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**The Effect of Various Surface Conditions on Corrosion Resistance
of Absorption Refrigeration Regenerators**

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ABSTRACT

Absorption water chillers/heaters are air-conditioning machines which do not use CFC gas that leads to depletion of the ozone layer and global warming. Although absorption water chillers/heaters use condensed lithium bromide solution, which is highly corrosive, as absorbent in a vacuum, developments of various corrosion inhibitors have helped minimize corrosion problems with absorption systems. However, their performance gradually deteriorates because corrosion occurs in some cases. Improvement of further corrosion resistance is therefore hoped for. The surface conditions of carbon steel and the heating rate at aging are considered as the major factors affecting corrosion resistance. Aging means a passivation process for vessel material at the beginning of refrigerator operation.

Then, in order to evaluate the effects of various surface conditions and the heating rate during aging on the corrosion resistance of carbon steel, which is used as a regenerator vessel material in the absorption refrigeration cycle, electrochemical measurements of carbon steel in a concentrated lithium bromide solution were carried out. As a result, it was found that when polished steel, as a defect due to mill scale on carbon steel, was corroded to some extent or when a metal/metal crevice was formed on polished steel surface, macro cells possibly continued to occur between the polished steel and the carbon steel covered with mill scale during or after the aging. On the other hand, it was found that when the heating rate during the aging was low, the macro cell current was large and that there was higher corrosion risk than at high heating rates.

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1. Introduction

In recent years, CFC-free gas absorption water chillers/heaters (hereinafter called “absorption systems”) have recaptured growing attention, against the alarming state of global environmental problems such as ozone depletion and global warming. However, absorption systems use a concentrated lithium bromide solution as absorbent in a vacuum. Therefore, numerous studies¹⁾⁻⁵⁾ on the corrosiveness of lithium bromide solution in a vacuum and on the effects of various corrosion inhibitors have helped minimize corrosion problems with absorption systems. In some rare cases, however, corrosion occurs.

Regarding rare corrosion cases of absorption systems, it has been revealed that such cases can be reproduced by using a mill-scaled specimen representing actual equipment and magnetite particles, i.e., corrosion products, as impurities in solution.

Nonetheless, the surfaces of carbon steel which is used in the absorption systems might be corroded due to atmospheric corrosion when storing it before aging. Moreover, metal/metal crevices might be present. These may be a cause of rare corrosion. Aging means a passivation process for vessel material by heating it in a concentrated lithium bromide solution containing a passivator as an inhibitor at the beginning of refrigerator operation. Therefore, in this study, steel surface conditions affecting the corrosion resistance of steel during and after aging were evaluated.

2. Experimental Method

2.1 Specimens

Specimens were prepared to simulate various surface conditions of actual equipment. Mill-scaled specimens were used to simulate carbon steel covered with mill scale. Polished specimens were used to simulate defects in mill scale. Corroded specimens simulated corrosion defects in mill scale. Specimens with crevices simulated metal/metal crevices. To make the corroded specimens, drops of tap water or sodium chloride tap water solution with 100 mg/l of total chloride ion concentration (hereinafter called 100 mg/l Cl⁻ solution) were used.

In addition, to reproduce repeated atmospheric wetting and drying, a drying process (333 K, 35% RH, 3 h) and a wetting process (313 K, 95% RH, 3 h) were repeated for nine cycles. Transition time was 1 h from drying to wetting and 1 h from wetting to drying. Table 1 shows the types of corroded specimens and water-dropping conditions.

Table 1 Corroded specimens preparation conditions

Surface condition	Test condition	
	drop	Dropping condition
Corroded (Slight)	Tap water	One 1 mℓ drop only at beginning
Corroded (Moderate 1)	100mg/ℓCl ⁻ solution	One 1 mℓ drop only at beginning
Corroded (Moderate 2)	Tap water	One 1 mℓ drop every 3 cycles
Corroded (Heavy)	100mg/ℓCl ⁻ solution	One 1 mℓ drop every 3 cycles

2.2 Electrochemical Testing

• Passive Current Measurement

In the simulated macro cell test, detailed below, it is necessary to confirm that macro cell corrosion has stopped. For this purpose, macro cell corrosion was judged to have stopped when the macro cell current decreased to the passive current density at the anode. Then, the passive current in polished steel was measured.

The test electrodes were maintained at 430 K in test solution, to stabilize the corrosion potential. Then, their passive current was measured at a maintained potential within the passive range [-600 mV, referenced to Ag/AgCl/KCl (sat.) at room temperature: 298K]

• Simulated Macro cell Test

The test simulated a macro cell between carbon steel covered with mill scale and a defect in mill scale, a corrosion defect in mill scale, and a metal/metal crevice. For standard testing, the temperature was increased to 430K in 1 h. In contrast, to ascertain the effect of heating rates, the temperature was increased to 430K in 4 h.

In macro cell current measurement, the electrode potential of the specimen was set to 0 mV, with respect to mill-scaled steel, to measure the current in the simulated macro cell between the specimen and mill-scaled steel. Figure 1 shows a schematic diagram of the test apparatus.

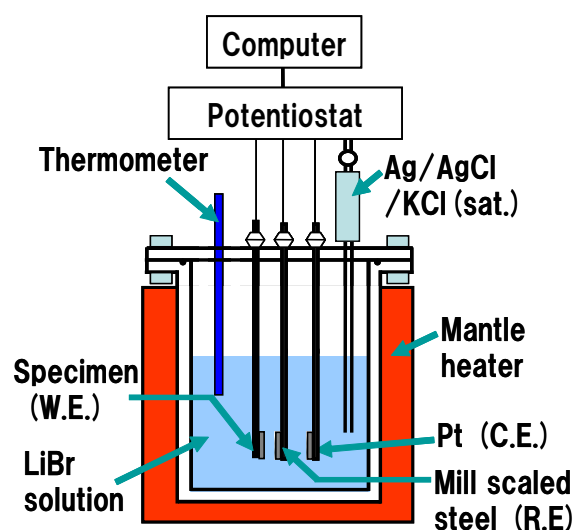


Fig.1 Schematic diagram of the autoclave system.

3. Results and Discussion

3.1 Observation of Corroded Specimens

The slightly corroded specimen was corroded over roughly half its size. The maximum corrosion depth was approximately 20 μm . The moderately corroded specimens were corroded almost all over their surfaces. The maximum corrosion depth of each specimen was approximately 40 μm . The heavily corroded specimens also were corroded almost all over their surfaces. The maximum corrosion depth was approximately 60 μm .

3.2 Measurement of Passive Current Density

After the polished specimen was maintained until passivation, anode polarization measurement was performed. The result was that the current density was roughly constant in the range of 7 to 8 $\mu\text{A}/\text{cm}^2$ from the corrosion potential of polished steel, which was from -630 mV to -590 mV. Then, passivity was considered to be retained for the polished steel in the range between the corrosion potential and -590 mV. On the other hand, it was verified that the potential of mill-scaled specimens stabilized between -640 and -590 mV. On the basis of these results, the passive current density was measured at -600 mV.

After the polished specimen was kept until its potential stabilized, the potential was ennobled to -600 mV and maintained at this value. Then the anodic current density was measured. After maintaining the potential at -600 mV, the anode current density decreased rapidly and stabilized below 0.2 $\mu\text{A}/\text{cm}^2$. Therefore, this current density was used as a reference in determining the cease of simulated macro cell corrosion.

3.3 Simulated Macrocell Test Results

- **Effects of Mill Scale Defects and Corrosion Defects**

Figure 2 shows the result of simulated macro cell current, which was measured from the onset of heating to 5 h, between a mill-scaled specimen and a polished specimen simulating a mill scale defect.

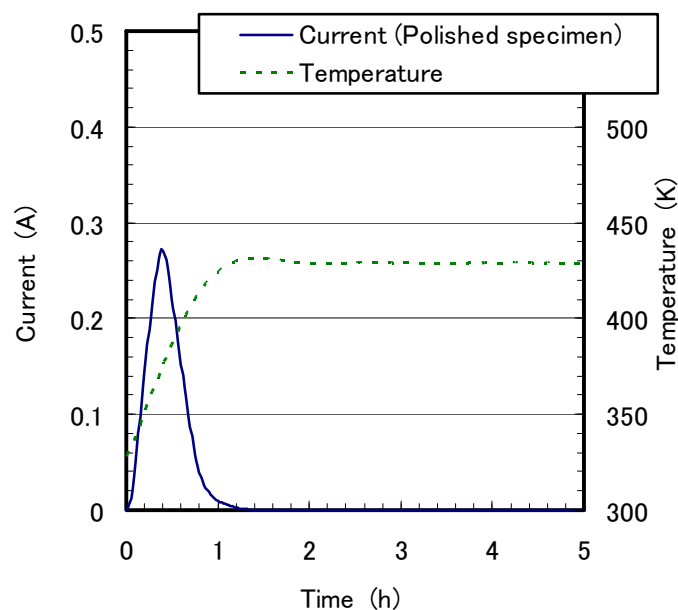


Fig.2 Time dependence of current in simulated macrocell between a polished specimen and a specimen covered with mill scale.

The measured anodic current simulating the macro cell current between the polished specimen and the mill-scaled specimen increased rapidly during heating and then decreased rapidly to 430K.

A trend similar to this was detected for the other types of simulated macro cells, including the corroded specimen and the creviced specimen in place of the polished specimen. Thus, it was thought that corrosion in any type of simulated macro cell would occur mainly during the heating process and that the degree of corrosion largely affected the continuation or cease of corrosion during cooling after the heating process.

Figure 3 shows the results of simulated macro cell current between a mill-scaled specimen and a polished specimen, a “slightly” corroded specimen, or a “moderate1” corroded specimen.

In the case of a polished specimen, the simulated macro cell current decreased below a passive current density of $0.2 \mu\text{A}/\text{cm}^2$ in approximately 50 h. After the test, the maximum corrosion depth was $12 \mu\text{m}$. In the case of the “slightly” corroded specimen (maximum corrosion depth: $20 \mu\text{m}$), the measured anodic current density fell to the passivity retention current of $0.2 \mu\text{A}/\text{cm}^2$ in 100 h. The maximum corrosion depth for this specimen was $24 \mu\text{m}$, and the progress of corrosion from the initial state (maximum corrosion depth: $20 \mu\text{m}$) was insignificant. In the case of “moderately” corroded specimens (maximum corrosion depth: $40 \mu\text{m}$) or heavily corroded specimens, the simulated macro cell current did not stabilize below the passive current density even after 100 h. The maximum corrosion depth for this specimen was a few tens of μm greater than that in the initial state.

From these results, it was thought that, in the case of mill scale defect only without corrosion, the macro cell corrosion did not continue because of the formation of passive layers over the defects for a few tens of hours after heating. On the other hand, it was thought that, in the case of corrosion defects in mill scale, passive layers might not be readily formed for over 100 h after heating and macro cell corrosion continued depending on the initial corrosion depth. From the present experimental results, it was thought that macro cell corrosion would continue if the initial corrosion depth of the defect in mill scale was $40 \mu\text{m}$ or more.

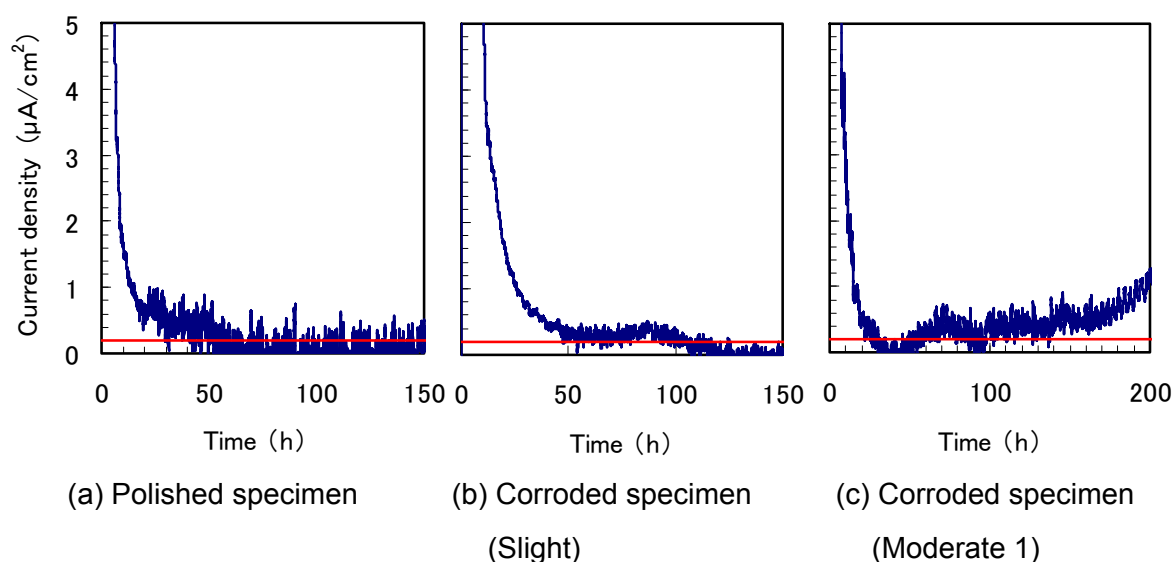


Fig.3 Time dependence of current density in simulated macrocell between various steel specimens with different degrees of corrosion and specimens covered with mill scale

- **Effects of Crevices**

Figure 4 shows the results of simulated macro cell current between a crevice specimen and a mill-scaled specimen. In the case of a metal/metal crevice, the simulated macro cell current did not decrease below the passive current density, even with no corrosion on the surface. The maximum corrosion depth of the specimen was 100 μm or more. As a result, in metal/metal crevices, it was thought that the macro cell corrosion between a metal/metal crevice and carbon steel covered with mill scale continued because passive layers might not be readily formed, irrespective of the corrosion.

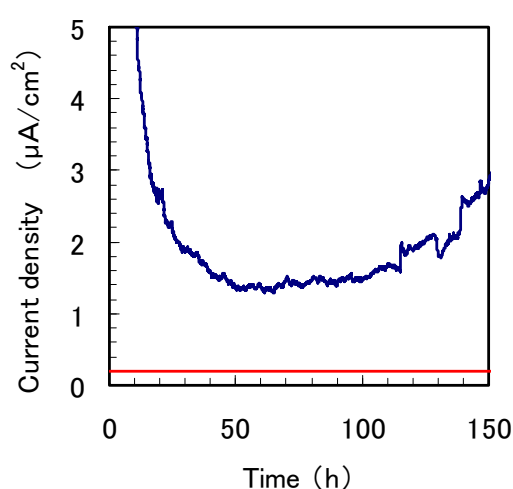


Fig.4 Time dependence of current density in simulated macrocell between specimens with metal/metal crevice and specimens covered with mill scale.

- **Effects of Heating Rate**

The results showed that when the heating rate was about 1/4 compared with the heating rate in standard testing, the simulated macro cell current between a polished specimen and a mill-scaled specimen decreased below the passive current density. However, the time during which the simulated macro cell current was large was 10 h longer at the low heating rate than at the standard heating rate. The maximum corrosion depth was about 40 μm , which was relatively large.

As a result, when the heating rate during the aging was low, it was thought that, although passive layers were formed, macro cell current was already large before the passive layer formation and that the corrosion depth would be larger.

4. Conclusion

This study focused on the effects of initial carbon steel surface conditions, which were defects or corrosion, and of the heating rate during aging on the corrosion resistance of steel used in the regenerators of absorption systems during and after aging. The results showed that

- (1) Macro cell corrosion between carbon steel covered with mill scale and defects of mill scale or crevice occurred during heating at aging. It was thought that macro cell corrosion, which occurred during heating, largely affected the continuation or cease of corrosion during holding process after heating.
- (2) When the defect was free from corrosion, the macro cell corrosion between the defect and carbon steel covered with mill scale would not continue during or after aging. On the other hand, when the mill scale defect was corroded to some extent, macro cell possibly continued to occur between the corrosion defects and carbon steel covered with mill scale during or after aging.
- (3) If a crevice was present in metal, it was highly probable that macro cell corrosion between a metal/metal crevice and carbon steel covered with mill scale would continue during or after aging.
- (4) When the heating rate during aging was low, the macro cell current was large and there was greater corrosion risk than at high heating rates.

Therefore, to improve the corrosion resistance of absorption systems, it was found that metal/metal crevices should not be made during construction, that careful management of steel material was necessary to avoid corrosion when storing it before aging, and that the heating should be as prompt as possible during aging.

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