A justification on Critical Pitting Temperature (CPT) Mechanism proposed by Salinas-Bravo and Newman Using Pencil Electrode/ Effect of nitrate ion addition

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Critical pitting temperature (CPT) has been defined by Salinas-Bravo and Newman as a temperature at which $i_{lim}=i_{crit}$ where i_{lim} is the diffusion limiting current density as a result of salt precipitation and i_{crit} is the critical (maximum) current density necessary for passivity in pit solution (1). The positive effect of nitrate ion on CPT of 2205 by increasing it towards higher temperatures due to its increasing effect on i_{lim} was presented in detail elsewhere(2). The objective of this work is to validate the theory mentioned above by investigating the effect of nitrate ion addition in chloride containing solution on critical current density of a 2205 duplex stainless steel (DSS 2205). Potentiodynamic polarization tests were conducted on 200 µm diameter DSS 2205 in a 5M HCl solution assuming creates simulated pit environment(3). To identify the effect of nitrate ion addition to the solution containing chloride ion, the critical current density for passivation on a DSS 2205 specimen annealed at 1050°C was measured in 5M HCl and 5M HCl+0.1M $NaNO_3$ solutions. Mentioning that addition of 0.1M NaNO3 to a 0.6M NaCl solution causes an increase of 30°C in CPT of DSS 2205(4).

Typical anodic polarization curves of specimen annealed at 1050°C obtained in 5M HCl and 5M HCl+0.1M $NaNO_3$ solutions at different temperatures are illustrated in fig. 1 (a) and fig. 1 (b). Depicted curves show that passivity occurs at temperatures up to 45°C and 55°C for 5M HCl and nitrate containing solution respectively. At temperatures higher than 45°C and 55°C, passivity does not occur and after a maximum current density g salt film precipitates and a diffusion controlled dissolution (dissolution under the salt) is established. The fluctuations in current density observed at diffusion control region is believed to be due to localized passivation followed by rapid reactivation under the salt film(5).

An increasing trend of Maximum current densities is observed for all conditions shown in fig 2. It is obvious that critical current density is marginally affected by nitrate ion addition and its values and also the slope of i_{crit} vs. temperature curve is slightly changed for nitrate containing solution in comparison with ones without nitrate.

According to the effect of nitrate ion addition on both limiting current density (i_{lim})(2) and critical current density (i_{crit}) of DSS 2205, it can be concluded that increase in critical pitting temperature (CPT) of DSS 2205 is a consequence of change mainly in i_{lim} rather than i_{crit} values. These results are in a good agreement with CPT theory proposed by Salinas-Bravo and Newman (fig 3). According to their proposed mechanism for CPT, the CPT can be affect by change in diffusion limiting current density, pit critical current density for passivation or both. The effect of addition of nitrate in increasing CPT can be related to an increase on diffusion limiting current density, although its addition has also changed marginally on critical current density.

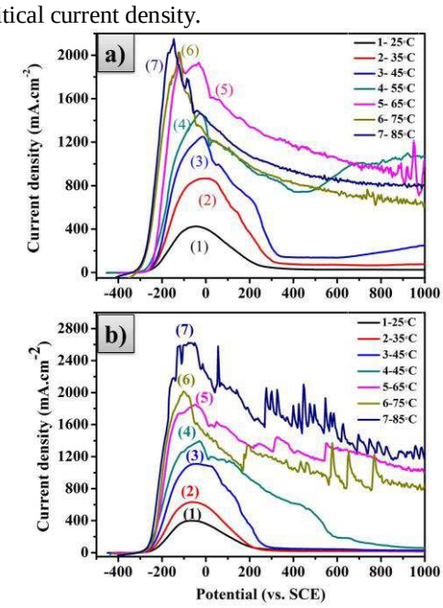

Figure 1. Potentiodynamic polarization curves of DSS 2205 alloy solution annealed at 1050°C mV in a) 5M HCl and b) 5M HCl+0.1M $NaNO_3$ solutions at different temperatures. Scan rate is 5 mV/Sec

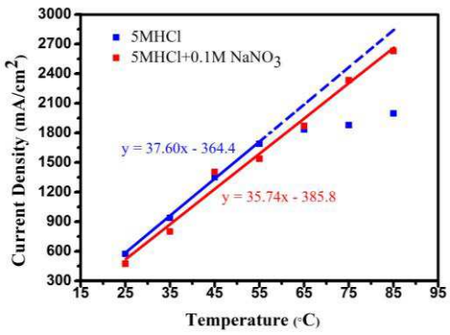

Figure 2. Critical current density vs. temperature obtained from potentiodynamic polarization curves of DSS 2205 alloy.

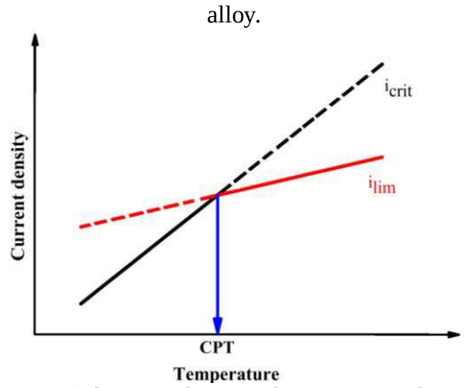

Figure 3. Schematic drawing showing i_{lim} and i_{crit} vs. temperature, the cross section is introduced as CPT by Salinas-Bravo and Newman

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