

# The effect of aliovalent impurities on the sulfidation kinetics of manganese and molybdenum

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**Abstract** The influence of aliovalent impurities on the kinetics and mechanism of manganese and molybdenum sulfidation has been demonstrated, as a function of temperature (1,073–1,273 K) and sulfur pressure (1– $10^4$  Pa). The results of these experiments have been considered in terms of Hauffe–Wagner theory of doping, which made it possible to explain the different influence of aliovalent impurities on the sulfidation kinetics of manganese and molybdenum. It has been shown that the same impurity may play both the positive or negative role in the corrosion behavior of a given metal and it is not possible to predict the type of this influence without the detailed knowledge of point defect structure of sulfide or oxide scales and, in particular, of the mechanism of impurity dissolution in the crystallographic structure of oxidation or sulfidation products.

**Keywords** Doping effect · Point defect structure · Sulfidation kinetics · MnS · MoS<sub>2</sub>

## Introduction

It is well known that small amounts of impurities in metallic materials may in some cases dramatically influence the rate of high-temperature corrosion in both oxidizing and

sulfidizing environments [1–3]. Of course, it should be noted that the impurity effect may play an important role, if the grain boundary diffusion can be neglected and the concentration of point defects in the growing scale is very low. In those cases only, the rate of corrosion, determined by volume diffusion of cations (or anions) through point defects, may considerably be influenced by doping effect. At present, it is generally assumed in the literature that this influence depends virtually only on the valency of impurity atoms [4]. It has been found, for instance, that trivalent chromium ions increase the oxidation rate of nickel [5] or cobalt [6] and those of lithium decrease oxidation rate of nickel [7]. However, several experimental results strongly suggest that additional factors may play analogous or even more important role. In addition to the concentration and the valency of impurity, the mode of its dissolution (incorporation) into the crystal lattice of the growing scale may decisively influence the rate of corrosion and the mechanism of scale growth. It must be stressed once again that the classical interpretation of doping effect in terms of Hauffe–Wagner theory [4] is possible only if the concentration of defects is very low and the scale is growing by the volume diffusion, being the slowest step of the overall corrosion rate (parabolic kinetics). If, on the other hand, grain boundary diffusion predominates and the impurities accumulate along grain boundaries, like in the case of chromium oxidation, their influence may not be considered in terms of doping in the classical sense of this term.

The present paper is an attempt to demonstrate that, considering all the restrictions mentioned above, the same impurity may in some cases accelerate and in others dramatically decrease the rate of corrosion of a given metal. These phenomena will be demonstrated by the results of the influence of aliovalent impurities on the sulfidation rate of manganese and molybdenum—two metals forming the scales with very low defect concentrations.

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### The influence of chromium and lithium on manganese sulfidation kinetics

The kinetics and mechanism of manganese sulfidation, as well as the defect structure and transport properties of manganous sulfide have been extensively studied by different authors, using various experimental techniques [8–17]. It has been shown that the nonstoichiometry and thereby defect concentration in  $\alpha$ -MnS, showing rock salt structure, is very low and this is the main reason why the sulfidation rate of manganese is several orders of magnitude lower than that of other transition metals [18, 19]. Over the major part of the phase field, corresponding to higher sulfur activities, this sulfide is a metal-deficit p-type semiconductor with the predominant defects being doubly ionized cation vacancies and electron holes (Mn<sub>1-y</sub>S) [12, 15, 17].

As the nonstoichiometry and thereby the concentration of defects in Mn<sub>1-y</sub>S, even at high temperatures, is very low ( $y < 10^{-3}$ ), they do not interact and are randomly distributed in crystal lattice. Thus, the formation of these defects can be described by the following quasichemical reversible reaction (Kröger–Vink's notation of defects is used throughout this paper [20]):



Applying to this defect equilibrium the mass action law and the appropriate electroneutrality condition ( $2[V''_{\text{Mn}}] = [h^\bullet]$ ) and considering the fact that the nonstoichiometry,  $y$ , is simply equal to defect concentration, expressed in site fraction, one obtains the following theoretical relationship [1, 3], describing the concentration of ionic and electronic defects in Mn<sub>1-y</sub>S, as a function of temperature and sulfur pressure:

$$y = [V''_{\text{Mn}}] = \frac{1}{2}[h^\bullet] = 0.63 \cdot p_{\text{S}_2}^{1/6} \cdot \exp\left(\frac{\Delta S_f}{3R}\right) \cdot \exp\left(-\frac{\Delta H_f}{3RT}\right) \quad (2)$$

where  $\Delta S_f$  and  $\Delta H_f$  are entropy and enthalpy of defect formation, respectively. The equilibrium constant,  $K_V$ , of this defect situation is given by:

$$K_V = [V''_{\text{Mn}}] \cdot [h^\bullet]^2 \cdot p_{\text{S}_2}^{-1/2} \quad (3)$$

In agreement with Eq. 2, it has been found that the nonstoichiometry,  $y$ , in Mn<sub>1-y</sub>S is the following function of temperature and sulfur pressure [21]:

$$y = 4.77 \cdot 10^{-2} \cdot p_{\text{S}_2}^{1/6} \cdot \exp\left(-\frac{41.5 \text{ kJ/mol}}{RT}\right) \quad (4)$$

From the comparison of Eqs. 2 and 4 it follows that  $\Delta S_f = -64.4 \text{ J/mol K}$  and  $\Delta H_f = 124.5 \text{ kJ/mol}$ . On the other hand, the mobility of these defects, the measure of which

defect diffusion coefficient,  $D_V$ , has been found to be independent on their concentration and is the following function of temperature [13]:

$$D_V = \text{const} \cdot \exp\left(-\frac{\Delta H_m}{RT}\right) = 1.97 \cdot 10^{-2} \cdot \exp\left(-\frac{83.4 \text{ kJ/mol}}{RT}\right) \quad (5)$$

where  $\Delta H_m$  is enthalpy of defect migration.

Consequently, the self-diffusion coefficient of cations in Mn<sub>1-y</sub>S, which is a product of defect concentration and their mobility [1, 3], can be calculated as a function of temperature and sulfur pressure:

$$D_{\text{Mn}} = [V''_{\text{Mn}}] \cdot D_V = 9.4 \cdot 10^{-4} \cdot p_{\text{S}_2}^{1/6} \cdot \exp\left(-\frac{124.9 \text{ kJ/mol}}{RT}\right) \quad (6)$$

From Wagner's theory of metal oxidation [22, 23], it follows, in turn, that in the simple case under discussion of noninteracting point defects, the parabolic rate constant of scale formation of a given metal is related to the self-diffusion coefficient of migrating species,  $D_{\text{Mn}}$ , determining the overall reaction rate, by the following equation:

$$k'_p = (1 + |p|) \cdot D_{\text{Mn}} \quad (7)$$

where  $k'_p$  is the parabolic rate constant, expressed in square centimeter per second and  $p$ —the degree of defect ionization, equals 2 in this case. Thus, using this relationship and empirical Eq. 6, the parabolic rate constant of manganese sulfidation could have been calculated:

$$k' = 3 \cdot D_{\text{Mn}} = 2.82 \cdot 10^{-3} \cdot p_{\text{S}_2}^{1/6} \cdot \exp\left(-\frac{124.9 \text{ kJ/mol}}{RT}\right) \quad (8)$$

and compared with experimentally determined one:

$$k'_p = 3.51 \cdot 10^{-3} \cdot p_{\text{S}_2}^{1/6} \cdot \exp\left(-\frac{127 \text{ kJ/mol}}{RT}\right) \quad (9)$$

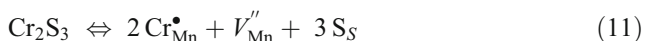
From this comparison, it follows clearly that the calculated parabolic rate constant of manganese sulfidation, as dependent on temperature and sulfur pressure, is in excellent agreement with experimentally determined data. The second important conclusion from this agreement is that the sulfide scale on manganese is growing by the outward volume diffusion of cations and consequently that the participation of grain boundary diffusion in this process may be neglected. Thus, the effect of impurities on the kinetics and mechanism of manganese sulfidation can be considered in terms of Hauffe–Wagner theory of doping [4].

From these short remarks, it follows that the activation energy of manganese sulfidation,  $E_p$ , being equal to the activation energy of cation self-diffusion in Mn<sub>1-y</sub>S scale,

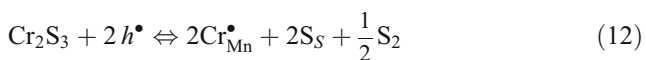
$E_D$ , is the sum of one third of enthalpy of defect formation,  $\Delta H_f$ , and the enthalpy of their migration,  $\Delta H_m$ :

$$E_p = E_D = \frac{1}{3} \Delta H_f + \Delta H_m = 127 \text{ kJ/mol} \quad (10)$$

Passing now to the influence of aliovalent impurities on manganese sulfidation kinetics, the effect of trivalent chromium and monovalent lithium ions will be presented and explained in terms of doping effect. At the beginning, the influence of chromium will be discussed. If, namely, one assumes that trivalent chromium ions are substitutionally incorporated into the cation sublattice of  $Mn_{1-y}S$  scale, this process can be presented by the following quasichemical reaction:



and



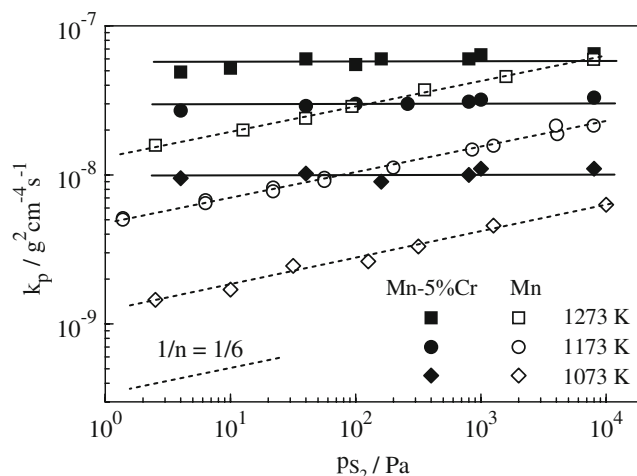
It follows from these defect equilibria that the concentration of cation vacancies in chromium-doped  $Mn_{1-y}S$  is higher than that in pure manganous sulfide and the concentration of electron holes is lower. Consequently, the growth rate of  $Cr_2S_3$ - $Mn_{1-y}S$  solid solution scale on Mn–Cr alloy must be higher than that of  $Mn_{1-y}S$  scale on pure manganese metal. The electroneutrality condition for this solid solution is given by:

$$[Cr_{Mn}^{\bullet}] + [h^{\bullet}] = 2 [V''_{Mn}] \quad (13)$$

When the concentration of dopant is much higher than that of electronic defects ( $[Cr_{Mn}^{\bullet}] \gg [h^{\bullet}]$ ), as in the discussed case, the above electroneutrality condition reduces to the following simplified form:

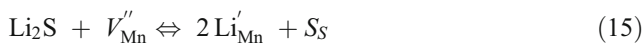
$$[Cr_{Mn}^{\bullet}] = 2 [V''_{Mn}] \quad (14)$$

It follows from these considerations that in agreement with experimental results [24], Figs. 1 and 2, the sulfidation rate of Mn–Cr alloy should be pressure independent and the activation energy of this reaction must be lower than that of pure manganese sulfidation. This last conclusion results from the fact that the activation energy of Mn–Cr alloy sulfidation is simply equal only  $\Delta H_m$  ( $E_p = E_D = \Delta H_m$ , see Eq. 10) because  $\Delta H_f$  is equal to zero due to the fixed concentration of cation vacancies on the constant level by dopant (see Eq. 14). This conclusion is in excellent agreement with experimental results, shown in Fig. 2, confirming the full applicability of Hauffe–Wagner doping effect in the case under discussion.

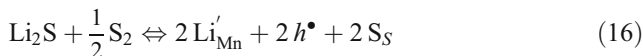


**Fig. 1** The pressure dependence of the parabolic rate constant of Mn–5% Cr alloy sulfidation for several temperatures on the background of pure manganese sulfidation data

Following this type of reasoning, the influence of monovalent impurity may also be considered in terms of this theory. Assuming, namely, that lithium ions are being substitutionally incorporated into the cation sublattice of the growing  $Mn_{1-y}S$  scale, this process can be presented by the following quasireversible reactions:



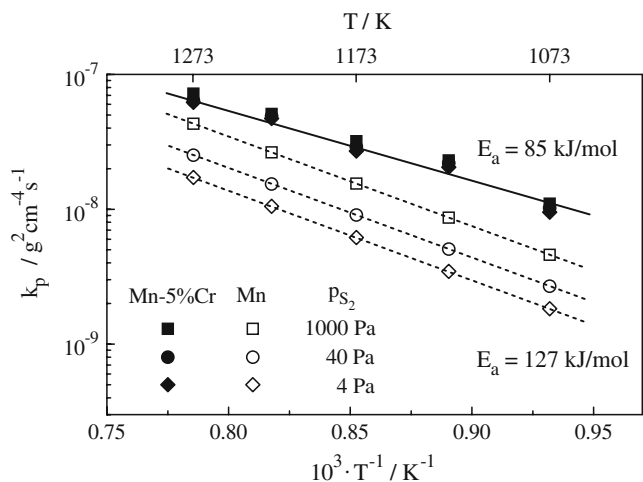
and



From these equations, it follows that the concentration of cation vacancies of lithium-doped  $Mn_{1-y}S$ , i.e., in  $Li_2S$ - $Mn_{1-y}S$  solid solution, should be lower and the concentration of electron holes higher than that in pure  $Mn_{1-y}S$ . Assuming further that, like in the case of Mn–Cr alloy sulfidation, the rate-determining step of the overall sulfidation rate of Mn–Li alloy is the diffusional transport of cations through cation vacancies (parabolic kinetics), the protective properties of lithium-doped  $Mn_{1-y}S$  scale should be better than those of pure  $Mn_{1-y}S$  scale. In addition, the activation energy of reaction should be higher and the rate of the reaction should increase more rapidly with increasing sulfur pressure. Both these conclusions result from the following theoretical considerations.

The electroneutrality condition for the case under discussion assumes the form:

$$[Li'_{Mn}] + 2 [V''_{Mn}] = [h^{\bullet}] \quad (17)$$



**Fig. 2** The temperature dependence of the parabolic rate constant of Mn–5% Cr alloy sulfidation on the background of pure manganese sulfidation data

Two limiting cases should be again considered. If  $[Li'_{Mn}] \gg [V''_{Mn}]$ , this electroneutrality condition reduces to the following form:

$$[Li'_{Mn}] = [h^\bullet] \tag{18}$$

Replacing now in the relationship (3) the electron hole concentration by that of dopant (Eq. 18), one obtains the following theoretical equation:

$$[V''_{Mn}] = \frac{K_V}{[Li'_{Mn}]^2} \cdot P_{S_2}^{1/2} \tag{19}$$

From these considerations, it follows that if the concentration of monovalent lithium dopant is high enough to fix the concentration of electronic defects in the growing  $Li_2S$ – $Mn_{1-y}S$  scale, the sulfidation rate of Mn–Li alloy should increase more rapidly with sulfur pressure, with the slope 1/2 (see Eq. 19) and the activation energy of this process should be higher than that of pure manganese sulfidation. This last conclusion follows from the fact that in the case of pure manganese sulfidation, the concentration of both ionic and electronic defects increase with increasing temperature and, consequently, only 1/3 of  $\Delta H_f$  participates in the activation energy of cation self-diffusion and thereby in the activation energy of manganese self-diffusion (Eq. 10). In lithium-doped  $Mn_{1-y}S$  scale, on the other hand, if the dopant content is sufficiently high, the electron hole concentration is fixed on the constant level (Eq. 18) and, consequently, the whole value of  $\Delta H_f$  participates in the activation energy of sulfidation. Eliminating, namely, from Eq. 19, the equilibrium constant,  $K_V$ , one obtains the following dependence of the concentration of cation

vacancies in  $Li_2S$ – $Mn_{1-y}S$  solid solution on sulfur pressure and temperature:

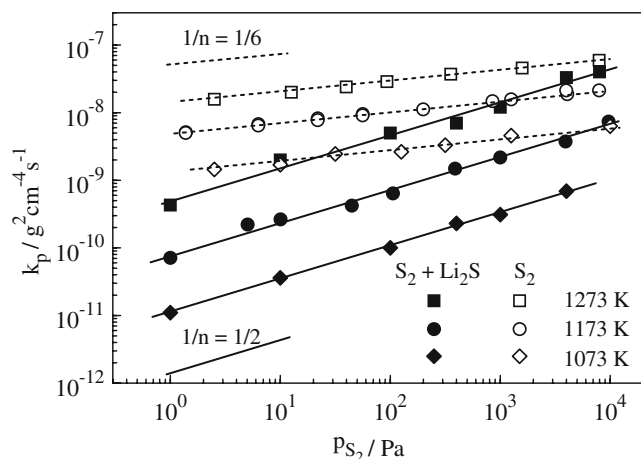
$$[V''_{Mn}] = \frac{1}{[Li'_{Mn}]^2} \cdot P_{S_2}^{1/2} \cdot \exp\left(\frac{\Delta S_f}{R}\right) \cdot \exp\left(-\frac{\Delta H_f}{RT}\right) \tag{20}$$

As can be seen, the concentration of cation vacancies in  $Li_2S$ – $Mn_{1-y}S$  scale on Mn–Li alloys must increase with increasing temperature more rapidly than in pure  $Mn_{1-y}S$  and, consequently, the activation energy of alloy sulfidation should be higher:

$$E'_p = E'_D = \Delta H_f + \Delta H_m > E_p = E_D = \frac{1}{3} \Delta H_f + \Delta H_m \tag{21}$$

where  $E'_p$  and  $E'_D$  denote the activation energy of alloy sulfidation and that of self-diffusion of cations in  $Mn_{1-y}S$ – $Li_2S$  solid solution, respectively. If one assumes that the enthalpies of defect formation and their migration in pure and lithium-doped  $Mn_{1-y}S$  are the same, from Eqs. 6 and 20, it follows that the activation energy of Mn–Li alloy sulfidation should be equal to  $\Delta H_f + \Delta H_m = 124.5 + 83.4 = 207.9$  kJ/mol, while in the case of pure manganese sulfidation, the activation energy of the reaction is lower and equal to  $1/3 \Delta H_f + \Delta H_m = 41.5 + 83.4 = 124.9$  kJ/mol (Eqs. 4 and 5).

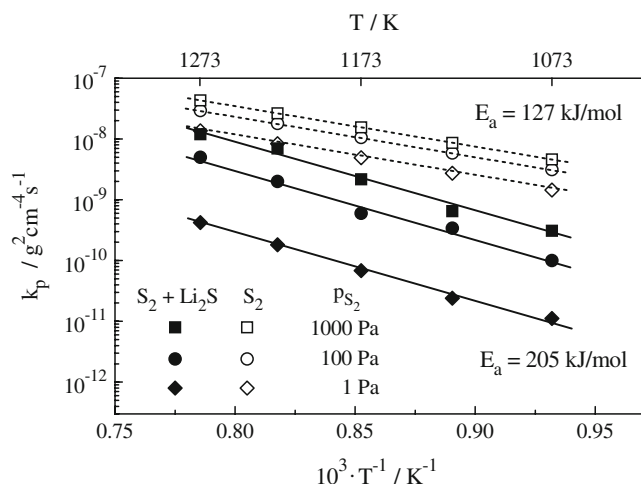
In order to prove this theoretical considerations, the influence of lithium on the sulfidation rate of manganese should have been investigated as a function of temperature and sulfur pressure [25]. However, Mn–Li alloys are very difficult to be prepared by the conventional metallurgical procedure and we have been unable to obtain such alloys of acceptable quality. Considering this difficult situation, the conclusion was that appropriate concentration of lithium may be incorporated into the growing MnS scale from “outside,” following the sulfidation rate of pure manganese samples in sulfur vapor atmosphere containing  $Li_2S$  vapor. In order to apply this experimental procedure to manganese sulfidation, the following experiments have been carried out. Quartz crucible with  $Li_2S$  powder has been located beneath the manganese sample in the reaction chamber of microthermogravimetric apparatus and the sulfidation rate under such conditions has been determined as a function of temperature (1,073–1,273 K) and sulfur pressure (1– $10^4$  Pa). Some of the results obtained in these experiments are presented in Figs. 3 and 4 in doubly logarithmic and Arrhenius plots, respectively. As can be seen, the influence of lithium on the sulfidation rate of manganese is in full agreement with theoretical predictions, based on Hauffe–Wagner theory of doping. The sulfidation rate, being about two orders of magnitude lower than that of pure manganese sulfidation, increases, namely, with sulfur pressure with the slope 1/2 (Fig. 3) and the higher activation energy of the



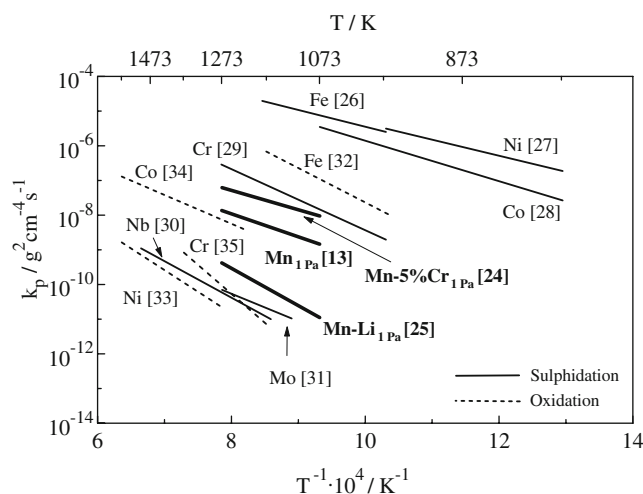
**Fig. 3** The pressure dependence of the parabolic rate constant of Mn sulfidation in pure sulfur vapor (*dashed line*) and in sulfur vapor containing  $\text{Li}_2\text{S}$  (*solid line*), for several temperatures

reaction is, as predicted, virtually equal to the sum of  $\Delta H_f + \Delta H_m = 205 \text{ kJ/mol}$  (Fig. 4).

It follows from these results that in agreement with Hauffe–Wagner theory [4], the protective properties of the sulfide scale on manganese may considerably be improved by appropriate doping effect. In order to visualize the important role of this effect, the temperature dependence of the parabolic rate constant of manganese sulfidation in lithium-containing sulfur vapors is compared in Fig. 5 with parabolic rate constants of oxidation and sulfidation of several metals. It follows from this comparison that protective properties of lithium-doped sulfide scale on manganese are comparable with those of the oxide scale on chromium and sulfide scales on niobium and molybdenum—three metals representing the highest resistance to oxide and sulfide corrosion, respectively. Thus, the final conclusion is that, in those cases when all



**Fig. 4** The temperature dependence of the parabolic rate constant of Mn sulfidation in pure sulfur vapor (*dashed line*) and in sulfur vapor containing  $\text{Li}_2\text{S}$  (*solid line*), for several sulfur vapor pressures



**Fig. 5** Comparison of the parabolic rate constant of Mn sulfidation in pure [13] and  $\text{Li}_2\text{S}$ -containing [25] sulfur vapor on the background of the sulfidation [26–31] (*solid lines*) and oxidation [32–35] (*dotted lines*) rates of several metals as well as Mn–5% Cr alloy sulfidation data [24]

assumptions of Hauffe–Wagner theory are fulfilled, doping effect may play an important role in improving the corrosion resistance of metals to high-temperature oxide and sulfide corrosion.

### The influence of chromium and lithium on molybdenum sulfidation kinetics

Due to the very low defect concentration in molybdenum disulfide,  $\text{MoS}_2$  [36], constituting the main part of sulfide scale on molybdenum, is one of the most resistant metals to sulfide corrosion [18, 37]. It has been shown that predominant defects in  $\text{MoS}_2$  are doubly ionized interstitial sulfur ions and electron holes [31, 38]. Consequently, the appropriate chemical formula of molybdenum disulfide should be written in the following form  $\text{MoS}_{2+\delta}$ , indicating that the extrinsic disorder in this sulfide results from sulfur excess. It has been shown also that very low growth rate of sulfide scale on molybdenum is determined by inward diffusion of sulfur [31, 39] and the parabolic rate constant of sulfidation, as dependent on temperature and sulfur pressure, can be described by the following empirical equation [39]:

$$k_p = 3.6 \cdot 10^3 \cdot p_{\text{S}_2}^{1/2} \cdot \exp\left(-\frac{166 \text{ kJ/mol}}{RT}\right) \quad (22)$$

It should be noted, however, that the defect structure of the discussed sulfide is more complex [31] because the extrinsic defects resulting from nonstoichiometry is highly dominated by intrinsic electronic disorder. Thus, in addition to the formation of interstitial anions and electron holes

resulting in nonstoichiometry, which may be described by the following quasi-chemical reaction:



it is necessary to consider the intrinsic electronic disorder:



Applying to both those defect equilibria the mass action law, one obtains the following relationships for corresponding equilibrium constants:

$$K_{23} = \frac{[S_i''] \cdot [h^\bullet]^2}{p_{S_2}^{1/2}} \quad (25)$$

and

$$K_{24} = [e'] \cdot [h^\bullet] \quad (26)$$

General electroneutrality condition in the case under discussion assumes the form:

$$2[S_i''] + [e'] = [h^\bullet] \quad (27)$$

Considering further the fact that the intrinsic electronic disorder prevails, general neutrality condition may be reduced to the following simplified form:

$$[e'] = [h^\bullet] = \sqrt{K_{24}} \quad (28)$$

Using this relationship, the Eq. 25 can be transformed into the following form:

$$[S_i''] = \frac{K_3}{K_{24}} \cdot p_{S_2}^{1/2} \quad (29)$$

It follows from this equation that the concentration of interstitial anions increases with increasing sulfur pressure with the slope 1/2. If one assumes further that the mobility of ionic defects (interstitial sulfur ions) does not depend on their concentration, the sulfidation rate of molybdenum should increase with increasing sulfur pressure in the same way because the parabolic rate constant of scale growth is directly proportional to the defect concentration [1, 2]. This conclusion is in full agreement with experimental results of molybdenum sulfidation kinetics, described by Eq. 22.

Passing now to the explanation of the influence of chromium on the sulfidation rate of molybdenum, again appropriate defect equilibria should be considered. From such theoretical analysis it follows that if one assumes that trivalent chromium ions are incorporated substitutionally into the cation sublattice of  $MoS_{2+y}$  scale, as shown by the following defect reaction:



and consequently the sulfidation rate should be decreased. On the other hand, when chromium ions dissolve intersti-

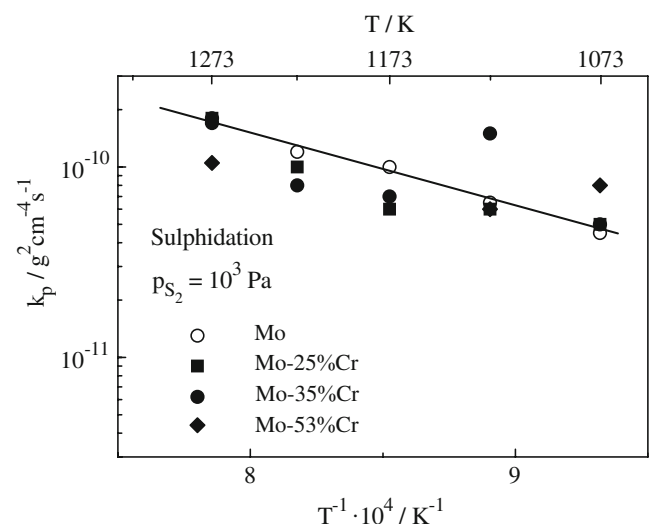
tially, the concentration of interstitial sulfur ions will increase as shown by this defect equilibrium:



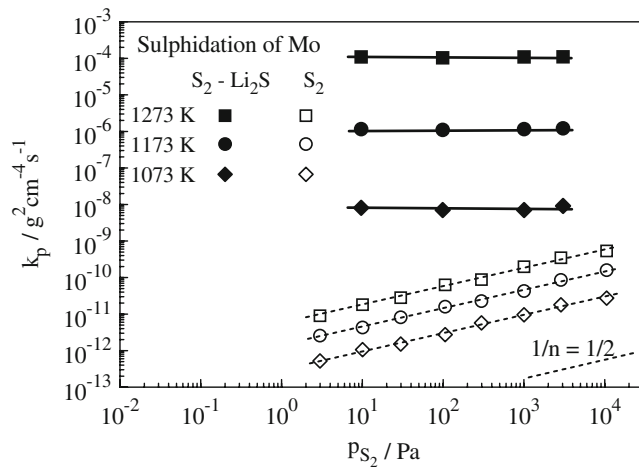
the sulfidation rate should increase. It has been found, however, that the sulfidation rate of Mo–Cr alloys even containing very high amount of chromium is virtually the same as that of pure molybdenum, Fig. 6, which implies that no influence of doping is observed [40]. The tentative explanation of these rather unexpected behavior is that chromium sulfide does not form solid solution with  $MoS_{2+y}$  at all.

As far as the influence of lithium on the sulfidation kinetics of molybdenum is concerned, again Mo–Li alloys was impossible to be obtained in conventional metallurgical procedure. Thus, as in the case of manganese sulfidation, lithium ions were incorporated from “outside” into the crystal lattice of  $MoS_{2+y}$  scale, growing on molybdenum [39]. Thus, the sulfidation rate of molybdenum in lithium-containing sulfur vapor has been studied as a function of temperature (973–1,273 K) and sulfur pressure ( $10^{-4}$ – $10^4$  Pa). Some of these results are presented in Figs. 7 and 8 in doubly logarithmic and Arrhenius plots, respectively. As can be seen, dramatic influence of monovalent lithium dopant on the sulfidation rate of molybdenum is clearly visible. In fact, the rate at highest temperatures in lithium-containing atmosphere is more than four orders of magnitude higher than that in pure sulfur vapor. In addition, from Fig. 7, it follows that the sulfidation rate does not depend on sulfur pressure at all.

In order to explain this peculiar doping effect, appropriate defect equilibria must be considered. If one assumes that monovalent lithium ions are substitutionally incorporated



**Fig. 6** The temperature dependence of the parabolic rate constant of Mo–Cr alloys sulfidation for several temperatures on the background of pure molybdenum sulfidation data [40]



**Fig. 7** The pressure dependence of the parabolic rate constant of Mo sulfidation in pure sulfur vapor (*dashed line*) and in sulfur vapor containing  $\text{Li}_2\text{S}$  (*solid line*), for several temperatures

into the cation sublattice of the  $\text{MoS}_{2+y}$  scale, the concentration of interstitial sulfide ions should decrease, as shown by the following defect equilibrium:



Thus, the sulfidation rate should dramatically be decreased, which in fact is in obvious contradiction with experimental results. From Figs. 7 and 8, it follows, namely, that the sulfidation rate of molybdenum is dramatically increased and not decreased by lithium doping. Consequently, the possibility of the second mode of lithium dissolution in  $\text{MoS}_{2+y}$  should be considered, by assuming that lithium ions dissolve interstitially in the crystal lattice of  $\text{MoS}_{2+y}$  scale. Assuming such a mechanism of doping, dissolution of lithium ions in cation sublattice of  $\text{MoS}_{2+y}$  can be described by the following quasi-chemical defect reaction:



Applying to this defect equilibrium the mass action law, one obtains the following equation for equilibrium constant of this reaction:

$$K_{33} = [\text{Li}_i^\bullet]^2 \cdot [\text{S}_i''] \quad (34)$$

The general electroneutrality condition, in turn, taking into account intrinsic electronic disorder, is given by:

$$[\text{Li}_i^\bullet] + [h^\bullet] = [e'] + 2[\text{S}_i''] \quad (35)$$

Assuming further that the concentration of dopant is higher than that of electronic defects, the above electroneutrality condition reduces to the following simplified form:

$$[\text{Li}_i^\bullet] = 2[\text{S}_i''] \quad (36)$$

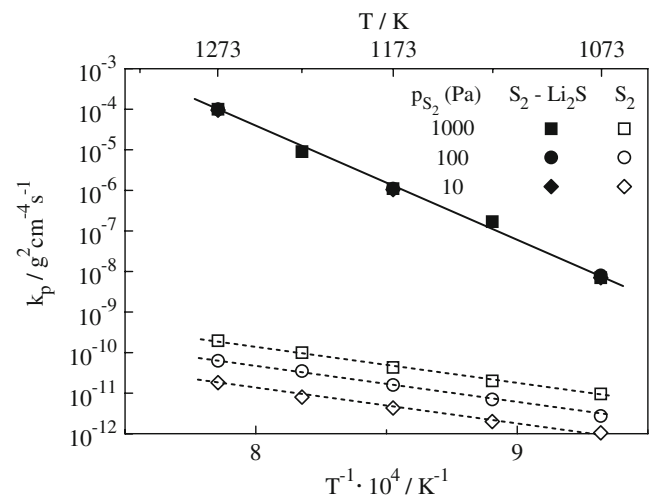
From above considerations, it follows clearly that, if the concentration of lithium in the growing scale on molybdenum is sufficiently high, the rate of the reaction in lithium-containing atmospheres should be higher (see Eq. 33) than in pure sulfur vapor. In addition, the sulfidation rate should be pressure independent because the concentration of ionic defects is fixed by the concentration of dopant in the  $\text{MoS}_{2+y}\text{-Li}_2\text{S}$  solid solution, forming the scale. Both these conclusions are in full agreement with experimental results presented in Figs. 7 and 8.

It is important to note that the described results of lithium influence on the sulfidation kinetics of molybdenum constitutes an excellent example of the importance of the dissolution mode of dopant in the growing scale. It has been shown, namely, that the rate of manganese sulfidation is considerably decreased by monovalent dopant, which indicates that lithium ions are substitutionally incorporated in cation sublattice of  $\text{Mn}_{1-y}\text{S}$  scale. The same effect would be observed in the case of molybdenum sulfidation, if lithium ions would also incorporate substitutionally into the cation sublattice of  $\text{MoS}_{2+y}$ . However, experimental results strongly suggest that, in this case, monovalent impurity dissolves interstitially and not substitutionally.

### Conclusions

Theoretical considerations and experimental results presented in this paper allow the following conclusions to be formulated.

One of the most important but rather pessimistic conclusion is that it is impossible a priori to predict the influence of aliovalent impurity on the sulfidation or oxidation kinetics of a given metal, basing on theoretical



**Fig. 8** The temperature dependence of the parabolic rate constant of Mo sulfidation in pure sulfur vapor (*dashed line*) and in sulfur vapor containing  $\text{Li}_2\text{S}$  (*solid line*), for several sulfur vapor pressures

considerations in terms of Hauffe–Wagner theory of doping. On the contrary, this theory may be used in explaining the experimental results of doping if the defect structure of the compound, forming the scale, is known. In particular, the mode of dissolution of impurity may be explained considering the appropriate defect equilibria of doping. This type of reasoning has been demonstrated in the present work on two examples, in studying the influence of aliovalent impurities on the kinetics and mechanism of manganese and molybdenum sulfidation.

## References

- Mrowec S (1980) Defects and diffusion in solids. Elsevier, Amsterdam-Oxford-New York
- Mrowec S (1982) An introduction to the theory of metal oxidation. National Bureau of Standards and National Science Foundation, Washington D.C
- Kofstad P (1972) Non-stoichiometry, diffusion and electrical conductivity of binary metal oxides. John Wiley, New York
- Hauffe K (1953) Progress Metal Phys 4:71
- Mrowec S, Grzesik Z, Rajchel B, Gil A, Dabek J (2005) J Phys Chem Solids 66:115
- Mrowec S, Grzesik Z (2003) J Phys Chem Solids 64:1387
- Pfeiffer H, Hauffe K (1952) Z Metallkunde 43:364
- Erlefaie FA, Smeltzer WW (1981) Oxid Met 16:267
- Perez M, Larpin JP (1984) Oxid Met 21:229
- Danielewski M (1986) Oxid Met 25:51
- Papaiacovou P, Schmidt H, Erhard H, Grabke HJ (1987) Werkstoffe und Korrosion 38:498
- Rau H (1978) J Phys Chem Solids 39:339
- Grzesik Z, Mrowec S, Walec T, Dabek J (2000) J Phys Chem Solids 61:809
- Rosner J, Carton D (1980) C R Acad Sci (Paris) Sci II 290:405
- Mrowec S, Grabke HJ, Danielewski M (1990) J Mater Sci 25:537
- Gilewicz-Wolter J, Danielewski M, Mrowec S (1997) Physical Rev B 56:8695
- Mrowec S, Danielewski M, Gilewicz-Wolter J (1999) Solid State Ionics 117:65
- Mrowec S, Przybylski K (1984) High Temp Mater Processes 6:1
- Mrowec S, Janowski J (1989) Similarities and differences in defect dependent properties of transition metal sulphides and oxides. In: Johannesen Q, Andersen AG (eds) Selected topics in high temperature chemistry, defect chemistry of solids. Elsevier, Amsterdam, pp 55–96
- Kröger F (1964) The chemistry of imperfect crystals. North Holland, Amsterdam
- Mrowec S, Grzesik Z (2001) Solid State Ionics 143:25
- Wagner C (1933) Z physik Chem B21:25
- Wagner C (1975) Progr Solid State Chem 10:3
- Mrowec S, Grzesik Z (2001) J Phys Chem Solids 62:1171
- Grzesik Z, Mrowec S (2006) Corr Sci 48:3186
- Mrowec S, Danielewski M, Stoklosa A (1980) Solid State Ionics 1:287
- Mrowec S, Czerski L, Werber T (1962) J Electrochem Soc 109:273
- Mrowec S, Danielewski M, Wójtowicz A (1998) J Mater Sci 33:2617
- Mrowec S, Danielewski M, Dabek J, Sieminska G (1987) Bull Acad Pol Sci Chem 35:199
- Danielewski M (1987) “Sulphidation behaviour of niobium”. In: Proc. of European Corrosion Meeting, Eurocorr’87, pp 223–228
- Przybylski K, Potoczek M (1994) Trans Mat Res Soc Jpn 14A:169
- Footner DK, Holmes DR, Mortimer D (1967) Nature 216:54
- Mrowec S, Grzesik Z (2004) J Phys Chem Solids 65:1651
- Mrowec S, Grzesik Z (2003) J Phys Chem Solids 64:1387
- Lillerud KP, Kofstad P (1980) J Electrochem Soc 127:2397
- Rau H (1980) J Phys Chem Solids 41:765
- Mrowec S (2003) High Temp Mater Processes 22:1
- Potoczek M, Przybylski K, Rekas M (2006) J Phys Chem Solids 67:2528
- Grzesik Z, Migdalska M, Mrowec S (2008) High Temp Mater and Processes 26:355
- Ito K, Habazaki H, Mitsui H, Akiyama E, Kawashima A, Asami K, Hashimoto K, Mrowec S (1997) Mater Sci Eng A226–228:910