Pitting corrosion of sensitised type 304 stainless steel under wet–dry cycling condition

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ABSTRACT

The pitting corrosion of sensitised stainless steel (SS) 304 during wet–dry cycling were investigated and compared with that of AR one. The average relative humidity for pitting corrosion during drying and repassivation during wetting correspondingly increased from 56% to 65% and from 67% to 79% by sensitisation. The decrease in pit potential and critical chloride concentration provides the degradation evidence of sensitised SS 304. The pitting probability and pit average size were promoted by sensitisation. The pit morphology changed from round to irregular shape. Such modification was possibly induced by preferential corrosion along grain boundaries where the pit initiated.

1. Introduction

Austenitic stainless steel (SS) demonstrates high corrosion resistance because of the formation of a passive layer markedly enriched chromium (Cr) content. Hence, such steel is used commercially in various industrial applications. However, in a marine atmospheric environment, airborne sea salts are deposited with moisture to form a thin electrolyte film and/or droplet in a wide range of relative humidity (RH). Under the action of highly concentrated aggressive chloride anion in such thin film, stainless steels suffer from pitting corrosion even below the relative humidity, at which general atmospheric corrosion of carbon and weathering steel can occur [1–4].

Pitting mostly initiates at surface active sites, such as inclusions or any place with a diminished passive film, as well as chromium-depleted zones [5–7]. Sensitisation, which is normally induced during welding or improper heat treatment, causes Cr depletion at the region adjacent to the grain boundaries [8–10]. Once the Cr content of the depleted zone falls below ~12 wt.%, the alloy becomes susceptible to corrosion because the passive film at such region is less protective. Therefore, researchers need to understand the role of sensitisation on pitting corrosion of austenitic stainless steel.

Many studies have reported about the pitting corrosion of stainless steel under the effect of sensitisation in solutions [11–17], but this topic has not been addressed in atmospheric environment or droplet conditions. Mudali et al. [15] reported that the pitting resistance in NaCl and H_2SO_4 solution decreased as the degree of sensitisation increased, and pitting attack was found at the grain boundaries and precipitate/matrix interfaces because of the precipitation of $Cr_{23}C_6$ carbides for 304 and 316 L stainless steel. The degradation of pitting corrosion resistance related to sensitisation was also verified by Rashid et al. [16]. Although previous studies provided many valuable information to extensively explore the role of sensitisation, the pitting potentials measured in bulk solution are not suitable for the atmospheric corrosion.

In marine atmospheric environments, RH is an important factor for the occurrence of pitting corrosion of stainless steel [19–22]. The droplet thickness variation due to RH changes directly effects on the oxygen reduction as cathodic reaction [19,20] and on Fe dissolution to form passive film [21]. However, chloride ions in droplet can be concentrated due to drying up of the thin water layer as RH decreases [22]. When the chloride ions exceed a critical concentration, passive film could be broken to generate pitting corrosion. In contrarily, when the chloride ions is decreased to critical concentration due to RH rises, repassivation likely occurs [3]. Therefore,

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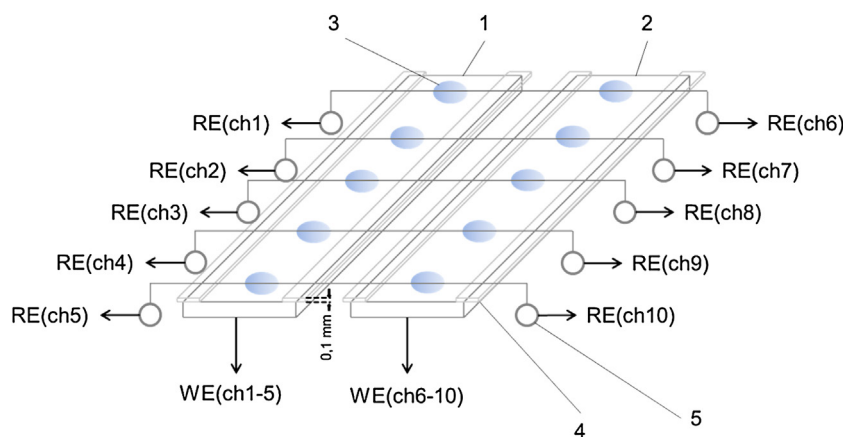
Fig. 1. Schematic diagram of cell for monitoring pitting corrosion under wet-dry condition; 1 the sensitised SS 304, 2 as-received SS 304, 3 $MgCl_2$ droplet, 4 acrylic plate as spacer, 5 Ag wires and their holders.

the essential features of pitting corrosion are the pitting RH (RH_{pit}) and the repassivation RH (RH_{rep}) for stainless steels. However, conventional electrochemical techniques, which are often used in bulk solution, are extremely difficult to evaluate the corrosion behaviour in the atmospheric environment, due to the problems associated with nonuniform current distribution for measurements where the potential is applied [23].

Over the past few decades, several electrochemical techniques have been used to investigate atmospheric corrosion. The vibrating Kelvin probe method has been demonstrated useful to measure surface potentials under solution droplets or thin electrolyte films [4,18]. Electrochemical impedance spectroscopy was employed by Nishikata et al. to evaluate the corrosion rate of metals covered with thin electrolyte film [23–25]. Electrochemical studies on atmospheric corrosion have also been published by other researchers [26].

The pitting corrosion of stainless steel has been described as a stochastic phenomenon [27,28]. Pitting corrosion tests should be conducted using as many samples as possible. In a previous study [29], a novel cell without epoxy resin was designed to evaluate RH_{pit} and RH_{rep} for the onset of pitting corrosion and repassivation, respectively. Such method can monitor the corrosion of 10 local spots under electrolyte droplets without crevice corrosion. They observed a potential drop at the onset of pitting when RH decreased, as well as a potential increase during the subsequent wetting stage, which is ascribed to the pit repassivation. They reported the determined value of RH_{crt} for pitting of SS 304 was approximately 65% RH during wet-dry cycling condition by using $MgCl_2$ droplet. In the current study, the pitting corrosion of SS 304 under the effect of sensitisation in wet–dry condition was investigated using the new cell. The potential variation during the wet–dry test was monitored, and the RH_{pit} and RH_{rep} were determined. Moreover, the pitting morphology and electrochemical behaviour in the simulated solution were discussed.

2. Experimental

Type 304 stainless steel plates in 4 mm thick were cut into 70 mm × 25 mm sheets and then cleaned as the specimen. The chemical composition is shown in weight percentages: C 0.050%, Si 0.55%, Mn 0.92%, P 0.031%, S 0.005%, Ni 8.09%, Cr 18.12%, Fe bal. Sensitisation treatment was conducted by annealing the plate at 700 °C for 24 h. Non-heat-treated samples were identified as "as-received" samples. All the specimens including sensitised and as-received plates were ground to 2000# by sandpaper before electrochemical measurement. The degree of sensitisation was evaluated by

double-loop electrochemical potentiokinetic reactivation (DL-EPR) in a solution containing 0.5 mol/L H_2SO_4 and 0.01 mol/L KSCN [30]. In DL-EPR test, the potential was swept from 50 mV lower than open circuit potential (OCP) up to 300 mV vs. SCE and then reversed to the initial potential with the scanning rate of 100 mV min^{-1}.

2.1. Wet–dry cycle test

Fig. 1 shows the schematic of cell for monitoring pitting corrosion under wet–dry condition. Two identical specimens, one sensitised and one solution treated, were placed in parallel on an acrylic plate. Five droplets of 50 μL 1.0 M $MgCl_2$ solution containing air (the initial volume: 8 mm diameter and ca. 1 mm thickness) were placed on the surface of each specimen. Five Ag wires (0.1 mm in diameter) as reference electrodes were placed horizontally in each droplet and then strained by fixing them to five holders on both side of the acrylic plate. The gape distance between the sample surface and the Ag wire was successfully maintained at about 0.1 mm by the insolation spacers and strains. The surface area of Ag wire that contacted the droplet is calculated about 0.02 cm^2.

The wet–dry cycle test was conducted in a temperature–humidity-controllable chamber without inert gas (IW222 Yamato). The temperature remained constant at 25 °C. Since the concentration of 1 M $MgCl_2$ was the equilibrium chloride concentration in droplet at 95% RH [19,22,31], maximum RH of 95% RH was employed to decrease the effect of droplet evaporation and save the experiment period. The RH was firstly reduced from 95% to 45% at a rate of 5% per hour and then increased from 45% to 95% at the same rate. Such wet–dry cycles were conducted seven times for one test to statistically investigate on the RH_{pit} and RH_{rep}. The potential of the 10 droplets was monitored using a multichannel electrometer (Keithley Model 2000 Digital Multimeter), which has no influence on the pitting process. By using this cell, the pitting corrosion of 10 droplets were evaluated on the sensitised and as-received samples respectively, by conducting two times of the whole test.

2.2. Corrosion morphology and EDX observation

Pitting photographs for all droplets after the wet–dry cycle test were observed firstly under a microscope (LV150 Eclipse, Nikon). In addition, one droplet spot from the surface for sensitised and as-received sample, that had the most pit numbers, was observed to determine the pit size respectively. The two droplet samples were etched with oxalic acid by applying a current density of 1 A/cm^2 before the examination. To expose the pitting initiation site, some