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# Two cases of high alloy austenitic steel failures

**Abstract:** The article presents failures of structures made of austenitic steels. The first part is concerned with accelerated (centrifugally) cast tubes ( $\phi$  52.6 x 5.8 mm) made of steel 25-35 CrNi exposed to high temperature and severe reducing environment (ac >> 1). The second part of the article presents test results related to a water meter element and a cooling water pipeline made of austenitic steel. In both cases, a relatively short period of service was accompanied by the appearance of leaks. The tests revealed that the failures were triggered by microbiological corrosion caused by a sulphur reducing bacteria and not by the welding technology applied.

**Keywords:** High alloy austenitic steels, centrifugally cast tubes, carburization, metal dusting, microbiologically influenced corrosion

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## Introduction

The article deals with different cases of high alloy austenitic steel failures. The first one is from the petrochemical industry, where high alloy centrifugally cast tubes are exposed to high temperatures and to carburizing environments.

The second ones talk about a microbiologically influenced corrosion attack (MIC) caused



Fig.1 Element mapping of exploited CCT (1000-1050°C/ 70 000 hrs) – inside surface

by SRB, which were present in relatively pure water. Even though the causes of both failures are not so typical, their high economical loses may arise.

# Metal dusting of 25/35 CrNi centrifugally cast tubes.

Centrifugally cast tubes, which are applied in ethylene or hydrogen production, have to withstand very high temperatures (up to 900-1150°C) and harsh environments. In dependence on the carburizing effect they may undergo different corrosion processes.

The most often used process is carburization of the pyrolysis tube internal surface during an ethylene production, when creation of the thick carbide network ( $M_{23}C_6$ and  $M_7C_3$ ) is involved, see EDX element mapping in Figure 1, [1]. The thick carbide formation occurs, if a carbon activity  $a_c < 1$ .

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In case of carbon activity  $a_c > 1$ , processes of coking or metal dusting may take place, especially in an H<sub>2</sub>-CO-H<sub>2</sub>O-CO<sub>2</sub> atmosphere, when in the consequence of carbon oversaturation ( $a_c > 1$ ) graphitization happens.

The coking process may result in wall pipe delamination (Fig.2a) during shutdowns due to high stresses created by a thick coke layer with a much lower thermal expansion coefficient (Fig.2b), [2].

Metal dusting is a localized degradation process that occurs in hot reactive gases containing carbon and hydrogen compounds but almost no oxygen. Local defects in the oxide scale allow carbon diffusion into metal, where firstly stable carbides M<sub>23</sub>C<sub>6</sub> and M<sub>7</sub>C<sub>3</sub> precipitate and when a carbon activity rises to values  $a_c >> 1$ , graphitization starts. The graphite growths into metal and disintegrates its structure such way, that a metal powder consisting of carbides, oxides and graphite originates [3]. Such a process may result in the formation of surface pitting and subsurface hollows, see sketch in

 $\alpha - \text{metal} \approx 19 \,\mu\text{m/m/K}$   $\alpha - \text{coke} \approx 4 \,\mu\text{m/m/K}$   $\Delta \varepsilon = \Delta \alpha \cdot \Delta T$ 

Fig. 2. Wall pipe delamination (a) and Coefficient of thermal expansion (b) [2]



Fig. 3 A mechanism, proposed by Zeng et al. [4], for metal dusting of both iron and nickel based alloys



Fig. 4 Hollows at outer tube surface



Fig. 5. EDX analysis of the graphite particle in the hollow

Figure 3. In our case 25/35 CrNiNb tubes of the hydrogen furnace were examined, Fig. 4 and 5 shows a presence of the graphite in the under surface hollow.

According to K. Natesan et al. [4] an economical loss caused by metal dusting in the hydrogen industry reaches up to \$ 220-290 million annually.

# Microbiologically influenced corrosion

There are more than 100 species of bacteria associated with the corrosion of metals. The main types are sulphate-reducing bacteria (SRB), sulphate-oxidizing bacteria (SOB), iron-oxidizing bacteria (IOB) and manganese-oxidizing bacteria (MOB).

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The SRB are considered to be the most dangerous ones. Besides of mild steels, they often attack stainless steels or Cu and Al alloys. SRB look for wet environments void of oxygen having temperatures between 25-60°C and with alow flow rate of liquid (standing water).

There are only limited possibilities how to distinguish them:

- presence of S in the corrosion products
- their typical "bottle" shape observed by microscopy
- unpleasant smell due to  $H_2S$  release.





Fig. 6. Bacteria on surface of corrosion pitting of stainless steel weldment [5]





Fig. 7 Leakages in weld of air separator unit



Fig. 8 Macroetches of weld attacked by SRB



Fig. 9 Leakages around the welds





Fig. 10 SRB attack of welds and around the welds SRB

Only specialized laboratories may provide the direct microscopical observation of the SRB on the surface of a corrosion pitting, see Fig.6, [5].

Irregularities of weld surface (weld reinforcement in the cap or root) as well as the HAZ oxide colour may serve as traps of the bacteria.

### *Leakage in air separator unit made of* stainless steel

An air separator of the water meter made of 1.4306 stainless steel was concerned [7]. The water meter was a part of a desalting plant in

> one of the African countries. It should be emphasized that SRB are almost always present in coastal sea waters.

A lot of leakages in the weld were revealed after a year of operation, see Figures 7 and 8.

### Failure of stainless steel pipeline

Girth welds of the  $\phi_{129\times 2}$  mm pipes made of 1.4301 stainless steel were examined [8]. A company applied stainless steel pipeline (instead of the usually used plastic or Zinc coated pipes) for transport of the cooling water from an old well. Already after 4 weeks several leakages were revealed, see Fig. 9 and 10. Especially, if a water unit is not in continuous service with residues of water inside after shutdowns. Higher content of sulfur, which probably comes from SRB was identified by EDX microanalysis of corrosion products inside a pit (Fig.11).

Repairing equipment or a pipeline by welding is practically impossible as attacks (inside – outside of welds)

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cannot be repaired. Microbiologically influenced corrosion (MIC) is a serious problem in a number of industries including power generation, petrochemical, gas transmission and shipbuilding. A conservative estimation of economical loss due to MIC is \$30 to 50 billion/year (EUR 27 to 44 billion), [6].



Fig. 11. EDX analysis of corrosion products

# Conclusions

The article deals with two less known corro- [3] Hrivňak I., Čaplovič Ľ., Bakay G., Bitter A.: sion cases of high alloy steels; however, it is very probable that their occurrence in practice is more frequent due to their inexact classification in our countries, but according to American references their impact on economic losses is significant.

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