INVESTIGATION OF CARBON STEEL CORROSION IN
DILUTED AMMONIACAL MEDIA

59

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ABSTRACT

Electrochemical measurements (steady-state current-voltage curves) were coupled with Mössbauer spectroscopy techniques to investigate the corrosion of carbon steel in diluted ammoniacal media. The corrosion current for carbon steel in diluted ammoniacal media was determined from galvanostatic measurements, through extrapolation of the Tafel segments at the corrosion potential. Mössbauer measurements were performed at room temperature in the transmission (TMS) and conversion electron spectroscopy (CEMS) using a conventional constant-accelerating spectrometer with a ⁵⁷Co-Rh source. The result of the corrosion is the layer appearance (nonstoichiometric iron oxide) on the sample surface.

KEYWORDS: ammoniacal media; carbon steel, corrosion, Mössbauer spectroscopy

RESUMO

A corrosão do aço de carbono em meio amoniaco diluído foi estudada usando técnicas de espectroscopia Mössbauer acoplada com medidas eletroquímicas (curvas potencial-corrente). A corrente de corrosão do aço carbono em meio amoniaco diluído foi determinada com medidas galvânicoestáticas, extrapolando os segmentos de Tafel no potencial de corrosão. As medidas Mössbauer foram efetuadas à temperatura ambiente com espectroscopia eletrônica de transmissão e conversão (EMT e EMCE) usando um espectrômetro convencional com aceleração constante e uma fonte de ⁵⁷Co-Rh. O resultado da corrosão é o aparecimento de uma camada (óxido de ferro não-estequiométrico) na superfície da amostra.

PALAVRAS CHAVE: aço de carbono, meio amoniaco, corrosão, espectroscopia Mössbauer

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INTRODUCTION

Industrial and residual waters containing ammonia/ammonium have been long neglected by researchers, as these were considered inoffensive to the environment and regarding the corrosion they exercise on the pipes used in cooling circuits especially in the ammonium-based fertilizers industry.

Recent research has demonstrated that waters containing ammonia/ammonium have negative actions on the environment concerning over-fertilization of surface waters resulting in the multiplication of the inferior organisms, e.g. phytoplankton and algae, in the toxic action on the live organisms in waters and in the destruction of oxygen through nitrification.^{1,2}

The corrosion action of the ammoniacal solutions is associated with the nitrification of the ammonium in two stages: first as a nitrite and then as a nitrate. The first stage is achieved by the *Nitrosomonas* bacteria that oxydate the ammonium ion. At the second stage, the nitrite is turned into nitrate in presence of *Nitrobacter* bacteria.

The first stage is very slow, but the second is relatively fast. This is why only residual concentrations of nitrite can be found. There have been many studies on the ammonium recovery from water through chemical procedures^{3,4} or through biological purification.^{5,6} The processes of corrosion or of inhibition can be studied by associating electrochemical measurements with analytical techniques.⁷

The aim of the present study is to investigate the carbon steel corrosion in diluted ammoniacal media by using electrochemical measurements.

In the carbon steel fabrication, no significant differences appear in the composition of different ingots, and this is why the corrosion rates do not differ under the same given conditions.

The variation in the ratio proportion of carbon manganese and silicon (elements that condition the value of the mechanic characteristics) does not influence the sensitivity to the corrosive action too much. Nevertheless, an increase in the ratio of these elements leads to some decrease in the sensitivity to the corrosive action, which is not the case with carbon steel. In the corrosion processes, the common carbon steels liberate a very small quantity of hydrogen. In the representative corrosion processes water appears as a solubilization agent, as a reactant and as favoring the ionic conductivity of the surface layer, a conductivity necessary to the transfer of ferrous ions.^{8,9}

The basic/alkaline media determine the start of punctiform corrosion process and its development in the classic way of the electrochemical corrosion.

Experimental details

The samples chosen for this investigation was carbon steel with the following composition: C = 0.35%, Mn = 0.65%, Si = 0.25%, S = 0.035% and the remainder iron up to 100%. For all experiments the samples were polished, cleaned in water, degreased in ethilic alcohol and dried in warm air.

The corrosion medium was produced from ammoniacal solutions that contained: 10^{-3} N NH_3 and different concentrations of NH_4Cl and NH_4NO_3 . The investigation has been done at a temperature of 25°C , while the corrosive medium has been kept in contact with air.

Electrochemical measurements

A standard corrosion cell was used to study polarization. The working electrode was a carbon steel plate with an area of 4 cm^2 . A calomel-saturated electrode was used as a reference electrode and the auxiliary electrode was a carbon steel plate identical to that of the working electrode. The galvanostatic measurements were made by using a continuous current supply in the circuit, a variable resistance, a miliampermetre and a milivoltmetre. Data were computerized.

RESULTS AND DISCUSSION

We have studied the corrosion process of the carbon steel in diluted ammoniacal solutions, which contain dissolved ammonia and different concentrations of ammonium chloride and ammonium nitrate.

The study of the carbon steel corrosion in diluted ammoniacal waters containing Cl^- anion

The anodic polarization curves in stationary conditions for the carbon steel sample in ammoniacal solutions containing 10^{-3} N NH_3 and different concentrations of NH_4Cl are presented in figure 1.

Figure 1. The anodic polarization curves for carbon steel in ammoniacal solutions containing different concentrations of NH_4Cl , such as: (1) 10^{-3} M ; (2) $3 \times 10^{-3} \text{ M}$; (3) $5 \times 10^{-3} \text{ M}$.

It can be observed that while the concentration of NH_4Cl increases, the anodic over-voltage decreases. Steel is active and dissolves after a Tafel-type slope b_a at 41 ± 6 mV.

The cathodic polarization curves are presented in figure 2. The supplementary cathodic polarization leads to an increase in the linear segments from 33.3 mV to 43.3 mV for a NH_4Cl concentration of 10^{-3} M. Also an increase in the NH_4Cl concentration is concurrent with the increase in the cathodic over-voltage (figure 2).

Figure 2. The cathodic polarization curves for carbon steel in ammoniacal solutions containing different concentrations of NH_4Cl such as: (1) 10^{-3} M; (2) 3×10^{-3} M; (3) 5×10^{-3} M.

The presence of Cl^- anion in the ammoniacal solution slightly decreases the pH value, while no spontaneous passivation of the metal surface can be observed. The polarization curve $E = f(I)$ in figure 3 proves that steel is active in the current density field under study, between 15 mA/dm^2 and 800 mA/dm^2 .

Figure 3. The polarization curve of carbon steel in the solution containing 10^{-3} N NH_3 and 5×10^{-3} M NH_4Cl .

For the determination of the corrosion current the anodic and cathodic polarization curves have been drawn for a sample of carbon steel in ammoniacal solution containing 10^{-3} N NH_3 and 10^{-3} M NH_4Cl for potentials far apart from the corrosion potential (figure 4).

Figure 4. The anodic and cathodic polarization curves for carbon steel in ammoniacal solution containing 10^{-3} N NH_3 and 10^{-3} M NH_4Cl .

By extrapolation of the linear segments at $y = 0$ the corrosion current has been determined. The results are presented in Table 1.

Table 1. The corrosion current for carbon steel in ammoniacal solution containing 10^{-3} N NH_3 and 10^{-3} M NH_4Cl .

	From anodic	From cathodic	From anodic + cathodic
I_{cor} (mA/dm ²)	8.87	3.32	4.31

The corrosion currents resulting from extrapolation of Tafel segments on the last part of the curves for different NH_4Cl concentration are presented in Table 2.

Table 2. The electrochemical parameters of the carbon steel sample in solution containing 10^{-3} N NH_3 and different NH_4Cl concentrations.

Conc. NH_4Cl (mol/L)	10^{-4}	10^{-3}	3×10^{-3}	5×10^{-3}
E_{cor} (mV)	126	90	37	33
I_{cor} anodic (mA/dm ²)	1.7	12.8	33	47
I_{cor} cathodic (mA/dm ²)	6.5	17	50	59
I_{cor} anodic + cathodic (mA/dm ²)	5	13	47	57

For the solution containing 10^{-3} M NH_4Cl at current densities higher than 100 mA/dm², it can be observed an increase of the corrosion current from 4.3 mA/dm² to 13 mA/dm², which shows that while the current densities increase, the electrode surface changes, the metal dissolves. Also compounds are formed such as $\text{Fe}(\text{OH})_3$, which precipitate in the solution and form non-adherent, porous and non-uniform layers on the metal surface, under which the corrosion process continues.

The cathodic reduction of the solvent requires a higher over-voltage for decreasing NH_4Cl concentrations. The cathodic process is also determined by the total transfer of all compounds reduced cathodically (O_2 , NH_4^+ and H_3O^+)

The study of the carbon steel corrosion in diluted ammoniacal waters containing NO_3^- anion

The anodic and cathodic polarization curves are presented in figure 5. The corrosion process is spontaneous, while the NO_3^- anion has hardly any influence on the solution pH. If experimentally the conditions created for the achievement of corrosion can differ from the real corrosion conditions, the dissolving of steel was inhibited by the presence of NO_3^- anions. The solution pH at the level of the corrosive spot increases with the NH_4Cl solution, leading to a slow down in the rate of dissolution. The development of the corrosive spot is evidently inhibited by NO_3^- anion or is a combined effect resulting from the synergetic action of the ammonium with NO_3^- .

Figure 5 The polarization curves for carbon steel in 10^{-3} N ammoniacal solution containing different NH_4NO_3 concentrations: (1) 10^{-3} M; (2) 3×10^{-3} M; (3) 5×10^{-3} M.

At low current densities the curve presents a significant leap from the corrosion potential to a potential of 600 mV, after which the process proceeds slowly (figure 6), with metal dissolving after a Tafel-type curve b_a at 43 ± 10 mV.

Figure 6. The polarization curves for carbon steel in ammoniacal solution containing 10^{-3} N NH_3 and 3×10^{-3} M NH_4NO_3 .

The cathodic process proceeds with depolarization of NH_4^+ , O_2 and of the solvent at cathodic over-voltages increases concurrent with the increases in NO_3^- concentration.

The corrosion currents were determined from the anodic and cathodic Tafel segments for the final portions of the polarization curves. Data are presented in Table 3.

Table 3. The electrochemical parameters for the carbon steel sample in ammoniacal solution 10^{-3} N NH_3 and different NH_4NO_3 concentrations.

Conc. NH_4NO_3 (mol/L)	10^{-3}	3×10^{-3}	5×10^{-3}
E_{cor} (mV)	138	128	132
$I_{\text{cor}}^{\text{anodic}}$ (mA/dm^2)	0.09	0.31	0.75
$I_{\text{cor}}^{\text{cathodic}}$ (mA/dm^2)	5.8	3.79	5.7
$I_{\text{cor}}^{\text{anodic} + \text{cathodic}}$ (mA/dm^2)	2.03	1.46	2.65

Irrespective of the NO_3^- concentration, the corrosion currents have very close values, which confirms the passivant role of the anion at current densities higher than $2 \text{ mA}/\text{dm}^2$. The corrosion currents are significantly smaller than in solutions containing NH_4Cl and have higher values than in solutions containing only dissolved ammonium.

Mössbauer spectroscopy was performed at room temperature in the transmission (TMS) and conversion electron spectroscopy (CEMS) using a constant accelerating spectrometer with a ^{57}Co -Rh source.

In figures 7 and 8 are presented the TMS and CEMS spectra of reference sample before corrosion processes. The best fitting of the TMS spectrum shows the presence of single sextet. The parameters of this singlet are practically the same as for α -Fe sample. The CEMS spectrum shows the presence of α -Fe.¹⁰

Figure 7. Transmission Mössbauer of the reference sample.

Figure 8. Conversion electron Mössbauer spectrum of an uncorroded sample.

The CEMS spectra of the sample corroded in 5×10^{-3} M NH_4NO_3 and 5×10^{-3} M NH_4Cl solutions are showed in figures 9 and 10.

Figure 9. CEMS spectrum of corroded sample in a 5×10^{-3} M NH_4NO_3 solution.

Figure 10. CEMS spectrum of corroded sample in a 5×10^{-3} M NH_4Cl solution.

The best fit of the CEMS spectra uses an additional wide line to the sextet. The parameters of the wide line correspond to a nonstoichiometric oxide. In all CEMS spectra intensities of the second and fifth peaks of the α -Fe spectrum with regard to the third and fourth peaks shows that the direction of the γ -ray and magnetic moments are nearly perpendicular.¹¹

There is a magnetical anisotropy on the surface of the samples. The result of the corrosion is the layer appearance (nonstoichiometric iron oxide) on the samples surface. The layer thickness increases for the corroded sample in NH_4Cl solution regard to in NH_4NO_3 solution.

CONCLUSIONS

The corrosion of carbon steel in diluted ammoniacal media comes from current densities ranging between 15 mA/dm^2 and 800 mA/dm^2 . The process becomes significant from densities of 130 mA/dm^2 . Steel is active and dissolves after a Tafel slope b_a of $41 \pm 6 \text{ mV}$.

The cathodic process proceeds with a depolarization of O_2 , NH_4^+ , H_3O^+ and of the solvent with slopes varying from 33.3 mV to 43.3 mV .

The corrosion current increases with the increase in the NH_4Cl concentration. No metal passivation was observed during the corrosion process.

The products precipitate in solution and do not form adherent and uniform layers under which corrosion continues.

The corrosion process of carbon steel in ammonium solutions containing NO_3^- proceeds spontaneously at low current densities, the polarization curves presenting a significant slope. Current densities higher than 2 mA/dm^2 retards the process because of the

passivant action of NO_3^- or because of a combined effect resulting from the synergistic action of the ammonium with NO_3^- .

The corrosion currents are significantly smaller than in solutions containing NH_4Cl , but higher than in waters containing only dissolved ammonium. Irrespective of the NH_4NO_3 concentration they have very close values, which proves that the development of the corrosion spot is inhibited by the NO_3^- anion. The cathodic process proceeds with the depolarization of the solvent, O_2 and NH_4^+ at a Tafel slope of 32.5 mV.

Mössbauer spectroscopy shows the presence of the nonstoichiometric iron oxide layer on the samples surface. The layer thickness increases for a corroded sample in NH_4Cl solution regard to the corroded sample in NH_4NO_3 solution.

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