

Stress corrosion cracking of carbon steel in methanol

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The stress corrosion cracking of carbon steel in methanol has been investigated. The role of water as a stress corrosion cracking inhibitor in liquid ammonia is well known and the same beneficial effect of water can be expected in the case of C1 – C2 alcohols. Many variables can affect corrosion in organic solutions, but chlorides and acidity appear to be the most relevant.

KEYWORDS: CARBON STEEL, STRESS CORROSION CRACKING, METHANOL, ORGANIC SOLVENTS.

INTRODUCTION

A systematic review on stress corrosion cracking (SCC) of carbon and low alloy CrNiMo steels in methanol shows that the phenomenon can occur over a limited range of environmental conditions, possibly in the range of industrial grade solvent. The authors have investigated three cases of stress corrosion cracking of carbon steel tanks containing industrial grade methanol.

In all cases the cracks appeared intergranular (Figg. 1,2) and related to high residual stress around non-post weld treated weldments (Fig. 3). Remedial actions are basically weld repairs, replacements and use of internal coatings.



Fig.1 - Intergranular stress corrosion cracking of carbon steel in industrial grade methanol (X Nital) / Tensocorrosione intergranulare dell'acciaio al carbonio in metanolo industriale (X Nital).

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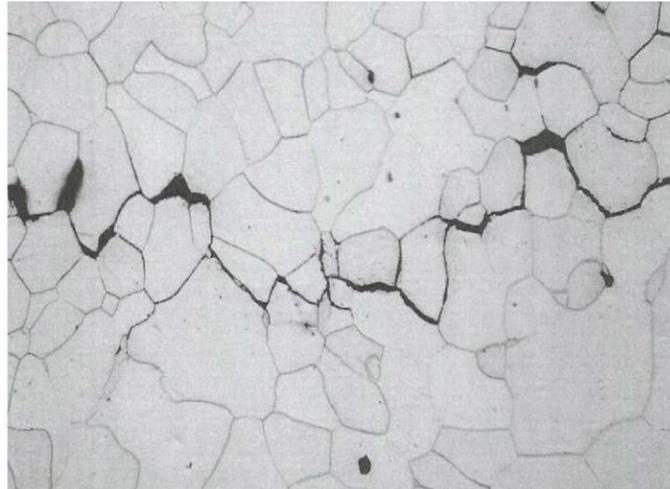


Fig.2 - As Fig. 1 at higher magnification (500x) / Come Fig. 1 a maggiore ingrandimento (500x).

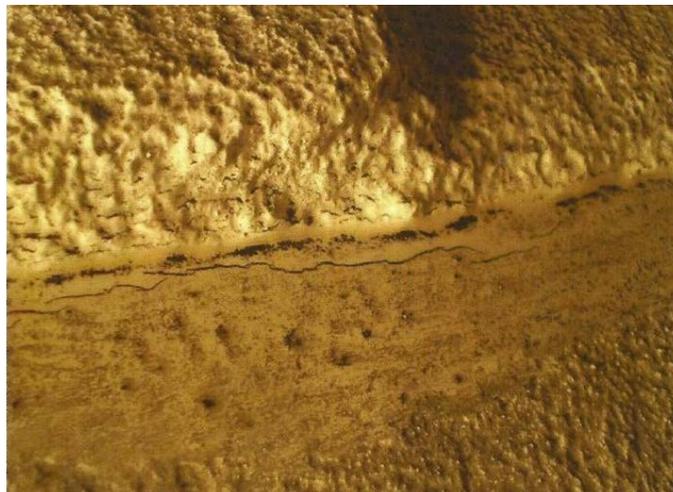


Fig.3 - Cracking on the bottom of a methanol tank / Fratture sul fondo di un serbatoio di metanolo.

The situation

In most cases corrosion processes would be thermodynamically similar in water and in alcohol. Therefore all the variables that affect corrosion in aqueous solutions can affect corrosion in organic solutions. These include temperature, redox potential, presence and concentration of salts, oxygen, acids and bases, fluid velocity (1).

However, there is a number of variables which are not to be found in aqueous solutions that can be important in organic solvents. Organic liquids encompass an extremely important variety of compounds.

Organic liquids may be classified into two main categories: aprotic, which are generally water insoluble, and protic,

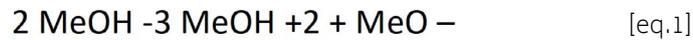
which are generally water soluble. Many solutions properties such as solvating power depend on the nature of the organic liquid. Thus, the protic nature of a given organic liquid will determine the solubility of various impurities and corrosion products.

Literature shows that the stress corrosion cracking of carbon and low alloy steels in methanol can be influenced by various impurities and that it can be inhibited by small quantities of water which ensure a certain degree of protection in relatively aggressive environments. (2,3)

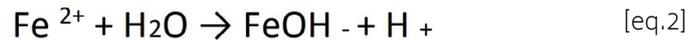
However, the role of water is not completely clarified. In alcohols small amounts of water (e.g. 0.1 – 0.2%) has a passivating effect but at higher concentration other corrosion

mechanisms are enabled to operate.

The oxide film on the surface of the steel is not resistant in solutions of methanol with water content of 200 to 450 ppm and it is dissolved at defective points, due to the intrinsic acidity of the protic medium:



The oxide-free areas dissolve rapidly, with a further acidification of the solution:



As water content increases a metal oxide compound forms from the water-metal bond, triggering off a new passive film. The corrosion process is therefore stopped and the same happen in chloride containing methanol to $\geq 1\%$.

The industrial practice does not always permit to operate with low water contents, consequently water addition turns out to be one effective measure to prevent liquid phase stress corrosion cracking, together with low residual stress (post weld heat treatment) and the use of low strength material (e.g. ASTM A 516 gr 60 max.).

The availability of oxygen to participate in corrosion reaction is expected to be generally greater in methanol, since its solubility is of an order of magnitude higher than that of water, as in ethanol.

SCC occurs over a range of rather oxidizing conditions and

therefore requires significant dissolved oxygen available. In deaerated conditions (oxygen < 30 ppb) much less susceptibility to stress corrosion cracking is reported, whereas cracking has been found in aerated environments (77 ppm of dissolved oxygen).

As water content in concerned, some tests seem to indicate that the maximum probability to SCC is for a water content of 0.2 % in methanol.

The metallurgical and mechanical factors that promote SCC in industrial grade methanol are the same of any carbon steel stress corrosion cracking phenomena, that is to say high tensile residual stresses around non post weld heat treated weldments. An increase in corrosivity going from water to methanol has been reported (Fig.4).

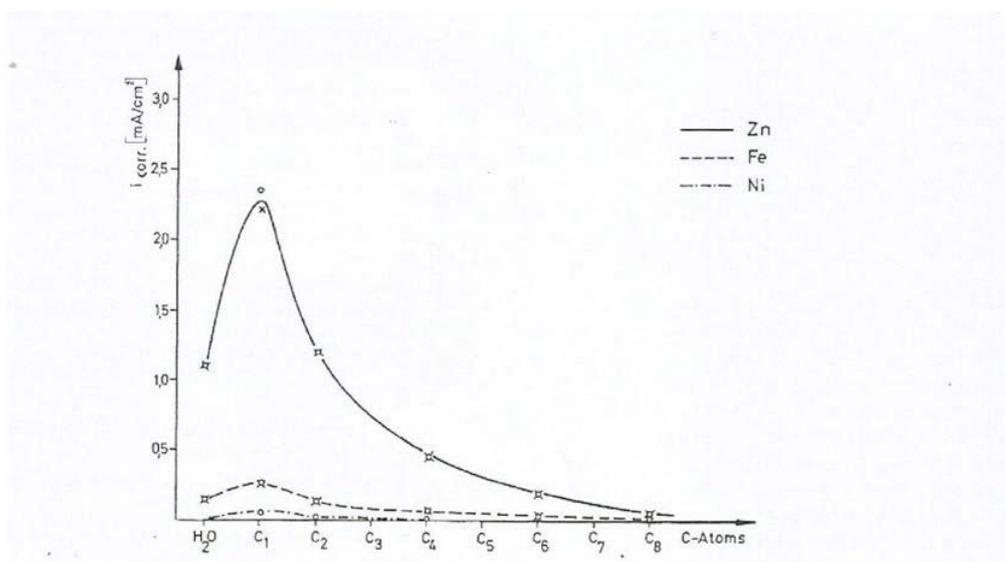


Fig.4 - Corrosion rate of Zn, Fe and Ni in primary alcohols vs carbon number of solvent: methanol C1, ethanol C2 / Velocità di corrosione per Zn, Fe and Ni in alcoli primary, in funzione del numero di carbonio del solvente.

The SCC in methanol was comparable in many ways to SCC of steel in liquid ammonia, in that case susceptibility can be affected by small additions of water. Whereas the role of water as SCC inhibitor in liquid ammonia is well proved (Fig.5), the same role in methanol solutions is not completely clarified, as previously said. (4)

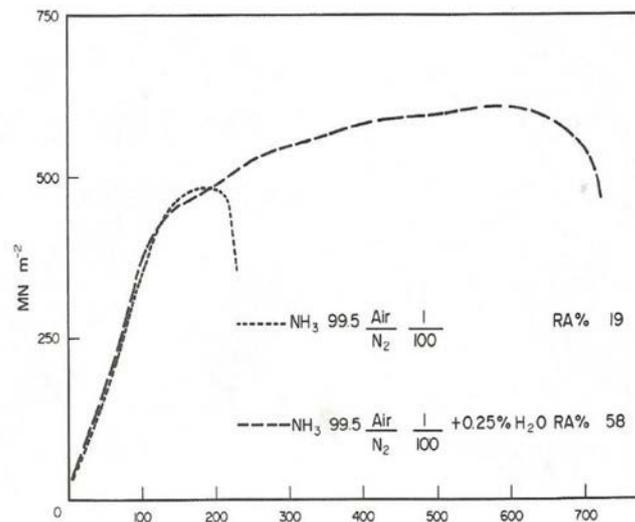


Fig.5 - Stress time curves for carbon steel in liquid ammonia. Time/s x 10³ /
Curve tempo sollecitazione per l'acciaio al carbonio in ammoniaca liquida. Tempo/s x 10³.

Water addition can act in the direction of accelerating the healing of the protective oxide layer, where it is damaged by mechanical stresses, as indicated by potentiodynamic anodic polarization and of anodic potentiostatic transients. (5).

A reason for the effect of water concentration on corrosion may be that the oxide film on the surface of the metal is not resistant in low water solutions and therefore is dissolved at defective points.

Methanol SCC is more severe than ethanol SCC and has occurred more regularly in practice. There may be similarities with the CO – CO₂ SCC and that in methanol and possibly in ethanol.

The range of SCC is limited by regions of passivity and active corrosion and SCC occurs in the transition between these modes of corrosion. (6)

Stress corrosion cracking of Ni Cr Mo low alloy steel has been also observed in methanol and ethanol (7).

Many similitudes can be found between stress corrosion cracking in methanol and ethanol; the dissolved oxygen content appears the most important factor to determine stress corrosion cracking susceptibility in these solvents.

Cracking has not been found under deaerated conditions (8).

As mentioned above oxygen solubility is an important point for corrosion process: the oxygen solubility in methanol and ethanol are similar. However, it is of an order of magnitude higher than that of water, therefore the availability of oxygen in the corrosion reaction is expected to be generally greater in methanol and ethanol than in aqueous solutions.

An analogy can also be found with the corrosion rate of zinc, iron and nickel in primary alcohols versus carbon number of solvents: there is an increase in aggressiveness going from water to methanol, which then decrease when increasing carbon number. (Fig 4).

The intergranular path of the methanol and ethanol SCC seems to indicate than an anodic mechanism is acting with dissolution of metal at metal boundaries. The cracking is often found in the vicinity of welds and they can be parallel to the weld (Fig.3) or transversal (Fig. 6). The cracks are typically branched (Figg. 1,2).



Fig.6 - Stress corrosion cracking observed on a welded vessel used as a storage for industrial grade methanol /
Tensocorrosione rilevata in un serbatoio di metanolo.

In the API study it was established that the cracks are intergranular, but again there is a critical amount of water that produce SCC in steel, less than 0.05 % to just below 1% volume.

The negative influence of chlorides and acidity on the stress corrosion cracking behavior of Ni Cr Mo alloys has been proved by means of slow strain rate tests. (fig.7)

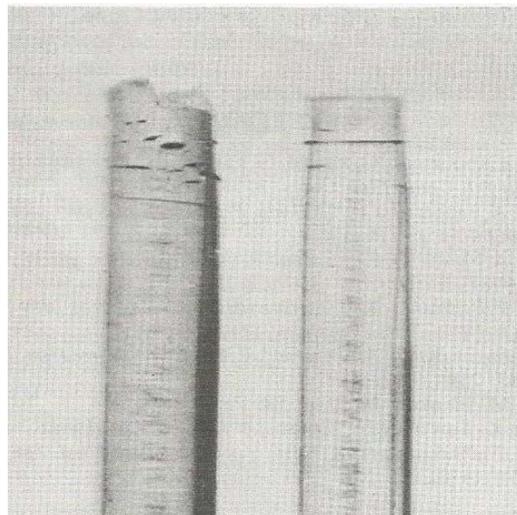


Fig.7 - Stress corrosion cracking of a Ni Cr Mo low alloy steel in methanol (left) and ethanol (right) (10^{-1} mol m $^{-3}$ LiCl, 10^{-1} mol m $^{-3}$ H $_2$ SO $_4$) / Tensocorrosione di un acciaio basso legato Ni Cr Mo in metanolo (sinistra) e in etanolo (destra) (10^{-1} mol m $^{-3}$ LiCl, 10^{-1} mol m $^{-3}$ H $_2$ SO $_4$).

CONCLUSIONS

The stress corrosion cracking of carbon steel in methanol has been investigated. The role of water as a stress corrosion cracking inhibitor in liquid ammonia is well known and the same beneficial effect of water can be expected in the case of C1 – C2 alcohols. Many variables can affect corrosion in orga-

nic solutions, but chlorides and acidity appear to be the most relevant.

In the industrial practice stress relieving and water addition are the most recommended practices in order to decrease the frequency of the stress corrosion cracking phenomena

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Tensocorrosione dell'acciaio al carbonio in metanolo

È stata studiata la tensocorrosione dell'acciaio al carbonio in metanolo. Il ruolo dell'acqua come inibitore della tensocorrosione, ben noto nel caso dell'ammoniaca liquida, viene ritenuto benefico anche nel caso degli alcoli C1 – C2. Fra le tante variabili che influenzano la corrosione nei solventi organici, le più rilevanti risultano i cloruri e l'acidità.

PAROLE CHIAVE: ACCIAIO AL CARBONIO, TENSOCORROSIONE, METANOLO, SOLVENTI ORGANICI