## Atmospheric corrosion of low alloy steels near seashore environment under high relative humidity condition

H. Masuda

Corrosion Analysis Group, MEL, NIMS, 1-2-1 Sengen, Tsukuba, Ibaraki, Japan 305-0047 TEL:0081-029-859-2542, Fax: 0081-029-859-2501 E-mail:MASUDA.Hiroyuki@nims.go.jp

#### Abstract

It is well known that the atmospheric corrosion of steel is accelerated by sea salt particles near seashore environment. However, the mechanism of atmospheric corrosion of steel has not been clarified because of the difficulty in experimental work. We have developed a new atmospheric corrosion test device. By using this device, the atmospheric corrosion tests have been carried out on low alloy steels under high relative humidity conditions with constant deposition rate of sea salt particles. Besides this experiment, certain amount of sea salt particles were attached on low alloy steels and the initiation of atmospheric corrosion was observed both by the super Kelvin force microscope (SKFM) and the colour laser microscope. Test specimens were two types of low alloy steels, SM50B and 3% Ni steel, mechanically polished up to 1µm.roughness. The atmospheric corrosion tests were done at 90% RH with the deposition rate of sea salt particles of 1mdd. The deposition rate of sea salt particles was estimated by using 30MHz of gold-coated quartz crystals. For SKFM and the colour laser microscope observations, sea salt particles were attached by using the new atmospheric corrosion test device under low humidity conditions for preventing the corrosion. The initiation of atmospheric corrosion was observed under humidity control conditions. The relative humidity was controlled by controlling the specimen surface temperature with cooler. The SKFM image was taken every 1 hour. Kelvin force microscope was also used to observe the detail of corrosion.

The atmospheric corrosion rate of SM50B was faster than that of 3%Ni steel at the beginning, but total amount of corrosion became the same with time. The in-situ SKFM observation showed that the area of the part where potential is more negative than that of usual sea salt particles attached spread rapidly once corrosion started. The increase of the area of negative potential part is considered due to the spread of thin liquid film of FeCl<sub>3</sub>. The thickness of this thin layer could not be estimated even by the highly magnified observations. The filiform corrosion that width is much more bigger than the diameter of sea salt particle attached also progressed. After the specimen surface was covered with thin liquid film, Cl ion can move at the corroding part to increase the corrosion rate. The trace of Cl ion movement was alos observed on SKFM images. The mechanism of atmospheric corrosion by sea salt particles under high relative humidity condition was similar on both SM50B and 3%Ni steel. The main difference was the initiation time of corrosion.

#### Keywords

super Kelvin force microscope, Kelvin force microscope, atmospheric corrosion, colour laser microscope, high relative humidity.

#### Introduction

Atmospheric corrosion of steels is most commonly observed phenomena in our life. It is well known that the atmospheric corrosion of steel is accelerated by sea salt particles near seashore environment. However, the mechanism of atmospheric corrosion of steel has not been clarified because of the difficulty in experimental work. We have developed a new atmospheric corrosion test device that can control the amount of attached sea salt particles. By using this device, certain amount of sea salt particles were attached on the low alloy steel and the initiation of atmospheric corrosion was observed by the super Kelvin force microscope (SKFM) [1].

## Experiment

The Kelvin force method used in SKFM was originally developed by Yasutake et al [2]. In this method, topography and surface potential can be obtained at the same time with noncontact mode. 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  $\mu$ m 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  $\mu$ m, so the scan area of 25.6 X 25.6  $\mu$ m 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  $\mu$ m of working distance and another is 0 X 0 X 40  $\mu$ m of working distance. After setting 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  $\mu$ m, the scan range can be chosen from 10 nm to 1 cm. The tip used for SKFM measurement was the conductive goldcoated Si tip with the resonant frequency of around 25 kHz. The SKFM image was taken every 1 hour with data points of 256 x 256.

Test specimens were two types of low alloy steels, SM50B and 3% Ni steel, mechanically polished up to 1µm.roughness. For SKFM observation, sea salt particles of 0.012mg/cm<sup>2</sup> were attached by using the new atmospheric corrosion test device under low relative humidity conditions (30%RH) for preventing the corrosion. The accumulation rate of sea salt particles of 0.2 to 1 mdd was used for constant humidity of 90% RH corrosion test,. The amount of attached sea salt particles is estimated by using 30MHz of gold-coated quartz crystals. The initiation of atmospheric corrosion was observed by SKFM under humidity control conditions. The relative humidity range of between 48 and 85%RH was used to study the initiation of atmospheric corrosion. In this case, relative humidity was controlled by controlling the specimen surface temperature with cooler. Kelvin force microscope and colour laser microscope were also used to observe the detail of corrosion. The nucleation of thin liquid film was observed by KFM and SKFM at RH of 35% to 40% after keeping the specimen at 85% RH for 1 h with attaching sea salt particles of 0.01 mg/cm<sup>2</sup>.

## **Result and discussion**

## SKFM observation of initiation of corrosion

Fig. 1 shows the SKFM images of SM50B tested under the humidity range between 48 and 85%RH. The amount of attached sea salt particles was  $12\mu g/cm^2$ . As the relative humidity increased, the area of the part where potential is more negative than that of usual sea salt particles attached increased rapidly (Fig. 1 (b) to (d)) and the potential of most observed area moved negative direction (Fig. 1 (e)). The filiform corrosion that width is much more bigger than the diameter of sea salt particle attached progresses rapidly. The increase of the area of negative potential part is considered due to the increase of the formation of FeCl<sub>3</sub>, because the amount of liquid increase due to that NaCl which is main composition of sea salt particle becomes liquid above 73%RH. The size of sea salt particle also increased due to the



Fig.1 SKFM observation of atmospheric corrosion of SM50B at RH of 48 to 85%.

increase of volume by the state change of NaCl from solid to liquid. The potential of corroding part was more negative than other part. After the relative humidity was decreased to 48% again, the area of negative potential part still remained (Fig. 1 (f)). Fig. 2 shows the optical microscope image immediately after corrosion test. The transparent liquid of green colour was observed at the corroding part. The former FT-IR microscope analysis showed [3] that this liquid was FeCl<sub>2</sub>. The volume of this liquid was over 100 times bigger than that of



Fig. 2 Optical microscope image immediately after corrosion test.

sea salt particle. The mechanism of the formation of the big liquid droplet is considered as follows: after the specimen surface was covered with thin liquid film, Cl ion can move at the corroding part to keep the electric neutrality. Cl ion was supplied by the sea salt particles near the corrosion part. Fig. 3 shows the distribution of sea salt particles of the square area indicating in Fig. 2 at the beginning (Fig. 3(a)) and 17 h after test started (Fig. 3(b)). The decrease of the height of sea salt particles shows the evidence of Cl ion movement. Thus the existence of very thin liquid film plays the important role on the mechanism of atmospheric corrosion near seashore environment.



Fig.3 Distribution of sea salt particles at the beginning (left image) and 17 h after test started (right image).

Observation of nucleation of thin liquid film

Fig. 4 shows the SKFM image of SM50B (left image) and 3% Ni steel. The existence of negative potential part indicates the existence of thin liquid film. The coverage ratio of thin liquid film on SM50B was bigger than that on 3% Ni steel, because 3% Ni steel is more

resistant than SM50B in corrosion. The corrosion product in which the potential is noble was observed within the negative potential part (Fig. 5). This also shows the thin liquid film was produced by corrosion. Fig. 6 shows the KFM image of the part where the potential was changed. No evidence of the existence of thin liquid film was observed on the surface profile image of SM 50B in spite of the maximum height difference on the surface profile was about 20nm. While small particles of 10nm in maximum height were observed at negative potential part on 3% Ni steel.



(a) SM50B

(b) 3% Ni





Fig. 5 Relation between corrosion product and thin liquid film (SM50B).



Fig.6 KFM image of low alloy steels near the potential boundary.

Constant relative humidity test

Fig. 7 shows the results of constant relative humidity test for low alloy steels with the sea salt

accumulation rate of 0.2mdd to 1mdd. When the sea salt accumulation rate was low, the corrosion rate of 3%Ni steel was mach lower than SM50B. While the corrosion rate became similar as the sea salt accumulation rate increased. Fig. 8 shows the optical microscope image of low alloy steels after test. The corrosion morphology was the same at the sea salt accumulation rate of 1mdd. Thus main difference between 3Ni steel and SM50B was the initiation time of atmospheric corrosion.



Fig. 7 Effect of accumulation rate of sea salt on corrosion rate for low alloy steels.





(a) 0.2mdd. Left 3% Ni steel and right SM50B. (b) 1mdd. Left 3% Ni steel and right SM50B.

Fig. 8 Optical microscope image of low alloy steels after constant humidity test.

# Conclusion

Atmospheric corrosion tests were carried out under high relative humidity condition. The results show that very thin liquid film was formed around the corrosion products once corrosion started. After the specimen surface was covered with thin liquid film, Cl ion can move at the corroding part to increase the corrosion rate. The mechanism of atmospheric corrosion by sea salt particles under high relative humidity condition was similar on both SM50B and 3%Ni steel. The main difference was the initiation time of corrosion.

## References

[1] H.Masuda, *Corrosion*, **57** (2001) 99
[2]M.Yasutake, D.Aoki and M.Fujihira, *Thin Solid films*, **273** (1996) 279
[3] H.Masuda and K.Noda, J. Electrochemical Society, Proc. Vol (The 196th Meeting of ECS) ,**99-28**, (2000)351