# FAILURE ANALYSIS OF PIPES IN RADIATE SECTION OF ETHYLENE CRACKING DECOMPOSITION FURNACE INDUCED BY SULFURIZATION

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## ABSTRACT

Failure analysis of pipes made from ACI HP40 alloy in the radiate section of an ethylene cracking decomposition furnace was carried out with an optical microscope (OP) and an energy dispersive spectrometer (EDS). The results show that besides the carburization attacks, sulfurizing attacks in the working environment occur at elevated temperatures since the sulfur content in the used medium is high. This attack results in sulfide formation at the grain boundary, which brings about embrittlement of the alloy and an overall degradation of its original mechanical properties.

**Key words:** Sulfurizing; Carburization; High-temperature corrosion; Failure analysis

## INTRODUCTION

Industrial environments are becoming increasingly complex and severe, with some applications requiring materials to perform in atmospheres with low oxygen and high carbon contents plus sulfur activities at elevated temperatures. Given that these environments do not allow an alloy component to form a protective oxide scale, the corrosion observed in these situations is typically severe and sometimes catastrophic. Not only does an alloy have to be sulfurization resistant, which typically infers a low Ni

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content; it must also resist internal carburization, which typically infers a high Ni content /1,2/.

The formation of carbon deposits on iron- or nickel-based alloys at elevated temperatures in gaseous carbon-bearing environments remains a subject of substantial technological interest. Such deposits can have significant detrimental effects in industrial processes, e.g., by reducing heat transfer efficiency in chemical engineering plants /3/ or in CO-cooled nuclear reactors /4/, or they may be associated with excessive carburization of the alloy and consequent structural impairment /5,6/.

For typical radiate pipes of an ethylene cracking decomposition furnace, HP40 has been commonly used due to its good carburization resistance. However, in a factory, the service life of the above pipes was less than one year, which was much shorter than expected /7,8/. To extend the service life of the equipment, the reason for failure of the pipes must be analyzed in this special working condition. In this contribution, this analysis has been carried out. Based on the analysis, a substitute material for the alloy is suggested.

The working environment of the pipes is as follows: The media in the ethylene cracking decomposition furnace are naphtha and diesel oil. The working pressure is 0.35 MPa, the temperature outside the pipe is 1073 K-1105 K. The pipe is ACI HP40 alloy (24%Cr, 34%Ni and 0.45%C in weight percentage), and the diameter and the thickness of the pipes are 88.9 mm and 5 mm, respectively.

## EXPERIMENTAL PROCEDURE

The corrosive internal surface of a failed pipe was cleaned with a 10% HCl solution, water and alcohol, in turn, and then dried. The samples were cut along the horizontal directions of the pipe to observe the section. The corresponding composition analysis of the pipes at four different distances from the internal surface with a space of 1 mm was made with an energy dispersive spectrometer (EDS) to obtain the composition grades of carbon and sulfur within the pipes along the distance of the internal surface. The microstructure of the samples was observed with an optical microscope (OP) to understand the details of the corrosion mechanism.

## RESULTS AND DISCUSSION

The composition analysis of the pipes at different distances from the internal surface is shown in Table 1, where both the carbon and the sulfur contents decrease from the inner to the outer surface. Note that the sulfur content is more than 1.5 wt.% even where the distance from the inner surface is 3 mm, which is about the same as the carbon content. Note that on the outer surface, the contents of both carbon and sulfur are equal to the original contents. Thus, the failure of the pipe takes place when sulfurization and carburization, leading to saturated contents of carbon and sulfur of 1.5 wt.% in the pipe, reaches about 60% of the full thickness of the pipe. As seen below, although the content of compounds in the rest of the thickness of the pipes is still lower, the compounds exist in a part of the interface where crack expansion has occurred and failure arises.

**Table 1**
Composition analysis of carbon and sulfur contents within the pipes where the layer distance is 1 mm (wt.%)

| | Inner surface | Second layer | Third layer | Fourth layer | Outer surface |
|---|---|---|---|---|---|
| C | 1.12 | 1.48 | 1.40 | 1.02 | 0.46 |
| S | >1.5 | >1.5 | ≥1.5 | 0.67 | 0.04 |

The macroscopy of the internal surface of the pipe is shown in Fig. 1, where the black areas in the photograph should be carbide or sulfide. Thus, most of the inner surface consists of the above compounds. As the distance

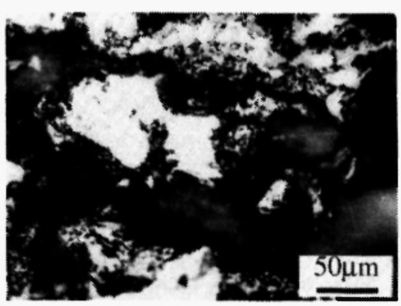


**Fig. 1:** Optical micrograph of the inner surface of the pipe.

from the inner surface increases, the compounds exist only along the grain boundaries that are present in Fig. 2. The results correspond to the composition analysis of Table 1 where the contents of carbon and sulfur are almost the same as the original contents. The result of Fig. 2 indicates that the grain boundary diffusions of carbon and sulfur are much faster than the volume diffusion. On the outer surface of the pipe, there are only light pits

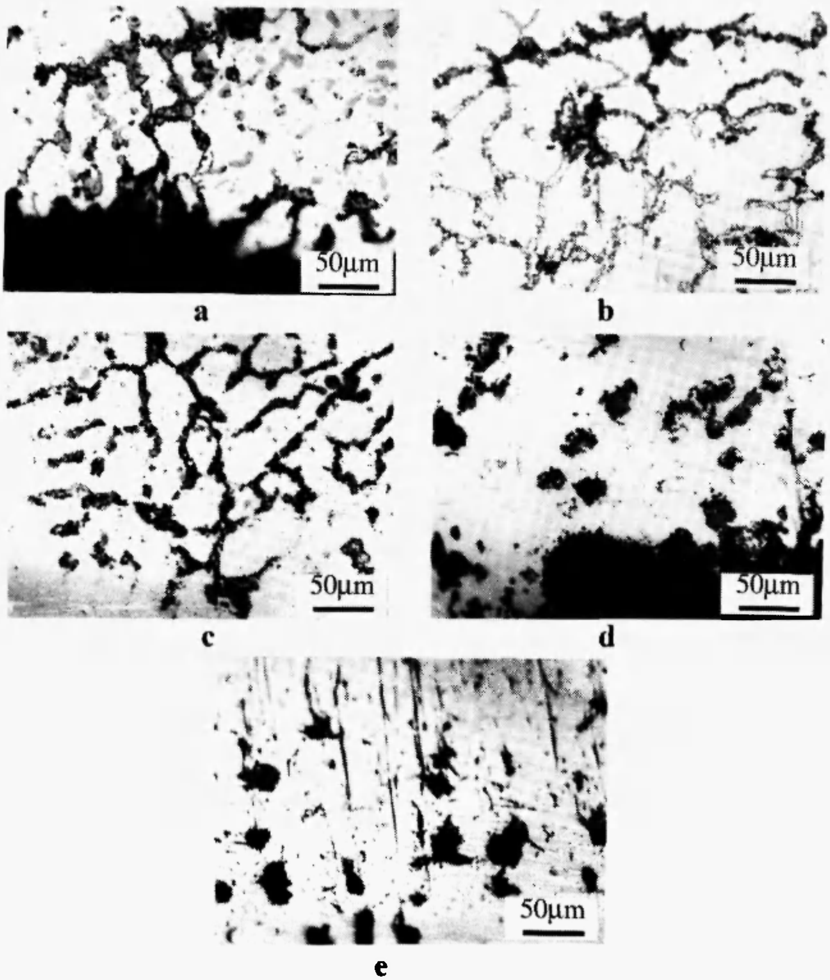


**Fig. 2:** Optical micrograph of the pipe. (a) The internal surface; (b) The second layer; (c) The third layer; (d) The fourth layer; (e) The outer surface of the pipe.

indicating the existence of $Cl^{-1}$ ions in the atmosphere /7,8/, since the furnace is located within a chlorine factory.

Fig. 3 shows that the crack propagates along the grain boundaries. This is because the brittle compound is formed at the grain boundaries, which leads to volume expansion and internal stress and, consequently, to crack formation and expansion. When the cracks extend along the full grain boundaries, the grains drop off from the matrix.

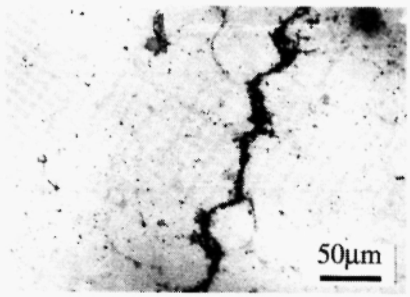


**Fig. 3:** Micrograph showing the surface cracks.

From the above results, it is known that the rapid failure of the pipe is due to the strong sulfurization tendency that was not considered during the instrument design. Since the original content of sulfur is only 0.04 wt.%, while the original carbon content is 0.4 wt.%, the volume expansion due to the formation of sulfide is more evident when the saturated contents of both the carbon and the sulfur is about 1.5 wt.%. The volume expansion should be the essential reason for the internal stress and cracks.

To improve the service life of the pipe, a substituted alloy with higher Cr and lower Ni contents should be selected. Based on this consideration, the ACI HD40 alloy (0.40% C, 30%Cr, 6%Ni and 2%Si) or the ACI HK40 alloy (0.40%C, 28%Cr, 18%Ni and 2%Si) should be utilized to substitute the HP40 alloy.

## SUMMARY

Sulfurization plus carburization attacks lead to a much shorter service life of pipes in the radiate section of an ethylene cracking decomposition furnace due to the high contents of sulfur in the working medium. Since carbide and sulfide are formed above the grain boundary, embrittlement of the alloy is present. HD40 alloy or HK40 alloy that has higher Cr and lower Ni contents should be selected to substitute the HP40 alloy in the above working environment.

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