

# Influence of H<sub>2</sub>S on metal dusting

## Einfluß von H<sub>2</sub>S auf metal dusting

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Presence of H<sub>2</sub>S 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 Fe<sub>3</sub>C is an intermediate, graphite deposition would initiate its decomposition but graphite nucleation is prevented by adsorbed sulfur. Thus continued Fe<sub>3</sub>C growth can be observed in the presence of H<sub>2</sub>S. Thermogravimetric studies in CO-H<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub>S mixtures have been conducted at 500 °C at various carbon activities a<sub>C</sub> and H<sub>2</sub>S/H<sub>2</sub>-ratios. With increasing a<sub>C</sub> higher H<sub>2</sub>S/H<sub>2</sub>-ratios are needed to suppress metal dusting, with increasing H<sub>2</sub>S/H<sub>2</sub>-ratio the kinetics of Fe<sub>3</sub>C growth change from diffusion controlled parabolic kinetics to linear carbon transfer controlled kinetics. At very high a<sub>C</sub> ≥ 1000 besides Fe<sub>3</sub>C also the Hägg carbide Fe<sub>5</sub>C<sub>2</sub> was observed as an outer layer on the cementite.

Die Gegenwart von H<sub>2</sub>S 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 Fe<sub>3</sub>C als Zwischenprodukt auf, und Graphitabscheidung würde den Zerfall des Zementit einleiten, jedoch wird die Graphitkeimbildung durch adsorbierten Schwefel verhindert. Daher kann fortgesetztes Fe<sub>3</sub>C-Wachstum in der Gegenwart von H<sub>2</sub>S beobachtet werden. Thermogravimetrische Untersuchungen in CO-H<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub>S-Gemischen sind bei 500 °C durchgeführt worden und bei verschiedenen Kohlenstoffaktivitäten a<sub>C</sub> und H<sub>2</sub>S/H<sub>2</sub>-Verhältnissen. Mit zunehmender Kohlenstoffaktivität a<sub>C</sub> sind höhere H<sub>2</sub>S/H<sub>2</sub>-Verhältnisse notwendig, um das metal dusting zu unterdrücken, weiterhin ändert sich mit zunehmendem H<sub>2</sub>S/H<sub>2</sub>-Verhältnis die Kinetik des Fe<sub>3</sub>C-Wachstums von der diffusionskontrollierten parabolischen Kinetik zu der linearen, durch die Kohlenstoffübertragung kontrollierten Kinetik. Bei sehr hohen Werten für die Kohlenstoffaktivität a<sub>C</sub> ≥ 1000 wurde neben Fe<sub>3</sub>C auch das Hägg-Karbid Fe<sub>5</sub>C<sub>2</sub> 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<sub>C</sub> > 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-H<sub>2</sub>-H<sub>2</sub>O 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-H<sub>2</sub>-H<sub>2</sub>O 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<sub>C</sub> > a<sub>C(Fe/Fe<sub>3</sub>C)</sub>), (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<sub>C</sub> → 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 H<sub>2</sub>S 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 Fe<sub>3</sub>C on Fe has been observed in CO-H<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub>S atmospheres [6–8].

## 2 Influence of H<sub>2</sub>S 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<sub>S</sub> on the carburization kinetics in a CH<sub>4</sub>, H<sub>2</sub> and H<sub>2</sub>S atmosphere has been studied at carbon activities a<sub>C</sub> < 1 by Grabke et al. [11–12]. By increasing the H<sub>2</sub>S content in the carburizing atmosphere, the reaction velocity decreases. At T = 850 °C the carburization

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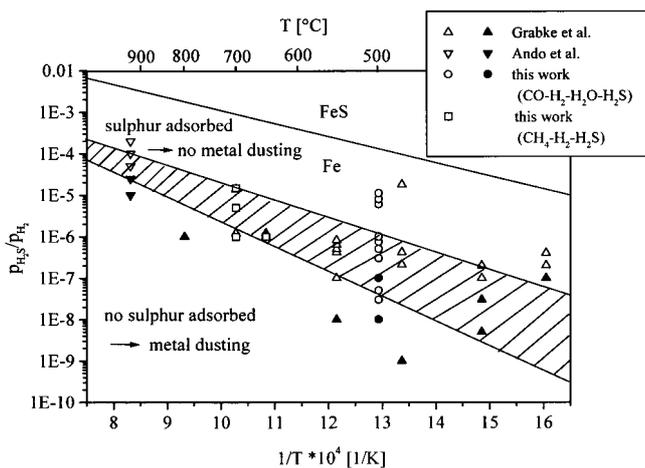
rate was retarded by a factor of 0.1 due to the presence of a small amount of H<sub>2</sub>S ( $p_{\text{H}_2\text{S}}/p_{\text{H}_2} = 10^{-5}$ ). In this case the surface coverage with sulfur was calculated to be  $\Theta_S \approx 0.9$ . The structure of an adsorption monolayer ( $\Theta = 1$ ) in 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, H<sub>2</sub>S retards the onset of cementite decomposition [6]. The influence of H<sub>2</sub>S on the growth and decomposition of Fe<sub>5</sub>C<sub>2</sub> must also be taken into account. Most probably sulfur has the same effect on Fe<sub>5</sub>C<sub>2</sub> as on cementite growth.

In Fig. 1 the influence of H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S 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  $\pm 1 \mu\text{g}$ . The carbon activity of the CO-H<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub>S gas mixture has been calculated by using the following equation [16]:

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

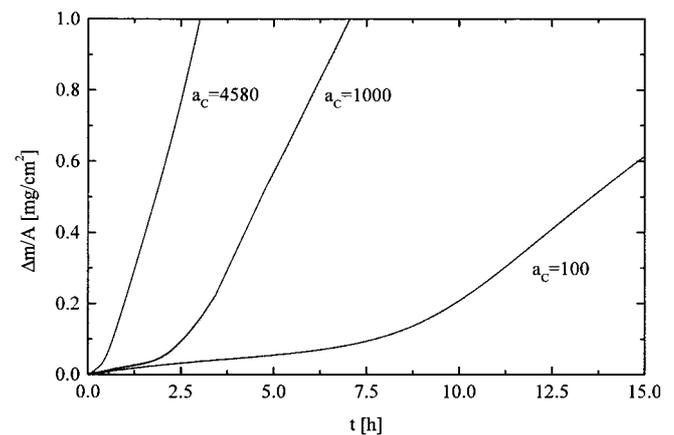
A H<sub>2</sub>-H<sub>2</sub>O mixture was obtained by passing H<sub>2</sub> through a mixture of oxalic acid and its dihydrate at a certain temperature. A H<sub>2</sub>-H<sub>2</sub>S mixture was obtained by passing H<sub>2</sub> through a mixture of iron and iron sulfide where its equilibrium content 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 H<sub>2</sub>S on the metal dusting behaviour of pure iron in CO-H<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub>S atmospheres at  $T = 500 \text{ °C}$ . In Fig. 2 TGA mass gain curves at 500 °C at different carbon activities without



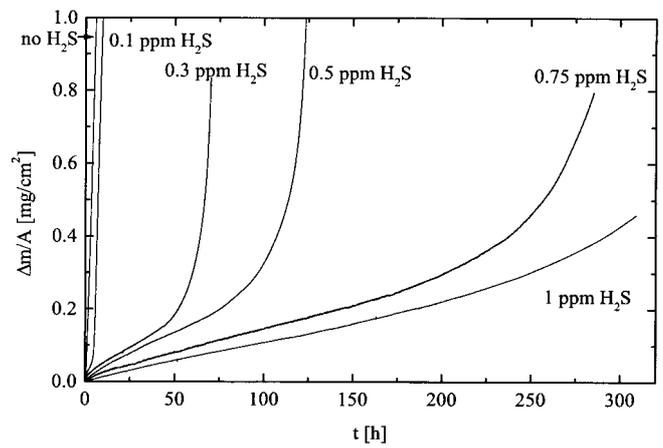
**Fig. 2.** Mass gain versus time for iron samples carburized in CO-H<sub>2</sub>-H<sub>2</sub>O mixtures at 500 °C. The onset of metal dusting is indicated by the change of the curvature into an almost quadratic mass gain

**Abb. 2.** Massezunahme aufgetragen gegen die Zeit für Eisenproben, die in CO-H<sub>2</sub>-H<sub>2</sub>O-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<sub>2</sub>S 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<sub>3</sub>C 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.

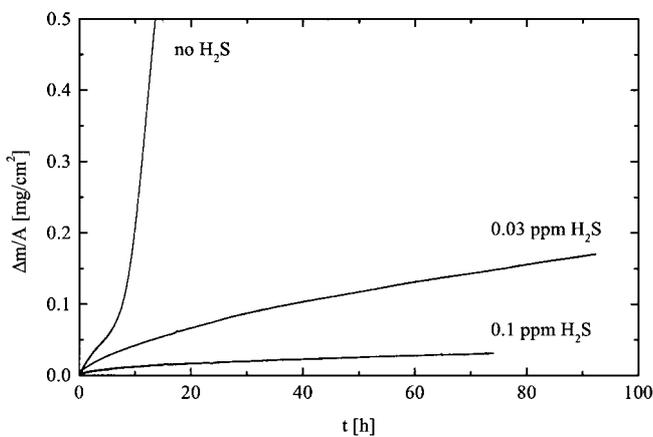
The influence of H<sub>2</sub>S has been studied for the cases of a<sub>C</sub> = 100, a<sub>C</sub> = 1000 and a<sub>C</sub> = 4580. It was observed that at high carbon activities a<sub>C</sub> ≥ 1000 a second carbide forms in addition to cementite. With X-ray diffraction analysis of the carburized samples this carbide was identified as Hägg carbide Fe<sub>5</sub>C<sub>2</sub> [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<sub>C</sub> = 100 and lower carbon activities no Fe<sub>5</sub>C<sub>2</sub> were detected. By using Auger electron spectroscopy it was shown, that at a<sub>C</sub> ≥ 1000 a layer sequence forms as follows: Fe/Fe<sub>3</sub>C/Fe<sub>5</sub>C<sub>2</sub>/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<sub>C(Fe<sub>3</sub>C/Fe<sub>5</sub>C<sub>2</sub>)</sub> required for the formation of Fe<sub>5</sub>C<sub>2</sub> is between a<sub>C</sub> = 100 and a<sub>C</sub> = 1000.

At a<sub>C</sub> = 100 the onset of metal dusting is retarded for at least 90 h by adding 0.03 ppm H<sub>2</sub>S 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<sub>2</sub>S 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<sub>C</sub> = 1000 the metal dusting kinetics slows down with increasing H<sub>2</sub>S 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<sub>2</sub>S, 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<sub>5</sub>C<sub>2</sub> also decomposes in a similar way. The microprocesses of metal dusting including the Hägg carbide will be investigated in the future.

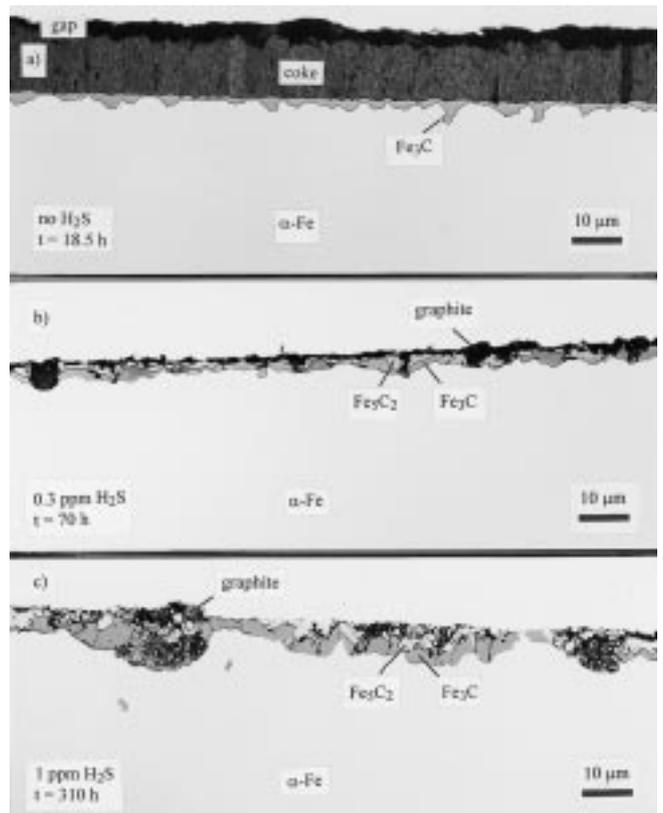


**Fig. 4.** Influence of H<sub>2</sub>S on carburization at a<sub>C</sub> = 1000  
**Abb. 4.** Einfluß des H<sub>2</sub>S auf die Aufkohlung bei a<sub>C</sub> = 1000

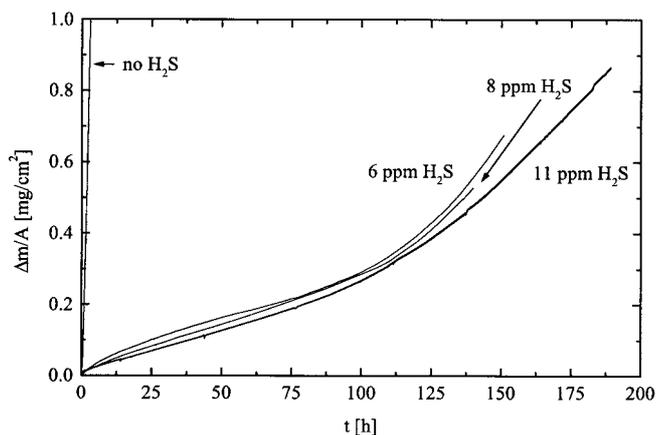
In Fig. 5 metallographic cross sections of three of these samples are shown. Fig. 5 c indicates carbide decomposition of cementite and Hägg carbide. It is striking that the cross section of the sample carburized without any H<sub>2</sub>S addition has no Fe<sub>5</sub>C<sub>2</sub>, as confirmed by XRD. Only a very small amount of Fe<sub>5</sub>C<sub>2</sub> was detected in the sample exposed to 0.1 ppm H<sub>2</sub>S. This observation can be explained assuming that, after super-



**Fig. 3.** Influence of H<sub>2</sub>S on carburization at a<sub>C</sub> = 100  
**Abb. 3.** Einfluß des H<sub>2</sub>S auf die Aufkohlung bei a<sub>C</sub> = 100



**Fig. 5.** Metallographic cross sections of iron samples carburized at a<sub>C</sub> = 1000: a) no H<sub>2</sub>S addition, b) 0.3 ppm H<sub>2</sub>S and c) 1 ppm H<sub>2</sub>S  
**Abb. 5.** Metallographische Querschnitte von Eisenproben, die bei a<sub>C</sub> = 1000 aufgekühlt wurden: a) ohne H<sub>2</sub>S-Zusatz, b) mit 0,3 ppm H<sub>2</sub>S-Zusatz und c) mit 1 ppm H<sub>2</sub>S-Zusatz



**Fig. 6.** Influence of H<sub>2</sub>S on carburization at  $a_C = 4580$

**Abb. 6.** Einfluß des H<sub>2</sub>S 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 H<sub>2</sub>S 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 Fe<sub>5</sub>C<sub>2</sub> or Fe<sub>3</sub>C. 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 H<sub>2</sub>S contents, 8 and 11 ppm H<sub>2</sub>S, 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 H<sub>2</sub>S 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 H<sub>2</sub>S and for  $a_C = 4580$  with 6 ppm H<sub>2</sub>S. The surface reaction controls the kinetics for  $a_C = 1000$  with  $\geq 0.75$  ppm H<sub>2</sub>S and for  $a_C = 4580$  with  $\geq 8$  ppm H<sub>2</sub>S. A sample carburized at  $a_C = 4580$  without any H<sub>2</sub>S addition showed only a small amount of Fe<sub>5</sub>C<sub>2</sub> in the X-ray diffraction pattern.

## 5 Conclusions

The influence of H<sub>2</sub>S 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 H<sub>2</sub>S content the onset of metal dusting can be retarded for longer times. At higher carbon activities a higher H<sub>2</sub>S content is required to obtain a similar retardation effect. The presence of H<sub>2</sub>S in the carburizing atmosphere retards the carbon transfer from the carburizing atmosphere into the sample. The H<sub>2</sub>S 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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