

## **The Scaling of Iron in Oxygen- and Sulfur-Containing Gases**

**Alfred Rahmel\***

*Received December 18, 1974*

---

*The following possible conditions for the simultaneous formation of oxide and sulfide on iron in oxygen- and sulfur-containing gases are considered: (1) simultaneous thermodynamic stability of oxide and sulfide; (2) temporal changes in gas composition; (3) intermediary cracking of the oxide film; (4) solubility and diffusion of sulfur in the oxide (lattice diffusion); (5) kinetic conditions for simultaneous oxide and sulfide formation at the scale-gas interface.*

---

**KEY WORDS:** oxidation-sulfidation; iron; oxygen; sulfur compounds.

### **INTRODUCTION**

The kinetics and mechanism of the reactions of metals and alloys with *one* gaseous oxidant, for example, with oxygen or gaseous sulfur, have been investigated relatively frequently and are today fairly well understood because of the fundamental studies of Carl Wagner.<sup>1-3</sup> In technical processes however, metals are seldom exposed to gases with only one oxidant. The main sources of energy are still fossilic fuels such as coal, oil, and natural gas. The combustion gases of these fuels very frequently contain oxygen *and* sulfur, or compounds of these two elements.

The engineer does not desire the formation of sulfides during the heating of metals in such gases, because sulfide formation increases or can increase

\*Dechema-Institut, Frankfurt am Main, Federal Republic of Germany.

the scaling rates of metals and because sulfide formation can have disadvantageous effects on the processing and welding properties of metallic materials. The old question of the conditions under which sulfides form alongside oxides and how sulfide formation can be prevented in technical processes is therefore still of great interest. A large body of practical experience has been gathered concerning this, for example, combustion of the S-containing fuel with a great excess of air, but our scientific understanding of the processes is still rather incomplete. Thermodynamic investigations of the equilibria in the gases, between gases and metals, and between gases, metals, oxides, and sulfides do not suffice alone. They must be supplemented by kinetic investigations.

In recent years, scientific workers have also made increased efforts to cast more light on the processes which occur when gases with two or more oxidants are brought into contact with metals. Apart from the simultaneous formation of oxides and sulfides, industry is also interested in other simultaneous reactions, for example, simultaneous oxidation and nitriding and simultaneous oxidation and carburization. Findings obtained in investigations of simultaneous oxide and sulfide formation can therefore contribute to an understanding of simultaneous oxidation and nitriding or simultaneous oxidation and carburization, and *vice versa*.

The following represents an attempt to summarize present knowledge of the behavior of iron in gases containing sulfur and oxygen and, in particular, the prerequisites to the simultaneous formation of oxide and sulfide.

### POSSIBLE CONDITIONS FOR THE SIMULTANEOUS FORMATION OF OXIDE AND SULFIDE

If a scale consists of oxide and sulfide, there are, in principle, several possible ways of explaining its formation :

1. The gas composition was such that oxide and sulfide were thermodynamically stable at the same time.
2. The composition of the gas varied over the course of time, so that oxide and sulfide were alternately stable and formed.
3. Intermediary cracking of the scale occurred, so that gas could penetrate through fine cracks to the interior of the scale or even to the surface of the metal.
4. Sulfur was soluble in the oxide and diffused through the oxide layer to the metal-scale phase boundary (lattice diffusion).
5. Simultaneous formation of oxide and sulfide occurred at the scale-gas phase boundary for reasons of reaction kinetics.

The alternatives are briefly discussed in the following.

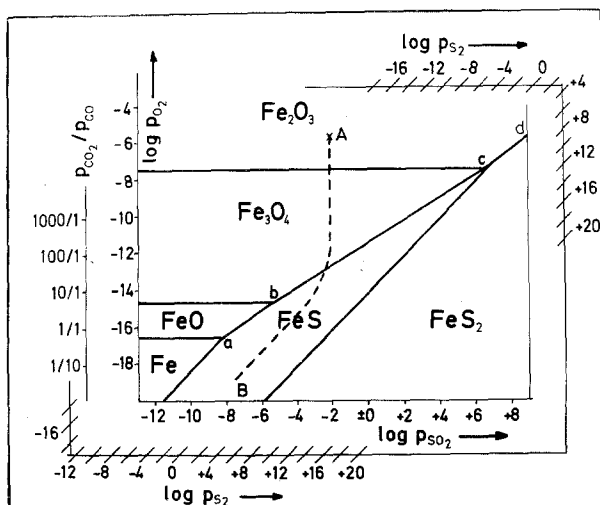


Fig. 1. Isothermal section of the system Fe-O-S at 900°C.

### Simultaneous Thermodynamic Stability of Oxide and Sulfide

The phase diagram Fe-S-O can be used to clarify this question. Figure 1 shows an isothermal section at 900°C. One notes that there is no field in which oxide and sulfide can coexist. Oxide and sulfide coexist only along the lines a-b, b-c, and c-d. The corresponding oxygen and sulfur pressures are exactly defined along these lines. The question of whether oxide and sulfide really form simultaneously in such gases has apparently not been investigated until now. Such experiments would also be difficult to perform, as small changes in gas composition could lead to conditions such as are discussed in the section Kinetic Conditions for Simultaneous Oxide and Sulfide Formation at the Scale-Gas Phase Boundary. This question has no technical significance; such exactly defined gas mixtures are not found in practice.

### Temporal Changes in Gas Composition

If the composition of gas varies over the course of time in such a way that oxide and sulfide are alternately stable, one should find a layered structure of alternating oxides and sulfides parallel to the metal surface. Unpublished laboratory experiments show that oxide and sulfide do in fact form alternating layers on iron. The prerequisite to this is, however, that diffusion in the scale is the rate-determining step in both oxidation and sulfidation (*cf.* the section Kinetic Conditions for Simultaneous Oxide and Sulfide Formation at the Scale-Gas Phase Boundary). This layered structure of

the scale, however, does not lead to a sharp increase in scaling rate, because the oxide layer or layers have an inhibiting effect.<sup>4</sup> In such a structure, the diffusion of the iron ions through the oxide layer is in fact usually the slowest step. Only when sulfide is deposited on the iron as the first step is its formation uninhibited. The formation of a second sulfide layer over an oxide film is inhibited by the oxide.

In the previous laboratory experiments, the atmosphere was only altered at time intervals of > 30 min. It still remains to investigate whether layer growth is also possible with very rapid changes of atmosphere. It is possible that a certain minimum time is necessary for the formation of complete layers. However, rapid changing of the composition of combustion gases must be expected in technical plants in which fossilic fuels are burned.

### Intermediary Cracking of the Oxide Film

If intermediary cracking of the oxide film occurs as a result of "growth stresses," the reaction gas can penetrate through fine cracks to the interior of the scale or even as far as the surface of the metal. In a growing oxide layer, oxygen activity decreases with depth. Due to the equilibria in the Fe-S-O system, sulfides can then be formed in the deeper part of the oxide for thermodynamic reasons. If, for example, a gas with the oxygen and sulfur partial pressures of point A in Fig. 1 reached the interior of the oxide layer, the gas composition would—given equilibrium between gas phase and solid (but without sulfide formation)—alter along the broken line A-B because the oxygen activity of the oxide decreases toward the interior. Sulfide formation would be thermodynamically possible at the intersection of the broken line A-B and the line c-b of the equilibrium Fe<sub>3</sub>O<sub>4</sub>-FeS. This corresponds to an oxygen partial pressure of about 10<sup>-13</sup> atm. Sulfide formation within the Fe<sub>3</sub>O<sub>4</sub> layer is therefore already possible in this case. The composition of the gas would then alter along the line A-B if no sulfide formation occurred. Because, however, sulfide formation begins at the intersection A-B-b-c, the gas will in fact alter along the line b-c and a-b on reaching the intersection A-B-b-c.

At what depth within the oxide film sulfide formation is possible depends on the sulfur content of the external gas. Sulfide formation is, however, only possible above a critical sulfur content of the gas; this is the case by virtue of the fact that the sulfur partial pressure must be greater than that of the Fe-FeS equilibrium at the oxygen partial pressure of the equilibrium Fe-FeO. In a gas which contains only the elements S and O and in which the sulfur and oxygen partial pressure is given by the equilibrium constant

$$K_1 = p_{\text{SO}_2}^2 / (p_{\text{S}_2} \cdot p_{\text{O}_2}^2) \quad (1)$$

according to the equilibrium of the reaction



the condition for sulfide formation is

$$p_{\text{S}_2} + \frac{1}{2}p_{\text{SO}_2} \geq p_{\text{S}_2}^{\text{Fe-FeS}} \quad (3)$$

Because the sulfur pressures of the equilibrium Fe-FeS are very small, for example, at 900°C,  $p_{\text{S}_2}^{\text{Fe-FeS}} = 1.3 \cdot 10^{-8}$  atm, even extremely small sulfur contents of the gas suffice to make sulfide formation theoretically possible. Under practical conditions, one will scarcely ever observe a reaction when the S content of the bulk gas is very small, because the amount of sulfur available for a reaction is very limited.

The condition shown in Eq. (3) is correct only for pure O<sub>2</sub>-SO<sub>2</sub>-S<sub>2</sub> mixtures. The reactions in technical combustion gases from fossilic fuels are more complex, because compounds of the elements H and C are also present. Here, one must consider further equilibria with, for example, H<sub>2</sub>S and COS.

The remarks on the formation of FeS in an oxide layer naturally also apply in the reverse case of the formation of oxide in sulfide layers. The above remarks not only apply to the system Fe-S-O but also can be formulated more generally for the systems Me-S-O. Analogous considerations can also be made for simultaneous oxidation and carburization and simultaneous oxidation and nitriding.<sup>5</sup>

### Solubility and Diffusion of Sulfur in the Oxide (Lattice Diffusion)

Sulfur can penetrate into an oxide layer in two fundamentally different ways: either in the form of gas through cracks and other mechanical faults in the oxide layer, or by lattice diffusion as a consequence of sulfur solubility in the oxide. Unfortunately, the literature provides very little information as to the solubility and diffusion of sulfur in oxides. According to Kor and Richardson,<sup>6</sup> sulfur is only very sparingly soluble in alkaline earth oxides at 1500 and 1600°C. Birks and Tattam<sup>7</sup> stated that sulfur could be soluble in NiO, but no quantitative measurements have been published. The surprisingly high diffusion coefficient of sulfur in Cr<sub>2</sub>O<sub>3</sub> has not been clearly proved to result from lattice diffusion.<sup>8</sup> According to Kor and Turkdogan,<sup>9</sup> FeO dissolves about 140 ppm sulfur at 1250°C; according to Kor,<sup>10</sup> the diffusion coefficient of sulfur in FeO is of the same order as the self-diffusion coefficient of iron in FeO which is in equilibrium with metallic iron.

Although the question of the solubility and diffusion of sulfur through oxides has not yet been clarified, one must give consideration to such a possibility. Certain prerequisites, however, must be fulfilled for sulfide formation in an oxide layer or at the metal-scale phase boundary. Sulfide

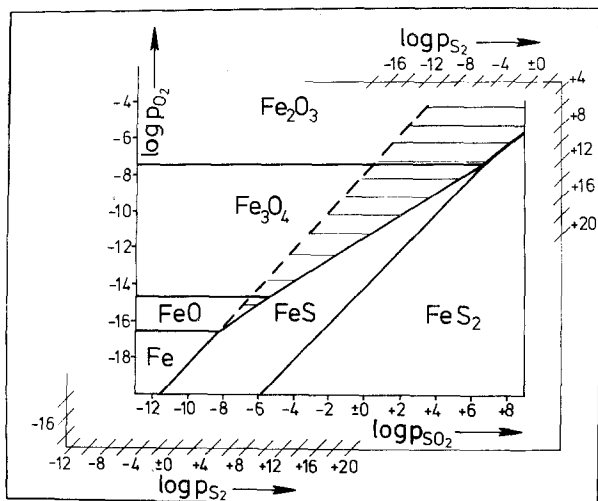


Fig. 2. Isothermal section of the system Fe-O-S at 900°C.

formation is possible only when the sulfur activity in the oxide or at the metal-scale phase boundary is greater than the sulfur activity of the Fe-FeS equilibrium. If the sulfur diffuses through the oxide layer from the oxide-gas phase boundary to the metal-scale interface, sulfur activity at the latter can only be less or equal to that at the oxide-gas phase boundary. For sulfide formation the following condition must be fulfilled:

$$p_{S_2}^{\text{gas}} \geq p_{S_2}^{\text{Fe-FeS}} \quad (4)$$

The condition (4) therefore differs from the condition for the formation of sulfides as a result of cracks in the oxide layer, which is given by Eq. (3). If one once again considers the isothermal section through the system Fe-S-O, the condition (4) is fulfilled in the shaded portion of Fig. 2. Until now no reports have been published on experiments which take into consideration the differing conditions for sulfide formation in oxides as the result of crack formation and lattice diffusion of the sulfur.

Analogous conditions apply for the formation of oxide in or under a dense sulfide layer due to the solubility and lattice diffusion of oxygen in sulfides.

#### Kinetic Conditions for Simultaneous Oxide and Sulfide Formation at the Scale-Gas Phase Boundary

The kinetic conditions for the simultaneous formation of oxide and sulfide at the scale-gas phase boundary in the reaction of iron in gases con-

Rate-determining step of reaction	Rate law	Concentration gradients in the scale and in the convective diffusion boundary layer	Effect of second oxidant on	
			1. rate	2. Composition of scale
Reaction at the Fe/FeX phase boundary	complex		no effect	Fe-oxides or Fe-sulfides
Diffusion in FeX	parabolic $x^2 = k \cdot t$		no effect	Fe-oxides or Fe-sulfides
Reaction at the FeX/X2 phase boundary	linear $x = l \cdot t$		rate increases	FeO + FeS
Transport in the gas phase	linear $x = l' \cdot t$		rate increases	FeO + FeS

Fig. 3. Influence of the second oxidant on the oxidation or sulfidation of iron depending on the rate-determining steps of the reaction.

taining sulfur and oxygen have been studied in more detail in recent years. A summary report was published recently.<sup>11</sup> The decisive factor is the rate-determining step of phase formation, which because of the bulk composition of the gas is thermodynamically stable. If, for example, oxide is the stable phase in a gas containing sulfur and oxygen, oxide and sulfide will always be simultaneously formed when either the transport of the oxygen from the gas to the surface of the scale or the reaction at the scale-gas phase boundary is rate-determining. If, on the other hand, the diffusion in the scale or the reaction at the metal-scale interface is the rate-determining step, only oxide—the thermodynamically stable phase in the gas—will be formed.

The same applies also when not the oxide but the sulfide is thermodynamically stable because of the bulk composition of the gas. The results are summarized in Fig. 3.

Until now these investigations have only been carried out with iron. One may assume that these conditions also apply to other metals on which oxide or sulfide scales grow by outward diffusion of cations and electrons.

### CONCLUSIONS

We have today reached a point at which we have begun to have a better understanding of the reaction of a pure metal with two oxidants. The problem

has some similarities with the oxidation of an alloy with one oxidant.<sup>12</sup> Unfortunately, our knowledge of the thermodynamics of the systems Me-O-S is not complete. There is, in particular, a lack of data on the solubility of sulfides in oxides, and *vice versa*. Better kinetic data, in particular those concerning the diffusion of sulfur in oxide and oxygen in sulfide, would be necessary to allow quantitative estimates. Also necessary in the analysis of the overall problem is a knowledge of the rate-determining step of the oxidation reaction, because the rate-determining step determines the simultaneous formation of oxide and sulfide at the scale-gas phase boundary.

The situation becomes even more complex when the reaction of an alloy in two oxidation agents is to be investigated. Such analyses are at present almost unknown.

## REFERENCES

1. C. Wagner, *Z. Phys. Chem. Abt. B* **21**, 25 (1933).
2. C. Wagner, *Z. Phys. Chem. Abt. B* **32**, 447 (1936).
3. C. Wagner, "Diffusion and High Temperature Oxidation of Metals," in *Atom Movements* (American Society for Metals, Cleveland, 1951), p. 153.
4. A. Rahmel and J. A. Gonzalez, *Corros. Sci.* **13**, 433 (1973).
5. F. S. Pettit, J. A. Goebel, and G. W. Goward, *Corros. Sci.* **9**, 903 (1969).
6. G. J. W. Kor and F. D. Richardson, *Inst. Min. Metall. Trans. Sect. C* **79**, 148 (1970).
7. N. Birks and N. Tattam, *Corros. Sci.* **10**, 857 (1970).
8. A. U. Seybolt, *Trans. Am. Inst. Min. Metall. Pet. Eng.* **242**, 752 (1968).
9. G. J. W. Kor and E. T. Turkdogan, *Metall. Trans.* **2**, 1571 (1971).
10. G. J. W. Kor, *Metall. Trans.* **3**, 2343 (1972).
11. A. Rahmel, *Corros. Sci.* **13**, 125 (1973).
12. C. Wagner, "General Aspects of High-Temperature Corrosion of Structural Materials," in *High Temperature Corrosion of Aerospace Alloys* (AGARD Conference Proceedings No. 120, 1972), p. 3.