

# The Use of Microelectrodes in the Study of the Effects of Electrolyte Composition, Potential and Metallurgical Conditions on Nucleation and Metastable Pitting of Stainless Steel 316

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The study of stainless steel 316 has been undertaken in electrolytes containing various concentrations of chloride ( $\text{Cl}^-$ ) and perchlorate ions ( $\text{ClO}_4^-$ ). The concentration of  $\text{Cl}^-$  and  $\text{ClO}_4^-$  in these electrolytes varied between 0.025 and 0.1 M in a variety of combinations.

This study utilized microelectrodes with surface areas of between  $2 \times 10^{-5} \text{ cm}^2$  and  $3.9 \times 10^{-4} \text{ cm}^2$ . One set of electrodes was prepared with commercially drawn wire, while another set was prepared with wires that were made by electropolishing commercially available bulk specimens down to microelectrode size. A specially constructed electrochemical cell was used in the electropolishing process.

The goal of this study was to describe the dependence of pit nucleation and metastable pitting on the concentration of aggressive ions ( $\text{Cl}^-$ ), applied potential, and metallurgical condition. Potentiostatic polarization experiments were carried out at potentials in the passive region of stainless steel 316 (SS 316). A two-electrode cell was employed to minimize electrochemical noise. A silver/silver chloride ( $\text{Ag}/\text{AgCl}$ ) electrode was used as a combined reference and counter electrode. Nucleation events with peak currents less than 1.6 pA in height were resolved by the use of a combination of Faraday cages and current amplifiers for data acquisition. Such nucleation events have been reported in the past in various  $\text{Cl}^-$  containing environments [1-5]. Figure 1 shows a typical current transient from potentiostatic polarization.

Regression analyses of the data yielded expressions for the frequency of nucleation and metastable pitting events as well as for the time constant. The data was also analyzed for the total number of nucleation and metastable pitting events, as well as the height of the nucleation events.

Results showed that the total number of events increased as  $[\text{Cl}^-]$  and potential increased. Figure 2 shows a plot of the average frequency of nucleation as a function of time. Although the number and frequency of nucleations decreased as  $[\text{ClO}_4^-]/[\text{Cl}^-]$  ratio increased, i.e. as  $[\text{Cl}^-]$  decreased (Figure 3), the percentage propagation rate of metastable pits from nucleations increased (Figure 4). The data also showed that the metallurgical condition of the sample affected the number of nucleations and metastable pits generated.

## References

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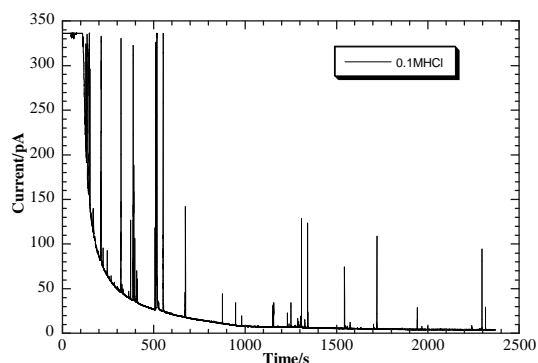


Figure 1. Current transient of SS 316 in 0.1M HCl at 0.2 V (SCE) for 2370 s.

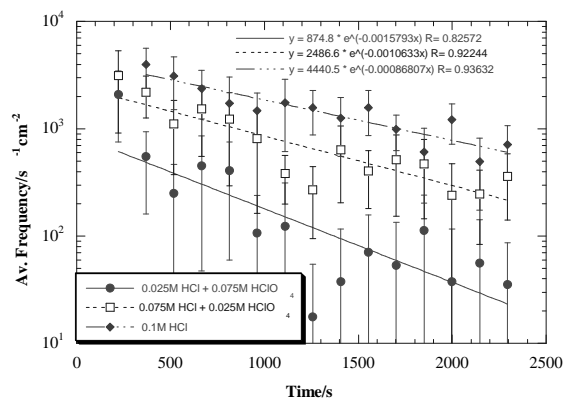


Figure2: Average frequency of nucleations per  $\text{cm}^2$  as a function of time in deaerated 0.025M HCl + 0.075M  $\text{HClO}_4$ , 0.075M HCl + 0.025M  $\text{HClO}_4$  and 0.1M HCl on SS316 at 0.2V(SCE) for 2370s.

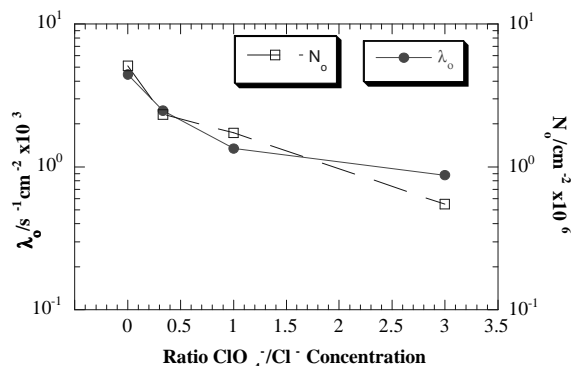


Figure 3: Total number,  $N_0$ , and initial frequency,  $\lambda_0$  of nucleations per  $\text{cm}^2$ , as a function  $[\text{ClO}_4^-]/[\text{Cl}^-]$  ratio on SS 316. Polarization: 0.2V(SCE) for 2370s.

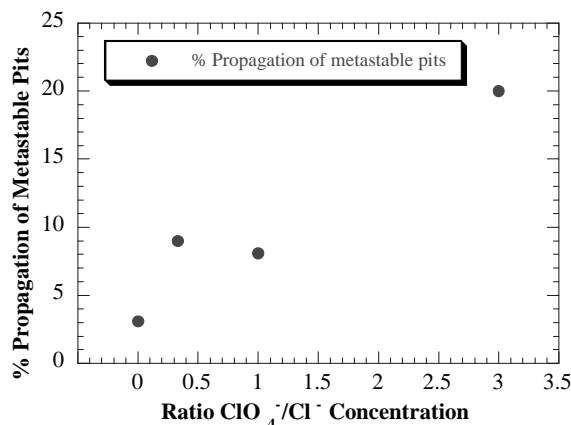


Figure 4: Percentage propagation of metastable pits as a function  $[\text{ClO}_4^-]/[\text{Cl}^-]$  ratio on SS 316. Polarization: 0.2V(SCE) for 2370s.