Sulfur Effect on Corrosion Behavior of Fe-20Cr-(Mn, Si) and Fe-20Ni-20Cr-(Mn, Si) in CO2-H2O at 650°C

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Model alloys, Fe-20Cr and Fe-20Cr-20Ni (wt%), and these alloys doped with 0.5% Si or 2% Mn, were exposed to Ar-20%CO2-20%H2O-0% (0.1%, 0.5%, 1.0%)SO2 gas mixtures at 650°C. The reaction kinetics were analyzed gravimetrically and the reaction products were characterized using X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. In sulfur-free gases, thick iron-rich oxide scales and internal carbides formed on alloys of Fe-20Cr-(2Mn) and Fe-20Cr-20Ni-(0.5Si). Additions of SO2 promoted the maintenance of protective chromia scale on these alloys, but had no benefit for the already highly corrosion resistant Fe-20Cr-0.5Si and Fe-20Cr-20Ni-2Mn alloys. The role of sulfur in retarding carburation is discussed with reference to its strong adsorption on oxide-metal interfaces and oxide grain boundaries.

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Extraction of energy from coal contributes greatly to the environmental problem of CO2 emissions. With the goal of limiting CO2 emissions and mitigating global warming, advanced combustion technologies have been developed for CO2 collection and sequestration, one of which is the oxyfuel process. In this process, coal is burnt in pure oxygen, so the flue gas is mainly CO2 and H2O, making CO2 capture feasible. Unfortunately, the corrosive nature of this gas, together with the increased operating temperatures adopted for higher efficiencies, provides severe operating conditions for materials of power plant construction, such as steel tubing for a boiler.

The Fe-Cr alloys which are able to form a protective chromia scale in air have been shown to suffer breakaway oxidation with subsequent extensive carburation in CO2. Even in conditions where a protective chromia scale was formed in CO2, carburation was observed in the alloy beneath its oxide scale. This phenomenon has recently been explained by the observation of carbon enrichment along chromia grain boundaries using atom probe tomography. Furthermore, the addition of H2O to CO2 rich gases is known to accelerate the onset of breakaway oxidation of Fe-Cr alloys.

Coal combustion also produces some SO2, since sulfur is a common impurity in fossil fuels. The corrosion rate of Fe-Cr alloys is related to the sulfur potential in a combustion gas. Growth of sulfide within and on top of Cr2O3 scale is observed in high sulfur potential and low oxygen potential gases, causing a transition from initial protective oxidation to breakaway corrosion due to a much faster rate of sulfidation. On the other hand, the presence of small amounts of sulfur in more oxidizing combustion gases leads to slower corrosion rates. In a previous paper, the addition of (0.1%~1.0%) SO2 was shown to promote the protective oxidation of Fe-9Cr alloy in 20% CO2-20%H2O gas at 650°C, with the suppression of carbon penetration and carbide formation. This was suggested to be due to the preferential adsorption of sulfur on scale grain boundaries or metal/oxide interface, impeding the diffusion of other species.

From a practical point of view, ferritic-martensitic alloys with Cr concentrations of 9–10% cannot resist oxidation at T ≥ 650°C, but higher Cr ferritic alloys might. Austenitic Fe-Cr-Ni alloys are to be preferred, with good corrosion resistance and mechanical properties. The effect of SO2 in CO2-H2O gas on the corrosion behavior of such high chromium ferritic and austenitic alloys is unknown, and is the subject of this study.

The presence of small amounts of silicon and manganese in Fe-Cr and Fe-Cr-Ni alloys can alter the kinetics and morphology of the corrosion reaction. Additions of 2% Mn significantly reduced carbon penetration and improved the corrosion resistance of Fe-20Cr and Fe-20Cr-20Ni alloys in CO2 and CO2-H2O gas at 818°C, due to the formation of MnCr2O4 spinel scale layers. However, Mn had no influence on the oxidation resistance of Fe-9Cr in CO2 gas, and accelerated the breakdown of its chromia scale, the formation of which is promoted by the presence of SO2 in CO2-H2O at 650°C. The role of a SiO2 scale layer acting as a diffusion barrier for Fe-(9, 20)Cr-(0.2, 0.5)Si and Fe-20Cr-20Ni-(0.2, 0.5)Si alloys in CO2 and CO2-H2O gas at 818°C has recently been reported. A SiO2 layer does not form on Fe-9Cr-0.5Si alloy in CO2-H2O gas at 650°C, but does so in the presence of SO2, which in turn promotes the formation of a protective chromia scale.

The aim of the present work was to investigate the influence of small SO2 additions and minor alloying elements (Si, Mn) on the corrosion behavior of model Fe-20Cr and Fe-20Cr-20Ni alloys at 650°C in Ar-20% CO2-20% H2O gas.

Materials and Methods

Six model alloys, Fe-20Cr, Fe-20Cr-0.5Si, Fe-20Cr-2Mn, Fe-20Cr-20Ni, Fe-20Cr-20Ni-0.5Si and Fe-20Cr-20Ni-2Mn (all in wt%) were prepared by arc melting pure metals of Fe (99.97%), Cr (99.995%), Ni (99.99%) and Mn (99.9%) under a protective Ar-5% H2 gas atmosphere, using a non-consumable electrode. Silicon was added using a master alloy of Fe-4.7Si to minimize the silicon loss during melting. Cast alloy buttons were annealed at 1100°C for 50 h in a flowing Ar-5% H2 gas for homogenization. The as-annealed materials had coarse and irregular grains, with average grain size 2.6 ± 2 mm for Fe-20Cr alloys, and 2.4 ± 1.8 mm for Fe-20Cr-20Ni alloys. Analysis by XRD confirmed that Fe-20Cr-(2Mn, 0.5Si) alloys were ferritic and Fe-20Cr-20Ni-(2Mn, 0.5Si) alloys austenitic. Rectangular specimens were cut and ground to approximate dimensions of (12–16) × (6–8) × (1–1.5) mm3, and a small suspension hole was drilled near an edge. Each sample was ground to a 1200 grit finish in water, and ultrasonically cleaned in ethanol prior to reaction.

Isothermal corrosion experiments were performed at 650°C in a flowing Ar-20%CO2-20%H2O-(0, 0.1, 0.5, 1.0)SO2 (volume %) mixture with a linear flow rate of 2 cm/s and a total pressure of 1 atm. Wet gases of controlled water vapor pressure were generated by passing a mixture of argon and carbon dioxide through a thermostatted water saturator. The demineralized water in contact with the gas mixture was set at such a temperature that an excess of water vapor was produced. This excess was subsequently condensed by cooling the wet gas in a distillation column at the temperature corresponding to the required water content. This wet gas was then mixed with Ar-5% SO2 to obtain the desired gas composition before introducing it into the reactor. Individual gas flows were regulated using mass flow controllers (Brooks 5850E serials).
Weight changes of reacted samples were measured using an analytic balance (Precisa 180A) with an accuracy of 0.1 mg. In weight gain kinetic plots shown in this work, each point represents the value from a separate sample. Corrosion samples were characterized by X-ray diffractometry (XRD; PANalytical Xpert MPD) with Cu-Kα radiation, optical microscopy, transmission electron microscopy (TEM; Philips CM200) and scanning electron microscopy (SEM; Hitachi S3400) with an energy dispersive X-ray spectrometer (EDS, Bruker). Using focused ion beam (FIB, XT Nova Nanolab 200) milling, electron-transparent slices were cut from specific parts of the samples after oxidation and lifted out for TEM observation. Metallographic examination employed Vilella’s reagent (7 ml saturated solution of picric acid in ethanol, 3 ml HCl, and 40 ml ethanol) to reveal alloy grain structure, and a modified glyceregia solution (10 ml glycerine, 6 ml HCl, and 3 ml HNO3) or Murakami’s reagent (1 g K₃Fe(CN)₆, 1 g KOH, and 10 ml H₂O) to reveal carbides.

Results

Fe-20Cr-(Mn, Si) alloys.—Corrosion kinetics.—Weight gain kinetics for the ferritic alloys is shown in Fig. 1. The plots for Fe-20Cr and Fe-20Cr-2Mn alloys in sulfur-free wet CO₂ gases exhibit rapid breakaway oxidation. The corrosion resistance of these two alloys is significantly improved with the addition of SO₂ to the gas, with generally lower weight gains following approximately parabolic kinetics over the experimental time period. The Fe-20Cr-0.5Si alloy in both sulfur-free and sulfur-containing gases exhibited much lower weight gains than the other two alloys.

The parabolic rate law was used to describe weight uptake kinetics in SO₂-containing gases. Parabolic rate constants, kₚ, can be calculated from the equation:

\[
\left( \frac{\Delta W}{A} \right)^2 = 2k_p t
\]

where ΔW is the weight gain, A the surface area of the reacted sample and t the reaction time. The values of kₚ summarized in Table I were obtained by regression of the reaction data in Fig. 1.

Linear weight uptake kinetics take effect after an initial period of parabolic growth for these three alloys exposed to sulfur-free wet CO₂ gases (Fig. 1). In this case, kₚ was obtained by regression of the reaction data for the initial parabolic growth stage. Due to the irregular weight uptakes for Fe-20Cr-0.5Si alloys in sulfur-containing gases, kₚ was not calculated for them. In sulfur-free gas, Fe-20Cr and Fe-20Cr-2Mn alloys oxidized five orders of magnitudes faster than did the Fe-20Cr-0.5Si alloy. The addition of 0.1% SO₂ lowered the corrosion rates for Fe-20Cr and Fe-20Cr-2Mn alloys by three orders of magnitudes. Further increasing the SO₂ level up to 1.0% had no additional effect on the corrosion rates of these two alloys.

External corrosion products.—Cross-sections of the reacted samples are shown in Figs. 2 and 3. Correlation with the XRD patterns shown in Fig. 4 allows identification of the morphology and constitution of the reaction products. It is clear that Fe-20Cr and Fe-20Cr-2Mn alloys exposed to wet CO₂ in the absence of SO₂ were, for the most part, covered with a thick iron-rich oxide scale, although a thin
Table I. Parabolic Rate Constants Calculated from Weight Gain Kinetics (10^{-10} \text{mg}^2 \text{cm}^{-4} \text{s}^{-1}).

| Alloys                  | 20CO_2-20H_2O | 20CO_2-20H_2O-0.1SO_2 | 20CO_2-20H_2O-0.5SO_2 | 20CO_2-20H_2O-1.0SO_2 |
|-------------------------|---------------|------------------------|-----------------------|-----------------------|
| Fe-20Cr                 | 2.5 \times 10^5 | 350                    | 350                   | 500                   |
| Fe-20Cr-2Mn             | 4.5 \times 10^4 | 500                    | 500                   | 500                   |
| Fe-20Cr-0.5Si           | 5             | *                      | *                     | *                     |
| Fe-20Cr-20Ni            | *             | *                      | *                     | *                     |
| Fe-20Cr-20Ni-2Mn        | *             | *                      | 35                    | 10                    |
| Fe-20Cr-20Ni-0.5Si      | *             | *                      | 100                   | 25                    |
| Fe-20Cr-20Ni-0.5Si      | *             | *                      | *                     | *                     |

*Kinetics constants are not available for these alloys due to the irregular weight uptakes.

Figure 2. Optical metallographic cross-sections of (a) Fe-20Cr, (b) enlarged image of iron-oxide scale in (a), (c) Fe-20Cr-2Mn alloy, (d) enlarged image of iron-oxide scale in (c), and (e) SEM cross section of Fe-20Cr-0.5Si alloy after reaction in sulfur-free wet CO_2 gas for 240 h.

Figure 3. SEM cross-sections of (a) Fe-20Cr, (b) Fe-20Cr-2Mn, (c) Fe-20Cr-0.5Si, and (d) optical metallographic cross-section of Fe-20Cr-0.5Si alloy after reaction in sulfur-free wet CO_2 gas for 500 h.

Figure 4. XRD patterns of Fe-20Cr-(Mn, Si) alloys reacted in CO_2-H_2O-1.0% SO_2 gas for 500 h.
Figure 5. TEM-bright field cross-sections of (a) Fe-20Cr, (b) Fe-20Cr-2Mn, and (c) Fe-20Cr-0.5Si after reaction in CO₂-H₂O-0.5% SO₂ gas for 500 h; and (d) and (e) EDS line profiles in (b) and (c), respectively (insert in (d) shows a higher S content in the outer scale).

(Fig. 4) reveals the coexistence of Fe₂O₃ and Cr₂O₃ in the external scale.

Severe spallation was observed on Fe-20Cr-0.5Si alloy after reaction in SO₂-containing gas (Fig. 6d), leading to an under-estimated value of the weight uptakes measured after oxidation. To rectify this effect, the weight uptakes during the period of oxidation were calculated from scale thickness measured in un-spalled locations. The scale was assumed to be a uniform chromia, and weight uptakes calculated on this basis for Fe-20Cr-0.5Si alloy in 0.1% SO₂ containing gas are shown in Fig. 1. As whiskers, iron oxide nodules and internal products were ignored in this calculation, the actual weight uptakes would be somewhat higher.

A high magnification TEM bright field image (Fig. 5c) of Fe-20Cr-0.5Si alloy reacted in 0.5% SO₂ containing gas shows a very thin layer (about 44 nm) underneath the chromia scale. An EDS line-scan in Fig. 5e shows this layer to be silicon rich, presumably silica. Some chromia also formed locally underneath the main silica layer, and a new continuous silica layer formed at the interface between this type of chromia and the alloy.

Whiskers were observed for all three alloys reacted in sulfur-bearing gas and Fe-20Cr-(Si) alloys in sulfur-free gas. Fine plate-shaped whiskers formed on top of the solid chromia layer in sulfur-free wet gas. Surface SEM views in Fig. 6 show two types of whiskers for alloys reacted in sulfur-bearing gas: fine plates and coarse rod-like whiskers. The fine structures appeared on the surface of all three alloys. The coarse rod-like whiskers were observed on Fe-20Cr and Fe-20Cr-0.5Si alloys, with a higher number density on the Si-containing alloy.

Internal corrosion products.—Reaction in SO₂-containing gas produced no internal oxides beneath the chromia scale (Fig. 3), although internal oxidation zones developed beneath iron oxide scales on these alloys reacted in sulfur-free wet CO₂ gas (Figs. 2b and 2d). Internal sulfide developed in Fe-20Cr reacted in SO₂-containing gas, predominantly along alloy grain boundaries (Fig. 7a), and sparsely distributed at a shallow depth beneath the chromia scale (Fig. 3a). Analysis by EDS identified the sulfides as chromium-rich (Fig. 7b). Internal sulfides were also found in Fe-20Cr alloys doped with Mn and Si (Figs. 3b and 3c). They were identified by EDS as chromium-rich sulfide in Fe-20Cr-0.5Si and (Cr, Mn)-rich sulfide in Fe-20Cr-2Mn (results not shown).

Internal carbides were revealed by etching. As shown in Fig. 8a, reactions in sulfur-free wet CO₂ gas also led to both intergranular and intragranular carbides in Fe-20Cr alloys beneath their iron-rich oxide scales. Alloying with Mn had no effect on the carburization of these alloys during reaction in sulfur-free gas. No carburization was observed in Fe-20Cr-0.5Si alloy exposed to sulfur-free wet CO₂ gas. The Fe-20Cr and Fe-20Cr-0.5Si alloys exposed to SO₂-containing gas developed only intergranular carbides (Figs. 8c and 8d), lying deeper within the alloy below the intergranular sulfide (Fig. 8d). The sulfide phase has been dissolved during etching, leaving only pores as...
Fe-20Cr-20Ni-(Mn, Si) alloys.—Corrosion kinetics.—Weight gain kinetics for Fe-20Cr-20Ni-(Mn, Si) alloys are shown in Fig. 9. Weight gains of Fe-20Cr-20Ni alloy in sulfur-free wet CO₂ gas increased slowly and irregularly over 380 h, and had accelerated somewhat by 1000 h. The addition of 0.1% SO₂ to wet CO₂ gas shows little effect on the weight gain kinetics of this alloy, which again exhibits irregular growth. However, the kinetic plots for reaction in 0.5% SO₂ and 1.0% SO₂ containing gases exhibit slower weight uptakes, with approximately parabolic growth over the experimental times. The addition of Mn seems to retard the breakaway oxidation of Fe-20Cr-20Ni alloy in sulfur-free wet CO₂ gas, as evident after 1000 h exposure. The Fe-20Cr-20Ni-2Mn alloy exhibits irregular growth after reaction in both wet CO₂ gas and with the addition of 0.1% SO₂ to the gas. The addition of 0.5% and 1.0% SO₂ had little effect on the weight gain of this alloy, but did lead to parabolic growth over the experimental times. Only the kinetic curves in Fig. 9 which showed regular parabolic behavior were used for regression on Equation 1. The resulting values for $k_p$ are shown in Table I.

Weight uptakes of Fe-20Cr-20Ni-0.5Si alloy in sulfur-free wet CO₂ gas show significant fluctuation within the experimental time. While the corrosion rate of Fe-20Cr-20Ni-0.5Si alloy is faster than that of Fe-20Cr-20Ni alloy in sulfur-free wet CO₂ gas, it was apparently slower in all SO₂-containing gases. However, these measurements were affected by scale spallation which occurred in SO₂-containing gases, and are therefore underestimated. For this reason, no $k_p$ values for Fe-20Cr-20Ni-0.5Si alloys are given in Table I.

External corrosion products.—The Fe-20Cr-20Ni alloy developed a thin chromia scale interrupted by small, sparsely distributed iron...
Figure 10. SEM cross-sections of (a) Fe-20Cr-20Ni, (b) enlarged image of chromia scale in (a), (c) Fe-20Cr-20Ni-2Mn, and (d) Fe-20Cr-20Ni-0.5Si reacted in sulfur-free CO₂-H₂O gas for 240 h.

oxide nodules in short term when exposed to wet CO₂ gases in the absence of SO₂ (Figs. 10a and 10b). However, long-term exposure up to 1000 h led to the extensive formation of iron-rich oxide scale. The Fe-20Cr-20Ni-2Mn alloy reacted in sulfur-free wet CO₂ is predominantly covered by a thin (Cr, Mn)-rich scale (Fig. 10c). Alloys of Fe-20Cr-20Ni and Fe-20Cr-20Ni-2Mn reacted in sulfur-bearing gas are also covered by nodule-free, thin scale. Cross-sectional SEM images of the thin scales on these alloys exposed to 1.0% SO₂ containing gas are shown in Figs. 11a and 11b. By correlating with the XRD patterns (Fig. 12), one can identify the constitution of the external scale as Cr₂O₃ for Fe-20Cr-20Ni, and both Cr₂O₃ and MnCr₂O₄ for Fe-20Cr-20Ni-2Mn. High magnification TEM bright field images (Figs. 13a and 13b) clearly show the chromia scale for Fe-20Cr-20Ni and a duplex scale for Fe-20Cr-20Ni-2Mn alloy exposed to gas containing 0.5% SO₂. Analysis by EDS (Fig. 13d) identifies the inner layer for Fe-20Cr-20Ni-2Mn alloy as mainly Cr₂O₃, and MnCr₂O₄ spinel, while the outer layer is MnCr₂O₄ spinel.

The Fe-20Cr-20Ni-0.5Si alloy partially developed a thin scale which was frequently interrupted by iron oxide scale when exposed to wet CO₂ gases in the absence of SO₂. The apparent fluctuations in weight uptakes are due to random variations in the nucleation of iron oxide nodules on different alloy specimens. No scale spallation was observed on this Si-containing alloy in wet CO₂ gas. Cross-section and surface view images of Fe-20Cr-20Ni-0.5Si alloy reacted in SO₂-containing gas (Figs. 11c and 14d) shows spallation had occurred, presumably during cooling. Therefore, the corrosion rate implied by measured weight uptake (Fig. 9c) is under-estimated. As the surface is still predominantly covered with a thin chromia scale at these experimental times (Fig. 13c), the actual weight gain during the period of oxidation was calculated from scale thickness, assuming a uniform chromia scale. Results for Fe-20Cr-20Ni-0.5Si alloy reacted in 0.1% SO₂ containing gas are shown in Fig. 9. It is seen that the weight uptakes are generally higher than measured gravimetrically, but still
much lower than for Fe-20Cr-20Ni-0.5Si alloy reacted in sulfur-free wet CO2 gas. A high magnification TEM bright field image of this alloy reacted in the 0.5% SO2 gas for 500 h reveals a very thin layer (about 26 nm) underneath the outer chromia scale (Fig. 13c), and EDS analysis indicates this layer to be silica (Fig. 13e).

Fine plate-shaped whiskers formed on top of the solid chromia layer in sulfur-free wet gas for the austenitic alloys.19 It is seen from SEM surface views (Fig. 14) that numerous whiskers form in the outer part of the external scale on all the austenitic alloys reacted in sulfur-bearing gas. Mixtures of fine-sized platelets and some coarse rod-like whiskers were observed for both Fe-20Cr-20Ni and Fe-20Cr-20Ni-0.5Si alloys. The SEM surface (Figs. 14c and 14d) and cross section views of the scale (Fig. 11c) show a high density of coarse rod-like whiskers on the outer surface of the Si-containing alloy. Only fine whiskers were observed for Mn-containing alloys.

Internal corrosion products.—No internal oxides were seen under the chromia scale for any of the Fe-20Cr-20Ni-(Mn, Si) alloys reacted in any gas. Internal sulfidation products in alloys reacted in SO2-containing gas were found beneath the chromia scale, either along alloy grain boundaries or sparsely distributed at a shallow depth (Fig. 11b for Fe-20Cr-20Ni-2Mn; Fig. 15a for Fe-20Cr-20Ni; and Fig. 15b for Fe-20Cr-20Ni-0.5Si). Intergranular carbides were observed for Fe-20Cr-20Ni and Fe-20Cr-20Ni-0.5Si alloy underneath both the chromia scale and iron-rich oxide scale developed in sulfur-free gas.19 No internal carbide was observed after etching for Fe-20Cr-20Ni-2Mn alloy reacted in sulfur-free gas, and in any of the austenitic alloys exposed to SO2 containing gases.

Figure 15. SEM image showing internal sulfides in (a) Fe-20Cr-20Ni and (b) Fe-20Cr-20Ni-0.5Si alloys reacted in CO2-H2O-1.0% SO2 gas for 500 h.

Discussion

The corrosion behavior of these alloys depends on whether or not a protective chromia scale can be formed and maintained. Discussion is therefore focused on the effects of SO2 addition and alloy composition on Cr2O3 scaling.

Effect of SO2 on chromia formation.—A scale of Cr2O3 is partially developed on the Fe-20Cr alloy surface exposed to sulfur-free CO2 gas, as seen in Fig. 2a, whilst a protective chromia scale almost completely covered this alloy when exposed to SO2-containing gas (Fig. 3a). This change in reaction morphology accounts for the much lower weight uptakes observed (Fig. 1). In the case of austenitic Fe-20Cr-20Ni alloy, there is a reduction in the frequency of nodule formation when SO2 is added to the gas (Fig. 10a and Fig. 11a). However, these nodules are in any case small and infrequent, so no significant change is seen in weight uptake kinetics (Fig. 9).

Whether or not an exclusive external chromia scale forms is determined by the Cr content of the alloy. During the initial transient stage of oxidation, iron oxide scale might form with Cr2O3 internally precipitated within the alloy. If the alloy Cr concentration exceeds a critical value, N21Cr, these precipitates coalesce laterally to form a continuous layer of chromia. The value of N21Cr can be calculated according to Wagner’s analysis:20

\[
N_{Cr}^{(1)} = \left( \frac{\pi g V_m D_{Fe} N_{Cr, Ni}}{2V_{Cr, Ni}, D_{Fe-Cr}} \right)^{1/2}
\]

where \( g \) is a critical volume fraction of oxide precipitates, generally approximated as 0.3,21 \( V_{m} \) and \( V_{Cr, Ni} \) the molar volumes of alloy and chromia, \( D_{Fe} \) the alloy diffusion coefficient of oxygen, \( D_{Fe-Cr} \) the alloy-inter-diffusion coefficient, and \( N_{Cr}^{(1)} \) the oxygen solubility at the scale-alloy interface.

In addition, in order to maintain exclusive external chromia scale growth, the alloy Cr concentration must exceed a critical value to produce sufficient Cr diffusion to the scale-alloy interface:22

\[
N_{Cr}^{(2)} = \left( \frac{\pi k_{e}}{2V_{Cr, Ni}} \right)^{1/2}
\]

where \( k_{e} \) is the parabolic rate constant for scale thickening.

These critical Cr levels have been evaluated using available thermodynamic and kinetic data.19 The results show that for Fe-20Cr alloy reacted in wet CO2 gas, \( N_{Cr}^{(1)} \) and \( N_{Cr}^{(2)} \) are 0.10 and 0.11, respectively, both below the actual alloy chromium content (\( N_{Cr}^{(1)} \approx 0.21 \)) for Fe-20Cr alloy. Thus diffusion theory predicts that this alloy should be able to form and maintain a chromia scale. This is indeed the case in carbon free oxygen gases, e.g. in air or oxygen where a protective chromia scale forms.23 However, it does not apply for wet CO2 gas, where breakaway oxidation is observed (Figs. 1 and 2).

Mechanisms of breakaway oxidation for Fe-20Cr alloys in CO2 gas have previously been discussed.23 Faster Cr2O3 scale growth in CO2 can accelerate mechanical failure of the scale as growth stresses rise with increasing scale thickness. Then scale cracking or spallation can allow gas access to a depleted alloy surface. Repeated scale failure and regrowth would further deplete chromium in the subsurface alloy, leading eventually to breakaway. High chromium levels sometimes permit the formation of a re-healing layer rich in chromium beneath the nodules, which slows the local corrosion rate. However, once iron-rich oxide nodules nucleate, internal carburization is observed beneath them as a consequence of carbon permeability being greater in the iron-rich oxide than in the chromia it replaces (Fig. 8a). Extensive precipitation of internal chromium-rich carbide leads to further depletion of chromium, rendering re-passivation of the alloy difficult or impossible.

Although the onset of breakaway is greatly accelerated by CO2, carburization of the alloy was seen not to be a necessary condition for breakaway.23 It is now known that carbon-bearing species are present on chromia scale grain boundaries,6 which could affect the scale mechanical properties, rendering it more susceptible to fracture.
The segregation of carbon can also affect grain growth and boundary diffusion. In addition, chromia whiskers form on top of the chromia layer if water vapor is present with CO₂ in the gas (refer to Ref. 19 for Fe-20Cr alloy). Whiskers are thought to increase growth stresses in the protective scale, increasing the risk of mechanical damage.²⁷

In the presence of sulfur, internal carburization occurred only in the form of intergranular carbides (Fig. 8c). The formation of only limited amounts of chromium-rich carbide beneath Cr₂O₃ scale has little effect on the matrix chromium concentration, and therefore does not affect the kinetic stability of the protective scale during steady-state growth. Similarly, the extensive carburization underneath the iron-rich oxide scale on Fe-9Cr in sulfur-free CO₂-H₂O gas at 650 °C was effectively inhibited and replaced by the formation of intergranular carbides when SO₂ was added to the gas.¹⁹ This effect of sulfur is attributed to its strong adsorption on oxide surfaces and grain boundaries, which retards carbon diffusion along these pathways.

The long-term oxidation behavior of a high-temperature alloy is determined not only by the effectiveness of the oxide scale as a barrier to transport of reactants but also by its resistance to mechanical failure. The replacement of carbon by sulfur segregation on grain boundaries might also change mechanical properties of the scale. Figure 16a shows the growth kinetics of chromia scale in terms of thickness, measured for Fe-20Cr alloys exposed to CO₂-H₂O-0.1% SO₂ gas. Chromia scale thickness on Fe-20Cr exposed to sulfur-free gas is included for comparison. It is seen that chromia scaling for Fe-20Cr in SO₂-containing gas was slightly faster than in SO₂-free wet CO₂ gas, indicating a slightly higher critical value of ωₖ.²⁴ In addition, the slightly thicker scale would generate marginally higher stress intensity. However, this alloy formed protective scales in S-bearing gases, but went into breakaway in S-free gas. Thus the effect of sulfur on Nₖ via carburization is very small, and its effect on ωₖ is mildly adverse. It is therefore suggested that the slower onset of breakaway oxidation for Fe-20Cr-20Ni alloy in sulfur-containing gas is not related to kinetic stabilization of the chromia scale. However, it could be due to a changed mechanical state of the scale resulting from exclusion of carbon by preferential adsorption of sulfur.

**Effect of Mn on chromia formation.—**Breakaway oxidation associated with extensive carburization was found to occur on Fe-20Cr-2Mn alloy exposed to wet CO₂ gas at 650 °C (Fig. 2c and Fig. 8b). The failure of the chromia scale for Fe-20Cr-2Mn alloy in wet CO₂, as discussed above, is suggested to be caused by growth stresses in combination with the presence of carbon within the scale. The addition of SO₂ significantly improved the corrosion resistance of Fe-20Cr-2Mn alloy with the formation of a protective chromia scale (Fig. 3b). The reasons for its stability are similar to those applying to the Fe-20Cr alloy. The Mn-bearing alloy does in fact form a thin scale rich in Cr and Mn in sulfur-free wet CO₂ gas (Fig. 2c), but this protective layer is short-lived. The effect of SO₂ is to preserve this layer to longer times. The thin scale grows at similar rates, whether or not SO₂ is present. The explanation is therefore not a simple kinetic issue, and the mechanical behavior of this layer is important. Since internal carburization of Fe-20Cr-2Mn alloy is suppressed by the SO₂ addition, it is concluded that the preferentially adsorbed sulfur excludes carbon from the scale, thereby improving its mechanical properties.

In the presence of sulfur, the outward diffusion of Mn leads to the formation of a discontinuous outer layer of mixed, chromium and manganese-rich oxide plus sulfide over the Cr₂O₃ scale on this alloy (Figs. 5b and 5d). This is due to the diffusivity of Mn being about two orders of magnitude greater than those of Cr and Fe in chromia layers grown on iron-base alloys.²⁴ This manganese-rich outer layer was not observed in the absence of SO₂ because of the fast growing of iron oxide scale. The formation of manganese-rich oxide plus sulfide on the scale surface is associated with external whisker morphology of a rather uniform and fine structure for this alloy (Fig. 6b), rather than the coarse rod-like whiskers developed at scale surfaces grown on Fe-20Cr in SO₂-bearing gas (Fig. 6a). As impingement of whisker roots within the solid chromia layer leads to higher stress levels, the reduction in whisker size after this stress and might thereby provide an additional benefit for continued protection by the chromia scale.

Formation of a thin (Cr₂O₃ + MnCr₂O₄) scale on the austenitic Fe-20Cr-20Ni-2Mn alloy is favored in wet CO₂ gas at 650 °C,¹⁹ despite the prediction from Equation 3 that Fe-20Cr-20Ni should fail. Since the scale growth rate is not effectively reduced with the addition of Mn, detected in sulfur-containing gases (Fig. 15), indicating that carbon did not penetrate the scale. Figure 16b shows that chromia scale growth kinetics for Fe-20Cr-20Ni alloy in SO₂-containing gas were slightly faster than those in SO₂-free wet CO₂ gas, indicating a small increase in the critical value of ωₖ.²⁴ Thus the effect of sulfur on Nₖ via carburization is very small, and its effect on ωₖ is mildly adverse. It is therefore suggested that the slower onset of breakaway oxidation for Fe-20Cr-20Ni alloy in sulfur-containing gas is not related to kinetic stabilization of the chromia scale. However, it could be due to a changed mechanical state of the scale resulting from exclusion of carbon by preferential adsorption of sulfur.

![Figure 16. Chromia scale thickness as a function of reaction time for Fe-20Cr-(Mn, Si) and Fe-20Cr-20Ni-(Mn, Si) alloys.](image-url)

For the austenitic Fe-20Cr-20Ni alloy, the calculated Nₖ(1) and Nₖ(2) values are 0.072 and 0.316, respectively,¹⁹ indicating that the chromium concentration of the alloy is sufficient for chromia scale formation but insufficient to maintain its growth (Nₖ(1) = 0.212 for Fe-20Cr-20Ni alloy). It should be noted that the rate of oxidation is very slow in the austenitic alloy because of NiFe₂O₄ formation in the scale and the slow diffusion in this oxide.²⁴ Nevertheless, the trend to breakaway oxidation was observed after long-term reaction, e.g. 1000 h in Fig. 9, in agreement with prediction.

Carburization in Fe-20Cr-20Ni alloy exposed to sulfur-free wet CO₂ gas was basically in the form of intergranular carbide under both chromia scale and iron oxide nodules.¹⁹ No internal carbide was
the development of a thin scale on Fe-20Cr-20Ni-2Mn is therefore attributed to a higher value of $D_{\text{diff}}$. The necessary acceleration in diffusion results from the existence of a cold worked alloy sub-surface region.\textsuperscript{19} The resulting high corrosion resistance was also observed for this alloy reacted in sulfur-bearing gas, although the scale grows a little faster than on Fe-20Cr-20Ni alloy (Fig. 16). The formation of uniform, fine whiskers (Fig. 14b) and the exclusion of carbon from the scale by preferentially adsorbed sulfur contribute to the high resistance of the scale to mechanical failure, and thereby the high corrosion resistance of this Mn-doped alloy.

**Effect of Si on chromia formation.**—The effect of 0.5% Si additions in postponing the onset of breakaway for Fe-20Cr alloy in sulfur-free wet CO$_2$ gas is evident in Fig. 1. The beneficial effect of Si addition is due to the formation of a Cr$_2$O$_3$ scale which acts as a diffusion barrier.\textsuperscript{18} However, the addition of 0.5% Si had no significant improvement on the corrosion kinetics for Fe-20Cr-20Ni alloy in sulfur-free wet CO$_2$ gas (Fig. 9), and breakaway oxidation occasionally occurred on both the undoped and Si-doped alloys. Silica formed underneath the Cr$_2$O$_3$ scale formed on Fe-20Cr-20Ni-0.5Si alloy, but not continuously, interrupted by iron oxide nodules. It is, therefore, deduced that a higher Si level is required in austenitic alloys than in ferritics for the formation of a continuous silica layer. This arises from the slower diffusion rates in FCC Fe, which results in a lower enrichment of Si in the IOZ.\textsuperscript{25}

The critical Si concentration to form an external silica layer is:

$$N_{\text{Si}}^{(1)} = \left( \frac{\pi g V_m D_m N_S}{2V_S D_S} \right)^{1/2}$$  \hspace{1cm} \text{(4)}$$

where $V_{SO_2}$ is the molar volume of silica and $D_S$ is the alloy diffusion coefficient of Si. The critical Si content to maintain the growth of a continuous silica layer is:

$$N_{\text{Si}}^{(2)} = \frac{V_m}{V_{SO_2}} \frac{\pi k_S}{2D_S} ^{1/2}$$ \hspace{1cm} \text{(5)}$$

where $k_S$ is the parabolic rate constant for silica layer thickening. These calculations have been carried out,\textsuperscript{18} yielding $N_{\text{Si}}^{(1)} = 1.2 \times 10^{-4}$ for both ferritic and austenitic alloys. The addition of 0.5% (weight percent) Si to Fe-20Cr and Fe-20Cr-20Ni alloys corresponds to $N_S$ of 9.7 $\times$ 10$^{-3}$ and 9.8 $\times$ 10$^{-3}$, respectively, indicating Fe-20Cr-0.5Si and Fe-20Cr-20Ni-0.5Si alloys are able to form an external silica layer. Similarly, it is found that $N_{\text{Si}}^{(2)} = 5 \times 10^{-4}$ for Fe-20Cr-Si alloy and $8 \times 10^{-4}$ for Fe-20Cr-20Ni-Si alloy in sulfur-free wet CO$_2$ gas, indicating the absence of the ferritic alloy to maintain a continuous silica layer. With $N_{\text{Si}}^{(2)} = 8 \times 10^{-4}$ for the austenitic alloy in sulfur-free wet CO$_2$ gas, the actual Si content of Fe-20Cr-20Ni-0.5Si is marginal for silica layer maintenance. Thus more Si may be required for enhanced corrosion resistance of this alloy in wet CO$_2$ gas.

In sulfur-bearing wet CO$_2$ gas, the addition of 0.5% Si had little influence on the already high corrosion resistance of Fe-20Cr and Fe-20Cr-20Ni alloys. Each of SiO$_2$ in the reaction gas and Si as an alloying element has a positive effects on the corrosion resistance of ferritic Fe-20Cr alloy in wet CO$_2$ gas, as does their combination. On the other hand, the presence of sulfur, rather than Si doping, is apparently the dominant factor influencing the corrosion resistance of austenitic Fe-20Cr-20Ni in wet CO$_2$ gas (Fig. 9). As a result of chromia scale formation and maintenance, a continuous, slow growing silicon oxide layer developed at the scale-alloy interface in sulfur-bearing wet CO$_2$ gas (Fig. 5c for Fe-20Cr-0.5Si and Fig. 13c for Fe-20Cr-20Ni-0.5Si). This layer provides an additional diffusion barrier together with the chromia layer.

Figure 17a shows the superimposed Cr-S-O and Si-S-O predominance diagrams calculated using FactSage.\textsuperscript{26} Here, the metal activities have been approximated as $a_{Cr} = 0.21$, and $a_{Si} = 9.7 \times 10^{-3}$. For the Fe-20Cr-20Ni-0.5Si alloys studied, the thermodynamic phase stability in a given atmosphere can be predicted from the predominance phase diagrams. The equilibrium sulfur and oxygen partial pressures of the reaction gas (calculated in a previous paper\textsuperscript{16}) are shown by point A, where Cr$_2$O$_3$ is stable. When Cr$_2$O$_3$ forms an external scale by selective oxidation of Cr, the diffusion path starts from point A, and moves toward lower oxygen potential. Beneath the scale, internal chromium sulfides exist within the alloy matrix, and the diffusion path is approximated by the line A-B-C-D. Point B corresponds to the interface between chromia and alloy containing internal sulfides of chromium. At an early stage, internal SiO$_2$ could co-exist with internal chromium sulfides underneath the chromia scale, represented by line B-C. The transport of silicon to the surface via alloy grain boundaries plays an important role in the process.\textsuperscript{27} The lateral coalescence of internal silica precipitates underneath chromia scale leads to the formation of a silica healing layer eventually. Chromium sulfides may form deeper in the alloy underneath the silica layer, represented by line C-D. The formation of silicon sulfide was not observed and has been excluded from the diffusion path.

**Effect of sulfur on scale spallation.**—The addition of SO$_2$ to wet CO$_2$ gas promoted the formation of Cr$_2$O$_3$ scale, and consequently the formation of SiO$_2$ scale. But SO$_2$ causes serious spallation on cooling for Si-bearing alloys (Figs. 11 and 14). The Fe-20Cr-0.5Si alloy exhibited an extremely low corrosion rate, being completely covered by slow growing scale (Fig. 2e) in S-free wet CO$_2$ gas. However, small iron-rich oxide nodules grew on this alloy in sulfur-bearing gas (Fig. 3d), consequently resulting in somewhat higher corrosion rates compared with that in sulfur-free gas (Fig. 1).

Spallation results from the application of sufficient stress to the scale-alloy interface. At least in principle, the addition of SO$_2$ to the gas could alter both the stress state of the scale-substrate system and the strength of the interface. Given that scale growth in sulfur-bearing gases is only slightly faster than in sulfur-free gases (Fig. 16), it would seem that neither the differences in scale-growth stresses nor in thermal stresses induced by cooling explain the observation of spallation of the reacted alloys in sulfur-bearing gases. Scale adhesion, however, is another matter.

It is long been known\textsuperscript{28} that sulfur segregates strongly to both Al$_2$O$_3$-metal and Cr$_2$O$_3$-metal interfaces. Such segregation is also responsible for weakening of the silica/ally interface,\textsuperscript{26,29} and leads to severe spallation for Si containing alloys in SO$_2$-containing gases. In the presence of sulfur, the chromia/alloy interface is stronger than for a silica/alloy interface.\textsuperscript{29} This difference accounts for the fact that scale spallation occurred on cooling of Si-doped alloys, but not for...
undoped Fe-20Cr and Fe-20Cr-20Ni alloys, after reaction in sulfur-bearing gas.

Factors affecting carbide formation.—Internal carbide formation has been shown to be possible in CO$_2$ gas for Fe-Cr and Fe-Cr-Ni alloys.\textsuperscript{3,5,16} The extent of carburization depends on gas atmosphere and alloy composition. In sulfur-free gas, both intragranular and intergranular carbides were observed underneath the oxide scale of Fe-20Cr (Fig. 8a). Addition of sulfur to the gas reduced carburization significantly, with very limited intergranular carbide formation in this alloy (Fig. 8c). A strong retarding effect of sulfur on carburization was also observed for the Fe-20Cr-20Ni alloy, as no carbide was formed in sulfur-containing gases. The effect of sulfur on carburization has been reported\textsuperscript{18} and is attributed to the strong adsorption effect of sulfur on interfaces and/or grain boundaries, which retards carbon penetration. Carburization is also affected by the presence of Si in the alloy. Carburization was suppressed in Si-bearing alloys in sulfur-free gas, with no carbide formation in the Fe-20Cr-0.5Si alloy.\textsuperscript{18} This phenomenon was explained by the formation of an additional, continuous silica layer which blocks carbon penetration and carburization underneath the scale. However, in the presence of sulfur, very limited intergranular carbides were identified (Fig. 8d) in this Si-containing alloy, indicating a rather complicated interaction between gas and alloy, which is still not understood.

It should be mentioned that internal silica may precipitate along alloy grain boundaries before its lateral coalescence due to favored diffusion of silicon at these locations. This intergranular silica, if it forms, provides little resistance to carbon diffusion because the silica-alloy interface provides an additional diffusion path. Thus intergranular carburization is limited, but still takes place.

In sulfur-free gas, Mn had no significant effect on carburization of Fe-20Cr (Fig. 8b), but had a strong retarding effect on carburization of Fe-20Cr-20Ni. This has been attributed to the formation of a protective scale of Cr$_2$O$_3$ + MnCr$_2$O$_4$, blocking carbon penetration effectively.\textsuperscript{19}

Conclusions

The addition of SO$_2$ enhanced the formation and maintenance of protective Cr$_2$O$_3$ scale on the un-doped ferritic Fe-20Cr and austenitic Fe-20Cr-20Ni alloys. Internal oxide and carbide formation was greatly suppressed in these alloys, with the formation of intergranular chromium sulfides in SO$_2$-containing wet CO$_2$ gas. It is proposed that the improved chromia scale performance in the presence of SO$_2$ is due to preferential adsorption of sulfur, and the prevention of carbon entry into oxide grain boundaries.

An Fe-20Cr-2Mn alloy also underwent breakaway oxidation in wet CO$_2$ gas, but maintained a protective (Cr$_2$O$_3$ + MnCr$_2$O$_4$) scale in sulfur-bearing gas. The addition of 2% Mn increased the corrosion resistance of Fe-20Cr-20Ni alloy in wet CO$_2$ gas with the formation of MnCr$_2$O$_4$ as part of the scale, which was maintained with the addition of SO$_2$. It is proposed that both the reduction in whisker size by the addition of Mn and the suppression of carbon ingress by sulfur provide benefits for mechanical properties of the chromia scale in sulfur-bearing gas.

Silicon additions markedly improved the corrosion resistance of ferritic Fe-20Cr alloy in wet CO$_2$ gas due to the formation of a silica layer which acted as a diffusion barrier. This enhanced corrosion resistance was maintained with the addition of SO$_2$. The addition of 0.5% Si, however, provided little improvement for the corrosion resistance of Fe-20Cr-20Ni alloy, allowing formation of iron-rich oxide scale regions during reactions in wet CO$_2$ gas. The corrosion resistance of Fe-20Cr-20Ni-0.5Si alloys was improved by the addition of SO$_2$.

Although the formation of a silica layer is beneficial in improving the corrosion resistance during reaction at high temperature, severe spallation was observed for the Si-containing alloys upon cooling in sulfur-containing wet CO$_2$ gases. The latter effect is attributed to weakening of the SiO$_2$-alloy interface by sulfur segregation.

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