

Volume 6 Paper H043

Metal dusting of binary Fe–Al alloys in CO–H₂–H₂O gas mixtures

A. Schneider, J. Zhang, G. Inden

*Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1,
40237 Düsseldorf, Germany, schneider@mpie.de*

Abstract

Iron aluminium alloys are reasonably resistant against high temperature oxidation and sulphidation. There is only little information available about carburisation and metal dusting of iron aluminium alloys. In this work metal dusting of Fe–Al alloys was investigated in CO–H₂–H₂O gas mixtures at different temperatures.

The effect of temperature on metal dusting was investigated on Fe–26Al alloys (compositions are given in at. %). By thermogravimetric analysis it was found that the carburisation rate reaches its maximum at about 600 °C. With increasing temperature and with increasing aluminium content from 15 to 40 at. % the tendency of the formation of a protective aluminium oxide layer on Fe–Al alloys becomes stronger. An alumina (Al₂O₃) layer was observed at the surface of a Fe–26Al sample carburised at 700 °C. In this case no metal dusting was observed for at least 72 h. By X-ray diffraction analysis (XRD) cementite (Fe₃C) was detected in the coke. The κ -phase Fe₃AlC_x was identified as a precipitate in the matrix. The graphite on the surface of the carburised samples was determined to consist mainly of fine filaments with iron-containing particles.

Keywords: Iron aluminides, metal dusting, carburisation, oxide layer, cementite, κ phase.

Introduction

Iron aluminium based alloys are generally regarded as promising for materials for high-temperature applications. High temperature corrosion studies of Klöwer [1] and Stott et al. [2] showed that iron aluminides exhibit a reasonable corrosion resistance to high temperature oxidation and sulphidation due to the formation of a dense protective alumina (Al_2O_3) scale. However, there is only little information about carburisation and metal dusting of iron aluminium alloys [1, 3–4].

Metal dusting is a high temperature corrosion process which attacks iron, low and high alloy steels and Co- or Ni-based alloys in strongly carburising gas atmospheres with carbon activities $a_C \gg 1$ at temperatures between 400 and 1000 °C [5]. Metal dusting of iron and steels at various conditions such as temperature and carbon activity has been studied by [6–17] using $\text{CO-H}_2\text{-H}_2\text{O}$ and $\text{CH}_4\text{-H}_2$ gas mixtures.

The metal dusting of iron and low alloyed steels during exposure to $\text{CO-H}_2\text{-H}_2\text{O}$ mixtures with carbon activities $a_C > a_C(\text{Fe/Fe}_3\text{C})$ has been explained by the following reaction mechanism [6–10]: (i) rapid supersaturation of the metal phase with dissolved carbon by transfer from the gas phase, (ii) growth of a cementite layer at the surface, (iii) graphite deposition, (iv) subsequent cementite decomposition $\text{Fe}_3\text{C} \rightarrow 3 \text{Fe} + \text{C}$ into graphite and fine metal particles, which (v) act as catalysts for coke deposition. Catalytic coke deposition can be observed in thermogravimetric experiments by a drastic acceleration of the mass gain kinetics.

The coke layer contains graphite and finely dispersed iron particles [ref 10] or carbide particles [ref 13–14, ref 17].

Protection of steels against metal dusting using chromium oxide (Cr_2O_3) layers was tested by [ref 18–20]. Chromium-containing steels are to a large extent resistant against metal dusting. This holds for the surface areas which are covered with Cr_2O_3 , while at defects of the chromia layers local metal dusting was observed.

Alumina (Al_2O_3) forming iron aluminium alloys are promising high-temperature materials for application in the petrochemical industry. Here the gaseous environments can have very low oxygen partial pressures. Thus only a very thermodynamically stable oxide such as Al_2O_3 can be considered to form a protective scale. First experiments on the metal dusting behaviour of Fe_3Al were performed by *Grabke* et al. [ref 3]. The constitution of the Fe–Al–C was investigated by *Palm* and *Inden* [ref 21]. A ternary carbide Fe_3AlC_x (κ -phase) exists in this system which might play an important role as suggested by *Grabke* [ref 3], but his first experiments revealed only the presence of cementite after metal dusting treatment of Fe_3Al alloys. The mechanisms of metal dusting of iron aluminium alloys are still not understood. The resistance of Fe–Al–Cr alloys against metal dusting was studied by *Klöwer* [ref 1]. The investigated alloys showed good resistance against corrosive attack in CH_4 – H_2 gas mixtures at 850, 1000 and 1100 °C.

In this work investigations on metal dusting of binary iron aluminium alloys are presented. Generally it can be expected that the process of metal dusting of iron aluminium alloys includes surface oxidation and carburisation reactions at defects of an oxide layer. The aim of the present work is to investigate metal dusting processes, which may occur at such defects or at the whole surface. The effect of pre-oxidation is not investigated.

2. Experimental

The iron aluminium alloys were processed by vacuum induction melting. The melts were cast into cylindrical copper moulds (32 mm in diameter by 186 mm in length). The as-cast alloys were then cut by spark-erosion to obtain disks with $d = 1$ mm in thickness. Quarter segments of the disks were used for the metal dusting experiments. Before starting the experiment the samples were ground (1000 grit). Thermogravimetric analysis (TGA) was carried out by measuring the mass gain versus time using a microbalance with an accuracy of $1\text{ }\mu\text{g}$. The samples were fixed at the mass balance by quartz filaments. At the end of the treatment the quartz filaments holding the sample were broken so that the sample fell on a quartz plate in the cold region of the TGA apparatus.

Gas mixtures of $\text{CO-H}_2\text{-H}_2\text{O}$ were used for the metal dusting treatment. The water vapour pressure was established by passing H_2 through a mixture of oxalic acid and its dihydrate at a certain temperature [22]. The gas velocities were controlled by capillary flow meters. The flow rate of the gas mixtures was fixed at 2 ml/s and the total pressure of the gas mixture was 1 bar. The diameter of the reaction tube is 27 mm.

The phases on the carburised samples were determined by X-ray diffraction (XRD) using Co-K_α radiation. The carburised samples were coated with nickel and then analysed by means of metallographic cross-sections. Surface analysis of the carburised samples was performed by scanning electron microscopy (SEM).

3. Results

The results of the thermogravimetric analysis (TGA) in Fig. 1 represent the mass gain kinetics of the carburisation of binary Fe-26Al samples (alloy compositions are given in at.%) in a 50%CO-49.3%H₂-0.7%H₂O gas mixture at temperatures from 500 to 700 °C.

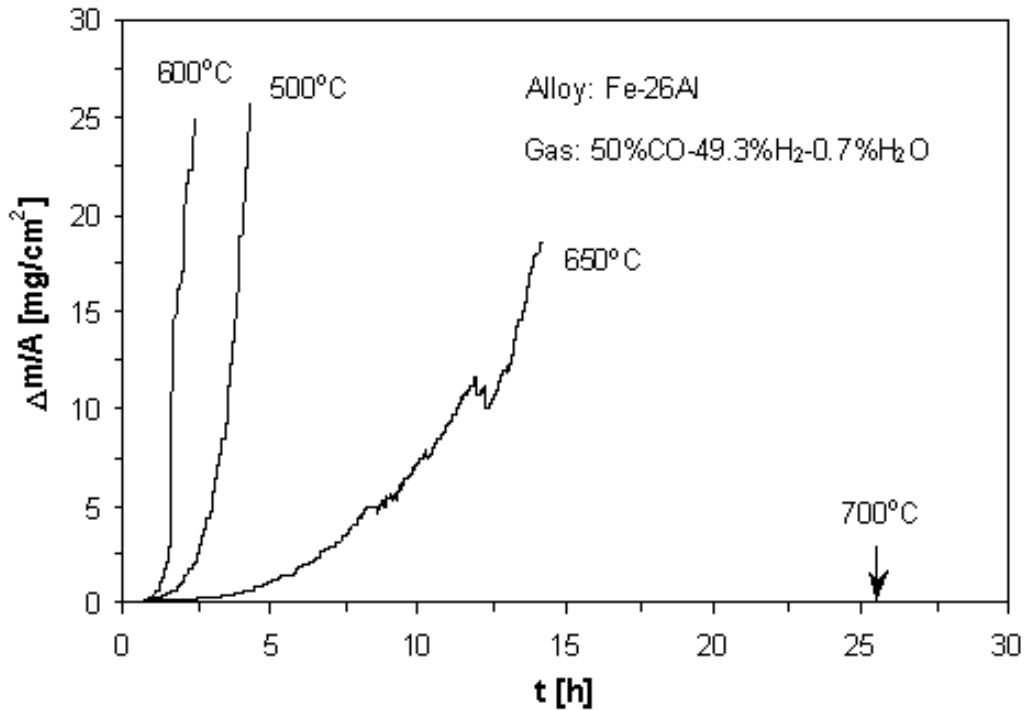


Fig. 1. Thermogravimetric analysis of Fe-26Al samples carburised in a 50%CO-49.3%H₂-0.7%H₂O gas mixture at different temperatures.

Fig. 1 shows that the rate of mass gain reaches its maximum at about 600 °C. Below 600 °C the rate of mass gain increases with increasing temperature. However, above 600 °C this rate decreases with increasing temperature. At 700 °C the mass gain is negligible even after 72 h. Metallographic cross-sections of the corresponding samples are shown in Fig. 2. After 17.4 h reaction at 500 °C the matrix/coke interface is coarsely serrated, indicating a more or less general metal wastage (Fig. 2a). After 2.5 h at 600 °C, large pits are formed (Fig. 2b).

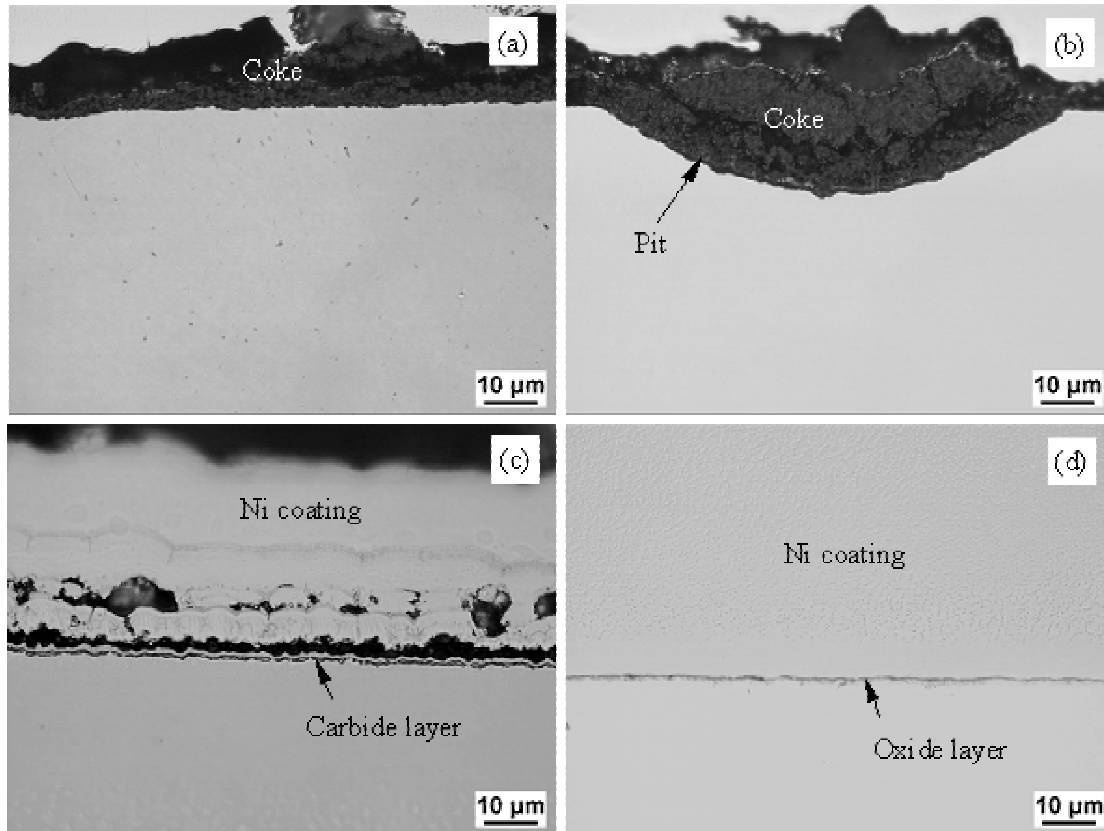


Fig. 2. Metallographic cross-sections of Fe-26Al samples carburised in a 50%CO-49.3%H₂-0.7%H₂O gas mixture at (a) 500 °C for 17.4 h ($a_c = 1720$), (b) 600 °C for 2.5 h ($a_c = 153$), (c) 650 °C for 22.25 h ($a_c = 55$), and (d) 700 °C for 72 h ($a_c = 22$).

The SEM micrograph in Fig. 3a shows these pits of circular form of about 200 µm in diameter. Each pit is filled with many carbon filaments (Fig. 3b). At the surface area which shows no pits, the scratches stemming from the sample grinding can be seen (Fig. 3c). Also at this surface area, which shows no pits carbon filaments are observed.

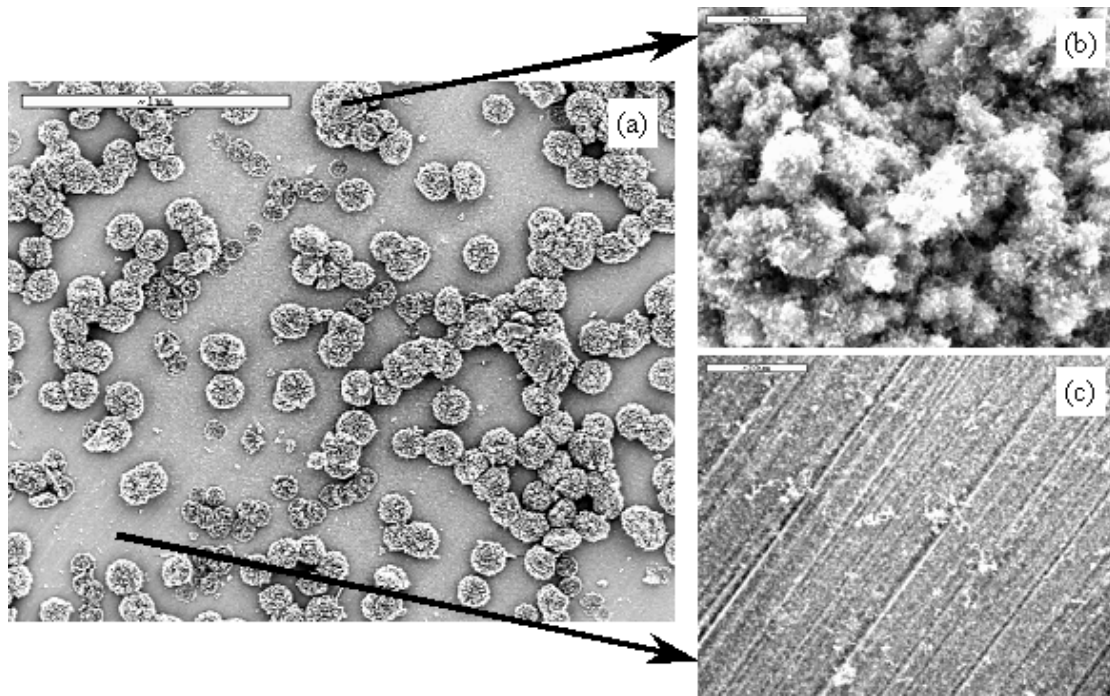


Fig. 3. SEM surface observation of a Fe-26Al sample carburised in a 50%CO-49.3%H₂-0.7%H₂O gas mixture at 600 °C for 2.5 h.

Fig. 2c shows the metallographic cross-section of a Fe-26Al sample carburised for 22.25 h at 650 °C. A thin carbide layer has formed underneath the sample surface which is covered with graphite or coke. The carbide layer is observed by light optical microscopy of an etched cross-section. Without etching no layer can be seen. The top-view of this sample by SEM shows the presence of some large pits (Fig. 4a). Carbon filaments are detected at both pitted and non-pitted areas (Figs. 4b and 4c). After metal dusting treatment for 72 h at 700 °C a very thin oxide layer is observed at the sample surface (Fig. 2d). This layer appears coloured by light optical microscopy which is typical for oxides. In this case metal dusting did not yet set on, but a few filaments have already formed on the surface (Fig. 5).

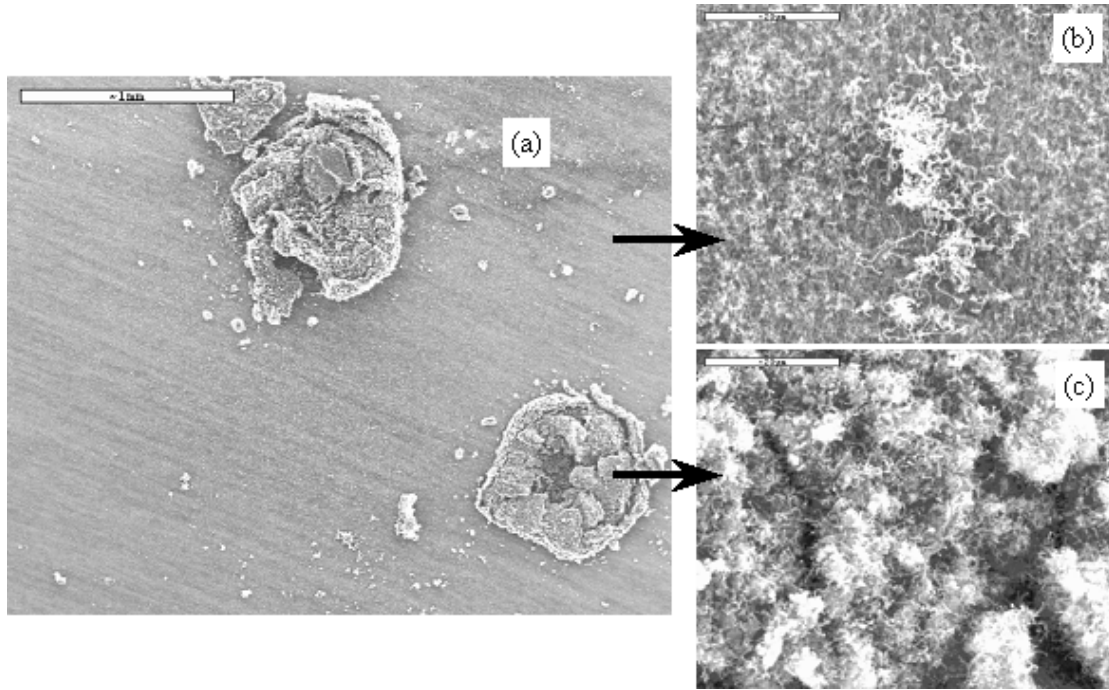


Fig. 4. SEM surface observation of a Fe-26Al sample carburised in a 50%CO-49.3%H₂-0.7%H₂O gas mixture at 650 °C for 22.25 h.

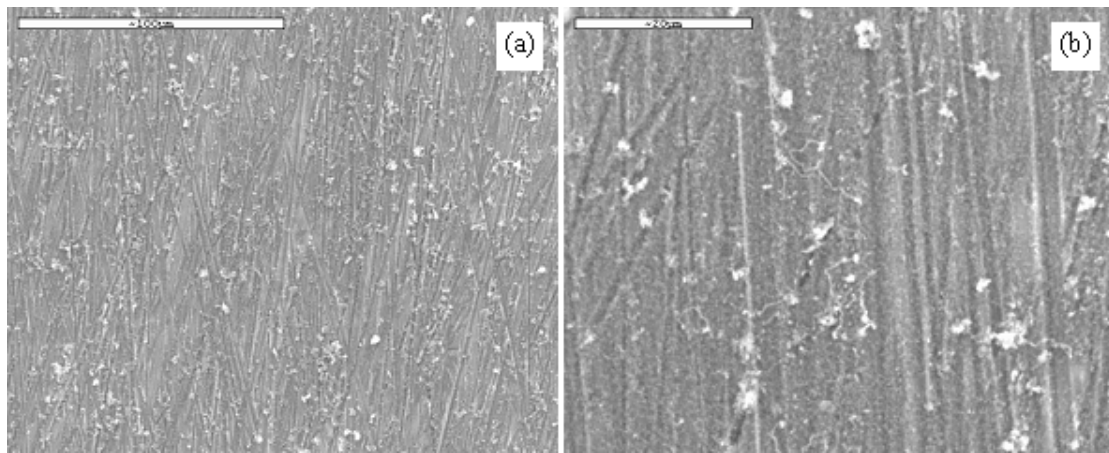


Fig. 5. SEM surface observation of a Fe-26Al sample carburised in a 50%CO-49.3%H₂-0.7%H₂O gas mixture at 700 °C for 72 h.

In Fig. 6 results of X-ray diffraction analysis (XRD) of some carburised Fe-26Al samples are presented. For the sample carburised at 500 °C besides the Fe₃Al peaks strong peaks for the κ -phase (Fe₃AlC_x) and also for cementite (Fe₃C) are detected. For the sample carburised at 600 °C smaller peaks for both cementite and κ phase are

detected. The XRD analysis of the sample carburised at 650 °C does not reveal the presence of any carbide, whereas the more detailed analysis of the coke separated from this sample shows Fe_3C peaks (Fig. 7). For the sample carburised at 700 °C no carbide was detected. For all temperatures oxides could not be detected by XRD.

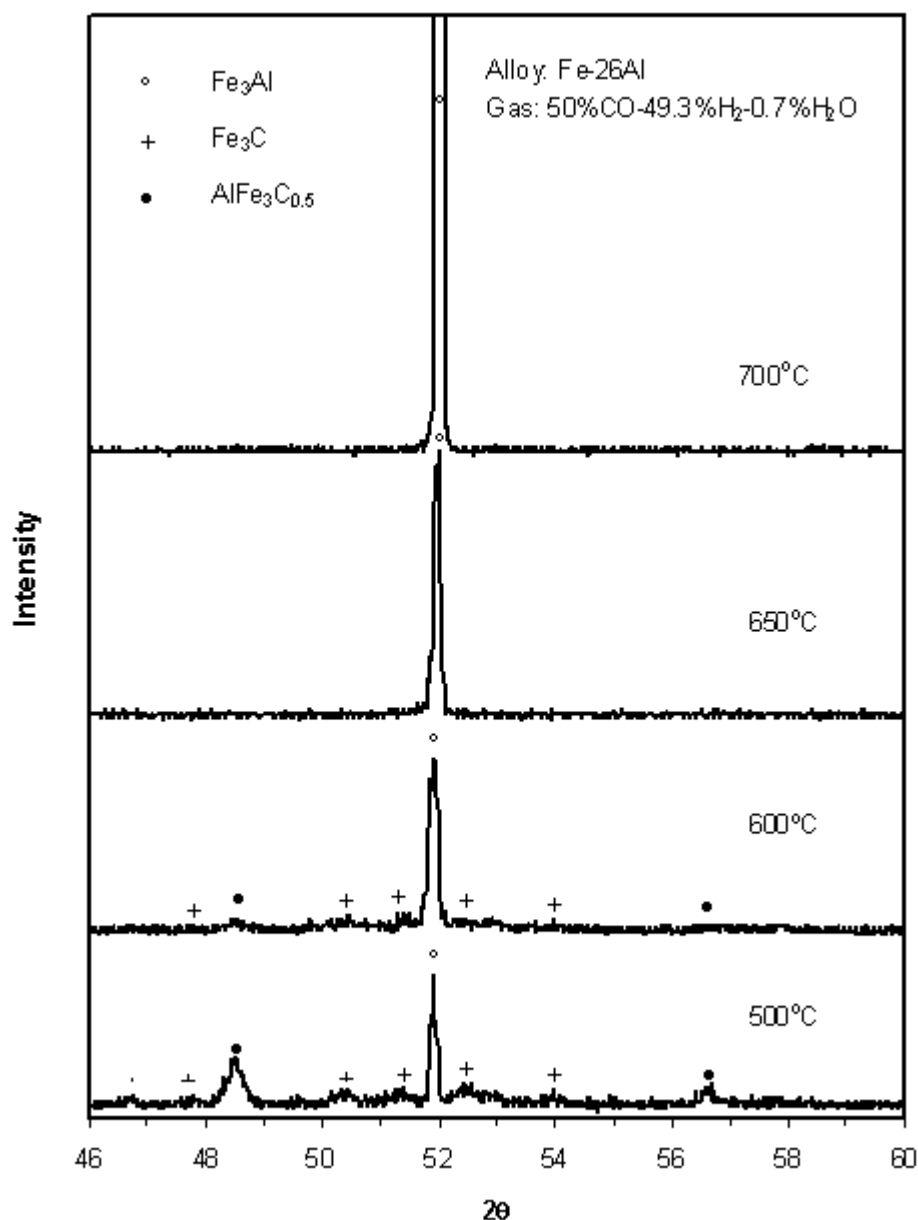


Fig. 6. XRD spectra of Fe-26Al samples carburised in a 50%CO-49.3%H₂-0.7%H₂O gas mixture at (a) 500 °C for 17.4 h, (b) 600 °C for 2.5 h, (c) 650 °C for 22.25 h, and (d) 700 °C for 72 h.

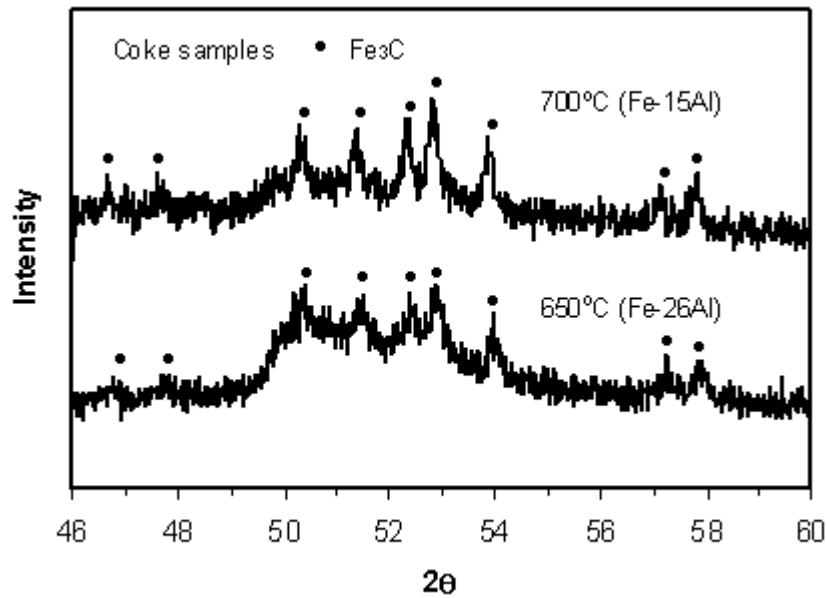


Fig. 7. XRD spectra of the coke removed from the surface of Fe–Al samples carburised in a 50%CO–49.3% H_2 –0.7% H_2O gas mixture at 650 °C for 22.25 h (Fe–26Al) and at 700 °C for 23 h (Fe–15Al).

The effect of gas composition on the carburisation rate was investigated by TGA experiments on Fe–26Al samples carburised at 650 °C in CO– H_2 – H_2O gas mixtures with different compositions. Here the H_2O content was fixed at 0.7 %. Fig. 8 shows that with an increasing CO content from 15% to 50%, that means with increasing carbon activity from $a_c = 28.4$ to 55.3, the carburisation reaction becomes faster.

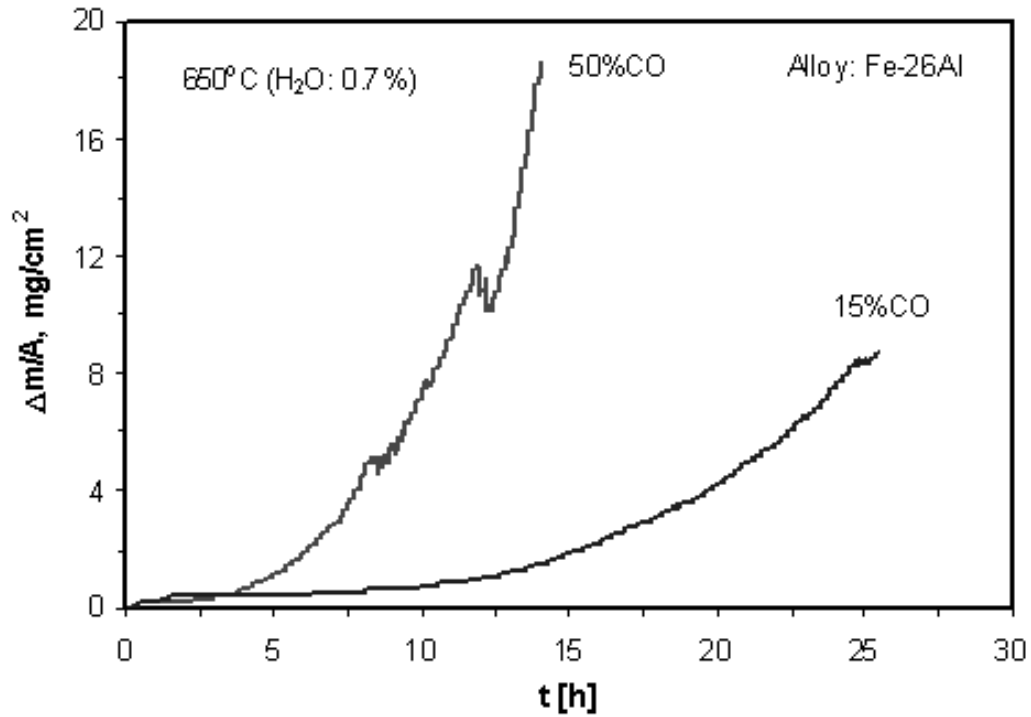


Fig. 8. TGA of Fe-26Al samples carburised in 15%CO-84.3%H₂-0.7%H₂O ($a_c = 28.4$) and 50%CO-49.3%H₂-0.7%H₂O ($a_c = 55.3$) gas mixtures at 650°C.

The effect of Al content of the iron aluminium alloys and temperature on the formation of protecting Al₂O₃ layers was also investigated.

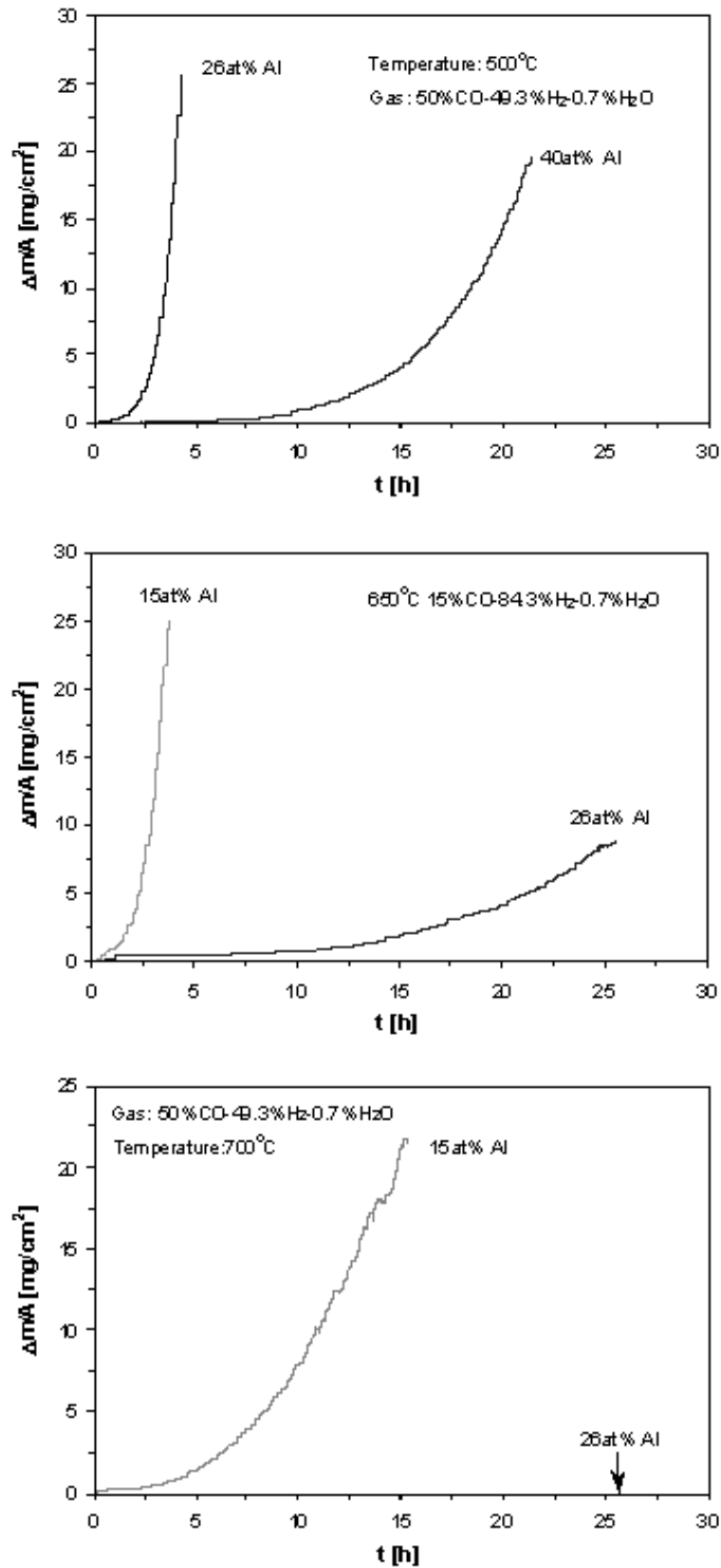


Fig. 9. Effect of aluminium content on the kinetics of the metal dusting process of Fe-Al alloys in CO-H₂-H₂O gas mixtures at (a) 500 °C, (b) 650 °C and (c) 700 °C.

In Fig 9. it is shown that an increase of the aluminium content generally leads to a lowered kinetics of the metal dusting process. For all temperatures the onset of metal dusting, which is represented by a drastic change in the mass gain kinetics, is suppressed for certain time periods with increasing Al content. Unexpectedly, at 500 °C metal dusting sets on fairly quick after about 20 h for an alloy with a high aluminium concentration of 40 at. %. The metallographic cross-section in Fig. 10 shows large pits at the surface. At 700 °C the Fe-26Al alloy is resistant against metal dusting for at least 72 h. However, at the same temperature the Fe-15Al sample is seriously attacked by a general metal wastage after 18.8 h at 700 °C in a 50%CO-49.3%H₂-0.7%H₂O gas mixture (Fig. 11a). The metallographic cross-section in Fig. 11a shows plate-like carbides close to the decomposition interface. Similar precipitates were also found in a Fe-15Al sample carburised for 4 h at 650 °C in a 15%CO-84.3%H₂-0.7%H₂O gas mixture (Fig. 11b).

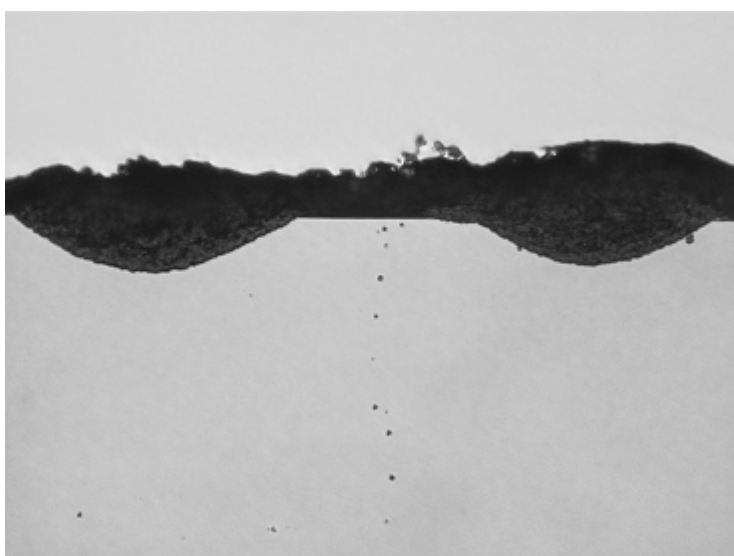


Fig. 10. Metallographic cross-sections of a Fe-40Al sample carburised in a 50%CO-49.3%H₂-0.7%H₂O gas mixture at 500 °C for 20 h.

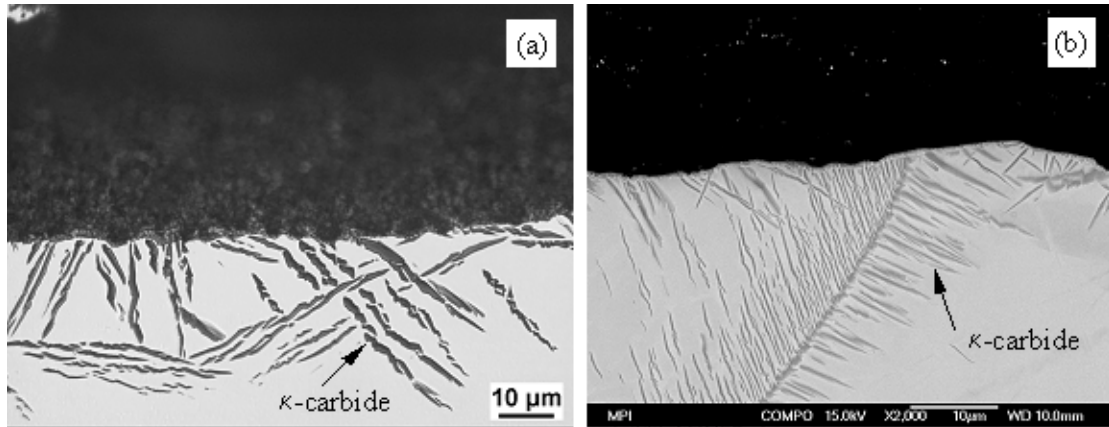


Fig. 11. Cross-section observation of Fe-15Al alloys carburised in (a) 50%CO-49.3%H₂-0.7%H₂O for 18.8 h at 700 °C (light optical microscopy) and (b) 15%CO-84.3%H₂-0.7%H₂O for 4 h at 650°C (SEM).

The plate-like precipitates were identified to be the κ phase Fe₃AlC_x [4]. XRD analysis of the coke removed from the Fe-15Al sample carburised for 18.8 h at 700 °C in the 50%CO-49.3%H₂-0.7%H₂O gas mixture shows that besides graphite only cementite is present in the coke (Fig. 7).

4. Discussion

Generally it can be expected that the process of metal dusting of iron aluminium alloys includes surface oxidation and the onset of metal dusting via carburisation reactions at defects of an oxide layer.

As mentioned above, the aim of the present work is to investigate metal dusting processes and not the effect of pre-oxidation on the resistance against metal dusting.

Regarding Al₂O₃ formation the following information is relevant for an understanding of metal dusting experiments of Fe-Al alloys in carburising and oxidising CO-H₂-H₂O atmospheres. Although

aluminium oxide was not detected by XRD analysis due to very small volume fractions its presence can be assumed because the oxygen partial pressure in the CO-H₂-H₂O gas mixtures is significantly higher than the value necessary for alumina formation. For example the equilibrium partial pressure of oxygen of the 50%CO-49.3%H₂-0.7%H₂O gas mixture is 5.05×10^{-32} bar at 500 °C and 3.77×10^{-25} bar at 700 °C. However, the oxygen partial pressure required for Al₂O₃ formation is only 2.77×10^{-65} bar at 500 °C and 8.99×10^{-50} bar at 700 °C. As it is shown for chromia forming alloys [ref 18-20] the formation of an oxide layer generally retards the carburisation process. Metal dusting attack occurs preferentially at defects of the oxide layer with subsequent pit formation (see Figs. 3a, 4a, and 10). At present, conclusions concerning details of the pit formation during metal dusting of iron aluminium alloys can not be drawn. Also the influence of size and distribution of defect in the oxide layer on the metal dusting kinetics is not yet understood. From the TGA results shown in Fig. 9 it can be deduced that an increase of the aluminium content leads to a retardation of the onset of metal dusting.

The metal dusting attack is differently characterised as pitting (Figs. 2b, 3a, 4a, and 10) or general metal wastage (see Figs. 2a, 11a and 11b). Concerning this simple distinction it should be mentioned that local attack with many fast growing pits and general metal wastage might be the same.

Some results of the present work confirm the assumption that the alumina formation depends on temperature, gas composition and aluminium content. At 500, 600 and 650 °C no oxides were detected in this work. However, the light optical microscopic observation of a thin oxide layer (Fig. 2d) on the Fe-26Al sample carburised at 700 °C indicates that an increase of the temperature enhances the formation of aluminium oxide. For this sample no metal dusting was detected (see also the TGA curves in Figs. 1 and 9c). Thus it can be concluded that the presence of the fairly dense oxide layer formed at a relatively high temperature of 700 °C leads to a significant protection against metal dusting. However, decreasing the aluminium content to 15 at. % leads to a serious attack (Fig. 9c).

At temperatures below 700°C no significant protection against metal dusting of Fe–Al alloys is observed. Thus it can be concluded that at relatively low temperatures there is no distinctive formation of protecting Al_2O_3 layers. This result confirms the reports that with increasing temperature the formation of a dense aluminium oxide layer is favoured [ref23]. The formation of $\alpha\text{-Al}_2\text{O}_3$ is optimal for materials protection because of its very dense crystal structure. However, $\alpha\text{-Al}_2\text{O}_3$ formation occurs at temperatures around 1000 °C or higher [ref24]. Therefore, a pre-treatment for oxide layer formation is required in order to protect iron aluminium alloys from metal dusting. The aspect of protective scales will be treated in future.

At those locations where carburisation can take place the formation of carbon profiles with decreasing carbon content from the surface to the matrix can be assumed. Supersaturation of the matrix with carbon will lead to carbide formation. Thermodynamic calculations showed that for a binary Fe–15Al alloy the formation of the κ -phase Fe_3AlC_x and for increased carbon contents additional cementite Fe_3C precipitation can be expected during carburisation at 650 °C [ref4]. In this work, κ -phase with Perovskite structure was detected by XRD on Fe–26Al samples carburised at 500 and 600 °C (Fig. 6). Plate- or needle-like Fe_3AlC_x precipitates are directly observed in the matrix close to the surface of a carburised Fe–15Al alloy (see Fig. 11). Cross-section analysis by light optical and scanning electron microscopy does not reveal the presence of cementite in the matrix, but with XRD analysis of the coke removed from this sample cementite was detected (Fig. 7). The experimental observation of cementite present in the coke leads to the assumption that there are similarities between metal dusting of iron and of iron aluminium. The mechanism of metal dusting of iron aluminium alloys will be studied in more detail in the future.

The TGA curves in Fig. 1 show that for Fe–26Al alloys the metal dusting rate reaches its maximum at about 600°C. This result is very similar to that of pure iron reported by Chun et al. [ref25]. In their report the rate of metal dusting has its maximum at 575°C. This finding supports the assumption of similarities between metal dusting of Fe and of Fe–Al.

5. Conclusions

In this work metal dusting of Fe-15Al, Fe-26Al, and Fe-40Al alloys was investigated in CO-H₂-H₂O gas mixtures at temperatures from 500 to 700 °C. Generally it can be expected that the main processes of metal dusting of Fe-Al alloys are oxide formation and carburisation at defects of the oxide at the surface. The effect of pre-oxidation was not investigated.

Thermogravimetric analysis (TGA) reveals that the onset time of metal dusting depends on temperature and alloy composition for a given gas composition. The metal dusting attack is characterised as pitting or general metal wastage.

The investigation of the influence of temperature on metal dusting on Fe-26Al reveals a maximum carburisation rate at about 600 °C. With increasing temperature and with increasing Al content the formation of an Al₂O₃ layer is favoured.

In the case of a Fe-26Al alloy carburised at 700 °C an Al₂O₃ layer was detected. For this sample metal dusting was prevented from starting for at least 72 h. Cementite Fe₃C and also the κ -phase were detected by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The role of carbides in the decomposition process still remains unclear. The coke on the surface of the carburised samples was determined to consist mainly of fine filaments with iron-containing particles at both pitted and non pitted areas.

6. Acknowledgements

The authors would like to thank Mrs. K. Angenendt and Mrs. M. Nellesen for SEM analysis and Mrs. H. Falkenberg for preparing the metallographic cross-sections. Support of this work by the Deutsche Forschungsgemeinschaft is greatly acknowledged.

7. References

!ref1 'High temperature corrosion behaviour of iron aluminides and iron aluminium-chromium alloys', J. Klöwer, Oxidation of intermetallics, H. J. Grabke and M. Schütze (Eds.), Wiley-VCH, Weinheim, pp203-220, 1997.

!ref2 'Oxidation-sulphidation of iron aluminides', F. H. Stott, K. T. Chuah, L. B. Bradley, Oxidation of intermetallics, H. J. Grabke and M. Schütze (Eds.), Wiley-VCH, Weinheim, pp221-232, 1997.

!ref3 'Metal dusting of Fe₃Al and (Fe, Ni)₃Al', S. Strauß R. Krajak, M. Palm, H. J. Grabke, *Mater. Corros.*, 47, pp701-702, 1996.

!ref4 'Metal dusting of ferritic Fe-Al-M-C (M = Ti, V, Nb, Ta) alloys in CO-H₂-H₂O gas mixtures at 650 °C', A. Schneider, J. Zhang, submitted to *Mater. Corros.*.

!ref5 'Mechanisms of carburisation, metal dusting and coking - ways and means for protection', H. J. Grabke, Proceedings of EUROCORR '97, Vol. II, E. Bardal (Ed.), European Federation of Corrosion, Trondheim, pp1-8, 1997.

!ref6 'On the mechanism of catastrophic carburization: metal dusting', H. J. Grabke, R. Krajak, J. C. Nava Paz, *Corros. Sci.*, 35, pp1141-1150, 1993.

- !ref7 'Metal dusting', J. C. Nava Paz, H. J. Grabke, *Oxid. Met.*, 39, pp437–456, 1993.
- !ref8 'Metal Dusting – eine korrosive Aufkohlung', H. J. Grabke, R. Krajak, *Härtereitech. Mitt.*, 49, pp150–156, 1994.
- !ref9 'Mechanisms of metal dusting of low and high alloy steels', H. J. Grabke, *Solid State Phen.*, 41, pp3–15, 1995.
- !ref10 'Microprocesses of metal dusting on iron', E. Pippel, J. Woltersdorf, H. J. Grabke, S. Strauß, *Steel Res.*, 66, pp217–221, 1995.
- !ref11 'Thermodynamics, mechanisms and kinetics of metal dusting', H. J. Grabke, *Mater. Corros.*, 49, pp303–308, 1998.
- !ref12 'Carburization and metal dusting on iron', H. J. Grabke, E. M. Müller-Lorenz, A. Schneider, *ISIJ Int. (Suppl.)*, 41, ppS1–S8, 2001.
- !ref13 'Effect of H₂S on formation and decomposition of Fe₃C and Fe₅C₂ under metal dusting conditions', A. Schneider, G. Inden, H. J. Grabke, Q. Wei, E. Pippel, J. Woltersdorf, *Steel Res.*, 71, pp179–184, 2000.
- !ref14 'Surface analytical studies of metal dusting of iron in CH₄–H₂–H₂S mixtures', A. Schneider, H. Viefhaus, G. Inden, *Mater. Corros.*, 51, pp338–343, 2000.
- !ref15 'Iron layer formation during cementite decomposition in carburising atmospheres', A. Schneider, *Corros. Sci.*, 44, pp2353–2365, 2002.
- !ref16 'Effect of gas composition on cementite decomposition and coke formation on iron', J. Zhang, A. Schneider, G. Inden, *Corros. Sci.*, 45, pp283–299, 2003.
- !ref17 'Characterisation of the coke formed during metal dusting of iron in CO–H₂–H₂O gas mixtures', J. Zhang, A. Schneider, G. Inden, *Corros. Sci.*, 45, pp1329–1341, 2003.

!ref18 'Resistance of 9–20%Cr-steels against metal dusting', H. J. Grabke, E. M. Müller-Lorenz, B. Eltester, M. Lucas, D. Monceau, *Steel Res.*, 68, pp179–185, 1997.

!ref19 'Carburization of high chromium alloys', T. A. Ramanarayanan, R. A. Petkovic, J. D. Mumford, A. Ozekcin, *Mater. Corros.*, 49, pp226–230, 1998.

!ref20 'Operational experience with diffusion coating on steam cracker tubes', B. Ganser, K. A. Wynns, A. Kurlekar, *Mater. Corros.*, 50, pp700–705, 1999.

!ref21 'Experimental determination of phase equilibria in the Fe–Al–C system', M. Palm, G. Inden, *Intermetallics*, 3, pp443–454, 1995.

!ref22 'The aqueous pressure of some hydrated crystals. Oxalic acid, strontium chloride and sodium sulfate', G. P. Baxter, J. E. Lansing, *J. Amer. Chem. Soc.*, 42, pp419–426, 1920.

!ref23 'Alloy design strategies for promoting protective oxide-scale formation', M. P. Brady, B. Gleeson, I. G. Wright, *JOM*, 52, pp16–21, 2000.

!ref24 'The oxidation of NiAl and FeAl', H. J. Grabke, M. W. Brumm, B. Wagemann, *Oxidation of intermetallics*, H. J. Grabke and M. Schütze (Eds.), Wiley-VCH, Weinheim, pp79–83, 1997.

!ref25 'Relationship between coking and metal dusting', C. M. Chun, T. A. Ramanarayanan, J. D. Mumford, *Mater Corros.*, 50, pp634–639, 1999.