METAL DUSTING OF INLET TUBE MADE OF ALLOY 800

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Metal dusting is a localized degradation that occurs in environments containing carbon and hydrogen compounds, but almost no oxygen. Metal dusting was observed in the inlet tube of a heat exchanger unit, where the high temperature reaction gas is employed for getting high temperature water steam. Alloy 800 was used for inlet tube manufacturing. Analysis of surface contaminants showed two forms of carbon in it: very fine globular, very probably amorphous and rod-like, which could be crystalline. Preferential diffusion of carbon through the broken oxide surface layer leads to precipitation of secondary phases and dusting of metal.

Key words: metal dusting, metallography, diffusion, hardness

1. Introduction

Metal dusting is a corrosion phenomenon, which leads to the disintegration of structural alloys turning them into a powder of fine metal particles and graphite (graphite wool) [1]. It occurs in environments containing carbon and hydrogen compounds, but almost no oxygen. Metal dusting occurs at temperatures of 450–800 ℃ [2] with high carbon activity (greater than 1) and very low oxygen partial pressures in the gas phase, the conditions that are prevailing in many chemical and petrochemical processes.

The combination of natural gas, i.e. methane, in the steam reforming, with steam at high temperature produces a mixture of gases commonly referred to as 'syngas' which contains mostly H_2, CO, CO_2, H_2O and some CH_4. Within the syngas environment, the reactions contributing most to carbon deposition are: the

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*corresponding author, e-mail: hrivnak@mtf.stuba.sk reduction of CO by hydrogen and the decomposition of CO ($2CO \leftrightarrow CO_2 + C$, the Boudouard reaction). The equilibrium constant for each of these reactions dips below one at about 750 ℃. The need for greater efficiency has reduced the quantity of steam used for the reforming process, resulting in lower steam-to-hydrogen ratios. Higher front-end pressures have also increased the CO content of the syngas. Lower H_2O/H_2 ratios in combination with higher CO/CO_2 ratios result in lower oxygen partial pressures and higher carbon activities, respectively, and may serve to increase the severity of metal dusting attack [2].

Two major issues of importance in metal dusting are:

– transfer of carbon by surface reactions into the alloy. This is influenced by carbon activity in the gas mixture and the availability of surface for carbon-producing reactions to proceed;

– the initiation of metal dusting in the alloy and subsequent propagation of the degradation.

The initiation period for metal dusting is determined by the carbon activity in the gas phase, resistance of the oxide surface layer to degradation, alloy chemistry, system pressure, and probably the exposure temperature. The incubation period for metal dusting attack in the case of high Ni-base materials may last up to more than 10,000 h [3].

Although metal dusting has taken place at temperatures as high as 1100℃ in strongly reducing gaseous environments, it generally occurs at temperatures from 450 to 800℃ [2, 4]. Deterioration and material wastage by metal dusting in carburizing gases at these temperatures result in pitting and overall wastage of steels with or without an oxidizing environment [3, 4]. Absorption and diffusion of carbon into the base alloy can lead to significant changes in the alloy mechanical properties, leading to possible alloy embrittlement. Variables that affect the carburization rate are the temperature, exposure time, alloy composition, and the partial pressures of H_2, CH_4, and H_2S. H_2S tends to retard alloy carburization rates. The addition of sulphur-containing compounds, however, cannot be used as they deactivate catalysts needed in the ammonia synthesis process.

In iron including low-alloyed steels [3, 4], the reaction starts with a transfer of C into the metal phase and oversaturation of the metal ($a_c > 1$ in the metal); then formation of cementite, M_3C, at the surface which acts as a barrier for further carbon ingress, thus causing: graphite precipitation, decreasing the carbon activity on the cementite to $a_c = 1$, whereby the M_3C becomes unstable and decomposes according to $M_3C \rightarrow C + 3\ M$; the carbon atoms from this decomposition are attached to graphite which grows into the cementite. The metal atoms diffuse through the graphite and agglomerate to small particles, and these particles act as catalyst for further carbon deposition and vast coke growth results [2, 4].

For nickel, Ni-base materials and steels with $Ni/Fe > 2/3$, another simpler reaction sequence applies [4, 5], not involving the unstable intermediate M_3C. After oversaturation of the metal phase, direct graphite growth occurs into the metal phase and destroys the metal.

Local defects in the scale allow carbon diffusion into the metal phase, its preferential diffusion at grain boundaries and precipitation of stable carbides $M_{23}C_6$ and M_7C_3. Then the carbon concentration and activities rise to values $a_c > 1$, and the disintegration of the material starts [5]. The metal particles generated by disintegration of the Fe- or Fe-Ni-matrix act as catalyst for carbon deposition and coke arises from the growing pit.

An adherent, protective, self-healing oxide surface layer is required for protection of an alloy against metal dusting attack. Although oxide formation may be stable, the oxide layer may still be susceptible to disruption. Higher levels of the scale forming elements like silicon, aluminium and chromium will then make the scale healing process more rapid and complete.

Most of the studies about metal dusting and carburization deal with those phenomena taking place at the samples' surface. However, carburization at high temperature, below the surface of structural elements in industrial equipment, can strongly diminish their mechanical properties.

Avoidance of metal dusting is often accomplished in industry by designing around the critical temperature range. Syngas is produced at temperatures above the critical range (> 800 ℃) and transferred to a boiler via a short transfer line where it is rapidly quenched to temperatures below the critical metal dusting range (< 450 ℃). This necessitates the use of materials which exhibit excellent resistance to metal dusting attack [2].

2. Failure case study

We have analysed the metal dusting occurring in the inlet tube, made of Alloy 800 alloy in the steam generator boiler. Into the reformer a methane gas CH_4 is flowed at higher pressure and temperature over 700 ℃ where it is mixed with a stream of water steam. A reaction which occurs is $CH_4 + H_2O \leftrightarrow CO + 3\,H_2$. The hot reaction product is then employed for production of high temperature steam in a boiler. Heat exchanger is of a tube type. Inside the heat exchanging tubes, made of low alloy CrMo steel a reaction gas, containing high portion of hydrogen, is flowing, outside the circulating water is heated up into steam. The critical part of the heat exchanger is the tube-to-tube sheet unit. The surface of the tube sheet is protected by fireclay and the openings in the tube sheet are protected by Alloy 800 inlet tubes, as seen from Fig. 1. Chemical composition of Alloy 800 is as follows (in wt.%): 32 % Ni, 21 % Cr, 45 % Fe, 0.9 % Mn, 0.1 % Si, 0.4 % Al, 0.4 % Ti, 0.007 % C.

After several years of operation the inlet tubes were checked and analysed. The appearance of the end of the investigated tube is shown in Fig. 2. The inside diameter of the tube is 28 mm, outer diameter 33 mm, its total length approx.

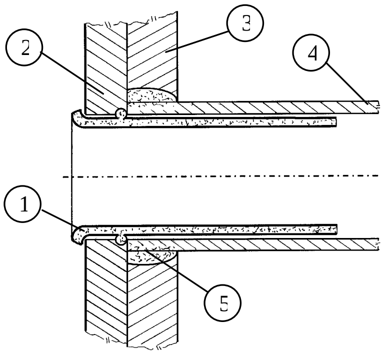

Fig. 1. The set-up of inlet tube (1) in fireclay (2) and tube-sheet (3), (4) – tube made of STN 15 020 steel, (5) – weld.

Fig. 2. A general view on the inlet tube made of Alloy 800.

270 mm. The front part of the tube, in the length 65 mm, was inside the fireclay and was not damaged by dusting phenomenon probably due to its higher temperature. The inlet tube was fixed into the tube sheet by a fixing ring. As seen from Fig. 2, the end of inlet tube was severely thinned and several pits and holes were observed in this region. The inner, as well as the outer surface of the tube were heavily contaminated by dust. The morphology of dust was analysed by scanning electron microscope (SEM) as well as by transmission electron microscope (TEM). A two-step celluloid-carbon replica was prepared from tube surface contaminants. In the first step one side of the celluloid film (Bioden) was softened by acetone and slightly pressed into the tube surface. After several minutes the celluloid strip was taken off the surface. A lot of contaminants covered this surface. In the second step a thin carbon film was evaporated into the active surface of celluloid strip in high vacuum, and subsequently the celluloid strip was dissolved in acetone. It is a usual procedure in transmission electron microscopy. Figures 3a,b show the morphology of contaminant dust. In Fig. 3a a SEM image shows many discrete particles on the surface of the tube. In Fig. 3b (TEM) several black extracted particles are parts of metal dust in the form of oxides and carbides but in between there is a very fine colloid dust of carbon. The detail of two carbon morphologies is shown in Fig. 4.

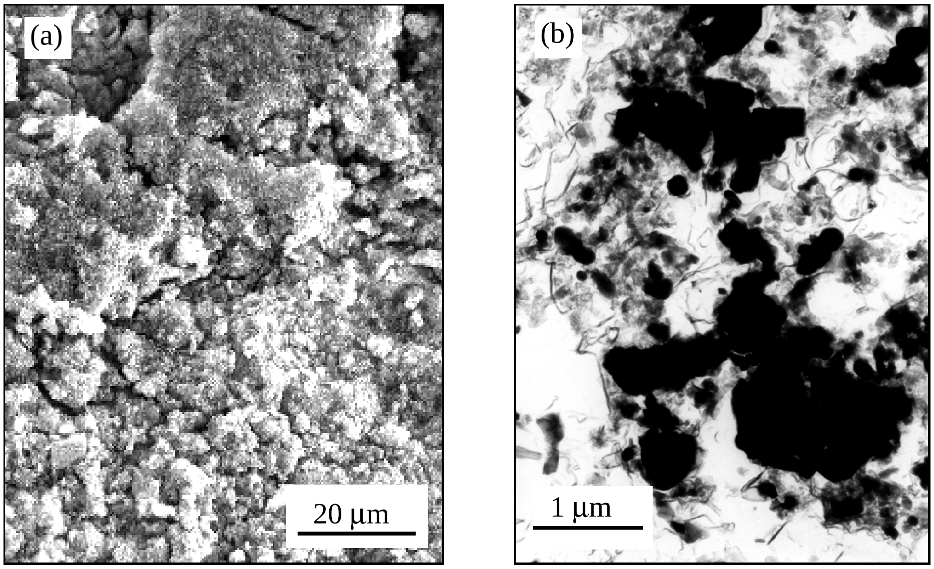

Fig. 3. Morphology of tube surface contaminants: (a) SEM, (b) TEM, two steps celluloid--carbon replica.

Except of fine amorphous carbon dust also fine rods of carbon were identified. By electron diffraction we have identified in the extracted dust also oxides of chromium, silicon, aluminium and, as to be expected, chromium carbides, but the diffraction rings from very fine ("background") particles were of very diffuse nature, the same as those of the carbon replica itself. By EDX analyses in TEM we have identified the occurrence of elements from alloy itself and also some Si, Al and Mg, which could come from the particles of fireclay. This means that except of carbon from the chemical reaction between methane and steam, the flowing gas is also entrapping particles from fireclay. These hard particles could then contribute to some abrasion of the tubes' surface, which was covered by chromium oxide film.

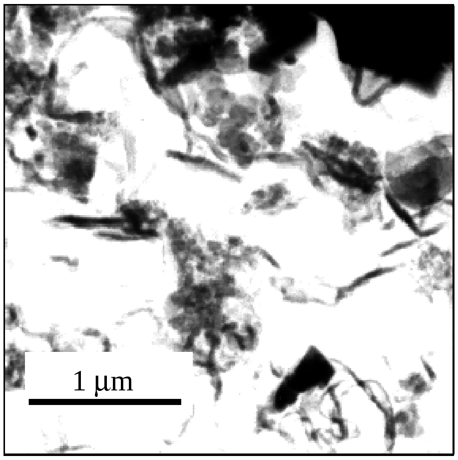

Fig. 4. Very fine globular and rod-like particles of carbon. TEM.

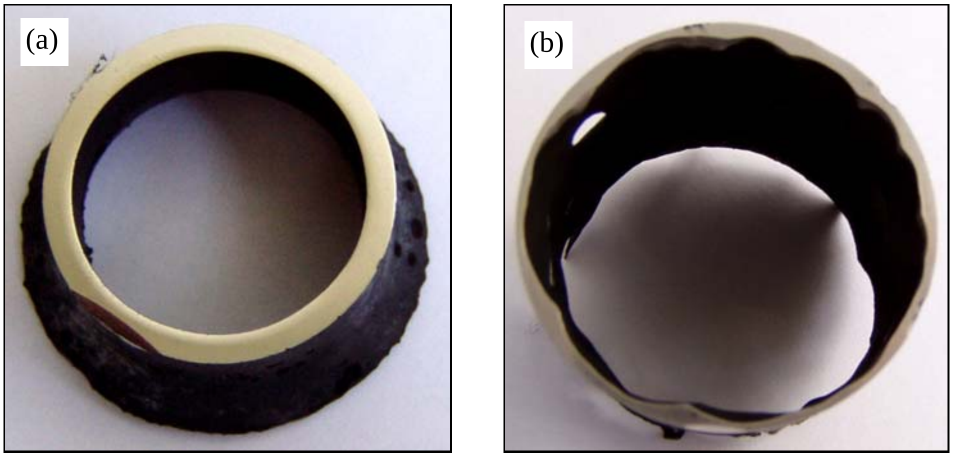

Fig. 5. Polished and etched cross-sections of the inlet tube at the front, non-damaged part (a) and at the end part damaged by dusting (b).

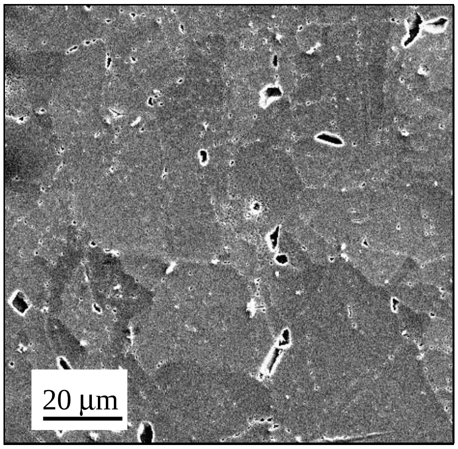

Fig. 6. Microstructure of the front part of tube, not damaged by dusting. SEM.

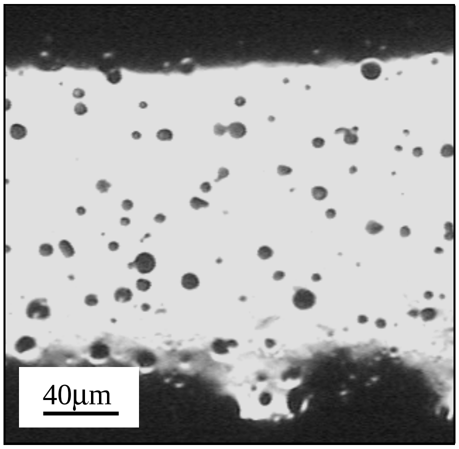

Fig. 7. Unetched metallographic specimen of the cross-section in the damaged part of the tube. Notice etch pits in the cross-section after electrolytic polishing.

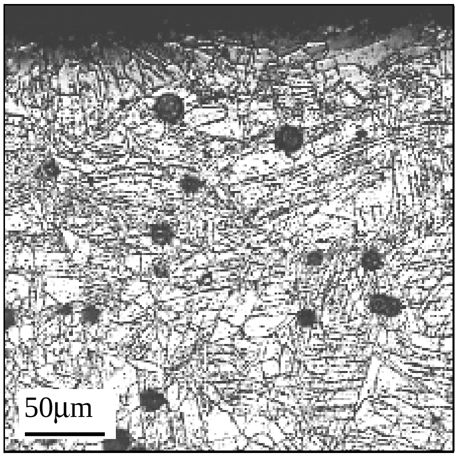

Fig. 8. Microstructure of tube cross-section in the area of dusting attack.

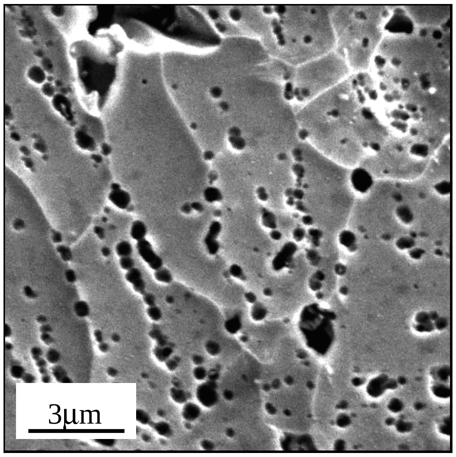

Fig. 9. Microstructure at higher magnification. SEM.

To analyse the microstructural features, we have prepared several samples from tube cross section, from the entry part of the tube, which was not damaged by dusting process, and from near the damaged end of the tube. The appearance of two polished and etched surfaces is shown in Figs. 5a,b. The microstructure of the tube entry part, which was not damaged, consists of polygonal austenite grains and second phase particles, which were oxides and carbides in nature. In between, some porosity of tube was also detected. Figure 6 shows the microstructure of that part of inlet tube. The cross section appearance in the damaged (thinned) part of the tube is in Fig. 7 (after electrolytic polishing) and its microstructure in Fig. 8. Grain and subgrain boundaries, and slip planes were etched preferentially. At these sites the occurrence of chromium carbides was detected. More detail of these sites is given in Fig. 9 (SEM) and the appearance of carbides in Fig. 10. Comparing to the entry part of the inlet tube, which was not damaged by dusting, we can conclude that the microstructure of the tube in the dusted area was very different. Grain boundaries and subgrain boundaries, as well as the slip planes, became sensitive to etching. The density of second-phase particles was much higher. They were composed of chromium carbides namely. At these etched sites also two kinds of carbon particles were detected. Very fine rods were of crystal nature while fine globular shapes were giving a very diffuse diffraction rings corresponding to amorphous phase.

We have also analysed the surfaces of pits and holes by SEM and TEM. Figure 11 shows the edge of corrosion pit after electrolytic polishing. Several contaminants (oxides) are still present. One of them, extracted into replica, is in Fig. 12. It was identified as Cr_2O_3 by electron diffraction. Except of oxides also very fine carbon

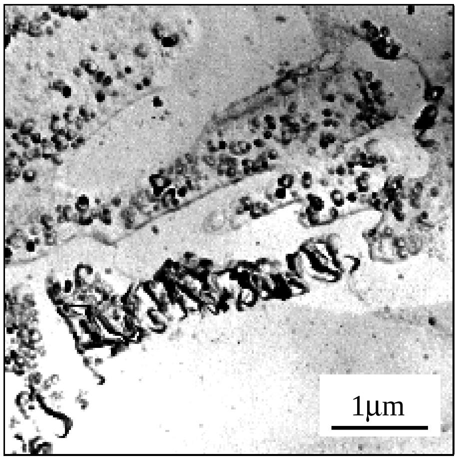

Fig. 10. Second-phase particles in the damaged part of the tube. TEM.

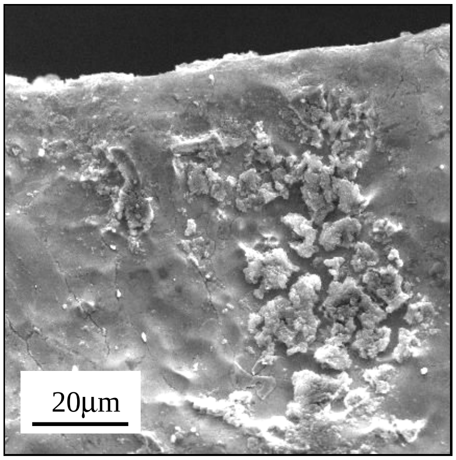

Fig. 11. An edge of the dusting hole after electrolytic polishing. SEM.

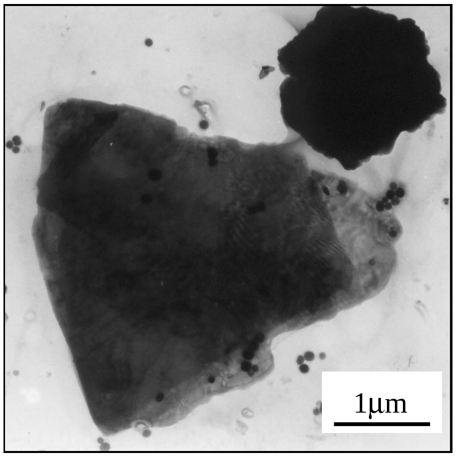

Fig. 12. Extracted Cr_2O_3 particles from Fig. 11. TEM.

particles were found on pit surfaces. They were again of two kinds: globular, as seen in Figs. 13a,b, and also very fine rod-like ones.

We have also measured the hardness of the inlet tube in the front area, not damaged by dusting and at places with intensive corrosion attack. The average hardness of not attacked alloy was 166 HV5, while the average hardness in damaged area was 160 HV5.

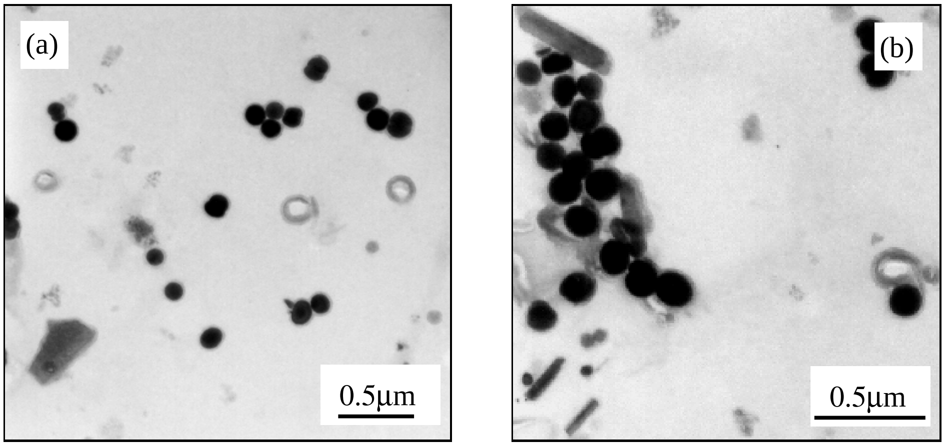

Fig. 13. Very fine globular (a) and rod-like (b) carbon particles extracted from the metallographic specimen in dusting region. TEM.

3. Discussion

Metal dusting is a very complex phenomenon, which cannot be fully investigated in laboratory conditions. On the other hand in industrial measure the process parameters are not exactly known and the problem arises when the structural part is either damaged or destroyed and must be repaired or replaced. One among the questions is which type of material has better or higher resistance to metal dusting in the given conditions. In the steam generator analysed it was Alloy 800, containing 21 % Cr, 0.1 % Si and 0.4 % Al as the scale forming elements. Baker and Smith [2] measured the maximum pit depth in the specimens corroded by dusting as a function of time for various alloys tested. The best fit was produced using the following summation (in wt.%): (Ni + Co) + 11 Cr + 5 Mo + 15 W + 52 Ti + 83 Si + 54 Al – 1.5 Fe for metal dusting resistance.

Equivalent value of this summation for Alloy 800 is about 240, while that for Alloy 602 CA about 600. This means that Alloy 602 CA is more resistant to dusting as Alloy 800. From that it follows that one of possible solutions is to replace the type of alloy. Probably due to local inhomogeneities (large grain size, TiN inclusions) it is difficult to obtain a dense and protective scale in Alloy 800.

According to information obtained from the plant, in the last time the amount of steam supplied into methane was decreased, which in turn increased the efficiency of the process. But lowering the steam/H_2 ratio tends to increase the CO/CO_2 ratio [1] and a tendency of free carbon production by Boudouard reaction.

Concerning the microstructural features it was found (Fig. 8) that diffusion of carbon and subsequent carbides formation is – to some extent – leading to fragmentation of an alloy and easier loss of material. The surface of pit (Fig. 11) is not very much dimpled, it is rather smooth, which prefers the view for nanoscale loss of material.

4. Conclusion

A metal dusting corrosion was observed in inlet tube made of Alloy 800 in methane converter plant. Thermal cracking of methane with oxygen in water steam produced hydrogen and also carbon monoxide/dioxide. In a lower steam/H_2 ratio, the amount of carbon monoxide is increasing, and the metal dusting phenomenon may occur.

It was proved that the surfaces of damaged tube were heavily covered by contaminants in which the prevailing part was colloid carbon, with small portion of graphite particles. In the dust also other elements were present coming from the fireclay and also from the composition of the inlet tube. Electron diffraction from extracted particles proved their crystalline nature.

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