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Pitting susceptibility of UNS NO. 8904 stainless steel in bromide-sulphide solution

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The effect of sulphide ion on the pitting corrosion behaviour of UNS* no. 8904 (904L) stainless steel (SS) in 0.6 M NaBr at 25 °C has been investigated by using potentiodynamic anodic polarization and electrochemical impedance spectroscopy techniques. The pitting potential, E_{pit}, in 0.6 M NaBr + 10^{-2} M Na_2S was more negative than that obtained in 0.6 M NaBr, and decreased with increasing temperature in the range 25–60 °C. Scanning electron microscopy observation showed that elemental sulphur formed on the steel surface before E_{pit} was reached in 0.6 M NaBr + 10^{-2} M Na_2S at 60 °C. E_{pit} of 904L SS was pH independent in the pH range from 3–10 of 0.6 M NaBr + 10^{-2} M Na_2S at 25 °C, while at high pH values the pitting was suppressed. The impedance measurements showed that the charge transfer resistance, R_t, decreased with time, when the controlled potential became higher than E_{pit}.

1. Introduction

The corrosion behaviour of stainless steels due to the presence of sulphur compounds dissolved in corrosive solutions has received the attention of many investigators due to its practical and fundamental standpoints [1–5]. Some of the practical cases are related to the oil and gas industry [6], to the production of heavy water by the Girdler–sulphide process [7], to paper machines [8] as well as microbial corrosion [9]. It has been reported that sulphide ions promote the corrosion of stainless steel by chloride ions [10]. A similar effect is observed for stainless steel in a mixture of chloride and thiocyanate ions, as well as chloride and thiosulphate ions [11]. In all cases, at a constant chloride concentration, the increase of suphur-containing anion concentration shifts the corresponding pitting potential towards more negative values.

904L stainless steel (SS) has been developed as a high molybdenum-containing steel for severe corrosive environments, especially for sea water when it is used as coolant in heat exchangers. However, many investigations showed the occurrence of some corrosion problems at elevated temperature for 904L SS in chloride–sulphate [12], chloride and sea water [13, 14], chloride–sulphide [15] solutions as well as in bromide solution at room temperature [16] under different environmental conditions. Therefore, in a continuation of our investigations [13–16] on the pitting corrosion behaviour of 904L SS in environments such as those encountered in several industries, the present work was performed to study the pitting corrosion behaviour of 904L SS in bromide–sulphide solution under different environmental factors such as temperature, the presence of sulphide ions, and pH values.

2. Experimental procedure

Each working electrode consisted of a commercial UNS NO. 8904 stainless steel. The percentage average chemical compositions is: C, 0.015; Mn, 1.55; S, 0.01; P, 0.028; Si, 0.58; Ni, 23.5; Cr, 20; Mo, 4.5; V, 0.24; W, 0.6 and the balance iron. The electrodes were cut from a 2 mm thick sheet and were mechanically polished with emery paper down to 600 grit. The back and edges of the electrodes were coated with epoxy resin, allowing 1 cm^2 to be exposed to the test solution. All solutions were prepared from analytical grade reagents and doubly distilled water. The pH of the solutions was adjusted to give values between 3 and 12 by adding acetic acid or NaOH. All the experiments were conducted under thermostatted conditions at the desired temperature. Potentiodynamic anodic polarization experiments were carried out using a scan rate of 600 mV h^{-1}, commencing at free corrosion potential after the electrode had been immersed for 30 min in the test solution. The potential of the working electrode was measured against a saturated calomel electrode (SCE). The E_{pit} was determined from the forward anodic polarization curves as mentioned elsewhere [14, 17]. The surface morphology of the electrode after potentiostatic anodic treatment at 200 mV,

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in 0.6 M NaBr + 10^{-2} M Na_2S at 60 °C, then water rinsing and gold coating, was observed by using scanning electron microscopy (SEM). The electrochemical impedance spectroscopy was carried out for 904L SS in different solutions under potentiostatic anodic condition at the desired thermostatted temperature. The impedance measurement unit (CNF-6378 circuit Design Block Co., Ltd) was used. The instrument was provided with a frequency response analyser (FRA) model S-5720, NF circuit Design Block Co., Ltd, serving to make the frequency sweep measured on a logarithmic scale from 0.1 Hz to 10 KHz using a small sinusoidal perturbation signal. The measurements were controlled by a personal computer (PC-9801 F, Nippon Electronic Corporation), and the data were memorized at the same time. Complex plane graphs of Cole–Cole plots were obtained using an *X–Y* plotter (MP 3300 Graphec Corop); more details are described elsewhere [18].

3. Results

3.1. The effect of temperature on E_{pit}

Fig. 1 illustrates the dependence of E_{pit} of 904 L SS on temperature in 0.6 M NaBr + 10^{-2} M Na_2S as well as 0.6 M NaBr + 0.1 M Na_2SO_4 in comparison with 0.6 M NaBr at pH 7.5. As seen, a linear dependence of E_{pit} on temperature is observed; these results indicate an occurrence of a temperature-affected change in the protective properties of the passive film, resulting in a decrease of its resistance to breakdown as temperature is increased.

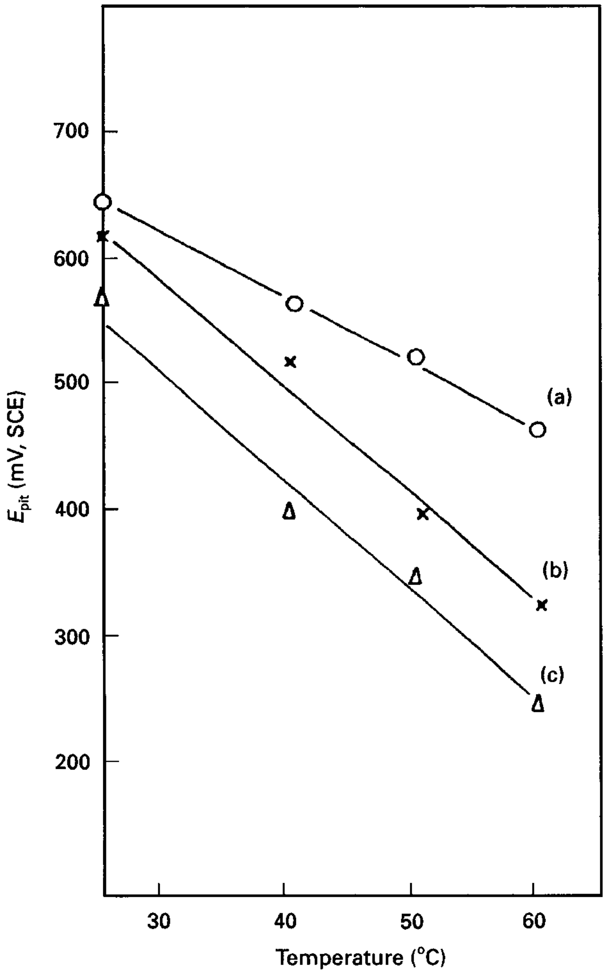

Figure 1 Temperature dependence of pitting potential, E_{pit}, of 904L SS in different solutions at pH 7.5. (a) 0.6 M NaBr + 0.1 M Na_2SO_4; (b) 0.6 M NaBr; (c) 0.6 M NaBr + 10^{-2} M Na_2S.

3.2. Behaviour of 904L SS in bromide–sulphide and bromide–sulphate solution

Potentiodynamic cyclic anodic polarization curves for 904L SS in 10^{-2} M Na_2S, 0.6 M NaBr and 0.6 M NaBr + 10^{-2} M Na_2S at pH 7.5 and at 25 °C, are shown in Fig. 2. On the positive-going potential scan in 10^{-2} M Na_2S (Fig. 2a), the scan exhibits a complete passivation with a passivation current, I_{pass}, of 150 $\mu A\,cm^{-2}$ and without any sign for passivity breakdown until oxygen evolution. This behaviour indicates the absence of pitting attack due to the high protectivity of the passive film formed in sulphide solution [15]. In 0.6 M NaBr (Fig. 2b), the alloy exhibited pitting corrosion at E_{pit} which amounted to 620 mV. It has been reported that bromide ions are more aggressive than chloride ions for high molybdenum alloyed stainless steel [19], titanium [20] and tantalum [21]. The anodic response of 904L SS in 0.6 M NaBr + 10^{-2} M Na_2S (Fig. 2c) displays two anodic current peaks prior to attaining the breakdown potential at 570 mV. The first anodic peak is associated with the formation of sulphide species film, then electro-oxidized to elemental sulphur at a potential value corresponding to the second peak [10, 22] (+ 200 mV); however, the electro-formation of elemental sulphur on the surface of 904L SS was confirmed by SEM as shown in Fig. 3. It has been reported [23–25] that various non-aggressive anions, e.g. OH^-, NO_3^-, SO_4^{2-} and ClO_4^-, when added to chloride solutions, shift E_{pit} to more noble values, accounting for an increased resistance to pitting. The influence of increasing amounts of SO_4^{2-} ions on the potentiodynamic anodic polarization of 904L SS in 0.6 M NaBr is shown in Fig. 4.

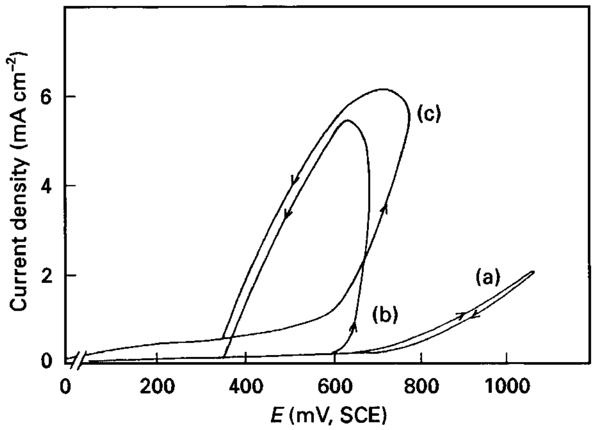

Figure 2 Potentiodynamic cyclic anodic polarization of 904L SS, at pH 7.5 and at 25 °C, in (a) 10^{-2} M Na_2S, (b) 0.6 M NaBr, (c) 0.6 M NaBr + 10^{-2} M Na_2S.

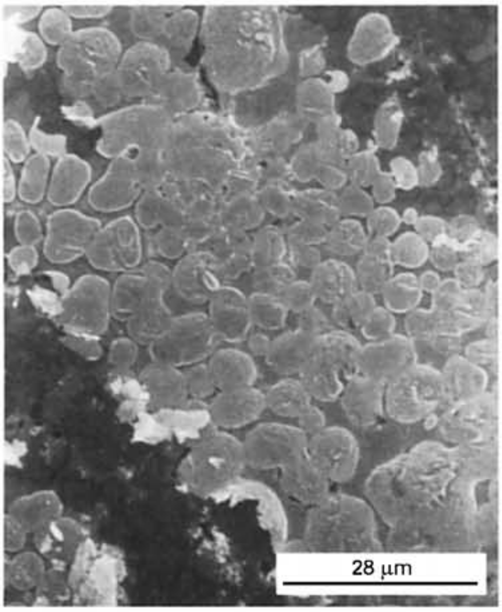

Figure 3 Scanning electron micrograph of the elemental sulphur deposit on 904L SS electrode after potentiostaic anodic treatment for 1h at 200 mV (SCE) in 0.6 M NaBr + 10^{-2} M Na_2S at 60 °C.

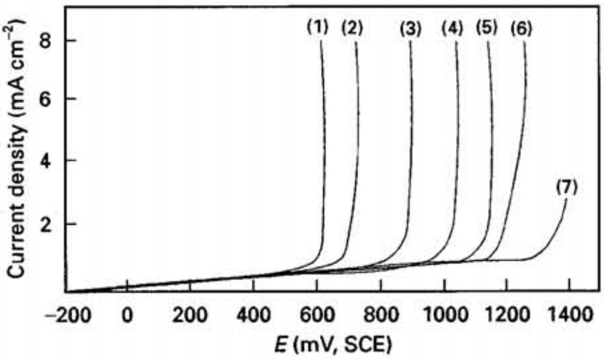

Figure 4 Potentiodynamic anodic polarization curves of 904L SS in 0.6 M NaBr with and without different additions of Na_2SO_4 at 60 °C. (1) 0 Na_2SO_4, (2) 0.1 M Na_2SO_4, (3) 0.3 M Na_2SO_4, (4) 0.6 M Na_2SO_4, (5) 0.9 M Na_2SO_4, (6) 1.2 M Na_2SO_4, (7) 0.1 M Na_2SO_4.

3.3. Effect of pH on E_{pit}

The effect of pH on the E_{pit} of 904L SS has been investigated in 0.6 M NaBr + 0.1 M Na_2SO_4 and 0.6 M NaBr + 10^{-2} M Na_2S at 25 °C, as shown in Fig. 5. In both solutions, E_{pit} amounts to 680 and 570 mV for bromide–sulphate and bromide–sulphide, respectively, while in strong alkaline solutions (pH $\geqslant$ 11), the pitting corrosion is completely inhibited.

3.4. Impedance spectroscopy measurements

Impedance spectroscopy was performed for 904L SS in 0.1 M Na_2SO_4, 0.6 M NaBr, 0.6 M NaBr + 0.1 M Na_2SO_4 and 0.6 M NaBr + 10^{-2} M Na_2S at 25 °C under potentiostatic conditions. Figs 6 and 7 show the typical changes of the impedance spectra measured in these solutions at the passive (+ 200 mV) and pitting (600 mV) potential values. For comparison, the impedance measurements were made in 0.6 M NaCl

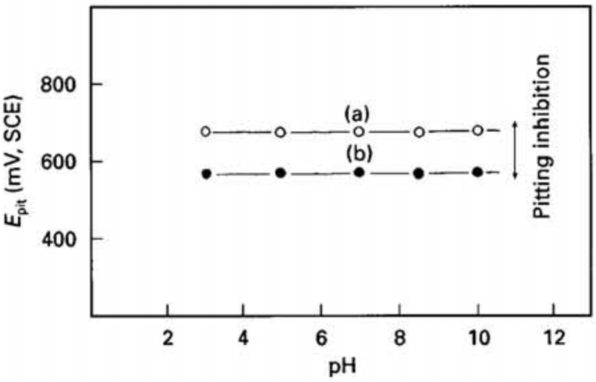

Figure 5 pH dependence of pitting potential, E_{pit}, of 904L SS, at 25 °C in (a) 0.6 M NaBr + 0.1 M Na_2SO_4, (b) 0.6 M NaBr + 10^{-2} M Na_2S.

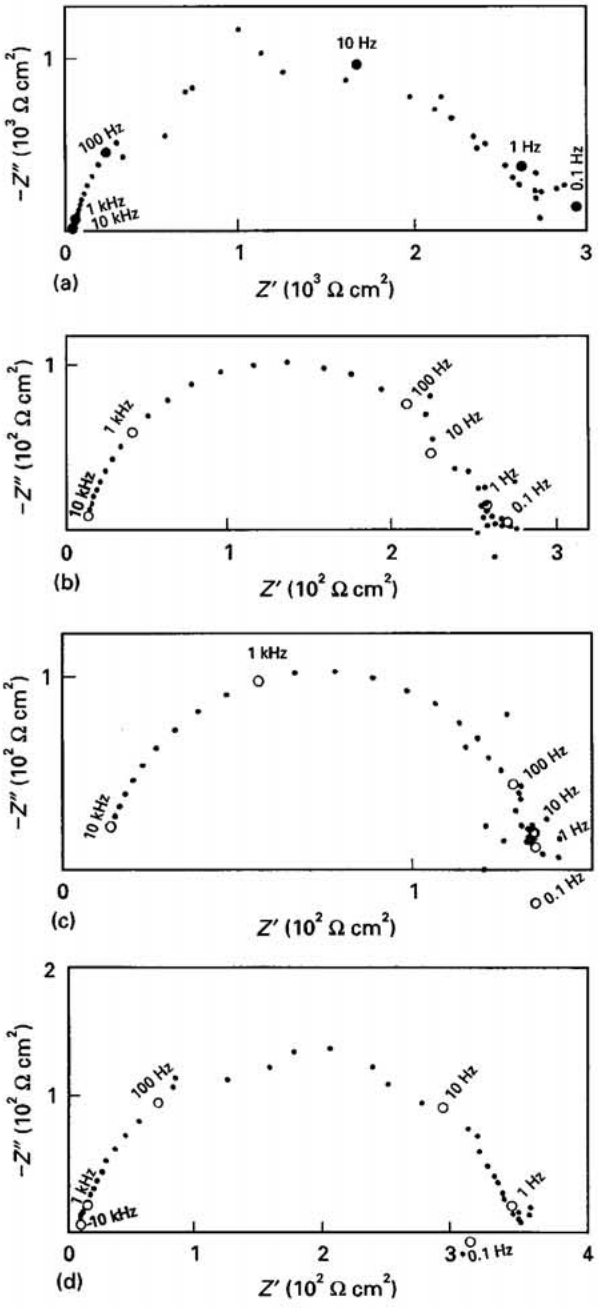

Figure 6 Cole–Cole plots for 904L SS under potentiostatic condition at 200 mV (SCE) and at 25 °C in (a) 0.1 M Na_2SO_4, (b) 0.6 M NaBr, (c) 0.6 M NaBr + 0.1 M Na_2SO_4, (d) 0.6 M NaBr + 10^{-2} M Na_2S.

solution under an applied anodic potential of 620 mV at 25 and at 60 °C, as shown in Fig. 8. The interfacial impedance spectra for 904L in all solutions under test are characterized by a capacitive semicircle at higher frequency region. The charge transfer resistance, R_t, was evaluated as the diameter of the capacitive semicircle. It is observed that the impedance did not change with time in sulphate- and bromide-containing solutions at the passive potential, as well as in chloride solution at a potential of 620 mV at 25 °C. The time dependence of the charge-transfer resistance, R_t, of 904L SS in 0.6 M NaBr at 650 mV and in 0.6 M NaCl at 620 mV, at 25 and at 60 °C, respectively is shown in Fig. 9.

4. Discussion

Two possibilities to explain the influence of temperature on E_{pit} may be taken into consideration. First,

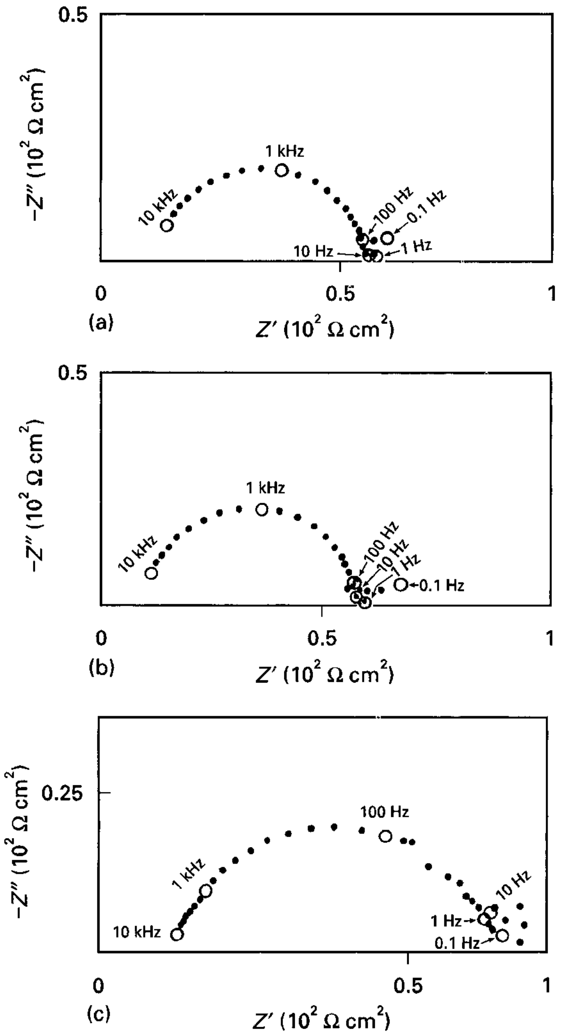

Figure 7 Cole–Cole plots for 904L SS under potentiostatic condition at 650 mV (SCE) and at 25 °C in (a) 0.6 M NaBr, (b) 0.6 M NaBr + 0.1 M Na_2SO_4, (c) 0.6 M NaBr + 10^{-2} M Na_2S.

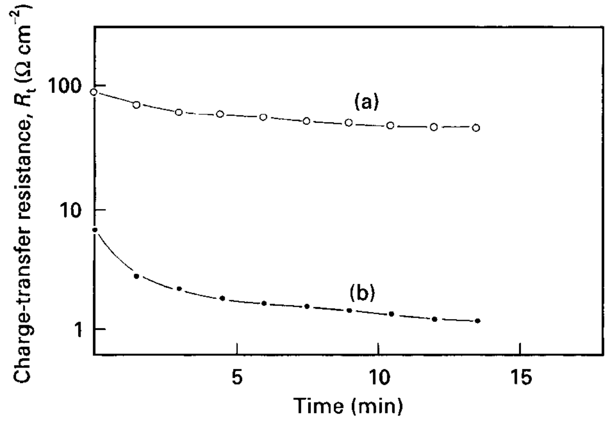

Figure 9 Time dependence of the charge-transfer resistance, R_t, of 904L SS in (a) 0.6 M NaBr at 650 mV (SCE) and at 25 °C, and (b) 0.6 M NaCl at 620 mV (SCE) and at 60 °C.

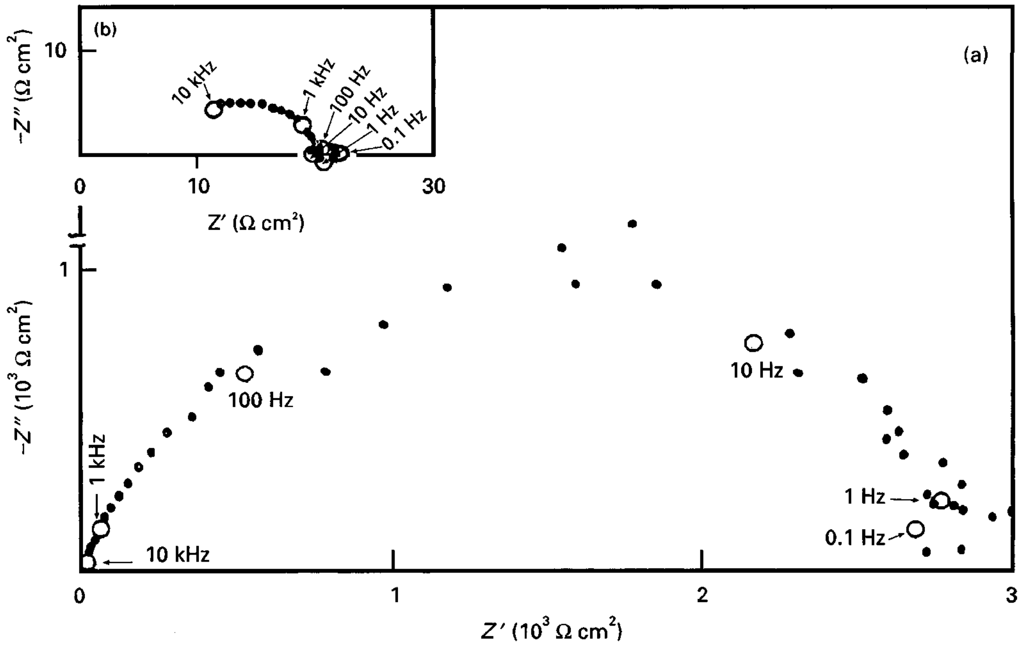

Figure 8 Cole–Cole plots for 904L SS in 0.6 M NaCl under potentiostatic condition at 620 mV (SCE) (a) at 25 °C, and (b) at 60 °C.

the porosity of the film increases with temperature. Second, the passive film undergoes an intrinsic modification of its chemical composition and/or physical structure. Based on the curves of Fig. 1, both possibilities must be considered. An increase in porosity with temperature is supported by the fact that halide ions have been found to be incorporated into the passive film on stainless steel at high temperature, but not in the lower temperature range [26]. For the second possibility, for example, Manning and Duquette [27] found that the oxide film on stainless steel changes from p-type at room temperature to n-type at higher temperature. However, insufficient information on the influence of temperature on the composition and structure of passive films is available to decide which of these two alternatives is correct. The present results indicate that 904L SS is susceptible to pitting in bromide-containing solutions at room temperature (25 °C), and the protective efficiency of the steel decreases with an increase in temperature. However, several investigators reported [12–14] that the corrosion resistance of this steel is very high in chloride-containing solution at room temperature, even when the potential is raised into the transpassive potential region at which the transpassive dissolution occurs.

The results in Fig. 2 and Fig. 3 clearly indicate that the decrease in the pitting corrosion resistance of 904L SS in bromide–sulphide mixture could be attributed to the formation of elemental sulphur on the surface, which accelerate the pitting corrosion [28]. Similar behaviour has been found for the same alloy in chloride–sulphide solution [15] at 60 °C. Shoesmith *et al.* [5] demonstrated that the formation of elemental sulphur on a stainless steel surface in aqueous H_2S solution could occur via an electrochemical mechanism in the absence of soluble iron. It is obvious from Fig. 4 that E_{pit} in 0.6 M NaBr moves to more positive values with increasing SO_4^{2-} ion concentration. At and above 0.6 M Na_2SO_4, no pitting occurs at all, the observed current increase being characteristic of transpassivity in the absence of Br^-. The curves of Fig. 4 indicate that sufficient SO_4^{2-} ion added to the Br^- solution inhibits pitting of 904L SS. This finding is in agreement with that previously reported in chloride for 904L SS [14] as well as for 18-8 stainless steel [29]. The result of Fig. 5 could be explained in view of the local acidification theory [30, 31], and agrees with that obtained for several kinds [13–15, 29] of stainless steels in chloride solution, especially in the acidic and natural pH range. The pitting inhibition occurring at higher pH values of these solutions is related to the well-established pitting inhibition effect of a high concentration OH^- [29, 32] ions as well as the fact that in bromide–sulphide solution, both SH^- and OH^- simultaneously attack the surface, yielding sulphide and oxide species, respectively [33].

It was observed (Figs 6 and 8) that the impedance spectra for 904L did not change with time in sulphate- and bromide-containing solutions at the passive potential as well as in a chloride solution at a potential of 620 mV at 25 °C. This behaviour indicates the presence of general corrosive attack with a low corrosion rate, and coincides with the surface observation which indicates the absence of pitting corrosion. When the applied potential was controlled at the pitting potential either in a bromide-containing solution at 25 °C (Fig. 7a) or in chloride solution at 60 °C (Fig. 8b), R_t values were less than that obtained either in a bromide-containing solution at the passive potential or in chloride at 25 °C, and also at the pitting potential, R_t, decreased with time (Fig. 9). The decrease of R_t with time indicates an increase of the pit-growth rate and/or area fraction at which pitting occurs [34]. However, Wang *et al.* [35] reported that the Nyquist and Bode diagrams for unpitted and pitted specimens of 304 SS in 1 M NaCl had the same character, but the R_t value was less when severe pitting was present. Mansfeld *et al.* [36, 37] demonstrated that when pitting or crevice corrosion occur, the dependence in the capacitive frequency region decreases greatly, and the dramatic changes of the impedance indicate the initiation and propagation of the pits.

As shown in Figs 6–8, if the capacitive loop at the higher frequency region is assumed to be a semicircle, the centre of the semicircle is usually depressed on the real axis, thus the θ value is defined as the angle between the line made by the intercept at higher frequency and the centre of the semicircle and the real axis. The θ value is considered to be a parameter corresponding to reaction uniformity at the interface. The results shown in Table I, indicate that the value of θ in all solutions under test, increases when pitting occurs; this behaviour arises from the surface heterogeneity due to the pitting attack. The time constant, τ_0, corresponding to the surface reactivity is represented as a product of the double layer capacitance, C_{dl}, by

TABLE I Impedance parameters obtained for 904L SS in different solutions under potentiostatic conditions

Solution	Passive region, where $E = 200$ mV (SCE), at 25 °C				Pitting region, where $E = 650$ mV (SCE), at 25 °C only Cl^- at 60 °C			
	R_t (Ω)	τ_0 (s)	C_{dl} (F)	θ (deg)	R_t (Ω)	τ_0 (s)	C_{dl} (F)	θ (deg)
0.1 M Na_2SO_4	3×10^3	1.4×10^{-2}	4.9×10^{-6}	5				
0.6 M NaBr	2.5×10^2	8.2×10^{-4}	0.4×10^{-6}	7	80	10^{-4}	3.2×10^{-6}	13
0.6 M NaBr + 0.1 M Na_2SO_4	1.7×10^2	3.2×10^{-4}	0.5×10^{-6}	6	50	2×10^{-4}	1.8×10^{-6}	12
0.6 M NaBr + 10^{-2} M Na_2S	3.5×10^2	7.5×10^{-3}	0.5×10^{-6}	7	50	10^{-3}	2.1×10^{-5}	14
0.6 M NaCl	3×10^3	8.3×10^{-3}	0.1×10^{-6}	9	6.7	10^{-4}	2.7×10^{-6}	22

R_t, i.e. $\tau_0 = R_t \cdot C_{dl}$. In the impedance spectra, τ_0 can be calculated from the top frequency, f_0, of the semicircle, where $\tau_0 = (2\pi f_0)^{-1}$. τ_0 is considered to be the parameter due to the reaction rate constant for the corrosion process, because τ has a dimension of time. However, it is obvious from Table I that τ_0 values decreases and C_{dl} values increased in all solutions under test when pitting was present. These results are in agreement with those reported for aluminium [34]. Therefore, it seems that the occurrence of pitting on 904L SS in aggressive anion (Cl^- at 60 °C or Br^- at 25 °C) is associated with a decrease in R_t value, and an increase in both θ and C_{dl} values.

5. Conclusions

1. E_{pit} of 904L SS in 0.6 M NaBr + 10^{-2} M Na_2S solution decreases linearly on increasing the temperature from 25 °C to 60 °C.

2. The anodic scan of 904L SS in bromide–sulphide solution displays two current peaks prior to attaining the breakdown potential. The peaks are related to the formation of sulphide species and elemental sulphur, respectively. The electro-formation of the elemental sulphur is confirmed by SEM.

3. E_{pit} of 904L SS is pH independent in bromide–sulphide in the pH range from 3–10, while at higher pH values, pitting corrosion is inhibited due to the effect of a high concentration of OH^- ions.

4. When pitting corrosion of 904L SS occurs in 0.6 M bromide at 25 °C or in 0.6 M chloride at 60 °C, the measured charge-transfer resistance decreases.

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