ELECTROCHEMICAL BEHAVIOUR OF OLT – 35 LOW CARBON STEEL IN ALKALINE (1M KOH) AQUEOUS SOLUTION

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ABSTRACT. Cyclic voltammetry, under rigorously controlled conditions (scan rates, positive and negative reversal potentials, polarizations at definite potentials and times) has been used to obtain details on the electrochemical behaviour of OLT – 35 low carbon steel in 1M KOH (pH 14) open aqueous solution. The formation of anodic layers and their reduction on the steel surface in various experimental conditions were investigated.

INTRODUCTION

Many works using a variety of different analytical techniques and voltammetry measurements have been reported in literature on the chemical and electrochemical properties of iron and iron oxides in various aqueous environments. [1 -6].

The study of electrochemical behavior of an alloy, such as low carbon steel OLT – 35, may give scattered results to those obtained on iron pure metal or monocrystals. Such studies provide relevant information about the corrosion of buried steel pipes or storage tanks in various soils and serve as a rational basis for evaluation of coating performance and determination of controlling parameters [7 -10].

In urban areas, residual wasters, slightly alkaline, containing carbonate, chloride and possibly sulfate ions, may be in contact with underground pipelines, made from mild steel coated with an electrically insulating paint system and cathodicaly protected. Each ionic species has a different effect on the electrochemical behaviour of mild low carbon steel depending on the ion concentration, potential, pH and temperature.

The corrosion of steel in soil is due to electrochemical oxidation of metal at the anodic sites coupled to the reduction of oxygen at cathodic sites. Despite these processes occur in presence of dissolved oxygen, the most of electrochemical studies of steel pipelines corrosion are done in anaerobic conditions [11 -13].

It was established that when the pipeline steel is under cathodic polarization, electrochemical reactions, such as oxygen or oxide reduction, occurring at a cathodic potential can greatly affect the integrity of the protective coating film at pipeline surface [14]. Disbanding of the protective coatings leads to corrosion of steel pipe.

The cathodic protection level is recommended to be lower (more negative) than – 0.85 V vs Cu /$CuSO_4$, equivalent to –0.78Vvs.SCE.

Depending of the soils properties, pipeline coating, anode placement and their geometry, the actual potential of cathodicaly protected pipeline can vary in a wide range and can easily reach to – 1.5 V vs SCE or even lower values. According to Song *et al.* in such conditions the pH in the vicinity of the pipeline may

increase, to a value higher than 13, either or both by oxygen reduction and/or by water reduction [15]. Because the volume of electrolyte in the crevice between disbanded coating and pipeline is obviously small, obtaining such a high pH environment is conceivable.

In such strong alkaline environments the fluctuation of the cathodic protection can make the solid passive iron oxide unstable, and the solid species will dissolve into the ground water as soluble species.

The objective of this research was to investigate the electrochemical behaviour of low carbon steel OLT – 35 in open aqueous alkaline solution (pH = 14) in the range of anodic active potential of iron. The voltammetric characteristics of surface films formed on OLT – 35 were studied.

EXPERIMENTAL

Cyclic voltammetry was used to investigate the electroformation and the electroreduction of various iron compounds on low carbon OLT – 35 steel whose composition is (wt%): C 0.17, Si <0.35, Mn <0.4, P <0.05, S <0.05, Fe 98.98.

The working electrode was a disk of OLT – 35 steel with a surface area of 0.154 cm^2. The disk was press-fitted into a Teflon holder in order to ensure a reproducible and well-defined surface area. Before each experiment the OLT-35 steel electrode surface was mechanically polished with abrasive paper, thoroughly rinsed with distilled water and cathodically polarized (for 5 minutes i.e.) in the range of hydrogen evolution potential, to provide a reproducible electroreduced steel surface.

The experiments were carried out using a three-compartment glass cell, at room temperature and quiescent solutions. The volume of the used experimental cell was large (~ 0.35 l) so that the concentration of eventually dissolved iron compound in the bulk of the solution could be neglected

Potentials were measured and referred to in the text with respect to a saturated calomel electrode (SCE) as reference. This was connected to the main compartment of the cell by a salt bridge and a Lugging capillary.

The counter electrode, separated from the main compartment of the cell by a Nafion membrane, was a platinum sheet of 5 cm^2 in area.

Aqueous solution of 1M KOH (pH 14) was used as electrolyte. The electrolyte solution was prepared from analytical grade reagents using high distillated water.

The cyclic voltammograms were obtained by sweeping the potential linearly in a positive direction from a certain starting negative potential to a maximum, at different sweeping rates and then the direction was reversed.

The measurements were performed with an Autolab PGSTAT 10 system.

RESULTS AND DISCUSSION

First informations about the corrosion system created at OLT – 35 low carbon steel/aqueous 1M KOH solution interface were obtained by measurements of open circuit potential (o.c.p.). In this experiment the freshly polished electrode was submerged in electrolyte and kept until the value of o.c.p. was constant, Fig.1.

In such experiment the system is not disturbed by any external voltage or current source, so that no additional corrosion effects are induced and the measured potential value must be considered as corrosion potential, E_{corr}.
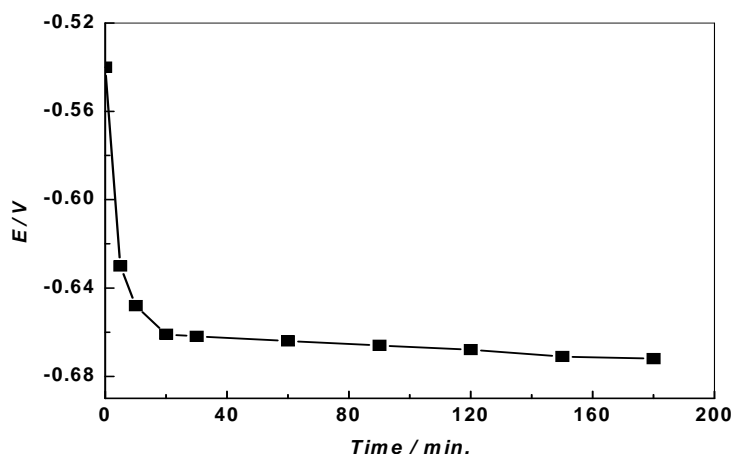
Fig. 1. Open circuit potential against time for OLT – 35 electrode in 1 M KOH solution (pH = 14).

At the beginning, the o.c.p. of the system was – 0.542 V but the potential decreased continuously (shifted in negative direction) with the exposure time before to reach, after around 180 minutes, a constant value at about – 0.672 V. This negativation of potential in time denotes a relative high corrosion tendency of OLT – 35 steel in our experimental conditions.

Fig. 2 (solid line curve) shows a typical cyclic voltammogram for OLT –35 steel in 1M KOH open aqueous solutions. Such voltammograms in steady-state could be obtained after a few cycles over the whole potential range. The range of the potential was varied from hydrogen evolution (-1.3V) to prepassive potential of iron (0.2V) so that no any oxygen evolution from electrolyte can occur.

The freshly polished electrode was submerged in electrolyte and kept until the change in the o.c.p. was less than 1mV / min. Starting at o.c.p., the potential of electrode was scanned, at 30 mV/ s, to the negative

direction until – 1.3 V when it was held for 10 min. in order to bring the electrode surface to the reduced metallic state.

The electrode was then cycled between –1.3V (the hydrogen evolution potential) and 0.1 V (the prepasive potential for our experimental conditions) for 15 times. The 2nd and the 15th cycle were recorded.

The recorded voltammograms (Fig.2.) show that, in our experimental conditions, the first 10 cycles have great influence on the shape or height of the oxidation and reduction peaks.
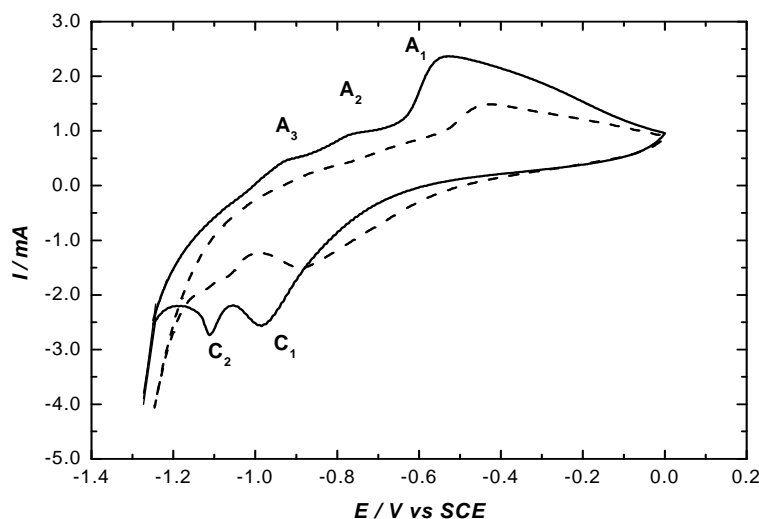
Fig. 2. Cyclic voltammograms of OLT – 35 steel electrode in aqueous 1M KOH (pH 14) open aqueous solution. Scan rate: v = 30 mV/s. Key: (----) 2nd cycle and (—) the 15th cycle.

The features of the 15th voltammogram in Fig.2. are similar to those reported by Gervasio *et al.* for a mild steel electrode in aqueous anaerobic 1M KOH solution [14].

The scan in the positive direction shows only one proeminent peak A_1 at around -0.56 V, which is attributed to the oxidation of $Fe(OH)_2$ to FeOOH according to the following reaction [16, 17]:

$$Fe(OH)_2 \rightarrow FeOOH + H^+ + e^-$$ (1)
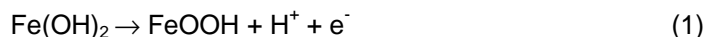
Some oxidation (positive current) waves are visible at approximatelly -0.76V (A_2) and -0.92 V (A_3). Shallow peaks A_2 and A_3 corresponds to the formation of $Fe(OH)_2$ from Fe metal (A_2):

$$Fe^0 + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2e^-$$ (2)
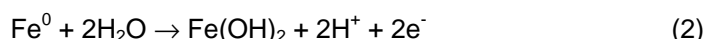
and (A_3) to the formation of a ferrous soluble compound (e.g. dihypoferrite):

$$Fe^0 + 2H_2O \rightarrow H FeO_2^- + 3H^+ + 2e^-$$ (3)
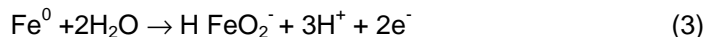
The formation of this dihypoferrite is in agreement with the iron potential – pH diagram (Pourbaix) which predicts that there are several regions where iron exists as soluble species [18]. One of the regions is in strong alkcaline solution (pH 14) and near –1.0V potential.

At potentials more positive than 0.1 V the steel surface appeared to be passivated. Other voltammograms (not included in this paper) indicate that although the positive potential was reversed at more high values (0.2 V or 0.3 V) no additional oxidation current would have been see before water is oxidized to molecular oxygen [19].

In the negative direction scan, there are two peaks before hydrogen evolution at -1.3 V. The first cathodic peak C_1 at -0.98 V is due principally to the reduction of FeOOH to Fe(OH)$_2$ [16, 17]:

$$FeOOH + H^+ + e^- \rightarrow Fe(OH)_2 \qquad (1')$$
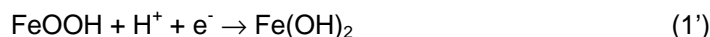
The second cathodic peak C_2 , at -1.13V corresponds to the reduction of Fe(OH)$_2$ to Fe metal:

$$Fe(OH)_2 + 2H^+ + 2e^- \rightarrow Fe^0 + 2H_2O \qquad (2')$$
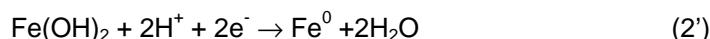
At the end of the scan in negative direction a large current can be seen at -1.3V. This is associated to water reduction to molecular hydrogen:

$$2H_2O + 2e^- \rightarrow H_2 + 2HO^- \qquad (4)$$

We have seen that the oxidation peak A_1 and the reduction peaks C_1 and C_2, corresponding to the electroformation and to the electroreduction of insoluble iron species, becomes larger with the increase of scans number, but the peaks A_2 and A_3 stayed the same in magnitude.

It seems that in our experimental conditions at pH 14 the dissolved ferrous state (H FeO$_2^-$) is more stable than solid state (Fe(OH)$_2$ or Fe) when the electrode potential passes −1.0 V during cycling.

This suggests that one possible route to the disbanding of insulating coating from steel pipelines may due to the dissolution of solid species (Fe(OH)$_2$, FeOOH or Fe) at the coating/oxide compounds/steel interface during cycling.

The effect of the polarization time (t_{pol}), in the cathodic range potential characteristic for hydrogen evolution, E_{pol}= -1.3V, just prior to the electrode potential sweep in the anodic direction, was investigated. The recorded voltammograms (Fig.3.) shows that the heights of the oxidation current peak A_1 and the reduction current peaks C_1 and C_2 increases with the polarization time, from t_{pol} = 15 min. to t_{pol} = 35 min., but the current peaks A_2 and A_3 heights are more less dependent of t_{pol}.
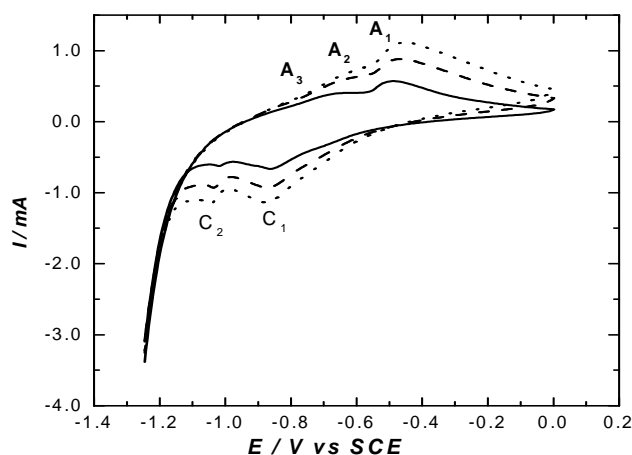

Fig. 3. Effect of polarization time, $t_{pol,}$ at E_{pol} = -1.3 V on the voltammograms of OLT – 35 steel electrode in aqueous 1M KOH solution. Scan rate: v = 30 mV/s.
Key: (—) t_{pol} = 15 min., (----) t_{pol} = 25 min., (...) t_{pol} = 35 min.

According to Simard *et.al.* this behaviour is more likely related to the adsorption and/or absorption of hydrogen on the electrode surface [20].

Consequentlly, in the following experiments, prior to each potential scan in the anodic direction, the working electrode was held 35 minutes at −1.3V in order to minimize the influence of hydrogen evolution on oxidation processes. Using this procedure the recorded voltammograms, for the same experimental conditions, were reproducible. Such results indicate that the OLT-35 surface films characteristics are strong function of the cathodic applied potential and polarization time.

Establishment of the sweep-rate dependence of an electrochemical process is of primary importance in determination of reaction mechanism, since it permits the identification of diffusion-controlled processes.

Figure 4 shows the effect of increasing the scan rate, from 10mV/s to 30 mV/s, on the voltammograms recorded on OLT-35 low carbon steel/ aqueous 1M KOH solution electrodes. Each voltammogram was taken after the electrode was cycled 15 times and held at −1.3V for 35 min.

For various sweeping rates the form of voltammograms changes slightly. The peaks current height increases with the increase of sweep rates and the peak potentials slightly shift towards more positive values (peak A_1) and towards more negative values, (peaks C_1 and C_2).
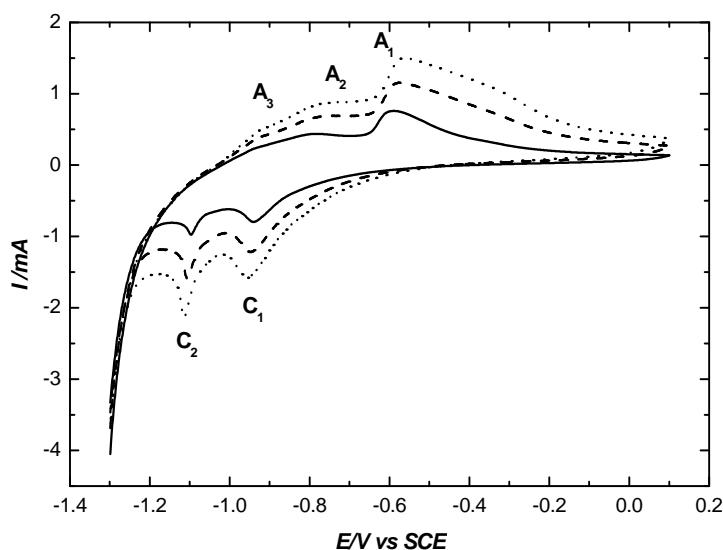

Fig. 4. Effect of scan rates on the voltammograms obtained for OLT – 35 steel electrodes in aqueous 1M KOH (pH = 14) solution. Key: (—) 10 mV/s, (----) 20 mV/s, (...) and 30 mV/s.

This would be consistent with a kinetically limited electrochemical process such as transfer of a species through a passive layer.

In the present experiments, all observed peaks exhibited a linear relationship between the peak current and the square root of the scan rate (Fig.5.).

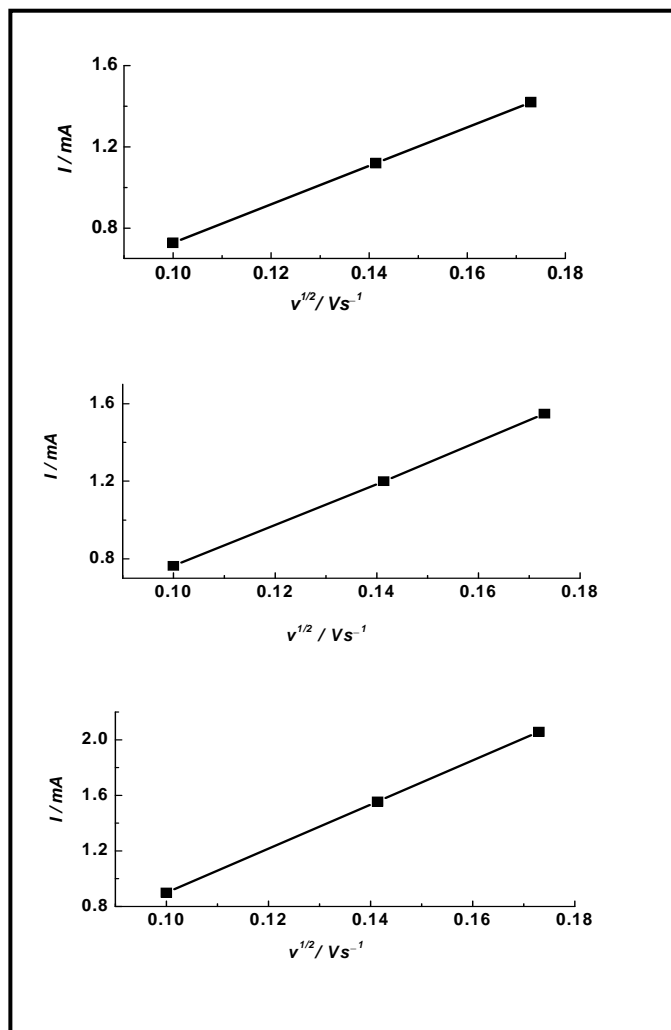This suggests that the processes are diffusion rather than activation limited.

Fig. 5. The peak current vs. (scan rate)$^{1/2}$ relations for: a) the anodic peak A_1; b) the cathodic peak C_1 and c) the cathodic peak C_2.

Correspondence between successive anodic and cathodic processes in a voltammogram can usually be demonstrated by slowly increasing the reversal potential along the anodic sweep.

Voltammograms with an increase in the anodic potential sweep limit ($E_{l,a}$) greater than –0.4V, for the OLT-35 steel electrode in 1M KOH aqueous solutions, are presented in Fig.6.
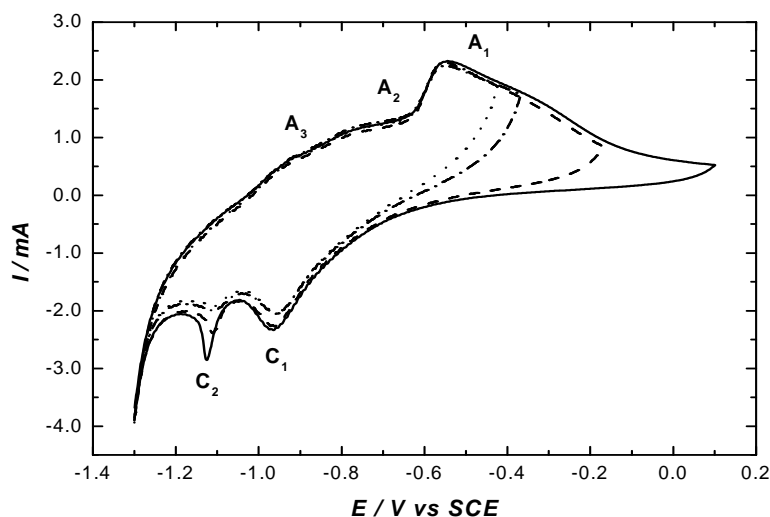
Fig. 6. Cyclic voltammograms of OLT – 35 steel electrode in aqueous
1M KOH (pH = 14) solution recorded for different anodic potential limits, $E_{I,a}$.
Key: (—) 0 V, (----) - 0.16 V, (-. -.) – 0.36 V, (...) – 0.42 V; v = 30 mV/s.

The potential and the current peak height for oxidation peak A_1 remained unchanged when the anodic potential sweep limit was increased.

The more anodic potential sweep limit, the higher the reduction current peaks C_1 and C_2.

It seems that this is due to longer time needed to reduce the greater amount of oxides, hydroxides or oxihydroxides formed at electrode surface when the upper anodic potential limit is higher. At higher than 0.2V potential the formation of γ-Fe_2O_3 has been proposed and at lower potentials, the presence of Fe_3O_4 is suggested [19-21].

Simultaneously increase of the cathodic current peaks C_1 and C_2 indicate that the product reduced at C_1 (more positive potential) is at higher oxidation state.

The fact that the changes in both C_1 and C_2 peaks, with increasing of the reversal anodic potential limit, are similar (Fig.6) and the fact that their peak current follows the same trend with regard to scan rate (Fig.5.), suggests that than two peaks represent successive steps which lead to complete reduction of oxide layer formed in above positive going scan.

The potential of both, C_1 and C_2, reduction peaks shifted in positive direction indicating that the anodic product changed with the increase of anodic potential scan limit.

Our voltammetry results make it clear that the C_1 and C_2 current peaks recorded in all experimental conditions are related to the presence, the amount and the properties of passive formed layer.

CONCLUSIONS

The voltammetry of OLT – 35 low carbon steel in open 1M KOH aqueous solution seems to be similar to that of iron in same conditions. Cyclic voltammetry provide a means for identifying various types of oxidated species formed on the OLT – 35 steel surface and monitoring their stability. The results indicated that the characteristics of OLT – 35 steel surface layers are strong function of the applied potential.

It seems that the rate – determining step, in active dissolution of OLT – 35 steel, in open alkaline aqueous solutions is a diffusion process.

The formation of soluble Fe^{2+} species ($HFeO_2^-$) during cycling at cathodic potential lower than –1.0V, where this dihypoferrite is stable with respect to iron and insoluble iron species ($Fe(OH)_2$ was confirmed.

We can say that our results are in agreement to that reported by Song *et al.* [15] according to which in strong alkaline environment in the presence of cathodic protection, temporal fluctuation of the pipelines potential, may cause chemical and possibly structural changes in the surface passive oxide layers. Such changes can lead to an instability of the the coating/steel interface. Voltammetric results suggest that one possible route to disbanding of coating layer from low carbon steel pipelines may be due to the dissolution of solid species at the steel/coating interface.

Thus, an excesive cathodic protection may produce an electrochemical environment in which the coating layer on steel pipelines may disbond.

Although the cyclic voltammetry enables us to accurately identify the changes in the electrode reactions, the method itself does not lead to an intimate study of these processes.

Further experimental works (maybe spectroscopic studies) are required to identification of the surface oxides layers formed under the experimental conditions of the present study.

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