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# A Model for Mild Steel Oxidation in $CO_2$

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*A model for the oxidation of mild steel in $CO_2$ is proposed, which is an extension of the ideas of Bruckman, Romanski, and Mrowec. A single layer of magnetite forms initially by short-circuit solid-state transport of cations. Lattice vacancies are injected into the underlying metal and eventually cause loss of scale–metal adhesion in some areas. Microchannels develop in the overlying oxide and the scale continues to grow at both oxide–metal and oxide–gas interfaces. In this duplex stage of growth, inner layer oxide nodules form in the vacancy condensation volume produced by departing metal. Their growth is restricted by a build-up of CO released by the oxidation reaction, so that a microporous structure is perpetuated. Breakaway oxidation is the result of local destruction of CO when a catalyst for the Boudouard reaction eventually forms. The inner layer crystals then grow in an atmosphere of higher oxygen potential, and deposited carbon produces a very porous structure.*

## INTRODUCTION

A consistent picture of the morphological development of oxide scales on mild steel in $CO_2$-based atmospheres has emerged from work in various laboratories.[1–5] A compact scale first grows at the scale–gas interface by diffusion of iron outwards. An inner layer of oxide may subsequently nucleate and grow at the scale–metal interface, in the volume made available by departing metal. Oxidation kinetics in both single and double layer stages are protective and approximately parabolic (scale thickness proportional to $\sqrt{t}$). The single-double layer transition may occur nonuniformly on a flat surface, depending on the type of steel and surface preparation, and develops preferentially on convex surfaces and corner sites.

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Formation of double-layered protective oxide seems to be a necessary prerequisite for breakaway oxidation, which has been reported in high pressure ($\gtrsim 10$ atm) $CO_2$. The porous breakaway oxide nucleates and grows entirely at the scale–gas interface, and gives rise to rapid linear oxidation kinetics. If nucleation is nonuniform, breakaway excrescences disrupt the overlying protective scale. Otherwise, the protective oxide is simply translated outwards from the metal surface. There is no definite association of scale stresses of either sign with protective oxidation, but there is a large compressive stress in breakaway scale.[5]

Duplex scale grows at a slow decreasing rate at both scale–metal and scale–gas interfaces. It is compact and has a low carbon content, $\lesssim 1$ wt. %. In contrast, breakaway oxide grows only in the vicinity of the scale–metal interface. It is very porous and contains a significant amount of carbon, generally $\sim 5$ wt. %. Both protective and breakaway scales are magnetite ($Fe_3O_4$), and are formed mainly by the reaction

$$3Fe + 4CO_2 \rightarrow Fe_3O_4 + 4CO \qquad (1)$$

Some oxide may be formed from water vapor when this is present. Carbon deposited in the oxide or injected into the metal is thought[2] to arise from CO liberated by the oxidation reaction (1). This CO disproportionates according to the Boudouard reaction,

$$2CO \rightarrow CO_2 + C \qquad (2)$$

This process of carbon deposition is favored by a high external $CO_2$ pressure[2] and seems to play a vital role in the nucleation and growth of breakaway oxide.[5]

Several investigators have discussed the mechanisms of protective and breakaway oxidation. Antill *et al.*[2] proposed solid state diffusion of iron in magnetite as the rate-controlling process in the protective stage, with scale dissociation at voids as a possible mechanism of inner layer growth. Breakaway oxidation was attributed to continual mechanical breakdown of the scale as a result of carbon deposited from the Boudouard reaction at the scale–metal interface. An alternative "vapor phase transport" mechanism was proposed by Surman and Castle.[6] These authors suggested that a volatile compound of iron is formed in CO-rich gas at the scale–metal interface and diffuses out through microchannels in the scale, to (decompose and) be oxidized at the scale–gas interface. Inner layer crystals grow in the volume made available by departing metal. A breakaway process was not clearly defined, but assumed to be associated with layer cracking to preserve a short constant diffusion distance for transport of volatile compounds.

This paper develops a new model for protective and breakaway corrosion of mild steel in $CO_2$-based gas mixtures, based on the earlier theories of Bruckman and Romanski[7] and Mrowec *et al.*[8–10] Inner layer growth is assumed to be the result of continual condensation of metal lattice vacancies injected by outward diffusion of cations,[11] and a build-up of CO at the scale–metal interface is invoked to explain the perpetuation of a microporous scale. The catalyzed destruction of CO with accompanying carbon

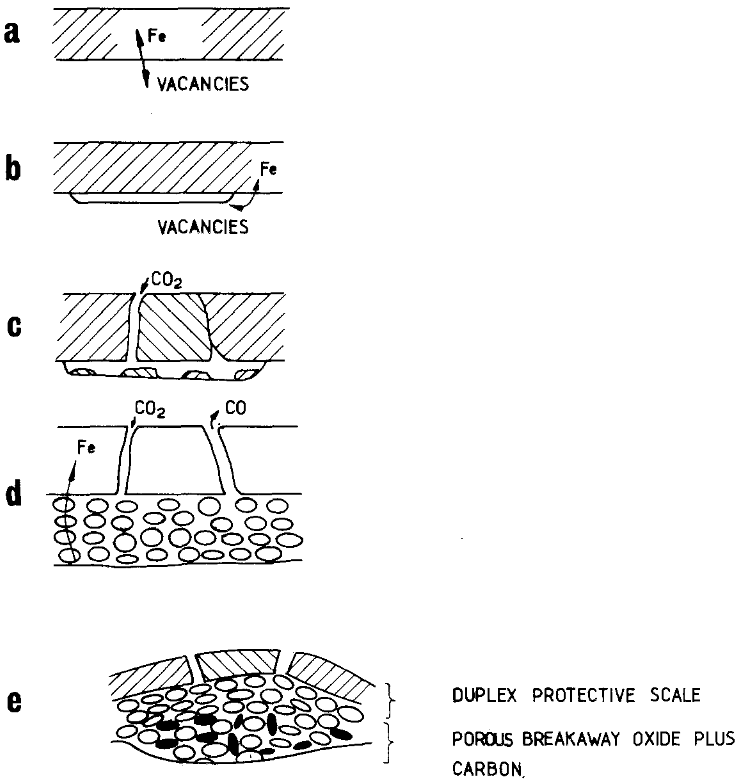

**Fig. 1.** A model for protective and breakaway oxidation of mild steel in $CO_2$. (a) Scale grows initially by cation diffusion outwards. (b) Vacancies are injected and lead to loss of scale–metal adhesion. (c) Oxide above voidage develops microchannels by cracking and/or dissociation along grain boundaries. (d) CO builds up at the scale–metal interface as a result of the oxidation reaction $3Fe + 4CO_2 \rightarrow Fe_3O_4 + 4CO$ and restricts local crystal growth so that a microporous structure is perpetuated. (e) Eventually a Boudouard catalyst is generated at the scale–metal interface. CO is then destroyed rapidly by the Boudouard reaction $2CO \rightarrow CO_2 + C$. The fall in local CO levels leads to rapid (breakaway) growth of inner layer crystals. Carbon deposited between crystals prevents complete sintering of the scale.

deposition is invoked to explain the nucleation and growth of breakaway oxide, but by a mechanism different from that proposed by Antill *et al.*[2]

## A MODEL FOR OXIDATION IN $CO_2$

The model described in this section is illustrated schematically in Fig. 1.

(a) A compact scale of $Fe_3O_4$ grows initially at the scale–gas interface by solid-state diffusion of iron outwards. In the temperature range of interest (350–550°C), iron diffusion is predominantly along "short-circuit" paths such as dislocations and grain boundaries in the oxide.

(b) Metal ions entering the oxide leave behind metal lattice vacancies.[11] Some of these may condense to give local loss of adhesion at the scale–metal interface. Scale–metal separation may also occur when vacancies are annihilated at the interface or within the metal, if the scale is not sufficiently plastic to maintain contact with the shrinking metal substrate. For obvious geometrical reasons, loss of adhesion is favored over convex surfaces and on corner sites.

(c) Oxide scale above a void is mechanically and thermodynamically unstable, and may develop microchannels by anisotropic dissociation or cracking. This possibility was pointed out some years ago by Bruckman and Romanski.[7]

(d) Once microchannels have been established, $CO_2$ has access to the scale–metal interface. The scale then continues to grow by reaction (1) at both scale–metal and scale–gas interfaces. At the scale–metal interface, the growth of an individual oxide crystal follows the scheme illustrated in Fig. 2. It is undercut by further vacancy condensation as it grows.

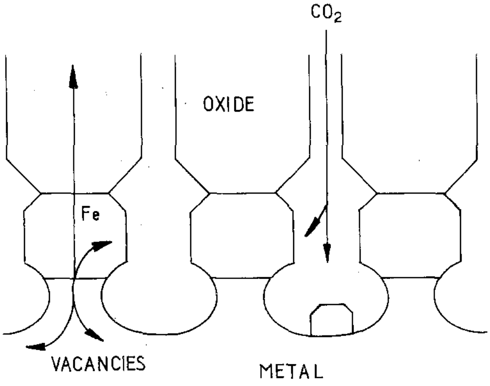

**Fig. 2.** Schematic diagram of oxide growth at the scale–metal interface, showing undercutting of oxide crystals by injected vacancies.

If protective scale is to continue to grow at the scale–metal interface indefinitely, a microporous structure must be perpetuated. That is, individual oxide crystals must be completely undercut before they completely fill the volume available for growth. This is possible because reaction (1) liberates CO which can escape only by diffusing out across the scale. (The low carbon content of protective scale shows that the Boudouard reaction is slow in this stage.) Accordingly, the $CO/CO_2$ ratio at the scale–metal interface rises toward the redox value and stifles local crystal growth.

In the duplex stage of growth, iron continues to be removed by short-circuit solid-state transport outwards. The inner layer of oxide then grows at the same rate as the outer layer in the vacancy volume made available.

(e) The $CO$–$CO_2$ gas mixture generated at the oxide–metal interface is carburizing with respect to iron. It is well known that if iron is exposed to a carburizing mixture for a prolonged period, it develops catalytic activity, allowing the Boudouard reaction (2) to proceed at a rapid rate. This is favored in high-pressure gas. When it happens at the oxide–metal interface there are two important consequences:

(i) The $CO/CO_2$ ratio drops because of the rapid destruction of CO. Thus, the oxygen potential of the local gas mixture rises and oxide crystals grow rapidly.

(ii) Carbon is deposited between the growing oxide crystals so that the scale cannot sinter up and become protective again. This is breakaway oxidation. An incidental consequence of carbon deposition is that oxide crystals may continue to grow at points of contact, if porous carbon is sandwiched between them. Compressive stresses will therefore develop in breakaway scale.

Experimental and theoretical evidence in support of this model is discussed below, with particular emphasis on the importance of solid-state rather than vapor phase transport of cations.

## THE IRON TRANSPORT MECHANISM

Table I gives typical parabolic rate constants for the growth of protective scales. Although they are clearly too large to be accounted for by lattice diffusion of iron in magnetite,[6] they are readily explained by short-circuit transport.[12] The associated activation energy[13] ($118 \pm 8$ kJ mole$^{-1}$) is also in the range anticipated for grain-boundary or dislocation-pipe diffusion.

It is clear from the table that there is no great difference between parabolic rate constants for growth of single and duplex oxide layers. When scale growth is only at the oxide–gas interface, there is no possibility of

Table I. Parabolic Rate Constants for Iron and Rimming Steel Oxidized in $CO_2$ at 773°K

| Material | Atmosphere | Scale structure | $k_p$, mg$^2$ cm$^{-4}$ h$^{-1}$ | Reference |
|---|---|---|---|---|
| Rimming steel | "Wet" $CO_2$, 2.8 MN/m$^2$ | Single layer | $1.9 \times 10^{-2}$ | Rowlands[4] |
| | "Wet" $CO_2$, 2.8 MN/m$^2$ | Single layer | $3.5 \times 10^{-2}$ | Gibbs *et al.*[5] |
| | "Dry" $CO_2$, $10^5$ N/m$^2$ | Single layer | $1.2 \times 10^{-2}$ | Price[19] |
| | "Dry" $CO_2$, 2.0 MN/m$^2$ | Double layer | $2.3 \times 10^{-2}$ | Antill *et al.*[2] |
| | "Wet" $CO_2$, 2.0 MN/m$^2$ | Double layer | $4.9 \times 10^{-3}$ | Antill *et al.*[2] |
| | "Wet" $CO_2$ + CO $10^5$N/m$^2$ | Double layer | $5.0 \times 10^{-3}$ | Antill *et al.*[2] |
| Pure iron | "Wet" $CO_2$, 2.8 MN/m$^2$ | Double layer | $7.1 \times 10^{-2}$ | Gibbs *et al.*[5] |
| | "Dry" $CO_2$, 2.0 MN/m$^2$ | Double layer | $3.4 \times 10^{-2}$ | Antill *et al.*[2] |
| | "Wet" $CO_2$, 2.0 MN/m$^2$ | Double layer | $1.4 \times 10^{-2}$ | Antill *et al.*[2] |
| | "Wet" $CO_2$ + CO $10^5$N/m$^2$ | Double layer | $4.0 \times 10^{-2}$ | Antill *et al.*[2] |
| | "Dry" $CO_2$, 13 kN/m$^2$ | Single layer | $3.4 \times 10^{-2}$ | Graham[20] |
| | "Dry" $CO_2$, $10^5$ N/m$^2$ | Single layer | $1.1 \times 10^{-2}$ | Curtis *et al.*[13] |

formation of volatile compounds at the metal surface. Thus, the fact that rates do not change dramatically when an inner layer forms argues qualitatively against a significant amount of vapor phase transport of iron. A quantitative argument is developed in the next section.

Solid state diffusion of iron across a magnetite scale grown on pure iron in oxygen has been investigated by Channing and Graham.[14] These authors oxidized foils to completion, the final specimens consisting of magnetite with an outer layer of $Fe_2O_3$. The reduction of $Fe_2O_3$ by iron diffusion across the magnetite was then followed by a Mossbauer absorption technique after successive vacuum anneals. In these conditions vapor phase transport is not possible, but an iron diffusion rate was observed which is adequate to account for the rate of protective oxidation. Further, the associated activation energy 126 ± 20 kJ mole$^{-1}$ agreed with that for the oxidation process.

## GASEOUS DIFFUSION ACROSS A PROTECTIVE SCALE

Both the present model and the "vapor phase transport" model for duplex scale growth propose diffusion of gaseous species through microporosity in the protective oxide. It is important to establish whether the diffusion coefficients required for the various species are mutually compatible, and reasonable for a scale with the observed structure.

### An Upper Limit

An upper limit for gaseous diffusion across protective scale may be estimated from the proximity of its density to that of nonporous oxide.

From the growth morphology of inner layer oxide it may be deduced that there is of the order of one microchannel per grain of oxide in a given cross section, and connected porosity must completely traverse the scale. If A is the cross-sectioned area of a channel, the fractional decrease in density associated with microporosity becomes

$$(\Delta\rho/\rho) \sim (A/d^2) \qquad (3)$$

where $d$ is the grain diameter. Two extreme forms of microchannel may be envisaged, "tubes" of diameter $\Delta d \sim A^{1/2}$ or grain-boundary channels with $A \sim d\Delta d$. The first assumption gives the larger value of $\Delta d$, and hence of diffusivity in a channel, and will be used here to calculate the limiting diffusivity. Measurements of the Pilling–Bedworth ratio of protective scale[5] and of the volume density of iron indicate that $\Delta\rho/\rho < 5 \times 10^{-2}$. Using a typical oxide grain size $d \sim 1\ \mu m$, the upper limit for $\Delta d$ is $\sim 2 \times 10^{-7}$ m. This is of the order of the mean-free path of a molecule in bulk gas, so that diffusion in a microchannel is dominated by collisions between molecules and the walls of the channel: Knudsen flow. The diffusivity in a channel is therefore[15]

$$D_k = (\Delta d/3)(8kT/\pi M)^{1/2} \qquad (4)$$

where $M$ is the mass of a diffusing molecule. The average diffusivity of gas across an area containing several microchannels is

$$D \sim (A/d^2)D_k \qquad (5)$$

Substituting $\Delta d \sim 2 \times 10^{-7}$ m in Eq. (4) together with $M \sim 7.4 \times 10^{-26}$ kg for a $CO_2$ molecule gives $D_k \sim 8 \times 10^{-5}\ m^2\ sec^{-1}$ at 773°K. From Eq. (5), an upper limit for the average diffusivity across a scale which falls 5% below theoretical density is $4 \times 10^{-6}\ m^2\ sec^{-1}$. A more realistic estimate, which allows for tortuosity of microchannels and assumes only 1% departure from theoretical density, reduces this value by about a factor of ten. Since it is unlikely that all of the porosity revealed by metallography and density measurements is connected, the actual diffusivity across a scale may be very much less than the upper limit:

$$D \lesssim 4 \times 10^{-7}\ m^2\ sec^{-1}$$

## Inner Layer Growth

A minimum value for the average diffusivity required to support inner layer growth may be deduced from the parabolic rate constant in the duplex stage of growth and the external $CO_2$ pressure. If $k_p$ is the rate constant expressed in units of $kg^2\ m^{-4}\ sec^{-1}$ and $W$ is the weight gain at thickness

$\Delta X$, the effective flow of oxygen molecules to the scale–metal interface must be

$$j_{O_2} = (k_p/4\,Wm) \text{ molecules m}^{-2}\text{ sec}^{-1} \tag{6}$$

where $m$ is the molecular mass in kilograms. Using typical values of $k_p = 2 \times 10^{-9}\text{ kg}^2\text{ m}^{-4}\text{ sec}^{-1}$, $W = 4 \times 10^{-2}\text{ kg m}^{-2}$ ($\Delta X = 30\,\mu\text{m}$) and $m = 5.4 \times 10^{-26}$ kg, the oxygen flux at 773 K is

$$j_{O_2} = 9.2 \times 10^{17} \text{ molecules m}^{-2}\text{ sec}^{-1}$$

Assuming that oxygen "molecules" are transported to the scale–metal interface as $CO_2$, the maximum possible concentration gradient driving diffusion is that for which the $CO_2$ concentration falls almost to zero at this interface. If $p$ is the external $CO_2$ pressure in N m$^{-2}$, the molecular concentration there is $c = (p/kt)$ molecules $m^{-3}$ and the maximum concentration gradient is $(c/\Delta X)$. Using Fick's first law

$$j = D(c/\Delta X) \tag{7}$$

the corresponding minimum diffusivity at 773°K for $p = 10^5\text{ N m}^{-2}$ (1 atm) is

$$D \sim 3 \times 10^{-12}\text{ m}^2\text{ sec}^{-1}$$

It is clear that scales of the observed density could easily have the required amount of connected porosity.

## Diffusion of Volatile Compounds

The calculation of the preceding section may be repeated for the diffusion of volatile compounds in the vapor phase transport model. The nature of the compounds has not been stated, but they are likely to have of the order of one iron atom per molecule.[16] Since the oxide composition is $Fe_3O_4$ and both layers of oxide grow at essentially identical rates,

$$j_{Fe} = (\tfrac{2}{3})j_{O_2} \tag{8}$$

Laboratory experiments with various gas mixtures have shown that volatile compounds formed at the scale–metal interface must represent $\lesssim 10$ vpm of the gas mixture.[16] Since the number of molecules of gas does not change during reaction (1), the total gas pressure at the scale–metal interface cannot exceed the external gas pressure and the maximum concentration gradient which could drive diffusion of volatile compounds is $(10^{-5}\,p/kT\Delta x)$. The minimum diffusivity required to account for outer layer growth when $T = 773$°K and $p = 10^5\text{ N m}^{-2}$ is therefore

$$D \sim 2 \times 10^{-7}\text{ m}^2\text{ sec}^{-1}$$

This is close to the upper limit estimated from scale density, and it will be shown in the next section that a diffusivity this high cannot support the required build-up of CO at the scale–metal interface.

## Volatile Compounds and the Build-up of CO

It seems to be generally agreed[2,6,17] that CO builds up at the scale–metal interface during protective oxidation until the local gas composition approaches the redox composition ($\sim 30\%$ CO). A high CO level is *essential* before volatile compounds of iron can form.[6,16]

It is possible to calculate the interfacial level of CO from certain limiting assumptions. If the CO produced by reaction (1) is lost only by outward diffusion, dynamic equilibrium requires that

$$j_{CO} = j_{CO_2} \tag{9}$$

Defining gas concentrations as in Fig. 3 and equating diffusivities of CO and $CO_2$, Eq. (9) may be rearranged using Fick's first law to give

$$(C_2/C_1) = [(C/C_1) - 1] + C_3/C_1$$

Duplex scale may form in pure flowing $CO_2$, and it is therefore permissible to consider the simpler case with $C_3$ set equal to zero. Using Fick's law again,

$$(C_2/C_1) = (1 - j_{CO_2}\,\Delta x/CD)^{-1} - 1 \tag{10}$$

If Eq. (10) is applied to duplex scale growth at 773°K as before, the diffusivity required to make $(C_2/C_1) = 0.43$ (30% CO) is found to be

$$D \sim 9.2 \times 10^{-12}\ \mathrm{m^2\,sec^{-1}}$$

Using this diffusion coefficient in the calculation of the previous section, the flux of volatile compounds of iron is found to be four orders of magnitude

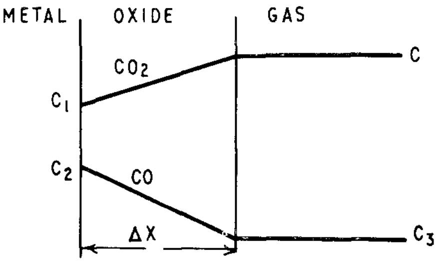

**Fig. 3.** Schematic representation of the variation of gas composition across a duplex oxide scale.

too small to account for outer layer growth. On the other hand, if gaseous diffusivity were as high as $2 \times 10^{-7}\,\mathrm{m}^2\,\mathrm{sec}^{-1}$, Eq. (10) shows that there would be no appreciable elevation of the CO level at the interface and volatile compounds could not form. This argument is strengthened if some CO is removed by volatile compound formation or by the Boudouard reaction. It must be concluded that volatile compounds of iron formed at the scale–metal interface do not make a significant contribution to outer layer growth.

## BREAKAWAY OXIDATION

During the protective oxidation of mild steel, carbide and sulfide particles originally present in the steel are included unoxidized in the inner layer of duplex scale.[1] This implies a low local oxygen activity and is consistent with the build-up of CO at the scale–metal interface, as described in previous sections. The onset of breakaway oxidation is characterized by the oxidation of these particles. This is consistent with the elevation of oxygen potential associated with the fall in local CO level at the start of a rapid Boudouard reaction. The association of the onset of breakaway oxidation with the formation of a Boudouard catalyst is also supported by the observation[2] that the carbon content of breakaway oxide is usually $\sim 5$ wt.%, whereas protective oxide contains $\lesssim 0.5$ wt.%. Finally, carburization, which is known to favor early formation of a Boudouard catalyst,[18] promotes the early onset of breakaway.

The morphology and growth kinetics of breakaway oxide lend additional support to the idea that rapid breakaway growth is a consequence of an increase in local oxygen activity. The nodular grain structure of breakaway oxide is indistinguishable from that of inner-layer protective oxide in the scanning electron microscope.[19] Breakaway oxide grains simply grow to the same size ($\sim 1\,\mu$m) at a faster rate. If individual nodules grow parabolically with a rate constant $k_p$, this should be related to the effective linear rate constant in breakaway $k_l$ by

$$k_p = (Wk_l/2) \tag{11}$$

where $W$ is the weight gain per unit area corresponding to a monolayer of crystals. At 773°K, Rowlands[4] finds $k_l = 3.1 \times 10^{-7}\,\mathrm{kg \cdot m^{-2}\,sec^{-1}}$ and the oxide grain size of $1\,\mu$m corresponds to $W \sim 1.3 \times 10^{-3}\,\mathrm{kg \cdot m^{-2}}$. Substituting into Eq. (11), this implies a parabolic rate constant $k_p \sim 2 \times 10^{-10}$ $\mathrm{kg^2\,mg^{-4}\,sec^{-1}}$. This is only slightly less than the parabolic rate constant observed for protective oxidation of the same material in $CO_2$ with a very low level of CO.

It follows from the above arguments that surface treatments or gas phase additions which inhibit the Boudouard reaction should also inhibit breakaway oxidation. This has now been confirmed, and the experiments will form the subject of a future paper.

## CONCLUSIONS

The rate-controlling process during the protective oxidation of mild steel in $CO_2$ is short-circuit solid state transport of cations. Volatile compounds of iron do not make a significant contribution to the outward flow of metal.

The inner layer of oxide of duplex scale grows in the vacancy-condensation volume made available by departing metal. A build-up of CO produced by the oxidation reaction controls the growth of oxide crystals at the scale–metal interface, so as to maintain a microporous structure.

If the CO generated at the scale–metal interface is destroyed locally by the Boudouard reaction, the local oxygen potential is raised. Oxide crystals then grow more rapidly but do not completely sinter because of the deposited carbon. This accounts for rapid breakaway attack in high-pressure gas.

The incubation period for breakaway oxidation is the time required to generate a Boudouard catalyst at the scale–metal interface.

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