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Pitting Corrosion of Type 430 Stainless Steel under Chloride Solution Films

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Introduction

Nowadays, stainless steel is widely used in construction of bridges and buildings because of its excellent corrosion resistance. However, stainless steel may suffer with corrosion in environments especially containing halide ions. Airborne chloride salt causes corrosion of stainless steel in seashore areas. Even though duplex stainless has excellent corrosion resistance, ferritic or austenitic stainless steels usually preferred from economic point of view. Therefore, investigation of mechanism of corrosion of ferritic and austenitic stainless steels under environments containing halide ions is important.

In marine atmospheric environments, airborne salts are deposited on the stainless steel surface. At night water vapor condenses to form droplets containing chloride on the stainless surface due to increasing relative humidity (RH) and declining temperature. During the daytime, the chloride ion concentration increases due to water evaporation. Water droplets/films with highly concentrated chloride solution cause pitting corrosion. The previous researches reported that critical concentration of chloride ion for occurrence of pitting corrosion is *ca.* 5M and 6M on stainless steel type 430 and 304, respectively. However, detailed investigation of the effect of droplet dimensions (thickness, diameter) on probability of occurrence of pitting corrosion is lacking. There is no report on the effect of cathodic reactions on pitting. Actually, cathodic reaction is a key factor for pitting corrosion. There are many reports on the study of mechanism of corrosion by immersing the sample into bulk solution. However, corrosion process under droplets (thin solution layers) is quite different from that in the bulk solution. Electrochemical techniques are very often used for evaluation of corrosion resistance of metallic materials and the mechanistic studies.

In addition, composition and structure of passive film formed on the stainless steel surface play as an index to its corrosion resistance, it is well known that chromium is one of the most beneficial elements for corrosion protection. There are lots of researches to improve chromium contents on the material surface by coating, planting, etc. In addition, the inclusions on the metal surface play as the preferable sites for occurrence of corrosion. Corrosion resistance of stainless steel will be improved with decreasing the surface inclusions. Nitric acid solution is employed as a common solution for improving the corrosion resistance in the both sites, industry and study. However, this solution is toxic with not only dilute but also concentrated content. Therefore, finding a non- toxic method has been posed urgently.

Experimental

The stainless steels type 430 (SS430), type 304 (SS304), and type 303 (SS303) were employed in this study. The samples were prepared approximately due to each experiment conditions.

For pitting corrosion tests: The specimens sizes were 80 mm x 35 mm x 4 mm (**chapter 2**) and 100 mm x 100 mm x 4 mm (**chapter 3**), respectively. The specimen surface was ground to a 1000 grit surface using silicon carbide paper and cleaned ultrasonically in distilled water. Five droplets of $MgCl_2$ solution were randomly deposited on the specimen sample with micropipette. The specimen was kept in a humidity- and temperature- controlled chamber. The relative humidity be controlled (fix or cyclic change) according to specific experiments.

For the electrochemical measurements: a three-electrode cell was employed. The working electrode (WE) was a stainless steel plate (1 mm × 10 mm), whereas platinum (1 mm × 10 mm) and silver plates (1 mm × 1 mm) acted as counter (CE) and reference electrodes (RE), respectively. All electrodes were embedded about 0.5 mm apart and parallel to each other in an

epoxy resin. **(Chapter 3)**. The end surface was ground to a 4000 grit surface and ultrasonically cleaned in distilled water. The AgCl was deposited on the RE surface by the galvanostatic polarization method for making an Ag/AgCl reference electrode. The cathodic polarization curves under thin electrolyte layers containing chloride ions were observed.

For the surface modification experiments: a SS430 plate (20 mm x 20 mm x 4 mm) was embedded in epoxy, the sample surface was ground with a 1000 grit SiC paper and then ultrasonically cleaned in distilled water. The specimen surfaces were modified in bulk NaNO_3 solution by potential cycling method. The treated specimens were undergone the corrosion tests for evaluating the corrosion resistance.

Results and Discussion

The mechanism of pitting corrosion of stainless steel type 430 under the cyclic change in relative humidity was investigated. Under the cyclic change in relative humidity between 95% and 45%, the solution layer thickness changed from ca. 1 mm ($2\text{M } [\text{Cl}^-]$ at 95%RH) to about 0.23 mm ($8.6\text{M } [\text{Cl}^-]$ at 45%RH). The corrosion potentials of stainless steel were simultaneously monitored. The results show that, the relative humidity ranges for occurrence of pitting (RH_{pit}) and repassivation (RH_{rep}) are 68%- 48% and 67%-73%, respectively. Besides, the RH_{pit} and RH_{rep} ranges are 58%-47%; 56%-70% for SS304, and 63%- 50%; 61%-72% for SS303, respectively. In addition, an increase in temperature resulted an increase in both RH_{pit} and RH_{rep} . In addition, the dissolutions of MnS inclusions for occurrence of pitting corrosion were discussed.

Furthermore, the pitting corrosion probability of SS430 under MgCl_2 solution films was investigated for thicknesses ranging between 1 and 70 μm and diameters of 1 to 13 mm. The results show that when the relative humidity exceeds 85%, no pitting corrosion occurs under solution films regardless of thickness and diameter. On the other hand, the pitting corrosion probability decreases when the solution film diameter and thickness decrease. No pitting corrosion occurred when the solution film diameter was approximately 1 mm, irrespective of solution film thickness and RH. Finally, a decrease in solution film thickness is supposed to suppress the anodic dissolution from nucleated pits, and a decrease in diameter is expected to reduce the effective cathodic area for pit growth.

According to the enhancement of pitting corrosion resistance, it was improved after 450 times of potential cycles between 0.5 V and 0.9 V in 5M NaNO_3 solution with a scan rate of 5 mV/s. Micro pits with 1-2 μm were found on the specimen surface. The pitting corrosion potential increase from 0.2V (as-polished) to ca. 0.5 V in 0.5 M NaCl solution. Besides, the pitting corrosion didn't occur on the treated specimen surface under relative humidity cyclic changes between 95% and 45%.