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# Corrosion by Hot CO<sub>2</sub> Gases

by David J. Young and Jianqiang Zhang

Heat-resisting alloys are designed to survive high-temperature oxidation by forming a slow-growing scale, usually Cr<sub>2</sub>O<sub>3</sub>, which acts as a barrier between the metal and its environment. However, alloys that succeed in this way when exposed to hot oxygen or air fail to do so in CO<sub>2</sub> gas. Instead, they exhibit rapid “breakaway” corrosion, developing oxides of alloy base metal iron and/or nickel. The growth of these non-protective scales is accompanied by internal carburization of the underlying alloy (Fig. 1). Carbon passes through the oxide, dissolves in the alloy, and precipitates chromium as carbide. Removal of chromium from its matrix makes the alloy incapable of reforming chromia, and recovery from breakaway becomes impossible.

This is a problem with practical implications. It was first studied after breakaway corrosion was seen in CO<sub>2</sub> gas-cooled nuclear reactions.<sup>1-7</sup> Since then, interest has been rekindled by potential greenhouse gas abatement technologies, oxyfuel combustion,<sup>8-10</sup> where the flue gas is largely CO<sub>2</sub> + H<sub>2</sub>O(g), concentrated solar power generation and fast nuclear reactors,<sup>11-14</sup> where supercritical CO<sub>2</sub> is used as a heat transfer medium and turbine working fluid.

There have been several difficulties in understanding how a relatively unreactive species like CO<sub>2</sub> can cause such destructive effects. Firstly, how does a gas with low carbon activity ( $a_C$   $1.6 \times 10^{-15}$  in atmospheric pressure CO<sub>2</sub> at 650°C) carburize the alloys? Secondly, how does the carbon transfer through the oxide scale, in which it is thought to be insoluble<sup>15</sup> to the alloy? This occurs not only through iron oxides but also through highly protective chromia scales (Fig. 2)<sup>16</sup>. Thirdly, what are the chemical processes at the scale gas interface (where the equilibrium  $p_{O_2}$  value is too low to account for observed iron oxide scaling rates) and at the scale-alloy interface (where carbon is made available and injected into the alloy)? Finally, of course, how can the destructive effects of high-temperature CO<sub>2</sub> corrosion be avoided or at least slowed?

## Thermodynamics of Carburization by CO<sub>2</sub>

Oxidizing and carburizing potentials are governed by the following gas phase reactions.



Equilibrium oxygen potentials due to (1) are relatively high (atmospheric pressure CO<sub>2</sub> yields  $p_{O_2} = 1.5 \times 10^{-8}$  atm at 650°C) and sufficient to oxidize both iron and nickel at relevant temperatures. Breakaway oxidation is therefore always thermodynamically possible.

As seen above, values of  $a_C$  resulting from equilibration of the two reactions are insufficient to carburize chromium. However, alloys exposed to CO<sub>2</sub> grow an oxide scale, and the metal is in contact with an oxide, not the gas. The situation is shown schematically in Fig. 3, where  $p_{O_2}$  varies between a high value at the scale surface characteristic of the gas and a minimum at the scale-gas interface where it is set by the local equilibrium between the reacting metal, M, and its oxide. Correspondingly, according to (1), the ratio  $p_{CO}/p_{CO_2}$  varies between a minimum at the scale surface and a maximum at the scale-alloy interface. In this case, according to the Boudouard equilibrium (2),  $a_C$  also varies between a minimum at the scale surface and a maximum at the scale-alloy interface.

Recognizing that CO is produced from CO<sub>2</sub> by oxygen consumption, it is seen that

$$p_{CO} + p_{CO_2} = p_T \quad (3)$$

where  $p_T$  is an unknown constant, which depends on the external CO<sub>2</sub> pressure and scale transport properties. Equations (1) – (3) can be

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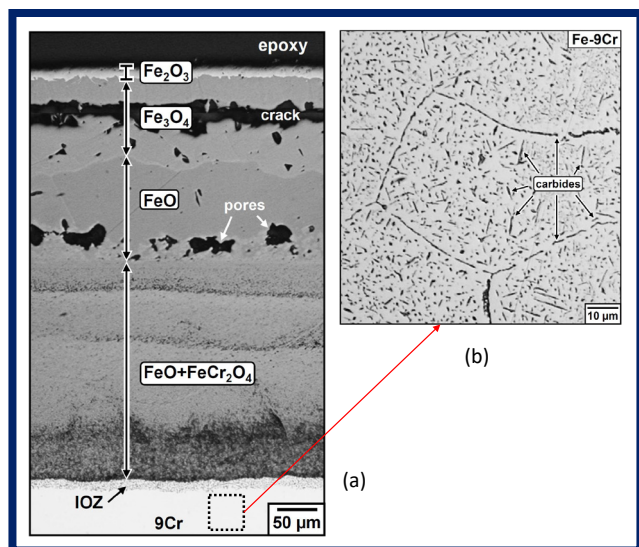


FIG. 1. Fe-9Cr reacted in Ar-20%CO<sub>2</sub> at 650°C for 1000 h (a) cross-section showing thick oxide scale and (b) dotted lined section in (a) etched by Murakami agent showing carbides in metal matrix.

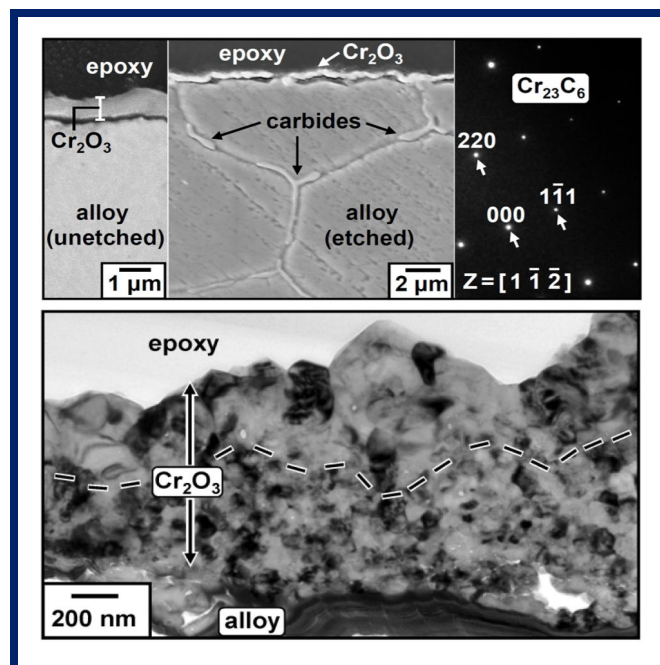


FIG. 2. Reaction products formed by Fe-20Cr exposed at 650°C to Ar-20%CO<sub>2</sub> for 24 h, and then to Ar-20%CO<sub>2</sub> for 70 h: upper – SEM views with SAD pattern identifying fcc Cr<sub>23</sub>C<sub>6</sub>; lower – bright field TEM image showing two-layered chromia scale.<sup>16</sup>

solved to yield

$$a_c = K_2 \frac{b^2}{1+b} p_T \quad (4)$$

with  $K_2$  the equilibrium constant for (2) and  $b = p_{CO}/p_{CO_2}$ , a value defined at the scale-alloy interface by the metal/metal oxide equilibrium.

This analysis has been tested<sup>17</sup> for the case of a model Fe-9Cr alloy exposed at 650°C to Ar-20CO<sub>2</sub>, forming the scale shown in Fig. 1. The value  $a_c = 0.52$  was calculated for the scale-alloy interface from the thermodynamic analysis. The volume fraction of carbide measured in the alloy adjacent to this interface was found from the phase diagram to correspond to  $a_c = 0.43$ , in good agreement with prediction. As seen below, the rate of alloy carburization is also consistent with the thermodynamically predicted  $a_c$  value.

## Carbon Transport Mechanisms

Information is available for the penetration of chromia scales by carbon.<sup>18,19</sup> The scale cross-section in Fig. 2 was produced by reacting the model alloy Fe-20Cr at 650°C, first for 24 h in O<sub>2</sub> and then for 70 h in CO<sub>2</sub>. The coarser-grained outer layer is characteristic of reaction in O<sub>2</sub>, while the finer-grained inner layer is characteristic of reaction in CO<sub>2</sub>. Clearly, the second stage reaction in CO<sub>2</sub> involves penetration of the first-formed outer layer by an oxygen species. Carburization of the alloy also took place during the second stage reaction, indicating that both carbon and oxygen penetrated the first-formed Cr<sub>2</sub>O<sub>3</sub>.

The rate at which the oxide scale thickness,  $X$ , increases with time,  $t$ , is diffusion controlled, leading to parabolic kinetics<sup>20,21</sup>

$$X^2 = 2k_p t \quad k_p = \int_{a_o}^{a_o''} D_i d \ln a_o \quad (5)$$

Here  $k_p$  is the parabolic rate constant,  $D_i$  the diffusion constant for the mobile species,  $a_o$  the oxygen activity within the scale, and  $a_o'$ ,  $a_o''$  the boundary values at the metal-scale and scale-gas interfaces (Fig. 3). Because the oxide lattice is so stable, diffusion in chromia scales is confined to grain boundaries and other extended defects.

Approximating the oxide grains in the chromia scale as being square in cross-section, then the fraction of sites within grain boundaries,  $f$ , is given by

$$f = 2d/L \quad (6)$$

with  $d$  the boundary width and  $L$  the grain size. Assuming  $L$  is almost constant with time,

$$k_p \propto 1/L \quad (7)$$

comparison of oxide scales grown in O<sub>2</sub> and CO<sub>2</sub><sup>19</sup> at 650°C yields  $L^{CO_2}/L^{O_2} = 0.6 \pm 0.1$  and  $k_p^{O_2}/k_p^{CO_2} = 0.8 \pm 0.2$ , confirming that chromia scale growth in CO<sub>2</sub> is supported by grain boundary diffusion.

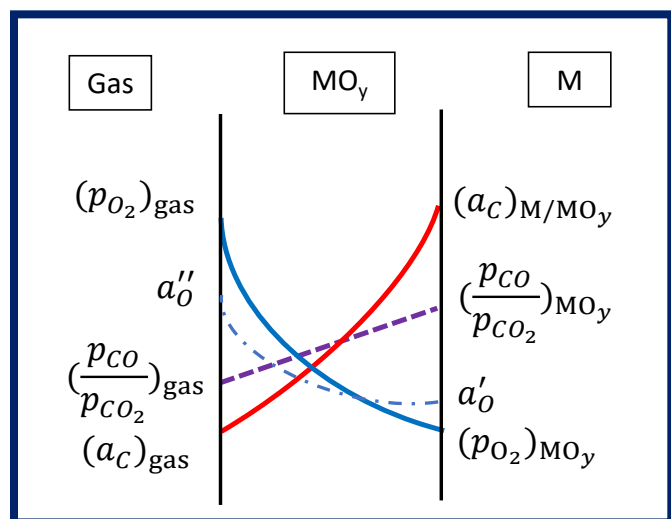


Fig. 3. Schematic illustration of  $p_{O_2}$ ,  $a_o$ , and  $a_c$  in growing oxide scale.

It is reasonable then to expect that carbon also penetrates the scale via its grain boundaries, as was proposed long ago.<sup>22,23</sup> The advent of atom probe tomography has allowed verification of this hypothesis. As seen in Fig. 4, a chromia scale grown in CO<sub>2</sub> has carbon decorating its grain boundaries as well as the scale-metal interface. The chemical state of this grain boundary carbon is unknown. Although elemental carbon is thermodynamically possible, it would presumably contribute negligibly to diffusion. Measurement of surface carbon concentrations yield about 5 atom nm<sup>-2</sup> on grain boundaries, much less than the 40 atom nm<sup>-2</sup> in a graphene sheet. Carbon must therefore be present in another form.

Once carbon has entered the alloy, it reacts with solute chromium to precipitate Cr-rich carbides. The rate at which the carburization depth,  $X_c$ , increases can be predicted from diffusion theory,<sup>21</sup> using the mass balance between carbon and chromium at the precipitation front

$$X_c^2 = 2k_p^C t \quad k_p^C = \frac{N_C^{(i)} D_C}{v N_{Cr}^{(0)}} \quad (8)$$

Where  $k_p^{(i)}$  is the parabolic rate constant for internal carburization,  $N_C^{(i)}$  the carbon concentration at the alloy-scale interface,  $D_C$  the carbon diffusion coefficient,  $v$  the C/Cr ratio in the carbide, and  $N_{Cr}^{(0)}$  the original alloy Cr mol fraction.

If the scale-alloy interface is at equilibrium, then  $a_c$  and therefore  $N_C^{(i)}$  are fixed, leading to the parabolic carburization kinetics observed commonly at high temperatures. Measurement of  $k_p^C$  can, in principle, be used to evaluate  $N_C^{(i)}$  and hence  $a_c$ , providing an additional check on the thermodynamic analysis. To do this properly requires taking into account the low stability of the carbides, which means some Cr remains in the metal matrix of the carburized region, and of the fact that Fe is dissolved in the carbides to a degree, which varies with  $a_c$ . These complexities can be dealt with numerically,<sup>17</sup> based on a description of partial precipitation.<sup>24</sup> For Fe-20Cr exposed to Ar-20CO<sub>2</sub> at 650°C, the carburization kinetics indicated a value  $a_c = 0.25$  at the alloy surface beneath Fe-rich oxide scales, still in reasonable agreement with the thermodynamic prediction.

At lower temperatures, the approach to equilibrium is slow<sup>25,26</sup> because the Boudouard reaction is so slow. Carbon drains away into the alloy, slowing the rate at which the carbon concentration at the surface increases (Fig. 5). Examination<sup>27</sup> of a 9Cr-1Mo steel after exposure at 600°C to pressurized (40 atm) CO<sub>2</sub> revealed that a 1mm thick cooling fin took more than 4000 h to reach carbon saturation at its surface. Obviously, the assumption of a fixed boundary condition must be abandoned in order to arrive at realistic lifetime predictions.

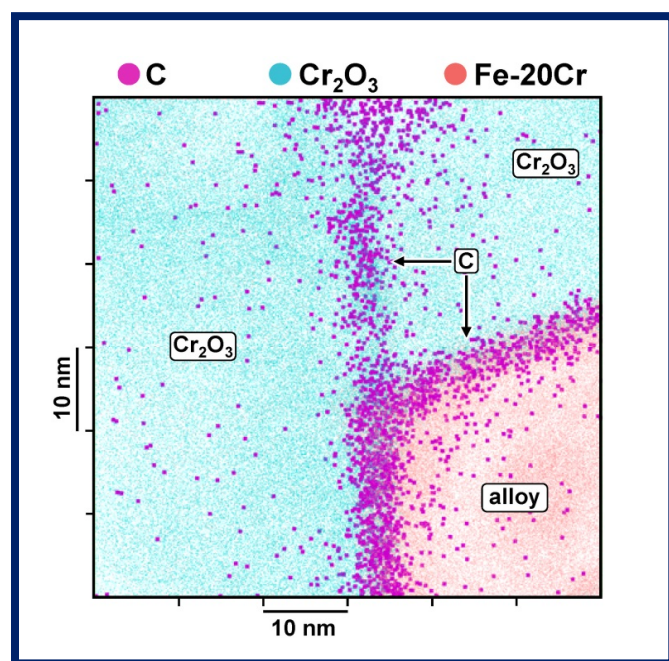
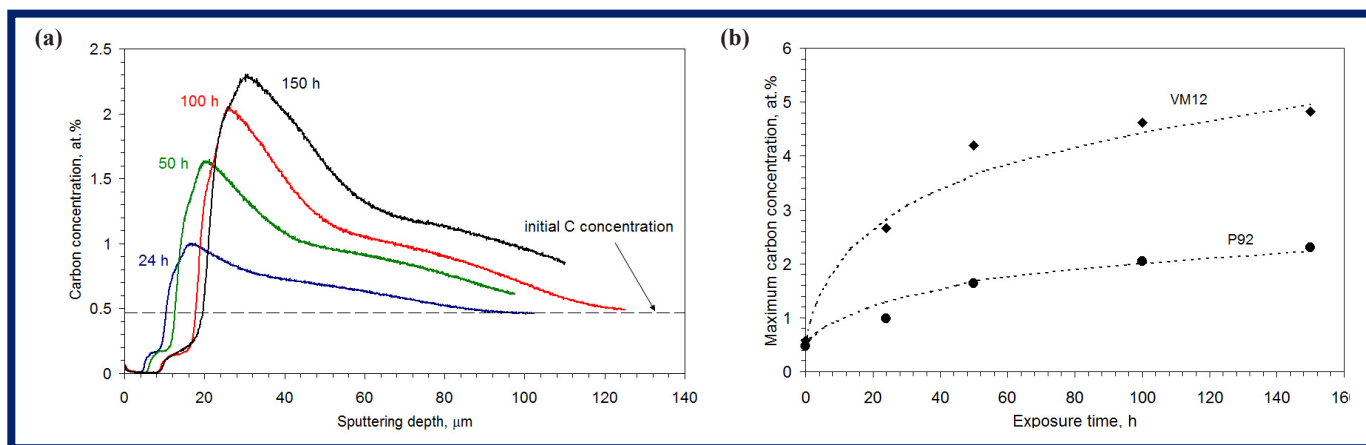


Fig. 4. Atom probe analysis of the Cr<sub>2</sub>O<sub>3</sub> scale of Fe-20Cr reacted at 650°C in Ar-20O<sub>2</sub> for 120 h.<sup>16</sup>



**Fig. 5.** (A) carbon concentration profiles (measured by GDOES) in 9% Cr steel P92 after different times of reaction in Ar-50%CO<sub>2</sub> at 550°C. (B) carbon concentration at oxide-alloy interface in P92 and VM12.<sup>25</sup>

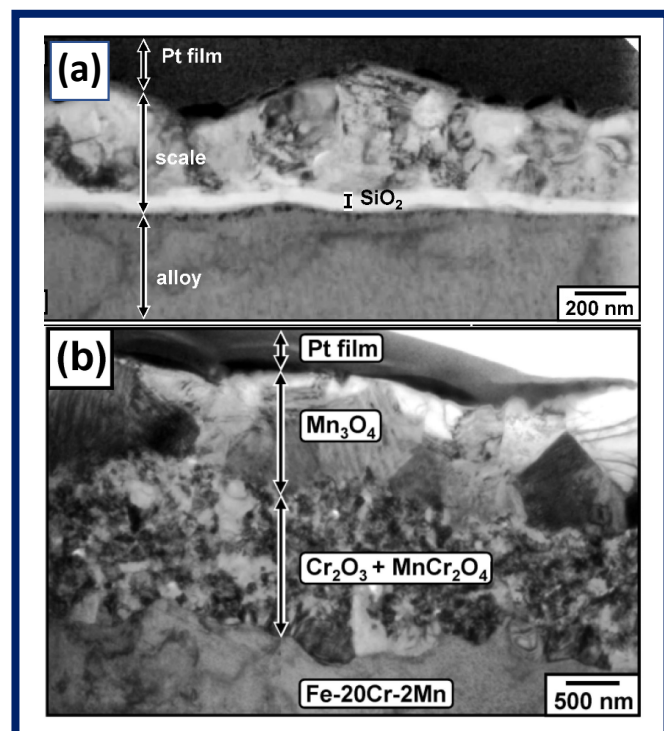
To proceed, it is necessary to develop a kinetic treatment for the processes of carbon formation and injection into the alloy. Recognizing that the Boudouard reaction must be catalyzed to occur at any significant rate, a model can be formulated for the interfacial kinetics.

## Scale-Alloy Interface

Much is happening at this boundary: metal is being oxidized; in the case of Fe-rich oxide, the metal is removed and diffuses outward, creating at least momentarily a vacancy. These vacancies can coalesce to form voids, which can then be encapsulated into the inward growing scale, accounting for its observed porosity. Alternatively, they can diffuse into the alloy, accommodating the volume change accompanying carbide precipitation and growth. They can also be filled with new oxide, resulting from a reaction with CO<sub>2</sub>. Before they vanish, voids at the scale-alloy interface present bare metal accessible to gas, allowing the catalytic process



to produce dissolved carbon, C.



**Fig. 6.** BF-TEM images of scales formed in reaction at 818°C with Ar-20CO<sub>2</sub> for 240 h: (a) Fe-9Cr-0.2Si, (b) Fe-20Cr-2Mn.

The carbon injection process can be modeled on the basis<sup>25,27,28</sup> that the flux of carbon into the alloy,  $J_C^{(i)}$ , is driven by the difference between the equilibrium carbon activity and its instantaneous value at the interface

$$J_C^{(i)} = A \{a_C^{eq} - a_C^{(i)}\} \quad (10)$$

Here the factor  $A$  combines the effect of any surface activation barrier with the pre-exponential factor for the Boudouard reaction itself. Eq. (10) then provides a boundary condition for the carbon diffusion equation. The latter is modified to reflect the partitioning of carbon between matrix and precipitates, as determined by the phase diagram for the system.

Numerical solutions, which treat  $D_C$  as an adjustable parameter, provide good agreement with the observed time dependence of  $N_C^{(i)}$  and  $X_C$ , as well as the shape of the  $N_C$  vs  $x$  profiles in Fig. 5.<sup>25</sup> Under the same reaction conditions, the rate constant  $A$  varies with the composition of the alloy, reflecting the catalytic role of the latter.<sup>25</sup>

It is found that  $D_C$  increases with depth within the carburized zone, only slightly near the alloy surface but strongly at greater depths.<sup>25,27,28</sup> Precipitate/matrix interfacial diffusion cannot account for this, as the interfacial surface area decreases with increasing depth. It is thought that precipitation-induced strain in the ferrite matrix accounts for the difference: inward vacancy migration from the alloy surface relieves the strain near the surface, but because interstitial carbon diffusion is faster than lattice diffusion, no such relief is available at greater depths.

## Controlling Carburization

In high alloy materials, carburization can be prevented by improving scale oxide quality, decreasing alloy carbon permeability, and lowering alloy carbide stability. Chromia scales provide much superior barriers to carbon entry and are obviously preferred. All three pathways are followed by choosing Ni- rather than Fe-base alloys. A relatively high alloy chromium content is required (~25Cr), and the materials choice can be economically unattractive. However, their superior performance in supercritical CO<sub>2</sub> has been established.<sup>29-31</sup>

Austenitic heat-resisting steels such as 310 stainless can perform rather well, but at the modest temperatures expected, ferritic-martensitic steels (9-12Cr) provide good creep life and are economically desirable. As seen above, these intermediate Cr level steels are subject to carburization and relatively rapid scale growth. However, their performance can be improved by minor alloying additions of Si and/or Mn.

Transfer of carbon from a chromia scale into the substrate alloy can be prevented by alloy addition of Si to develop a silica sublayer at the scale-alloy interface. This strategy has been proven to succeed for both ferritic and austenitic alloys in dry CO<sub>2</sub>.<sup>32-34</sup> As shown in Fig. 6a, the addition of 0.2% Si in Fe-9Cr alloy leads to the formation of a thin sublayer of silica underneath the chromia layer in CO<sub>2</sub> at 818°C. This

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thin amorphous silica layer serves as an additional diffusion barrier for oxygen and carbon diffusion, and as a result, significantly reduces the scaling rate.<sup>32</sup>

Prevention of carbon entry into chromia scale grain boundaries can also be achieved by alloying with Mn to form an additional, outermost scale layer of Mn-rich oxide. These have been shown to resist carbon entry in both CO<sub>2</sub> and CO<sub>2</sub>-H<sub>2</sub>O gases<sup>35-37</sup> for Fe-20Cr and Fe-20Ni-20Cr alloys. Fig. 6b shows Fe-20Cr-2Mn alloy in Ar-20CO<sub>2</sub> after 240 h reaction at 818°C, forming outermost Mn<sub>3</sub>O<sub>4</sub> and inner Cr<sub>2</sub>O<sub>3</sub>+MnCr<sub>2</sub>O<sub>4</sub> scale. However, this beneficial Mn effect does not appear for Fe-9Cr, as a thick oxide scale forms in that case.

In addition to Si and/or Mn alloying, another strategy to reduce carburization is to modify the scale surface/grain boundaries by sulfur uptake. As is well known, sulfur adsorbs strongly on many surfaces. It is expected that sulfur in the gas will be preferentially adsorbed on oxide scale surfaces and grain boundaries, reducing the

occupancy by carbon of these sites. As a result, carbon penetration via oxide grain boundary is retarded, as is carburization.<sup>38-40</sup> It was found<sup>40</sup> that adding only 0.1%SO<sub>2</sub> reduced the carburization kinetics of Fe-9Cr-0.5Si alloy significantly (Fig. 7a). Cross-section views in Fig. 7b reveal that addition to the gas of 1% SO<sub>2</sub> prevented breakaway oxidation of Fe-9Cr, achieving largely protective oxidation.

## Conclusions

CO<sub>2</sub>-rich gas produces not only oxidation but also carburization of heat-resisting chromia-forming alloys, accelerating their corrosion. Although carbon activity of the gas is too low for alloy carburization to occur, high carbon activities are produced beneath oxide scales by local equilibrium with the low oxygen activity at the alloy-scale interface. This thermodynamic analysis explains the formation of carbide in low carbon activity CO<sub>2</sub> gas.

Carbon penetration through chromia scales as CO<sub>2</sub> via oxide grain boundaries is confirmed by APT. This suggests possible strategies to resist CO<sub>2</sub> corrosion: alloying with Si and/or Mn to form additional diffusion barriers or modifying grain boundaries by adding sulfur (SO<sub>2</sub>) to the gas. The effectiveness of these methods of enhancing corrosion resistance of chromia-forming alloys in CO<sub>2</sub> gases has been demonstrated.

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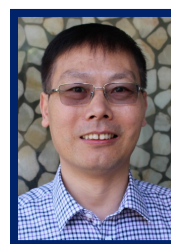


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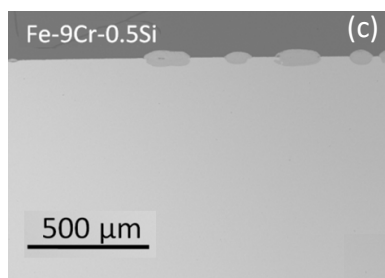
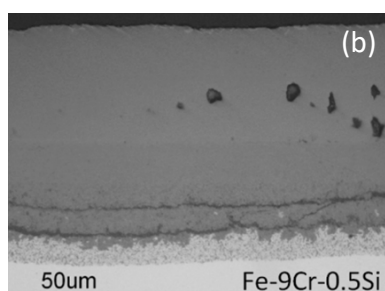
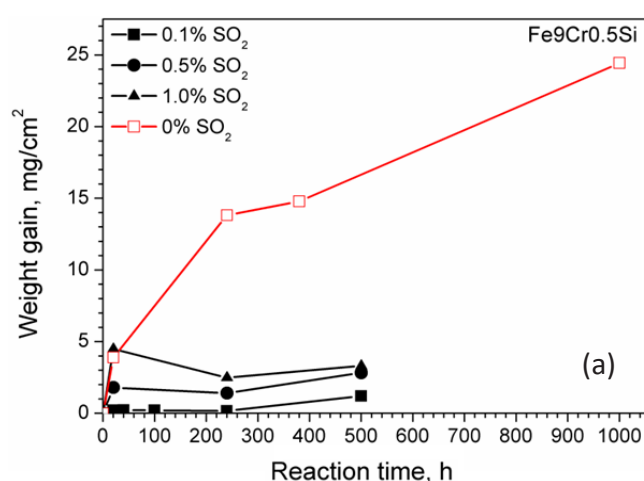
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**FIG. 7.** (a) Weight gain as a function of reaction time for Fe9Cr-0.5Si in Ar-20CO<sub>2</sub>-20H<sub>2</sub>O with and without SO<sub>2</sub>, and cross-sections of this alloy in (b) SO<sub>2</sub>-free gas for 240 h, and (c) 1.0% SO<sub>2</sub> gas for 240 h.

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