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# Pitting of AISI 304 stainless steel in bicarbonate and chloride solutions

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Metastable and stable pitting on 304 stainless steel (SS304) in 0.1–0.5 M NaCl aqueous solution (pH ~8) has been investigated using a potentiodynamic, a potentiostatic and a weak anodic current galvanostatic techniques. The addition of bicarbonate (0.025–0.5 M) to the solution had an inhibiting effect, manifested by a shift of the pitting potentials to more positive values, a longer induction time for pitting and reduced pit nucleation. The pit nucleation frequency and growth, in the metastable and stable states, decrease as the $NaHCO_3$/NaCl molar concentration increases and pitting is no longer observed for $NaHCO_3$/NaCl molar ratios higher than 3 (four times larger % wt of $NaHCO_3$). Pitting events never occurred at a potential below –0.1 V, fewer metastable events were observed at higher temperature (50°C) and none were observed in chloride free bicarbonate solutions. The inhibiting behaviour of oxyanions is discussed.

## 1. Introduction

The pitting susceptibility of metals and alloys is generally investigated by measuring the pitting potential, usually based on polarization techniques. It was observed that the increase in buffer concentration leads to an increase of pitting potential, thus making more difficult for pitting to start. Galvele [1] concluded that a linear relation between the pitting potential and the logarithm of the buffer concentration is true only if there is a Tafel relation between the electrode potential and the current density of metal dissolution inside the pit. However, even when reliable experimental procedures are carefully followed [2], wide scatter in stainless steel data is commonly obtained. The pitting potential values approximately follow a normal probability distribution and pit generation is considered to be a stochastic process so the stochastic approach has been adopted to study localized corrosion [3–7].

Recently, there has been increased interest in analysing potential or current transients to detect the initiation and propagation of localized corrosion [8–16]. It is well established that metastable pits, the precursor of stable pits, occur more frequently and with greater intensity at potentials approaching the pitting potential. The corrosion current associated with metastable pits may be limited to a few microamperes. Metastable pit growth may terminate at any time and only a few pits will achieve stability but, in each case, a minimum potential or current has to be reached before localized corrosion occurs and a finite time is necessary for the pits to attain stability. Investigation of metastable events is particularly attractive because it could lead to a nondestructive technique for obtaining information about a metal's resistance to localized corrosion.

It is characteristic of stainless steel that pitting corrosion starts in the form of metastable pits, which either repassivate before achieving stability or grow to become stable pits [8–19]. Metastable pits occur over a wide potential range, well below the pitting potential, and are manifested by the random occurrence of short potential drops or a small rise in current transients whenever localized corrosion is initiated. These transients seem to vary in magnitude and shape. Susceptibility to metastable pitting is affected by microstructural defects, changes in the composition of the metal surface or surface pretreatment. For example, the probability of pits formation on stainless steel increases with the surface roughness or the presence of sulfide inclusions and decreases with the addition of molybdenum [8, 15, 20–22].

The alloy composition, surface film properties and the solution chemistry all contribute to pitting corrosion. Ionic species such as inorganic electrolytes are either helpful or detrimental in metal and alloy passivation [23–32] but why they play different roles is not clearly understood. As far as bicarbonate/carbonate aqueous solutions are concerned, the corrosion of stainless steel in such media has not been extensively explored, despite the fact that carbon dioxide is commonly present in all water systems, as well as in the oil and gas industry. However, recent studies on 304 stainless steel (SS304) in bicarbonate aqueous solutions of pH8 [33, 34] illustrate the presence of a broad range of passivity at low potentials, depassivation at 0.4 V vs SCE and a second passivity region before oxygen evolution. No metastable or stable pit formation was observed.

The present work investigates the effect of bicarbonate/carbonate ions on the metastable and stable pitting of SS304 induced by the presence of chloride ions. The influence of different parameters such as the chloride and bicarbonate/carbonate ion concentrations, electrode potential, anodic current and polarization time is considered. Potentiodynamic determination of the pitting potentials together with potentiostatic and galvanostatic measurements of the frequency and lifetime of current or potential transients were performed. Weak anodic current galvanostatic measurements offer an attractive approach to obtaining information about pits nucleation and growth.

## 2. Experimental details

The working electrode was made of austenitic 304 stainless steel (SS304) with the following chemical composition (wt %): C 0.009, Mn 1.67, p 0.034, S 0.020, Si 0.51, Cu 0.35, Ni 8.2, Cr 19.4, V 0.07, Mo 0.30, Co 0.14, Sn 0.018, Al 0.006, Ti 0.006, Nb 0.033 and the balance, Fe. The SS304 rod was machined in the shape of a cylinder and the experiments were carried out on the top of this cylinder, in a meniscus position, with the exposed surface area 0.19 cm$^2$. The electrode was mechanically polished with an alumina suspension to a mirror-like finish and rinsed with distilled water. This surface was examined before and after each experiment using a Bausch & Lomb optical microscope (70×) paying special attention to crevice corrosion. If an attack was observed, the data were discarded and the experiment was repeated. At the beginning of each experiment, the electrode was immersed in the solution and cathodically polarized at –0.8 V for 60 s to remove surface oxides but the surface film on the electrode was not completely reduced, regardless of the cathodic potential applied. The auxiliary electrode was a platinum grid, while a saturated calomel electrode (SCE) connected to the cell by a bridge with a Luggin capillary served as the reference electrode; all potentials quoted in the paper refer to this electrode. The experiments were performed in a Faraday cage.

The solutions were prepared from analytical grade materials (BDH) and deionized water. The pH value was about 8, which was adjusted by adding NaOH. The cell capacity was about 600 ml, which ensured that the buildup of dissolved ions in the bulk of the solution during the course of a given experiment would be negligible. All solutions were deaerated using high purity nitrogen before each experiment and a flow of nitrogen was established above the solution during the measurements. The experiments were performed at 25 °C and 50 °C.

## 3. Results and discussion

### 3.1. *NaCl Solutions*

The polarization curves for the SS304 electrode in 0.1, 0.3 and 0.5 M NaCl unbuffered solutions are presented in Fig. 1 which show that chloride has little or no influence on the wide passive region located at low potentials. The greatest effect of chloride is observed at higher potentials in the form of oscillation in the passive region arising from the propagation and repassivation of metastable pits. The polarization curves terminate with the formation of a stable pit. Both the metastable and the stable pitting potentials decrease with the increasing $Cl^-$ ion concentration. The pitting potential was determined at a scan rate of 0.5 mV s$^{-1}$, which is a reasonable approximation of the steady-state conditions. The pits were considered stable for a current of 50 $\mu$A (266 $\mu$A cm$^2$). Although

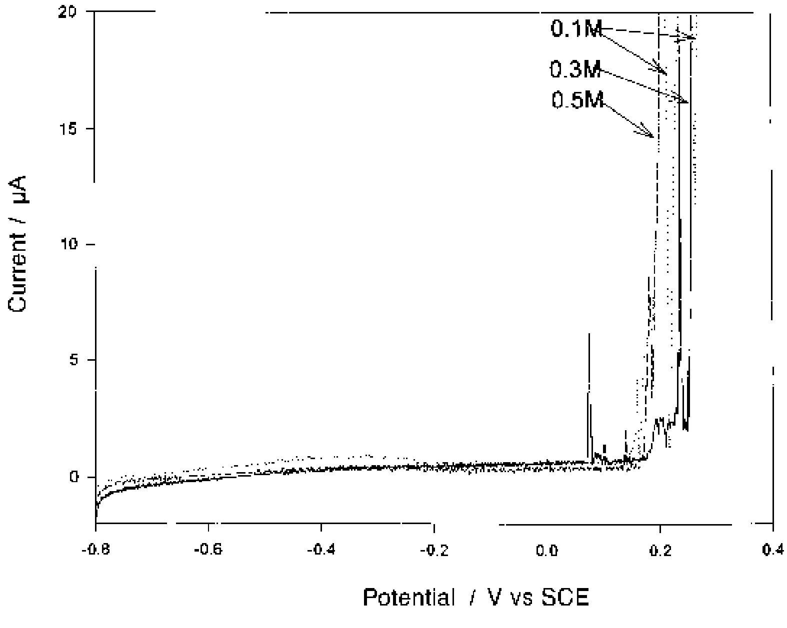

Fig. 1. Polarization curves for SS304 electrode (0.19 cm$^2$) in 0.5, 0.3 and 0.1 M NaCl solutions, d$E$/d$t$ = 0.5 mV s$^{-1}$, 25°C.

*Table 1.*

| *Solution at 25* °C | Stable pitting potential,$E_B$ /mV |
|---|---|
| 0.1 M NaCl | 270, 304, 324, 343, 352 |
| 0.1 M NaCl + 0.1 M $NaHCO_3$ | 490, 542, 547, 550, 580 |
| 0.1 M NaCl + 0.2 M $NaHCO_3$ | 562, 590, 603, 612, 615 |
| 0.1 M NaCl + 0.3 M $NaHCO_3$ | metastable pits |
| 0.1 M NaCl + 0.4 M $NaHCO_3$ | no pits |
| 0.3 M NaCl | 146, 158, 170, 270, 290 |
| 0.3 M NaCl + 0.1 M $NaHCO_3$ | 368, 370, 390, 430, 530 |
| 0.3 M NaCl + 0.3 M $NaHCO_3$ | 323, 340, 440, 470, 490 |
| 0.3 M NaCl + 0.5 M $NaHCO_3$ | 500, 506, 570, 600, 630 |
| 0.5 M NaCl | 17, 59, 75, 107, 162 |
| 0.5 M NaCl + 0.5 M $NaHCO_3$ | 380, 400, 422, 456, 480 |

special attention was paid to creating identical experimental conditions, a large variation was observed among the pitting potentials (Table 1).

So far, the pitting potentials reported in the literature have been used mainly as practical values for comparing metals and alloys in different environments with respect to their tendency to exhibit localized corrosion. However, the pitting potential is also linked to other parameters such as surface preparation, surface roughness or chemical pretreatment [17–19]. Furthermore, all pits begin in the metastable state whether they die there or grow to become stable. The effect of the parameters mentioned above on the metastable pitting process and the transition to the formation of stable pits may be significant.

Potentiostatic anodic current transients linked to the nucleation of metastable pits in chloride solutions were noticed above –0.1 V. Figure 2 shows a typical train of current transients at 130 mV for the SS304 electrode in 0.1 M NaCl solution at 25 °C and 50 °C. Metastable pits generated at 25 °C had a very limited lifetime, after which they repassivated and the current returned to the passive value. During repassivation, the chloride anions at the pit surface must be replaced by a passive film. Under potentiostatic conditions at

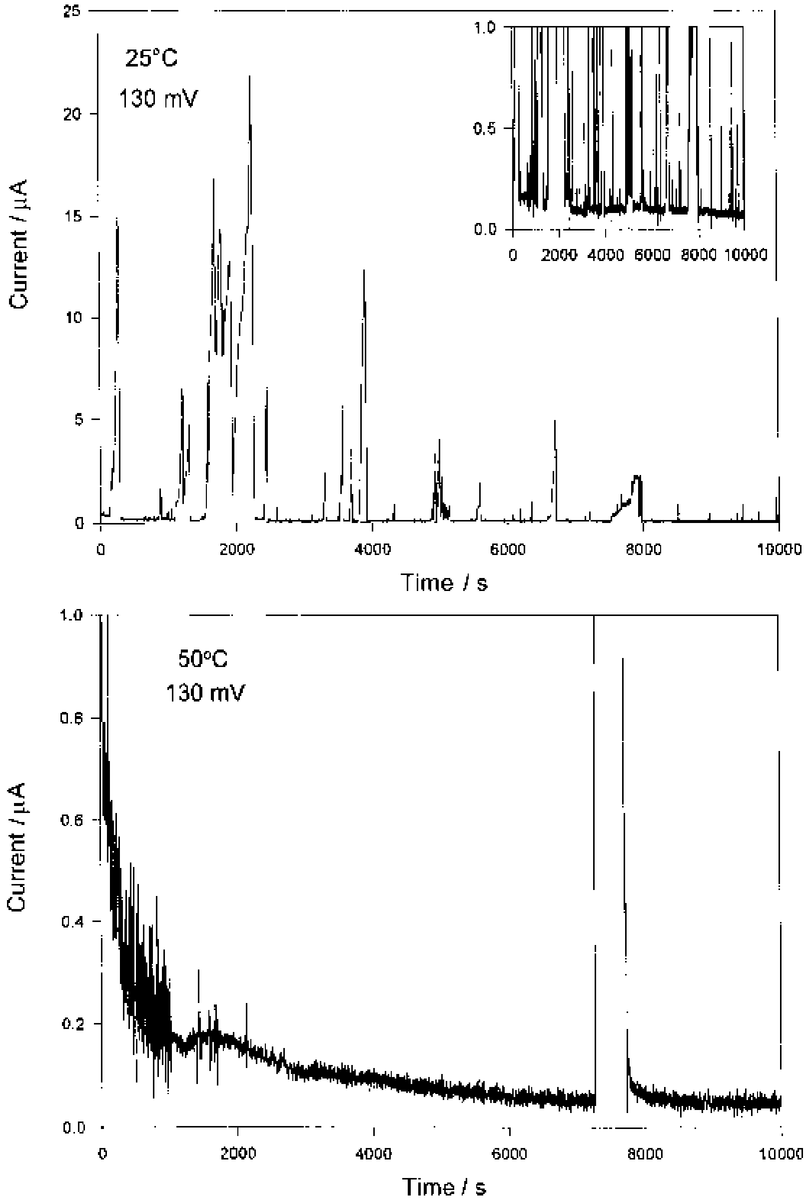

Fig. 2. Potentiostatic current–time transients of metastable pits on the SS304 electrode (0.19 $cm^2$) held at 0.13 V in a 0.1 M NaCl solution, at 25 °C and 50 °C. Inset: Current range 0–1 μA.

$E > -0.1$ V, fewer metastable events are observed at 50 °C than at 25 °C. No current transient rises smoothly, although repassivation appears to occur suddenly, as witnessed by a steep curve. The initiation of pitting must incorporate the development of a concentrated chloride solution at the side of pit growth. The concentration of dissolution products within pits influences the dissolution rate and repassivation of the pit [16]. When the concentration decrease below saturation, the rate of dissolution increases. The decreasing dissolution rate with increasing concentration is necessary for repassivation. The aggressive anions contained in the pits have to diffuse from the pit electrolyte to the bulk solution. The formation of a salt film is linked to the balance between rates of dissolution into a pit and diffusion out of pit. Pitting is unstable below a critical pit radius, diffusion from the pit dominates and repassivation takes place.

Typical potential transients from the metastable growth and repassivation of pits are depicted in Fig. 3 for the galvanostatic measurements with a weak anodic current of 0.1 $\mu$A (0.53 $\mu$A cm$^{-2}$) for the SS304 electrode in 0.1, 0.3 and 0.5 M NaCl solutions. As long as localized corrosion is absent, the potential rises continuously. However, when the potential reaches the pitting or crevice initiation potential, a sudden fall is noticed and localized corrosion is observed. The pit grows throughout the time that the potential is falling and/or remains constant and repassivation begins at the point where the potential starts to rise again. The magnitude of the potential transients reflects the size to which pits grow and can thus be taken as an indication of the pits survival probability. The frequency of the potential variations increases with the test duration as the potential increases and fewer transients are noticed at 50 °C than at 25 °C. As reported for the potentiostatic anodic current transients, no metastable or stable events were observed below $-0.1$ V. The low value of applied current indicates that pitting could start in any small defect in the oxide film but the use of a weak anodic current poses a stability problem for a pit, since normal pits grow with continually increasing current.

The SEM pictures in Fig. 4 show a pit on SS304 in a 0.1M NaCl solution. Within the micropit distinct crystallographic planes are visible. Increasing dissolution time led to growth of the pit and finally to the development of a rough, etched surface texture, indicating that different surface elements may alternatively depassivate and repassivate. The precipitation of salt at the edge occurs. However, the micrographs do not prove whether the voltage and current transients were generated by the initiation or propagation of a particular pit.

The key role of chloride ions in localized corrosion is generally accepted but the corrosion mechanism is still not clear. The strong effect of the anion, apart from electrostatic attraction, is also due to the hydration of anion and the hydrophobicity of the metal, since hydrophobic metals facilitate anion adsorption. Recently [35, 36], well known chloride aggressivity was attributed to a combination of the ion size and Gibbs energy of dehydration, which favours the adsorption of chloride ion compared to other anions. Chloride ions can be adsorbed on the active sites randomly distributed on the surface film and then desorb with surface cation. The process is favoured in cases where the anion has a tendency to complex with a cation, as in the case of iron in chloride solutions. The increase in anodic current can be ascribed to the formation of a chloride complex and metal dissolution while current decay is regarded as due to passive film growth controlled by the metal oxidation rate. Accelerated dissolution acidifies the solution, which prevents passive film formation and further accelerates dissolution because of the high acidity. The cathodic reaction on the passive surface around the pit supports pit growth until the dissolution is stopped by repassivation.

Different mechanisms could lead to pit initiation, mainly depending on the pretreatment and composition of the metal surface. Impurities and inclusions such as sulfides have a decisive influence on pit nucleation.

### 3.2. *Bicarbonate effect*

Aggressive and inhibiting anions compete at energetically preferred sites at the metal surface. For example, the presence of $HCO_3^-/CO_3^{2-}$ in the chloride solution results in a shift of the metastable and stable pitting events toward more positive potentials (Table 1). The electrochemical behaviour of the SS304 electrode in a bicarbonate solution (without $Cl^-$ ions) at pH 8 at 25 °C and 50 °C, is illustrated by the voltammograms in Fig. 5. The polarization curves are characterized by a broad passive region at low potentials, followed by depassivation of the electrode with no formation of visible pits and repassivation prior to the onset of the oxygen evolution. The passive film present at low potentials is partially dissolved at ~0.4 V by a $CrO_4^{2-}$ ion formation; the reaction rate depends on the bicarbonate concentration and temperature. In the transpassive region, simultaneously with the oxygen evolution process, iron dissolution by the formation of ferrate ions has been suggested [33, 34, 37]. It is thought that the superficial ferrate in a $HCO_3^-/CO_3^{2-}$ solution, stabilizes but that the free ferrate decomposes faster than in NaOH solution due to the pH requirements. The passive film formed on the SS304 electrode is not completely reduced, regardless of the applied cathodic potential used for that purpose. A detailed analysis of the electrochemical behaviour of SS304 in bicarbonate solutions has been given elsewhere [33, 34].

The effect of bicarbonate/carbonate ions on the chloride attack on the SS304 electrode is demonstrated by adding bicarbonate to the chloride solution. The fact that localized corrosion begins at low anodic current indicates that pitting could start at any small defect in the oxide film. Pitting potentials

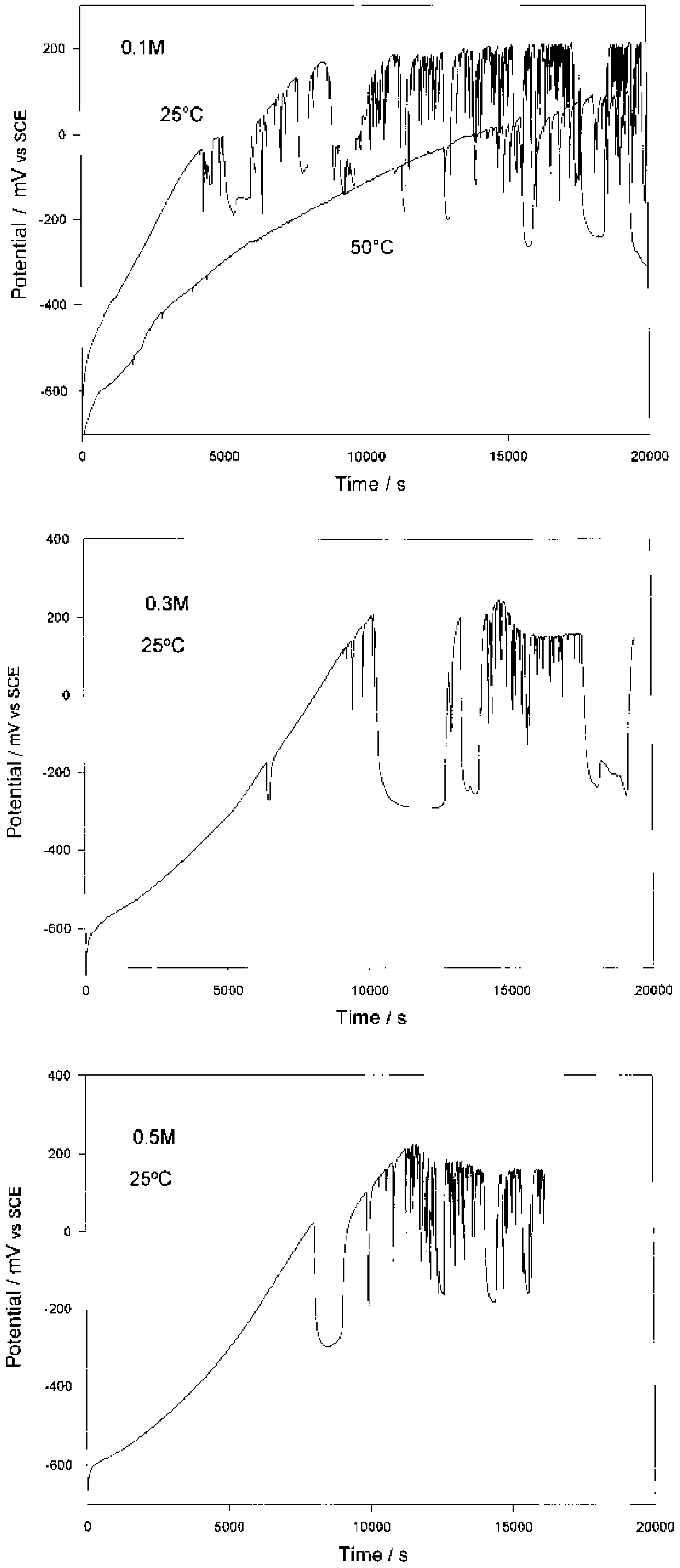

Fig. 3. Potential–time transients for the galvanostatic test with anodic current of 0.1 $\mu$A (0.53 $\mu$A cm$^{-2}$ ) applied to the SS304 electrode in 0.1, 0.3 and 0.5 M NaCl solutions.

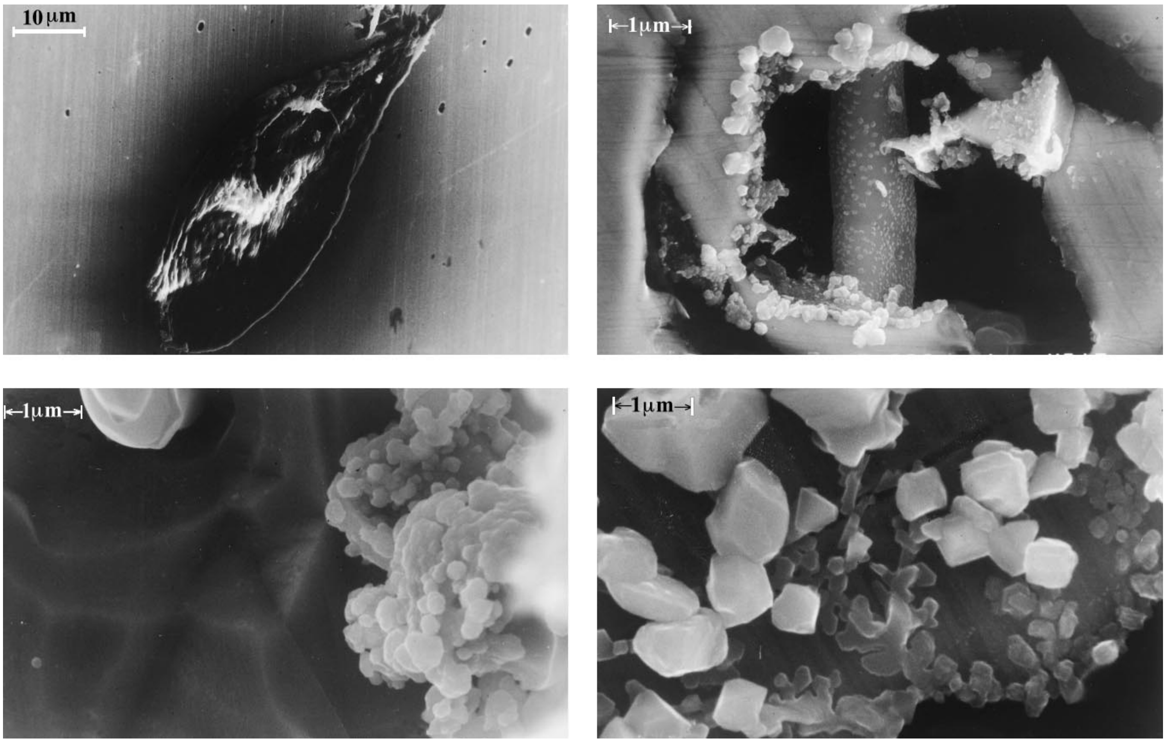

Fig. 4. SEM pictures of pits on the SS304 electrode in 0.1 M NaCl solutions; the other experimental conditions are those in Fig. 1.

for the various chloride and bicarbonate concentrations are reported in Table 1 and the plots in Fig. 6 show the tendency of the pitting potential values to increase at higher bicarbonate concentrations. No stable pits were observed for a $NaHCO_3/NaCl$ molar ratios greater than 3.

The potential–time plots in Fig. 7 were obtained for galvanostatic anodic polarization of 0.1 $\mu$A (0.53 $\mu$A cm$^{-2}$) and a constant chloride to bicarbonate molar ratio 1:1, with both ion concentrations increased from 0.1 to 0.5 M. The induction time for pitting increases at higher bicarbonate concentrations. The metastable pitting events begin after 15 000 s in 0.1 M $NaHCO_3$ solution, after 20 000 s in 0.3 M $NaHCO_3$ and after 35 000 s in 0.5 M $NaHCO_3$. When 0.025 M $NaHCO_3$ is added to 0.1 M NaCl solution, pitting events begin after only 13 000 s (Fig. 8). In this weak current test, the increased bicarbonate concentration in solution prevent the $Cl^-$ ion from inducing metastable and stable pitting events, and the results indicate that the $HCO_3^-/CO_3^{2-}$ ions prevent the pitting process.

The current and potential transients do not have the same shape. Figure 9 shows the potentiostatic

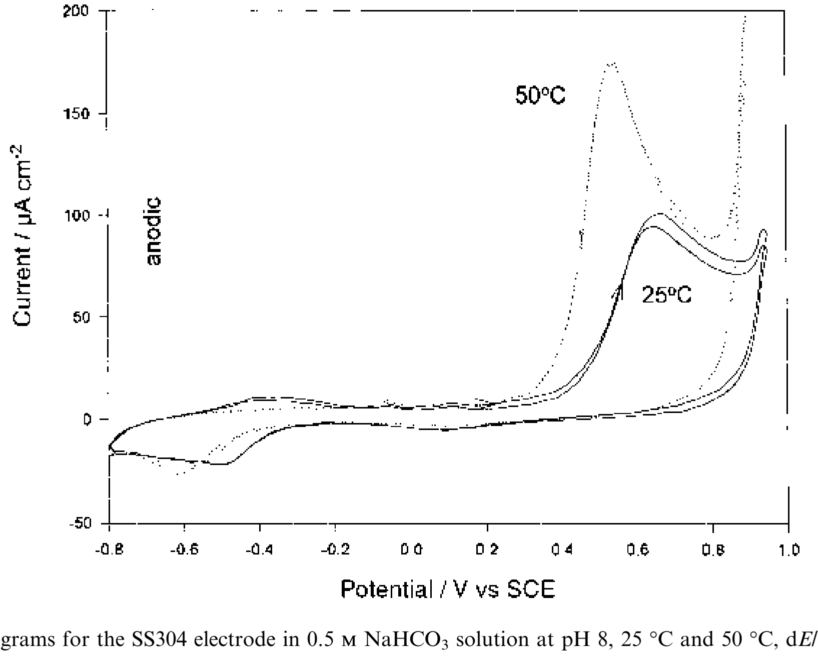

Fig. 5. Cyclic voltammograms for the SS304 electrode in 0.5 M $NaHCO_3$ solution at pH 8, 25 °C and 50 °C, $dE/dt$ = 5 mV s$^{-1}$

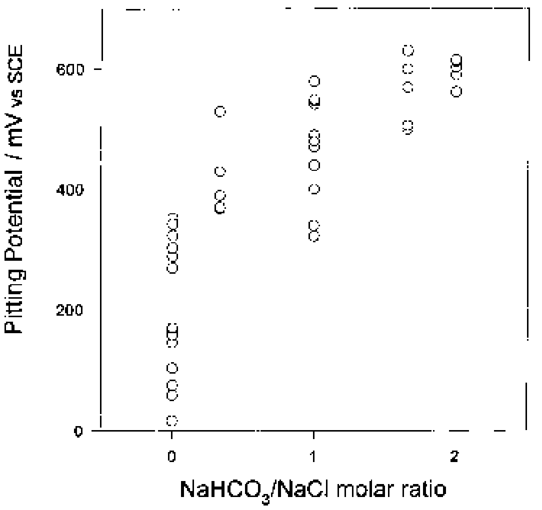

Fig. 6. Pitting potential for the SS304 electrode as a function of the NaHCO$_3$/NaCl molar ratio.

current/time transient at 750 mV on the SS304 electrode for a 1:3 molar ratio of 0.1 M NaCl + 0.3 M NaHCO$_3$ solution. The anodic current decreases to a value of about 60–30 nA, without pitting events. The small current pulses seem to reflect the dynamic state of cracking and healing of the passive film at this high positive potential.

These results indicate that adding bicarbonate to the chloride solution increases the efficiency of passive film formation on SS304, an efficiency which depends on a competitive effect between OH$^-$, HCO$_3^-$, CO$_3^{2-}$ and Cl$^-$ anions, with the concentration of each species in the solution playing an important role. The pitting by chloride can be also altered by addition of appropriate concentration of different anions such as borate, acetate, phthalate, nitrate, chromate, phosphate, sulfate, chlorate or perchlorate [8, 19, 24–27, 38, 39]. All these anions cause the shift of pitting potential value to more positive potentials. Different mechanisms of localized corrosion and inhibition have been suggested but no direct experimental results have corroborated any of the hypotheses put forward.

The ability of different oxyanions to suppress halide ion corrosion on various metals is discussed in the literature [23–32]. The probable explanation is that oxyanions act as adsorption inhibitors as well as pH buffering agents in a way that facilitates surface oxidation. A strong influence of the nature of the anions of the electrolyte and their concentration on the oxide film on noble metals has been observed [40]. The development of surface oxidation depends on the adsorption characteristics of the anions and is facilitated by the presence of adsorbed oxyanions, which affect the state of the oxide film generated in their presence. The effect is enhanced when ClO$_4^-$ or SO$_4^{2-}$ is replaced by CO$_3^{2-}$ or B$_4$O$_7^{2-}$ anions. These solutions have a larger buffer capacity than solutions brought to the same pH by adding of NaOH. An adequate solution buffer capacity is important in order to keep the surface pH constant. The pH drops in pits owing to hydrolysis of the cations evolved during anodic metal oxidation, and the pH may increase at cathodic sites on the outside open-circuit pits. The passivation provided by a relatively dilute borate solution is as effective as a large concentration of other anions (bicarbonate/carbonate, acetate, phthalate) at the same pH or even more so. This may be associated with polymeric nature of the borate [40], which causes stronger adsorption, and it suggests a direct participation of borate anions in the passive oxide film formation.

Direct anion participation in the anodic oxidation process by incorporation in the surface charge transfer complex (SCTC) is discussed by Kolotyrkin *et al.* [41, 42]. Such complexes form during the water ad-

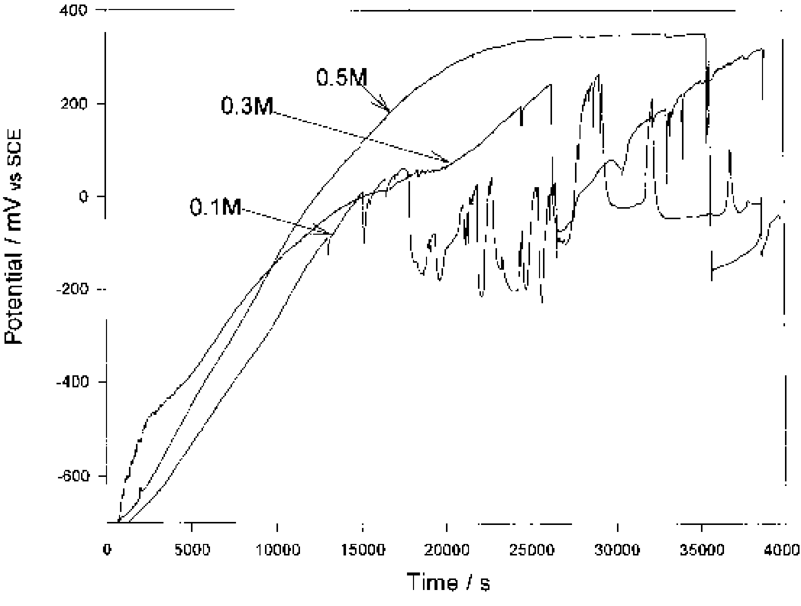

Fig. 7. Potential–time transients for the galvanostatic test with an anodic current of 0.1 $\mu$A (0.53 $\mu$A cm$^{-2}$) applied to the SS304 electrode in 0.1 M NaCl + 0.1 M NaHCO$_3$, 0.3 M NaCl +0.3 M NaHCO$_3$ and 0.5 M NaCl + 0.5 M NaHCO$_3$ solutions at pH 8.

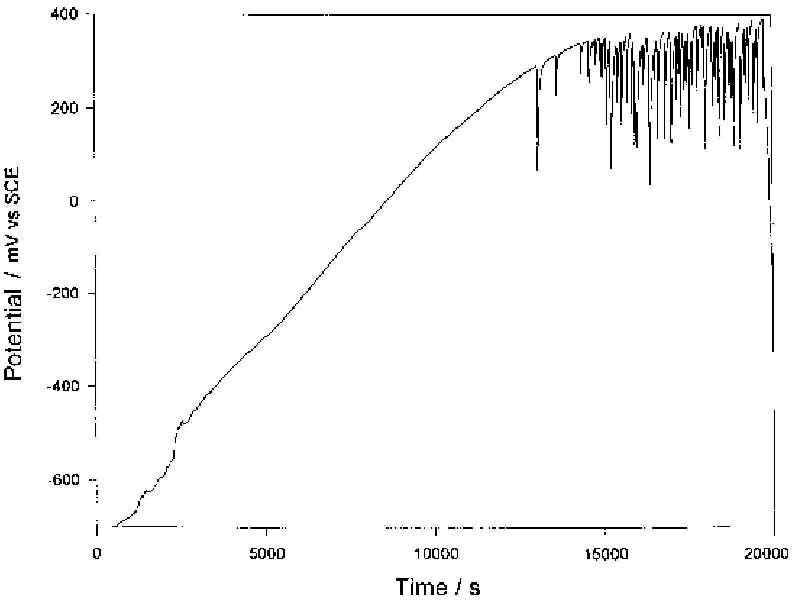

Fig. 8. Potential–time transients for the galvanostatic test with an anodic current of 0.1 $\mu$A (0.53 $\mu$A cm$^{-2}$) applied to the SS304 electrode in 0.1 M NaCl + 0.025 M NaHCO$_3$ solution at pH 8.

sorption process at the nonhomogeneous (with respect to energy) surface of iron and the anions facilitate partial charge transfer in the adsorbed water molecules. Passivation is due to the dehydration of two neighbouring hydroxy groups. The coupling of hydroxy groups is enhanced by the incorporation of single-charged anions in SCTC, the anion charge being neutralized by the proton of the adsorbed water.

Penetration of the protective film by both aggressive and inhibiting ions occurs through preferential sites on the surface, however there are different types of defects in oxide films and they are having different susceptibilities to breakdown passivity. The common feature in the behaviour of inhibiting oxyanions is the fact that they undergo reduction inside the protective oxide film containing an excess of metal ions and trapped electrons [32]. This behaviour is related to the oxide film formation. The reduction of oxyanions is also assumed to supply oxygen atoms, allowing displacement of the chloride species [32]. The relative quantities of oxygen species generated by this process depend on the nature of both the metal and the anions of the electrolyte as well as anion concentration. An analysis of passive films on Cr-rich alloys revealed that most of the oxygen lattice is not fixed but labile and readily exchangeable [43].

In the cases, the inhibitive action can arise through the formation of surface metal ion–anion complexes, which retard dissolution as a result of the formation of sparingly soluble salts [19, 44], or possibly as a result of stabilization of the ferric state. At higher pH levels, the solubility constants of iron hydroxides

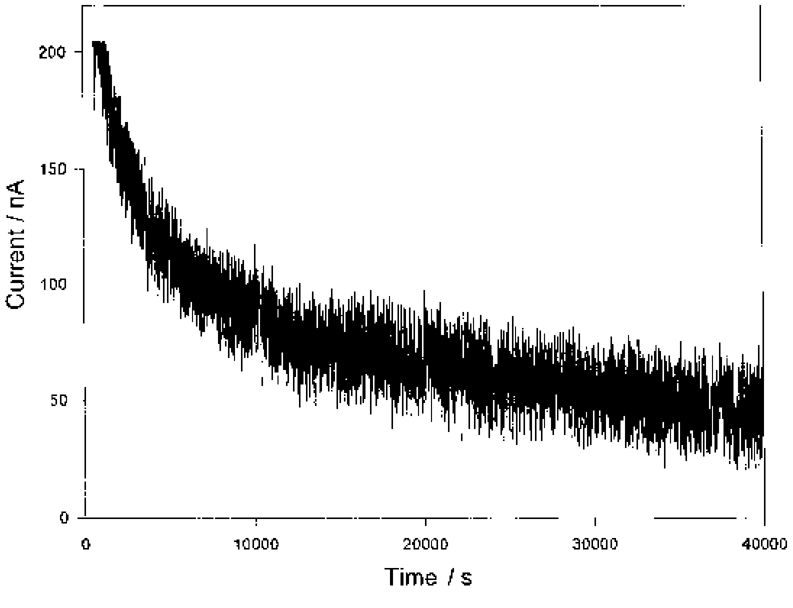

Fig. 9. Potentiostatic current–time transient for the SS304 electrode held at 0.75 V in 0.1 M NaCl + 0.3 M NaHCO$_3$ solution at pH 8.

($Fe(OH)_2$ $K_{sp} = 4.9 \times 10^{-17}$, $Fe(OH)_3$ $K_{sp} = 2.6 \times 10^{-39}$), oxides and carbonate ($FeCO_3$ $K_{sp} = 3\times10^{-11}$) are lower, which facilitates passivation. The Pourbaix diagram for $Fe–CO_2–H_2O$ [45] indicates that $FeCO_3$ is a solid phase and that passivation could occur by the transformation of $FeCO_3$ to $Fe_2O_3$ inside the passive film. It is considered that chemical and electrochemical processes play a key role and may be equivalent to the effect of potential increase.

## 4. Conclusion

The addition of bicarbonate to a pH 8 chloride solution improves the resistance of 304 stainless steel to the initiation and the propagation of pits, with the degree of protection increasing with the $NaHCO_3$ concentration. This effect is explicable in terms of the effect of bicarbonate on the solubility of the metal cations in the pits. The pit nucleation and the pit growth are different processes, the latter is under diffusion control.

No pitting events were observed for a $NaHCO_3$/NaCl molar ratio greater than 3. At 50 °C, the protection properties of the passive film are better than at 25 °C and a longer induction time is needed for both metastable and stable pits to occur. At low potentials, below –0.1 V, the metastable and stable pits are inhibited, and pits propagation was never achieved.

An analysis of potential transients during the low anodic current galvanostatic measurement gives useful information about localized corrosion without damage to the SS304 electrode surface.

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