

Transport Properties of Sulfide Scales and Sulfidation of Metals and Alloys

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Received November 21, 1984

Defect and transport properties of metal sulfides are discussed, showing the differences from and similarities with oxide systems. The sulfidation kinetics and mechanism of metals and alloys are compared with oxidation processes.

KEY WORDS: defects; diffusion in sulfides and oxides; sulfidation; oxidation of metals and alloys.

Progress in the theory of high-temperature corrosion of metallic materials is closely related to sulfidation processes. The first experimental proof of the validity of Wagner's theory of metal oxidation was obtained 50 years ago by Wagner himself during the sulfidation of silver using the pellet method.¹ That fundamental work is still cited in the literature and has initiated many systematic studies of the kinetics and mechanism of metal sulfidation, contributing greatly to a better understanding of not only sulfide corrosion but also to the general rules governing gas corrosion phenomena. In this paper, actual situations in the field of metal sulfidation are discussed on the basis of defect structures and transport properties of sulfides.

First, it should be stressed that metal sulfides are less stable thermodynamically (Table I) than their corresponding oxides, free energies of their

This paper is a summary of a lecture presented at the Gordon Research Conference on Corrosion, held in New London, New Hampshire, U.S.A., 21-27 July 1983. A complete description of the problem in question has been published in *High Temperature Materials and Processes*, **6**, 1 (1984).

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Table I. Free Energies of Formation for Sulfides and Oxides at 1123 K
(kcal/g atom S or O)^a

Sulfide	$-\Delta G_{1123K}$	Oxide	$-\Delta G_{1123K}$
FeS	21.9	FeO	45.0
NiS	15.4	NiO	32.0
CoO	17.0	CoO	37.5
Cr ₂ S ₃	34.9	Cr ₂ O ₃	66.5
MnS	46.5	MnO	77.5
MoS ₂	18.5	MoO ₂	47.0
TiS	44.0	TiO	98.5
TiS ₂	31.3	TiO ₂	88.5

^aFrom Ref. 2.**Table II.** Melting Points of Some Sulfides and Oxides and Metal-Sulfide Eutectics^a

Sulfide	Melting point (K)	Oxide	Melting point (K)
TiS	2273	TiO	2023
La ₂ S ₃	2353	La ₂ O ₃	2490
Ce ₂ S ₃	2333	Ce ₂ O ₃	1963
NbS ₂	?	NbO ₂	2353
ThS ₂	2198	ThO ₂	3323
US ₂	2123	UO ₂	3113
Y ₂ S ₃	1873	Y ₂ O ₃	2683
CrS	1823	Cr ₂ O ₃	2607
Cr ₂ S ₃	?	MoO ₂	2200
MoS ₂	1431	MnO	2058
MnS	1598 ^b	FeO	1697
FeS	1468	Cu ₂ O	1515
Cu ₂ S	1403	CoO	2083
CoS	1373	Al ₂ O ₃	2319
Al ₂ S ₃	1373	In ₂ O ₃	2273
In ₂ S ₃	1326	NiO	2230
NiS	1083	InO	1325
Ni ₃ S ₂	1061		
InS	965		
Metal sulfide eutectics			
Mn-MnS	1513		
Cu-Cu ₂ S	1343		
Fe-FeS	1258		
Co-Co ₄ S ₃	1153		
Ni-Ni ₃ S ₂	918		

^aFrom Refs. 3-6.

formation being as a rule approximately one-half those for oxides. Also, metal sulfides melt at lower temperatures than the corresponding oxides (Table II).

As a rule the sulfides of common metals show much higher deviations from stoichiometry than oxides. There are, however, some exceptions. As can be seen in Table III, in the case of Fe_{1-y}S and Fe_{1-y}O , maximum nonstoichiometry is practically the same, since wustite shows an exceptionally large (for oxides) homogeneity range. On the other hand, manganous sulfide shows a smaller homogeneity range than Mn_{1-y}O .

Most of the work has been done on the defect structure of ferrous sulfide.^{11,32-35} This sulfide shows large deviations from stoichiometry (metal deficient) which is associated with the defected cation sublattice, the

Table III. Maximum Deviations from Stoichiometry of Some Metal Sulfides and Oxides at 1273 K^a

Sulfide	Formula	Ref.	Oxide	Formula	Ref.
Fe_{1-y}S	$\text{Fe}_{0.76}\text{S}$	Rosenqvist (1954)	Fe_{1-y}O	$\text{Fe}_{0.88}\text{O}$	Vallet and Raccach (1965)
	$\text{Fe}_{0.85}\text{S}$	Rau (1976)		$\text{Fe}_{0.88}\text{O}$	Kleman (1965)
Ni_{1-y}S	$\text{Ni}_{0.87}\text{S}$ (1260 K)	Laffitte (1959)	Ni_{1-y}O	$\text{Ni}_{0.999}\text{O}$	Mitoff (1961)
	$\text{Ni}_{0.91}\text{S}$ (1260 K)	Rau (1975)		$\text{Ni}_{0.9997}\text{O}$	Tretyakov and Rapp (1969)
	$\text{Ni}_{0.94}\text{S}$ (1250 K)	Lin <i>et al.</i> (1978)		$\text{Ni}_{0.9994}\text{O}$	Volpe and Reddy (1970)
Co_{1-y}S	$\text{Co}_{0.86}\text{S}$	Hansen and Anderko (1958)	Co_{1-y}O	$\text{Co}_{0.993}\text{O}$	Fisher and Tannhauser (1966)
	$\text{Co}_{0.84}\text{S}$	Rau (1976)		$\text{Co}_{0.993}\text{O}$	Error and Wagner (1968)
$\text{Cr}_{2+y}\text{S}_3$	$\text{Cr}_{2.11}\text{S}_2$	Mikami <i>et al.</i> (1972)	$\text{Cr}_{2+y}\text{O}_3$	nonstoichiometry small	Kofstad (1980)
	$\text{Cr}_{2.18}\text{S}_3$	Le Brusq and Delmaire (1974)			
	$\text{Cr}_{2.03}\text{S}_3$	Rau (1977)			
Mn_{1-y}S	$\text{Mn}_{0.999}\text{S}$	Le Brusq and Delmaire (1974)	Mn_{1-y}O	$\text{Mn}_{0.984}\text{O}$	Hed and Tannhauser (1967)
	$\text{Mn}_{0.998}\text{S}$	Rau (1978)		$\text{Mn}_{0.988}\text{O}$	Fender and Riley (1970)
Cu_{2-y}S	$\text{Cu}_{1.83}\text{S}$	Rau (1974)	Cu_{2-y}O	$\text{Cu}_{1.998}\text{O}$	O'Keeffe and Moore (1962)
	$\text{Cu}_{1.87}\text{S}$	Le Brusq and Delmaire (1974)		$\text{Cu}_{1.996}\text{O}$	Mrowec <i>et al.</i> (1974)

^aFrom Refs. 7-31 and 131. The nickel sulfides were tested at the temperatures indicated.

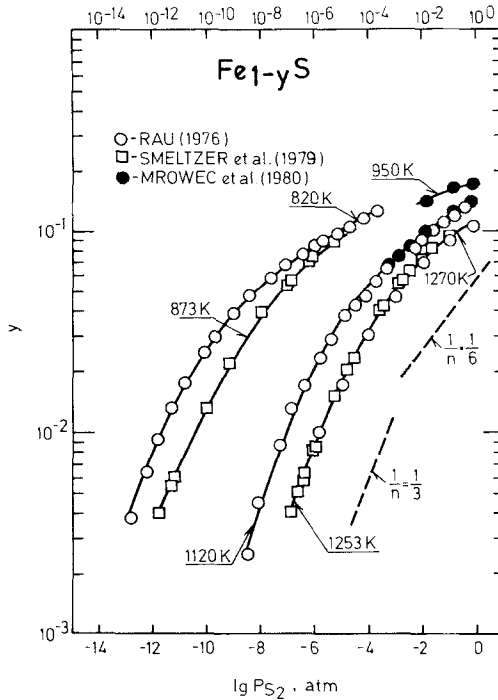


Fig. 1. Dependence of nonstoichiometry, y , in Fe_{1-y}S on sulfur pressure for several temperatures. (From Refs. 11, 32, 33.)

predominant defects being cation vacancies. As can be seen in Fig. 1, the dependence of nonstoichiometry on the sulfur-vapor pressure is not a simple power function as in the case of noninteracting defects. In addition, the defect concentration decreases with increasing temperature, similar to ferrous oxide, which is unusual for simple defect structures. Libowitz³⁴ has shown that this nontypical character of the dependence of nonstoichiometry on sulfur pressure and temperature results from strong repulsive interactions between cation vacancies.

From this theory it follows that the logarithm of the square root of sulfur pressure divided by nonstoichiometry should be a linear function of the product of y and $2 - y$, which is in agreement with experimental data (Fig. 2). From the slope of these lines, the energy of interaction between cation vacancies can be calculated and compared with theoretical values evaluated from the Libowitz model. The agreement is satisfactory.

From the comparison of the dependence of nonstoichiometry in Fe_{1-y}S and Fe_{1-y}O on sulfur and oxygen pressure, it follows that in both cases

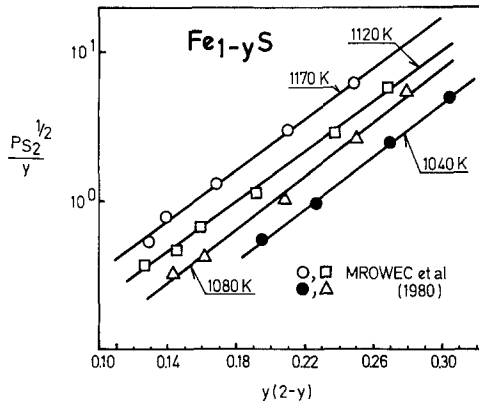


Fig. 2. The dependence of nonstoichiometry in $Fe_{1-y}S$ on sulfur pressure for several temperatures expressed in terms of the Libowitz model. (From Ref. 32.)

these effects are analogous, and the values of nonstoichiometry are comparable (Fig. 3). These great similarities do not imply, however, the existence of completely analogous defect structures. In both compounds the predominant defects are doubly ionized cation vacancies, but in ferrous oxide

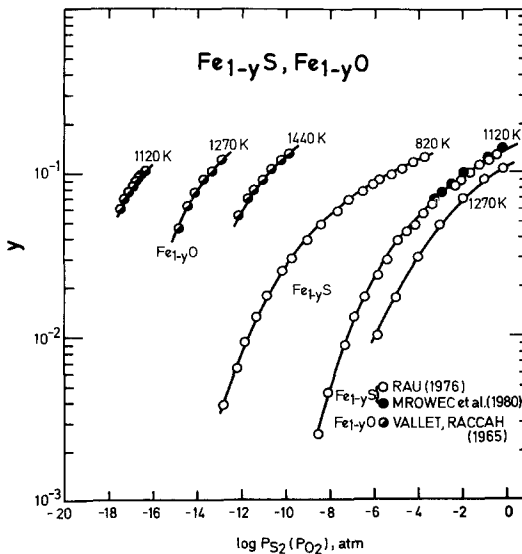


Fig. 3. The dependence of nonstoichiometry in $Fe_{1-y}S$ and $Fe_{1-y}O$ on sulfur and oxygen pressures, respectively, for several temperatures. (From Refs. 11, 15, 32.)

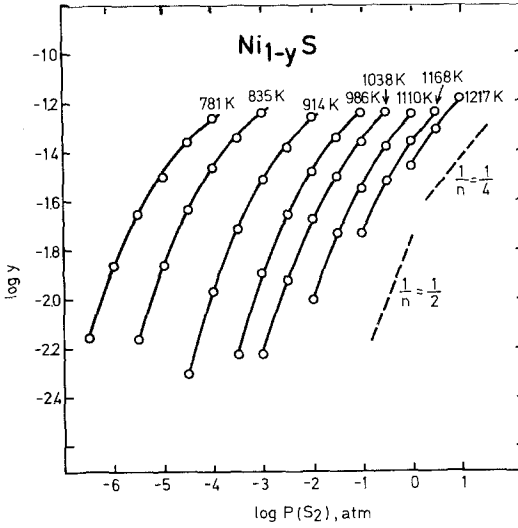


Fig. 4. The dependence of nonstoichiometry in Ni_{1-y}S on sulfur pressure for several temperatures. (From Ref. 36.)

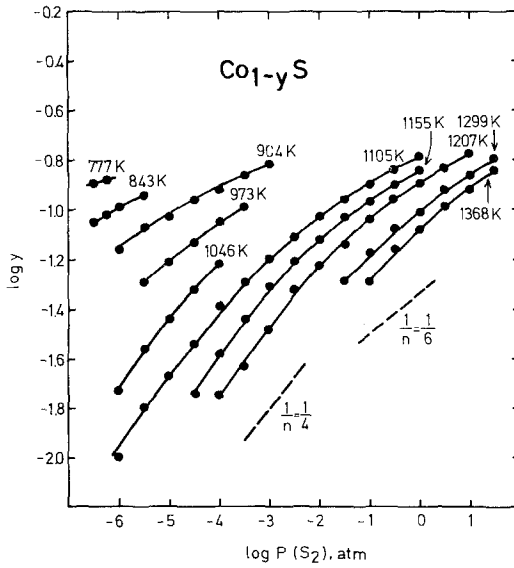


Fig. 5. The dependence of nonstoichiometry in Co_{1-y}S on sulfur pressure for several temperatures. (From Ref. 13.)

there are also interstitial cations of relatively high concentration, which together with cation vacancies form extended defects, so-called Koch-Cohen type clusters.

In ferrous sulfide, on the other hand, interstitial cations have not been found, and as a consequence, there are no three dimensional defect clusters in this material. An analogous defect situation exists in Ni_{1-y}S (Fig. 4) and in Co_{1-y}S (Fig. 5). In both these cases the nonlinear dependence of nonstoichiometry on sulfur pressure in a log-log plot can also be explained by the Libowitz model.

Chromium sulfide, Cr_2S_3 , is a metal-excess, n-type semiconductor,^{8,37,38} the predominant defects being interstitial cations. Consequently, nonstoichiometry of this sulfide decreases with increasing sulfur pressure, as shown in Fig. 6. Despite the large scatter of the experimental data obtained by different authors, from this plot it follows that the slope of the log-log dependence of nonstoichiometry on sulfur pressure decreases with increasing temperature, which is in agreement with theoretical predictions. Considering the defect equilibria in this sulfide, one arrives at the conclusion

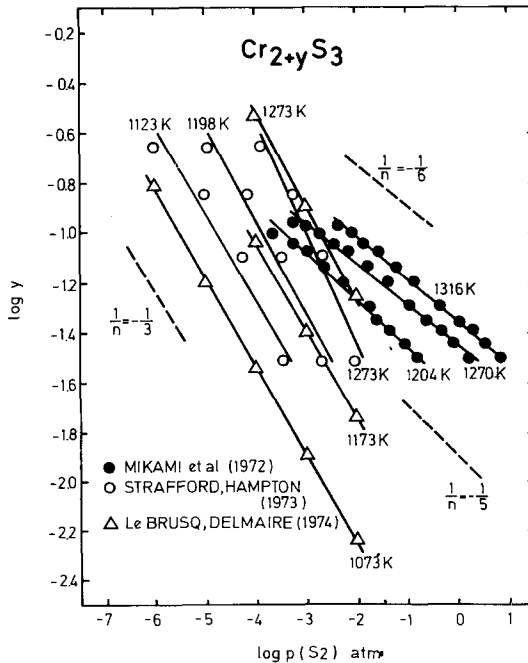


Fig. 6. The dependence of nonstoichiometry in $\text{Cr}_{2+y}\text{S}_3$ on sulfur pressure for several temperatures. (From Refs. 8, 37, 38.)

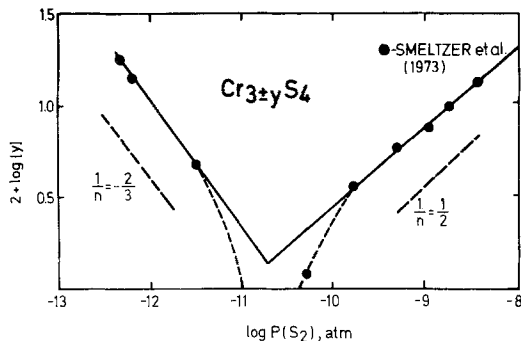


Fig. 7. The dependence of nonstoichiometry in $\text{Cr}_{3\pm y}\text{S}_4$ on sulfur pressure for 973 K. (From Ref. 41.)

that a decreasing slope is equivalent to an increase in the degree of defect ionization. In fact, from the experimental results it follows that at about 1000°C, doubly ionized interstitial cations predominate.

The nonstoichiometry in chromium oxide, Cr_2O_3 , has not yet been determined due to its very low values. Kofstad and Lillerud^{19,39} assume that the predominant defects in this oxide at low oxygen pressures are similar to those in the sulfide, e.g., interstitial cations. At high oxygen pressures, on the other hand, cation vacancies seem to be the predominant defects in this oxide.⁴⁰ At any pressure, however, the defect concentration in chromium oxide is many orders of magnitude smaller than in chromium sulfide.

The character of deviations from stoichiometry in the second chromium sulfide, Cr_3S_4 , indicates that this compound can exist with both excess metal or metal deficiency ($\text{Cr}_{3.11}\text{S}_4$ – $\text{Cr}_{2.9}\text{S}_4$). Smeltzer *et al.*⁴¹ have shown that the absolute value of nonstoichiometry in this sulfide decreases initially with increasing sulfur pressure and subsequently increases, as can be seen in Fig. 7. This dependence can be explained if one assumes that interstitial cations are the predominant defects at lower pressures, and cation vacancies predominate at higher pressures.

Another sulfide which deserves special attention is manganous sulfide, which is the main constituent of the sulfide scale on manganese. This sulfide is a metal-deficient, p-type semiconductor, the predominant defects being cation vacancies.^{8,10} The nonstoichiometry of this compound as a function of sulfur pressure is shown in Fig. 8. It can be seen that at all temperatures, the deviation from stoichiometry increases with sulfur pressure according to a simple power function, typical for noninteracting defects. The slope of these lines, close to $\frac{1}{6}$, indicates that the predominant defects are doubly ionized cation vacancies. It should be noted that, in comparison with other sulfides, manganous sulfide shows exceptionally small deviations from

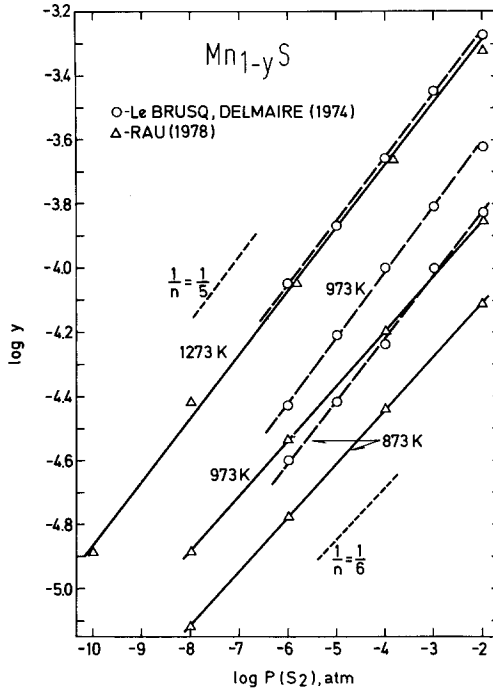


Fig. 8. The dependence of nonstoichiometry in $Mn_{1-y}S$ on sulfur pressure for several temperatures. (From Refs. 8, 10.)

stoichiometry. As can be seen in Fig. 9, these are nearly one order of magnitude lower than the nonstoichiometry of manganous oxide, having the same type of predominant defects under analogous thermodynamic conditions. However, manganous oxide shows (as does wustite) an exceptionally high nonstoichiometry for oxides which decreases with increasing temperature. This is, as in the case of wustite, due to the formation of extended defects.

To summarize this brief discussion of defect properties of metal sulfides, a comparison of nonstoichiometry of some sulfides and oxides is presented in Fig. 10. It is clearly seen that sulfides of important common metals show much higher deviations from stoichiometry, and thereby significantly higher defect concentrations than in the corresponding oxides. The only exception is manganous sulfide, which has a lower nonstoichiometry than the oxide. On the other hand, the unusually high nonstoichiometry of wustite is comparable with that of ferrous sulfide.

It should be stressed once again that in the case of high nonstoichiometry, the defect concentration in oxides of manganese and iron,

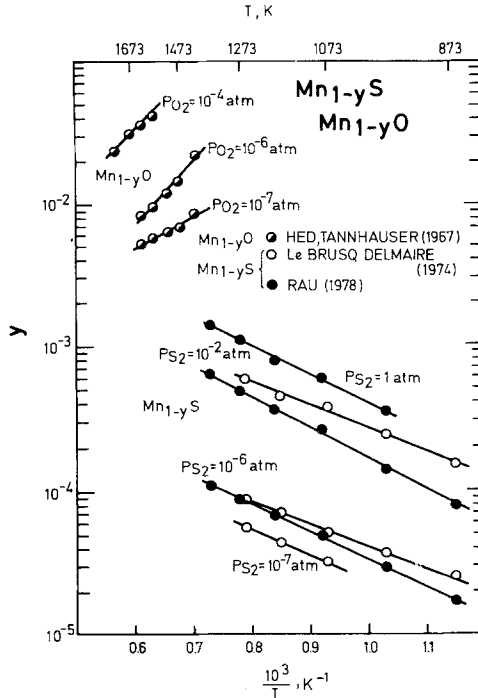


Fig. 9. The dependence of nonstoichiometry in $Mn_{1-y}S$ and $Mn_{1-y}O$ on temperature for several sulfur and oxygen pressures. (From Refs. 8, 10, 20, 21.)

as well as in the sulfides of iron, nickel, and cobalt, decreases with increasing temperature. In the case of sulfides, this behavior is due to strong repulsive interactions between cation vacancies, and in the case of oxides, it is due to the formation of extended defects. Finally, it should be mentioned that the defect structure in refractory metal sulfides has not been explained so far, and it is due to very low, and consequently difficult to measure, deviations from stoichiometry. Rau has shown, for instance, that the nonstoichiometry of molybdenum sulfide at about 1000°C is smaller than 8×10^{-5} mole of sulfur per mole of the sulfide. The defect concentration in refractory metal sulfides is thus assumed to be very low.

Consideration of the transport properties suggests that at high temperatures matter transport in metal sulfides (as in oxides) proceeds mainly through point defects. Thus, these properties can be described by self-diffusion and chemical diffusion coefficients. In contrast to oxides, however, the transport properties of metal sulfides are less known. In a few cases

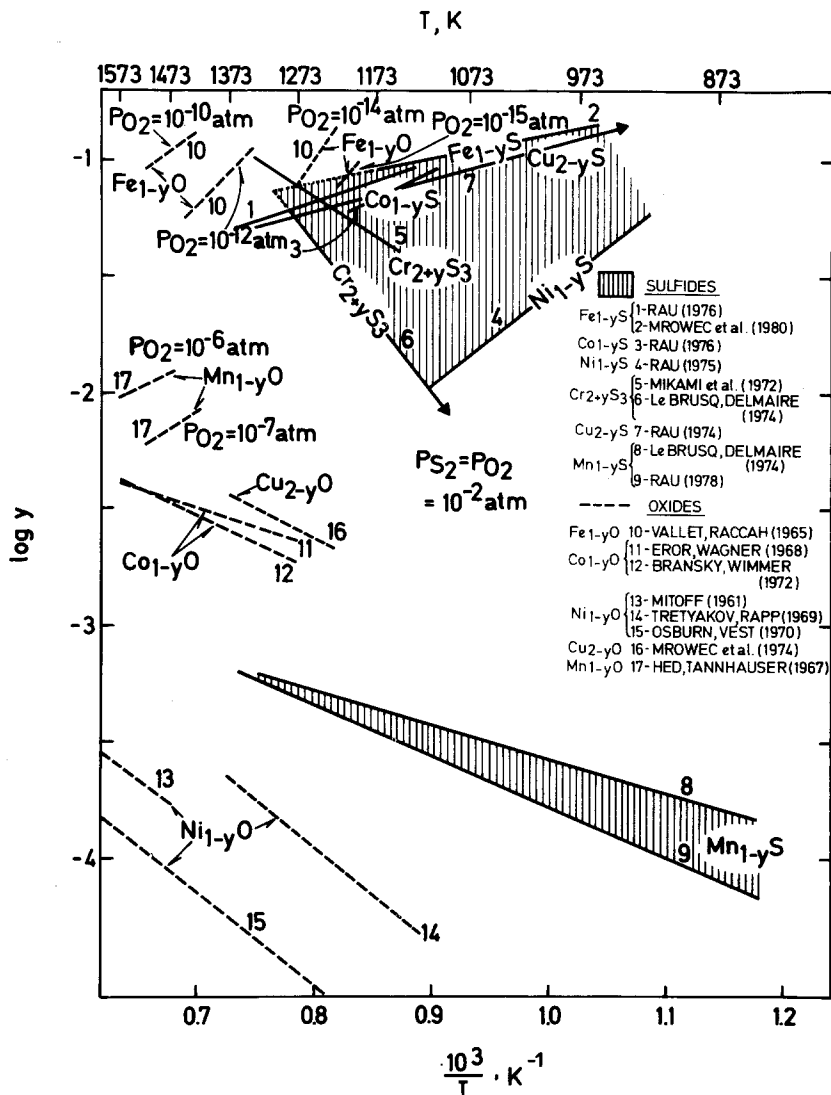


Fig. 10. Collective plot of the temperature dependence of nonstoichiometry for several metal sulfides and oxides. (From Refs. 8, 9-15, 20, 21, 25, 26, 29, 38, 42, 43.)

only, the chemical and self-diffusion coefficients have been determined as a function of temperature and sulfur pressure. These results are discussed below. However, in order to obtain a more complete picture, the fragmentary diffusion data and the results of sulfidation kinetics have been utilized in order to estimate at best the order of magnitude of the diffusion coefficients.

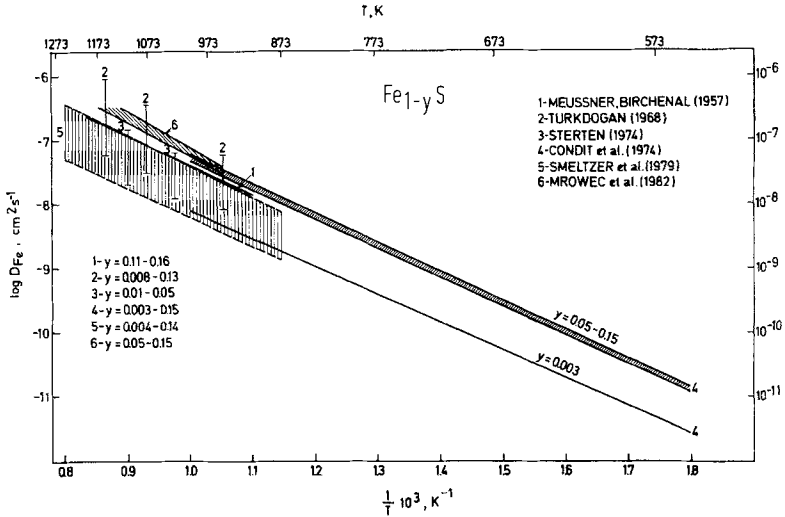


Fig. 11. Collective plot of the temperature dependence of iron self-diffusion in Fe_{1-y}S for several deviations from stoichiometry. (From Refs. 33, 44, 47-49, 45.)

Also in this field of research, ferrous sulfide has been the most extensively studied. Self-diffusion of iron and sulfur in single crystals of Fe_{1-y}S has been studied by Condit *et al.*⁴⁴ by the tracer method. Self- and chemical diffusion has also been studied in polycrystalline material by means of kinetics methods.^{32,33,45-49} Condit *et al.* have shown that, in agreement with the defect model of Fe_{1-y}S , the self-diffusion coefficient of sulfur in this material is many orders of magnitude lower than that of iron. Figure 11 shows a collective plot representing the dependence of the iron self-diffusion coefficient on temperature and the deviation from stoichiometry. As can be seen, the values of this coefficient, calculated for polycrystalline material and determined directly in single crystals, are in good agreement. This shows clearly that diffusion of iron in ferrous sulfide proceeds only through point defects. It has also been shown that the chemical-diffusion coefficient is nearly independent of composition over the whole homogeneity range of Fe_{1-y}S , as can be seen in Fig. 12. These data include the directly measured values and those calculated from self-diffusion coefficients and from deviations from stoichiometry. The temperature dependences of the self- and chemical diffusion coefficients in Fe_{1-y}S and Fe_{1-y}O are compared in Fig. 13 in order to show the great similarities in transport properties for the oxide and sulfide of the same metal.

Self-diffusion coefficients of nickel in nickelous sulfide have been determined in single and polycrystalline materials, as well as calculated from

Fig. 12. Collective plot of the dependence of the chemical diffusion coefficient in $Fe_{1-y}S$ on nonstoichiometry for several temperatures. (values for c -axis of ferrous sulfide). (From Refs. 33, 45, 46, 48.)

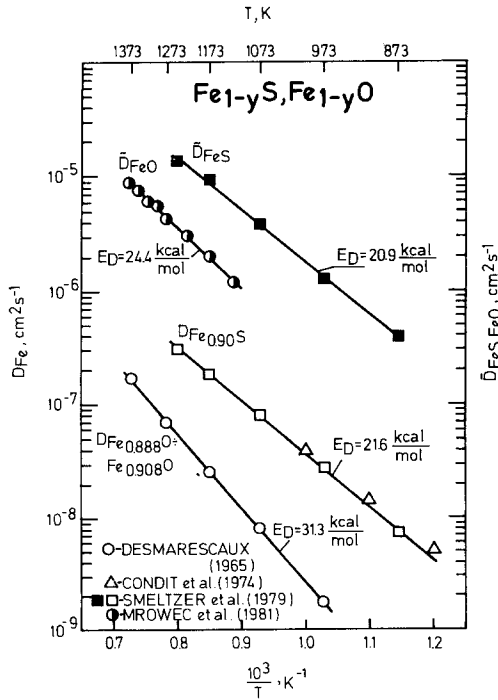
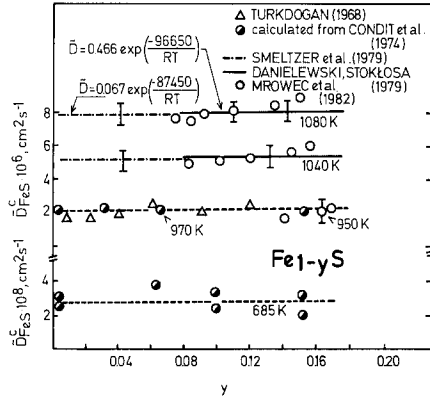


Fig. 13. The dependence of D_{Fe} and \tilde{D} in $Fe_{1-y}S$ and $Fe_{1-y}O$ on temperature. (From Refs. 33, 44, 50, 51.)

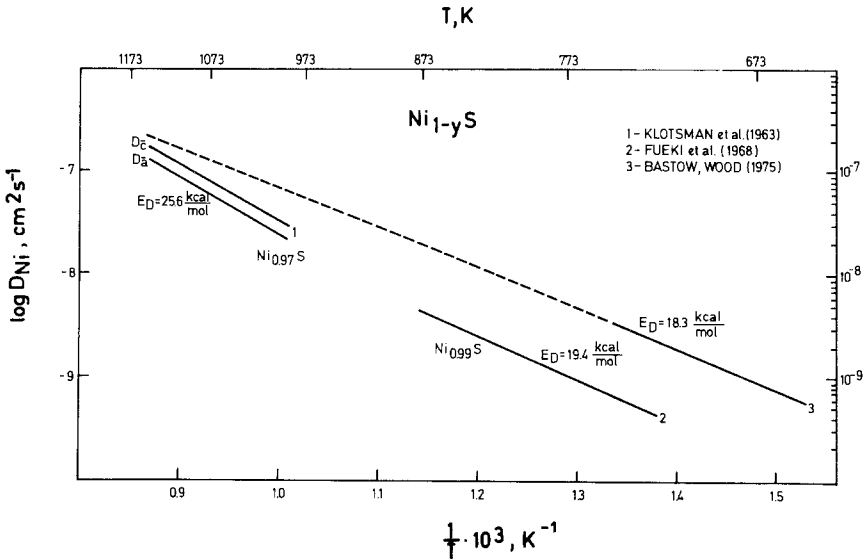


Fig. 14. Collective plot of the temperature dependence of self-diffusion of nickel in single and polycrystalline $Ni_{1-y}S$. (From Refs. 52-54.)

nickel sulfidation kinetics. These results are shown in Fig. 14. The results obtained by Bastow and Wood⁵⁴ concern polycrystalline material, and as such, they include lattice and intergranular diffusion. It should be expected that at relatively low temperatures, the participation of grain-boundary diffusion of nickel in polycrystalline $Ni_{1-y}S$ is significant. The absolute values of self-diffusivities determined by Bastow and Wood⁵⁴ should then be higher than those obtained for a single crystal, whereas the activation energy of diffusion in the polycrystalline material should be lower. These conclusions are in agreement with the experimental results (Fig. 14).

Self-diffusion of manganese and sulfur in $Mn_{1-y}S$ has unfortunately not been determined as yet. On the other hand, the kinetics of manganese sulfidation have been extensively studied.⁵⁵⁻⁵⁹ Because the sulfide scale on manganese grows by the outward diffusion of metal, it was possible to calculate self-diffusion coefficients of manganese in $Mn_{1-y}S$ from parabolic sulfidation kinetics. The results of these calculations are shown in Fig. 15. As predicted, the self-diffusion coefficient of manganese increases with sulfur pressure with a slope of $\frac{1}{6}$. Absolute values of diffusion rates calculated from kinetic results obtained in sulfur vapor below 1273 K are, however, slightly lower than those obtained in H_2/H_2S mixtures. These differences can result either from different atmospheres used, or from different purity of materials. The above mentioned differences are also reflected in slightly

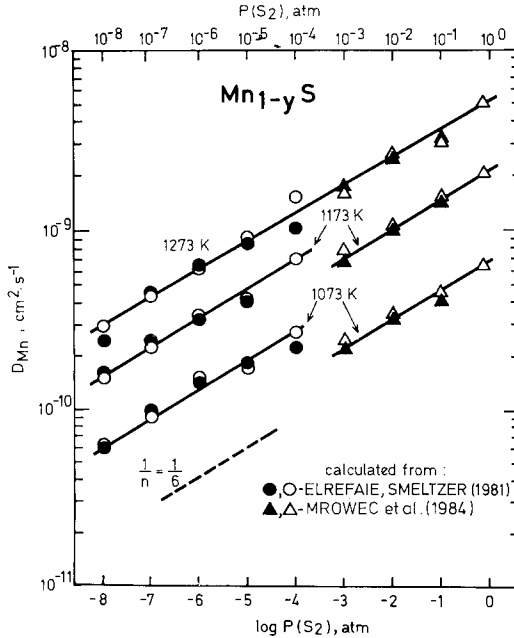


Fig. 15. The dependence of D_{Mn} in $Mn_{1-y}S$ on sulfur pressure for several temperatures. (From Refs. 55, 57, 60.)

different values of the activation energy of diffusion, as can be seen in Fig. 16. Chemical diffusion in manganous sulfide has not been studied so far. The rate of this process can, however, be estimated on the basis of self-diffusion coefficients and defect concentrations. The results of these calculations are shown in Fig. 17. As can be seen, the chemical diffusion coefficient in $Mn_{1-y}S$ is nearly independent of defect concentration but, again, values calculated from self-diffusion data referred to different atmospheres are slightly different. These differences are also reflected in different activation energies of chemical diffusion, as shown in Fig. 18.

Nevertheless, these results show clearly that the defect structure and diffusion mechanism in manganous sulfide are relatively simple and are atypical of the majority of metal sulfides. The deviations from stoichiometry in $Mn_{1-y}S$ are very small, and consequently, the predominant defects are completely ionized, noninteracting cation vacancies. In contrast to this, the defect structure in manganous oxide, and thus the diffusion mechanism in this oxide, are more complicated. The predominant defects in $Mn_{1-y}O$ are also cation vacancies, but their concentration is much higher and due to interaction and clustering of defects; the diffusion mechanism in this compound remains unclear.⁶¹

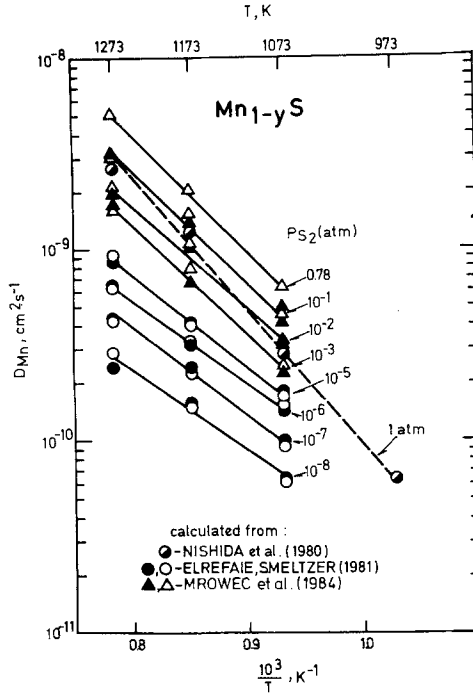


Fig. 16. The temperature dependence of self-diffusion of manganese in $Mn_{1-y}S$ for several sulfur pressures. (From Ref. 60.)

There is no information concerning self- and chemical diffusion rates in other sulfides. Only a rough estimate of these rates could be made for cobaltous and chromium sulfides, using sulfidation kinetics data and deviations from stoichiometry. As far as the refractory metal sulfides are concerned, only self-diffusion coefficients could be estimated approximately from parabolic sulfidation kinetics. With respect to this, it should be stressed that marker experiments have shown that the compact sulfide scale on molybdenum and tungsten grows by inward diffusion of sulfur.⁹⁸ Consequently, estimated values of self-diffusion coefficients in MoS_2 and WS_2 relate to sulfur diffusion.

Figure 19 shows a collective plot of all measured, calculated, and estimated values of self-diffusion coefficients in metal sulfides as well as the self-diffusion rates in oxides. It follows from the plot that the activation energy of diffusion in sulfides is significantly lower than that in oxides. Besides, it is clearly visible that the self-diffusion rate in several sulfides is of the same order of magnitude as in some oxides. These are $Mn_{1-y}S$ and

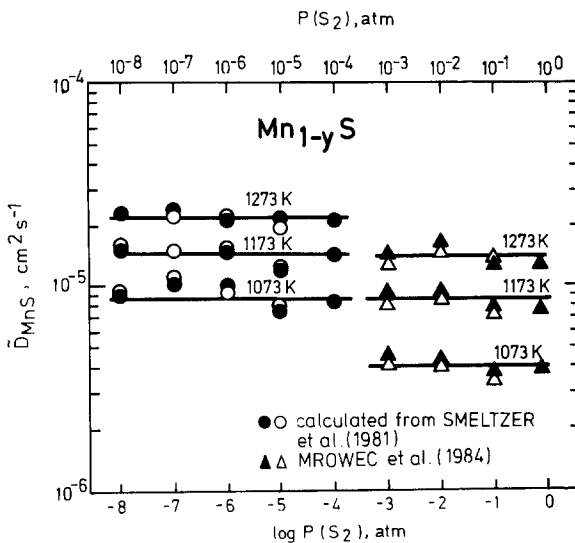


Fig. 17. The dependence of the chemical diffusion coefficient in Mn_{1-y}S on sulfur pressure for several temperatures. (From Refs. 57, 60.)

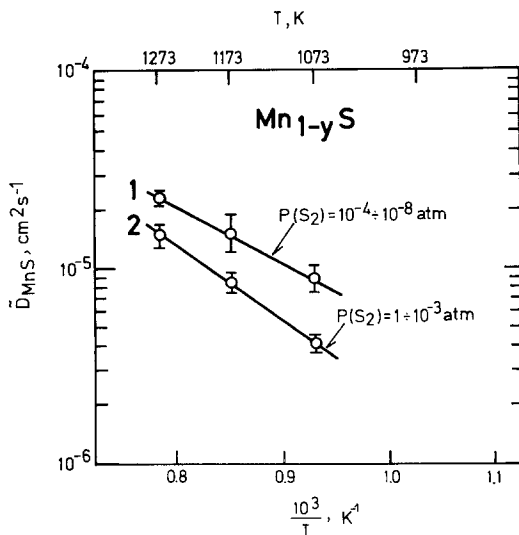


Fig. 18. The dependence of \bar{D}_{MnS} in Mn_{1-y}S on temperature. (From Ref. 60.)

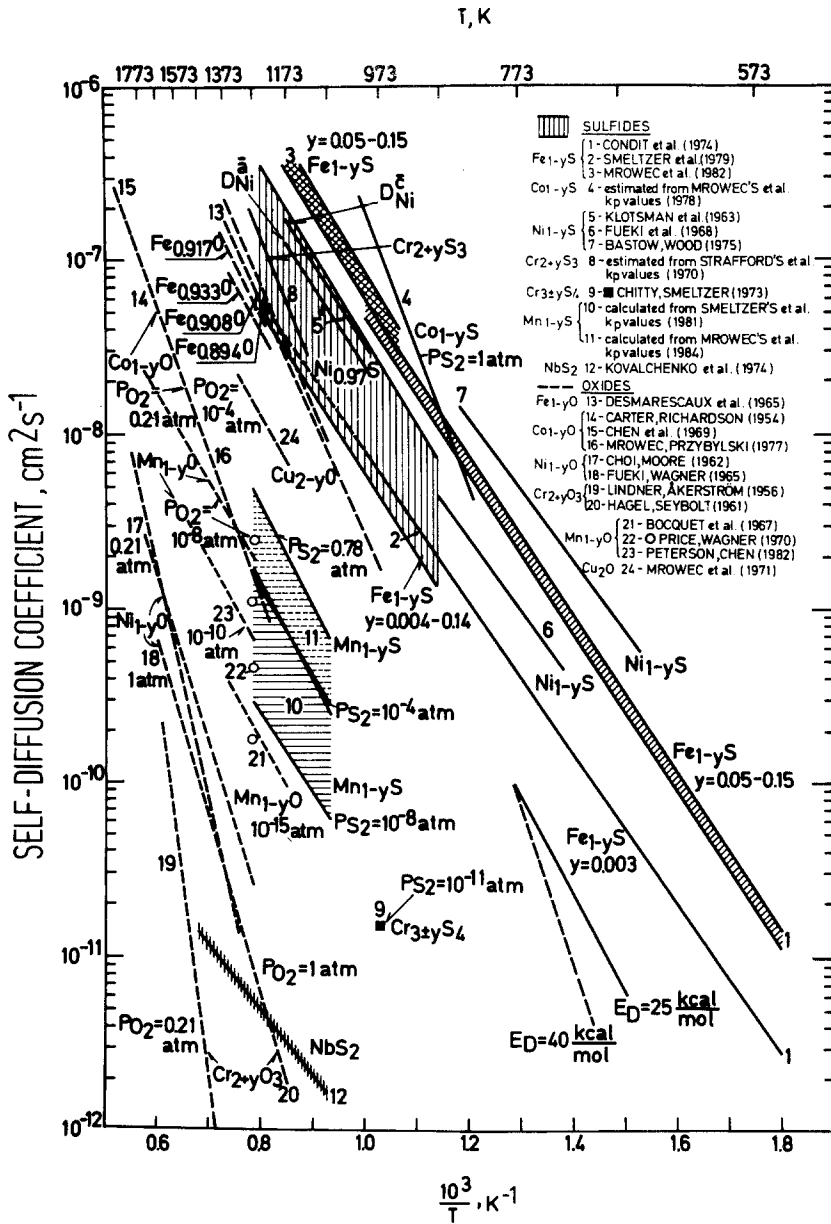


Fig. 19. Collective plot of self-diffusion coefficients in some metal sulfides and oxides. (From Refs. 32, 33, 44, 45, 51, 52-54, 57, 60, 62-76.)

$Mn_{1-y}O$, $Fe_{1-y}S$ and $Fe_{1-y}O$, as well as the refractory metal sulfides and oxides. The rate of self-diffusion, on the other hand, in a number of other sulfides is orders of magnitude higher than in oxides. In particular, the rate of self-diffusion in sulfides of such important metals as cobalt, nickel, and chromium is several orders of magnitude higher than in their corresponding oxides.

A question then arises. Why is the diffusion rate in metal sulfides generally higher than that in oxides? Because the self-diffusion coefficient is a product of defect mobility and their concentration, deviations from stoichiometry and chemical diffusion coefficients should be compared in both groups of these materials. Figure 20 shows a comparison of chemical-diffusion coefficients in some oxides and sulfides. It follows from this plot that the rate of this process and consequently the mobility of defects in metal oxides and sulfides do not differ significantly. In fact, the rate of chemical diffusion is generally higher in metal sulfides, but the differences do not exceed one order of magnitude. This means that in a majority of cases, the significantly higher rate of self-diffusion in metal sulfides results from higher defect concentrations and not from greater defect mobility. There are, however, some exceptions.

For instance, the mobility of defects in manganous sulfide is higher than in the oxide, whereas the defect concentration is lower. Due to this compensation effect, the self-diffusion rates in $Mn_{1-y}S$ and $Mn_{1-y}O$ are comparable. Ferrous sulfide and oxide, in turn, exhibit comparable deviations from stoichiometry, but the chemical diffusion coefficient in the oxide is lower. As a consequence, the self-diffusion rate in $Fe_{1-y}S$ is correspondingly higher than in the oxide. It is interesting to note that the activation energies of chemical diffusion in metal sulfides and oxides are comparable, whereas the activation energy of self-diffusion in metal oxides is much higher than in sulfides. This is generally due to a higher enthalpy of defect formation in oxides than in sulfides.

From the above considerations, it follows that sulfide scales on common metals should possess poor protective properties. An example of a scale with the poorest protective properties known is the sulfide scale on silver, the growth rate of which represents the most rapid reaction in the solid state. It is enough to mention that a silver plate, 1 mm thick, is completely sulfidized after 1 min at 400°C. Sulfidation of copper is almost equally rapid and that of nickel only slightly slower.

Figure 21 shows, for illustration, the sulfide "scales" on silver, copper, and nickel grown by Wagner's pellet method in our laboratory. It is evident that the rate of sulfidation of these metals is very high indeed. Of course, such thick scales are obtainable only with the pellet method, in which the metal consumption zone is fully compensated without any restrictions,

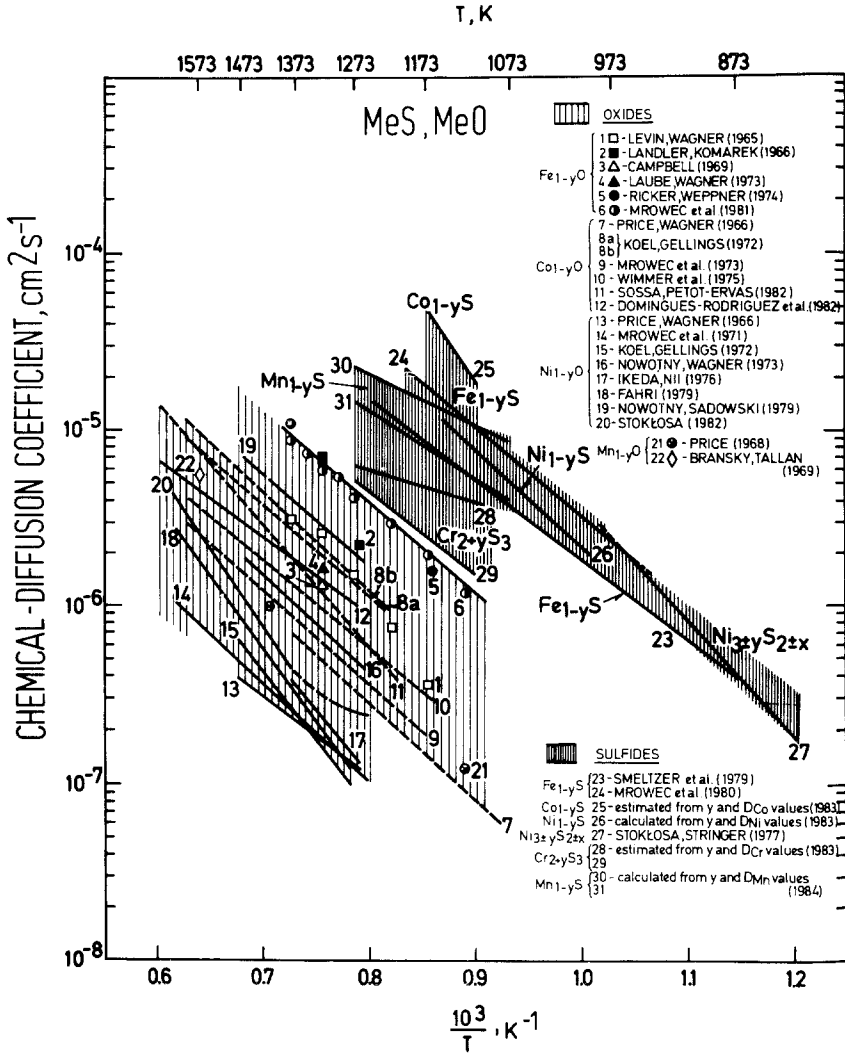


Fig. 20. Collective plot of chemical diffusion coefficients in some metal sulfides and oxides. (From Refs. 32, 33, 50, 60, 77-96.)

because the scale can move freely down together with the pellet following the receding metal surface. This method, however, can be used only in special, selected cases such as silver or copper sulfidation. Thus, the kinetics of metal sulfidation are usually studied, as in the case of oxidation, by thermogravimetric techniques. However, much greater experimental difficulties are encountered in studying sulfidation as compared to oxidation

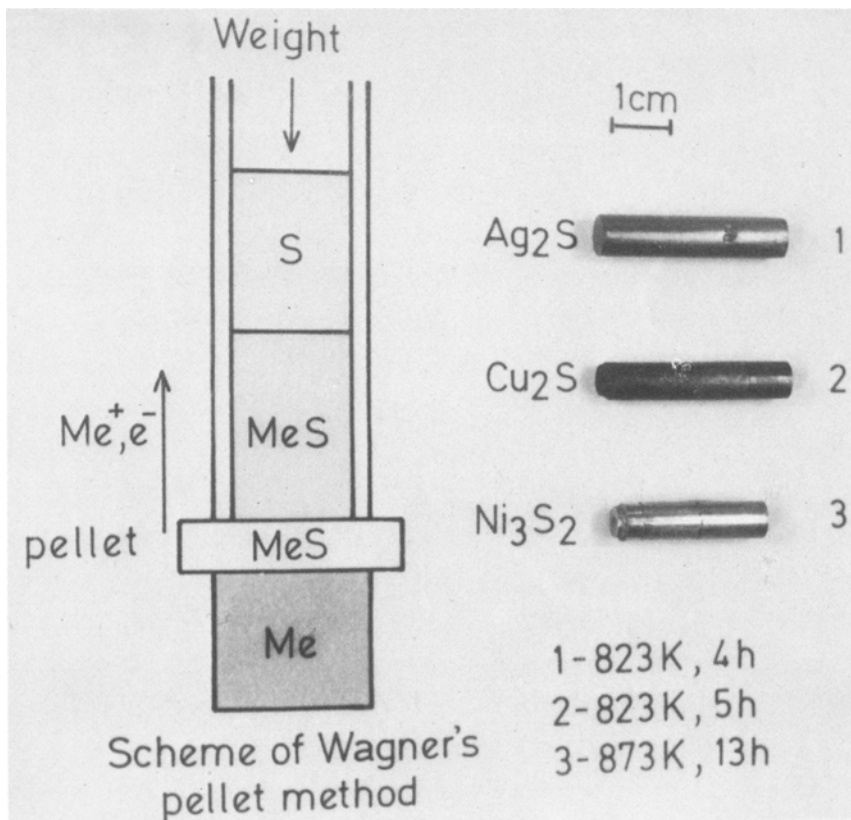


Fig. 21. Sulfide "scales" grown on silver, copper, and nickel in Wagner's pellet system.

reactions, which results from the fact that sulfur is not gaseous under normal conditions, and its vapors are extremely aggressive. Consequently, standard thermogravimetric equipment commonly used in kinetics measurements of metal oxidation cannot be used under these conditions.

As far as the results of metals sulfidation is concerned, again we must limit ourselves only to some general conclusions, concentrating mainly on the similarities and differences between sulfidation and oxidation processes. One of the most important conclusions is that, as in the case of oxidation, sulfide scales on all common metals grow primarily by the outward diffusion of cations, and on refractory metals by the inward diffusion of sulfur. This is illustrated in Fig. 22, showing cross-sections of sulfide scales formed on nickel and tungsten with platinum and gold markers. This important analogy results from the same type of predominant defects in sulfides and oxides.

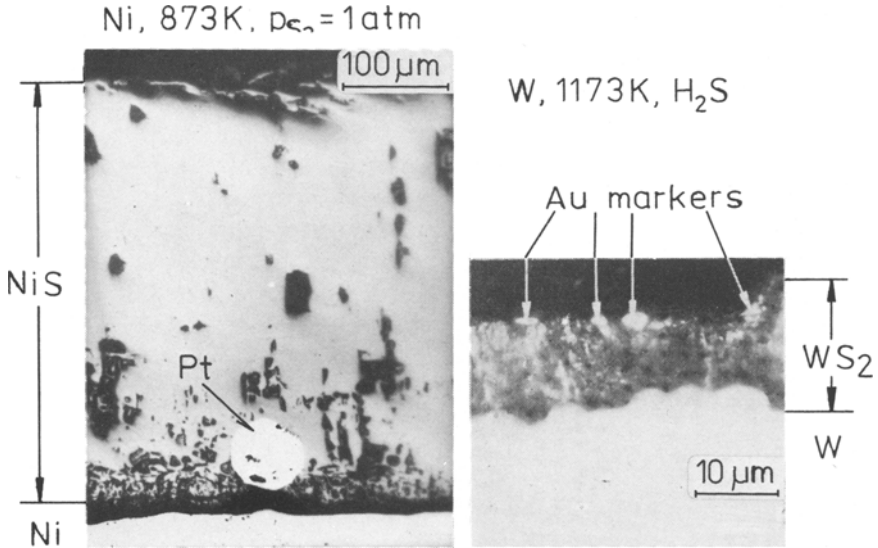


Fig. 22. Cross-sections of sulfide scales formed on nickel and tungsten. (From Refs. 97, 98.)

The great difference, however, is observed in the kinetics of these processes. Despite the parabolic nature of the reaction, the rate of sulfide corrosion of common metals is as a rule many times higher than in an oxygen atmosphere.

Figure 23 shows a collective plot of the temperature dependence of sulfidation and oxidation rates of some metals. From this plot it follows clearly that sulfidation rate of such important metals as cobalt, nickel, and chromium is significantly higher than that of oxidation. Manganese is in an intermediate position, as its sulfidation rate, due to the previously mentioned compensation effect, is comparable to that of oxidation. On the other hand, refractory metals are highly resistant to sulfide corrosion, their sulfidation rate being comparable to the oxidation rate of chromium, which represents one of the most resistant metals to oxide corrosion. It should be emphasized that the sulfidation rate of niobium is about 7 orders of magnitude lower than that of iron. The oxidation rates of refractory metals have not been marked in Fig. 25, since these processes do not, as a rule follow a parabolic rate law, due to cracking or vaporization of the scale.

As far as the sulfidation of alloys is concerned, again, analogies and differences can be noted. Figure 24 shows a collective plot of the sulfidation rate of iron-chromium, nickel-chromium, and cobalt-chromium alloys as a function of their composition. From the plot it follows that at higher pressures ($>10^{-2}$ atm), the character of this dependence is analogous for

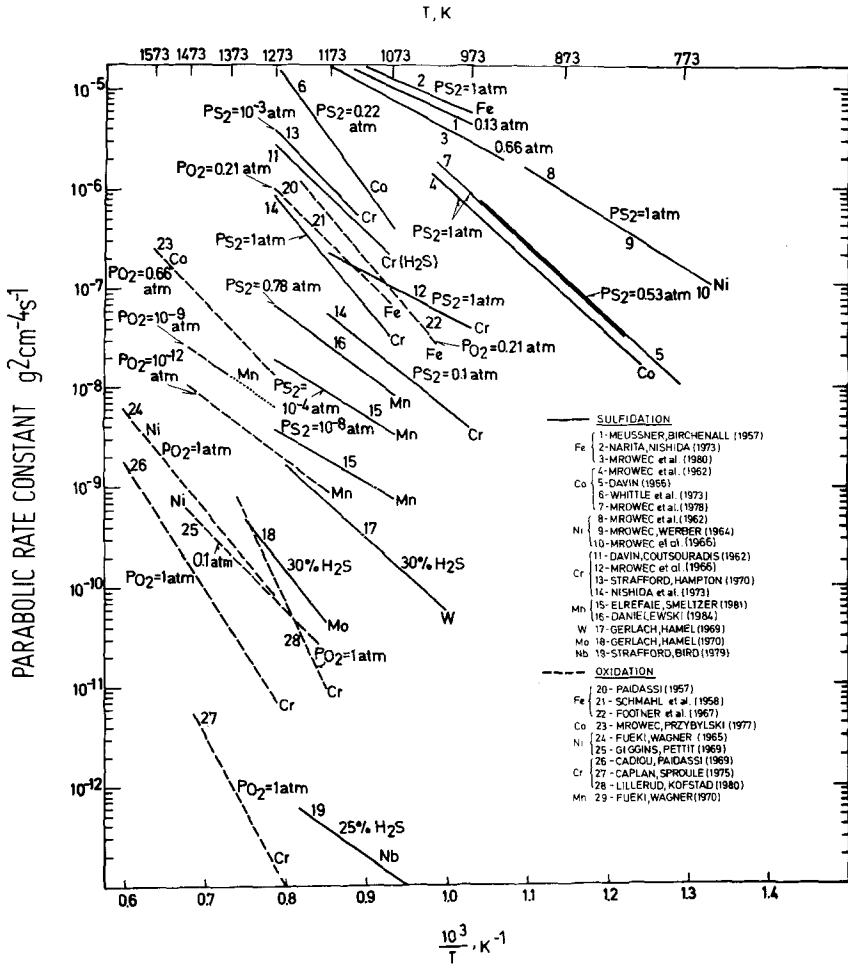


Fig. 23. Collective plot of the temperature dependence of sulfidation and oxidation rates of pure metals. (From Refs. 6, 32, 45, 47, 57, 59, 62, 63, 70, 97-113.)

all three alloy groups and can be shown schematically in Fig. 25. Three composition ranges can be distinguished, differing in the influence of chromium concentration on sulfidation kinetics. This is due to a different phase composition of the scales in every concentration range. In field I (up to about 2% Cr) where the sulfidation rate is comparable (Fe-Cr alloys) or higher (Co-Cr and Ni-Cr) than that of base metal, the scale is single phase and consists of base-metal sulfide doped with chromium. The higher sulfidation rate of these alloys as compared to the pure based metal results

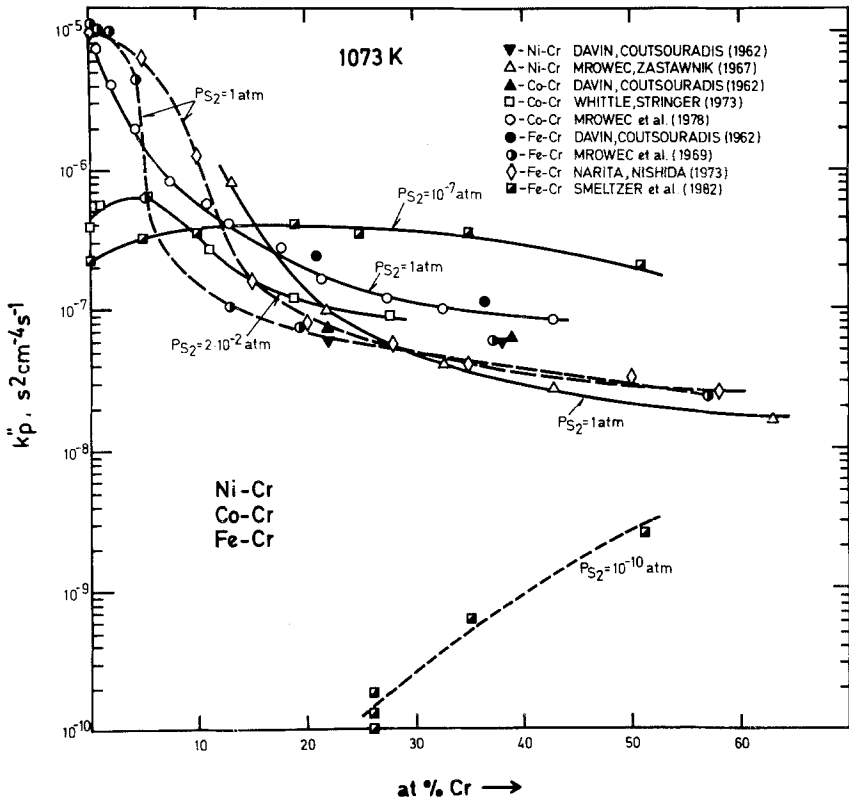


Fig. 24. Collective plot of the dependence of the sulfidation rate of Fe-Cr, Ni-Cr, and Co-Cr alloys on composition at 1073 K. (From Refs. 6, 62, 100, 114-117.)

from a higher concentration of cation vacancies in the scale due to the doping effect.

In field II the rate of sulfidation decreases abruptly with increasing chromium content due to the formation in the scale of an inner barrier layer consisting either of a sulfo-spinel or of chromium sulfide-base metal sulfide solid solutions. In field III the scale on all the alloys is again single phase and consists of chromium sulfide doped with base metal, the growth rate being comparable to pure chromium. Marker studies have shown that the scale on all the alloys, over the entire concentration range, grows by the outward diffusion of both alloying components, as can be seen in Fig. 26. It should be noted that the kinetics and mechanism of oxide scale formation on the alloys discussed depend similarly on chromium concentration, but the oxidation rate in fields II and III is many orders of magnitude smaller than that of sulfidation.

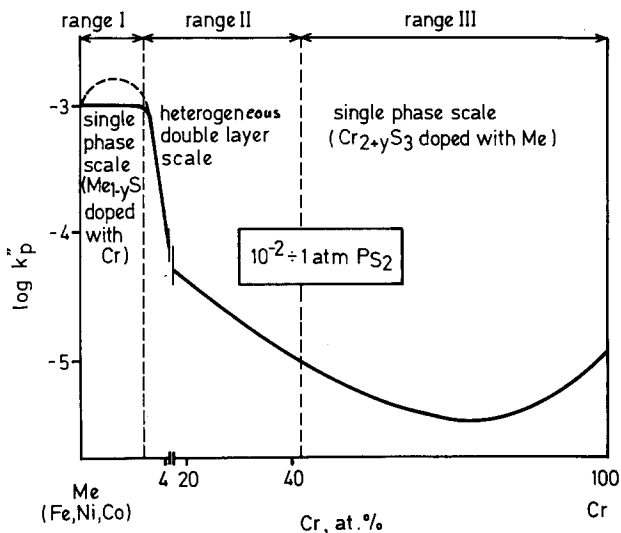


Fig. 25. Schematic dependence of sulfidation rate on composition for Fe-Cr, Ni-Cr, and Co-Cr alloys.

At very low sulfur pressures, lower than the dissociation pressure of the base-metal sulfide, the influence of chromium content on the sulfidation rate is completely different (Fig. 24). Under these conditions, the sulfidation rate increases rapidly with chromium concentration in the alloy, since the overall reaction rate is determined by diffusion in the metallic phase.¹¹⁷

Aluminum additions to binary alloys discussed above improve their resistance to sulfide corrosion, but this effect, in contrast to oxygen atmospheres, is rather weak even at very high aluminum concentrations. A very protective scale is formed only at sulfur pressures lower than the dissociation pressure of the base-metal sulfide (comparable to an Al_2O_3 scale). Figure 27 shows a collective plot of the sulfidation rate of the alloys discussed, containing about 20% Cr, as a function of aluminum content at high-sulfur pressures. As in the case of binary alloys of field II, a double-layer scale is formed, which grows by the outward diffusion of metals. The inner, barrier layer consists of a mixed sulfospinel, $\text{Fe}(\text{Fe}_x\text{Al}_y\text{Cr}_{2-x-y})\text{S}_4$, containing the base metal, chromium, and aluminum, the concentration of the latter increasing with aluminum content in the alloys, which results in a gradual improvement of the protective properties of the scale. This effect, however, is rather weak even if the aluminum concentration in the alloy exceeds 30 at.%, which is in contrast to oxygen atmospheres.

Figure 28 shows the effect of sulfur pressure on the sulfidation rate of iron-chromium-aluminum alloys in comparison to the analogous

Fe-Cr, 1173K, $p_{S_2} = 1 \text{ atm}$

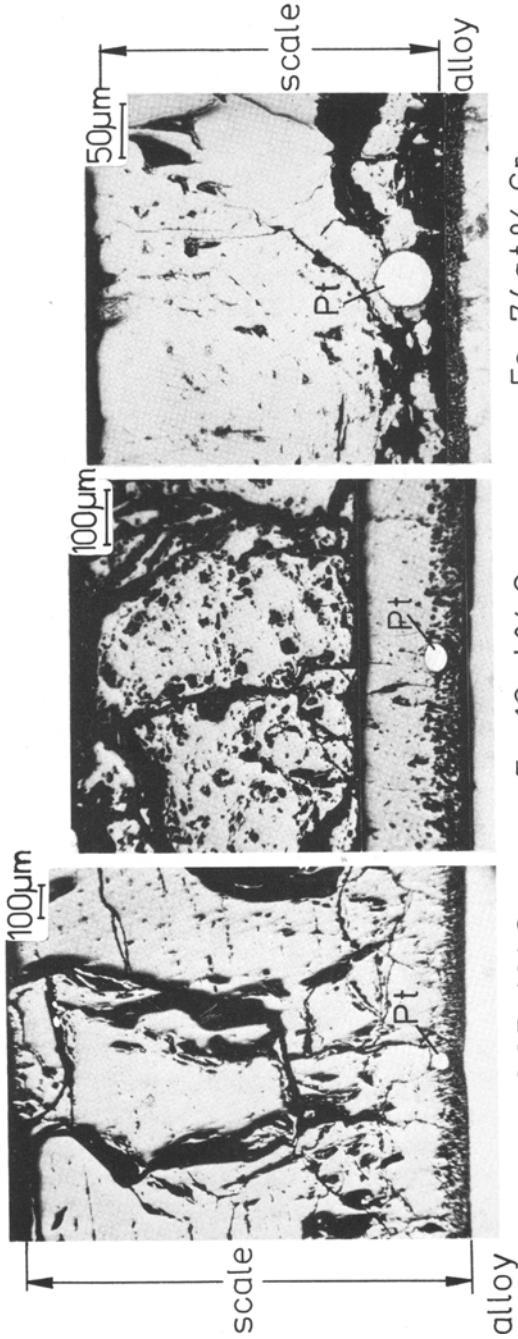


Fig. 26. Cross-sections of sulfide scales formed on Fe-Cr alloys for compositions corresponding to the three concentration ranges depicted in Fig. 25. (From Ref. 115.)

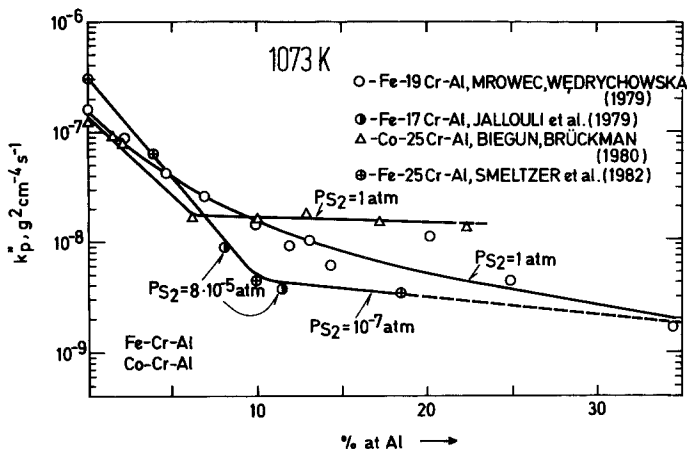


Fig. 27. The effect of aluminum content in Fe-Cr-Al alloys on the sulfidation rate at 1073 K for various sulfur pressures. (From Refs. 118-121.)

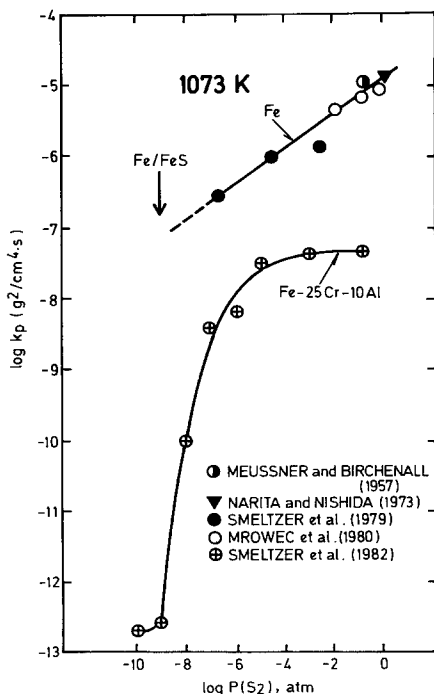


Fig. 28. The influence of sulfur pressure on the sulfidation rate of iron and an Fe-25Cr-10Al alloy at 1073 K. (From Refs. 32, 47, 111, 121, 122.)

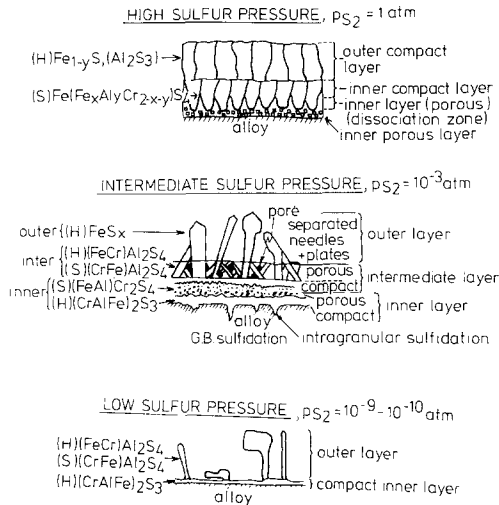


Fig. 29. Schematic morphology of sulfide scales formed on Fe-Cr-Al alloys at various sulfur pressures. (From Refs. 118, 123.)

dependence of pure iron sulfidation. It can be seen how dramatically sulfur-vapor pressure influences the corrosion rate of these alloys. For example, at pressures less than the dissociation pressure of ferrous sulfide, the sulfidation rate of the alloy is more than 5 orders of magnitude lower than that of pure iron extrapolated to the same pressure. The sulfidation rate increases rapidly with sulfur pressure, and above 10^{-5} atm it becomes practically independent of pressure, being only 2 orders of magnitude lower than that of pure iron. This is due to the fact that with increasing pressure, important changes occur in the chemical composition and crystal structure of the scale.

These differences are schematically visualized in Fig. 29 for three different sulfur pressures. Scale growth occurs by the outward diffusion of cations at all sulfur pressures, but at very low pressure a thin irregular scale is formed which consists only of sulfospinel and of hexagonal sulfides containing iron, chromium, and aluminum. Internal sulfidation occurs also beneath the scale at low pressures. At higher pressures the scale grows faster due to the formation of rapidly growing ferrous sulfide.

Figure 30 shows a comparison of the sulfidation and oxidation rates of some metals and alloys. It follows from this plot that not only pure metals but also highly oxidation-resistant alloys corrode several orders of magnitude faster in sulfur-containing atmospheres than in oxygen. This is due to the fact that in oxygen atmospheres, highly protective layers of Cr_2O_3 or Al_2O_3 are formed by the selective oxidation of these metals. However, in

T, K

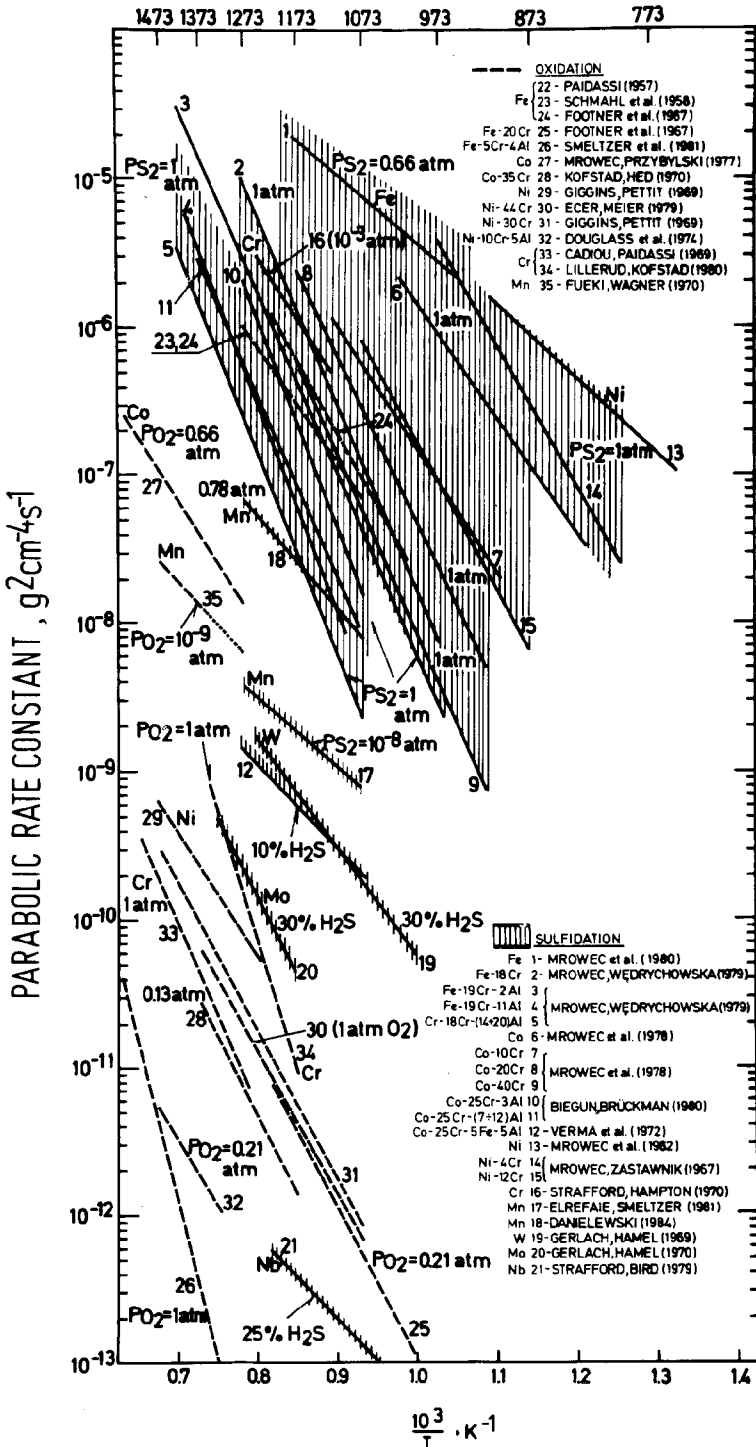


Fig. 30. Collective plot of the temperature dependence of sulfidation and oxidation rates

sulfur atmospheres, even at significantly higher concentrations of chromium and aluminum, heterogeneous scales are formed which have poor protective properties. It should be stressed, however, that even if the scale consisted exclusively of chromium sulfide, the corrosion process in a sulfur atmosphere would be much faster than in oxygen due to a much higher concentration of defects in chromium sulfide compared to chromium oxide.

There are no data for diffusion rates in aluminum sulfide, but the results of sulfidation kinetics of Fe-Cr-Al and Co-Cr-Al alloys clearly indicate that a continuous layer of aluminum sulfide is never formed during sulfidation, even if the aluminum concentration in the alloy exceeds 30 at.%. This behavior is in sharp contrast to that in oxygen atmospheres. Only at very low sulfur pressures, lower than the dissociation pressure of the base-metal sulfide, can protective scales be formed on these alloys. Thus, from a practical point of view, aluminum is not promising as an alloying addition to improve sulfide-corrosion resistance. It seems, however, that the refractory metals are very promising in this respect, because they show outstanding resistance to sulfur. On the other hand, the high thermodynamic stability of their sulfides suggests that a relatively low concentration of these metals in conventional alloys might greatly improve the protective properties of scales by selective sulfidation.

CONCLUSIONS

Metal sulfides show the same type of predominant defects as metal oxides. These are cation defects in Fe_{1-y}S , Co_{1-y}S , Ni_{1-y}S , Mn_{1-y}S , $\text{Cr}_{2+y}\text{S}_3$, Cu_{2-y}S and anion defects in refractory metal sulfides. The defect concentration in most sulfides is much higher than in the corresponding oxides; the inverse situation exists in Mn_{1-y}S and in the refractory-metal sulfides.

Defect mobilities in sulfides are only slightly higher than in oxides. Thus, the much higher diffusivities in most sulfides are due to the higher concentration of defects. In the case of Mn_{1-y}S , which has a lower defect concentration but higher mobility, the self-diffusion rate is comparable to that in Mn_{1-y}O (compensation effect). The same type of predominant defects in sulfides and oxides is the main reason for the analogous growth mechanism of sulfide and oxide scales on metals: outward cation diffusion in the case of common metals and inward diffusion of sulfur in the case of refractory metals.

The most important difference between sulfidation and oxidation of metals is in the kinetics of these processes. Despite the formation of a compact scale and the parabolic course of the reaction, the sulfidation rate of common metals is much higher, and of refractory metals much lower, than that of oxidation. This is due to the differences in defect concentrations

in sulfides and oxides. The reason why common scaling-resistant alloys are rapidly attacked by sulfur is that chromium and aluminum only slightly decrease the very high sulfidation rate of these materials. Only at very low sulfur pressures, lower than the dissociation pressure of the base-metal sulfide (FeS, CoS, NiS), can a protective scale be formed, comparable to α -Al₂O₃.

It seems that a significant reduction of the sulfide corrosion rate could be attained by alloying metallic materials with refractory metals, which have excellent resistance to sulfur. Further data are urgently needed on the defect structure and transport properties of refractory-metal sulfides, as well as on the sulfidation behavior of these metals.

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