The Effect of Crack-Tip Strain Rate and Potential on the Propagation Rate of Stress Corrosion Crack for 321 Stainless Steel in Boiling 42 Pct MgCl₂ Solution

D. LI and X. MAO

The decay law of current with time on the bare surface of scratched 321 stainless steel in boiling 42 pct MgCl₂ solution has been studied by the rapid scratching technique under potentiostatic condition. Based on the decay law and the model of slip-bare metal dissolution-repassivation, a theoretical equation of stress corrosion crack propagation rate as a function of crack-tip strain rate and potential for 321 stainless steel in boiling 42 pct MgCl₂ solution has been proposed as

\[
\frac{da}{dt} = 3.6 \times 10^4 \frac{M}{zF\rho Nn_b \varphi} \frac{\varepsilon}{0.03 - E} \left[ 1 - \exp \left( -\frac{Nn_b \varphi (0.03 - E)}{e} \right) \right]
\]

The theoretical calculation shows that when the crack-tip strain rate changes from \(10^{-4}/s\) to \(10^{-2}/s\), the crack propagation rate changes from 0.01 mm/h to 3 mm/h at natural corrosion potential (-0.35 V(SEC)). If the crack-tip strain rate is above \(10^{-2}/s\), the crack propagation rate should correspond to the upper bound determined by the maximum metal dissolution rate. When the crack-tip strain rate is below \(10^{-3}/s\), the crack propagation rate is below 0.01 mm/h. The sensitive potential \(E_c\) to cracking is -0.35 V(SEC); above the sensitive potential \(E_c\), the crack propagation rate varies slowly with potential. However, below \(E_c\), the crack propagation rate decreases rapidly with potential decreases. The crack propagation rate of 321 stainless steel in 42 pct MgCl₂ solution has been measured using a slow strain rate test technique. The theoretical calculation is consistent with the experimental results.

I. INTRODUCTION

The susceptibility of austenitic stainless steels to stress corrosion cracking (SCC) in boiling MgCl₂ solution has been studied by many workers.\(^{[1-7]}\) The importance of crack-tip strain rate and potential during SCC has been recognized for many years.\(^{[1-5]}\) Several authors\(^{[9-12]}\) showed that there was a critical range of applied strain rate and potential to SCC. For a variety of systems, SCC occurs only if the strain rate is within a critical range, limited by the upper and lower bound critical strain rates \(\varepsilon_1\) and \(\varepsilon_2\).\(^{[9]}\) Many workers\(^{[8,13]}\) investigated the relationship between applied strain rate and crack-tip strain rate. The results show that when the applied strain rate is above \(10^{-5}/s\), the crack-tip strain rate is two orders of magnitude higher than the applied strain rate. The processes of SCC have long been associated with the disruption of a passive film at the crack tip of an advancing crack, as a result of slip processes followed by anodic dissolutions of the exposed bare metal.\(^{[14,15,16]}\) The model of slip-bare metal dissolution-repassivation has been suggested to evaluate the processes of SCC for stainless steel in boiling MgCl₂ solution.\(^{[14]}\)

A significant limitation in previous studies of SCC is the lack of quantitative theoretical research. Obviously, the theoretical analysis of the effect of the crack-tip strain rate and potential on the SCC is of great importance for understanding the SCC processes.

OBTAINING THE DECAY LAW OF CURRENT WITH TIME ON THE SLIP STEP AT THE CRACK TIP IS A KEY ISSUE TO ESTABLISH THE RELATIONSHIP BETWEEN THE CRACK PROPAGATION RATE AND CRACK-TIP STRAIN RATE AS WELL AS POTENTIAL. Many authors have studied the repassivation kinetics of bare metal surfaces using the rapid scratching\(^{[18-24]}\) and straining electrode techniques\(^{[25,26]}\) for numerous systems. However, the results obtained from these techniques were not directly used to study SCC.

The aims of this work are the following: (1) to obtain the decay law of current with time on the bare surface of scratched 321 stainless steel in boiling 42 pct MgCl₂ solution by the rapid scratching technique; (2) to propose a theoretical equation of stress corrosion crack propagation rate as a function of the crack-tip strain rate as well as the potential for 321 stainless steel in boiling 42 pct MgCl₂ solution and a calculation based on the decay law of current with time and the model of slip-bare metal dissolution-repassivation; and (3) to measure the crack propagation rate of 321 stainless steel in 42 pct MgCl₂ solution using a slow strain rate test technique and to compare the calculated results with the experimental results.

II. EXPERIMENTAL

A. Rapid Scratching Test Technique

The rapid scratching experimental device is shown in Figure 1. It consists of a rapid scratching system and a follow-up recording system. The rapid scratching system is composed of a rotating disk electrode and a scratching
The experimental apparatus used for rapid scratching under potentiostatic control: (1) specimen; (2) steel rod with a diamond bit welded at the top; (3) microlathe; (4) counterelectrode; (5) reference electrode; (6) rotating apparatus; (7) electrolytic cell; (8) potentiostat; and (9) tachometer.

The scratching apparatus, made of a microlathe and a steel rod with a diamond bit welded at one end, moves in three-dimensional directions. The follow-up recording system is a computer with a 12 bit A/D fast transcriber with a sampling frequency of 20,000/s. The electrolyte was a boiling 42 pct MgCl₂ solution made from analytical grade reagent and deionized water.

The specimen used in the rapid scratching test was made from 321 stainless steel with the following chemical compositions (wt pct): C0.07, Si0.7, Mn1.8, S0.03, P0.03, Cr18.6, Ni9.9, Ti0.62, Fe balance. Its dimensions are shown in Figure 2.

The specimen was installed to the axis of the rotating apparatus, as shown in Figure 1, and rotated at 50 Hz. It was scratched using the scratching system at constant potential. The current was recorded by the computer during and after scratching. The linear velocity of the cylindrical surface of the specimens was 1.57 m/s. The scratch scar was about 4.6 to 4.8 mm, which was a part of the cylindrical surface of the specimen. Its length depended on the contacting time of the diamond bit with the specimen. The contacting time was about 2.5 ms and it was measured by the computer. The width of the scratch ranged between 20 to 25 μm, and the depth was approximately 1.5 μm.

By fitting the recorded data, the current density measured on the scratched bare surface as a function of time can be expressed by

\[ i(t) = i_0 \exp(-\beta t) \]  

where \( i_0 \) is the current density on the fresh surface and \( \beta \) is the decay constant.

The \( i_0 \) and \( \beta \) vary with the potential. In the range of \(-0.65 \) V to \(0.15 \) V(SEC), they can be expressed by

\[ i_0 = 4 + 6E \]  

and

\[ \beta = 0.03 - E \]

where \( E \) is the potential.

**B. Slow Strain Rate Test Technique**

The SCC test was conducted at free corrosion potential using the slow strain rate test (SSRT) technique.\(^{[27]}\) The tensile strain rates were \(1.25 \times 10^{-4}\) and \(2.5 \times 10^{-5}\) mm/s. The SCC testing specimen was made from 321 stainless steel with the same composition as the specimen used in the rapid scratching test. The specimen dimension is shown in Figure 3. The specimen was annealed in vacuum at 1080 °C for 1 hour. The specimen was kept for 5 hours in MgCl₂ solution before the SSRT. The crack length was measured directly by traveling microscopy to obtain the crack propagation rate.

**III. THEORETICAL ANALYSIS AND CALCULATION**

Stress corrosion cracking may well occur by rupture of surface passive film due to slip and the consequent action of electrolyte solution on what is essentially a fresh bare metal surface. The processes of slip, bare metal dissolution, and subsequent repassivation collectively determine the propagation rate of stress corrosion crack. The crack-tip strain rate determines the formation rate of slip step at the crack tip, and the crack-tip potential determines the rates of both bare metal dissolution and repassivation. When a slip step forms on a passive surface, the surface may be rapidly attacked.

As shown in Figure 4(a), if the formation rate of slip step at the crack tip is assumed to be \( \nu \), the time to form a slip step is \( 1/\nu \). The average current density of the anodic dissolution at the crack tip can be expressed by

\[ i_a = \frac{1}{(1/\nu)} \int_0^{1/\nu} i(t) \, dt \]  

where \( i(t) \) is the current density on the fresh surface and \( \nu \) is the strain rate.