4th International DAAAM Conference
"INDUSTRIAL ENGINEERING – INNOVATION AS COMPETITIVE EDGE FOR SME"
29 - 30th April 2004, Tallinn, Estonia

INFLUENCE OF TECNOLOGICAL STRESSES ON THE CORROSION OF WELDED PIPES

Ščekaturovienė, D.; Višniakov, N.

Welded as well as not welded steel elements are used for exploitation in various environments, including the aggressive one. Construction steel fracture mechanisms in corrosive environment are the following: decrease in adsorption strength, corrosion solubility and hydrogen embrittlement (Parton). Decrease in adsorption strength dominates under high stresses in the material, i.e. when stress intensity coefficient is high. Corrosion solubility depends on the medium: the aggressivity of the exploitation environment. Tap water is not very aggressive. The present paper deals with the influence of technological stresses, i.e. stresses obtained during cold working, on fine grained carbon steel hydrogen embrittlement.

Key words: carbon steel, cold working stresses, hydrogen embrittlement, tap water, welded pipe.

1. INTRODUCTION

Various methods may be employed to research metal corrosion resistance: statistical, regression analysis, electrochemical, in salt spray, controlled humidity etc. Laboratory experimentation allows electrochemical corrosion resistance in a certain aggressive environment: salt spray, sea water etc. But specific exploitation environment with different chemical and physical parameters, i.e. differing from the standard, as well as metal production technology often modify the standard research results. In investigating an in service failure, the analyst must consider a broad spectrum of possibilities or reasons for its occurrence. A large number of factors affect corrosion behaviour, and therefore there is no universal corrosion test. .In such cases, tests in which all exploitation conditions are taken into account are necessary, i.e. carried out by observing the behaviour of the elements under research in their working environment.

Construction steel fracture mechanisms in corrosive environment are the following: decrease in adsorption strength, hydrogen embrittlement and corrosion solubility (Parton, 1990.). Decrease in adsorption strength dominates under high stresses in the material, i.e. when stress intensity coefficient is high. Then crack growth is very rapid and other fracture mechanisms are not rapid enough to occur. Atomic hydrogen, which is always present in hydro-electrolytes, may diffuse to metal, especially, when the metal is not covered with an oxide layer, and thus make conditions for hydrogen induced cracking. Hydrogen diffusion speed in metals exceeds carbon or nitrogen diffusion speed: in α-iron, under 20 °C, hydrogen diffusion speed is 10^{12} times greater than that of carbon or nitrogen (Archakov, 1985). Crystal cell defects and dislocations play an important role here because electrolyte hydrogen solubility in a crystal cell is very small. At room temperature hydrogen solubility in iron crystal cells is very low. Therefore, during electrolyte processes, hydrogen solubility manifests itself through hydrogen adsorption and concentration in grain boundaries and at non-metal inserts, carbides and metal matrix resolution surface as well as pores and internal cracks, providing for the high pressure in microvolumes, under which the conditions for the movement of hydrogen molecules occur. Thus, dislocations and other crystal cell defects have great influence on hydrogen inducing. Under cold deformation, as the number of dislocations increases, inter-crystal relation becomes weaker and hydrogen solubility enhances. Hydrogen solubility may be retarded when, with the participation of oxygen, the oxide film forms (Archakov, 1985).

Different types of relations may occur between solute hydrogen atoms and dislocations: chemical, electric and elastic. Inter-phase borders become longer and hydrogen solubility increases during electrolytic processes as the amount of carbon increase. During the recent years, hydrogen influence on metals has been investigated with the HELP (Hydrogen enhanced localized plasticity) mechanism consisting of a twofold act: microscopic plasticity increases at the hydrogen penetration sites (i.e. dislocation movement enhances), and shear localization in macrovolume takes place. While hydrogen influence is limited to microvolume, micro-fractures do not form; they appear only during localization of dislocations in macrovolume (Sofronis et al, 2001).

Corrosion solubility depends on the medium: the aggressivity of the exploitation environment. Tap water is fresh water, which is not very aggressive. Corrosion in fresh or salt water always results from an electrochemical reaction of two parts: the anode reaction where the metal is oxidized and the cathode reaction where oxidizer is reduced. Neither of these reactions will occur without the other; and oxygen is necessary for these reactions to take place. When the corroding metal is iron or steel, the following reactions occur:

$$O_2 + 2H_2O + 4\,e^- \rightarrow 4OH^-$$
$$2Fe \rightarrow 2Fe^{++} + 4\,e^-$$
$$2Fe^{++} + \tfrac{1}{2}\,O_2 + 4OH^- \rightarrow Fe_2\,O_3 + 2H_2O \text{ and (or)}$$
$$4Fe^{++}\,O_2 + 10H_2O \rightarrow \rightarrow 4Fe_3\,(OH)_3 + 8H^+$$

When the dissolved in water oxygen concentrates in small area (at water impurities for example), corrosion pits, covered with crust of metal oxides, form. Pits consist of a tubercle, the interior of which contains a solution of ferrous chloride and sulphate ions in concentrations greater than those in the water with a pH of approximately 6. Hydrogen sulphide is occasionally present. This liquid is covered by a black inner crust consisting of hydrous Fe_3O_4, which, being magnetic, is attracted to the iron to form porous columnar fibres. The outer crust consists of reddish brown ferric hydroxide or hydrated ferric oxide. In ferrous metals such pits generally become inactive after a period of time. The flow of current protects the metal in the immediate vicinity of pit. When this occurs, they no longer protect the metal in their vicinity, and new pits develop. Apparently the tubercles become so impermeable that ions cannot diffuse through, and since the solution inside must maintain electrical neutrality, no additional iron ions are formed. If values of pH are low (<6), crust layer no longer prevents the further formation of ferric ions and new corrosion pits develop. Values of pH a little less than 7 are usually encountered in waters of low alkalinity and low dissolved solids. Under these conditions, uniform corrosion results and in absence of pitting, perforation is slow and facilities often have reasonably long life. Corrosion in fresh water is conditioned by complex processes which depend on water impurities. Groundwater brings microorganisms, flora decay products, dissolved calcium, magnesium, potassium and ferric salts, and suspended colloid particles. Listed substances and other water characteristics, such as pH, temperature and movement speed, affect composition and structure of corrosion products.

Though tap water contains low dissolved oxygen, it is not very aggressive because the cathode area of the metal is coated with a thin layer of calcium carbonate that develops from carbonates of the running water. The calcium carbonate film on the cathode surface almost stops the corrosion reaction because the diffusion of oxygen to the metal-electrolyte interface is greatly retarded. Water hardness indicator points out the amount of calcium carbonate: the harder the water, the more carbonate it contains.

In order for calcium carbonate film to form on the cathode, three conditions must be met: 1) water must have a Langelier Index of about zero; 2) it must contain a significant bicarbonate ion concentration, and 3) it must be flowing over the metal surface. Water has a Langelier Index of zero when it is in equilibrium with calcium carbonate. The Langelier Index is defined as $L = pH - pH_s$, where pH_s is the pH at which the water is just saturated with calcium carbonate. Thus, if the pH of water having zero indexes is increased, it will have a tendency to precipitate calcium carbonate, but water pH can not exceed 8.6. With such pH it is possible that water alkalinity occurs due to the dissolute bicarbonates. When the amount of calcium carbonates is great, pipe holes may even get blocked with them.

Calcium carbonate film formation is a dynamic process – chemically because the hydroxyl ion is produced by the corrosion reaction itself, and physically because it forms only where there is turbulent flow. When flow is turbulent in a pipe, there is always a thin layer or rather a film according to its thickness of laminar flow adjacent to pipe wall. Thus ions, HCO_3^{--}, OH^- , Ca^{++}, that have developed due to the chemical reactions have to diffuse through a thin laminar layer. Under turbulent flow carbonates are constantly provided. When flow is turbulent, diffusion of ions that make up carbonates towards the surface is low (Rossum).

Corrosion speed in tap water depends on the following parameters of the exploitation environment: water impurities, water temperature and pH, amount of oxygen, amount of carbonates (water hardness), and speed of water flow. Such water has relatively no oxygen and no carbon dioxide, but it is more corrosive than that having a small amount of such gas. Soft water is also more corrosive than hard water.

Mentioned factors of corrosion fracture are generally interrelated. Furthermore, fracture process is affected by steel microstructure and (exploitation or technological) stresses.

3. EXPERIMENTAL

The present paper deals with the influence of technological stresses, i.e. stresses obtained during mechanical processing, on steel resistance to corrosion in hot tap water.

Welded as well as not welded steel elements are used for exploitation in various environments, including the aggressive one. Quality of the surface conditions hydrogen penetration into metals: surface pickling by nitric acid increases hydrogen permeability ten times and, vice versa, advance oxidization greatly decreases hydrogen permeability. According to the researchers, the main factors having influence on hydrogen permeability through metal are surface conditions and chemical composition of oxide layers (Geld, Riabov, 1974). In order to increase steel corrosion resistance in atmosphere and in water, zinc or paint coatings are usually used. To prepare the surface for painting or galvanizing, chemical cleaning processes are usually applied: hot alkali treatment is used to remove the organic surface pollutants and acid treatment is used to remove surface rust and mill scale. Thus, during the surface preparation, electrolytic processes take place and hydrogen adsorption and concentration occur in places with weaker inter-crystal relation. During chemical cleaning processing more hydrogen dissolves in cold worked volume than in cold non-worked one because of additional crystal cell defects. When crystal cell defects appear unevenly, hydrogen is distributed unevenly on the surface layer of a metal during the electrolytic processes. If the steel has been severely cold worked in a small region, the hydrogen can be trapped in the steel, causing hydrogen embrittlement when the part is put under stress during use.

Annealing at around 250 °C enables hydrogen to escape from the steel. Baking after painting and exposing at a temperature of hot tap water for a long time makes conditions to escape from the material and painting.

The case when during baking of the paint the high pressure gas (hydrogen) delaminate the zinc layer from the steel, gas expanded and escaped through the soft layers to the surface and caused the appearance of the crater is shown by Torkar M, Godec M.

2. METHODS

The object of the research is the pipe of low carbon steel, composed of 0.20% C, 0.25% Mn, 0.2 % Si, 0.15% Cr, 0.025% S and P, of 18 mm diameter with 1.2 mm wall thickness. The steel is fine-grained; ferrite and perlite grains are of 9–10 points according to DIN 50601. Production technology of the pipe is welding.

With the aim to make strains, the pipe of 18 mm in diameter was bent in order for the two bends to be formed (Fig. 1). Bending radius of the pipe axis is 60 mm. Corrosive environment of the pipe is hot tap water. Water characteristics were established in the water research laboratory three times during the exploitation period: temperature 40 ºC - 60 ºC, pH 7.05-7.55, general hardness 4.2 – 4.6 mg-ekv/l, alkalinity 4.0 – 4.1 mg-ekv/l, free chlorine – 0.0 mg/l.

In order to prepare the external surface of the pipe for the painting, the surface underwent double pickling: 1) oils, grease and soluble paints were removed by putting it into hot 10% nitric alkali solution, and 2) surface rust was pickled in 15% nitric acid solution and prefluxed in a liquid flux to prevent oxidation prior to painting.

Three painted pipe elbows were installed in the hot water supply system in an apartment building and exploited until they started to leak. At the end of the exploitation of these pipe elbows, the following tests of the corrosion pits were carried out: spectrometric, macroscopic and microscopic. Equipment used constitutes the following: spectrometer Spectroport,

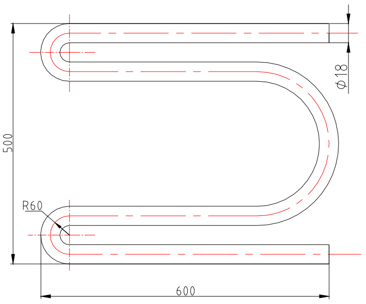

Fig.1. Construction element sample - pipe elbow.

stereoscopic microscope MBS 9, metalographic microscope MIM 7 with digital picture fixation.

4. RESULTS

Corrosion intensity was evaluated on the internal and external surfaces by cutting the pipe along the trough corrosion pit. On the external surface of the pipe only trough corrosion pits are clearly seen by the mark or the cracked paint (Fig. 1) The inner surface of the pipes had corrosion pits, which were denser in the weld seam and its heat affected zone. The inner surface of the pipes had corrosion pits, which were denser in the weld seam and its heat affected zone. The general corrosion produced deep trough corrosion pits which were noticed in a different part (in regard to their position along the crosscut) of each of the pipe elbow under research: on the opposite part of the weld seam, on the weld seam and at heat affected zone of the weld seam. In regard to the construction of the pipe elbow, trough corrosion pits were situated in the same part: 75-85 mm away from the furthest point of the elbow and on the upper part of the elbow in regard to its position in the water supply system (Fig. 1). This part of the pipes is on the passage of influence of cold processing stresses that formed during bending. Corrosion pit geometry has the form of a funnel, with its peak directed towards the external painted surface of the pipe. Corrosion products do not cover the whole surface of the corrosion pit. On the spherical part of the corrosion pit surface near the painted surface there are no corrosion products. It is the result of the hydrogen gas pressure (Fig. 2a and 2b). It cannot be the result of oxygen as there is no oxide film. This assumption is confirmed by the fact that there are gas pores on the painted layer of the external surface of the pipe (Fig. 3).


a)


b)

Fig. 2. Corrosion pit on the internal surface of the pipe after exploitation (longitudinal cut): a) corrosion pit geometry, x 5; b) spherical area without oxide film next to the corrosion affected surface, x 30

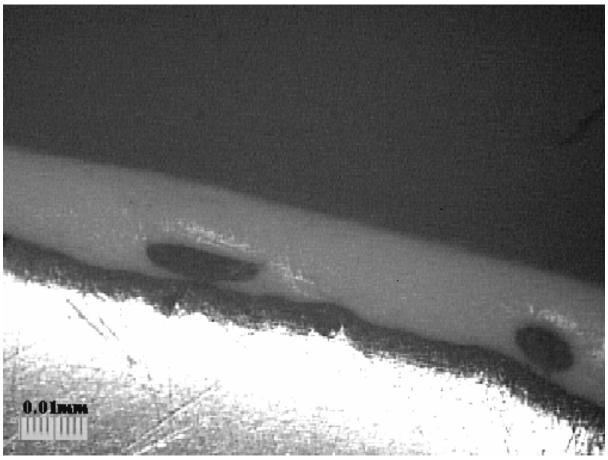

Fig. 3. Hydrogen pores under the layer of paint

On the internal surface of one of the pipes there are carbonates acting as corrosion retarding mechanisms in hard and medium hard water. As pipe elbows were exploited by the water supply system of the same building, but in different points of the tap, then carbonate formation was conditioned by the different mode of water movement in the pipes and not by the water characteristics. Water turbulence in the pipes may be judged by characteristic semi-circles in the carbonate coating on the internal surface of the pipe.

6. CONCLUSIONS

1. Stresses that develop during cold bending enhance negative hydrogenation influence on corrosion.
2. Weld seam and its heat affected zone are more susceptible to corrosion when stresses develop there.

REFERENCES

Archakov, J.I. *Hydrogen corrosion of steel (*1985), Moscow.

Geld P.V. Riabov P.A. *Hydrogen in metals and alloys* (1974). Metallurgia. Moscow.

Parton V.Z. *Fracture mechanics* (1990). Nauka. Moscow.

Sofronis P. Liang Y. Aravas N. (2001). Hydrogen induced shear localization of the plastic flow of metals and alloys. *European Journal mechanic A/solids,* Vol.20. Nov.-Dec. 2001 p.857-872, ISSN: 0997-7538.

Rossum, J.R. Fundamentals of Metallic Corrosion in Fresh Water. *www.roscoemoss.com.*

Tokar M. Godec M. (2003) Surface defects in car paint from recombination of atomic hydrogen. *Engineering Failure Analysis*, Vol.10, June 2003 p.325-328, ISSN: 1350-6307.