Effect of Solution Temperature on the Cavitation Corrosion Properties of Carbon Steel and its Electrochemical Effect

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In the open system (vessel and pipe), the maximum corrosion rate of carbon steel at *ca.* 80 °C was obtained due to the decrease of dissolved oxygen by increasing the solution temperature. Effect of temperature on the cavitation damage can be explained through several mechanisms. Moreover, when cavitation occurs on the surface of metal and alloys, whether cavitation is erosion or corrosion is still controversial. This work focused on the effect of solution temperature on the corrosion of carbon steel under cavitation in an open system, Tests were performed using an electrochemical cavitation corrosion tester in 3.5% NaCl solution and the effect of solution temperature of carbon steel was discussed. Cavitation corrosion rate can be increased by cavitation, but when the temperature increases, a dissolved oxygen content reduces at a very high speed and thus the maximum cavitation corrosion temperature changed from 80 °C to 45 °C. Below the maximum cavitation temperature, the electrochemical effect was more dominant than the mechanical effect by increasing temperature, but over the maximum cavitation temperature, the mechanical effect was more dominant than the electrochemical effect by increasing temperature.

Keywords: Carbon steel, Cavitation Corrosion, Electrochemical Cavitation, Solution Temperature

1. Introduction

The facilities in power plants, ships, and marine plants etc. use sea water as a cooling water to operate them. Sea water give a plenty of advantages in engineering aspects, but induces a variety of corrosion problems. Specially, it is well known that general corrosion has been occurred in carbon steel or low alloy steels [1-4].

Since they use sea water as a cooling water, the scales due to salt and various factors form on the surface and various corrosions form in the heat exchanger's tubing, and thus the leakage from the tubes has been occasionally reported [5]. Chloride ions in sea water have been well known as a representative aggressive ion, and they facilitate the corrosion of the inside of tube with dissolved oxygen and elevated temperature [6-8]. To solve these kinds of problem, the inside-coated tube has been used [9-11]. This coatings can afford the barrier layer to protect the contact from sea water, and protect the corrosion and

increase the lifespan of tube and reduce the cost of repair. The coating methods can be summarized as follows; rubber lining [12] and epoxy resin coating [13,14].

The effect of ultrasonic amplitude on cavitation erosion properties of epoxy coatings was described elsewhere [15]. If the coating was damaged during the operation of the plants, the matrix – carbon steel will be severely corroded by the environments. In the sea water-using facilities, corrosion of the steel can be affected by seasonal factors. – The temperature of sea water shows the high value in summer season but reveals the low value in winter season [16]. Particularly, the solution temperature is one of the factors affecting corrosion, which factors include dissolved oxygen, salt concentration, weather, ocean current, and season [17]. The sea water temperature from the intake to drainage can be changed due to the operation of heat exchanger. Usually, a temperature or pressure increase directly leads to a high corrosion rate because electrochemical reactions generally occur faster at high temperature. Increasing temperature raises diffusion rate and reaction rate [18]. These chemical rates are in effect in all corrosion mechanisms for all materials [19]. There

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are multiple corrosion mechanisms in metals and, again, diffusion and reaction rates or kinetics affect how much material is affected. Diffusion influences the delivery of the oxygen to the metal. The effect of solution temperature on corrosion of metals and alloys can be explained using the limiting current density, i_L and the concentration of dissolved oxygen [20]. When corrosion process is under diffusion-control of oxygen, corrosion of the steel can be duplicated every 30 °C increment. In the open system, the maximum corrosion rate of carbon steel at *ca.* 80 °C was obtained due to the decrease of dissolved oxygen by increasing the solution temperature. However, in the closed system, the increasing solution temperature, corrosion rate of metals and alloys will be increased until the oxygen was consumed [21,22].

Effect of temperature on the cavitation damage can be explained through several mechanisms [23-26]; 1) Thermodynamic effects upon bubble growth and collapse due to the fact that the growth and collapse begin to vary significantly from isothermal behavior as the temperature is raised, 2) Change in dissolved gas content due to temperature variation, 3) Change in material properties due to temperature variation.

Recent work [27] proposed the corrosion steps of carbon steel at the initial stage under cavitation condition in 3.5 % NaCl. When the cavitation strength is relatively low, corrosion of the steel is more affected by the electrochemical process than by the mechanical process; but when the cavitation strength is relatively high,

corrosion of the steel is affected more by the mechanical process than by the electrochemical process. However, there is little about the effect of solution temperature on the corrosion of steel under cavitation corrosion condition. Therefore, this work focused on the effect of solution temperature on the corrosion of carbon steel under cavitation in an open system, Tests were performed using an electrochemical cavitation corrosion tester in 3.5% NaCl solution and the effect of solution temperature of carbon steel was discussed.

2. Experimental Methods

2.1 Materials

Carbon steel of 0.42%C - 0.2%Si - 0.7%Mn was used in this work [27]. The dimensions of the specimen are 29 mm diameter, and 5mm thickness.

2.2 Cavitation Degradation Test

The cavitation degradation tester (R&B-RB111-CE, Korea) was made by a magnetostrictive driven method and by modifying ASTM G32 standard [28]; Maximum power output of the tester was 1,000 W, and an ultrasonic transducer showing ($20 \pm 5 \mathrm{kHz}$) was used. The horn tip was made by super duplex stainless steel (Fe-25.8Cr-2.3Mo-0.2W-0.5Si-10.7Ni-0.65Mn-0.03C-0.42N), and its diameter was 16 mm. The distance between the horn tip and specimen was 0.5 mm and a freshly ground (#2,000 SiC) horn tip was used in every test. Fig. 1 shows

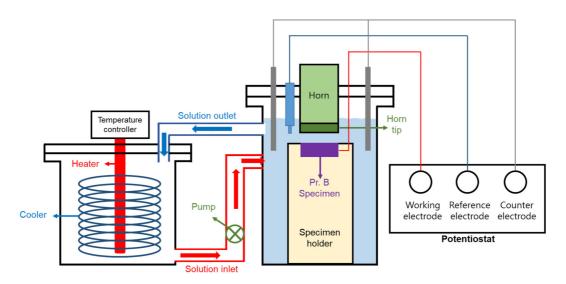


Fig. 1. Schematic of the cavitation degradation test equipment [28]

a schematic of the cavitation degradation tester using an indirect cavitation method.

2.3 Electrochemical Measurement During a Test

Test specimen having a diameter of 29 mm after connecting an insulated copper wire was mounted using an epoxy resin. After the surface was ground using a SiC paper of #2,000, the specimen was installed in the corrosion cell. For polarization test, a saturated calomel electrode (SCE) was used as a reference electrode, and high-density graphite electrode was used as a counter electrode. Polarization test was performed using a potentiostat (Gamry DC 105, USA) from -200 mV at open circuit potential at the scanning rate of 1 mV/sec. Test solution was 3.5 % NaCl at 10 °C, 30 °C, 45 °C, 65 °C, and polarization curves were measured at every one hour after the initiation of cavitation. i_{corr} was obtained by Tafel extrapolation.

To find electrochemical cavitation corrosion rate, i-t curves were obtained during cavitation corrosion test for 1 hour at an open circuit potential. After the test, the average cavitation corrosion rate was obtained by weighing the weight loss and the electrochemical cavitation corrosion rate was obtained by i-t curves.

2.4 Surface Analysis

Surface morphology was observed using a digital

camera, 3D stereographic microscopy (Hirox, KH-7700, Japan), and FE-SEM (Tescan, LYRA 3 XMH, Czech Republic).

2.5 Dissolved Oxygen measurement

Dissolved oxygen was measured using a Portable Dissolved Oxygen Meter (Hanna instruments, HI9146, UK) and the oxygen sensor was placed near ultrasonic horn tip. Dissolved oxygen over 60 °C used the referenced data [21,29].

3. Results and Discussion

3.1 Effect of solution temperature on the cavitation corrosion rate of carbon steel

Fig. 2 shows the effect of solution temperature on the surface morphologies of carbon steel by the cavitation corrosion test in 3.5% NaCl at each temperature. The ultrasonic amplitude was 85 µm and the cavitation was operated for 6 hours. The inner circle of the photo is the cavitated area and the outer area was also corroded due to the exposure to corrosive solution. When the temperature of the solution increased, the extent of cavitation corrosion was increased. But cavitation corrosion effect was reduced at 60 °C. As described elsewhere [27], corrosion steps of carbon steel at the initial stage under cavitation condition

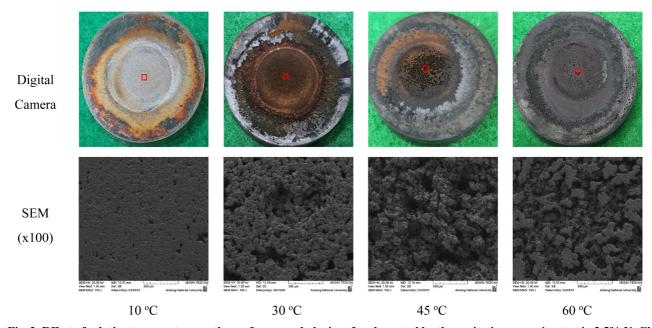
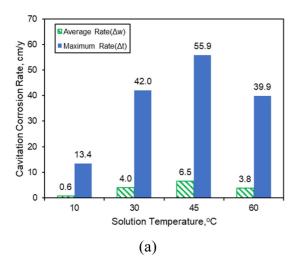


Fig. 2. Effect of solution temperature on the surface morphologies of carbon steel by the cavitation corrosion test in 3.5% NaCl at each temperature (ultrasonic amplitude 85 μ m, cavitation time 6 h)



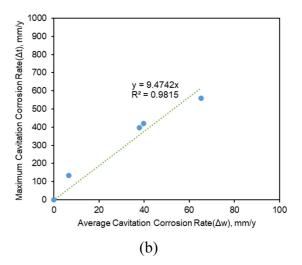


Fig. 3. (a) Average cavitation corrosion rates obtained by weight loss and maximum cavitation corrosion rate by cavitated depth of carbon steel in 3.5% NaCl (ultrasonic amplitude 85 μm, cavitation time 6h) and (b) Relationship between the rates

at 15 °C were proposed; Step 1- Ferrite corrodes in the ferrite and pearlite phases, and cementite remains. Step 2- Ferrite corrodes severely. Step 3- Enlarged ferrite corrosion. Step 4- Detachment of the ferrite and pearlite phases. As shown in Fig. 2, the morphologies after 6 hours in each cavitation corrosion test were severely damaged by cavitation corrosion. We investigated why the maximum cavitation corrosion occurred at 45 °C.

Fig. 3a reveals the average cavitation corrosion rates obtained by the weight loss and the maximum cavitation corrosion rate by the cavitated depth of carbon steel in 3.5% NaCl from Fig. 2. The maximum cavitation corrosion rate was 20.8 times higher than the average cavitation corrosion rate. Fig. 3b depicts the relationship between the maximum cavitation corrosion rate and the average cavitation corrosion rate.

Fig. 4 shows the effects of cavitation and solution temperature on the average degradation rate of carbon steel in 3.5% NaCl. The corrosion rate of 'No Cavitation' was obtained from the immersion test. As shown in Fig. 4, the maximum corrosion rate was obtained at 80 °C, and this result was same as that of E. Baral, H. Uhlig, and R. Winston's result [21,22]. Corrosion rate was obtained after 24 hours-immersion test. Generally, many factors influence the rate at which diffusion takes place. While diffusion go forward in the presence of a concentration gradient substance, several factors affect the rate of diffusion. The greater the difference in concentration is, the more rapid the diffusion is. The closer the distribution of substance

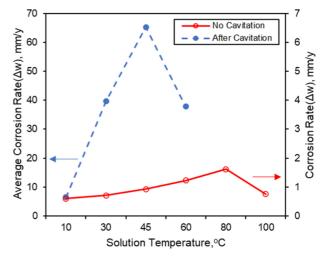


Fig. 4. Effects of cavitation and solution temperature on the average degradation rate of carbon steel in 3.5% NaCl (ultrasonic amplitude 85 μ m, cavitation test time 6 h)

gets to equilibrium is, the slower the rate of diffusion is. Heavier ions move more slowly and therefore diffusion more slowly. Similarly lighter ions diffuse faster. Higher temperature increases the energy and therefore the movement of the ions, increasing the rate of diffusion. Lower temperatures decrease the energy of the ions, thus decrease the rate of diffusion. However, when the solution temperature increases, the concentration of dissolved oxygen decreases. Therefore, it is well-known that the maximum corrosion rate of carbon steel in the no-cavitation condition was obtained at 80 °C in a neutral solution.

In the cavitation condition, as shown Fig. 4, corrosion rate of carbon steel in 3.5% NaCl solution was increased from ca. 10 to 70 times by cavitation corrosion. In a neutral solution, corrosion of carbon steel was controlled by the cathodic reaction of oxygen reduction and the limiting diffusion current density, i increases and thus, corrosion rate increases. Therefore, cavitation increased the limiting diffusion current density. Moreover, cavitation increased the mechanical damage on the surface (Mechanical and electrochemical effects will be discussed below). We investigated the maximum cavitation rate's temperature move from 80 °C to 45 °C. Fig. 5 reveals the variation of dissolved oxygen contents with solution temperature in the conditions under no-cavitation [21,29] and during cavitation in 3.5% NaCl. The oxygen content during cavitation was measured, but we couldn't the content over 45 °C because of the instrument's limitation. As shown in Fig. 5, the dissolved oxygen content greatly increased by the cavitation process. The increased dissolved oxygen was one of the reasons for the increased cavitation corrosion rate than that of 'No-Cavitation' condition of Fig. 4. Moreover, it should be noted that the increased dissolved oxygen content reduced very greatly.

From the observation of Fig. 4 and Fig. 5, we proposed the cavitation corrosion model of carbon steel showing the solution temperature's effect. Fig. 6 depicts the cavitation corrosion model of carbon steel by the corrosion parameters in 3.5% NaCl; when cavitation

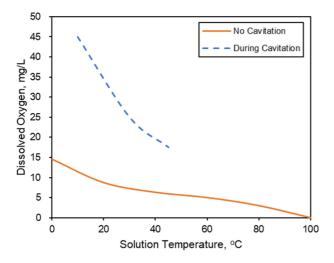
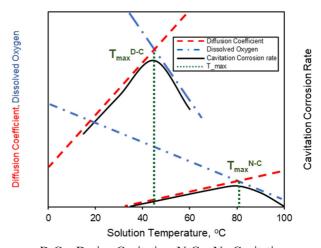


Fig. 5. Variation of dissolved oxygen contents with solution temperature in the conditions under no-cavitation [21,29] and during cavitation (3.5% NaCl, ultrasonic amplitude 85 μ m, cavitation time 6 h)



D-C = During Cavitation, N-C = No Cavitation

Fig. 6. Cavitation corrosion model of carbon steel by the corrosion parameters in 3.5% NaCl (ultrasonic amplitude 85 μ m, cavitation time 6 h)

occurs, cavitation reveals three kinds of effects – 1) increasing the limiting diffusion current density, 2) increasing the mechanical damage effect, 3) the air ingression by bubble formation increased the dissolved oxygen content. Therefore, cavitation corrosion rate can be increased by cavitation. On the other hands, when the temperature increases, a dissolved oxygen content reduces at a very high speed. Therefore, the maximum cavitation corrosion's temperature changes from 80 °C to 45 °C [30,31].

3.2 Electrochemical effect in cavitation corrosion of carbon steel

Fig. 7 shows the effect of cavitation on the polarization behavior of carbon steel after 10 minutes of every each hours in 3.5% NaCl (The tests were begun after 10 minute at open circuit potential). '0 h' means 'no-cavitation condition'. In the case of cathodic polarization, the limiting diffusion current densities were greatly increased. In the case of anodic polarization, anodic dissolution current densities were also greatly increased but showed a similar trend. On the other hand, the variation of corrosion potential is a little complicated. When the cavitation starts, corrosion potentials were increased, and the longer cavitation's time, the increased corrosion potentials go to saturation. Therefore, it is considered that the increased corrosion potential was due to the variation of cathodic polarization, *i.e.* cathodic controlled process.

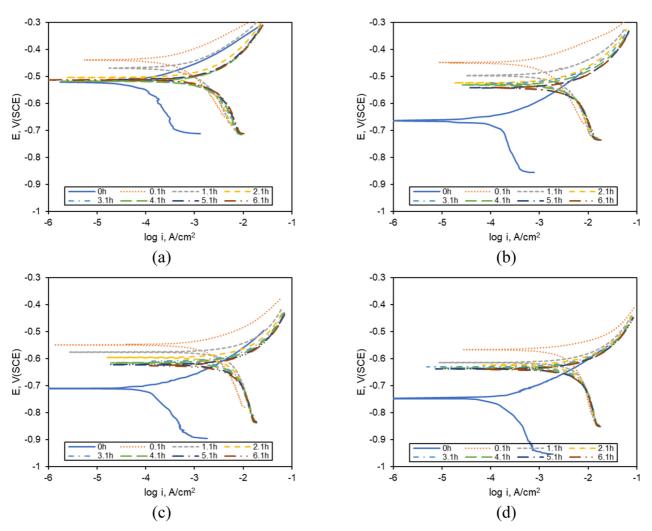


Fig. 7. Effect of cavitation on the polarization behavior of carbon steel after 10 minutes of every each hours in 3.5% NaCl (ultrasonic amplitude 85 μm); (a) 10 °C, (b) 30 °C, (c) 45 °C, (d) 60 °C

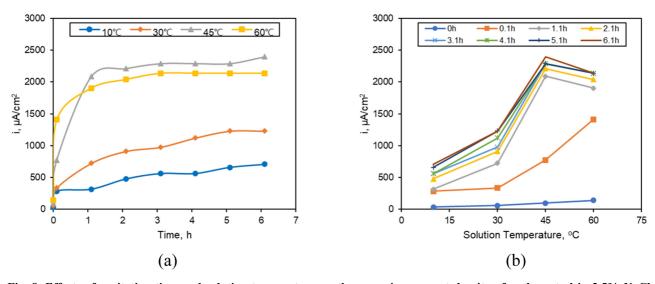
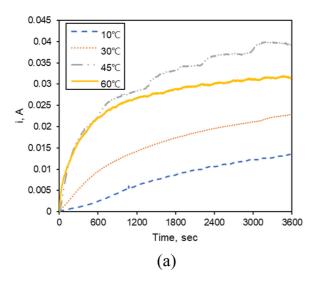


Fig. 8. Effects of cavitation time and solution temperature on the corrosion current density of carbon steel in 3.5% NaCl (ultrasonic amplitude 85 μ m); (a) corrosion current density with time, (b) corrosion current density with solution temperature



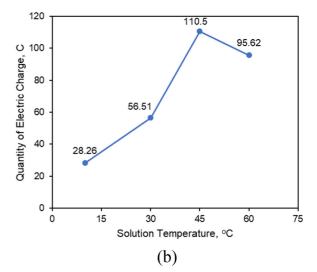


Fig. 9. Variation of corrosion current density of carbon steel with cavitation time in 3.5% NaCl (ultrasonic amplitude 85 μm)

Fig. 8 reveals the effects of cavitation time and solution temperature on the corrosion current density of carbon steel in 3.5% NaCl. Corrosion current density was obtained from Fig. 7. Increasing cavitation time, corrosion current density was initially greatly increased and after 1 hour cavitation, it was gradually increased (Fig. 8a). On the other hand, in the cases of no-cavitation or initial stage (0.1 hour), corrosion current density was increased with solution temperature (Fig. 8b). As longer as cavitation time, the maximum corrosion current density's temperature was obtained and its temperature was same to that of Fig. 4.

In order to get the electrochemical degradation rate during the cavitation process, the anodic dissolution test was performed during the cavitation test. Fig. 9a depicts the effect of cavitation time on the anodic current at open circuit potential and its electric charge from the currenttime curve was calculated as shown in Fig. 9b. This electric charge means the accumulated corrosion amount during 1 hour. We could calculate the cavitation degradation rate from the electric charge as shown in Fig. 10. Fig. 10a shows the effect of solution temperature on the total cavitation degradation rate and the electrochemical corrosion rate of carbon steel in 3.5% NaCl. Total cavitation degradation rate (by Δw , green color) means the rate obtained from Fig. 4, and the violet-colored rate was obtained by electric charge from Fig. 9. Two kinds of rates showed a similar trend and the same maximum corrosion temperature at 45 °C. It should be noted that the electrochemical corrosion rate was $(69.7 \sim 92)$ % of the total cavitation degradation rate. This implies that, in the case of carbon steel in 3.5% NaCl, the electrochemical factor was more important than the mechanical damage.

Fig. 10b shows the effect of solution temperature on the electrochemical and mechanical degradation rate below the maximum cavitation degradation temperature, 45 °C, while Fig. 10c shows the effect of solution temperature on the electrochemical and mechanical degradation rate over the maximum cavitation degradation temperature, 45 °C. Mechanical effect was obtained from the difference between the total cavitation degradation rate and the electrochemical rate. Below the maximum cavitation degradation temperature, 45 °C of Fig. 10b, increasing solution temperature, the increasing rate (the slope) of electrochemical effect was greater than that of mechanical effect (the slope). This behavior implies that electrochemical effect was more affected by the temperature increase, and in spite of the increased cushion effect at lower temperature [23,24]. Moreover, when the solution temperature increases, the cushion effect was reduced but the mechanical effect was increased, and this behavior may be induced by the increased corrosion damage. Over the maximum cavitation degradation temperature, 45 °C of Fig. 10c, increasing solution temperature, the decreasing rate (the slope) of mechanical effect was greater than that of electrochemical effect (the slope). This behavior implies that mechanical effect was more affected by the temperature increase, and the

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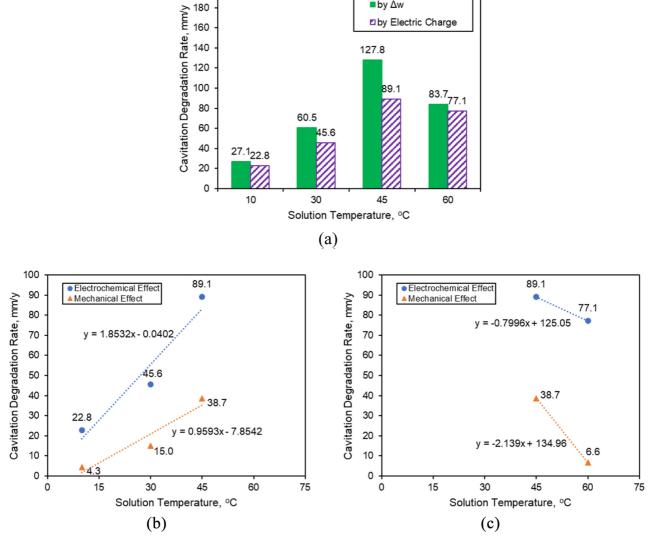


Fig. 10. Effect of solution temperature on (a) the total cavitation degradation rate and electrochemical corrosion rate of carbon steel in 3.5% NaCl (ultrasonic amplitude 85 µm, cavitation time 1h) and on the electrochemical and mechanical effects (b) below T_{max} , (c) over T_{max}

reduced cushion effect at higher temperature [25,26] decreased the mechanical cavitation effect greatly.

4. Conclusions

In this work, carbon steel was used, and the cavitation corrosion of carbon steel was evaluated in 3.5% NaCl with temperature using an indirect ultrasonic cavitation method (Ultrasonic Amplitude 85 µm). The following conclusions were derived:

1) When cavitation occurs on the surface carbon steel, cavitation reveals three kinds of effects -1) increasing the limiting diffusion current density, 2) increasing the mechanical damage effect, 3) the air ingression by bubble formation increased the dissolved oxygen content. Therefore, cavitation corrosion rate can be increased by cavitation. On the other hands, when the temperature increases, a dissolved oxygen content reduces at a very high speed. Therefore, the maximum cavitation corrosion temperature was changed from 80 to 45 °C.

2) Cavitation degradation can be divided into the electrochemical and mechanical effects; below the maximum cavitation temperature, the electrochemical effect was more dominant than the mechanical effect by increasing temperature, but over the maximum cavitation temperature, the mechanical effect was more dominant than the electrochemical effect by increasing temperature.

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