

Influence of H₂S on metal dusting

Einfluß von H₂S auf metal dusting

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Presence of H₂S in a carburizing atmosphere causes S-adsorption which retards carbon transfer and deposition and can suppress metal dusting of iron and steels. In the latter process cementite Fe₃C is an intermediate, graphite deposition would initiate its decomposition but graphite nucleation is prevented by adsorbed sulfur. Thus continued Fe₃C growth can be observed in the presence of H₂S. Thermogravimetric studies in CO-H₂-H₂O-H₂S mixtures have been conducted at 500 °C at various carbon activities a_C and H₂S/H₂-ratios. With increasing a_C higher H₂S/H₂-ratios are needed to suppress metal dusting, with increasing H₂S/H₂-ratio the kinetics of Fe₃C growth change from diffusion controlled parabolic kinetics to linear carbon transfer controlled kinetics. At very high a_C ≥ 1000 besides Fe₃C also the Hägg carbide Fe₅C₂ was observed as an outer layer on the cementite.

Die Gegenwart von H₂S in einer aufkohlenden Atmosphäre führt zu Schwefeladsorption, diese verlangsamt die Kohlenstoffübertragung und Kohlenstoffabscheidung und kann das metal dusting von Eisen und Stählen unterdrücken. Beim metal dusting tritt Zementit Fe₃C als Zwischenprodukt auf, und Graphitabscheidung würde den Zerfall des Zementit einleiten, jedoch wird die Graphitkeimbildung durch adsorbierten Schwefel verhindert. Daher kann fortgesetztes Fe₃C-Wachstum in der Gegenwart von H₂S beobachtet werden. Thermogravimetrische Untersuchungen in CO-H₂-H₂O-H₂S-Gemischen sind bei 500 °C durchgeführt worden und bei verschiedenen Kohlenstoffaktivitäten a_C und H₂S/H₂-Verhältnissen. Mit zunehmender Kohlenstoffaktivität a_C sind höhere H₂S/H₂-Verhältnisse notwendig, um das metal dusting zu unterdrücken, weiterhin ändert sich mit zunehmendem H₂S/H₂-Verhältnis die Kinetik des Fe₃C-Wachstums von der diffusionskontrollierten parabolischen Kinetik zu der linearen, durch die Kohlenstoffübertragung kontrollierten Kinetik. Bei sehr hohen Werten für die Kohlenstoffaktivität a_C ≥ 1000 wurde neben Fe₃C auch das Hägg-Karbid Fe₅C₂ als äußere Schicht auf dem Zementit beobachtet.

1 Introduction

Metal dusting is a corrosion process, which attacks iron, low and high alloy steels and Co- or Ni-based alloys in strongly carburizing gas atmospheres with a_C > 1 in the temperature range 400 to 700 °C. Gas carburizing involves reactions at the gas/metal interface and carbon-diffusion within the metal. The carburization reaction in a CO-H₂-H₂O gas atmosphere is



The carbon transfer into the bulk is established by the surface reactions $\text{CO} = [\text{C}] + \text{O}_{\text{ads}}$ and $\text{O}_{\text{ads}} + \text{H}_2 = \text{H}_2\text{O}$. These surface reactions are very fast compared to those of other carburizing gas mixtures. The metal dusting of iron and low alloyed steels in CO-H₂-H₂O atmospheres can be explained by the following reaction mechanism [1–5]:

(i) rapid supersaturation of the metal phase with dissolved carbon by transfer from the gas phase (a_C > a_{C(Fe/Fe₃C)}), (ii) growth of a cementite layer at the surface, which acts as a barrier for the carbon transfer, causing (iii) graphite deposi-

tion, which lowers a_C → 1 rendering cementite unstable. (iv) The subsequent cementite decomposition $\text{Fe}_3\text{C} \rightarrow 3\text{Fe} + \text{C}$ yields graphite growth and formation of fine metal particles, which (v) act as catalysts for coke deposition. The presence of H₂S leads to sulphur adsorption, which retards the carbon transfer and coke deposition. The adsorbed sulfur also suppresses graphite nucleation, thus preventing step (iii) and stopping the reaction sequence. In fact continued growth of Fe₃C on Fe has been observed in CO-H₂-H₂O-H₂S atmospheres [6–8].

2 Influence of H₂S on carburization

Sulfur is a very surface active element. It tends to adsorb or segregate at surfaces or interfaces. In this study adsorption of sulfur is established by the equilibrium



The enthalpy of adsorption is $\Delta H \approx -100$ kJ/mol for sulfur on polycrystalline iron [9–10]. Sulfur on iron surfaces retards gas carburizing and nitriding processes by site blocking [11–12]. The influence of sulfur activity a_S on the carburization kinetics in a CH₄, H₂ and H₂S atmosphere has been studied at carbon activities a_C < 1 by Grabke et al. [11–12]. By increasing the H₂S content in the carburizing atmosphere, the reaction velocity decreases. At T = 850 °C the carburization

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rate was retarded by a factor of 0.1 due to the presence of a small amount of H₂S ($p_{\text{H}_2\text{S}}/p_{\text{H}_2} = 10^{-5}$). In this case the surface coverage with sulfur was calculated to be $\Theta_S \approx 0.9$. The structure of an adsorption monolayer ($\Theta = 1$) in the case of Fe(100) surfaces is $c(2 \times 2)$ [13]. In principle carbon transfer should be prevented by such a monolayer S on the iron surface, but vacancies in this monolayer lead to continued carburization.

Metal dusting of iron occurs at carbon activities $a_C \geq a_{C(\text{Fe}/\text{Fe}_3\text{C})}$. In this case carburization is followed by cementite formation. It has been found that sulfur also prevents graphite from nucleating on cementite [14]. Since graphite formation would lower the carbon activity $a_C \rightarrow 1$ which starts cementite decomposition, H₂S retards the onset of cementite decomposition [6]. The influence of H₂S on the growth and decomposition of Fe₅C₂ must also be taken into account. Most probably sulfur has the same effect on Fe₅C₂ as on cementite growth.

In Fig. 1 the influence of H₂S on metal dusting of iron in strongly carburizing atmospheres is shown as a function of temperature and the ratio $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$. Most data points in this diagram were obtained in an earlier study [6]. Open symbols represent experiments where the onset of metal dusting was retarded for more than 48 h, filled symbols correspond to an earlier onset of metal dusting. In this diagram the hatched region represents the transition to an iron surface saturated with sulfur. The upper boundary of this hatched region corresponds to saturation with adsorbed sulfur ($\Theta = 1$) and the lower to $\Theta = 0.9$. This diagram (Fig. 1) includes data of a study by Ando et al. [15], who investigated the effect of H₂S on carbon filament growth which in fact was metal dusting at 950 °C.

3 Experimental

Thermogravimetric analysis (TGA) was carried out on samples of pure iron (1 mm × 10 mm × 20 mm) exposed to a flowing carburizing atmosphere in a furnace. The samples

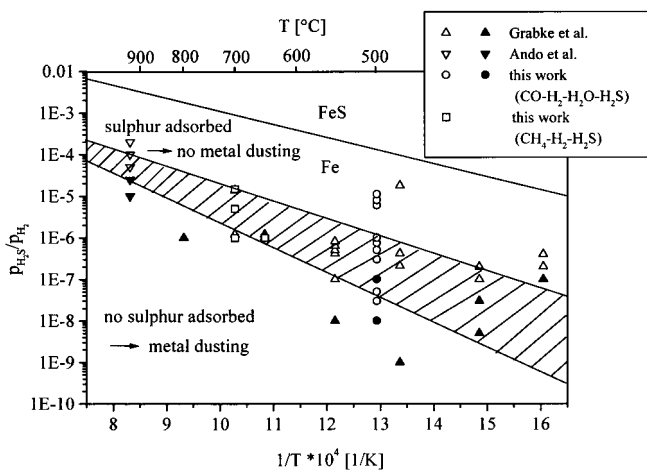


Fig. 1. Influence of H₂S on metal dusting as a function of temperature and the ratio $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$. The hatched region represents the transition to an iron surface saturated with sulfur

Abb. 1. Einfluß des H₂S auf das metal dusting als Funktion der Temperatur und des Verhältnisses $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$. Der schraffierte Bereich zeigt den Übergang von der freien Eisenoberfläche zu einer mit Schwefel gesättigten Oberfläche

were ground (1000 grit) and cleaned in acetone before inserting into the furnace. The mass gains were measured with a microbalance with an accuracy of ± 1 µg. The carbon activity of the CO-H₂-H₂O-H₂S gas mixture has been calculated by using the following equation [16]:

$$\lg a_C = \lg \left(\frac{p_{\text{H}_2} \cdot p_{\text{CO}}}{p_{\text{H}_2\text{O}}} \right) + \frac{7100}{T} + 7.496 \quad (3)$$

A H₂-H₂O mixture was obtained by passing H₂ through a mixture of oxalic acid and its dihydrate at a certain temperature. A H₂-H₂S mixture was obtained by passing H₂ through a mixture of iron and iron sulfide where its equilibrium content is established according to [17]:

$$\lg \left(\frac{p_{\text{H}_2\text{S}}}{p_{\text{H}_2}} \right) = -\frac{3132}{T} + 0.165 \quad \text{for } T = 139 - 907 \text{ °C} \quad (4)$$

The gas velocities were controlled using capillary flow meters and the composition of the gas mixture was continuously monitored by quadrupole mass spectroscopy. The phases on the carburized samples were determined using X-ray diffraction (XRD). Surface analysis was done by Auger electron spectroscopy (AES), here the different peak energies and signal shapes of carbon in graphite and in carbide can be distinguished. In order to analyse the layer structure of the carbides formed metallographic cross sections of the samples were prepared. After etching the samples in sodium picrate, the two iron carbides, cementite and Hägg carbide, are pale blue of different brightness.

4 Results and discussion

The results presented in this paper describe the influence of H₂S on the metal dusting behaviour of pure iron in CO-H₂-H₂O-H₂S atmospheres at T = 500 °C. In Fig. 2 TGA mass gain curves at 500 °C at different carbon activities without

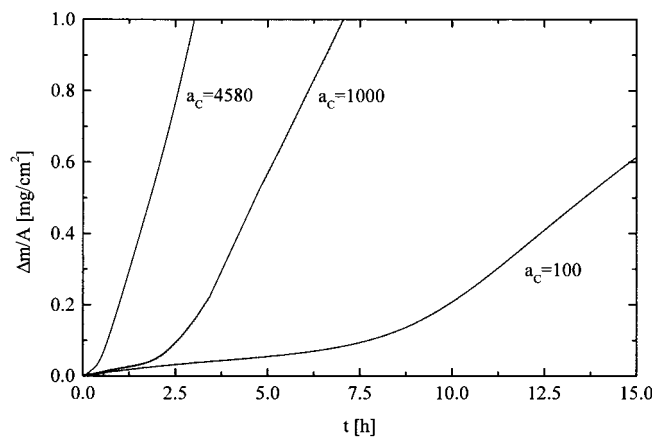


Fig. 2. Mass gain versus time for iron samples carburized in CO-H₂-H₂O mixtures at 500 °C. The onset of metal dusting is indicated by the change of the curvature into an almost quadratic mass gain

Abb. 2. Massezunahme aufgetragen gegen die Zeit für Eisenproben, die in CO-H₂-H₂O-Gemischen bei 500 °C aufgekühlt wurden. Das Einsetzen des metal dusting wird durch den Wendepunkt angezeigt und den Übergang der Kurven in eine nahezu quadratische Massezunahme

any H_2S addition are shown, the higher the carbon activity, the faster the metal dusting kinetics. At first the iron samples are supersaturated with carbon and Fe_3C formation occurs, later on the accelerating mass gain indicates start of metal dusting and is due to the carbon deposition caused by the catalytic effect of the fine metal particles formed.

The influence of H_2S has been studied for the cases of $a_C = 100$, $a_C = 1000$ and $a_C = 4580$. It was observed that at high carbon activities $a_C \geq 1000$ a second carbide forms in addition to cementite. With X-ray diffraction analysis of the carburized samples this carbide was identified as Hägg carbide Fe_5C_2 [18]. The d-spacings obtained were compared with those for cementite [19–20] and for Hägg carbide [21–22]. Additionally, theoretical diffraction patterns were calculated and compared with the measured ones. For $a_C = 100$ and lower carbon activities no Fe_5C_2 were detected. By using Auger electron spectroscopy it was shown, that at $a_C \geq 1000$ a layer sequence forms as follows: $Fe/Fe_3C/Fe_5C_2/gas$. This was done by evaluating the peak height ratios of the Auger peaks of carbon and iron for the two layers. These results indicate that the carbon activity $a_{C(Fe_3C/Fe_5C_2)}$ required for the formation of Fe_5C_2 is between $a_C = 100$ and $a_C = 1000$.

At $a_C = 100$ the onset of metal dusting is retarded for at least 90 h by adding 0.03 ppm H_2S to the carburizing atmosphere (Fig. 3). During the first period the mass gain is nearly parabolic with time, thus it can be assumed that the kinetics is controlled by diffusion of carbon through the growing cementite layer. By adding 0.1 ppm H_2S the mass gain is approximately linear with time, in this case most probably the site blocking effect of adsorbed sulphur is so strong that the surface reaction (1) controls the kinetics. In Fig. 4 it can be seen that also for $a_C = 1000$ the metal dusting kinetics slows down with increasing H_2S content. The onset of metal dusting, which is indicated by a change of curvature into an almost quadratic mass gain, can be retarded for times up to 300 h. Upon adding 0.75 or 1 ppm H_2S , the mass gain is almost linear over a long time period. During this period layers of cementite and Hägg carbide form. Then graphite nucleation starts and initiates the decomposition of cementite and probably of Hägg carbide, too. The microprocesses of cementite decomposition at lower carbon activities have been studied in detail [5]. Most probably the metastable Fe_5C_2 also decomposes in a similar way. The microprocesses of metal dusting including the Hägg carbide will be investigated in the future.

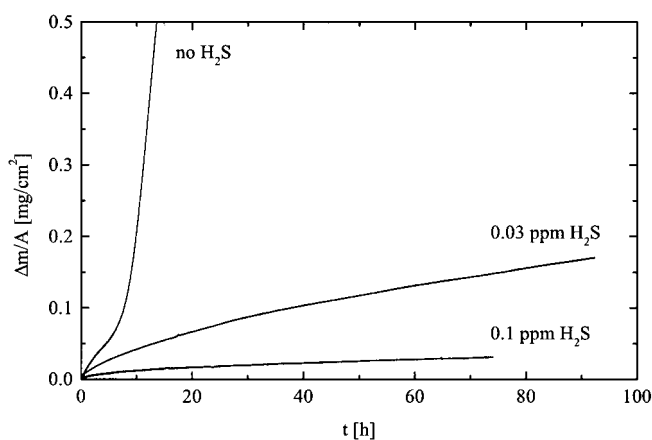


Fig. 3. Influence of H_2S on carburization at $a_C = 100$

Abb. 3. Einfluß des H_2S auf die Aufkohlung bei $a_C = 100$

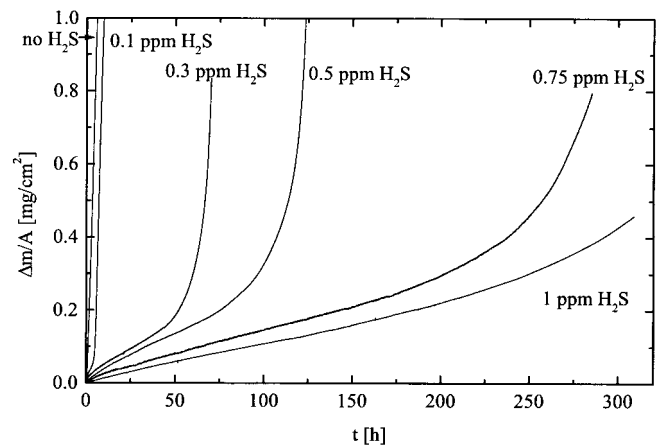


Fig. 4. Influence of H_2S on carburization at $a_C = 1000$

Abb. 4. Einfluß des H_2S auf die Aufkohlung bei $a_C = 1000$

In Fig. 5 metallographic cross sections of three of these samples are shown. Fig. 5 c indicates carbide decomposition of cementite and Hägg carbide. It is striking that the cross section of the sample carburized without any H_2S addition has no Fe_5C_2 , as confirmed by XRD. Only a very small amount of Fe_5C_2 was detected in the sample exposed to 0.1 ppm H_2S . This observation can be explained assuming that, after super-

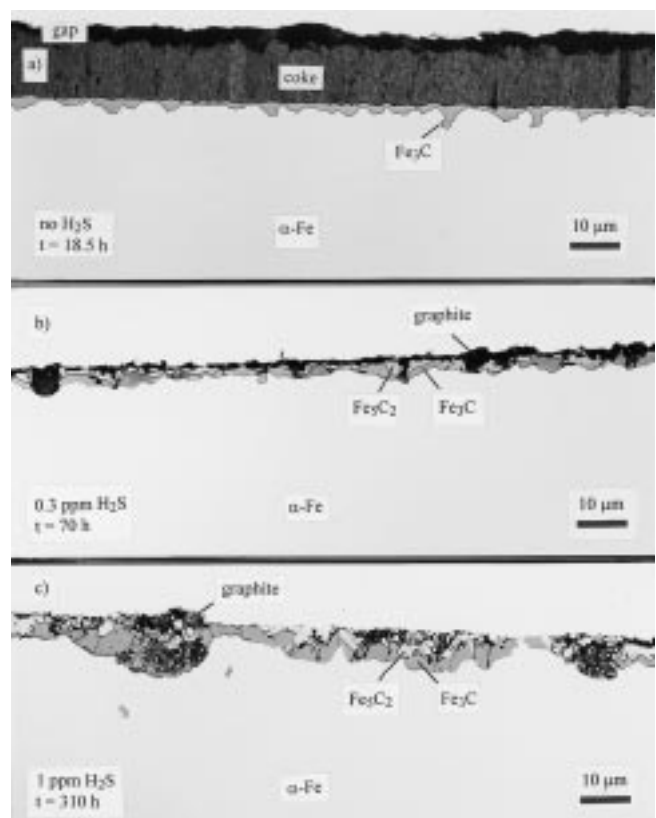


Fig. 5. Metallographic cross sections of iron samples carburized at $a_C = 1000$: a) no H_2S addition, b) 0.3 ppm H_2S and c) 1 ppm H_2S

Abb. 5. Metallographische Querschnitte von Eisenproben, die bei $a_C = 1000$ aufgekühlt wurden: a) ohne H_2S -Zusatz, b) mit 0,3 ppm H_2S -Zusatz und c) mit 1 ppm H_2S -Zusatz

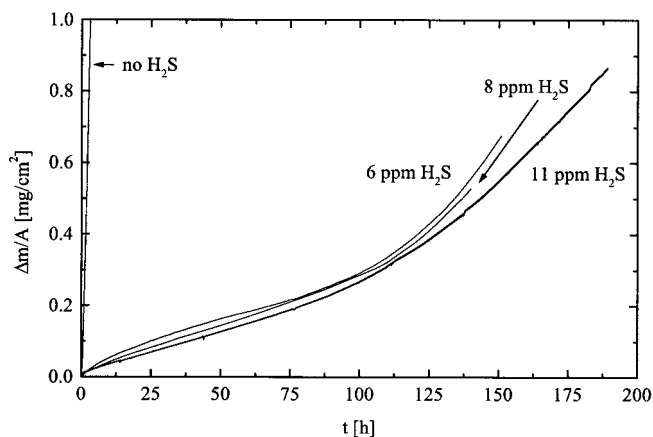


Fig. 6. Influence of H₂S on carburization at $a_C = 4580$

Abb. 6. Einfluß des H₂S auf die Aufkohlung bei $a_C = 4580$

saturation with dissolved carbon, cementite nucleates first and then Hägg carbide forms. Additions of 0.3 and 0.5 ppm H₂S retard graphite nucleation for a period of 30 to 60 h. For these special cases it has been observed, that the kinetics of the carbide formation is controlled by diffusion of carbon through Fe₅C₂ or Fe₃C. This is indicated by a parabolic growth rate. Fig. 5b indicates, that the carbides form tight layers before decomposition starts.

For $a_C = 4580$ the results are qualitatively the same (see Fig. 6) except that higher H₂S contents, 8 and 11 ppm H₂S, are required to achieve similar retardation effects as for $a_C = 1000$. During the first period the mass gain is almost linear with time. The comparison of the experiments shown in Figs. 4 and 6 leads to the conclusion, that the influence of H₂S depends on the carbon activity a_C . For example, carbide growth under diffusion control could be observed for $a_C = 1000$ with 0.3 ppm H₂S and for $a_C = 4580$ with 6 ppm H₂S. The surface reaction controls the kinetics for $a_C = 1000$ with ≥ 0.75 ppm H₂S and for $a_C = 4580$ with ≥ 8 ppm H₂S. A sample carburized at $a_C = 4580$ without any H₂S addition showed only a small amount of Fe₅C₂ in the X-ray diffraction pattern.

5 Conclusions

The influence of H₂S on metal dusting of pure iron has been investigated at $T = 500$ °C. The presence of sulfur retards the start of metal dusting. With increasing H₂S content the onset of metal dusting can be retarded for longer times. At higher carbon activities a higher H₂S content is required to obtain a similar retardation effect. The presence of H₂S in the carburizing atmosphere retards the carbon transfer from the carburizing atmosphere into the sample. The H₂S contents, which are necessary for an effective retardation of metal dusting, are in good agreement with values predicted earlier [6]. At carbon activities $a_C \leq 100$ cementite is the only intermediate, whereas at carbon activities $a_C \geq 1000$ metal dusting of pure iron occurs most probably via decomposition of cementite and Hägg carbide.

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