Comparison of stress-corrosion cracking susceptibility of mild and low alloy steels in phosphate environments

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Comparison between anodic behaviour and susceptibility to stress-corrosion cracking (SCC) in phosphate solutions (NaH_2PO_4, pH = 4) of two kinds of construction steels – low carbon (0.17% C) and low-alloy (2.0% Cr) steels has been carried out using the potentiodynamic polarization method with slow and fast potential sweep rates (10 and 300 mV/min) as well as slow strain rate techniques. It has been established, that both steels undergo active to passive state transition in phosphate medium, more clearly expressed for the low-carbon steel. For this steel, the susceptibility toward SCC is much higher than that of the low-alloy steel. The occurrence of SCC depends strongly on the potential and it is expressed only within a narrow range of potentials for both steels: –0.3–0.0 V (SCE) for the low-carbon and –0.1+0.3 V (SCE) for the low-alloyed steel. The SCC susceptibility decreases strongly with the increase of temperature and lowering solution concentration. The most severe SCC extent has been registered in 1 N NaH_2PO_4 solutions at 20°C. It is also shown that under SCC conditions a surface film, containing iron phosphates, is formed on both kinds of steels. The conditions of SCC correspond well to the regions of active-passive state transition in the polarization curves for both materials and are in good agreement with the regions, predicted by the potentiodynamic polarization method with slow and fast potential sweep rates. On the basis of the results obtained, a conclusion is drown for the higher mechano-corrosion stability of the low-alloy steel, compared to that of the low-carbon steel.

Key words: Stress-corrosion cracking, anodic behaviour, phosphate solutions, low-carbon steel, low-alloy steel.

INTRODUCTION

A survey of failure cases and analyses [1] show that the share of carbon and low-alloy steels in the stress-corrosion cracking (SCC) cases is 24%. It is well known today, that this type of steels undergoes SCC in hydroxide, nitrate and carbonate solutions. Some works on susceptibility to SCC of these materials and Armco iron in phosphate media were published as well [2–7].

SCC takes usually place in alloys in passive state and within some ranges of potentials. For carbon steels this region is close to the critical potential of passivation, where the passive film is not very stable [8]. Parkins proposed a simple method for predicting this potential range using a potentiodynamic polarization method with fast and slow potential sweep rates [3, 9, 10].

In our previous works, the detailed investigations concerning the effect of pH, solution concentration and temperature on SCC [11–13] as well as the film composition under SCC conditions [14] of mild and low-alloyed with Cr steels in phosphate media were represented. Taking into account that the low-alloyed steels are used as an alternative material for replacing the low-carbon ones, it is important to compare their SCC behaviour. The aim of the presented work was to make a comparison of SCC susceptibility and electrochemical behaviour of low-carbon and low-alloy (2% Cr) steels in phosphate environment.

EXPERIMENTAL

Materials and solutions: The studies were carried out with samples of:

- mild construction steel of the following composition (wt.%): C 0.17; Cr 0.06; Mn 0.36; Si 0.016; S 0.029; P 0.01; Ni 0.06 and Cu 0.11. The mechanical parameters of the steel (produced as hot-rolled bars) were: ultimate tensile strength σ_B = 440.0 MPa and yield strength σ_S = 354.7 MPa.

- low-alloy steel of the following composition (%): C 0.066; Cr 1.89; Mn 0.61; Si 0.23; S 0.034; P 0.015; Ni 0.066; Cu 0.15 and Al 0.08. The mechanical parameters of the steel (produced as hot-rolled sheets) were: ultimate tensile strength σ_B = 392.0 MPa and yield strength σ_S = 261.7 MPa.

Orthophosphate solution having pH = 4, prepared of $NaH_2PO_4 \cdot H_2O$ (p.a.) with small amounts of H_3PO_4 (p.a.) or NaOH (p.a.) for pH adjustment, was used as a corrosion medium.

Polarization studies on non-stressed electrode

Disk sample-electrodes (working area of 1 cm^2) installed on a special Teflon holder, three-compartment electrochemical cell and conventional experimental procedure were used for the polarization measurements [11, 12]. The potentiodynamic polarization method with fast (300 mV/min) and slow (10 mV/min) potential sweep rate was applied for assessment of the approximate potential range for cracking [10–13]. The potentials were measured and reported against saturated calomel electrode (SCE).

SCC tests

The measurements were made using the slow strain rate technique *in situ* (strain rate 2.34×10^{-5} s^{-1}) under potentiostatic conditions at different potentials. Tensile testing specimens were: for the mild steel – cylindrical specimens of 180 mm overall length, 10 mm diameter and 3 mm reduced gauge diameter, and for the low-alloy steel - sheet specimens 3 mm thick, 170 mm overall length and 3 mm reduced gauge width.

The electrochemical cell, the tensile testing apparatus and the experimental procedure were described elsewhere [15, 16]. The susceptibility to SCC was evaluated by comparison of the mechanical parameters (tensile strength σ_B and reduction in the specimen cross-sectional area RA) at fracture in the corrosion medium and inert atmosphere.

RESULTS AND DISCUSSIONS

Fig. 1 and Fig. 2 show typical potentiodynamic polarization curves (10 mV/min) of mild and low-alloy steels in phosphate solutions at concentrations 0.05–2 M NaH$_2$PO$_4$, pH = 4, 20°C. As it can be seen, both kinds of steels undergo active to passive state transition. The maximum in the active state (the critical potential) shifts in positive direction while the width of the passive region is reduced upon lowering solution concentration, more strongly expressed for the low-alloy steel. At low concentrations (0.05 M for the low-carbon and 0.1 M for the low-alloy steel) the steels are in an active state within the whole potential range. In more concentrated solutions, the polarization curves show "double peak", i.e. a region of "primary passivity" at potentials more negative than the potential of deep passivity, clearly expressed for the low-carbon steel. Upon increasing the temperature, this region for both kinds of steels shrinks and shifts to more negative potentials.

According to Kolotyrkin [17] the region of "primary passivity" for iron in phosphate media is related to formation of a surface film, composed of

two layers. The first one is thin, protective, created by adsorption of phosphate ions and their interaction with iron atoms from the metal surface. The second (external) layer is formed as a result of a secondary chemical reaction between iron and phosphate ions, composed of Fe$_3$(PO$_4$)$_2$.8H$_2$O, without any protective properties. The presence of a phosphate layer in the region of active to passive state transition was proved by our Mössbauer study of surface films, formed on the steels in phosphate solutions [12].
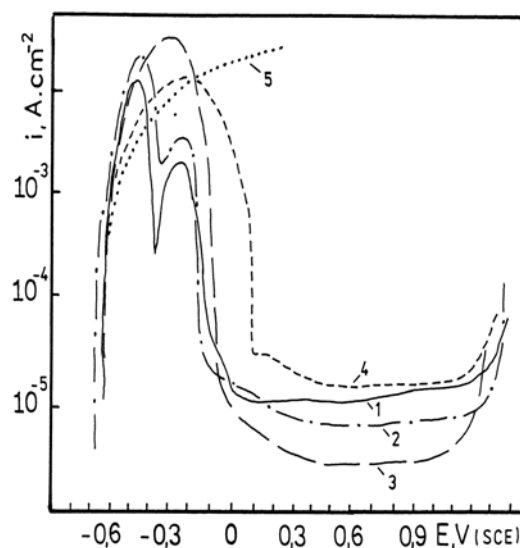

Fig. 1. Potentiodynamic polarization curves (10 mV/min) of low-carbon steel in solution of NaH$_2$PO$_4$, pH = 4, 20°C with concentrations (g-eqv/l): 2.0 (1); 1.0 (2); 0.5 (3); 0.1 (4) and 0.05 (5).
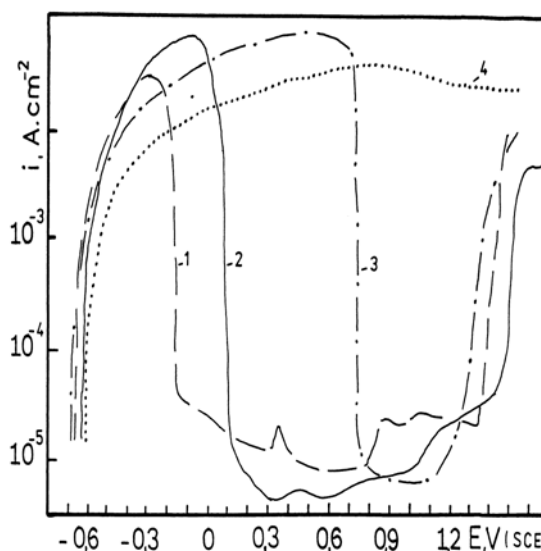

Fig. 2. Potentiodynamic polarization curves (10 mV/min) of low-alloy steel in solution of NaH$_2$PO$_4$, pH = 4, 20°C with concentrations (g-eqv/l): 2.0 (1); 1.0 (2); 0.5 (3) and 0.1 (4).

The differences in the polarization curves of the two kinds of steels can be explained by the different

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steel composition. Probably, the lower carbon content and the presence of chromium in the low-alloy steel affect the process of film formation on the metal surface and its properties.

The potentiodynamic polarization curves with fast (f) and slow (s) sweep rate under the most severe SCC conditions for both kinds of steels: 1 N NaH_2PO_4, pH = 4, 20°C as well as the ratio of current densities i_f/i_s are represented in Fig. 3 and Fig. 4. As it is known, the idea of this method is to determine the range of potentials with high metal activity (in the absence of film, high rate) and low metal activity (in the presence of a film, low rate) and in this way to define the region of most favorable electrochemical conditions for SCC development [10–12].
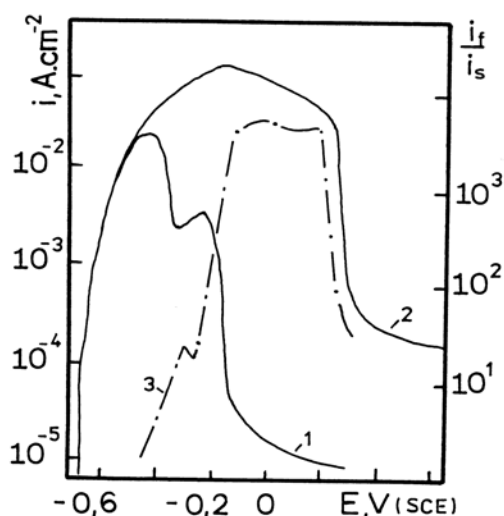

Fig. 3. Potentiodynamic polarization curves with 10 mV/min (1) and 300 mV/min (2) sweep rate, and i_f/i_s ratio (3) for low-carbon steel in 1 N NaH_2PO_4.
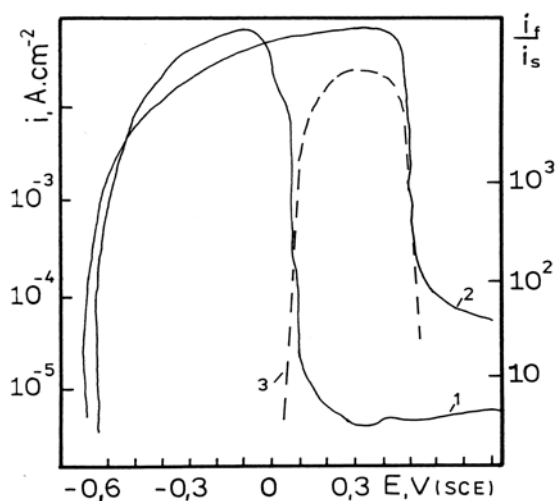

Fig. 4. Potentiodynamic polarization curves with 10 mV/min (1) and 300 mV/min (2) sweep rate and i_f/i_s ratio (3) for low-alloy steel in 1 N NaH_2PO_4.

Using this method the electrochemical conditions for SCC for both kinds of steels were defined and verified by slow strain rate SCC test. Fig. 5 and Fig. 6 show that the reduction of steel tensile strength σ_B can be observed actually in the area, predicted by the polarization curves. In support of this result comes also the dependence of the relative reduction in the specimen cross-sectional area at fracture RA% on the potential. For low carbon steel in all solution concentrations (0.1–2 g-eqv/l) the tensile strength of the steel σ_B decreases (compared to this one in air) in the potential range –0.3–0.0 V(SCE) (Fig. 5) corresponding to the zone of active-passive state transition of the metal in the range of rising current ratio i_f/i_s. The susceptibility to SCC however strongly depends on the phosphate concentration in the solution. The most severe cracking is registered in 1 M solution, where the tensile strength at potential about –0.15V is reduced more than 2.5 times compared to the tensile strength in air. The reduction of σ_B in 2 M and 0.1 M solutions is only about 10%, as it was expected in view of the change of i_f/i_s ratio. These results are confirmed also by the relationship between the reduction in specimen cross-sectional area RA% and potential (Fig. 5). It was also established that SCC susceptibility decreases with the increase of temperature.
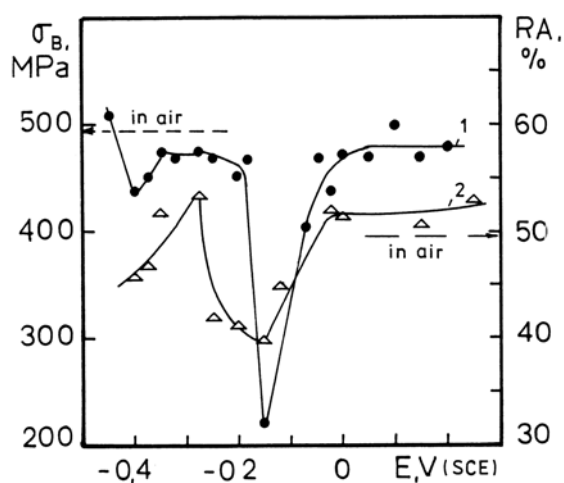

Fig. 5. Dependence of tensile strength σ_B (1) and of the reduction in area RA (2) on the potential for the low-carbon steel in 1 N NaH_2PO_4, pH = 4.

The SCC susceptibility of the low-alloy steel is much lower in comparison to that of the low-carbon steel (Fig. 6). The most severe decreasing of the tensile strength σ_B (15%) is registered in 1 N solutions at 20°C in the zone of active-passive state transition of the metal (–0.1+0.3 V) in the range of rising current ratio i_f/i_s. Like SCC of mild steel, the SCC of low-alloy steel is very weak at higher temperatures and lower solution concentrations.
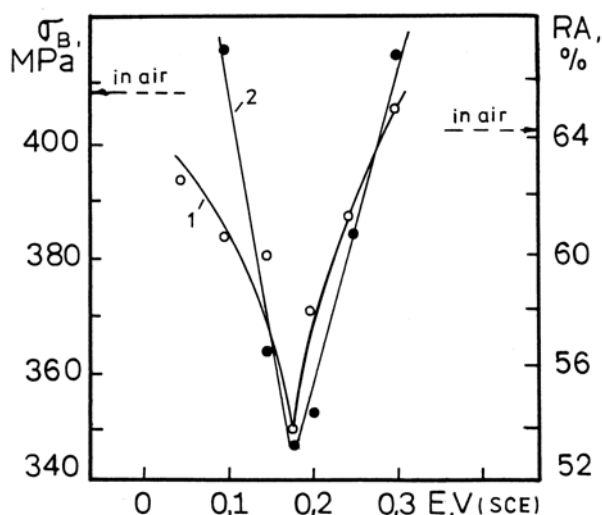
Fig. 6. Dependence of tensile strength σ_B (1) and of the reduction in area RA (2) on the potential for the low-alloy steel in 1 N NaH$_2$PO$_4$, pH = 4.

The lower SCC susceptibility of the low-alloy steel compared with the low-carbon steel can be explained by the differences in the steel structure and composition.

The steel composition and especially the carbon distribution in the steels are very important in respect to homogeneity and protective properties of the surface films. The mild steel has a ferrite structure with well defined grain boundaries and more strongly expressed carbon segregation (carbon content 0.17%) along the grain boundaries compared to the low-alloy steel. The carbon segregation facilitates the formation of a film on the grain boundaries with weak protective properties and lower mechanical strength compared to the film, formed on the metal grain itself [4, 5] and thus, it creates favourable conditions for breakdown of the film and highly localized corrosion attack under stress, i.e. for SCC. The intergranular paths of cracking, registered by SEM and metallographic observations [11, 12], are obviously related to the detrimental effect of carbon segregations on the properties of the passive film. The carbon content in the low-alloy steel is lower (0.07%), which leads to lower carbon segregation and formation of more uniform film with better protective properties (facilitated also by the presence of Cr), resulting in lower susceptibility to SCC of this type of steel.

CONCLUSIONS

The main results of the comparison of SCC susceptibility of low-carbon and low-alloy with Cr steels are as follows:

- In phosphate environment both kinds of steels undergo active-passive state transition, more strongly expressed for the low-carbon steel. There is a region of "primary passivity" in the polarization curve for this steel, missing in case of the low-alloy steel.

- Both kinds of steels undergo SCC in solutions of NaH$_2$PO$_4$ (pH = 4) however the SCC susceptibility of the mild steel is higher (reduction of the tensile strength about 2.5 times for the low-carbon and only 15% for the low-alloy steel).

- The SCC susceptibility is strongly dependent on the potential and it occurs in a relatively narrow potential range: for the mild steel this range is –0.3 –0.0 V and for low-alloy steel it is –0.1+0.3 V.

- The SCC susceptibility of both kinds of steels depends strongly on temperature and solution concentration. It diminished with increasing the temperature and lowering solution concentration. For both kinds of steels the most severe SCC is registered in 1 N solutions at 20°C.

- The SCC conditions for both kinds of steels, determined by SCC tests, correspond well with the region of active-passive state transition and are in a good agreement to the regions, predicted by the potentiodynamic polarization method with slow and fast potential sweep rates.

- SCC of both kinds of steels is related to the presence of phosphates in the surface film.

- The low-alloy steel has higher mechano-corrosion stability compared to that of the low-carbon steel studied.

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СРАВНЕНИЕ НА СКЛОННОСТТА КЪМ КОРОЗИОННО НАПУКВАНЕ НА НИСКОВЪГЛЕРОДНА И НИСКОЛЕГИРАНА СТОМАНИ ВЪВ ФОСФАТНИ СРЕДИ

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(Резюме)

Посредством метода на потенциодинамичните поляризационни криви с ниска и висока скорост на изменение на потенциала (10 и 300 mV/min), както и на метода на динамично деформиране на образците *in situ* с ниска скорост на деформация, е направена сравнителна оценка на анодното поведение и склонността към корозионно напукване (КН) във фосфатни среди на два вида стомани: нисковъглеродна (0.17% C) и нисколегирана (0.07% C, 2.0% Cr). Установено е, че и двете стомани проявяват склонност към КН в разтвори на NaH_2PO_4 (pH 4), която е по-силно изразена за нисковъглеродната стомана (намаление на границата на якост на материала в средата 2.5 пъти за нисковъглеродната и само 15% за нисколегираната стомана). Корозионното напукване зависи силно от потенциала и се проявява в тясна област от потенциали и за двете стомани: –0.3–0.0 V (SCE) за нисковъглеродната и –0.1+0.3 V (SCE) за нисколегираната стомана. Склонността към КН намалява силно с повишаване на температурата и разреждането на разтвора. Условията за КН, определени чрез корозионно-механичните изпитания, съответстват на областите на активно-пасивен преход на стоманите и са в добро съответствие с областите за КН, прогнозирани от поляризационните криви. Установено е, че развитието на КН и за двата вида стомани е свързано с присъствие на фосфати в повърхностния филм. Направено е заключение за по-високата корозионно-механична устойчивост на нисколегираната в сравнение с обикновената нисковълеродна стомана.