

KINETIC STUDIES OF LOCALIZED CORROSION OF 204 STEEL IN CHLORIDE SOLUTION

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ABSTRACT

The present work deals with the method of finding a rate equation and possible kinetic mechanism for passivity breakdown of austenitic steel due to pitting in chloride solution.

It is seen that the rate is dependent on temperature, chloride content of the solution, passivity curve etc. The order of reaction with respect to chloride ion is found out. The rate can be expressed as an equation, $\text{Rate} = A K (\text{Cl})^{1/3}$. Where K is the rate constant and Cl is the concentration of Cl ion. The activation energy for pit initiation process has also been found. It comes out to be around 90 kJ/m. Studies of kinetic data by Reduced Time plot indicate that initiation of pitting follows a mixed mechanism of diffusion and chemical controlled reaction.

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INTRODUCTION

It is well known that austenitic stainless steels have excellent corrosion resistance in aqueous solution due to a protective surface passive film. However stainless steel is prone to localized corrosion, in the form of pitting, in presence of chloride ions due to breakdown of this passive film.

Numerous studies have been carried out on various aspects of pitting, viz. Pitting potential, effects of temperature, concentration,

mechanisms etc, but limited literature is available on the kinetic aspects of pitting. Nisancioglu et al¹ studied the relation between incubation time, pitting potential and rate constant on pitting of aluminum in chloride solution. Engell and Stolica² determined the order of reaction with respect to chloride ion for aluminum, Beccaria and Poggi³ worked on the kinetics of aluminum corrosion in NaCl solution with some surface treatments.

In the present work studies have been conducted to find the factors influencing the rate of passivity breakdown on stainless steel from the concept of induction time. An equation expressing the rate has been established. It is also attempted here to find a rate controlled mechanism through the concept of a Reduced Time Plot.

THEORY AND EXPERIMENTAL SET UP

The steel sample is potentiostatically polarized into the passive region, a known concentration of chloride ion is injected into the solution. The current starts increasing due to the generation of pits and then a steady state value is reached. The induction time (t) is taken as the time required for the current to attain the steady state value⁴. If t is the induction time, then 1/t is taken as the rate of pitting that is the number of events per unit time. So the rate equation for initiation of pitting is given by

$$1/t = K (\text{Fe}^{++})^m (\text{Cl}^-)^n \dots\dots\dots(1)$$

Where K is the rate constant and m & n are orders of reaction with respect to Fe⁺⁺ and Cl⁻ ions respectively.

$$\text{Thus } \log(1/t) = \log K + m \log (\text{Fe}^{++}) + n \log (\text{Cl}^-) \dots\dots\dots(2)$$

Taking K, m and (Fe⁺⁺) as constants, plot of log (1/t) Vs log (Cl⁻), gives the order of reaction with respect to concentration of chloride ion.

$$\text{Again } K = K_0 e^{-E/RT} \dots\dots\dots(3)$$

So from equations (2) and (3), keeping chloride concentrations fixed and varying temperature, activation energy can be found out.

REDUCED TIME PLOTS

Identification of rate controlled mechanism

is possible by "Reduced Time Plots, first introduced by Sharp et al⁵ and Giess⁶ Here kinetic relationships are first expressed in the form

$$g(f) = kt \dots\dots\dots(4)$$

Where f is the fraction corroded in t time and k is the rate constant. If t_{0.5} be the time for 0.50 fraction reacted then

$$g(f)/g(f=0.5) = t/t_{0.5} = t_r \dots\dots\dots(5)$$

where t_r is the dimensionless time scale, reduced time. The above expression is independent of the rate constant k and is dimensionless. It only depends on the form of g(f) (Table 1). Plotting f vs. t_r for all possible reaction mechanisms from Table 1, a master chart can be obtained. Thus if a reaction is controlled by a particular reaction mechanism, all the data points would fit into the curve for that mechanism, irrespective of nature of the system, temperature or any other factors that influence the rate.

The experiments were conducted with variation of chloride concentrations (0.1N, 0.2N & 0.3N KCl) in 1N H₂SO₄ solutions and temperatures maintained at 303 K, 313 K and 323 K. AISI 304 stainless sample (Table – 1) about 1 cm diameter. One of the circular faces of the sample was polished with 00, 1/0, 2/0, 3/0 emery papers and finally on wet cloth, until a mirror finished surface was obtained. The sample was then observed under optical microscope at 50X magnification to ensure that no pits, scratch or cracks were present. The sample was tightly covered with Teflon around its round surface up to the edges so that no crevice could form. About 200ml of each batch above solution was taken in a glass reactor with arrangement for thermometer, salt bridge, electrodes etc. The temperature of solution was maintained within + -1 deg. C, using Remi heater stirrer. The sample was then introduced into the solution through one of the holes in the top of the vessel. It was then polarized, with scan rate of 50mV per 5 minute interval, using a Wenking standard Potentostat model St-72, according to methodology of ASTM G5 – 72. The sample was anodically polarized to different starting potentials (0.30v, 0.35v, 0.40v vs. SCE) within the passive region, when a fixed concentration of chloride ion was injected.