of 53.4%H2–5.7%CO–18.4%CO2–22.5%H2O (gas 1) at 14.3 atm and 593 °C with a carbon activity (ac) of 31. After exposure, the specimen was cut and a metallographic mount of the cross-section was prepared. The cross-section samples were mechanically polished on both sides to a thickness of 70μm. Care was taken to minimize decomposition and contamination during sample preparation. The X-ray nanobeam (beam size of 200 nm × 300 nm) was scanned across the cross-section at both the pit and non-pit areas from the surface to the interior of the alloy. Non-pit areas have not yet been attacked by metal dusting. Surprisingly, strong diffraction (2θ at 42.2°) from a Fe/Ni metal phase was observed in the oxide scale of non-pit areas (Fig. 1a). The diffraction peak position of the metal particles in the oxide scale is different from the peak position (2θ at 41.1°) of the alloy, which indicates that the lattice parameters of these embedded metal particles in the scale are different from the metal particles in the substrate alloy. Alloy 321 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 used. However, the metal particles in oxide scale showed a ferritic structure with the 110 diffraction peak at 42.2° (d-space at 2.03 Å).

Both (Fe, Cr) spinel and Cr$_2$O$_3$ phases were observed by X-ray diffraction (XRD) at non-pit areas. There were two strata in the oxide layer at the pit area and only spinel phase was observed in both layers. No diffraction from metal particles or Cr$_2$O$_3$ was seen in the oxide layer at the pit area (Fig. 1b). However, it is surprising that the nickel content in the inner layer of the scale is higher than that in the substrate alloy (Fig. 1c). This result was also confirmed by energy dispersive X-ray (EDX) analysis, but EDX could not establish the valence of the nickel in the oxide layer. On the other hand, nanobeam X-ray near-edge absorption analysis showed that the chemical shift of nickel in most locations of the oxide layer is close to metallic nickel (see Fig. 1d).

The presence of metallic nickel particles in the oxide layer. These Ni particles are amorphous and were not seen in a conventional XRD scan (Fig. 1b).

EDX analysis was also carried out on the cross-section of Alloy 321. The thickness of oxide scale at non-pit areas is only a few micrometres, whereas the thickness of oxide layer at pit areas is over 50 μm. Bright spots in sizes ranging from several tens of nanometres to 800 nm were observed in the SEM image of oxide scale at the non-pit area (Fig. 2a). EDX analysis indicated that these bright spots are rich in iron and nickel but contained less oxygen and chromium. There are no such bright spots in the oxide layer at pit areas of Alloy 321, but two distinct strata were observed in the oxide layer. EDX analysis indicated more oxygen and iron in the outer layer than in the inner layer, whereas the concentrations of chromium and nickel were less in the outer layer than in the inner layer (Fig. 2a).
Atomic force microscopy has been used extensively in corrosion research. Typically, MFM is used to characterize well-defined features; however, low-contrast MFM imaging can also couple structural and magnetic information with disordered materials. The particles in oxide scale at the non-pit area identified as Fe- and Ni-rich in the EDX analysis are probably composed of ferromagnetic iron, nickel or Fe/Ni alloy. Whereas the magnetic domains will presumably be isotropically oriented, those domains that have stray fields oriented perpendicular to the sample can produce contrast in an MFM image. Iron chromate, FeCr₂O₄, conversely, is paramagnetic and chromium oxide, Cr₂O₃, is antiferromagnetic at room temperature. These substances, which are among the materials traditionally identified as making up oxide scale, will provide no contribution to MFM contrast. The XRD and near-edge X-ray absorption analysis indicated that other ferromagnetic or ferrimagnetic oxides did not form in the low-\(pO_2\) environment in this area. Therefore, we scanned through the regions containing bright spots in the SEM micrographs of the oxide scale at non-pit area using MFM. Figure 2c shows MFM data exhibiting magnetic contrast correlating with the regions containing the particles (Fig. 2b), thus indicating ferromagnetism (or ferrimagnetism) in these locations. Correlation between the MFM image and the SEM image is not perfect owing to such factors as potential distortion of nanoparticle magnetic domain orientations by the sample holder and/or the MFM probe and the fact that the MFM can only probe stray fields perpendicular to the sample plane. However, the observation of magnetic contrast and its correlation with bright features from the electron micrograph, when viewed in the context of the XRD data, indicates the presence of ferromagnetic Fe/Ni particles with ferritic structure in the oxide scale.

Metal nanoparticles were also observed in the oxide scale of other alloys and in other test environments. Figure 3a shows the cross-section of oxide scales on Alloy 310 (Fe-19.5%Ni–25.5%Cr–1.7%Mn–0.7%Si–0.03%C) after 1,636 h exposure to a carburizing gas consisting of 65.1%H₂–4%CO₂–30%CO–0.9%H₂O (gas 2) at 1 atm and 593°C with an \(a_C\) of 104. Pits were observed after the short exposure period, even though the chromium content in this alloy is high. The density of metal particles in the oxide
layer in the pit area is higher than that at the non-pit area. An almost continuous channel of metal particles was observed from the surface through the oxide layer to the substrate alloy. Because carbon can rapidly diffuse through metals\textsuperscript{24}, this metallic network could enable transport of carbon in a matrix of oxides. In the non-pit regions, the particles have probably not formed continuous channels and the orientation of the metal clusters is probably parallel rather than perpendicular to the alloy surface (Fig. 3a), thereby resulting in less metal-dusting attack. The figure also shows a schematic representation of possible orientation of carbon-transfer channels in the two regions.

Because the electrical conductivity of metallic nickel and iron is 100 million times higher than that of spinel\textsuperscript{29}, the electrical resistivity of the oxide scale at the pit area will be much lower than that at the non-pit area if metal clusters connect to form channels in the pit area. The procedure for detecting low-resistance areas on the surface of alloys is to deposit metal (such as copper) particles by an electrochemical method in which copper is deposited on the alloys by immersing them in CuSO\textsubscript{4} solution and applying a voltage across the electrodes\textsuperscript{11}. The areas with low resistance will have deposits of copper particles because current can pass through them easily. Deposited copper particles thus act as an indicator to locate the carbon transfer channels\textsuperscript{11}. Figure 3b shows the copper-deposited region of a pit on the surface of Alloy 310. Such areas can be identified under a microscope and probably indicate regions of active degradation by metal dusting\textsuperscript{11}.

A metallic network was also observed in the oxide scale in the pit region of Alloy 353MA (composition: Fe–24.4%Cr–34.7%Ni–1.4%Mn–1.3%Si–0.1%Mo–0.18%N–0.06%V–0.05%C) after 1,130 h exposure to a metal-dusting gas mixture consisting of 40.2% H\textsubscript{2}–0.2%CO–19.8%CO–0.1%H\textsubscript{2}O (gas 3) at 1 atm and 593 °C with an a\textsubscript{c} of 200 (Fig. 3c). It seems that these networks form along the grain boundary regions (average grain size of 700 nm) in the (Fe,Ni)\textsubscript{2}Cr\textsubscript{4}O\textsubscript{9} spinel phase. When the spinel decomposes, the ductile nickel particles detach from the grain and concentrate in the grain boundary regions to self-assemble into a metallic network. These metallic networks could act as pathways for the transport of carbon into alloys and lead to metal-dusting corrosion. The proposed models for carbon diffusion are shown in Fig. 3d. In the earlier model, carbon-containing gases such as CO and CO\textsubscript{2} diffuse through pores, cracks or grain boundaries of oxides and the diffusion of carbon atoms through the scale is not considered. However, in the proposed Model A, carbon atoms diffuse through oxide scale via metallic networks present in the scale. Model B represents a hybrid between the earlier model and proposed Model A. Carbon-containing gas molecules diffuse through the external oxide scale and deposit carbon atoms onto a metallic network in the scale. Atomic carbon, dissolved in the metal, diffuses into the substrate alloy through the metallic networks in the oxide scale. In the earlier model, oxygen can also diffuse into the alloy and form a new oxide scale and self-heal the oxide scale to stop the further diffusion of carbon into alloys. However, in the proposed Models A and B, the metallic network acts as a filter to allow only carbon atoms to diffuse into alloys while preventing the diffusion of oxygen because the diffusion rate of carbon in Ni is much faster than that of oxygen\textsuperscript{24}. The carburization process will not be stopped by the self-healing process because a new oxide scale cannot form when oxygen cannot diffuse in\textsuperscript{11,24}. The continuous ingress of carbon finally leads to metal-dusting corrosion.

The large difference of carbon transport rate at the area with a metallic network from the area without a metallic network leads to a localized corrosion. The results presented above indicate occurrence of pitting corrosion when the metal particles join together to form a continuous channel through oxide scale for carbon transfer, whereas, in the oxide scale of the non-pit area, the metal particles have not formed such a continuous channel. Metallic nanoparticles are randomly distributed in oxide scale, so the statistical likelihood of forming a continuous channel is low. A consequence of this situation is that the pit density could be less than one per cm\textsuperscript{2}. The density of metallic nanoparticles in oxide scales can be affected by the phase composition of the scale. Cr\textsubscript{2}O\textsubscript{3} cannot be reduced into metallic particles in a metal-dusting environment, but (FeNi)Cr\textsubscript{2}O\textsubscript{4} spinel can be. Greater spinel content in oxides is expected to lead to increased density of metallic corrosion.
The oxide layer at a position close to the surface (Fig. 1d). Although the pit area of Alloy 321, Ni\(^{2+}\) was observed at the outer layer of the oxide layer at a position close to the surface (Fig. 1d). Although nanoparticles in oxide scale and, therefore, a greater likelihood to form a continuous channel. Indeed, we have observed that the pit density increases with increasing iron content\(^a\), because the spinel content in oxide scale increases with increasing iron content in the following reaction:

\[
\text{Fe} + \text{Cr}_2\text{O}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{FeCr}_2\text{O}_4.
\]

In the pit area of Alloy 321, Ni\(^{2+}\) was observed at the outer layer of the oxide layer at a position close to the surface (Fig. 1d). Although pure NiCr\(_2\)O\(_4\) is not stable in the reducing environment of the present study, a small amount of Ni\(^{2+}\) may enter the Fe\(^{2+}\) sites in FeCr\(_2\)O\(_4\) to form a (Fe, Ni)Cr\(_2\)O\(_4\) solid solution. The maximum concentration of Ni\(^{2+}\) in the solid solution is 15.2% in gas 1 at 14.3 atm and 593 °C, calculated from thermochemical data\(^b\). However, the calculated value for the maximum concentration of Ni\(^{2+}\) at the oxide–substrate interface, where the oxygen partial pressure is much less than in gas 1, is only 1.2 × 10\(^{-3}\)% Therefore, the concentration of Ni\(^{2+}\) in the spinel should be high at the gas side of the oxide scale and it will be low in the oxide on the alloy side of the scale.

In the early stage of oxide scale formation, nickel could be oxidized to 2\(^+\) at the gas–oxide surface and dope into the solid solution of (Fe, Ni)Cr\(_2\)O\(_4\). When cations continue to diffuse out, the nickel-containing spinel is buried inside. The pO\(_2\) in the inner layer of the oxide scale decreases with increasing thickness of the oxide scale, and Ni\(^{2+}\) will be reduced to nickel metal when the pO\(_2\) drops below the critical value. Such a process leads to the formation of nickel particles in oxide scale. FeCr\(_2\)O\(_4\) spinel itself is not stable either. Iron ions can also be reduced to metallic particles in the oxide scale. Therefore, formation of the metallic nanoparticles can occur owing to the reduction of nickel and iron ions in the spinel phase during the growth of the oxide scale.

Nickel oxidation and reduction processes can occur only if iron is present in alloys because pure NiCr\(_2\)O\(_4\) spinel will not form in a reducing environment. Only when FeCr\(_2\)O\(_4\) forms, Ni\(^{2+}\) can dope into iron-containing spinel to form a (Fe, Ni)Cr\(_2\)O\(_4\) solid solution. In the absence of iron, nickel will not be subjected to the oxidation–reduction process. Therefore, the spinel phases in oxide scale can lead to formation of unstable iron-rich regions and act as a solvent for the formation of Ni\(^{2+}\); the Ni\(^{2+}\) will eventually be reduced to nickel metal (over a long time), thereby enabling development of carbon transfer channels.

According to the analysis above, metal dusting would be greatly retarded if the alloys could develop an oxide scale without the formation of metal nanoparticles or nanonetworks. In the absence of iron in the alloy, the scale would not contain an iron-containing spinel and NiCr\(_2\)O\(_4\) would be thermodynamically unstable in the reducing environment of reformers. Therefore, it is desirable to prepare alloys that can develop an oxide scale without the spinel phase. We designed and prepared several nickel-base alloys with low iron content. The chromium content of Alloy ANL1 (74.5% Ni, 22% Cr, 2.3%Al, 0.7%Fe, 0.3%Ti, 0.2%Zr, and 0.1%Co) is similar to commercial Alloy 601 (61.8%Ni, 21.9%Cr, 1.4%Al, 14.5%Fe, 0.3%Ti, 0.1%Nb, and 0.03%C), but the Fe content of the ANL1 alloy is only 0.7% compared with 14.5% in Alloy 601.

Raman scattering spectra indicate formation of spinel phase on the surface of commercial Alloy 601 but not on the surface of the low-iron alloy after 12,858 h exposure in gas 2 at 1 atm and 593 °C. A large metal-dusting pit with depth of 490 µm was observed, but the surface of ANL alloy was still smooth.
mechanisms of these metallic nanoparticles and networks should be further studied with the twin goals of controlling their formation for applications such as reducing the electrical resistance of oxide scale on metallic interconnects for solid-oxide fuel cells or improving the bonding between alloys and oxide scales and minimizing their formation to avoid metal dusting, carburization and hydrogen embrittlement.

**METHODS**

Nanobeam X-ray analysis was carried out at the 2D-D beamline of the APS at Argonne National Laboratory. Using a Si(001) double-crystal monochromator and zone-plate optics, the X-ray nanoprobe in the experimental station produces a monochromatic X-ray beam of size 200 nm with a photon flux of $5 \times 10^{35}$ photons s$^{-1}$ with an X-ray energy bandwidth $(\Delta E/E)$ of 0.01%. The focal plane of the zone-plate optics was adjusted so that the minimum spot size was obtained at the surface of the specimen. Figure 5 shows the scattering and data acquisition geometry for the synchrotron radiation experiments: the beam is incident on the region of interest on the specimen, and the scattering intensity in a section of reciprocal space is captured by a flat, two-dimensional detector (CCD camera). Samples for the synchrotron radiation experiments were prepared in a similar manner as for the cross-section analysis in scanning electron microscopy. 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.

MFM measurements were carried out using a vibrationally damped Vecco MultiMode V system with silicon probes coated with CoCr alloy (approximately 25 nm tip radius of curvature).

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**Figure 5** Schematic diagram showing the geometry of data acquisition at the synchrotron beamline.

**References**


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**Author contributions**

Z.Z. and K.N. planned the experiments and analysed the data, Z.C. carried out the APS nanobeam experiment and S.B.D. carried out MFM measurements and contributed to data analysis and interpretation.

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