Assessment of Corrosive Attack of Fe9Cr1Mo alloys in Pressurised CO_2 for Prediction of Breakaway Oxidation

Supplementary Materials: Derivation of Analytical Solution for Oxidation

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1 Description of moving interface position/velocity governed by 'oxygen' diffusion field

To appeal to the observed parabolic oxidation kinetics, we introduce an oxygen-containing species in the spinel phase region, with its concentration C_{O} governed by:

$$\dot{C}_{\mathrm{O}} = \boldsymbol{\nabla} \cdot \left(D_{\mathrm{O}} \boldsymbol{\nabla} C_{\mathrm{O}}\right) \tag{1}$$

where D_{O} is the diffusion coefficient, as illustrated in Figure 7 in the main text. The initial concentration in the substrate C_{O}°, and boundary concentrations at the magnetite/spinel interface C_{O}^{+} and at the spinel/substrate interface $C_{\mathrm{O}}^{\star}$ are assumed to be constant.

The velocity of the spinel/substrate interface (relative to the magnetite/spinel interface) $\boldsymbol{v}^{+\to\star} = \boldsymbol{v}^{\star}$ is given by the mass balance at the spinel/substrate interface, consistent with:

$$\boldsymbol{v}^{\star}\left(C_{\mathrm{O}}^{\star} - C_{\mathrm{O}}^{\circ}\right) = -D_{\mathrm{O}} \boldsymbol{\nabla} C_{\mathrm{O}}^{\star} \tag{2}$$

The observed oxidation kinetics at the protective region shows parabolic behaviour, for simplicity D_{O} is assumed compositional-independent, i.e.

$$\dot{C}_{\mathrm{O}} = D_{\mathrm{O}} \boldsymbol{\nabla}^2 C_{\mathrm{O}} \tag{3}$$

For a 1D domain relative to the spinel/magnetite interface (i.e. $z_x^{+} = 0$), Equations (2) and (3) have the following explicit solution by using the similarity method (which is detailed in the next two sections),

$$z_x^{\star}\{t\} = \beta \sqrt{D_{\mathrm{O}} t + \left(z_x^{\star,\circ}/\beta\right)^2} \tag{4}$$

where $z_x^{\star,\circ}$ is the initial thickness of the spinel phase region at $t = 0$; the parameter β is defined implicitly as the solution of Equation (5):

$$\sqrt{\pi}\beta\left(C_{\mathrm{O}}^{\star} - C_{\mathrm{O}}^{\circ}\right)\operatorname{erf}\{\beta/2\} = 2\left(C_{\mathrm{O}}^{+} - C_{\mathrm{O}}^{\star}\right)\exp\left\{-\beta^2/4\right\} \tag{5}$$

Here superscripts $^{+}$, *, $^{\diamond}$ and $^{\times}$ denote interfaces of magnetite/spinel, spinel/substrate, gas/substrate and gas/magnetite, respectively.

2 System of equations

For a 1D domain with a fixed left boundary and a moving right boundary, satisfying:

$$\begin{aligned} \dot{C} &= \boldsymbol{\nabla} \cdot (D_{\mathrm{O}} \boldsymbol{\nabla} C) \\ C &= C_0 \quad \text{when } t = 0, \\ C &= C_{\max} \quad \text{at } z_x = 0, \\ C &= C_{\min} \quad \text{at } z_x = X\{t\}, \end{aligned} \tag{6}$$

where $C_{\max}$, $C_{\min}$, D_{O} and C_0 are constants; $X\{t\}$ is the position of the moving interface, with its velocity governed by the mass balance at the interface consistent with:

$$\dot{X}\{t\}(C_{\min} - C^{\star}) = -D_{\mathrm{O}} \frac{\mathrm{d}C}{\mathrm{d}z_x} \tag{7}$$

where $C^{\star}$ is the concentration at the right-hand side of the moving interface $X\{t\}$.

The initial size of the moving domain is X_0, i.e. $X\{0\} = X_0$ where X_0 is a constant.

See illustration in Figure 1 for definitions.

3 Analytical solution by using the similarity method

We modify the well-known similarity method (e.g. Crank [1]) to treat a moving oxidation region in which we have boundary conditions given in Equation (6) at both $z_x = 0$ and on a moving boundary $X\{t\}$. Since in this case we have an initial region $X\{0\} = X_0$ we use the transformation given in Equation (8) below to transform the partial differential equation to an ordinary one.

The time shift t_0 is chosen to satisfy the condition $X\{0\} = X_0$. For consistency, the derived solution requires that the concentration profile for $0 < z_x < X_0$ satisfies Equation (17).

Defining:

$$\eta = \frac{z_x}{\sqrt{D_{\mathrm{O}}(t + t_0)}} \tag{8}$$

we can convert the governing PDE to an ODE:

$$F''\{\eta\} + \frac{\eta}{2} F'\{\eta\} = 0 \tag{9}$$

where $C = F\{\eta\}$.

Solving Equation (9), we have:

$$F\{\eta\} = c_2 + c_1 \cdot \sqrt{\pi} \cdot \operatorname{erf}\{\eta/2\} \tag{10}$$

We also have the boundary condition:

$$\eta = 0 \quad \text{when } F = C_{\max} \tag{11}$$

$$\eta = \beta \quad \text{when } F = C_{\min} \tag{12}$$

where $X\{t\} = \beta\sqrt{D_{\mathrm{O}}\,(t + t_0)}$, is the assumed expression for the moving domain required for the solution of the ordinary Equation (9).

This gives:

$$F\{\eta\} = C_{\max} + \frac{(C_{\min} - C_{\max})\operatorname{erf}\{\eta/2\}}{\operatorname{erf}\{\beta/2\}} \tag{13}$$

and

$$F'\{\eta\} = \frac{(C_{\min} - C_{\max})\exp\left\{-\eta^2/4\right\}}{\sqrt{\pi} \cdot \operatorname{erf}\{\beta/2\}} \tag{14}$$

We can also transform the mass balance Equation (7) as:

$$\frac{\beta}{2}\left(C_{\min} - C^{\star}\right) = -F'\{\beta\} \tag{15}$$

Equations (14) and (15) give $\beta \approx 1.2401$, if $C_{\min} = 0.5$, $C_{\max} = 1$ and $C^{\star} = 0$.

t_0 is obtained from the condition $X\{0\} = X_0$ as:

$$t_0 = \frac{X_0^2}{\beta^2 D_{\mathrm{O}}} \tag{16}$$

Initial concentration profile following Equation (17) in 1D (i.e. $t = 0$ of Equation (13)) should give the initial steady state.

$$C\{z_x\} = C_{\max} + \frac{(C_{\min} - C_{\max})}{\operatorname{erf}\{\beta/2\}}\operatorname{erf}\left\{\frac{\beta z_x}{2X_0}\right\} \tag{17}$$

References

[1] J. Crank, The mathematics of diffusion, Oxford University Press, 1975.

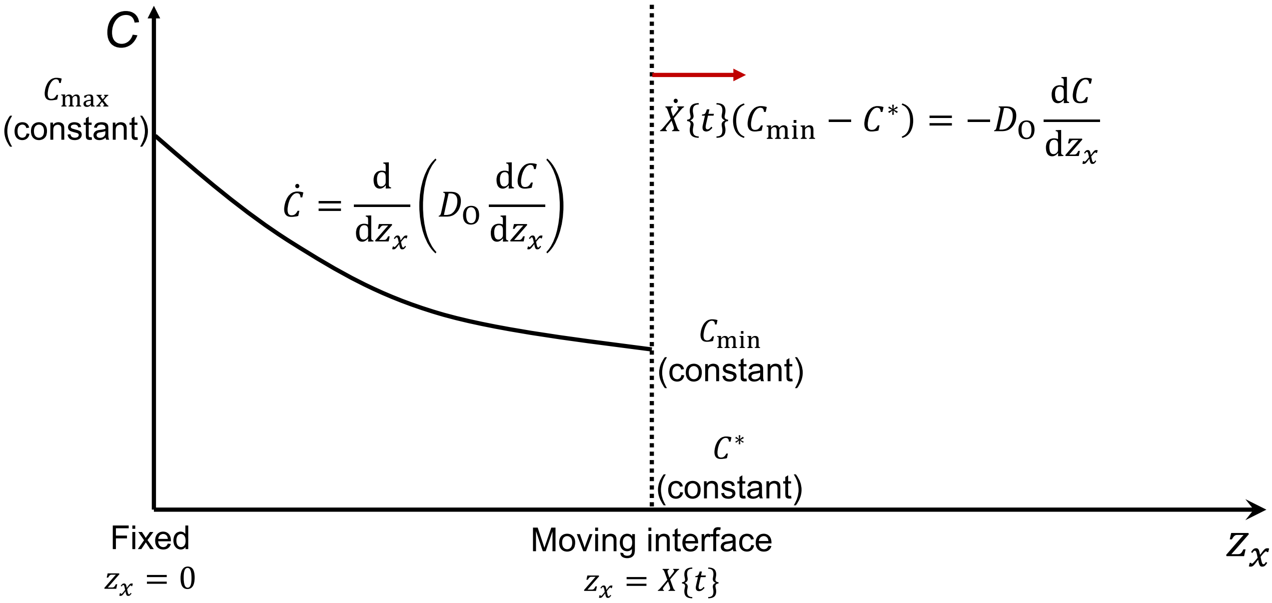

Figure 1: Definitions for solving the moving interface problem.