

SKFM Observation of Corrosion on SUS304 Stainless Steel

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Super Kelvin force method (SKFM) which is one of AFM measurement method is very useful for corrosion study, because the surface morphology and potential distribution can be obtained at high accuracy. The most cases the atmospheric corrosion is accelerated by sea salt. The initial corrosion mechanism of steels by sea salt particles is not well known. In-situ observation of corrosion initiated from a small water droplet of $MgCl_2$ was done by SKFM and the mechanism of atmospheric corrosion is discussed. The test specimen used was a SUS304 stainless steel. SKFM measurement was done under the constant temperature (297 ± 0.5 K) and the relative humidity range of 40 to 50 %. The test specimen was dry-polished up to 0.3 μm roughness and droplets of $MgCl_2$ with diameter of 0.3 - 0.8 mm were attached on the specimen, then they were kept the condition mentioned above. The corrosion morphology can be divided into 2 types: 1. Corrosion progressed inside of specimen with corrosion product when the liquid layer of $MgCl_2$ was thin. 2. Corrosion progressed inside of specimen without corrosion product when the liquid layer of $MgCl_2$ was thick. The corrosion product is invisible when the liquid layer of $MgCl_2$ was thin. Potential of the part where the droplet is attached becomes more negative as the thickness of liquid layer increased after corrosion started. Enrichment of chloride ion occurred at corroding part and water is supplied by the deliquescence of metal chloride.

Keywords : Super Kelvin Force Microscope, $MgCl_2$, SUS304, atmospheric corrosion, liquid thickness

1. Introduction

One of the biggest problems when we use stainless steels near seashore environments is the visible rust formation by sea salt particles. It is commonly said that critical amount of attached sea salt particles exists for the visible rust formation.¹⁾ To study the mechanism of visible rust formation, $MgCl_2$ droplets with different concentrations were attached on the stainless steel and the rust formation was studied by using a super Kelvin force microscope (SKFM) which we have developed recently,²⁾ an optical microscope and EDX image mapping.

2. Experimental method

2.1 SKFM Equipment

The scanning device for X-Y direction is used an accurate X-Y stage. The accuracy of the X-Y stage is less than 0.1 μm for repeated positioning. The X-Y stage can move up to 10 X 10 cm, but the maximum scanning area is limited to 1 X 1 cm. The minimum step of the X-Y stage is 0.1 μm , so the scan area of 25.6 X 25.6 μm is the minimum scan area for the stage scan mode when the acquired data points are 256 X 256. The specimen size

of 20 X 20 X 2.5 cm can be observed. Two types of piezo scanner can be used. One is 100 X 100 X 15 μm of working distance and another is 0 X 0 X 40 μm of working distance. After the tip is set the observing position, the scan mode can be chosen either the stage scan mode or the piezo scan mode. If we use the scanner of 100 X 100 X 15 μm , the scan range can be chosen from 10 nm to 1 cm. The tip used for SKFM measurement was the conductive gold-coated Si tip with the resonant frequency of around 25 kHz. The SKFM image was taken every 1 hour or 2 hours with data points of 256 x 256.

2.2 Atmospheric corrosion test

The test specimen used was a SUS304 stainless steel and was dry-polished up to 0.3 μm roughness. Droplets of 0.025 - 1 % $MgCl_2$ with diameter of 0.3 - 0.8 mm were attached on the specimen, then they were kept under the constant temperature (297 ± 0.5 K) and the relative humidity range of 40 to 50 %. The temperature and the relative humidity were monitored every 5 minutes. Beside SKFM observation, EDAX analysis and the optical microscope observation were also done. The equivalent salinity, ES, is estimated by the following formula:

$$ES = (D \cdot V \cdot C \cdot MCl_2) / (A \cdot MM_{MgCl_2}) \quad (1)$$

Where D: relative density at certain concentration, V: volume of attached droplet which can be estimated from the topography, C: concentration at certain relative humidity, M: molecular weight and A: area of attached droplet.

3. Result and discussion

3.1 0.025 % MgCl₂

Figure 1 show the SKFM image of SUS304 stainless steel with attaching 0.025 % MgCl₂. The equivalent salinity is estimated 0.3 mg/dm². The potential of the part where the droplet of MgCl₂ was attached was about 120 mV more negative than that of dry-polished part on the average and the potential of the part where the corrosion proceeds was about 120mV more negative than that of the part where the droplet of MgCl₂ was attached. However, after 6 hours corrosion stopped and the potential of the part where the corrosion proceeded before had become about 100mV more positive than that of the part where the droplet of MgCl₂ was attached and the potential of the part where the droplet of MgCl₂ was attached was about 80 mV more negative than that of dry-polished part on the average (Figure 1(b)). The corrosion initiated other part after 20 hours (Figure 1(c)). Thus corrosion proceeds with repeating initiation and extinction of pitting type of corrosion. The main difference of corrosion morphology between pure iron and SUS304 steel is the number of corrosion initiation site.

3.2 0.1% MgCl₂

Figure 2 show the SKFM image of SUS304 stainless steel with attaching 0.1 % MgCl₂. The equivalent salinity is estimated 1.0 mg/dm². The potential of the part where the droplet of MgCl₂ was attached was about 20 mV more negative than that of dry-polished part on the average at the beginning (Figure 2(a)). The potential of the part where the droplet of MgCl₂ was attached, however, became more negative with time. The potential difference between the part where the droplet of MgCl₂ was attached and the dry-polished part became 0.9V at maximum 14 hours after the droplets had been attached (Figure 2(b)). The macro anode and cathode site were detected at corroding part. The increase of the height of corrosion product indicates the progress of corrosion. The macro anode and cathode site changed with time. The potential difference between anodic and cathodic site was 0.26 V after 14 hours (Figure 2(b)) and became 0.66V after 50 hours (Figure 2(c)). The liquid layer became thin at the left side of the droplet where corrosion did not occur. EDAX analysis (Figure

3) showed the enrichment of chloride ion and the lack of magnesium ion near corroding part. Since oxide was partly observed at corroding part, the corrosion product was composed with the mixture of rust and liquid of metal chloride. MnS inclusion was detected inside the droplet, but was not detected at corroding part.

3.3 1% MgCl₂

Figure 4 shows the SKFM image of SUS304 stainless steel with attaching 1 % MgCl₂. The equivalent salinity is estimated 6.5 mg/dm². The asperity of spokewise starting from the corroding part was formed on the liquid surface (Figure 4(a)) and it grew with time (Figure 4(b)). From now I call this type of corrosion as 'Pit's eye'. The liquid thickness of MgCl₂ at the corroding part decreased with time. The potential of upper part of liquid in Figure 4 (a) was nobler than that of bottom part. This is considered owed to the time delay by scanning. That is, the potential difference between the part where the droplet of MgCl₂ is attached and that of dry-polished part is small at the beginning of the scanning, because the surface is passive condition as is shown in Figure 2(a). The potential difference becomes large once corrosion starts. The scanning starts from the upper part of the image, so the change of the potential in the droplet is seemed owed to the initiation of corrosion. The potential of the part where the droplet of MgCl₂ was attached was about 1.2 V more negative than that of dry-polished part at maximum after 6 hours (Figure 4(b)).

3.4 Optical microscope observation

Figure 5 shows the optical microscope observation of SUS304 steel after SKFM observation. In the case of SUS304 steel with attaching 0.025% MgCl₂, the corrosion product of 20 μm diameter or less was observed several parts 108 hours after the start of the test by an optical microscope (Figure 5(a)), but no corrosion (rust) was observed by the visual observation. While in the case of SUS304 steel with attaching 0.1% MgCl₂, the optical microscope observation (Figure 5(b)) shows that liquid of brown color existed at the corroding part and rust was observed by the visual observation. In the case of SUS304 steel with attaching 1% MgCl₂, a hall without corrosion product (Figure 5(c)) was observed in the middle of the droplet.

3.5 Mechanism of atmospheric corrosion on SUS304 stainless steel

The mechanism of atmospheric corrosion on stainless steels can be divided into two categories. One is the initiation and the other is the growth up to the visual size.

Fig. 1. SKFM images of atmospheric corrosion of SUS304 stainless steel with attaching 0.025% MgCl₂.

Fig. 2. SKFM images of atmospheric corrosion of SUS304 stainless steel with attaching 0.1%MgCl₂.

Fig. 3. EDAX analysis of corroding part of SUS304 stainless steel after 52 hours with attaching 0.1% MgCl₂.

Fig. 4. SKFM images of atmospheric corrosion of SUS304 stainless steel with attaching 1% MgCl₂.

is less than 3.53 mol/ kg (equivalent relative humidity is 65%). This result indicates that NaCl which is the main component of sea salt does not play an important role on the initiation of atmospheric corrosion of SUS304 stainless steel. The relative humidity is the critical factor for the initiation of the atmospheric corrosion on stainless steels. Recently Motoda¹⁾ reported very interesting results about the relation between the visible rust formation and the equivalent salinity. That is, the critical equivalent salinity exists for the growth of rust up to the visual size. The critical equivalent salinity is reported about 0.4 mg/dm² for SUS304 stainless steel. Our experimental result shows that no visible rust was found when equivalent salinity is low and that visible rust was found when the equivalent salinity is above 1 mg/dm². The equilibrium concentration of MgCl₂ solution at 40 % RH is about 25 wt%. In this concentrated MgCl₂ solution, the dissolved oxygen concentration is very low. The dissolved oxygen concentration becomes lower by the oxidation of metal ion once corrosion starts. When MgCl₂ liquid layer is thin, oxygen can be supplied to the specimen surface from the air because the diffusion layer in the liquid is thin. While when the liquid layer is thick, oxygen can not be supplied to the specimen surface from the air. This may be the reason that no rust was formed at corroding part and that the tarnished area is produced by the oxidation of Fe²⁺ ion diffused from the corroding part when the liquid layer was thick. The absence of dissolved oxygen also influences on the potential difference between the part where the droplet of MgCl₂ is attached and that of dry-polished part. As the lack of dissolved oxygen proceeds, the cathode reaction in neutral solution changes from $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-$ to $\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ and the potential moves the negative direction. This phenomenon explains the increase of potential difference between the part where the droplet of MgCl₂ is attached and that of dry-polished part with the thickness liquid layer. The enrichment of chloride ion at corroding part and the existence of brown liquid indicated that corrosion progressed with supplying water by the deliquescence of metal chloride.

Fig. 5. Optical microscope images of atmospheric corrosion of SUS304 stainless steel.

As for the initiation of atmospheric corrosion on stainless steels, Muto³⁾ studied the relation between the concentration of Cl ion and the initiation of atmospheric corrosion and showed that the critical Cl ion concentration increased with the increase of corrosion resistant of stainless steel. For example corrosion does not initiate on SUS304 stainless steel with the attached droplet of which concentration

4. Conclusions

In-situ observation of corrosion initiated from a small droplet of MgCl₂ solution was done under low relative humidity condition by Super Kelvin force microscope (SKFM) which we have developed recently. At the same time EDX image mapping analysis and the optical microscope observation were done. The results show that the corrosion morphology can be divided into 2 types. 1. Corrosion progressed inside of specimen with corrosion

product when the liquid layer of MgCl_2 was thin. 2. Corrosion progressed inside of specimen without corrosion product when the liquid layer of MgCl_2 was thick. Potential of the part where the droplet is attached becomes more negative as the thickness liquid layer increased after corrosion started. Enrichment chloride ion occurred at corroding part and water seems to be supplied by the deliquescence of metal chloride.

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