J Appl Electrochem (2009) 39:1703–1708
DOI 10.1007/s10800-009-9863-9

ORIGINAL PAPER

Effect of temperature change rate on the critical pitting temperature for duplex stainless steel

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Received: 23 August 2008 / Accepted: 4 March 2009

Abstract The effect of temperature change rate on the critical pitting temperature (CPT) for two kinds of duplex stainless steels (DSS, namely UNS S31803 and UNS S32750) in 1 mol L^{-1} NaCl solution was investigated using the potentiostatic current transient technique. The values of CPT for two DSSs all increased as the temperature change rate (υ) increased. A linear relationship between the CPT and the square root of temperature change rate ($\upsilon^{1/2}$) was found. Furthermore, deriving from the point defect model (PDM), this particular relationship received theoretical support at low temperature change rates.

Keywords Duplex stainless steel · Pitting corrosion · Critical pitting temperature · Temperature change rate · The point defect model

List of symbols

J_{ca}	Cation diffusion rate at the metal/film interface/$\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$
J_{m}	Rate of elimination of cation vacancies at the metal/film interface/$\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$
t	Incubation time for passivity breakdown at a single site/s
J^0	Parameter defined by Eq. 3
u	Parameter defined by Eq. 4
F	Faraday's constant (96,487 °C mol^{-1})
V_{ext}	Applied potential with respect to a reference electrode/V
R	Gas constant (8.314 J $\mathrm{K}^{-1}\ \mathrm{mol}^{-1}$)
T	Absolute temperature/K
a_{Cl^-}	Activity of chloride ion/mol L^{-1}
K	Parameter defined by Eq. 6
$D^*_{V_M^{\chi'}}$	Cation vacancy diffusivity/$\mathrm{cm}^2\ \mathrm{s}^{-1}$
N_v	Avogadro's number ($6.023 \times 10^{23}\ \mathrm{mol}^{-1}$)
ΔG_{S}^0	Change in Gibbs energy for Schottky-pair reaction/J mol^{-1}
ΔG_{A-1}^0	Standard Gibbs energy change for absorption of an aggressive species into an oxygen vacancy at the film/solution interface/J mol^{-1}
$\phi_{\mathrm{f/s}}^0$	Constant/V
D_0	Diffusion coefficient/$\mathrm{cm}^2\ \mathrm{s}^{-1}$
ΔE	Diffusion activation energy/J mol^{-1}
T_{cpt}	Critical pitting temperature for passivity breakdown at a single site/K
ΔT	Over temperature for passivity breakdown at a single site/K

Greek letters

τ	Time for passivity breakdown at a single site once a critical vacancy condensation had been achieved/s
ξ	Critical concentration of cation vacancies for passivity breakdown/cm^{-2}
χ	Stoichiometry of the passive film, $MO_{\chi/2}$, and the oxidation state of the cation
α	Dependence of potential drop across the film/solution interface on the applied potential
Ω	Mole volume of the barrier layer per gram-atom of the cation/$\mathrm{cm}^3\ \mathrm{mol}^{-1}$
β	Dependence of potential drop across the film/solution interface on pH
ε	Field strength in the passivity film/V cm^{-1}
ξ'	Defined by Eq. 12
υ	Temperature change rate/K s^{-1}

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1 Introduction

It is generally accepted that temperature is one of the most important factors affecting pitting corrosion. The temperature dependence of an electrochemical reaction rate for pitting corrosion occurring on the surface of stainless steels is determined conventionally in two ways, measuring current densities under constant temperature conditions (thermostatic) and recording controlled varying potentials (voltammetry) over a number of different temperatures. The concept of critical pitting temperature (CPT) was first introduced by Brigham and Tozer and has since been widely used as a criterion for ranking pitting susceptibility in stainless steels [1, 2]. The literature on this subject is large. Qvarfort [3] and Newman [4] argued that stable pitting did not occur below the CPT, at least not before the onset of transpassive corrosion; but above the CPT, stable pitting occurred well below transpassive potentials. The CPT was usually measured in fairly concentrated chloride solutions, but they were independent of chloride concentration in the range 0.01 M–5 M [3, 4] and of pH in the range 1–7 [3]. However, the CPT may be influenced by high sulphate [5] or thiosulphate [6] concentrations, and different results were obtained when chlorides in the test solution were replaced by bromides [7]. The CPT was also dependent on surface roughness of the samples [8].

The CPT, regarded as more sensitive than the more-often measured pitting potential, was introduced the ASTM standards in 1997 [9]. Brigham [10] proposed controlling the sample potentiostatically in chloride solution. The CPT was the temperature at which the current density increased sharply to a value of 10 μA cm^{-2}. Salinas-Bravo and Newman [11] determined the CPT of duplex stainless steel via a zero resistance ammeter (ZRA). The current flowing between the two specimens increased abruptly as the solution was heated, giving a rapid measurement of the CPT. Qvarfort [3] obtained the CPT of austenitic steels with different Mo contents by plotting the pitting potential (E_p) as a function of the test temperature. Using a potentiostatic technique to measure the CPT, the temperature of the test solution was required to increase at a constant temperature change rate. This was similar with pitting potential (E_p) obtained using the potentiodynamic anodic polarization at a constant potential sweep rate (υ). Several papers reported that E_p was affected by potential sweep rate. Macdonald [12–14] pointed out that on the basic of the point defect model (PDM) a relationship between pitting potential and potential sweep rate existed. In parallel, the pitting potential was a linear function of the square root of potential sweep rate at low sweep rates. Some work has investigated the effect of temperature change rate on the critical pitting temperature [15] and whether a particular relationship between CPT and temperature change rate also exists.

In this work, we aimed primarily at investigating the effect of temperature change rate on the CPT using the potentiostatic current transient technique. A further aim was to elucidate the underlying mechanisms of the effect of temperature change rate on pitting behavior.

2 Experimental

The specimens chosen were fabricated from commercial duplex stainless steel tubes with dimension 1.2 cm × 1.2 cm, UNS S31803 (SAF 2205) and UNS S32750 (SAF 2507). The chemical compositions are shown in Table 1.

All electrochemical measurements were carried out using a potentiostat (PARSTAT2273). A platinum foil and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. Unless otherwise stated in this paper, all potentials recorded are referred to SCE. The samples acting as the working electrodes were embedded in epoxy resin. Prior to each experiment, the working electrode was ground mechanically using successive grades of emery paper up to 1,000 grit, rinsed with distilled water and dried in air. In order to avoid crevice corrosion, the area of the specimen near the interface between the resin and the specimen was sealed with special silica gel sealant and dried in air. The exposed electrode surface area was 1 cm^2. The test solution, 1 mol L^{-1} NaCl, was made up from analytical grade reagents and distilled water.

The potentiostatic technique was based on recording the current flowing system at constant applied potential as a function of system temperature. The temperature was controlled externally using a programmable temperature controller (Zjnbth No.THCD-09) capable of a wide range of temperature change rates. The relative error in establishing the real temperature of the system in relation to the applied temperature was 0.1%. The temperature change rates were in the range 1.67×10^{-3}–4.17×10^{-2} K s^{-1}.

Table 1 Chemical compositions (wt.%) of UNS S31803 and UNS S32750

Materials	C	Si	Mn	P	S	Cr	Ni	Mo	N	Cu
UNS S31803	0.016	0.43	1.57	0.03	0.002	22.46	5.39	3.11	0.18	0.25
UNS S32750	0.022	0.55	0.69	0.029	0.002	25.15	6.74	3.43	0.27	0.13

In order to determine the CPT, the working electrodes were firstly cathodically polarized at −900 mV SCE for 300 s [16]. Secondly, specimens of UNS S31803 and UNS S32750 were allowed to stabilize at open circuit potential for 400 s at 303 K and 328 K, respectively. Then an anodic potential of 750 mV SCE was applied and the solution temperature increased at different temperature change rates. The current density was recorded simultaneously with the temperature throughout the test (except for the first 5 s following the applied anodic potential). The experiment was stopped when the current density reached 100 μA cm^{-2} and remained at that value for 60 s. The CPT was defined as the temperature at which the current density equaled 100 μA cm^{-2} [9]. The electrolyte was bubbled with pure nitrogen gas (N_2) to get eliminate oxygen gas (O_2) throughout the whole test. Each electrochemical measurement was repeated at least three times.

3 Results and discussion

The UNS S31803 and UNS S32750 specimens were tested three times under each experiment condition. The mean and standard deviation of the data obtained are summarized in Table 2. The reproducibility of measurement decreased (i.e. the standard deviation increased) as the temperature change rate increased.

Figure 1 shows typical current density versus temperature curves obtained from the specimens UNS S31803 in 1 mol L^{-1} NaCl solution with different temperature change rates at an anodic potential of 750 mV SCE. The arrows in the figure denote the values of the CPT, which increased with increasing temperature change rate. The current density kept steady at a lower value of about 1 μA cm^{-2} during the initial heating, corresponding to stainless steel being protected well by a passive film. With elevation of solution temperature, many current peaks, regarded as metastable pitting events [17], were observed below the CPT: this is associated with film breakdown occurring in metastable pits. As the temperature increased further above the CPT, the current density rose abruptly and increased continuously, indicating the occurrence of stable pitting. In a word, it could be concluded that temperature played an important role in the change of the composition and structure of passive film.

Figure 2 depicts typical current density versus temperature curves for specimens UNS S32750 in 1 mol L^{-1} NaCl solution with different temperature change rates at an anodic potential of 750 mV SCE. A lower current density value and some metastable pits were also observed below the CPT, while above the CPT the current density increased abruptly.

Comparing Figs. 1 and 2 the value of CPT for UNS S32750 is higher than that for UNS S31803 under the same conditions, indicating higher pitting resistance for the former. In previous work, this phenomena had been explained [18]. From the results above (Figs. 1, 2), the relationships between critical pitting temperature (CPT) and temperature change rate (υ) for UNS S31803 and UNS S32750 could be deduced, as shown in Figs. 3 and 4, respectively. Both schematics showed a linear dependence, and the measured CPT is a linear function of the square root of υ (the values of the parameter χ^2 describing the quality of fitting for Figs. 3 and 4 were both lower than 10^{-4}). Derived from the point defect model (PDM) the experimental findings received theoretical support.

According to the PDM [19–21] passivity breakdown results from the condensation of metal cation vacancies at the metal/film interface. This process may occur under the condition where the cation diffusion rate is so high that all the vacancies cannot be eliminated at the metal/film

Table 2 Reproducibility of the CPT measurements for UNS S31803 and UNS S32750 at 750 mV in 1 mol L^{-1} NaCl

Materials	Temperature change rates/K s^{-1}	Mean/K	Standard deviation/K
UNS S31803	0.00167	324.6	0.10
	0.00833	328.4	0.25
	0.01670	331.1	0.25
	0.02500	333.8	0.43
	0.03330	335.8	0.50
	0.04170	338.0	1.05
UNS S32750	0.00167	357.0	0.20
	0.00833	359.5	0.24
	0.01670	361.9	0.50
	0.02500	363.7	0.53
	0.03330	365.3	0.81
	0.04170	368.0	1.00

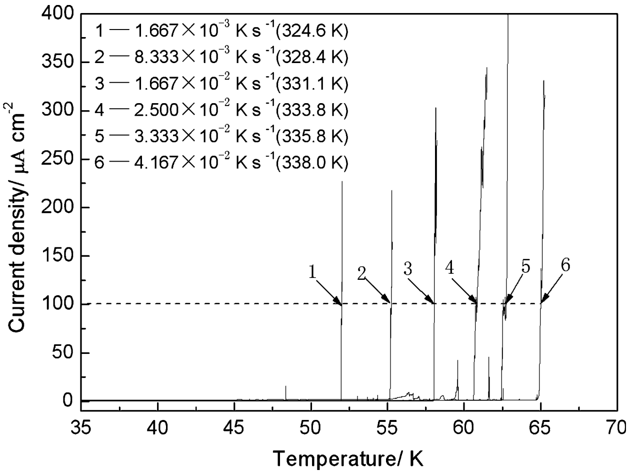

Fig. 1 Curves of current density and temperature for UNS S31803 in 1 mol L^{-1} NaCl solution with different temperature change rates at an applied potential of 750 mV SCE

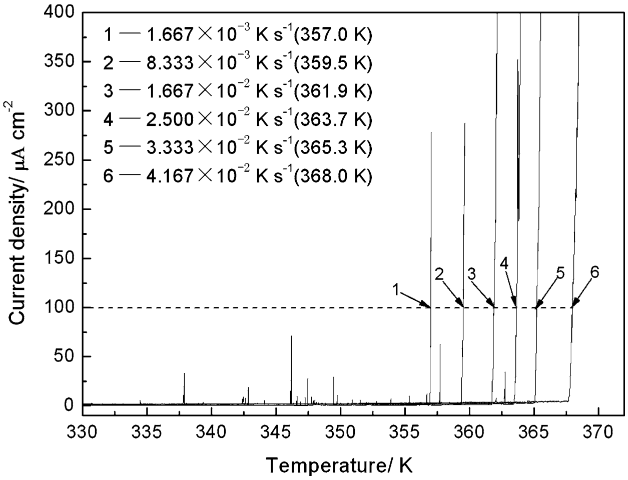

Fig. 2 Curves of current density and temperature for UNS S32750 in 1 mol L^{-1} NaCl solution with different temperature change rates at an applied potential of 750 mV SCE

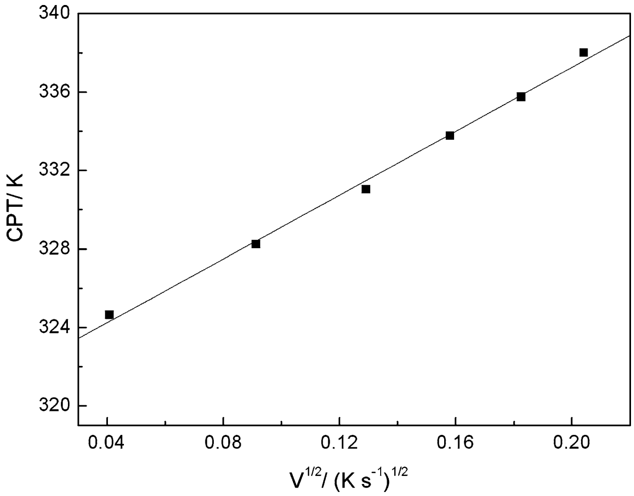

Fig. 3 Curves of critical pitting temperature and different temperature change rates in 1 mol L^{-1} NaCl solution for UNS S31803 at an applied potential of 750 mV SCE

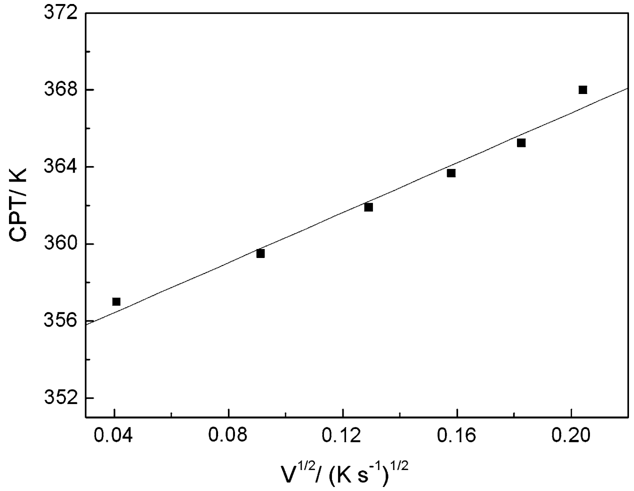

Fig. 4 Curves of critical pitting temperature and different temperature change rates in 1 mol L^{-1} NaCl solution for UNS S32750 at an applied potential of 750 mV SCE

interface. These residual vacancies are condensed at the metal/film interface to form a void. When the void grows to a certain critical size, the passive film suffers local collapse, marking the end of the pit incubation period. Subsequently, the collapsed site dissolved much faster than other locations on the surface, leading to pit growth. Thus, the critical condition for pit initiation may be expressed as follows

$$(J_{\mathrm{ca}} - J_{\mathrm{m}})(t - \tau) \geq \xi \tag{1}$$

Based on the references [19, 21], Eq. 1 can be expressed further as

$$\left[J^0 u^{-\frac{\chi}{2}} \exp\left(\frac{\chi F \alpha V_{\mathrm{ext}}}{2RT}\right)(a_{\mathrm{Cl}^-})^{\frac{\chi}{2}} - J_{\mathrm{m}}\right] \times (t - \tau) \geq \xi \tag{2}$$

where

$$J^0 = \chi K D^*_{V_M^{\chi'}} \left(\frac{N_V}{\Omega}\right)^{1+\frac{\chi}{2}} \exp\left(-\frac{\Delta G_{\mathrm{S}}^0}{RT}\right) \tag{3}$$

and

$$u = \frac{N_V}{\Omega} \exp\left(\frac{\Delta G_{A-1}^0 - F\beta pH - F\phi_{\mathrm{f/s}}^0}{RT}\right) \tag{4}$$

The cation vacancy diffusivity $D^*_{V_M^{\chi'}}$ can be calculated as

$$D^*_{V_M^{\chi'}} = D_0 \exp\left(-\frac{\Delta E}{RT}\right) \tag{5}$$

K is a parameter defined as

$$K = \frac{F\varepsilon}{RT} \tag{6}$$

The parameters appearing in these equations are listed in the List of Symbols and are defined in the literature [19, 22, 23].

Equation 2 shows that pit initiation does not occur if

$$J^0 u^{-\frac{\chi}{2}} \exp\left(\frac{\chi F \alpha V_{\mathrm{ext}}}{2RT}\right) (a_{\mathrm{Cl^-}})^{\frac{\chi}{2}} < J_{\mathrm{m}} \tag{7}$$

and that the critical pitting temperature, CPT, is given by the equation

$$J_{\mathrm{m}} = J'^0 u'^{-\frac{\chi}{2}} \exp\left(\frac{\chi F \alpha V_{\mathrm{ext}}}{2RT_{\mathrm{cpt}}}\right) (a_{\mathrm{Cl^-}})^{\frac{\chi}{2}} \tag{8}$$

where J'^0, u' were obtained under the critical pitting temperature conditions.

The analysis presented above yields an analytical function for another important parameter in pitting corrosion—the incubation time. Substitution of Eq. 8 into Eq. 2 gives

$$\left[J^0 u^{-\frac{\chi}{2}} (a_{\mathrm{Cl^-}})^{\frac{\chi}{2}} \exp\left(\frac{\chi F \alpha V_{\mathrm{ext}}}{2RT}\right) - J'^0 u'^{-\frac{\chi}{2}} (a_{\mathrm{Cl^-}})^{\frac{\chi}{2}} \times \exp\left(\frac{\chi F \alpha V_{\mathrm{ext}}}{2RT_{\mathrm{cpt}}}\right)\right] (t - \tau) \geq \xi \tag{9}$$

or

$$J'^0 u'^{-\frac{\chi}{2}} (a_{\mathrm{Cl^-}})^{\frac{\chi}{2}} \exp\left(\frac{\chi F \alpha V_{\mathrm{ext}}}{2RT_{\mathrm{cpt}}}\right) \left[\frac{T_{\mathrm{cpt}}}{T} \exp\left(\frac{A \Delta T}{2RT_{\mathrm{cpt}} T}\right) - 1\right] \times (t - \tau) \geq \xi \tag{10}$$

where $\Delta T = T - T_{\mathrm{cpt}}$, $A = 2\Delta E + 2\Delta G_{\mathrm{s}}^0 + \chi \Delta G_{A-1}^0 - \chi F \beta pH - \chi F \phi_{\mathrm{f/s}}^0 - \chi F \alpha V_{\mathrm{ext}}$. Equation 10 shows that when the chloride concentration in the solution is fixed (i.e., $a_{\mathrm{Cl^-}}$ and T_{cpt} are constants), the incubation time, t, is a function of ΔT. Mathematically, this can be expressed as

$$t = \xi' \left[\frac{T_{\mathrm{cpt}}}{T} \exp\left(\frac{A \Delta T}{2RT_{\mathrm{cpt}} T} - 1\right)\right]^{-1} + \tau \tag{11}$$

where

$$\xi' = \xi \Big/ J'^0 u'^{-\frac{\chi}{2}} (a_{\mathrm{Cl^-}})^{\frac{\chi}{2}} \exp\left(\tfrac{\chi F \alpha V_{\mathrm{ext}}}{2RT_{\mathrm{cpt}}}\right) \tag{12}$$

When determining T_{cpt} using the potentiostatic method, it is well known that the observed critical pitting temperature $[\equiv T_{\mathrm{cpt}}(\upsilon)]$ depends on the temperature change rate, υ. The PDM may be used to predict the relationship $T_{\mathrm{cpt}}(\upsilon)$ as follows. In the potentiostatic method, ΔT increases linearly with time (t) as the temperature is changed at a constant rate (υ); that is

$$\Delta T = \upsilon t \tag{13}$$

This relationship between ΔT and υ may be expressed mathematically by the following equation obtained by substituting Eq. 11 into Eq. 13 and setting $\tau = 0$ [19].

$$\upsilon = \frac{J_{\mathrm{m}} \Delta T}{\xi} \left[\frac{T_{\mathrm{cpt}}}{T} \exp\left(\frac{A \Delta T}{2RT_{\mathrm{cpt}} T} - 1\right)\right] \tag{14}$$

For small values of ΔT, and hence for low temperature change rates, Eq. 14 becomes

$$\upsilon = \frac{J_{\mathrm{m}}}{\xi} \cdot \frac{A \Delta T^2}{2RT^2} \tag{15}$$

and hence

$$\Delta T = B^{1/2} \upsilon^{1/2} \tag{16}$$

or

$$T_{\mathrm{cpt}}(\upsilon) = B^{1/2} \upsilon^{1/2} + T_{\mathrm{cpt}}(\upsilon = 0) \tag{17}$$

where $T_{\mathrm{cpt}}(\upsilon = 0)$ is defined as the critical pitting temperature at zero temperature change rate, $B = \frac{2R\xi T^2}{\left(2\Delta E + 2\Delta G_{\mathrm{s}}^0 + \chi \Delta G_{A-1}^0 - \chi F \beta pH - \chi F \phi_{\mathrm{f/s}}^0 - \chi F \alpha V_{\mathrm{ext}}\right) J_{\mathrm{m}}}$. Equation 17 predicts that the critical pitting temperature is a linear function of the square root of temperature change rate, which confirms the experiment findings.

The relationship between critical pitting temperature and temperature change rate is the same as that between pitting potential and potential sweep rate.

4 Conclusions

The critical pitting temperatures for UNS S31803 and UNS S32750 in 1 mol L^{-1} NaCl solution were obtained at different temperature change rates by the potentiostatic technique. The values of CPT for two DSSs increased with increasing temperature change rate and a linear relationship between the CPT and the square root of temperature change rate was observed at low temperature change rate, i.e. CPT $\sim \upsilon^{1/2}$. Based on the PDM, the experiment findings were supported by theoretical analysis.

Acknowledgements This work was supported by the National Natural Science Foundation of China (grant. No.10621063 and 50871031), Chinese National Science and Technology Infrastructure Platforms Construction Project (Grant. No. 2005DKA10400-Z13), Shanghai Science and Technology Development Funds (0725nm004), China Postdoctoral Science Foundation (No.20080430670) and Shanghai Leading Academic Discipline Project (No. B113).

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