

EFFECT OF HEAT TREATMENT ON STRESS-CORROSION CRACKING OF LOW-CARBON STEEL IN PHOSPHATE SOLUTIONS

ВЛИЯНИЕ ТЕРМИЧЕСКОГО ТРЕТИРОВАНИЯ НА КОРРОЗИОННОЕ РАССТРЕКИВАНИЕ НИСКОУГЛЕРОДИСТОЙ СТАЛЕЙ В СРЕДАХ ФОСФАТОВ

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Abstract: The effect of structure on the anodic behaviour and susceptibility to stress-corrosion cracking (SCC) in phosphate solutions (1M NaH₂PO₄, pH 4) of thermally treated carbon steel (0.17% C) 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 the change in structure results in change in the active-passive zone and especially in the zone of "primary" passivity of the metal. The quenched and annealed (200-600°C) steel does not show the susceptibility towards SCC while the non-treated steel has a high susceptibility. The obtained results are related to the effect of the structure and carbon distribution on the surface film formation.

KEYWORDS: STRESS-CORROSION CRACKING, ANODIC BEHAVIOUR, PHOSPHATE SOLUTIONS, HEAT TREATMENT

1. Introduction

It is well known today [1-3], that the carbon and low-alloy steels undergoes SCC in solutions of hydroxides, nitrates, carbonate-bicarbonates, etc. The share of this type steels in the stress-corrosion cracking (SCC) cases is 24% [4].

Although SCC of carbon steels in phosphate environments is rarely observed compared to SCC in hydroxide and nitrate media, the interest in this phenomenon is determined by the widespread use of phosphates (mineral fertilizers, corrosion inhibitors, metal surface treatment, etc.) and hence – by the potential risk for its observation in practice.

The data in the literature for the environmental conditions that provoke SCC of steels in phosphate media are limited [5-11]. Shroeder and Partridge [5] first observed SCC of mild steel in Na₃PO₄ solutions; later SCC was reported for mild steel [6, 11], C-Mn steels [7], Armco iron [8] in environment of various phosphates with pH in the range 3 to 7 with some discrepancy in the data for the cracking mode and environmental conditions for SCC.

One of the major problems concerning SCC is predictability of the environmental conditions under which it is likely to occur. According to Parkins [12] carbon steels contains susceptible paths for corrosion (usually grain boundaries) that cause a local galvanic cell. Their distribution on the steel structures is related to the paths followed by stress-corrosion cracks. Parkins has proposed [13, 14] slow and fast (rapid) *potentiodynamic scanning method* to determine both the relative susceptibility to slip-film rupture-repassivation SCC, as well as possible ranges of potentials where SCC might occur. The validity of this method relies on the notion that SCC requires some critical balance between active and passive behaviour, which only occurs when crack walls are readily passivated while the crack tip dissolves at a high rate due to continual destabilization of the passive film. In this method, the rapid scan anodic polarization curve provides a measure of the bare dissolution kinetics over a range of anodic potentials. A slow anodic potentiodynamic scan provides a measure of the passive crack flank dissolution kinetics over the same range of potential. No standard exists for this method [15].

The method was first applied to predict a potential range for SCC of mild steel in carbonate-bicarbonate environment [13]. Parkins proposed some *empirical* rules [14], which in the case of phosphate solutions, needs to be précised.

The potentiodynamic polarization curves in phosphate media produced by Middleton [5] using 1000 and 20 mV/min do not allow accurate prediction of his observed potential range for cracking; this range was reasonably accurately predictable from potentiodynamic polarization data with 300 mV/min and 10 mV/min in the work of Parkins [7]; according to Flis (sweep rates 1 V/min and 1 V/h) [8] the method does not manifest a high sensitivity in phosphate solutions and this region may be best revealed by

potentiostatic or very slow potentiodynamic polarization curves. Smart et al. [11] found that the use of the fast vs. slow sweep rate (4 – 300 mV/min) technique to predict the cracking potential ranges was not successful.

In our previous works [16, 17], investigations concerning the effect of pH, solution concentration and temperature on SCC as well as the film composition under SCC conditions of mild steel in phosphate media were represented. It was established, that the steel undergo active to passive state transition in phosphate medium, the SCC depends strongly on the potential and it is expressed only within a narrow range of potentials: -0.3–0.0 V (SCE). The SCC susceptibility decreases strongly with the increase of temperature and lowering solution concentration. The most severe SCC extent has been registered in 1M NaH₂PO₄ solutions (pH 4) at 20°C. It was also shown that under SCC conditions a surface film, containing iron oxides and phosphates, was formed [17]. The conditions of SCC correspond well to the regions of active-passive state transition in the polarization curves and are in good agreement with the regions, predicted by the potentiodynamic polarization method with slow (10 mV/min) and fast (300 mV/min) potential sweep rates.

The extent to which metal surface will exhibit active-passive transition depends not only on the nature of the environment, but also on the composition and the structure of the metal. During the heat treatment the susceptibility to SCC depends on the phase and structural transformations due to the metallurgical and structural changes and residual stress introduced during the treatment.

The effect of heat treatment and carbon content on passivation and SCC of iron and mild steel in phosphate media was studied by Flis [9, 10]. Studying six iron materials with different carbon content, the effect of carbon on the protectiveness and stability of the passivating film and its relation to intergranular SCC was evaluated. It was established, that heat treatment affects the susceptibility to cracking to a different extent, depending on the carbon content.

The aim of the presented work was assessment of the effect of heat treatment on the SCC behaviour of carbon steel (0, 17% C) in phosphate environment and the possibility to predict the SCC behaviour and potential range on the base of the electrochemical data.

2. Experimental

2.1 Materials and heat treatment

Carbon 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 was used. The steel (produced as hot-rolled bars) has pearlite-ferrite structure and mechanical parameters: ultimate tensile strength $\sigma_B = 440.0$ MPa and yield strength $\sigma_S = 354.7$ MPa.

Specimens of the material were quenched by heating at 930°C in salt bath and cooling in water. The quenched specimens were annealed in the temperature range 200 - 900°C for 24 min in argon atmosphere.

It is well known [18] that by quenching carbon steel the formed constituent is martensite where the carbon is dissolved in the ferrite. Because of supersaturated carbon, the martensite is very hard constituent. It is usually annealed (heated to a temperature between approximately 420 and 650°C) to allow some of the carbon to precipitate out as a carbide phase, usually cementite or pearlite, most clearly appeared at about 600°C. At temperatures over 600°C growing of ferrite grains and accumulation of carbon and another elements at grain boundaries is produced. At about 900°C the typical ferrite-pearlite structure (as in the untreated steel), with small carbide precipitates in the matrix is produced.

2.2 Solution, cell and measurements

1M orthophosphate solutions (pH 4), prepared of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (p.a.) with small amounts of H_3PO_4 (p.a.) or NaOH (p.a.) for pH adjustment, were used as a corrosion medium.

Disk sample-electrodes (working area of 1cm^2) installed on a special Teflon holder, three-compartment electrochemical cell and conventional experimental procedure were used for the *polarization measurements*. The potentiodynamic polarization method with fast (300 mV/min) and slow (10 mV/min) potential sweep rate as well as *current decay* measurements at potentiostatic conditions in the region of active-passive transition were carried out for both assessment of stability of passivation and the approximate potential range for cracking. The potentials were measured and reported against saturated calomel electrode (SCE).

SCC tests were performed using the slow strain rate technique *in situ* (strain rate $2.34 \times 10^{-5}\text{s}^{-1}$) under potentiostatic conditions at different potentials. Tensile testing specimens were cylindrical specimens of 180 mm overall length, 10 mm diameter and 3 mm reduced gauge diameter. Unused surface was isolated with inert PVC coating.

The electrochemical cell, the tensile testing apparatus and the experimental procedure were described elsewhere [19]. The susceptibility to SCC was evaluated by comparison of the mechanical parameter tensile strength σ_B at fracture in the corrosion medium and in air.

3. Results and discussion

Potentiodynamic polarization curves (sweep rate 10mV/min) on thermally treated steel and not treated one are shown on fig.1. Comparing the polarization curves we can say, that the change in structure and carbon distribution does not affect strongly on corrosion parameters, except annealing at 200°C. The most important effect is on the active-passive transition zone and especially on the "double peak"- zone of "primary passivity" at potentials more negative than the potential of deep passivity on the polarization curve. As can be seen on the quenched and annealed at 200°C structures (i.e. martensite) this peak is absent; raising the temperature of annealing small indications are shown at 400°C and 600°C (carbide precipitation) and clearly formed for steel, annealed at 900°C and the base steel (ferrite-pearlite structure).

Polarization curves with different sweep rate (10 and 300 mV/min) for thermally untreated and annealed at 200°C steel structures are represented at fig.2 and fig.3, where the lack of the primary passivity in the slow curve of the annealed steel is shown clearly, and at figs.4 and 5 *current-time* curves at the potentials from the zone of active-passive transition are represented. Fig.4 shows gradually change in current density as the potential increase, i.e. gradually transfer from totally active to entirely passive surface. The slow current is indicative of slow passivation, favoring lateral dissolution; the intermediate situation involves correct balance between dissolution and passivation and possible crack formation, while the fast drop of current shows the onset of passivity in few

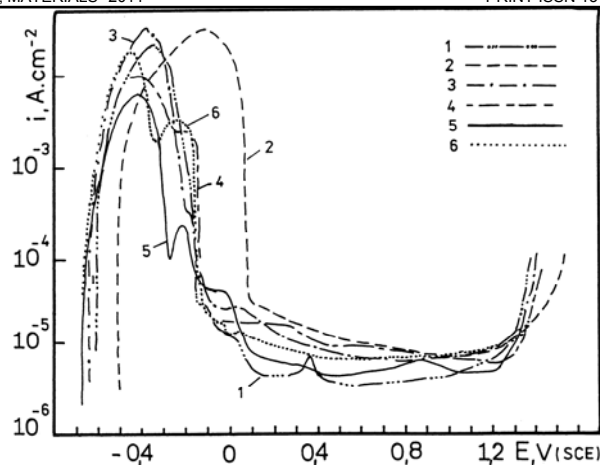


Fig.1 Potentiodynamic polarization curves (10 mV/min) for heat treated carbon steel: quenched (1); annealed at 200°C (2); 400°C (3) и 600°C (4); 900°C (5) and untreated steel (6).

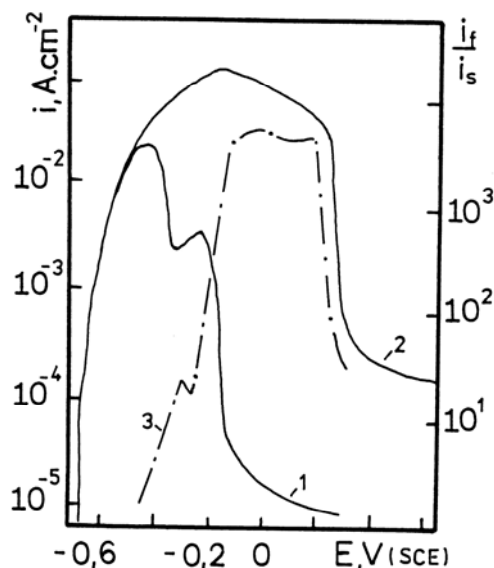


Fig.2 Potentiodynamic polarization curves with scan rate 10 mV/min (1), 300mV/min (2) and ratio i_f/i_s (3) for untreated steel

minutes. The situation on fig.5 is very different - for the intermediate potentials current oscillations for a long period are present, which can be related to instability of the formed surface films. The same was the behaviour for the others steel structures.

According to Kolotykin [20, 21] the region of "primary passivity" for iron in phosphate media is related to formation of a surface phosphate film, composed of two layers. The first one is thin, protective, created directly on the dissolving metal surface by adsorption of phosphate ions and subsequent electrochemical reaction with surface metal atoms, which explain the dependence of the potential of primary passivity on the phosphate solution concentration. Iron phosphate is formed not only on the metal surface, but in solution also, which means that the iron dissolution is produced also by the usual mechanism $\text{Fe} \rightarrow \text{Fe}^{2+}$ with secondary chemical reaction between iron and phosphate ions. The second one is without protective properties. It means that the surface film on the iron is composed by two layers - thin protective and thick, without passive properties composed of $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. The residue is deposited not on the whole surface, but only on the separate places, the most useful for the accelerated dissolution, or for salt crystallization (precipitation). After a time the residue is formed on the other places on the surface.

The presence of a phosphate layer in the region of active to passive state transition was reported by others authors [7-10] and

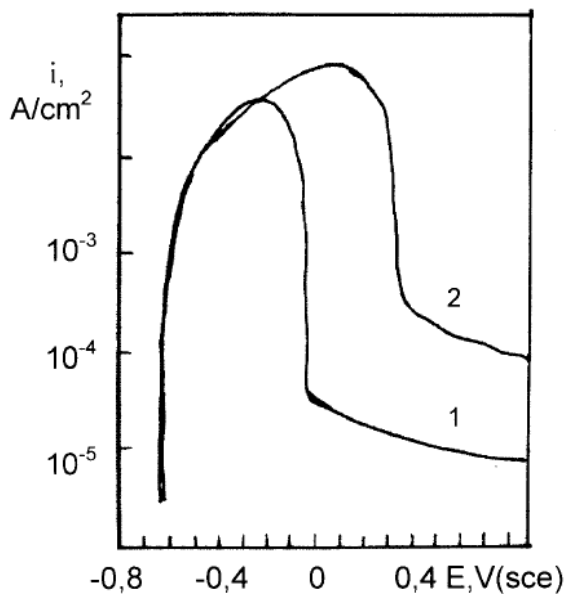


Fig.3 Potentiodynamic polarization curves with scan rate 10 mV/min (1), 300mV/min (2) for annealed at 200°C carbon steel.

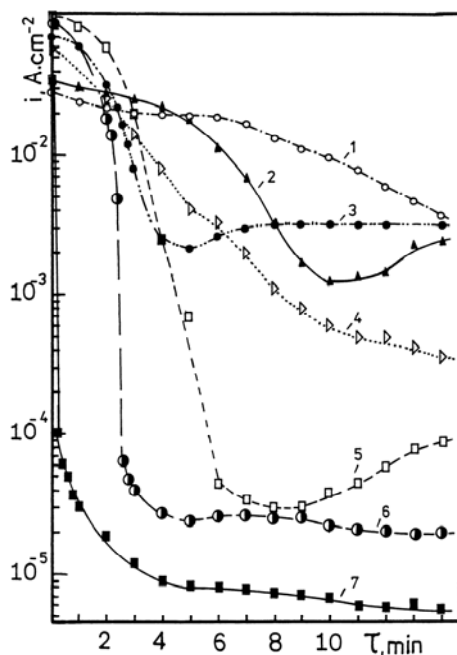


Fig. 4 Current-time curves for untreated carbon steel at potentials: -0,45V (1); -0,40V (2); -0,30V (3); -0,15V (4); -0,1V (5); -0,05V (6) and 0V (7)

proved by our Mössbauer study of surface films, formed on the steels in phosphate solutions in SCC region [17].

The lack of the primary passivity on the martensite and annealed to 600°C steels and presence mainly on the ferrite-pearlite structure, shows clearly the dependence of phosphate formation on the structure and carbon content and its distribution. Following the idea for adsorption of phosphate ions and deposition of the residue on special places [20, 21] it can be proposed, that the places where the processes of phosphate films formation are carbides and grain boundaries. Probably, in support of this idea are the strong current oscillations, produced on the structures where formation of these films is very difficult because of the lack or insufficiency of carbon segregations. Current oscillations were reported also by Flis [10]

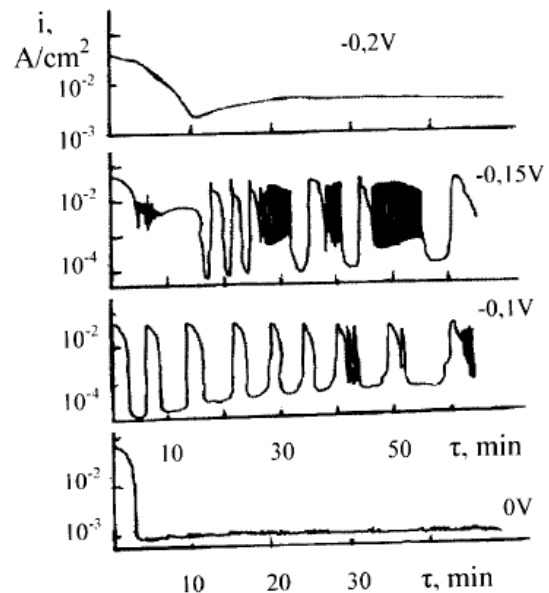


Fig.5. Current-time curves for annealed at 200°C carbon steel

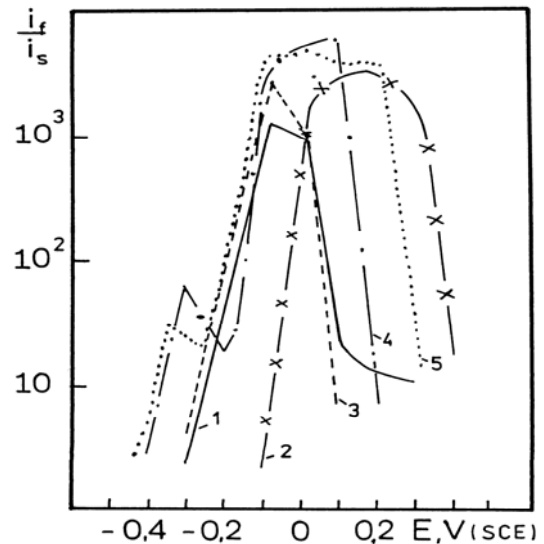


Fig.6 Dependence of ratio i_f/i_s on electrode potential of heat treated carbon steel: quenched steel (1); annealed at 200°C (2); 400°C (3) and 600°C (4) and untreated steel (5).

who proposed that carbon retards the passivation of iron and this effect is at the potentials of SCC stronger than at nobler ones. For this region Parkins [7] proposed electrochemical reaction of formation of $\text{Fe}_3(\text{PO}_4)_2$ and Fe_3O_4 (magnetite) and secondary chemical reaction for $\text{Fe}_3(\text{PO}_4)_2$. At more positive potentials in the passive region electrochemical reactions of transformation of $\text{Fe}_3(\text{PO}_4)_2$ and Fe_3O_4 in Fe_2O_3 were proposed [7].

The dependence of the ratio i_f/i_s (i_f – current density from the fast curve; i_s – from the slow curve) as a function of electrode potential was used for the potential SCC ranges to be determined and is represented on fig.4 for all steel structures. Following the empirical rules [13, 14] ($i_f/i_s > 10^3$) it can be assumed that SCC is probably most possible for annealed at 900°C and for not-treated steels (biggest i_f/i_s ratio), the probability for the other structures is smaller, and for the quenched steel is likely not possible. The ranges of potentials for SCC are very narrow (0,1 – 0,2V) for each structure and are in the range $-0,20 \div 0,15$ (SCE).

Stress-corrosion tests in wide potential range ($-0,4 \div 0,2V$) shown SCC only for annealed at $900^{\circ}C$ steel in the potential range ($-0,3 \div 0,0V$) and for the untreated one in the same potential range, which can be explain with the same (ferritic-pearlite) structure. At $-0,15V$ the tensile strength is about 2,5 times decreased for the untreated steel and about once for the annealed at $900^{\circ}C$ steel. All other structures in heat-treated steel did not show SCC in the whole studied potential range. The structures resulting of quenching and annealing in the temperature range $200-600^{\circ}C$ did not show decreasing of σ_B and this one in the air was attained. This result shows that only ferritic-pearlitic structures undergo SCC in phosphates. The SCC was in a narrow potential range ($-0,3-0V, SCE$), in the active-passive transition zone. After a test, specimens with SCC were covered with a black deposit on the surface and white-greenish deposit over it and in solution –i.e. magnetite and $Fe_3(PO_4)_2 \cdot 8H_2O$ [10, 17]. The presence of magnetite on the specimens undergoing SCC was reported also by Parkins [7] who proposed, that the absence of cracking might be associated with the lack of nucleation or growth of a passivating film. The domain within SCC observed is probably associated with the formation of mixed iron oxide-phosphate films, with stress corrosion failure ceasing at potentials where only Fe_2O_3 films are produced.

It is well known that the quenched structures have high residual stresses as a result of structure transformation and high corrosion activity and SCC behaviour compared to untreated steel would be expected. In fact, the result is opposite, which is indication, that in the case of phosphates not mechanical stresses but environmental conditions are the most important for SCC development.

It is clear, that the SCC development is related to formation of magnetite and phosphates, which is represented by the zone of primary passivity on the slow polarization curve and is related to carbon (carbides) segregation. Probably these segregations promote phosphate ions adsorption and give the opportunity for the electrochemical reaction of magnetite and phosphate formation, while quenched steel with a martensite structure as well the others structures (annealed at $200-600^{\circ}C$) do not propose this opportunity. Flis proposed [9, 10] that the detrimental effect of carbon can be explain in terms of its effect on the anodic dissolution and, in particular, on the passivation of steel. The effect of carbon in promoting the cracking may be due to blocking the surface and modifying protective properties of corrosion products. Apparently, it deteriorates a passivating film of ferric oxide, but on the other hand, it promotes the formation of black deposits of magnetite, which hinder corrosion.

It is known [10, 21], that surface film, formed on the iron during the passivity in phosphate solution contains mainly γFe_2O_3 with small quantity of phosphates. According to Kolotyркиn et al. [20, 21] the formation of Fe_2O_3 is as a result of interaction between the iron and dissolved oxygen or oxidizing agent. It is proposed, that the iron phosphate layer formed as a deposit of the corrosion products from the bulk solution troubles the oxygen access towards the responsible sites on metal surface and by this way hinder the formation of dense layer of Fe_2O_3 and probably stimulate the reaction of magnetite formation. Probably these responsible sites are grain boundaries and carbide segregations.

4. Conclusions

1. The electrochemical behaviour of heat treated steel ($0,17\%C$) in 1M phosphate solutions was assessed. The heat treatment has the strongest effect on the region of active-passive transition and especially on the zone of primary passivity on the slow ($10mV/min$) polarization curves, which is related to formation of film composed by magnetite and phosphates.

2. Only the steels with ferrite-pearlite structures have shown the SCC behaviour in a narrow potential range. For the martensite structures (quenched and annealed in temperature range $200-600^{\circ}C$ steels) SCC was not developed. This result is related to carbon (carbides) distribution in metal structure and its influence on the

composition and properties of formed the surface film.

3. The method of potentiodynamic polarization curves with scan rate 10 and $300 mV/min$ gives good predicative possibilities.

4. Heat treatment of carbon steel ($0,17\%C$) do not suggest any complementary risk of SCC of the steel in phosphate environment.

5. Literature

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