DETERMINATION OF THE CRITICAL PITTING TEMPERATURE AND THE CRITICAL ION (Cl⁻) CONCENTRATION INDUCING PITTING OF AISI 304L STAINLESS STEEL IN 0.5 M H₂SO₄

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Abstract

Corrosion of AISI 304L stainless steel in aqueous solutions of 0.5 M H_2SO_4 + 0.01 M KCNS + x M NaCl was studied at different temperatures (25, 40, and 50 °C). The critical ion (Cl⁻) concentration (CIC) and the critical pitting corrosion temperature (CPT) were determined on the basis of characteristic corrosion parameters (i_{crit}, i_{pass}, E_{pp}), which were obtained through potentiodynamic scanning experiments. The activation energy of the process was found to be equal to –42.0 (1 ± 0.08) kJ mol⁻¹. As the temperature increased, the pitting potential, E_{pp}, was shifted towards more negative values linearly with the reciprocal of temperature, when the concentration of added NaCl was above the CIC. In contrast, at concentrations very close to the CIC, the straight lines changed slopes. This result may indicate of the approximate boundary between metastable pitting and the beginning of stable pitting.

Introduction

Formation of metal oxides on metallic surfaces in contact with electrolyte solutions (passivation) protects the metal against corrosion, resulting in an almost zero rate of metal dissolution. The electrical current through the metal electrolyte system may oscillate within a wide potential region. The maximum and minimum current values correspond to the active and the passive states, respectively. Several chemical species in solution attack the passive oxide film leading to passivity breakdown. Pitting corrosion involves the formation of deep local active areas (pits) on the passive metal surface. The metal inside pits is in contact with the corrosive environment (active state) and it dissolves. Pitting is one of the most insidious and destructive forms of localized attack. Initiation of pitting corrosion starts with localized dissolution of the passive metal surface (oxide-covered) due to the attack on metal by certain dissolved ions. Halide ions

such as Cl⁻, Br⁻ and I⁻ are considered as "aggressive ions" since they result in local destruction of the passive oxide film and pitting corrosion.[1-3]

Smialowska[4] proposed that four stages of pitting corrosion could be distinguished: (1) processes occurring on the passive film, at the boundary of the passive film and the solution; (2) processes occurring within the passive film, when no visible microscopic changes occur in such a film; (3) the formation of so-called metastable pits which initiate and grow for a short period of time below the critical pitting potential and then repassivate (this is an intermediate step in pitting); and finally (4) stable pit growth, which starts above a certain potential termed the critical pitting potential.

Pit growth generally occurs at high rates. Increasing temperature additionally weakens the oxide film, and thus pitting occurs much more easily at higher temperatures. The reason for this behaviour is the higher number of locally limited defects in the film and the increased tendency of oxide films to incorporate ions at higher temperatures.[5,6]

The breakdown of the passivity of iron and stainless steels and the initiation of pitting corrosion induced by halides are of great technological importance and have attracted the interest of several research groups for a number of years. Usually, evaluation or comparison of the pitting resistance of stainless steels through accelerated testing methods involves the determination of characteristic pitting potentials, E_{pp}.

For pitting corrosion it was found that a critical pitting corrosion temperature (CPT) exists.[7-12] Below this temperature pitting is not possible and only transpassive corrosion occurs. In addition, there exists a critical concentration of metal chlorides, which is required to form a salt film on the metal surface that prevents growth of the passive film.[13,14] However, above the critical ion (Cl⁻) concentration (CIC) the pit will stabilize and grow, and below it, the pit will repassivate.

The breakdown or pitting potential is found from potentiodynamic scanning experiments and using this method it is possible to determine the critical pitting temperature and the critical ion concentration.

It is well known that the 300 series of austenitic stainless steels, are prone to pitting in the presence of halide ions, particularly chloride ions. This to a certain extent has limited their use in a wide range of engineering applications. The goal of this paper was to study the electrochemical behaviour of the stainless steel AISI 304L in 0.5 M

H_2SO_4 at various concentrations of chloride ion. The work was extended to investigate the effect of temperature on the breakdown potential due to Cl^- ions and finally, with the help of the kinetic parameters of corrosion, the CPT and CIC were determined.

Experimental

Cylindrically-shaped specimens were made from a rod of austenitic stainless steel AISI 304L (composition in wt %: C, 0.03, S, 0.014, Si, 0.58, Cr, 17.51, Ni, 9.29, Mn, 1.32, P, 0.023). The samples used for electrochemical experiments had a diameter of 16 mm and a thickness of 10 mm. The metal surface was hand polished with grit silicon carbide paper of grades 600, 800, 1000 and 1200, followed by polishing with 9μm and then with 3μm diamond paste to near mirror quality. Finally, the specimen was degreased with ethanol. The test electrolyte solutions used in our experiments were mixtures of 0.5 M H_2SO_4 + 0.01 M KCNS + x M NaCl.

Weight loss measurements were based on weighing of specimens before and after each polarisation measurement. After each test, specimens were rinsed in distillate water, ethanol, dried and weighed with a precision balance with an accuracy of ± 0.1 mg.

Polarization scans were run from –0.6 to 1.8V and back at a scan rate of 2 mV s^{-1}. This was to ensure, that the scan reached the highest potential applied during the potentiodynamic experiments in the transpassive region.Before each measurement, the sample was cathodically polarized at –1.0 V (SCE) for 10 min and then allowed to reach a stable open-circuit potential which was attained in about 30 min. The test solution was held thermostatically at the desired temperature (25, 40 and 50 °C ± 1 °C). Potentiodynamic polarization measurements were carried out using a SOLATRON 1287 Electrochemical Interface.

Results and discussion

The effect of the chloride ion concentration and the temperature on the polarization curves of AISI 304L SS is shown in Figure 1. Clearly, the chloride ion concentration and the temperature have only a slight effect on the change in the cathodic part of the polarization curves, but they have a pronounced influence in the anodic part and on the passive behaviour of the chosen steel. In the absence of chloride ions, we see

pronounced passivation, reflected by a decrease in the current by about two orders of magnitude. This passive film is seriously damaged by increase of the temperature to 40 °C. On further increase of concentration of chloride ions, i.e. at $c = 0.25$ M and for a temperature of 50 °C, the polarization curve shows no sign of passivity at all.
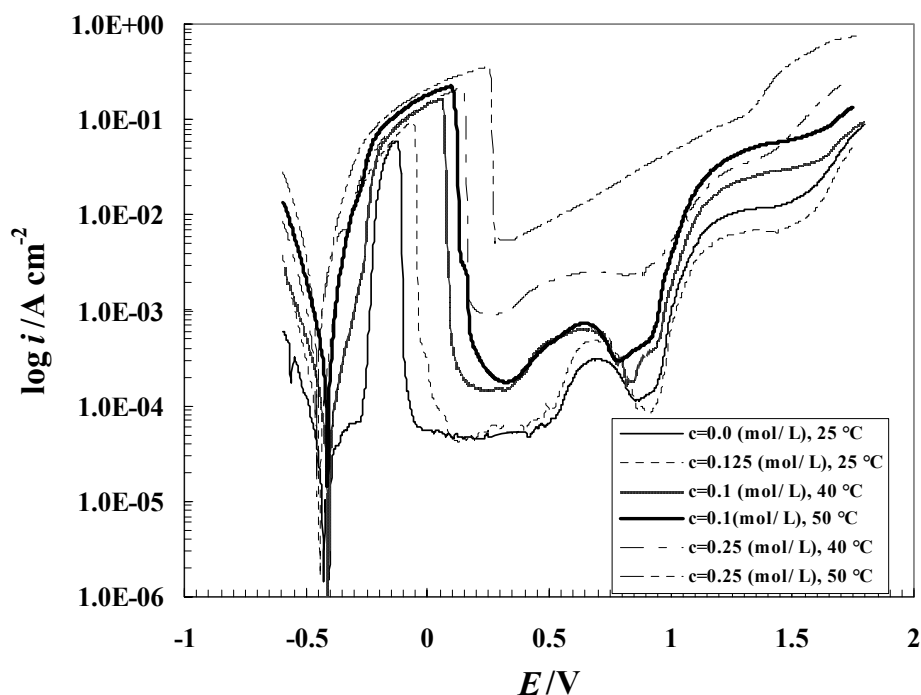
Figure 1. Temperature dependence of the anodic polarization curves of the AISI 304L SS in a mixture of 0.5 M H_2SO_4 + 0.01 M KCNS with and without chlorideions.

The shape of the return curve determines the ability of an alloy to repassivate. If pitting corrosion occurs, the polarization curve has the shape of a loop (hysteresis). The potential at which this loop finishes on its reverse scan is the protective potential, sometimes known as the repassivation potential, E_{rp}. For $E_{rp} = E_{pp}$ there is a small tendency for the occurrence of pits, whereas at E_{rp} potential, which is more positive than E_{pp}, there is no such tendency. However, for the case of E_{rp}, which is more negative than E_{pp}, the occurrence of pits is possible and the larger the loop, the greater is the tendency for the occurrence of pitting corrosion. The results of the cyclic polarization tests are shown in Figures 2a-c. At 25 °C, the hysteresis circle appeared for $c > 0.125$ M NaCl. The shape of a loop has changed, when the temperature increased from 25 °C to 40 °C; it became broader and a small hysteresis circle is observed for $c = 0.125$ M NaCl.

Finally, for the third temperature i.e. for 50 °C, hysteresis occurs for all the concentrations of Cl⁻ ions.
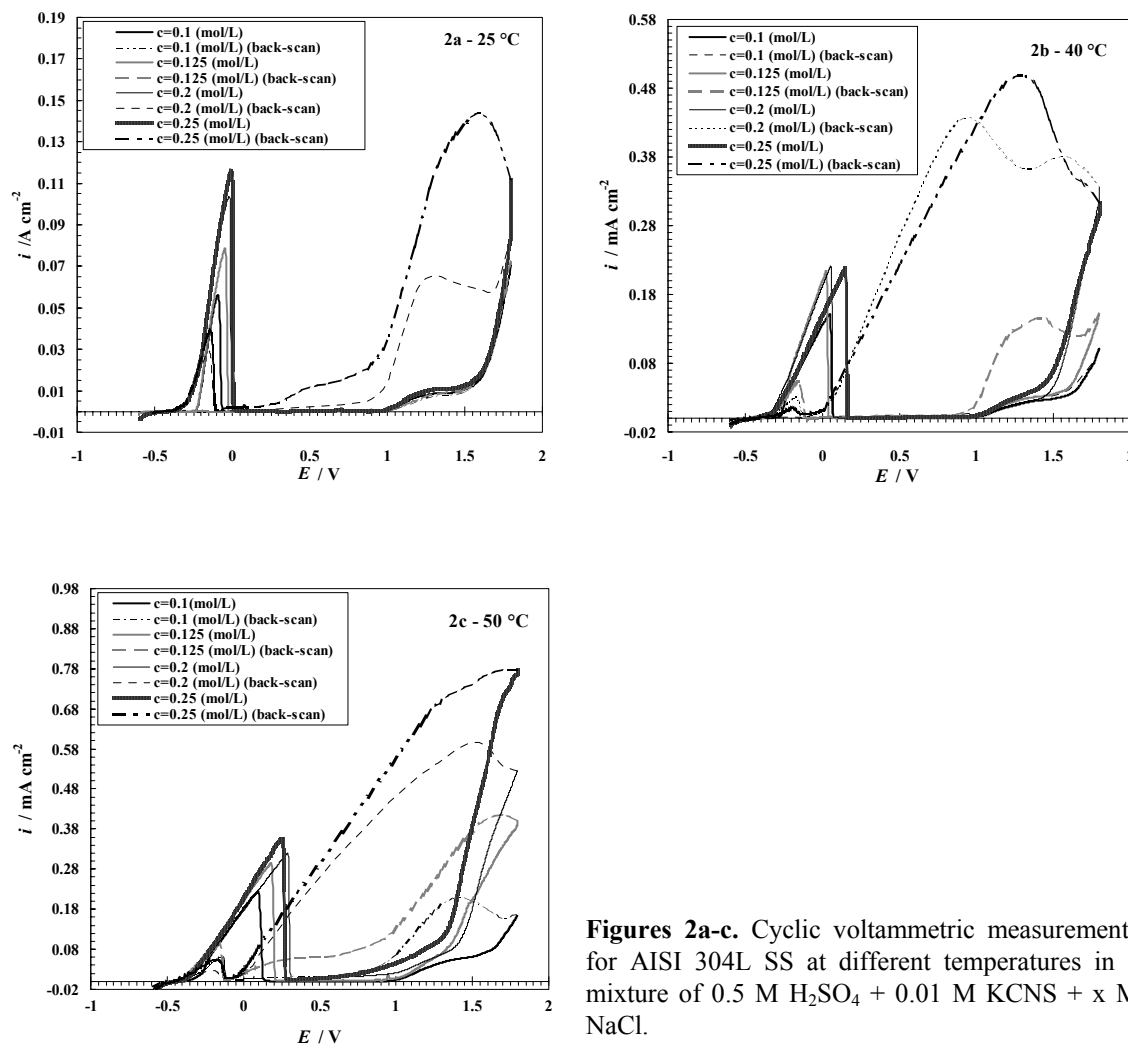
**Figures 2a-c.** Cyclic voltammetric measurements for AISI 304L SS at different temperatures in a mixture of 0.5 M H_2SO_4 + 0.01 M KCNS + x M NaCl.

The influence of the chloride ion concentration on the corrosion process is reflected in the characteristic corrosion kinetic parameters of, critical anodic current density i_{crit}, the breakdown or pitting potential E_{pp}, and through the passive current density at the pitting potential i_{pass} (Figures 3-5).

The corrosion parameters of AISI 304L SS were obtained from the polarization curves and presented collectively in Table 1.

Table 1. Corrosion parameters for AISI 304L stainless steel at different temperatures in a mixture of 0.5 M H_2SO_4 + 0.01 M KCNS + x M NaCl.

25 °C									
0.5 M H_2SO_4	i_{crit} /mAcm^{-2}		i_{corr} /mAcm^{-2}		i_{pass} /mAcm^{-2}		E_{pp} /V		m/g
+ x M NaCl	1st cycle	3st cycle	1st cycle	3st cycle	1st cycle	3st cycle	1st cycle	3st cycle	
0.0	85.2	53.3	0.070	0.010	0.047	0.043	0.53	0.53	0.0063
0.1	85.4	59.7	0.074	0.015	0.048	0.044	0.52	0.53	0.0067
0.125	95.2	79.2	0.095	0.020	0.058	0.046	0.51	0.515	0.0078
0.2	108.1	100.1	0.106	0.082	0.063	0.122	0.51	0.51	0.0255
0.25	123.7	120.2	0.109	0.087	0.094	0.140	0.51	0.49	0.0507
40 °C									
0.5 M H_2SO_4	i_{crit} /mAcm^{-2}		i_{corr} /mAcm^{-2}		i_{pass} /mAcm^{-2}		E_{pp} /V		m/g
+ x M NaCl	1st cycle	3st cycle	1st cycle	3st cycle	1st cycle	3st cycle	1st cycle	3st cycle	
0.0	120.0	139.9	0.46	0.066	0.049	0.046	0.49	0.49	0.0213
0.1	141.1	152	0.52	0.097	0.193	0.055	0.47	0.49	0.0266
0.125	163.0	176.3	0.56	0.183	0.194	0.087	0.43	0.46	0.0496
0.2	207.0	212.8	0.57	0.555	0.346	0.490	0.41	0.38	0.1959
0.25	213.6	239.3	0.58	0.589	0.618	0.906	0.40	0.33	0.6102
50 °C									
0.5 M H_2SO_4	i_{crit} /mAcm^{-2}		i_{corr} /mAcm^{-2}		i_{pass} /mAcm^{-2}		E_{pp} /V		m/g
+ x M NaCl	1st cycle	3st cycle	1st cycle	3st cycle	1st cycle	3st cycle	1st cycle	3st cycle	
0.0	189.5	218.7	0.078	0.278	0.051	0.055	0.49	0.49	0.0428
0.1	230.5	236.2	0.095	0.362	0.203	0.186	0.35	0.38	0.0907
0.125	256.7	274.2	1.03	0.453	1.5	3.900	0.32	0.31	0.2347
0.2	290.6	320.0	1.04	1.460	3.7	5.200	0.31	0.23	0.6102
0.25	321.3	359.2	1.07	1.500	4.7	5.470	0.27	0.22	0.889
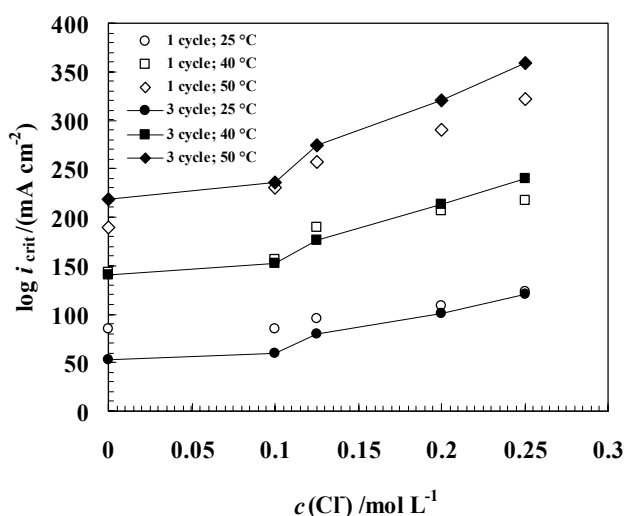
Figure 3. Logarithm of the critical anodic current density i_{crit}, vs. chloride ion concentration at T = 25, 40, and 50 °C for AISI 304L SS in 0.5 M H_2SO_4 + 0.01 M KCNS.
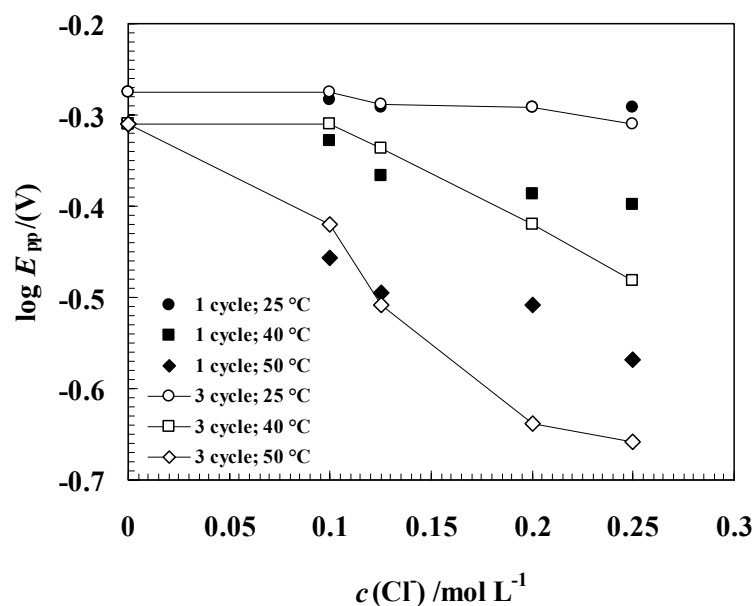
Figure 4. Logarithm of the pitting potential E_{pp}, vs. chloride ion concentration at T = 25, 40, and 50 °C for AISI 304L SS in 0.5 M H_2SO_4 + 0.01 M KCNS.
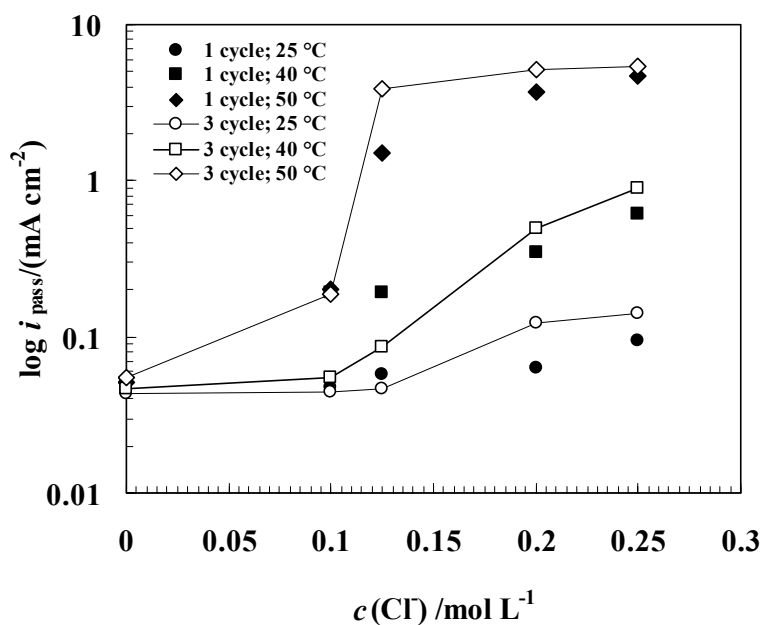
Figure 5. Logarithm of the passive current ipass at Epp, vs. chloride ion concentration at T = 25, 40, and 50 °C for AISI 304L SS in 0.5 M H_2SO_4 + 0.01 M KCNS.

Figures 3-5 represent the variation of the logarithm of the corrosion kinetic parameters, i.e. i_{crit}, E_{pp}, and i_{pass} (in the active and passive regions) at chloride ion concentrations and at three different temperatures. From all of them it could be noticed that addition of Cl$^-$ ions at low concentration has only a slight effect on the mechanism of SS passivity, while higher concentration of these ions accelerate the dissolution of SS in both, the active and passive regions. On the basis of the kinetic parameters of corrosion presented in Figures 3-5 it could be stated that when the concentration of chloride ions exceeds the value of $c = 0.125$ M NaCl, the slopes change markedly, and they become steeper with increasing temperature. A difference in the corrosion behaviour between the first and the third cycle is also observed. At the temperature of 25 °C i_{crit} in the third cycle decreased in comparison to the first one. Similar behaviour was observed in Figure 4, where E_{pp} did not change appreciably between cycles, but the curves in Figure 5 display higher values of i_{pass} in the third cycle when $c > 0.125$ M NaCl. These results may be due to changes in the nature of the passive film, and indicate that the protection properties of the passive film formed are altered. The corrosion susceptibility of SS increased when the temperature increased from room temperature to 40 °C and even more drastically with increasing molarity of added Cl$^-$ ions (above 0.125 M NaCl). The aggressiveness of halide anions could be ascribed to their ability to be adsorbed on the surface of the passive film, penetrating through the weak points and pores, in this way causing the film to rupture. For this reason, renewal of the passive layer (at high concentrations of aggressive ions) takes place at a high passive current density, until the dissolution rate of the passive layer becomes absolutely higher than the rate of repassivation. Finally, this causes, the passivation process to stop.

As the temperature of the solution and the concentration of Cl$^-$ ions increase the rate of oxide film formation decreases rapidly. This process is accompanied by a considerable shift of E_{pp} towards more negative values and by an appreciable increase in i_{pass}. In our case, where at $T = 50$ °C, and at $c = 0.125$ M NaCl, it was shown that i_{pass} increased by two orders of magnitude (Figure 5) and passivity was entirely lost.

The weight-loss m, of AISI 304L SS specimens after polarisation measurements, when they have corroded in mixtures of 0.5 M H$_2$SO$_4$ + 0.01 M KCNS + x M NaCl at 25, 40 and 50 °C are presented in Figure 6. The effects shown in Figure 6 are in accordance with results which were obtained from potentiodynamic scanning

experiments. On the basis of the data obtained from electrochemical measurements (Figures 3-6) it could be concluded that the critical ion (Cl⁻) concentration for stable pitting for AISI 304L SS in 0.5 M H_2SO_4 + 0.01 M KCNS occurs when c >0.125 M NaCl. Furthermore, the critical pitting temperature could be limited to 40 °C in the chosen corrosion medium. As the temperature of the solution increases up to 50 °C, the rate of oxide formation decreases progressively. This behaviour could be attributed to the increase of the solubility of the surface oxide film or film porosity with increasing temperature in that solution. The CIC at that temperature dropped to a lower concentration of Cl⁻ ions, of 0.1M NaCl.
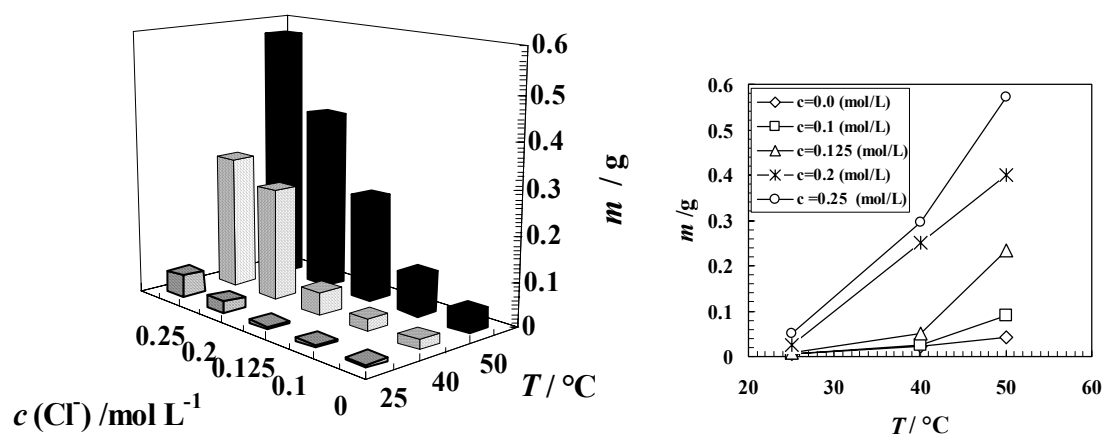
Figure 6. Weight-loss *m* of AISI 304L SS specimen after polarisation measurements in mixtures of 0.5 M H_2SO_4 + 0.01 M KCNS + x M NaCl at 25, 40 and 50 °C.

The activation energy of the corrosion process was obtained from the linear relation between the rate of the corrosion reaction, assigned as the corrosion current density, icorr, with temperature, which obeys the familiar Arrhenius equation. This linear relation is represented as (Eq.1),

$$\frac{d \log i_{corr}}{d\left(\frac{1}{T}\right)} = \frac{E_a}{2.303R} \tag{1}$$

where, E_a is the activation energy of the corrosion process. At each temperature, the corrosion current, i_{corr}, was obtained from the polarization measurements. The linear

plots at five different concentrations of added NaCl are presented collectively in Figure 7.
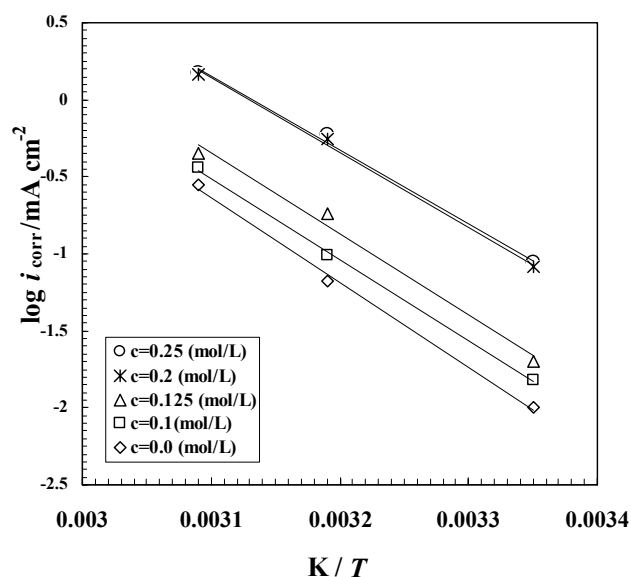
Figure 7. Arrhenius plots of the corrosion current i_{corr} in the Tafel region of the polarization curves of the AISI 304L SS in mixtures of 0.5 M H_2SO_4 + 0.01 M KCNS + x M NaCl.

The calculated values of the activation energy are -45.84, -43.84, -43.82, -40,32 and -39.86 kJ mol^{-1} for c = 0.0, 0.1, 0.125, 0.2 and 0.25 M NaCl, respectively. It is clear that the values of the activation energy, taking into account the experimental error (8 %), do not change much with concentration, suggesting the same underlying mechanism for the passivation process. The small decrease in the activation energy values with increasing concentration of chloride ions could be interpreted as diminishing stability of the passive film.
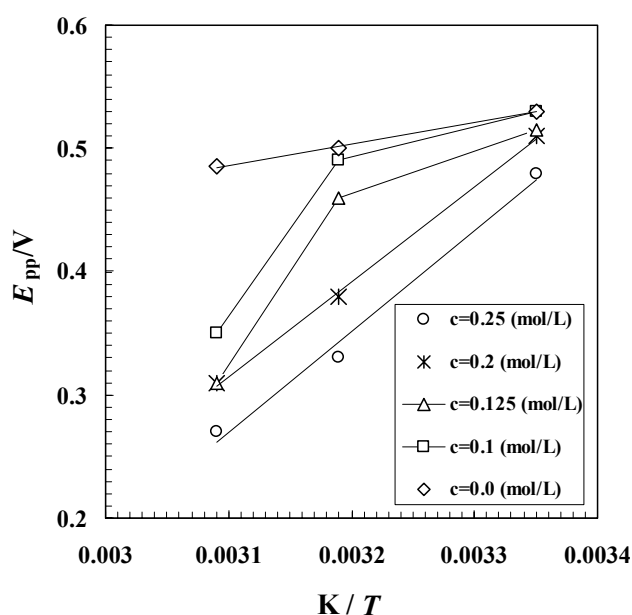
Figure 8. Variation of the of pitting potential E_{pp} with the reciprocal of temperature in mixtures of 0.5 M H₂SO₄ + 0.01 M KCNS + x M NaCl.

The Figure 8 shows a linear relation between the pitting potential Epp, and the reciprocal of temperature in chloride-free solution and at concentrations c = 0.2 and 0.25 M of added NaCl. In the interval 0 < c < 0.2 M NaCl a change of slope is observed close to the CIC and at the CPT. It could be speculated that this interval exhibits the approximate limit between metastable pitting and the growth of stable pits. Besides, it is true that the onset of stable pitting is accompanied by a sharp rise in the current at the pitting potential.6

Conclusions

- Simultaneous increase in temperature and the concentration of aggressive ions causes a drastic change in the corrosion behaviour of AISI 304L stainless steel in mixtures of 0.5 M H₂SO₄ + 0.01 M KCNS. The time of anodic arrest increases, while the rate of oxide film formation decreases.

- The critical ion (Cl⁻) concentration (CIC) and critical pitting corrosion temperature (CPT) were determined on the basis of the characteristic corrosion parameters which were obtained through potentiodynamic scanning experiments. The initiation of stable pits on the passive metal cannot occur unless the concentration of aggressive ions in the solution is above a certain value. The

corrosion resistance of AISI 304L stainless steel was limited to temperatures below 40 °C and concentrations of chloride ion below $c = 0.125$ M NaCl.

- As the temperature of the solution was increased to 50 °C the oxide formation rate decreased progressively. In this case the passive current density increased by two orders of magnitude and finally at $c = 0.25$ M NaCl the polarization curve showed no sign of passivity at all. This behaviour could be attributed to the increase of the solubility of the surface oxide film or film porosity with increasing temperature in that solution. The CIC at that temperature (50 °C) dropped to the lower concentration of Cl^- ions of 0.1 M NaCl .

- The results of return scans are consistent with the conclusions from the anodic polarization measurements.

- The activation energy of the process was found to equal $-42.0 (1 \pm 0.08)$ kJ mol^{-1}

- The region of parameters near the CIC and CPT seems to represent the border between metastable and stable pitting.

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Povzetek

Proučevali smo korozijsko odpornost avstenitnega jekla AISI 304L v vodnih raztopinah 0,5 M H_2SO_4 + 0,01 M KCNS + x M NaCl pri temperaturah 25, 40, in 50 °C. Kritično koncentracijo kloridnih ionov (CIC), ter kritično temperaturo (CPT) potrebno za začetek točkaste korozije, smo določili na podlagi parametrov odčitanih iz potenciodinamskih polarizacijskih krivulj. Za izbrano jeklo, v že prej omenjenem korozivnem mediju, sta njuni vrednosti sledeči; $c > 0,125$ M NaCl, ter $T = 40$ °C. Z naraščajočo temperaturo se E_{pp} pomika proti negativnejšim vrednostim. Odvisnost E_{pp} z $1/T$ daje linearno zvezo, razen v neposredni bližini CIC in CTP, kjer premica spremeni naklon. Predvideli smo, da to območje predstavlja okvirno mejo med 'metastabilnim in stabilnim pittingom'.