INFLUENCE OF STEEL CONTAMINATION IN PETROLEUM PRODUCTS ON FORMATION OF NON-METALLIC INCLUSIONS

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Abstract

It is generally recognized that the high content of non-metallic inclusions in structural steels alter their physical and mechanical properties. Formation of non-metallic inclusions is a complex phenomenon that depends on the composition, pressure and temperature of the working media. By use of different surface analysis techniques we analysed an austenitic stainless steel pipe that has been contaminated by petroleum products as a result of diffusion and concluded that the liquid medium penetrates relatively far into the metal by adsorptive migration, resulting in formation of chemically active sites that promote the formation of intermetallic compounds. It is important to understand this mechanism as it directly influences corrosion and further failure of the steel, leading to problems that translate into human and economic losses.

Keywords: stainless steel, non-metallic inclusions, corrosion

1. INTRODUCTION

Petroleum equipment, especially under the conditions of processing sulfur-containing oils, is subject to strong corrosion, and therefore is put out of commission rapidly. Metal wear is caused by vapors of petroleum products and hydrogen sulfide, moisture, and atmospheric oxygen entering the oil [1]. With this in mind we first analysed stainless steel specimens that did not present any visible trace of corrosion on visual inspection, as the contamination of steel in petroleum products takes place by diffusion mechanisms.

Uncontrolled contamination of petroleum products causes biodeterioration problems that translate into substantial economic loss. Biodeterioration's adverse economic effects constitute one cost of quality category [2].

Deterioration of fuels and oxidation of hydrocarbons by microorganisms, and corrosion of metals in the presence of microorganisms are strictly established facts [3] and they lead to contamination of the steel, corrosion and failure [4, 5].

Also in [6] the authors have also reviewed the fuel biodeterioration, concluding that all grades of conventional, bio and synthetic fuel are subject to biodeterioration.

It is generally recognized that ferrous metals, particularly structural steels, contain considerable amounts of nonmetallic inclusions; increased contamination of steel with such inclusions alters their physico-mechanical properties [7, 8]. Since the properties of steel depend both on the amount of inclusions and their composition (type), size, and shape, the influence of contamination on the properties of steel (especially in liquid media) is very complex.

It must also be noted that defects exiting to the surface do not play the decisive role in the influence of the medium on the physico-mechanical properties of a contaminated metal; their importance probably lies in initiating formations of jogs, through which the ambient medium can penetrate relatively far into the metal by adsorptive migration [9].

According to [2] in the first stage, hydrogen atoms and ions H+ and H– are formed by anodic-cathodic reactions of the medium containing hydrogen sulfide with the metal. Those atoms and ions are adsorbed on iron atoms at adsorption sites, with the iron sulfides deposited as a hump, which results in a galvanic cell with cathode on the iron sulfides at anode on the surface of the microcrack.

The chemisorbed hydrogen produces submicrocracks at the surface (initial stage of submicrocrack formation) with a layer of H–. The negative hydrogen ions are located at the sides and tip of an ideally sharp microcrack, which favors the breakage of maximally stressed interatomic bonds in the metal lattice.

During the first stage, hydrogen atoms and ions are transported by dislocations in the region of the microcrack, particularly at the tip, so a stress concentration appears which weakens the bonds in failure by the microcleavage mechanism.

The objective of this work is to investigate the effects of petroleum products on steel surface in order to assess its influence on the microstructure. For this we characterized the samples by use of surface analysis techniques and after that we investigated the microstructure and chemical composition.

2. EXPERIMENTAL ANALYSIS AND RESULTS

For analysis we used austenitic stainless steel samples cut from petroleum products transmission pipes. Because corrosion in this field is initiated from the inner surface the investigation was divided into several steps and started with surface analysis using Scanning Electron Microscopy (SEM). Inside the pipe we found a black homogeneous deposited layer that was quite adhesive (Fig 1).

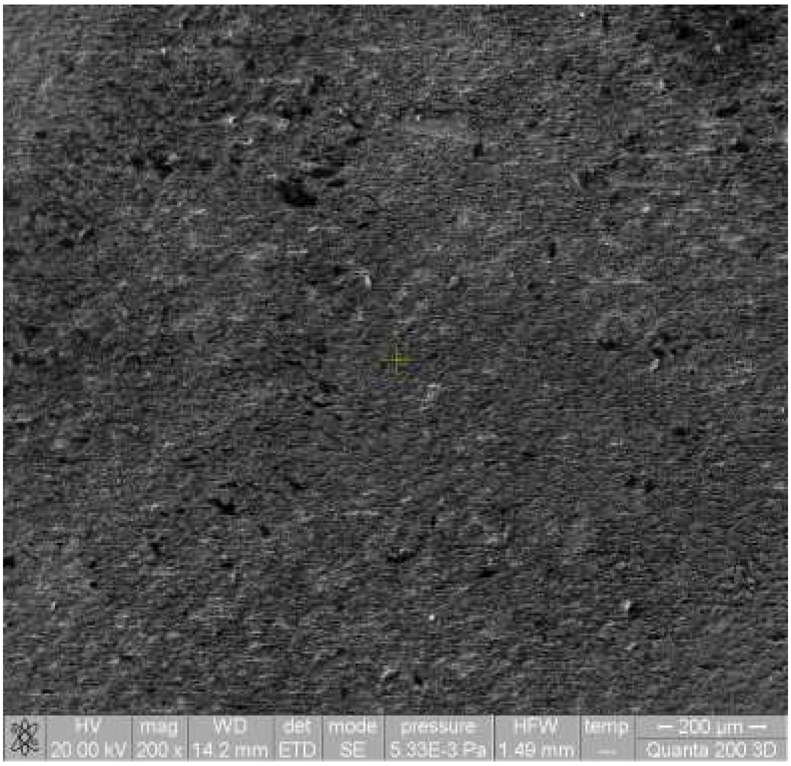

Fig. 1 SEM micrograph of the internal wall surface

Using X-ray photoelectron spectroscopy (XPS) we analysed the deposited layer elemental composition. Results are presented in Fig 2.

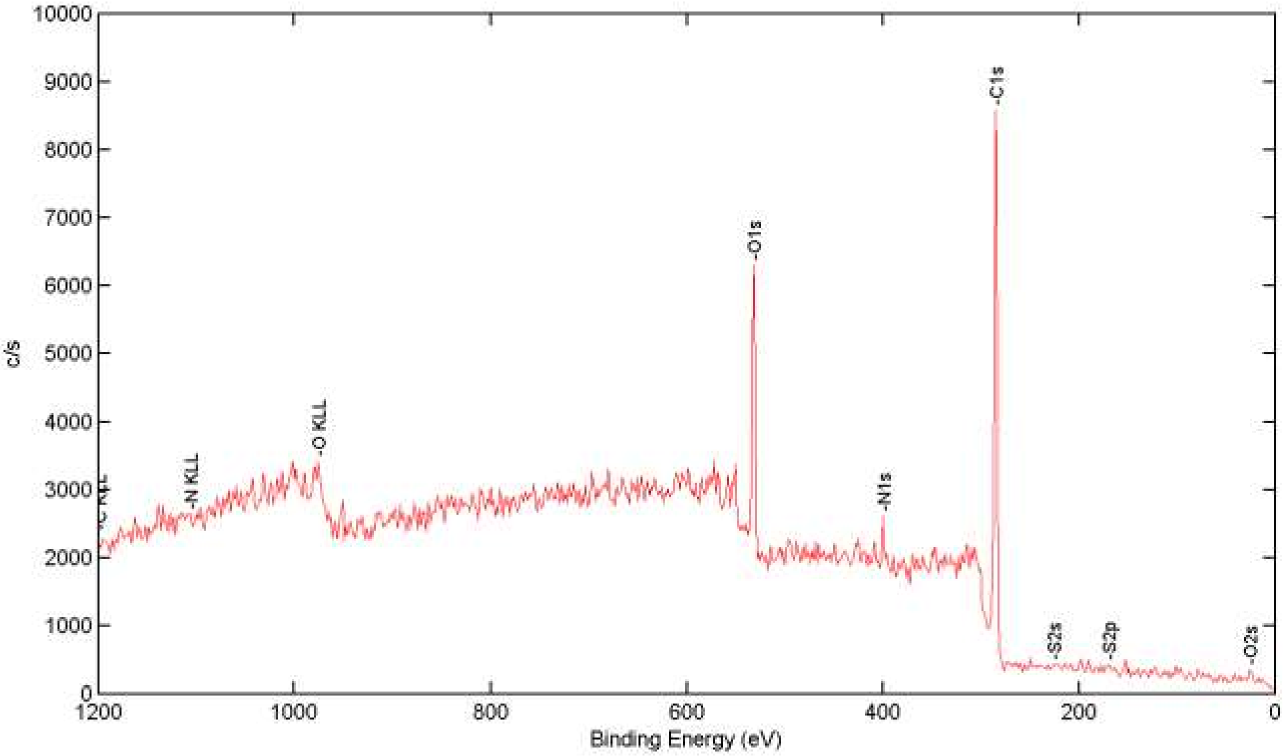

Fig. 2 XPS spectrum of the deposition

After surface analysis we cut the samples in cross section and analysed them by optical microscopy. The effects of corrosion can be seen in Fig. 3.

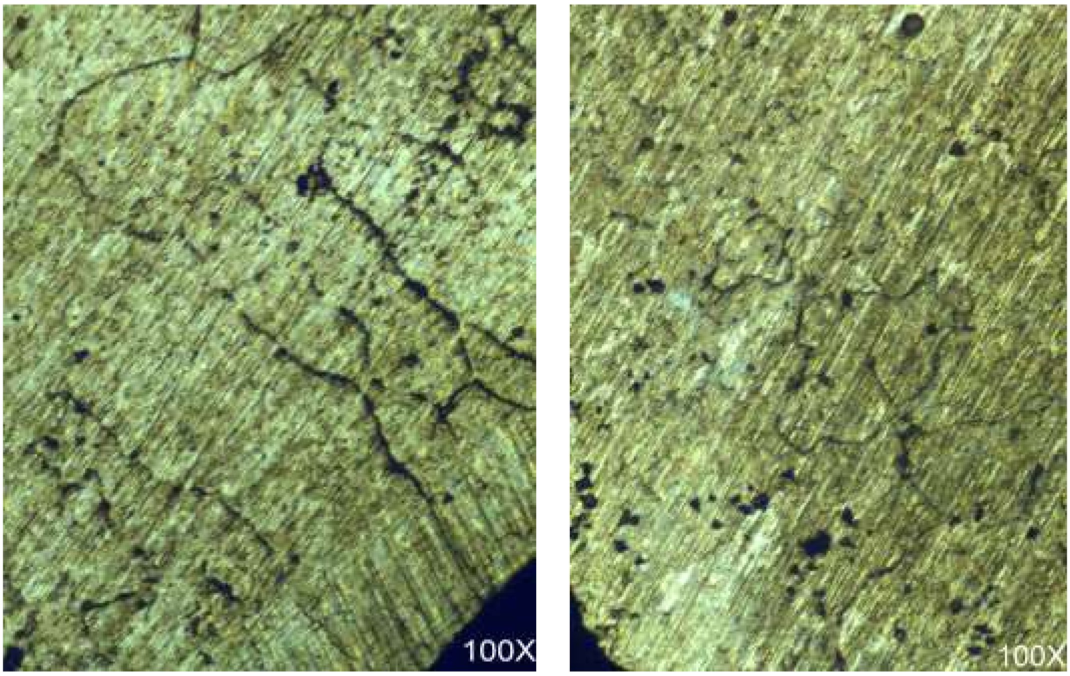

Fig. 3 Optical microscopy of the samples

Using SEM we analysed the chemical composition from the inner wall to the external wall and obtained the graphs with the variation (Fig. 4).

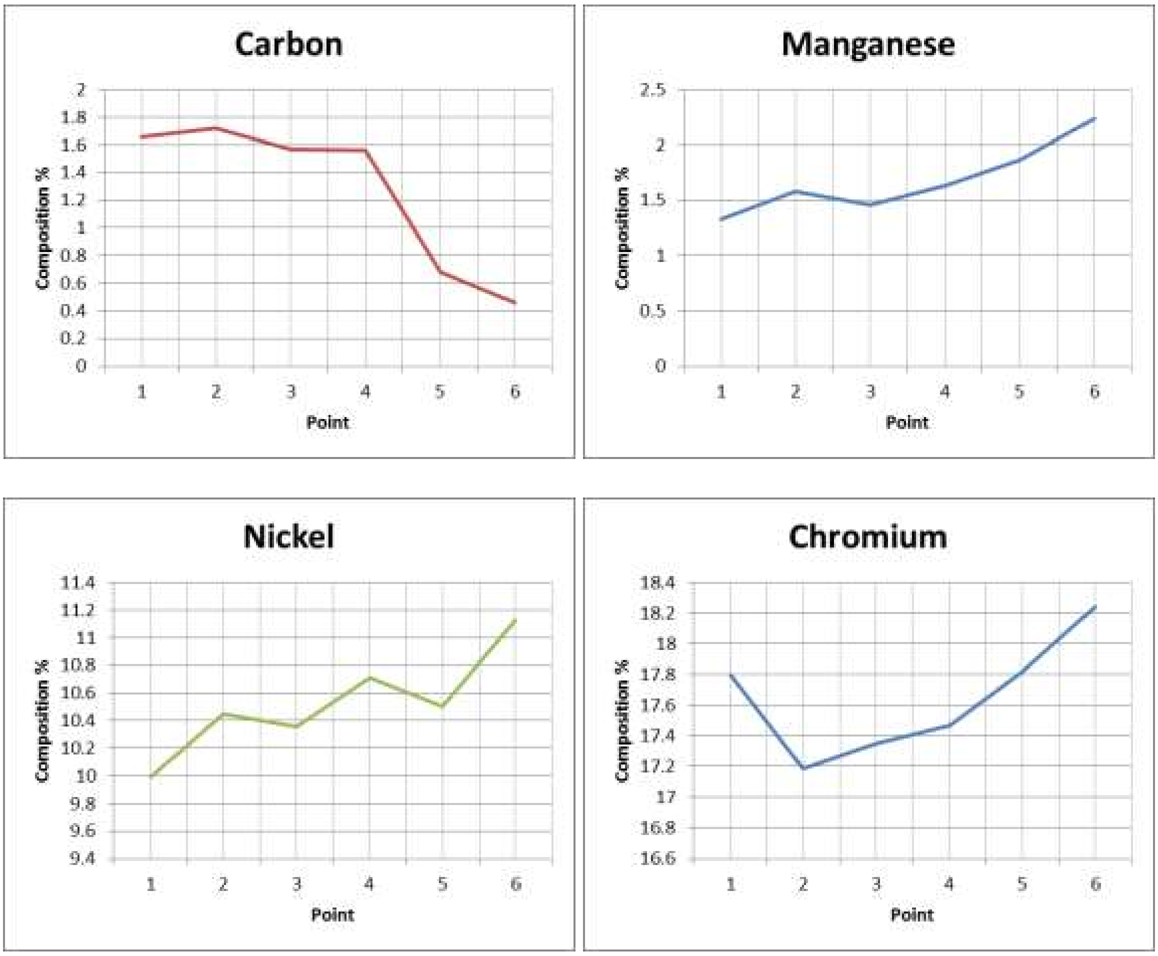

Fig. 4 Chemical composition variation in points from external wall (point 1) to the internal wall (point 6)

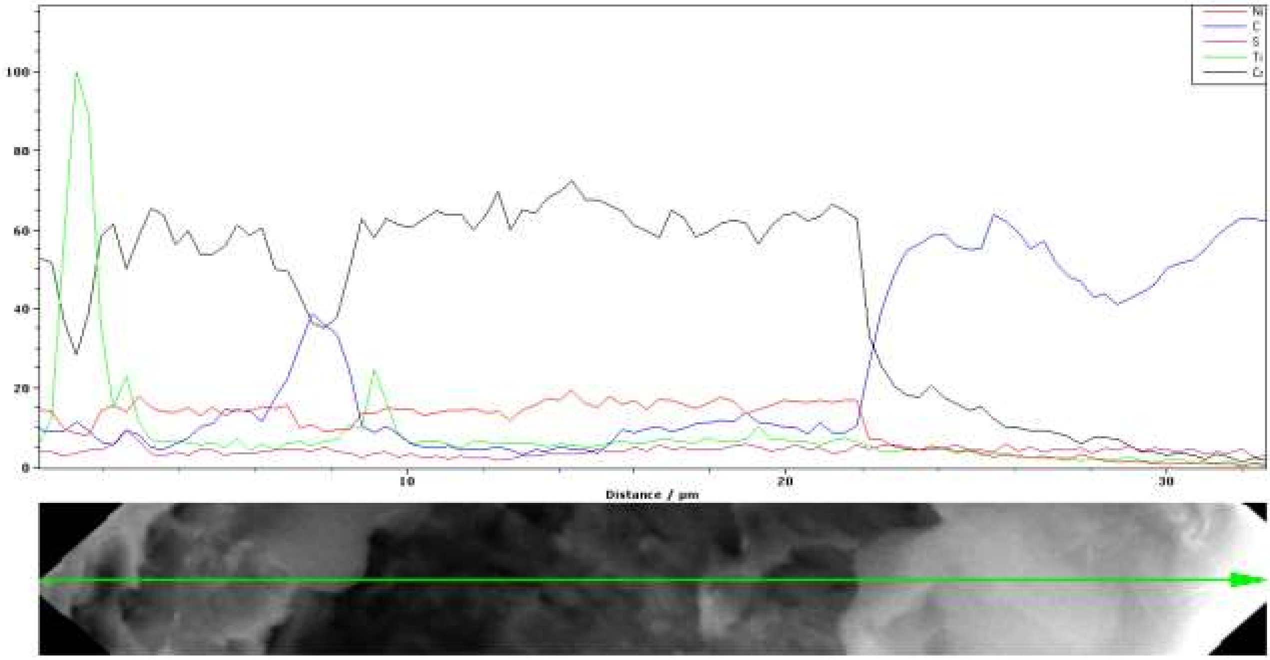

Fig. 5 EDAX of the chemical composition at grain boundaries

After fracturing the samples we used Energy Dispersive X-ray analysis (EDAX) to determine the chemical composition at grain boundaries. There can also be seen a composition variation due to the presence of non-metallic elements (Fig. 5).

3. DISCUSSION

The XPS spectrum shows that the surface is contaminated and the layer is quite adhesive. A strong S 2p pair of peaks is observed at binding energies of 164 and 165 eV, consistent with the presence of thiophenic sulfur and sulfoxide forms at 168 eV. Two peaks may be fit to the curve at binding energies characteristics of pyridinic (398 eV) and pyrrolic (400 eV) type nitrogen. At 285 eV the C 1S indicates the variation in content of aromatic and aliphatic carbon containing species. The sub peak at lower binding energy (530 eV) corresponds to the ferrous oxide film and sub peak at higher binding energy (531 eV) can be attributed to the carbon single and double bond with oxygen atom. The formation of sulfoxide species on stainless steel surface can simply be explained by interaction of sulfur with ferrous oxide film as well as the O 1s spectra analysis on stainless steel surface revealed the presence of ferrous oxide film. The nitrogen spectrum indicates the presence of pyridinic and pyrrolic species [10, 11].

All these elements seem to contaminate the steel by diffusive mechanisms. This resulted in lowering the carbon content and increasing the manganese, nickel and chromium content as seen in Fig. 4. This can be explained by migration of the atoms and formation of non-metallic inclusions. In [12] the author described the mechanism by dividing it into the following stages:

- diffusion of the oxidizing agent to the steel surface
- adsorption of the oxidizing agent particles to the steel
- chemical reaction of the oxidizing agent with the steel
- desorption of the reaction products from the steel surface
- diffusion of the reaction products from the steel in the petroleum product volume.

According to [9], as a result of diffusion, there is a considerable increase in the contact area and there is an intensification of the contact between the medium and the metal, so that the adsorptive, corrosive (electrochemical), and absorptive (hydrogen-saturation) effects of liquid media are far stronger for contaminated steel than for refined metal (purified of non-metallic inclusions).

CONCLUSION

- carbon, oxygen, sulfur and nitrogen elements revealed presence of carboxylic, thiophenic, thiol, pyridinic and pyrrolic type functional groups on the surface. The XPS spectral analysis indicated presence of thiophenic, sulfoxide, ferrous oxide, pyrolic, pyridinic, C-H species in aromatic and aliphatic form and carbon-oxygen bond species
- the deposited layer contaminates the steel and leads to formation of non-metallic inclusions, which worsen the steel’s mechanical properties
- formation of non-metallic inclusions is a complex phenomenon that depends on the composition, pressure and temperature of the working media
- intergranular corrosion could not be detected by non-destructive analysis, although the surface of the samples did not present any defect, which makes it extremely dangerous as it leads to problems that translate into human and economic losses.

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