

Initial Stage of Pitting Corrosion of SUS 304 under Thin Electrolyte Layers Containing Chloride Ions

Yusuke TSUTSUMI, Atsushi NISHIKATA and Tooru TSURU

Department of Metallurgy and Ceramics Science
Graduate School of Science and Engineering
Tokyo Institute of Technology
2-12-1 O-okayama, Meguro-ku, Tokyo, Japan

Introduction

In marine atmospheric environment, airborne salt particles adhere to metal surface. The moisture present in the atmosphere combined with them causes formation of electrolyte droplets or thin layers containing chloride ions. It is said that as these droplet or thin layers are drying, the concentration of chloride ions increases, leading to occurrence of pitting corrosion of stainless steel. In this study, we investigated the effects of drying rate, amount of airborne salt and pretreatment on the chloride concentration $[Cl]_{pit}$ at the onset of pitting.

Experimental

Figure.1 is the schematic diagram of the cell. A thin $MgCl_2$ solution layer was formed on this cell and was dried at various drying rates. Electrodes were mounted in a hard, cold-curing epoxy resin. SUS304 stainless steel was employed as working electrode. The exposed metal-epoxy interface was covered with electrodeposition paint to prevent crevice corrosion. Initiation of pitting corrosion was detected by monitoring the corrosion potential with respect to Ag/AgCl reference electrode during drying. Simultaneously, the solution resistance R_s was monitored by a pair of Inconel625 electrodes to determine $[Cl]_{pit}$. This cell was mechanically polished by #1000 SiC paper, and cleaned in distilled water before starting experiment.

Results and Discussion

The pitting corrosion tests of as-polished SUS304 were carried out at various drying rates and different amounts of $MgCl_2$ deposits on the specimen. The results are shown in **Fig.2**. The drying rates were varied by changing the relative humidity from 95 to 25% RH at different speeds. In this study, the drying rate v was defined as the $(\Delta RH\%/\Delta t)$ and varied from 1.75 to 70 %/h. The amounts of $MgCl_2$ deposits were varied between 1.98 and 79.2 g/m^2 by changing the initial thickness, d_0 , of electrolyte layer and the initial chloride concentration, $[Cl]_0$, which are shown in **Fig.2**. At 79.2 g/m^2 $MgCl_2$ deposit, the $[Cl]_{pit}$ was not so sensitive to the drying rate, and varied from 6 to 9.92 M which is the concentration of crystallization of $MgCl_2$. The $[Cl]_{pit}$ showed a minimum value (5.8 M) around $v = 6\%/h$ at 39.6 g/m^2 of $MgCl_2$ deposit. Pitting corrosion was hard to occur by the decrease of amounts of deposits to 9.90 and 1.98 g/m^2 .

The effect of immersion in $MgCl_2$ solution with different concentrations as pretreatment was examined. Before the corrosion test, the cell was immersed in 3~6 M chloride solutions ($MgCl_2$) for 24h. $MgCl_2$ deposits of 39.6 g/m^2 and drying rate of 5.8%/h were employed, which was the most aggressive condition in this study as shown in **Fig.2**. The results are shown in **Fig.3**. It's obviously that the probability of pitting corrosion $F(x)$ which means the ratio of pitting/non-pitting specimens was lowered by pretreatment in the higher concentration solution. The observation of metal surface by optical and laser microscope was also carried to explain these results.

The pitting corrosion mechanism based on the distribution of defect sites of SUS304 surface is discussed.

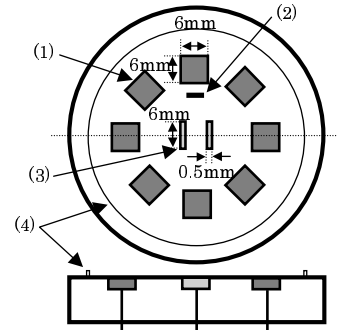


Fig.1 Schematic diagram of cell for electrochemical measurement (1)W.E: SUS304 (2) R.E: Ag (3) Inconel625 (4) bank

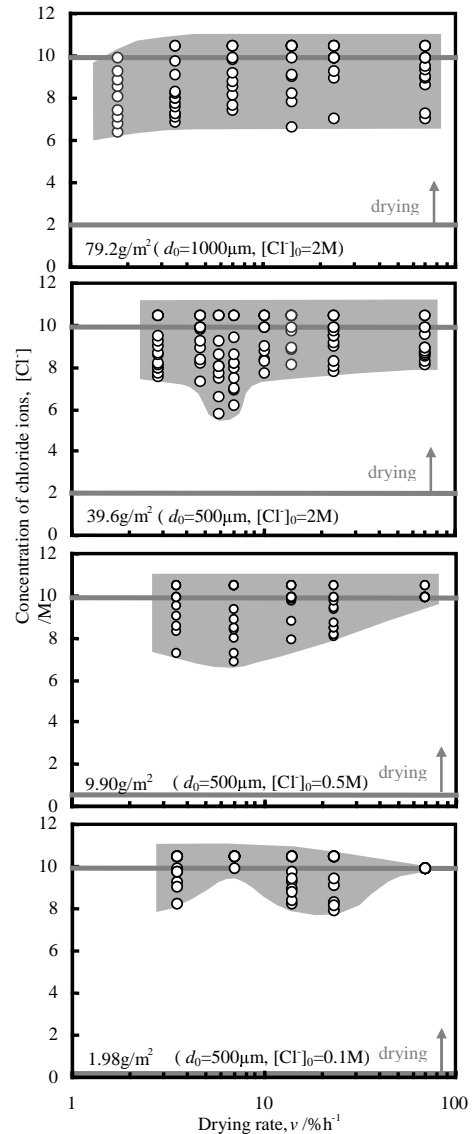


Fig.2 Effect of drying rate, v , on concentration of chloride ions, $[Cl]_{pit}$, at the onset of pitting corrosion

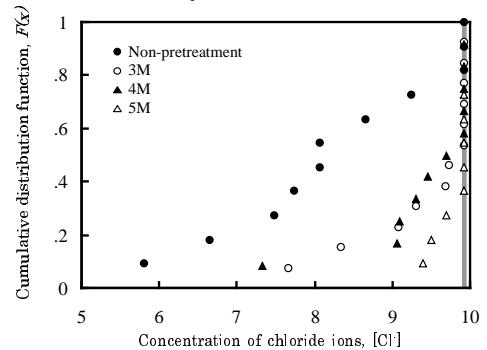


Fig.3 Effect of pretreatment due to immersion in 3M, 4M and 5M chloride solutions for 24h