

## The Influence of Temperature on the Electrochemical Behavior of Austenitic Stainless Steel in MgCl<sub>2</sub>

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Received: April 25, 1994; November 25, 1994

Foi estudada a influência da temperatura sobre o comportamento eletroquímico de um aço inoxidável austenítico AISI 304 em uma solução 35% de MgCl<sub>2</sub>. Foi analisada a velocidade de repassivação via ensaios de tração rápida, além de flutuações do potencial de corrosão através da técnica de ruído eletroquímico. Os resultados obtidos mostram a forte influência da temperatura sobre a estabilidade da interface metal/solução.

The influence of temperature on the electrochemical behavior of austenitic stainless steel AISI 304 in a 35% MgCl<sub>2</sub> solution was studied. The repassivation kinetics was evaluated by fast strain rate experiments, and small amplitude fluctuations of the corrosion potential were investigated by means of the electrochemical noise technique. The results show that the stability of the system is strongly influenced by temperature.

**Keywords:** *stainless steel, corrosion potential, electrochemical noise*

### Introduction

The failure processes of austenitic stainless steels, related to stress corrosion cracking (SCC), are easily simulated under laboratory conditions by immersion tests in hot MgCl<sub>2</sub> solutions. The actual mechanism involved in this kind of failure has not yet been clearly explained. The understanding of the role of the passive film formed on the metal surface during the SCC phenomenon is a basic requirement for the mechanistic approach. Some aspects concerning film aging, composition, physical structure and the effect of temperature on these properties are thought to determine SCC susceptibility, as reported by several authors<sup>1-3</sup>. Grast *et al.*<sup>1</sup>, for example, consider film properties more important than film thickness for SCC incidence. Shibata *et al.*<sup>2</sup>, on the other hand, correlate film thickness with corrosion rate in MgCl<sub>2</sub> solutions.

Electrochemical techniques are sufficient for the observation and study of SCC, as they permit the accurate *in situ* detection of the electrochemical reactions occurring at the metal-electrode interface, while being simple experimental

techniques. In the present work, electrochemical fluctuations of the corrosion potential were used as a source of information regarding the electrochemical properties of the film formed on the surface of AISI 304 stainless steel in the presence of MgCl<sub>2</sub>. The results obtained from current density transients, registered in fast strain rate tests, are also presented and compared to electrochemical noise measurements, in the time and frequency domain in terms of Power Spectral Density (PSD), at different temperatures.

### Experimental

The chemical composition of the AISI 304 stainless steel used in this work is shown in Table 1.

The material was normalized at 1050 °C for 1 h in argon atmosphere, and quenched with water. The surface of the samples was ground to grit 600 with emery paper and polished with alumina. After surface preparation, the samples were washed with distilled water and alcohol, and dried with hot air. The electrochemical tests were conducted in a aerated 35% weight MgCl<sub>2</sub> solution, at tempera-

**Table 1.** Chemical composition of AISI 304 stainless steel.

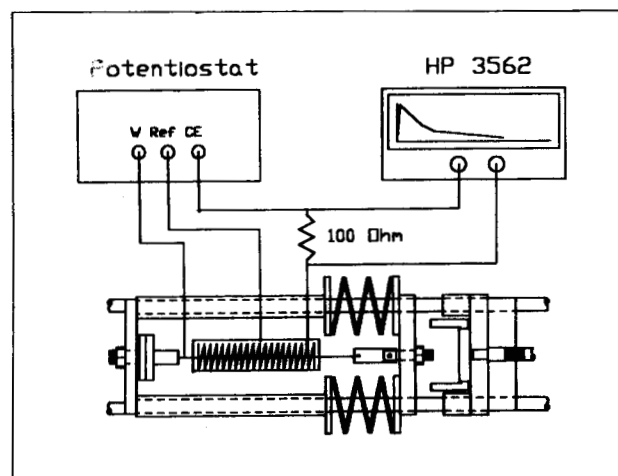
% C	% S	% Ni	% Cr	% Fe
0.081	0.005	8.14	18.2	balance

tures of 25, 60 and 90 °C, using a standard saturated calomel electrode as the reference electrode.

The samples for the SCC tests were wires 1.1 mm in diameter and 170 mm long. Fast strain rate tests were performed on a tensile test machine adapted by springs in order to permit ultra-high strain rates (up to 1.8 s<sup>-1</sup>). The spring was compressed to the desired displacement and released by the fall of a hammer to apply 10% total strain to the specimen. The tests were conducted under potentiostatic regulation at the corrosion potential ( $E = E_{\text{corr}}$ ). A low noise potentiostat developed at the Laboratoire Physique des Liquides et Electrochimie was employed. The current generated across the cell, as a consequence of the deformation of the sample, was registered by using a 100Ω series resistance (Fig. 1). The transient was recorded by a Hewlett Packard 3562 Signal Analyzer, triggered by the rising portion of the current signal, when it overcame a trigger level previously established (arbitrarily chosen as 2 mA/cm<sup>2</sup>).

Electrochemical noise measurements were performed using the same HP 3562 Signal Analyzer. Unstrained samples of the same steel, having a flat surface and embedded in Teflon™, were used. The fluctuations of the corrosion potential were analyzed after reaching a steady state of the mean value (-360 mV<sub>sc</sub>) after 1 h. These fluctuations were amplified after suppressing the DC level by means of a low noise amplifier also developed at the Laboratoire Physique des Liquides et Electrochimie.

The Power Spectral Density of these fluctuations, numerically calculated by the HP 3562 using Fast Fourier Transform, is mathematically equivalent to the fourier

**Figure 1.** Schematic view of the device used for fast strain rate experiments.

transform of the auto-correlation function  $R_{VV}(\tau)$ , according to Eqs. 1 and 2:

$$R_{VV}(\tau) = E[V(t) \cdot V(t + \tau)] \quad (1)$$

$$\phi_{VV}(\omega) = \int_{-\infty}^{+\infty} R_{VV}(\tau) \cdot e^{-j\omega\tau} d\tau \quad (2)$$

## Results and Discussion

A complete mechanism for SCC, supported by experimental observations, is not available. Several different models have been proposed in order to explain the stress corrosion cracking process: i) kinetic instability of the film<sup>4</sup>, ii) enhanced surface mobility<sup>5</sup>, iii) cleavage induced by the film<sup>6</sup>, and iv) hydrogen embrittlement<sup>7</sup>. Of these, the idea of the kinetic instability of the film stands out, due to the experimental evidence which correlates the reduction of the resistance to SCC (evaluated with ordinary SCC tests) with changes in the electrochemical properties of the system, such as electrode potential and chloride concentration. This correlation is emphasized when the temperature of the environment increases. It is important to note that the susceptibility of AISI 304 steel in MgCl<sub>2</sub> solutions to SCC is observed only at high temperatures. Therefore, in the present work, the influence of temperature on the stability of metal-solution interface was analyzed at 25, 60 and 90 °C, using fast strain rate tests and the electrochemical noise technique. The fluctuations in the corrosion potential are interpreted by many authors as being the result of several elementary processes of rupture and repassivation of the film<sup>3,8-10</sup>. Thus, the measurement and interpretation of the corrosion potential fluctuations, in both the time and frequency domain may be an interesting method for obtaining kinetic information about the electrochemical processes involved in SCC.

Temperature can affect the behavior of an electrochemical system by reducing the content of O<sub>2</sub> dissolved in the electrolyte. In the case of AISI 304 stainless steel immersed in hot MgCl<sub>2</sub> solution, oxygen reduction is an important cathodic reaction related to the corrosion process. This reaction should be less intense at higher temperatures, as the corrosion would be inhibited under these conditions. However, this hypothesis was not confirmed when electrochemical measurements were performed in aerated and deaerated MgCl<sub>2</sub> solutions, as pointed out by Schroeder and Müller<sup>11</sup>. The mean value of the corrosion potential and the polarization curves remain unchanged under both conditions. On the other hand, hydrogen reduction could be operative, especially inside occluded cells generated by cracking and by the onset of localized corrosion induced by chloride. The former process is the basis for the mechanism of hydrogen embrittlement in AISI 304 stainless steel<sup>7</sup>.

Transient techniques, such as scratching and fast strain rate are very effective for promoting film rupture processes. Wide areas of bare metal are created and the electrochemical response of the material in these conditions can be analyzed. The kinetics of the film rupture and its reconstitution is related to SCC susceptibility<sup>4,12</sup>, considering that a critical value of the time constant associated with repassivation is necessary for the initiation and propagation of cracks. The imposition of a "step" of instantaneous deformation to the specimen gives rise to a transient current density.

The results obtained in this work at different temperatures (total elongation = 10%) are shown in Fig. 2. A few milliseconds after the deformation there is a sharp increase in the current density, followed by an exponential decay.

The occurrence of the current density peak is attributed to the rupture of the film followed by anodic reactions at the bare metal, such as the oxidation of the metal, oxygen evolution and oxidation of electrochemical species. The subsequent transient decay is attributed to repassivation and some other processes such as the formation of the double layer. The relative influence of each contribution will depend on the nature of the system and the experimental conditions. In this work, the values of electrical charge  $Q$  determined by fast strain rate under potentiostatic control are presented in Table 2. These values were calculated by the integration of the transient current density vs. the time signal at the specified temperatures. The elapsed time considered for these calculations was between the instant of the maximum current density and  $t = 10$  ms and  $t = 200$  ms, respectively.

Vetter<sup>14</sup> suggests that the charge density of the double layer can be evaluated by the following equation:

$$Q_{DL} = C_{DL} \cdot \Delta V \quad (3)$$

where  $C_{dl}$  is the capacitance of the double layer and  $\Delta V$  is the difference of electrical potential between the passive film and the bare metal. The same author considers that a characteristic value for  $C_{dl}$  is  $40 \cdot 10^{-6} \text{ F cm}^{-2}$ . Thus, consid-

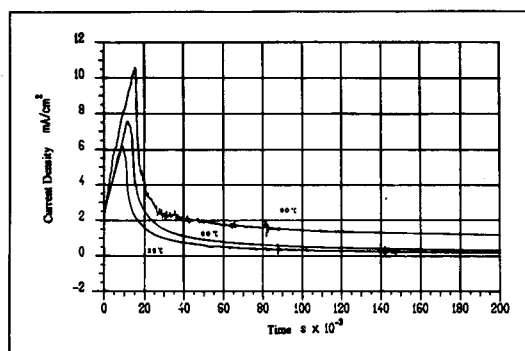


FIGURE 2 - Transient current density after a mechanic deformation

Figure 2. Transient current density after an instantaneous deformation.

Table 2. Total electrical charge density.

T (°C)	Q (mC cm <sup>-2</sup> ) / t = 10 ms	Q (mC cm <sup>-2</sup> ) / t = 200 ms
25	0.39	1.10
60	0.66	2.76
90	0.74	4.88

ering an overestimated value of 1 V for  $\Delta V$ , the charge density calculated with Eq. 3 would be  $0.04 \text{ mC cm}^{-2}$ . This value, compared to those presented in Table 2, indicates that the process of double layer charging is a secondary contribution to the transients registered during fast strain rate tests.

Some electrochemical contributions such as oxygen evolution and oxidation of electrochemical species are not considered in this case. Oxygen evolution occurs at very high potentials and no contribution from the oxidation of other species should be expected under these experimental conditions.

Consequently, one may assume that the transients obtained are mainly due to the metallic dissolution followed by the repassivation of the electrode. A comparison of the transients registered at different temperatures indicates that only the amplitude of the transients is affected by temperature. The time constants remain unchanged for all temperatures.

In order to obtain more information about the influence of temperature on this system, the electrochemical noise technique was used. Fluctuations of the electrode potential were recorded in the time domain, and the PSD of these signals was calculated for unstressed specimens.

The analysis of these fluctuations through Power Spectral Densities should at least consider the condition of a stationary signal (broad sense). Therefore, the measurements of electrochemical noise (time domain and PSD) were performed about one hour after the immersion of the samples.

Figures 3 and 4 show time records of the fluctuations in the corrosion potential at 25 and 90 °C for 80 s. The rise in temperature always caused the amplitude to increase, but the oscillation pattern only changed in the 90 °C test. This was observed mainly at 10 and 20 s. These changes in the oscillation pattern were not observed at test temperatures of 25 and 60 °C.

The PSD of the potential fluctuations at 25, 60 and 90 °C are shown in Fig. 5. The lack of a low frequency plateau in these spectra may be interpreted as an indication of the existence of electrochemical phenomena characterized by very low time constants. Such an interpretation may be justified by the fact that the DC value of the corrosion potential remains constant during the measured intervals, and that the PSD slope obeys a  $1/f^\alpha$  law, for  $\alpha > 1$ . The determination of the power spectrum density with  $\alpha = 1$  is considered by many authors to be of little physical significance and very difficult to interpret<sup>15-17</sup>.

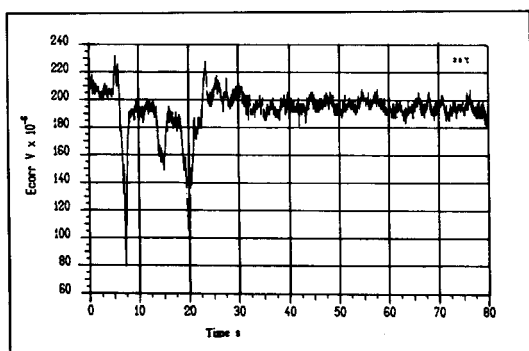


Figure 3. Time record of potential fluctuations at 25 °C

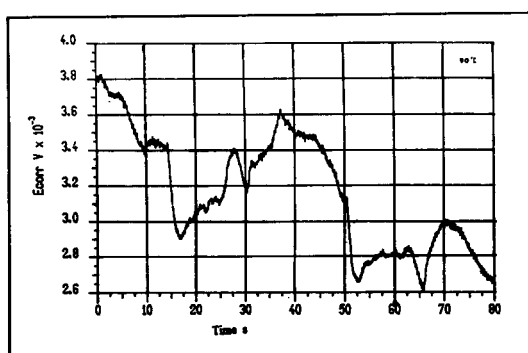


Figure 4. Time record of potential fluctuations at 90 °C.

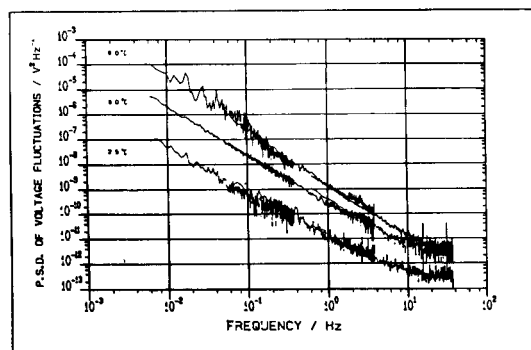


Figure 5. PSD of potential fluctuations at 25, 60 and 90 °C.

At 25 and 60 °C, the PSD shows a  $1/f^2$  relationship to the frequency (the power of the signal is inversely proportional to the square of its frequency). This result indicates that an increase in temperature from 25 to 60 °C simply affects the amplitude and not the oscillation pattern of the corrosion potential, as previously mentioned. However, at 90 °C, the PSD shows a decay which corresponds to  $1/f^3$  in an intermediate frequency (about 0.1 Hz), which can be attributed to changes in the oscillation pattern. These changes in the oscillation pattern at 90 °C were observed

both in the time and frequency domains, and correspond to an increase in the SCC susceptibility of this steel. These results agree with the Staehle<sup>4</sup> theory, which states that an increase in SCC susceptibility is followed by a change in the kinetics of the passivation processes, probably due to modifications in the activity of chloride ions.

Nevertheless, the pattern changes identified at 90 °C by electrochemical noise are not detected in the transient decay of the current density at the same temperature (Fig. 2). This result may be related to the existence of an effect associated with the regulation device of the interface as pointed out by Oltra *et al.*<sup>18</sup>. According to these authors, there is a limitation in measuring the intrinsic kinetics of repassivation in the case of transient techniques where new depassivated areas are created. Probably there is an interaction between the electrochemical processes and the regulation device. With the sudden localized rupture of the film, the adjacent passive regions would supply the necessary electrical charge to allow the repassivation of the bare areas created. Afterwards, the potentiostat would supply the charge to this passive region, re-arranging the system as a whole. In this way, the decay of the transients presented in Fig. 2 would be a joint effect of electrochemical processes and a regulation device that would hide the temperature effects of the repassivation kinetics. Electrochemical noise techniques can prevent this problem, as they perform measurements without the influence of the regulation device.

## Conclusions

1 - The results presented here show a clear dependence of the electrochemical behavior of AISI 304 stainless steel on the temperature in the system investigated. This effect is related to pattern modifications of the corrosion potential fluctuations at 90 °C, and the increase of the amplitude of both PSD and transient peaks of fast strain rate tests.

2 - The transient techniques were not able to detect changes in the kinetics of the passivation processes. The same tests do not reveal any difference in the time constants of the current density *vs.* the time decay. In the present work, this limitation is attributed to a joint effect of electrochemical processes and the regulation device.

3 - Electrochemical noise techniques, as performed in this work, proved to be adequate for investigating the temperature effects on the electrochemical behavior of the system under consideration. The information obtained with DSP clearly demonstrated that at higher temperatures, where stress corrosion cracking occurs, there is a change in the frequency distribution from  $1/f^2$  at low temperatures to  $1/f^3$ , around 0.1 Hz.

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