Mechanism of SCC on SUS316L Stainless steel

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The stress corrosion cracking (SCC) of stainless steel is one of the biggest problems for maintaining atomic power and chemical plants. However the mechanism has not been solved because of difficulty in observing hydrogen movement. In order to solve this problem, the author has developed a new SCC test method that enables the super Kelvin force microscope (SKFM) and the Kelvin force microscope (KFM) observations. By using this test method, the crack tip deformation and surface potential distribution on SUS316L stainless steels were observed by SKFM and KFM. The existence of hydrogen-induced martensite was examined by the magnetic force microscope (MFM) observations. The results showed that the less noble potential region existed near the crack tip. MFM and KFM observation showed hydrogen-induced martensite existed at the less noble potential region. Repeated SKFM observations revealed that the crack is formed by the movement of hydrogen-induced martensite.

Introduction

The stress corrosion cracking (SCC) of stainless steel is one of the biggest problems that have not been solved. Many excellent research works (1-8) have been done from the aspects of mechanical factors (applied stress, residual strain), environmental factors (temperature, pH, DO) and material factors (additional element, structure) to clarify the mechanism of SCC on stainless steel. Three basic mechanisms of SCC have been proposed, such as active path dissolution, hydrogen embrittlement and film induced cleavage. However, no clear mechanism of SCC has been found in the above-mentioned environment. We have developed a new SCC test method (9) that enables the SKFM (10) (super Kelvin force microscope) observation. By using this test method, surface potential distribution was observed on the whole crack of SUS304, SUS310S (11) and SUS316L (12) stainless steel. We have found that less noble potential region existed near the crack tip on SUS304 stainless steel and around the crack on SUS310S stainless steel. Ag decoration (13) was done at the same time to study the relation between the less noble potential region and hydrogen distribution. The results showed there is a good correlation between them (11, 12, 14). MFM and KFM observation at less noble potential region on SUS310S stainless steel revealed that hydrogen-induced martensite existed at less noble potential region. SUS316L stainless steel is austenitic stainless steel which is commonly used at atomic power plant. To clarify the mechanism of SCC on SUS316L stainless steel, the crack morphology and surface potential distribution were observed by SKFM and KFM. The existence of hydrogen-induced martensite was examined by MFM observations. Moreover, The crack growth behavior was studied by repeating SKFM observation. The mechanism of SCC is discussed from the results of these observations.

Experimental procedure
SPM Equipment

SKFM was originally developed by the author. The Kelvin force method used in this device was originally developed by Yasutake et al (15). In this method, topography and surface potential can be obtained at the same time with non-contact mode. The scanning device of SKFM for X-Y direction used is an accurate X-Y stage. The accuracy of the X-Y stage is less than 100 nm for repeated positioning. The X-Y stage can move up to 10 x 10 cm², but the maximum scanning area is limited to 1 x 1 cm². The minimum vertical movement is 0.2 mm. KFM and MFM observation were done by SPI8000 (SII). The tip used for KFM and SKFM measurement was the conductive gold-coated Si tip with the resonant frequency of around 25 kHz, while the tip used for MFM measurement was the magnet-coated Si tip with the resonant frequency of around 125 kHz. The SKFM image was taken with a scanning speed of between 0.03 and 0.06 Hz with data points of 256 x 256, while KFM and MFM image were taken with a scanning speed of 0.1 Hz with data points of 256 x 256. The bright part corresponds to less noble potential part in SKFM and KFM image based of electrode potential, while the bright part corresponds to the part where attractive force is operating (martensite part) in MFM image.

SCC Test

Test specimen used was commercial SU S316L stainless steel (Cr: 17.37, Ni: 12.11, Mo: 2.05, C: 0.014, Si: 0.58, Mn 1.54, P: 0.031, S: 0.002) with the size of 50 mm in length, 20 mm in width, 0.2 mm (HV: 310, 50gf) in thickness. The test part of specimen was mechanically polished up to 300 nm in roughness. Stress was applied by bending the specimen with a jig of 40 mm to 45 mm in length. The stress distribution of specimen, F, was estimated from the following formula:

\[ F = z \times \frac{E}{R} \]

where \( z \) is distance from the center part of thickness of specimen, \( E \) is Young’s modulus and \( R \) is curvature of radius near the centre of the test specimen. Thus the tensile stress is maximum at the surface and zero at the center part of thickness of specimen. More than 10 pieces of 25% MgCl₂ droplet of 2 mm³ in volume were attached on the specimen. Test was done at 343 K and 28% RH. The specimen was washed by water and dried after the test. At first, crack was observed by the color laser microscope and then observed by SKFM or by both KFM and MFM.

Crack growth Test

The following (a) to (d) were repeated for the crack growth test; (a) The specimen with more than 10 pieces of 25% MgCl₂ droplets attached was kept at 343 K and 28% RH with maximum applied stress of 1080 MPa for 1 day. (b) The specimen was washed by water and dried and observed by the color laser microscope. (c) SKFM observation was done at 298K and below 20% RH for 2 days. (d) MgCl₂ droplets were attached again on the specimen nearly the same place as before.

Results and Discussion
Fig. 1 Image of crack produced at applied stress of 1030 MPa for 4 days. (a) Optical microscope image, (b) topography and (c) potential distribution image. Image size: 0.8 mm x 0.8 mm.

Fig. 2 Images of crack produced at applied stress of 1030 Mpa for 4 days. (a) Optical microscope image, (b) topography, (c) potential distribution image, (d) magnetic force distribution image. Bright part correspond to less noble potential part in potential distribution image and to attractive force region in magnetic force image. Image size: 0.08 mm X 0.08 mm.

SKFM observation
Figure 1 shows (a) optical microscope image, (b) topography and (c) potential distribution image of a crack produced at applied stress of 1030 MPa for 4 days. The crack usually initiated from a pit and propagated to the maximum stress direction. The less noble potential region was observed near the crack tip of upper side.

MFM and KFM observation

In order to clarify the phase of less noble potential region observed on SKFM measurement, both MFM and KFM observation were done at the same region. Fig. 2 shows (a) optical microscope image, (b) topography, (c) potential distribution image and (d) magnetic force distribution image of the crack tip surrounded by square line in Fig. 1 (a). Less noble potential region was observed ahead of the crack tip (Fig. 2 (c)). MFM observation shows that the less noble potential region corresponds to the region where the attractive force exists. Since the attractive magnetic force does not generate on austenite phase, martensite phase must exist. This martensite is considered hydrogen-induced martensite, since there is no correlation between plastic deformation and martensite phase and this martensite phase moves with time. From this result, it is concluded that hydrogen-induced martensite can be observed by surface potential measurement.

Fig. 3 SKFM and optical microscope image of a pit and AFM image surrounded by square line in SKFM and optical microscope image. (a) Topography, (b) surface potential distribution image, (c) optical microscope image and (d) topography after 1 days loading test. Image size: (a), (b), (c) 0.25 mm X 0.25 mm, (d) 0.06 mm X 0.06 mm.
Crack growth test

Fig. 3 shows (a) topography, (b) potential distribution image and (c) optical microscope image of a pit and (d) topography surrounded by square line in the SKFM and optical microscope image after 1 day loading test. Less noble potential region is observed around the pit. Less noble potential region spreads upside as shown in Fig. 3(b). The magnified image of this region ((Fig. 3(d)) shows the evidence of plastic deformation without crack formation. This means that the plastic deformation occurs before crack initiation. Two examples are shown to clarify the mechanism of crack growth. Fig. 4
show SKFM images of whole crack and optical microscope images surrounded by square line in SKFM images. Less noble potential region (hydrogen-induce martensite phase) was observed ahead of the crack tip surrounded by square line (Fig. 4(b)) after 2 days loading test. Crack was not formed in this region at this moment (Fig. 4(c)). New plastic deformation occurred ahead of the crack tip after 3 days loading test (Fig. 4(d)) and less noble potential region increased ahead (Fig. 4(e)). Then discontinuous cracks were formed (Fig. 4(f)). New plastic deformation occurred again ahead of the crack tip after 4 days loading test (Fig. 4(g)) and less noble potential region moved ahead and the potential of this region became more noble (Fig. 4(h)). Then discontinuous cracks were formed (Fig. 4(i)). From the results of Fig. 4, it is clear that crack was formed when hydrogen moved. Fig. 5 shows SKFM images of whole crack and optical microscope images surrounded by square line in SKFM images. Less noble potential region was observed ahead of the crack tip (Fig. 5(b)) after 1 days loading test. Crack was not formed in this region at this moment (Fig. 5(c)). New plastic deformation occurred ahead of the crack tip after 2 days loading test (Fig. 5(d)) and less noble potential region moved ahead (Fig. 5(e)). Then crack was formed on the region where less noble potential was observed after 2 days test (Fig. 5(f)). In this case, crack was also formed when hydrogen moved.

Fig. 5 SKFM images and optical microscope images surrounded by square line in SKFM images. Topography (a) after 1 day test and (d) after 2 days test, surface potential distribution image (b) after 1 day test and (e) after 2 days test and optical microscope image (c) after 1 day test and (f) after 2 days test. Image size: (a), (b), (d), (e) 0.4 mm X 0.4 mm and (c), (f) 0.08 mm X 0.08 mm.

Crack growth mechanism
Narita et al. (16) studied hydrogen-related phase transformations in austenitic stainless steel by using X-ray diffraction technique and reported that volume increase occurs when hydrogen is charged on austenitic stainless steel, and tensile stress generates when charged hydrogen is lost by aging. The volume increase when hydrogen is charged on austenitic stainless steel was also reported by Ulmer et al. (17). In the case that the crack initiates from a pit, at first hydrogen-induced martensite is formed around the pit, which generates compressive stress. As the results, plastic deformation occurs at the maximum stress direction and hydrogen moves the plastic deformation region. In this state, crack is not formed as shown in Fig.3. Crack is formed when hydrogen is moved. From repeated SKFM observations as shown in Fig.4, it is clear that hydrogen tends to accumulate plastic deformation region ahead of the crack tip. This accumulation of hydrogen is considered to generate compressive stress. As the result, plastic deformation occurs when the accumulated hydrogen reaches certain amount. Then hydrogen moves to newly created plastic deformation region and tensile stress generates at the region where hydrogen-induced martensite phase changes austenite phase. The tensile stress increases with the movement of hydrogen to cause crack. Thus the crack growth is caused by the hydrogen movement under loading condition.

**Conclusion**

The crack tip deformation and surface potential distribution were observed by SKFM. The existence of hydrogen-induced martensite was examined by MFM and KFM. The results showed that the less noble potential region existed near the crack tip. The MFM and KFM observation showed hydrogen-induced martensite existed at the less noble potential region. Repeated SKFM observations revealed that the crack is produced when hydrogen-induced martensite phase changes former austenite phase.

**References**