

Investigation of the Pitting Corrosion Behaviour of 403 Martensitic Stainless Steel in Bromide and Iodide Solutions

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1- Introduction

Various aggressive anions have been reported that are capable to induce pitting corrosion of stainless steels (SSs). The most studied anion is normally chloride due to its commonplace presence in almost all environments. It has been reported that bromide and iodide can also provoke pitting in the case of stainless steels.

Most studies on SSs report that the aggressivity of halide anions increases in the order of: $I < Br < Cl$. In other words, pitting potential, E_{pit} , of SSs with low content of Mo, has the highest value in chloride bearing environments and the least one in iodide bearing one.

This work aims to examine the effect of bromide and iodide on both stable and metastable pitting of 403 martensitic SS. It is also intended to probe possible correlations between metastable pitting characteristics and stable pitting.

2- Experimental

403 martensitic SS was used in this study. It was composed of 0.165 wt% C, 11.64 wt% Cr, 1 wt% Ni, 0.83 wt% Mn, 0.29 wt% Si, 0.16 wt% Cu, 0.04 wt% Mo, 0.04 wt% N, 0.04 wt% Co, 0.03 wt% V, 0.03 wt% P and 0.01 wt% S. To impede the risk of crevice corrosion in mount/alloy interface, specimens were primarily pre-passivated in 0.1 M Na_2SO_4 solution by applying the constant potential of 850 mV_{SCE} to them for 900 s. The specimens then served as working electrode (WE) in a three-electrode cell alongside with saturated calomel (SCE) and platinum plate as reference and auxiliary electrodes, respectively. Prior to each electrochemical experiment, working electrodes were wet grinded by SiC paper up to 1200 grit. WEs were then rinsed by distilled water, dried by flowing warm air and put into use. Studied solutions were also made using analytical grade reagents of NaBr and NaI in concentrations of 0.01, 0.1, 0.2, 0.5 and 1 M.

In order to investigate stable pitting, potentiodynamic experiments were implemented. Polarization in these experiments was began from 50 mV below the open circuit potential (OCP) up to onset of pitting corrosion at high potentials. Sweep rate was 30 mV/min. Before running the experiment, OCP was

recorded for 3600 s to obtain steady state condition. Potentiostatic experiments which also served for studying the metastable pits, were performed by applying the constant potential of -50 mV_{SCE} to the specimens for 900 s. OCP recording for obtaining steady state condition in this case was last for 600 s. To check data reproducibility, each electrochemical experiment was repeated three times.

3- Results and Discussion

Potentiodynamic experiment showed that OCP in different concentrations of NaBr and NaI solutions are approximately equal. It was also found that 403 SS is passive in both solutions and undergoes pitting corrosion at higher potentials. Pitting potentials, E_{pit} , of 403 SS in NaBr and NaI solutions are shown in Fig. 1. It is observable that E_{pit} for each specific concentration is lower in the case of bromide. As reported by other scholars, there is a linear relationship between E_{pit} and logarithm aggressive anion concentration. This relationship is calculated for each solution by means of linear fitting to E_{pit} s. The more negative slope of the fitted line as well as lower intercept in the case of NaBr solution confirm that bromide has more aggressivity for 403 SS compared to iodide.

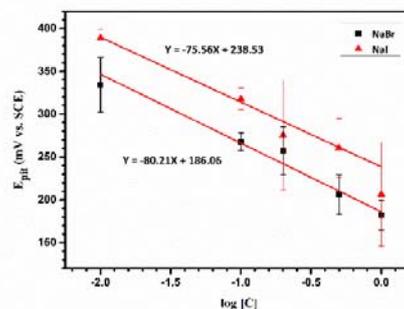


Fig. 1 Average of 403 SS pitting potential in NaBr and NaI solutions as a function of concentration. Linear fit has also been shown for each solution. Error bars are representing 95% confidence limit

Potentiostatic experiments showed that 403 SS is passive at the potential of -50 mV_{SCE} in both 0.5 M solutions of NaBr and NaI. Metastable pits were also observed in both environments as current fluctuations in the potentiostatic experiments. Fig. 2 shows the occurrence frequency of metastable pits. The values shown in Fig. 2 are calculated using 3 identical potentiostatic experiments. According to this figure, occurrence frequency of metastable pits was found to have greater values in NaBr solutions in comparison with NaI one. In other words, it was found that the presence of bromide activates more sites for

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metastable pitting nucleation. That is, bromide has more aggressive activity in the nucleation stage of pitting which can be attributable to its lower anionic radius. Bromide's smaller anionic radius increases the probability of its diffusion toward the passive film and initiating a localized breakdown. Declining trend of metastable pits occurrence frequency which is observable in Fig. 2 for both environments, is also attributed to diminishing the potential sites for pit nucleation over the working electrode exposure time.

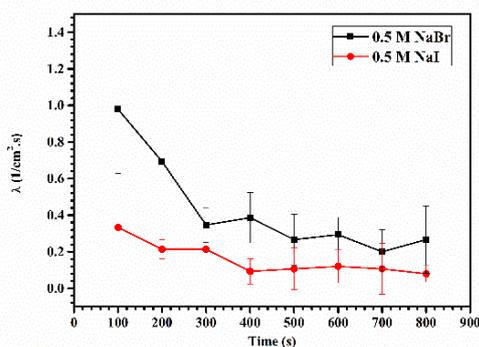


Fig. 2 Occurrence frequency of metastable pits during the time obtained from 3 identical potentiostatic experiments in NaBr and NaI solutions. Error bars are representing 95% confidence limit

Other metastable pitting characteristics such as lifetime, peak current, radius and stability product were also assessed in this study. Lifetime which is defined as the difference between nucleation and re-passivation times in the current-time curve, was found to be 0.8 s lower in NaBr solution compared to NaI one. However, metastable pits peak current was averagely 450 nA higher in NaBr solutions in comparison with NaI ones. Peak current is also defined as the difference between passive background current and the greatest current during the metastable pit growth. Possessing current-time curve for each individual metastable pit, its radius was calculated by using Faraday's law. Metastable pits radii were found to be approximately equal to 2 μm for both NaBr and NaI solutions.

Galvele has proposed a criterion for transition from metastability to stability. According to his criterion, if the stability product which is defined as the product of pit current density and its radius exceeds a critical value, the pit will become stable. Current density can be itself calculated by dividing metastable pits peak current per their surfaces ($2\pi r^2$, which a denotes radius). The values of metastable pits stability product have been represented in Fig. 3. As can be seen, stability product has slightly a higher value in NaI solutions in comparison with NaBr one. The median value for stability products in NaBr and NaI solutions are respectively 0.018 and 0.024 mA/cm. As observed in spite of higher E_{pit} of 403 SS in NaI solution, metastable pits stability product is greater in comparison with NaBr solution. In other words, metastable pits developed in presence of iodide have grown more than those initiated in presence of bromide. Onset of stable pitting at higher potentials in

NaI solution in spite of its greater stability product may stem from harder salt precipitation in that environment and also from lower occurrence frequency of metastable pits which is an indicative of initiation stage of pitting.

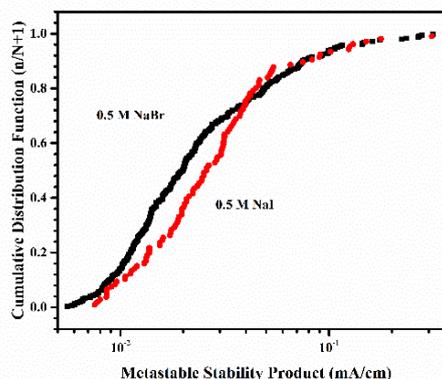


Fig. 3 Cumulative distribution of metastable pits stability product for 403 SS in 0.5 M solutions of NaBr and NaI. The values have obtained by considering 3 identical experiments for each environment

4- Conclusions

The effects of bromide and iodide anions on pitting corrosion of 403 martensitic stainless steel were studied in this work by means of potentiodynamic and potentiostatic experiments.

It was found that pitting potential of 403 SS is lower in NaBr solution in comparison to NaI solution. Hence, it can be said that bromide anion has more aggressivity for 403 SS compared to iodide.

Occurrence frequency of metastable pits was also found to be higher in presence of bromide which means that bromide is capable to activate more potential sites for pit nucleation in comparison to iodide.

Comparing NaBr and NaI solutions, it was also found that the lifetime of metastable pits was also shorter in the case of NaBr. However, metastable pits peak current was approximately 450 nA greater in 0.5 M NaBr solution compared to NaI. Metastable pits radii were found to be almost equal in both media. Nevertheless, metastable pits stability product was nearly 0.006 mA/cm greater in the case of iodide. The less probable stable pitting in NaI solution (higher E_{pit}) can be attributed to possibly harder precipitation of salt in the pit bottom as well as lower pit initiation events (lower occurrence frequency of metastable pits).