

### Investigation on the effect of nitrate ion on the critical pitting temperature (CPT) of duplex stainless steel using pencil electrode

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It is well known that resistance against pitting corrosion decreases as temperature increases. The concept of critical pitting temperature (CPT) was introduced by Brigham as a temperature below which the steel will not pit regardless of potential and exposure time(1).

Duplex stainless steels (DSS) are iron based alloys that their usage has been limited to temperatures below which pitting corrosion occurs. To encompass a higher temperature application and improve the pitting resistance of stainless steels in halide media, using inorganic-based corrosion inhibitors has been recommended (2-4). In the 1960s, Uhlig and Gilman(5), were reported Nitrate ( $\text{NO}_3^-$ ) inhibition of pitting in Fe-Cr-Ni alloys. The positive effect of nitrate ion on CPT of a high-entropy alloy has been reported by Chou and coworkers(3).

The aim of this research is to find out the effect of Nitrate addition to the chloride containing solution on CPT of a 2205 duplex stainless steel (DSS 2205). The CPT of DSS 2205 was measured in 0.6M NaCl and 0.6M NaCl+0.02M  $\text{NaNO}_3$  solutions by potentiodynamic polarization technique. Temperature, at which the breakdown potential drops steeply, was considered as CPT and the breakdown criterion was defined as the potential where the current density exceeded  $100 \mu\text{A}\cdot\text{cm}^{-2}$ (2, 6). The obtained results revealed that addition of 0.02M  $\text{NO}_3^-$  to 0.6M NaCl solution, increases the CPT for  $10^\circ\text{C}$ . As shown in Fig.1 at  $55^\circ\text{C}$ , alloy suffers from pitting corrosion in 0.6M NaCl solution while in solution containing 0.02M  $\text{NaNO}_3$ , increasing the current density at ca. 1100 mV (vs. SCE) is due to transpassivity.

In Second stage, a mechanistic approach has been sought based on CPT theory proposed by Salinas-Bravo and Newman, corresponding the CPT to a temperature in which  $i_{\text{crit}} = i_{\text{lim}}$  where  $i_{\text{crit}}$  is the critical current density necessary for passivity and  $i_{\text{lim}}$  is the anodic limiting current density in the pit nucleus(7). Newman and Ajjawi who used austenitic stainless steel pencil electrodes to simulate the chemistry of a pit, reported that no inhibiting effect of nitrate on active (film-free) dissolution(8). Thus it comes to mind that the addition of nitrate, would not affect the  $i_{\text{crit}}$ . So the effect of adding nitrate ion ( $\text{NO}_3^-$ ) on  $i_{\text{lim}}$  in a single growing pit was investigated using pencil electrode of DSS 2205. To make a pencil electrode, narrow strip of DSS 2205 thickness was reduced to  $80\mu\text{m}$  by electro-polishing in phosphoric acid. The pencil electrode potentiostatically polarized at a potential well above pitting potential at  $65^\circ\text{C}$  in 0.6M NaCl and 0.6M NaCl+0.02M  $\text{NaNO}_3$  solution and by applying Faraday's second law pit depth was calculated. As an example, fig.2 depicts the current density versus pit depth in diffusion controlled regime established by salt film precipitation. The observed fluctuations are reproducible and have been related to localized passivation and rapid reactivation under the salt film when the salt film locally reduces in

thickness or dissolves(8). The curves revealed higher current density for an identical pit depth in presence of nitrate ion. Based on anodic diffusion limiting current density (fig. 2), it is obvious that  $\delta \cdot i_{\text{lim}}$  value increases in presence of nitrate ion. In other words, in the same pit depth, the value of  $i_{\text{lim}}$  in presence of nitrate is noticeably higher than pure chloride solution. Hence it is concluded that increasing in critical pitting temperature (CPT) of DSS 2205 in nitrate containing solution is a consequent of increase in limiting current density. It means that for precipitation of salt film (requisite condition for stable pit) at the presence of  $\text{NO}_3^-$  ion the temperature has to be increases.

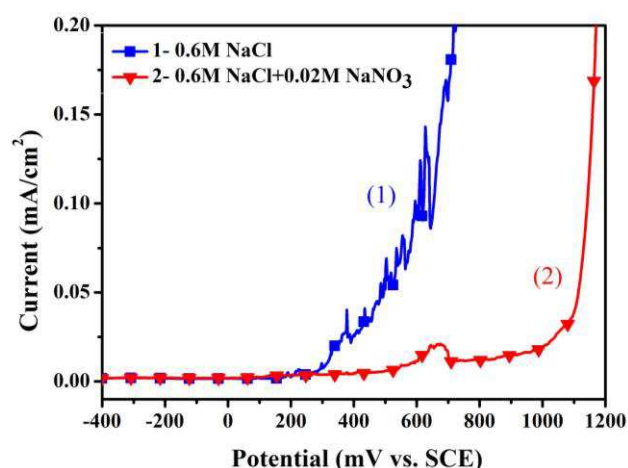


Figure 1. Potentiodynamic polarization curves of DSS 2205 alloy in 0.6M NaCl and 0.6M NaCl+0.02M  $\text{NaNO}_3$  at  $55^\circ\text{C}$ . Scan rate was 0.5 mV/ Sec.

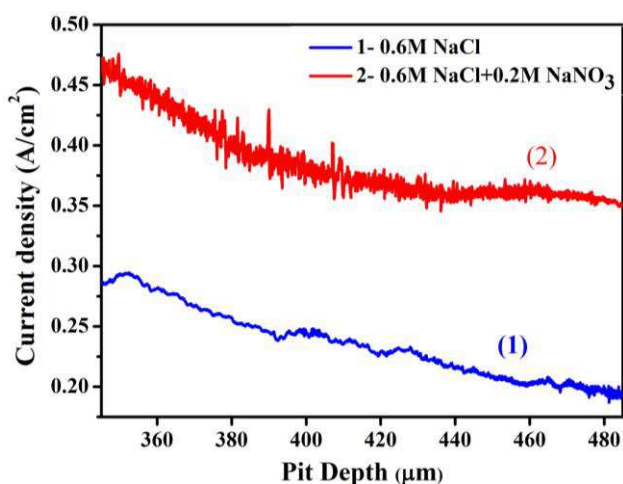


Figure 2. Current density-pit depth curves at diffusion controlled region for  $80\mu\text{m}$  dia. pencil electrode of DSS 2205 at  $850 \text{ mV}_{\text{SCE}}$  at  $65^\circ\text{C}$  in 1) 0.6M NaCl and 2) 0.6M NaCl+0.02M  $\text{NaNO}_3$

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