

Occurrence of metal dusting – referring to failure cases

H. J. Grabke* and M. Spiegel

Twelve years of research on metal dusting at the Max-Planck-Institut für Eisenforschung have led to comprehensive knowledge on the mechanisms and kinetics of metal dusting and on ways and means for prevention of this corrosion phenomenon, – this knowledge is shortly summarized in this paper.

In spite of this state of understanding, the present opinion in industry is that metal dusting is mysterious and not predictable and cannot be controlled. This paper is intended to show that the occurrence of metal dusting and its reasons can be well understood, by describing and explaining five failure cases.

1 Metal dusting – present knowledge

In carburizing atmospheres with carbon activities $a_C > 1$, carbon transfer into iron and nickel and their alloys leads to oversaturation and disintegration into fine metal particles and graphite. This metal dusting is caused by the high thermodynamic tendency for graphite formation and in fact, graphite growth into the materials causes the destruction [1–6]. Two mechanisms have been observed [7, 8]:

- I. Direct inward or internal growth of graphite occurs on Ni and Ni-base alloys. Carbon atoms from the oversaturated solution attach to the graphite basal planes which grow into the metal matrix.
- II. On iron and steels the instable carbide Fe_3C is formed which after graphite nucleation on its surface, decomposes by inward growth of graphite.

In these processes metal particles are created, very fine particles in mechanism II, coarser particles by mechanism I which act as catalysts for carbon deposition from the atmosphere, i.e. “coking” [9, 10].

The kinetics and mechanism of metal dusting and coking have been studied in detail in H_2 -CO- H_2O atmospheres on iron and low alloy steels. At temperatures up to 540 °C the rate of metal wastage is controlled by the continuous decomposition of a cementite layer



which is described by a linear time law. The decomposition reaction is independent of a_C and partial pressures, its activation energy is about 170 kJ/mol. The metal dusting attack on iron and steels reaches a maximum at about 600 °C. For iron the rate decreases since a dense Fe-layer is formed by the decomposition reaction, through which the carbon must diffuse outwards, so carbon diffusion becomes rate determining in the higher temperature range.

Metal dusting can be inhibited or even prevented by the presence of sulfur. The sulfur inhibition is caused by three effects of sulfur: i) the carbon transfer from the atmosphere is retarded, since adsorbed sulfur blocks the surface reaction in the carburization, ii) adsorbed sulfur hems the nucleation of graphite, thus the start of cementite decomposition (1) is retarded, iii) sulfur inhibits the graphite growth, so reaction (1) is slowed down [11, 12]. Also the coking is reduced by the presence of sulfur. The adsorption of sulfur on the metal phase and on the cementite occurs by the reaction



this means a certain amount of H_2S must be present in the atmosphere (also formed from additions such as CS_2 , $(CH_3)_2S_2$, etc.). It has been shown that only relatively small sulfur activities $a_S = K_S \cdot p_{H_2S}/p_{H_2}$ are needed for formation of a monolayer S(adsorbed) on iron [13, 14] and thus for protection of iron and steels, e.g. about $p_{H_2S}/p_{H_2} = 10^{-6}$ is sufficient at 600 °C – but with increasing temperature this value increases which must be considered in operation (see part 2.3).

Besides sulfur inhibition, the other more important way of protection is by oxide scales. In the temperature range in question, a protective scale generally consists of two layers: an outer spinel $MnCr_2O_4$ and an inner chromia Cr_2O_3 layer. Such layer can be formed on ferritic steels with > 11% Cr and on austenitic steels with > 17% Cr, the latter steels need more Cr since the Cr-diffusivity is lower in the austenitic lattice. Even at a low p_{O_2} , as established in process gases by the presence of some CO_2 and/or H_2O , these oxides are stable. But such scale may have defects, where carbon ingress and metal dusting can start and will lead to the well-known appearance of pits and holes in high alloy steels. The defects can be caused by heterogeneities in the surface, inclusions and precipitates (TiN, WC, NbC ...), scratches or edges [15]. Defects may also arise from oxide cracking and spalling, due to creep, fatigue and thermal cycling. The first step in the metal dusting of high alloy materials is the precipitation of internal carbides (MC , M_7C_3 , $M_{23}C_6$), oversaturation follows and then materials disintegration by one of the mechanisms described above. Pits are formed which grow together in the case of very sus-

* H. J. Grabke, M. Spiegel
Max Planck-Institut für Eisenforschung GmbH,
Max-Planck-Str. 1, D-40237 Düsseldorf (Germany)

ceptible alloys (P91, Alloy 800 and 600) so that attack becomes uniform. The chromium of course ends up in oxides, chromia and/or spinels.

At temperatures $< 650\text{ }^{\circ}\text{C}$ a protective Cr-rich scale is not formed for sure, due to slow Cr-diffusion Fe-rich oxides may form which are less protective [16–18]. The growth of the Cr-rich scale must be fostered by fast-diffusion paths, i.e. grain boundaries, subboundaries and dislocations. Therefore a fine-grain microstructure is advantageous and surface-near deformation by surface working: grinding, sandblasting, shot-peening etc. The positive effect of a fine grain microstructure and of grinding has been proven by metal dusting exposures of various steels at $500\text{--}600\text{ }^{\circ}\text{C}$ [16]. In contrast, pickling or electropolishing have negative effects on metal dusting resistance of steels since any surface deformation is removed. Surface near deformation clearly enhances the Cr-diffusivity in steels as shown by tracer diffusion studies and by taking SNMS profiles of the Cr-depletion beneath the oxide scale after different surface treatments and oxidation at $600\text{ }^{\circ}\text{C}$.

Alloying additions of Al, Si and Mn can be helpful to increase the metal dusting resistance [15]. Since generally not more than a few wt% can be added to the usual high temperature materials, no continuous scales of these elements are formed but they help in the formation of protective scales.

High Ni-contents are favorable since the carbon solubility and diffusivity decrease with increasing Ni-content, so the carbon ingress is retarded. In fact, some Ni-base alloys have proven to be rather resistant against metal dusting [19, 20]: Alloy 600 is still rather susceptible, due to its low Cr-content of about 15% Cr; Alloy 601 is much better with 23% Cr but it shows a tendency to form a small number of solitary pits; and Alloy 602 with 25% Cr and 2.3% Al and Alloy 690 with 30% Cr are very resistant. But even Alloy 602 is attacked by metal dusting, after pickling or electropolishing, and at the weldments, although made of the same material.

2 Failure cases

2.1 Metal dusting in a heat exchanger for synthesis gas

The heat exchanger, built mainly of Alloy 800 failed after 23 000 hours by local thorough wastage of the 10 mm thick sheet. The hole was closed by welding a patch of Alloy 601 on the wall, but after 31 000 hours the heat exchanger was taken out of service. Metallographic cross sections of the wall material indicate nearly uniform metal wastage all over the surface. Fig. 1 a shows a piece of Alloy 800 which was attacked from both sides, and is still covered with some coke but without the typical carburized zone. On Fig. 1 b of a wall section from another place, both carburized zone and coke are visible, the grain boundaries are marked by carbon ingress. A weldment in the wall attacked from both sides shows metal dusting of the base material Alloy 800 and a somewhat slower attack of the Ni-base weld material (\sim Alloy 600), see Fig. 2 a, b.

Since the wall of Alloy 800 was wasted from 10 mm to 3–0 mm in different places, a metal wastage rate results of 2–3 mm/year. Such rates were measured in laboratory tests on Alloy 800 and other steels in the temperature range $525\text{--}550\text{ }^{\circ}\text{C}$ [21, 22]. Since the heat exchanger operated in the temperature range $575\text{ }^{\circ}\text{C}$ to $350\text{ }^{\circ}\text{C}$, one can conclude that the walls made of Alloy 800 were attacked from the begin of operation. The large grained material is very susceptible to metal

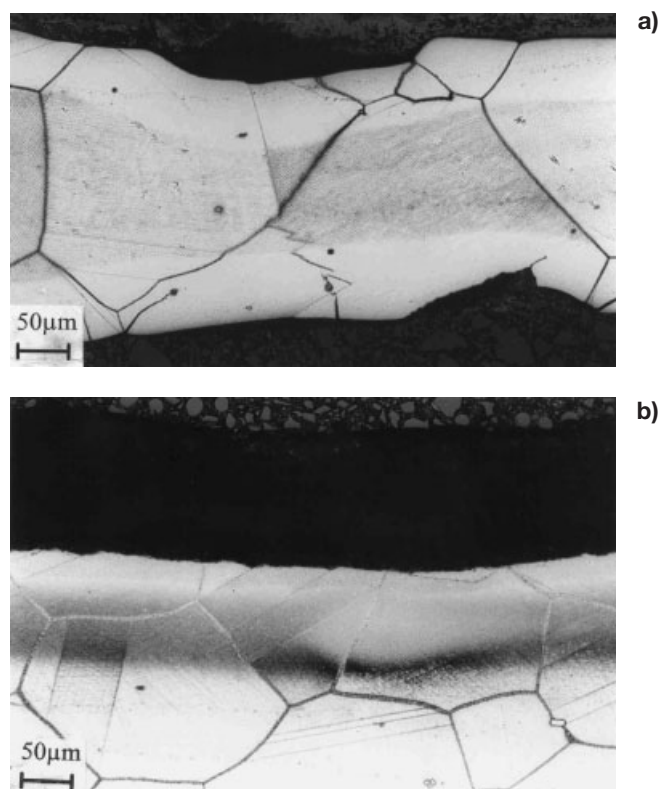


Fig. 1. Metal dusting attack on the wall of a heat exchanger, made of large grained Alloy 800, metallographic cross sections; a) wall segment, thinned from both sides from 10 mm to 2–3 mm, b) uniformly attacked wall surface, typical appearance of metal dusting: coke layer, carburized zone

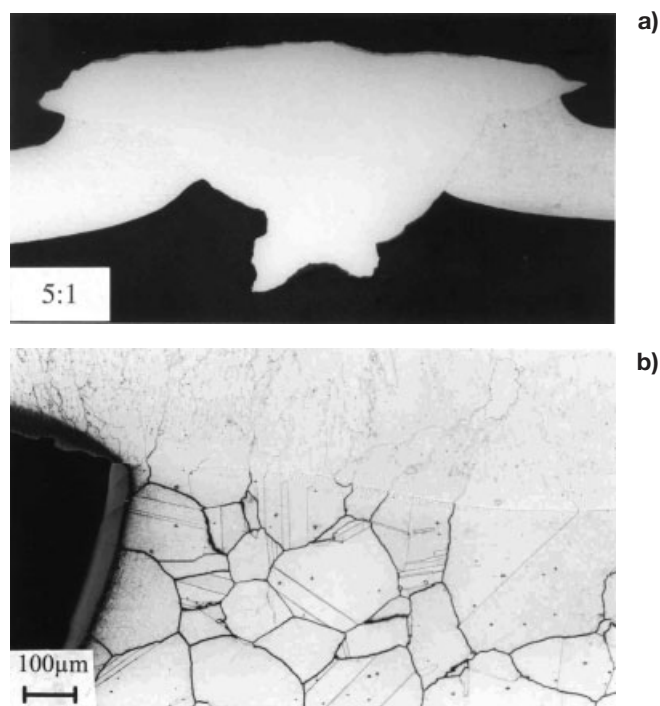


Fig. 2. Metal dusting attack on a weldment in the wall of the same heat exchanger, metallographic cross sections: a) total view, weld material less attacked than the base material (unetched), b) corner of the weldment, showing carburized zone in the weld and base material

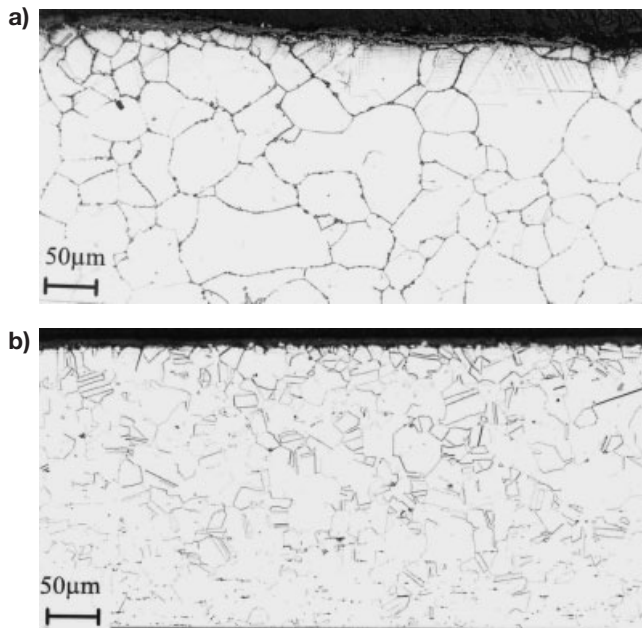


Fig. 3. Metallographic cross sections of parts from the same heat exchanger (see Figs. 1 and 2), not attacked by metal dusting but covered with a protective scale, parts made of fine grained materials: a) 21Cr-12Ni-0.7 Si steel, b) 17Cr-9Ni-0.5Si-0.33Ti steel

dusting and has no chance to form a Cr-rich protective scale at the relatively low temperatures, due to insufficient Cr-diffusion and –supply to the surface [16–18]. In contrast, some small metal parts which had been in the same heat exchanger, exposed to the same atmosphere and temperature range, showed no sign of metal dusting attack, see Fig. 3 a, b. Both were made of fine grained steels with about the same Cr-content, a nut made of a 21Cr-12Ni-0.7Si-steel, and a stainless steel sheet of 17Cr-9Ni-0.5Si-0.33Ti steel. Both materials had formed a protective oxide scale, the stainless steel in the temperature range 460–550 °C. For both steels the fine grained microstructure was of importance for the oxide formation, providing many fast diffusion paths for transport of Cr and Si to the surface. The analysis of the oxide scales showed a high content of Si at the outer surface, so presumably the relatively high Si-content of the steels led to an initial SiO_2 -formation and was helpful in formation of a protective dense scale which prohibited carbon ingress and start of metal dusting.

2.2 Metal dusting in the gas heaters of a direct reduction plant

A strong attack by metal dusting was investigated in detail [23] which had occurred in the gas heaters of a direct reduction plant, where a H_2 -CO-CO₂-H₂O mixture is heated from ambient temperature to reduction temperature, about 950 °C. The heater coils had been produced from centrifugally cast tubes of the steel HK 40. This steel has the nominal composition 25 Cr-20 Ni-1.2 Si, but in the case described the Cr-content was at the lower level 22–23% Cr which was one reason of the failure. The material has a coarse dendritic microstructure with large carbide precipitates (M_{23}C_6). At elevated temperature the steel tends to ageing by precipitation of fine secondary carbides and σ -phase. The inner walls of the straight

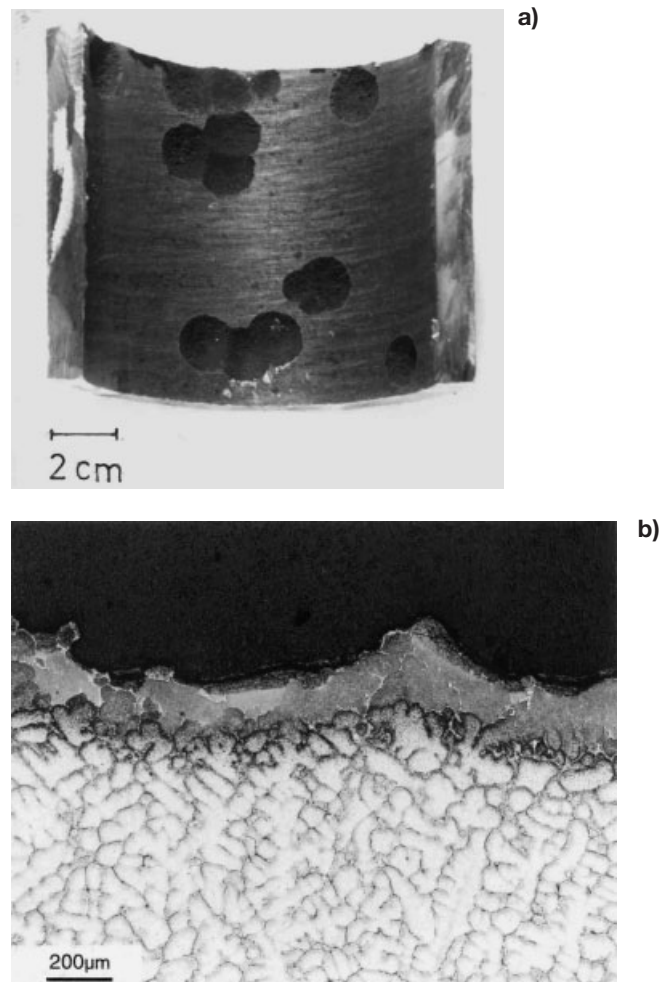


Fig. 4. Metal dusting attack in the heater tube of a direct reduction plant at about 600 °C; a) tube section of HK40 (cast 25%Cr-20%Ni steel) with deep pits, b) metallographic cross section, showing pits and carburized zone

tube segments are machined, the cast surface with its pores is removed and additionally a certain surface-near deformation is introduced. The heaters are operated usually under introduction of sulfur, by dosing DMDS, $(\text{CH}_3)_2\text{S}_2$ which should decompose at process temperature yielding a sufficient level of H_2S for protection. A constructional error in the plant caused that for some time one of the heaters was not supplied with DMDS. Short time after, leaks occurred and strong metal dusting attack was detected in wide regions of the coils. Depending on the temperature more or less deep pits were found in the inner wall of the tubes, see Fig. 4 a, b. The welds or the heat affected zones near the weld, were attacked even stronger than the straight machined sections. Since heaters of this type are used generally without severe failures for many years, when sulfur is supplied continuously, the lack of H_2S in the atmosphere obviously was the main reason of this failure. Additionally, the low Cr-content of the steel was a weakness, and the microstructure and composition of the welded joints caused enhanced attack.

2.3 Failure of a platformer unit in a refinery

In Continuous Catalyst Regeneration (CCR) units there are heaters for heating naphtha or other feedstock to the critical temperature range about 600 °C. The tubes are made of 2.25 Cr-, 5 Cr- or 9 Cr-steels depending on the temperature range. Two failure cases by metal dusting have been reported [24, 25], both most probably due to an increase of operation temperature and insufficient supply of sulfur at the higher temperature. One of these cases happened in a plant where the unit had been operated with 5%Cr-steel tubes for 25 years without failure. Some changes preceded the failure: i) in the heater concerned, new tubes made of 9%Cr-steel had been installed, ii) the amount of sulfur in the feedstock had been reduced, due to the introduction of a new catalyst, and iii) the operation temperature was raised up to about 675 °C. The new 9% Cr tube failed after short time, due to metal dusting obviously coke deposits had formed in certain

regions which led to overheating and crack formation. The overheating could be deduced from changes in the steel microstructure and the formation of a "red scale" on the outer tube wall.

By analyses of intact old tubes from the same CCR unit, hints were found to explain why the pipes installed earlier did not fail. The metallographic cross section shows an internally carburized zone and a scarred surface, see Fig. 5 a, b, i.e. indications of metal dusting. Auger-spectra taken on the surface showed graphitic deposits or metallic areas covered with adsorbed sulfur, see Fig. 5 c, d. Obviously the material had been largely protected by adsorbed sulfur and a coke layer, and only very slow metal dusting had taken place. In contrast, the new tube had no chance to obtain such protective coating, due to the enhanced operation temperature and the insufficient level of sulfur in the atmosphere.

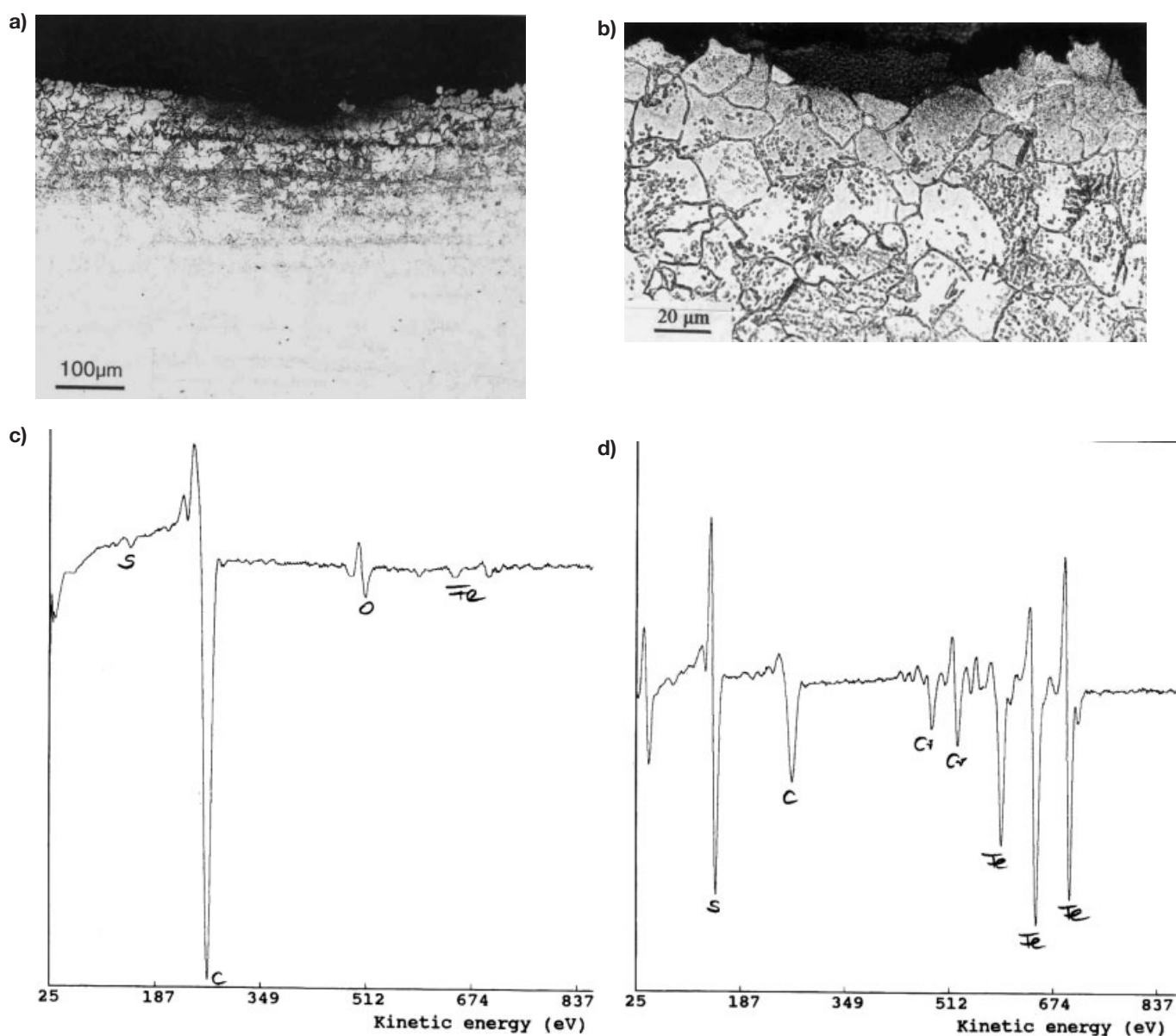


Fig. 5. Metal dusting of the inner tube wall in a refinery heater (CCR unit); a) and b) metallographic cross sections, showing only moderate attack of the 5%Cr-steel, c) and d) Auger spectra demonstrating the protecting carbon and sulfur layer on the surface

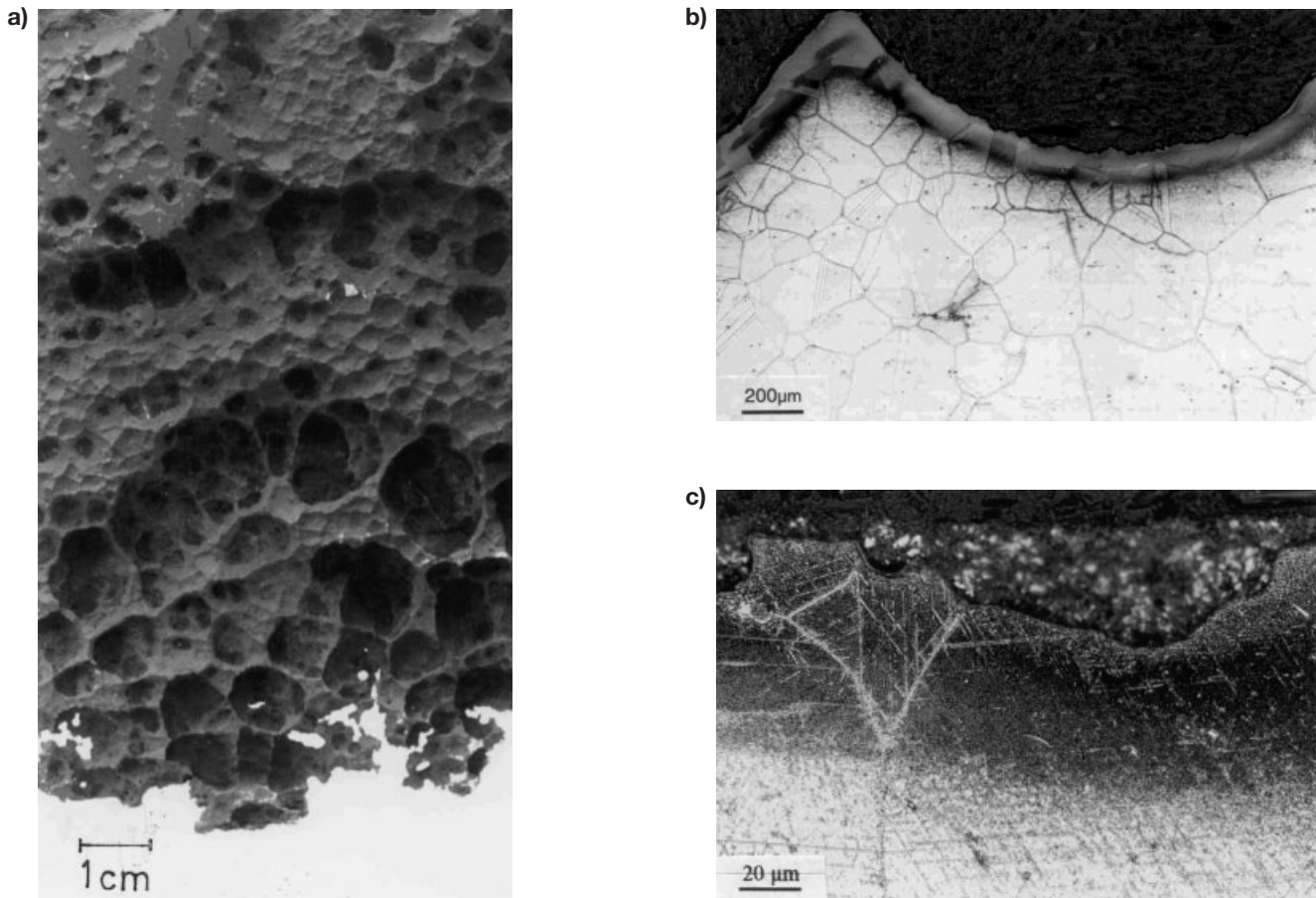


Fig. 6. Severe metal dusting attack on a steel sheet (Alloy 800) from a direct reduction furnace; a) piece of the steel sheet with vast erratic pitting, b) and c) metallographic cross sections, showing pits with carburized zone and coke

2.4 Metal Dusting in a direct reduction furnace

In this case, sheets of Alloy 800 suffered a very strong attack (see Fig. 6 a, b, c) within about 6 month, after 20 years operation with only minor attack. These sheets serve for guiding the cooling gas from the lower part of the shaft furnace into the upper part, where the reduction gas enters. The ore is reduced on its way from the top of the furnace and leaves as iron sponge at its bottom. In the region in question the temperature is 400–500 °C and the H_2 -CO-CO₂-H₂O atmosphere has carbon activities between $a_C = 2000$ to 100. The material Alloy 800 is rather susceptible, but the sulfur content ~ 10–12 ppm H₂S should effectively retard the metal dusting attack so that the 20–25 mm thick sheet could serve for many years. Some additional attack must have caused the acceleration. EDS analysis of the corrosion products indicated presence of chlorides, and it was known that chlorine had been introduced in the process line for controlling the growth of algae in a cooling unit. Obviously the presence of chlorine and the formation of chlorides hindered the formation of protective oxide scale and the very severe attack is due to the combined action of chloridation and metal dusting.

2.5 Metal Dusting in a heat exchanger of an ammonia Plant

A tube section which had been in service for 2¼ years was received for failure analysis, it showed severe attack by metal dusting on the outer surface (Fig. 7 a, b) and locally some greenish spots. These spots were deposits of mineral salts, as shown by EDS and AES analysis and most probably stemmed from an ingress of steam at the gas side, ½ year before the failure and inspection. In addition to the alloying elements the analyses detected: K, Na, Mg, Ca, Cl and S, which should not be carried by the process gas and should not be present on the tube. It may be concluded that deposition of mineral salts from the impure steam on the tube has locally destroyed the protective oxide layer on the Alloy 601. Preliminary tests on the effect of salt deposits, chlorides, sulfates and carbonates have shown accelerated start and enhanced attack by metal dusting on several materials.

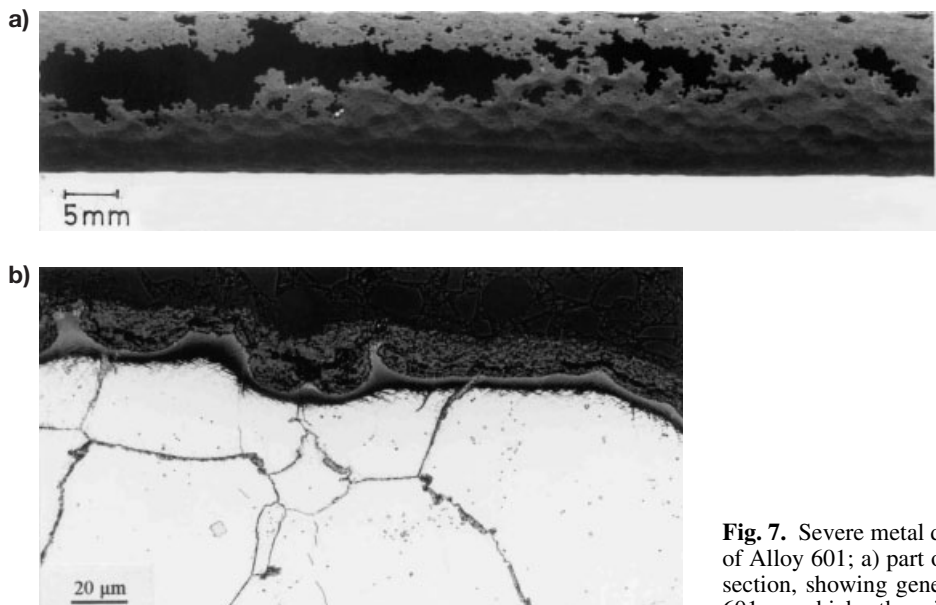


Fig. 7. Severe metal dusting attack on a heat exchanger tube made of Alloy 601; a) part of the corroded tube, b) metallographic cross section, showing general metal dusting – quite unusual for Alloy 601 on which otherwise single hemispherical pits occur

3 Conclusions

Metal dusting is a corrosion phenomenon which may start immediately on susceptible materials such as low alloy steels, Alloys 800 and 600, and sometimes unexpectedly, but mostly after some change in the operation conditions, repairs or changes of material and sudden ingress of impurities. On the base of the present knowledge the occurrence of metal dusting generally can be explained. Some failure cases and their reasons are presented.

One way of protecting steels is the presence of an appropriate partial pressure of H_2S in the atmosphere, the concentrations necessary for suppressing metal dusting have been determined [11, 12]. One failure case is described, of the heater in a direct reduction plant, where metal dusting of HK40 started, due to a total lack of sulfur supply. In the second case, of a CCR unit in a refinery, the sulfur content was lowered and the temperature increased, so that newly installed tubes suffered immediate metal dusting, due to too low pH_2S at the raised operation temperature.

In two other cases, the start of metal dusting was caused by ingress of impurities, chlorine in the case of a reduction furnace and mineral salts in the case of a heat exchanger. Both impurities obviously destroyed protective oxide scales, so that metal dusting attack started at numerous points and caused erratic attack.

4 References

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