

Area Effect on Galvanic Corrosion of Condenser Materials with Titanium Tubes in Nuclear Power Plants

Seong Sik Hwang, Joung Soo Kim, and Uh Chul Kim

Korea Atomic Energy Research Institute

(Received January 29, 1993)

Titanium 전열관을 사용하는 원전 복수기 재료의 Galvanic Corrosion에 미치는 면적의 영향

황성식 · 김정수 · 김우철

한국원자력연구소

(1993. 1. 29 접수)

Abstract

Titanium tubes have recently been used in condensers of nuclear power plants since titanium has very good corrosion resistance to seawater. However, when it is connected to Cu alloys as tube sheet materials and these Cu alloys are connected to carbon steels as water box materials, it makes significant galvanic corrosion on connected materials.

It is expected from electrochemical tests that the corrosion rate of carbon steel will increase when it is galvanically coupled with Ti or Cu in sea water and the corrosion rate of Cu will increase when it is coupled with Ti, if this couple is exposed to sea water for a long time. It is also expected that the surface area ratios, R_1 (surface area of carbon steel/surface area of Ti) and R_2 (surface area of carbon steel/surface area of Cu) are very important for the galvanic corrosion of carbon steel and that these should not be kept to low values in order to minimize the galvanic corrosion on the carbon steel of the water box. Immersed galvanic corrosion tests show that the corrosion rate of carbon steel is 4.4 mpy when the ratio of surface area of Fe/surface area of Al Brass is 1 while it is 570 mpy when this ratio is 10^{-2} . The galvanic corrosion rate of this carbon steel is increased from 4.4 mpy to 13 mpy at this area ratio, 1, when this connected galvanic specimen is galvanically coupled with a Ti tube. This can be rationalized by the combined effects of R_1 and R_2 on the polarization curve.

요 약

Titanium재료는 해수에서 좋은 내식성을 가지는 이유로 최근 원자력발전소 복수기에 사용되고 있다. 그러나, Ti이 tubesheet재료인 Cu 합금에 접하고 이것이 water box 재료인 탄소강에 접하게될 경우 접촉금속에 심한 galvanic corrosion이 일어나게 된다.

전기화학적 실험에 의하면, 탄소강이 해수속에서 Ti이나 Cu에 접할때 탄소강의 부식속도는 증가할 것이며, Cu가 Ti에 해수속에서 장기간 접촉할 경우에는 Cu의 부식속도가 증가할 것으로 생각된다. 또한 표면적비, R_1 (surface area of carbon steel/surface area of Ti)와 R_2 (surface area of carbon steel/sur-

face area of Cu)가 탄소강의 galvanic corrosion에 매우 중요하며, Water box 재료인 탄소강의 부식속도를 최소화하기 위해서는 이들 표면적비가 낮게 유지되어서는 안될 것이라고 생각된다. 침지 galvanic 부식 시험결과 surface area of Fe/surface area of Al Brass값이 1일때 탄소강의 부식속도는 4.4mpy이었으나 이 비가 10^{-2} 일때는 570mpy이었다. 이렇게 연결된 galvanic 시편에 Ti tube를 연결한 경우에는 이 비가 1일때 탄소강의 부식율이 4.4mpy에서 13mpy로 증가 하였다. 이는 R_1 과 R_2 가 분극곡선에 복합적인 영향을 미치는것으로 설명할 수 있다.

1. Introduction

Titanium tubes have been used recently in condensers of nuclear power plants since titanium has very good corrosion resistance to sea water. However, when it is connected to Cu alloys as tube sheet materials and Cu alloys are connected to carbon steels as water box materials, significant galvanic corrosion can take place and has been experienced on connected materials in nuclear power plants^(1,2). It was reported that the galvanic corrosion current is much more evenly distributed in the case of high conductivity than it is for lower conductivity⁽³⁾ and that galvanic current density increases with the increasing average free stream velocity of sea water⁽⁴⁾. It was also reported that the galvanic corrosion of carbon steel coupled to Pt shows the maximum value in the solution containing about 1% NaCl and its galvanic corrosion value is almost constant in the pH range from 5 to 9⁽⁵⁾. While rubber lining or epoxy coating is applied on the inner surface of water boxes and epoxy materials are painted on some tube sheets in order to reduce galvanic corrosion in nuclear condensers, some lined or painted parts are not protective after a long period of exposure to flowing sea water and this greatly changes the cathodic to anodic surface area ratio. This work was performed to evaluate the area effect on the galvanic corrosion in nuclear condensers since the reported data are limited.

2. Experimental

2.1. Materials and Test Solution

Cylindrical specimens of commercially pure Ti(%), Cu(%) and SA 285 grade C carbon steel were made to have a 0.63cm diameter and 3.0cm length for electrochemical tests. ASTM B-338 grade 2 seam welded titanium tubes, carbon steel and Al-Brass were machined and assembled as in Figure 1 for immersed galvanic corrosion test to investigate area effect and applied potential effect. The surface area ratio was controlled by painting of lacquer(MICCROSTOP). Their chemical compositions are listed in Table 1. The solution for the electrochemical test had 18,500 ppm Cl^- as NaCl and pH was adjusted to 8 with NaOH. Natural sea water was used for the immersion tests. Table 2 gives analyzed data for natural sea water.

2.2. Electrochemical Test

Cylindrical specimens were prepared with SiC papers down to 600 grade. These were degreased with acetone and rinsed with distilled water before the tests. A Princeton Applied Research Model

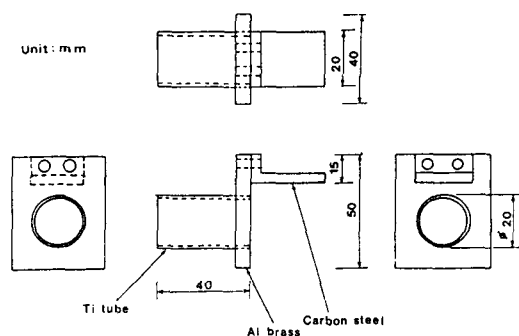


Fig. 1. Schematic Drawing of a Immersed Galvanic Test Specimen

Table 1. Chemical Compositions of Test Specimens for Electrochemical and Immersed Galvanic Tests.

Material	Chemical Composition(Weight %)
AST, B-338* grade 2 Ti	0.01 Fe, 0.14 O, 0.0035 N, 0.0019 H, Bal Ti
Al-Brass*	76.12 Cu, 20.43 Zn, 3.22 Al, 0.08 Ni, 0.04 Fe, 0.02 Mn, 0.02 Si
Carbon Steel*	98.60 Fe, 0.49 C, 0.32 Mn, 0.28 Al, 0.14 Co, 0.08 Si, 0.06 Cu 0.02 S, 0.01 Cr
SA 285 grade C	0.57 Mn, 0.15 C, 0.017 P, 0.006 S, Bal Fe
Commercially Pure Ti	0.0016 H, 0.111 O, 0.115 N, 0.004 C, 0.1 Others, Bal Ti
Commercially Pure Cu	0.047 O, 0.0006 S, 0.039 Pb, 99.89 Cu

* Materials for immersed galvanic corrosion tests

Table 2. Analyzed Data for Natural Sea Water Used for Immersed Galvanic Test

pH	8.13	Fe*	0.19
Tatal Cond. (μ S/cm)	41960	NH ₄ *	N/D
C.O.D.*	1.76	SO ₄ *	2646
D.O.*	7.7	SiO ₃ *	1.35
Turbidity	0.56	Cl*	18742
Ca*	348	Suspended Solid*	1.95
Mg*	1293		

* ppm

173 Potentiostat, Model 376 Logarithmic Current Converter, Model 175 Universal Programmer and X-Y recorder were used for electrochemical tests. A saturated calomel electrode and two graphite electrodes were used as a reference electrode and counter electrodes, respectively. Anodic and cathodic scanning were started from corrosion potentials right after the specimen preparation described above, scanning rate 30mv/min to get polarization curves.

2.3. Immersed Galvanic Corrosion Test

Specimens were finally ground with SiC 600 grade paper, degreased with acetone in a ultrasonic cleaner and rinsed with distilled water. The specimens were painted with a commercial lacquer

(MICCROSTOP) except exposure areas to control area ratio. Specimens were tested for 3 weeks and the solution was changed every 2 days. The specimens were treated with a nylon brush in flowing water, cleaned ultrasonically and dried after the tests. Weight losses were measured before and after the tests. Corrosion rates were calculated by the following formula⁽⁶⁾.

$$\text{Corrosion rate(mpy)} = K.W/A.T.D$$

Where K : constant(3.45×10^6)

T : time of exposure in hours

A : area in cm²

W : mass loss in g

D : density in g/cm³

Brinkman Model MP 81 Potentiostats were used to apply potentials.

3. Results and Discussion

3.1. Electrochemical Tests

Corrosion potentials were measured as a function of time in the solution containing 18,500 ppm Cl⁻ as NaCl at pH 8.0 and 30°C in Figure 2. The corrosion potentials for Cu and SA 285 grade C slightly decreased to -0.2 V after a 22 hour test and to -0.7 V after a 7 hour test respectively. However, the corrosion potential for Ti increased gradually from -0.55 V to -0.1 V during this test.

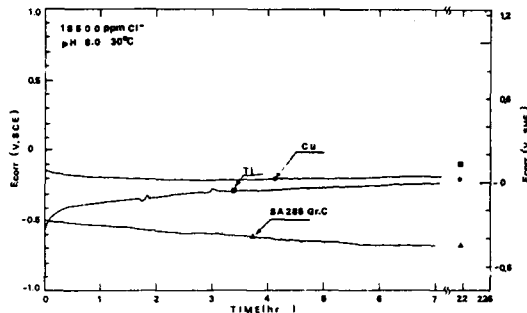


Fig. 2. Corrosion Potentials for Cu, Ti and SA 285 Grade C as a Function of Exposed Time.

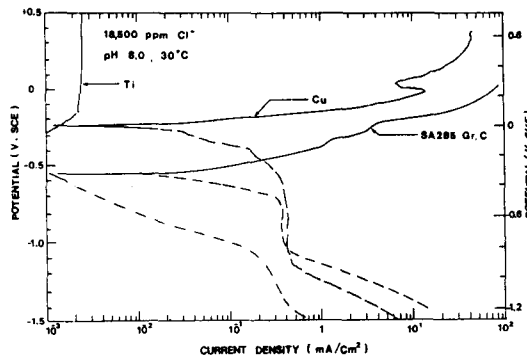


Fig. 3. Polarization Curves for SA 285 Grade C, Cu and Ti (Dotted Lines Mean Cathodic Current Density).

From Figure 2 it is expected that the corrosion rate of carbon steel, SA 285 grade C, will increase when it is galvanically coupled with Ti or Cu which is the major element of Cu alloy tube sheet materials. It is also expected that the corrosion rate of Cu will increase when it is coupled with Ti, if this galvanic couple is exposed in the sea water for a long time. Figure 3 shows polarization curves for SA 285 grade C, Cu and Ti in the same condition. The corrosion rate of SA 285 grade C will be greatly increased from this curve if its corrosion potential is raised due to galvanic contact with Ti or Cu. The similar tendency will occur for Cu after some exposure time when it is galvanically coupled with Ti.

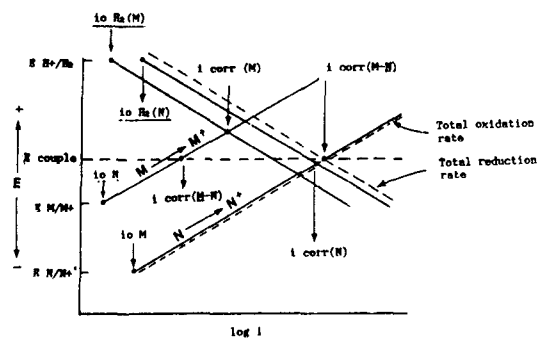


Fig. 4. Galvanic Couple Between Two Corroding Metals⁽⁷⁾.

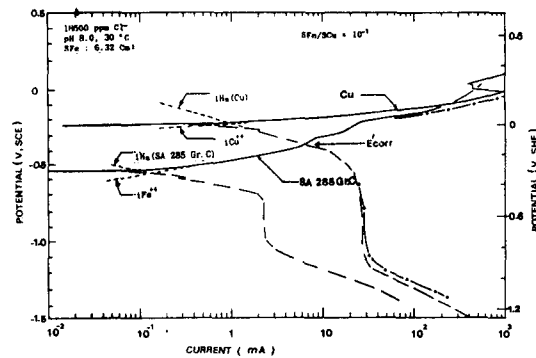


Fig. 5. Change of Corrosion Potential for SA 285 Grade C When it is Galvanically Coupled With Cu.

Figure 4 explains fundamental galvanic coupling between two corroding metals⁽⁷⁾. The corrosion rate of metal N ($i_{\text{corr N}}$) will be increased to $i_{\text{corr M-N}}$ by the galvanic contact with metal M when total oxidation and total reduction rates are considered. When a metal surface area increases, its current will increase. From the polarization curves for SA 285 grade C and Cu with a surface area ratio $S_{\text{Fe}}/S_{\text{Cu}} = 0.1$, the corrosion current and corrosion potential (E'_{corr}) for SA 285 grade C can be obtained in Figure 5 by considering total oxidation and total reduction rates as in Figure 4, when it is galvanically coupled with Cu. The current curve for Cu will be shifted as its surface area is changed. The surface area of SA 285

grade C was 6.32 cm^2 .

The effect of surface area ratios of S_{Fe}/S_{Ti} and S_{Fe}/S_{Cu} were plotted on the polarization curve for SA 285 grade C in Figure 6. The corrosion potentials for SA 285 grade C coupled galvanically were obtained as in Figure 5 by increasing Cu and Ti surface areas with the same surface area of SA 285. When R_2 (surface area of Fe/surface area of Cu) is decreased from 1 to 10^{-2} , the corrosion rate of SA 285 grade C is greatly increased. R_2 is more effective on its corrosion than R_1 (surface area of Fe/surface area of Ti). Titanium condenser tubes are expanded to tube sheets and these tube sheets are connected to water boxes in nuclear power plants and these surfaces contact sea water. Since the number of Ti tubes in a condenser ranges from 47,664 to 100,296 in Korean nuclear power plants, a large surface area of Ti is expected. The carbon steel surface of the water box is usually lined by rubber or painted with epoxy materials and the Cu alloy surface of tube sheet is sometimes painted with epoxy materials too. However, some parts of these surfaces are exposed to flowing sea water during long-term service and these exposed areas change ratios R_1 and R_2 . In order to minimize the galvanic cor-

rosion on the carbon steel of the water box, R_1 and R_2 should not be kept to low values. In the case of R_2 , the corrosion rate of the carbon steel can be lowered by painting the exposed Cu surface frequently. In the case of R_1 , exposed Ti surface area can not be reduced. If the exposed Fe surface area is increased, galvanic corrosion rate is reduced but the corrosion occurs in wide area. Therefore, cathodic protection is applied. However, the cathodic protection can produce hydrogen and it reacts with Ti easily to form hydrides. This can make a hydrogen embrittlement problem. Therefore, the potential range for the cathodic protection should be optimized by considering galvanic corrosion⁽²⁾ and hydrogen embrittlement⁽¹⁾. R_3 (surface area of Cu/surface area of Ti) effect was plotted on polarization curves for Ti and Cu in Figure 7 and 8. If R_3 is increased to 1, corrosion rate for Ti is slightly increased but its value is very low ($1 \mu\text{A}/\text{cm}^2$). In addition, R_3 is usually much less than 1 since Ti condenser tube surface area is relatively very large. R_3 does not increase the corrosion of Cu in Figure 8. However, corrosion potentials for Cu and Ti are changed as a function of time and the corrosion potential for Ti is higher than the value

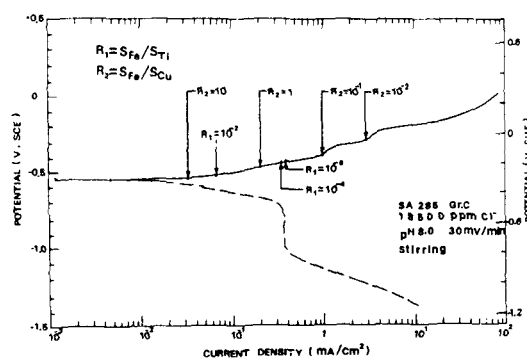


Fig. 6. Effect of Surface Area on Ratio on Galvanic Corrosion of SA 285 Grade C on Its Polarization Curve When it is Coupled With Ti or Cu.

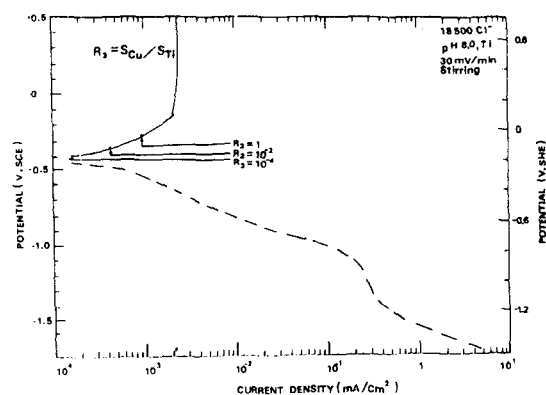


Fig. 7. Effect of Surface Area Ratio on Galvanic Corrosion of Ti on Its Polarization Curve When it is Coupled With Cu.

for Cu after 22 hour exposure in Figure 2. Therefore, it is expected that this R_3 can affect the corrosion of Cu if the polarization curve for Ti is obtained after stabilizing the Ti specimen in the solution for 22 hours.

3.2. Immersed Galvanic Corrosion Tests

Specimens shown in Figure 1 were immersed in natural sea water for 3 weeks with or without Ti tubes. The effect of the area ratio (surface area of Fe/surface area of Al Brass) on the galvanic corrosion rate of a carbon steel was plotted in Figure 9. Its corrosion rate without a Ti tube is 4.4 mpy when this area ratio is 1, while it is 570 mpy when the area ratio is 10^{-2} . This kind of tendency was expected in Figure 6, even though the values by immersion tests are lower than the values obtained from polarization curves by considering 1 mA/cm^2 is equivalent to 461.8 mpy. When this ratio was maintained at 10^2 , the corrosion rate was 0.04 mpy. The corrosion of this carbon steel was increased from 4.4 mpy to 13 mpy at the area ratio, 1, when it is galvanically coupled with a Ti tube. This can be rationalized by the increase of corrosion potential due to the combined effects of R_1 and R_2 in Figure 6 since the additional R_1

effect raises the potential further.

The effect of the applied potential and area ratio on the corrosion rate of carbon steel was shown in Figure 10. The corrosion potential at the interface between a carbon steel plate and a Al Brass plate with a Ti tube reached -0.48 V after 40 minutes exposure in the natural sea water. When the surface area of Fe/surface area of Al Brass is 1 and R_1 is 8.0×10^{-2} , the corrosion rate of carbon steel is 12.9 mpy. However, its corrosion rate is reduced to 1 mpy at -0.9 V . Its corrosion rate is greatly increased to 1230 mpy when the surface area of Fe/surface area of Al Brass is 10^{-2} and $R_1 = 2.7 \times 10^{-3}$. As the potential is applied cathodically, its corrosion rate is decreased. However, its value is 45.3 mpy at -0.9 V . This indicates that cathodic protection is not so

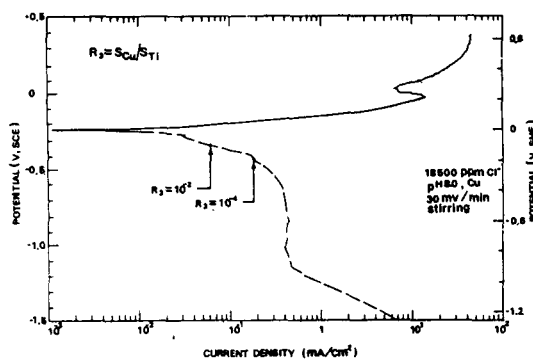


Fig. 8. Effect of Surface Area Ratio on Galvanic Corrosion of Cu on Its Polarization Curve When it is Coupled With Ti.

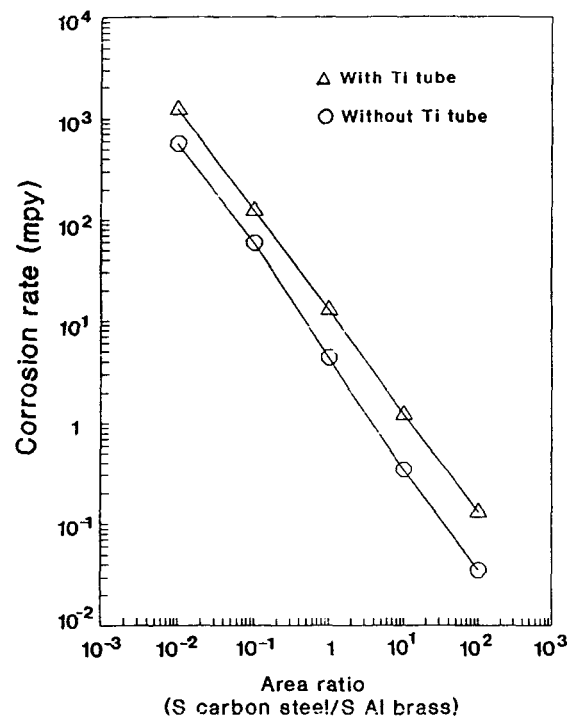


Fig. 9. Effect of Area Ratio on the Corrosion Rate of a Carbon Steel Coupled With Al Brass With or Without a Ti Tube.

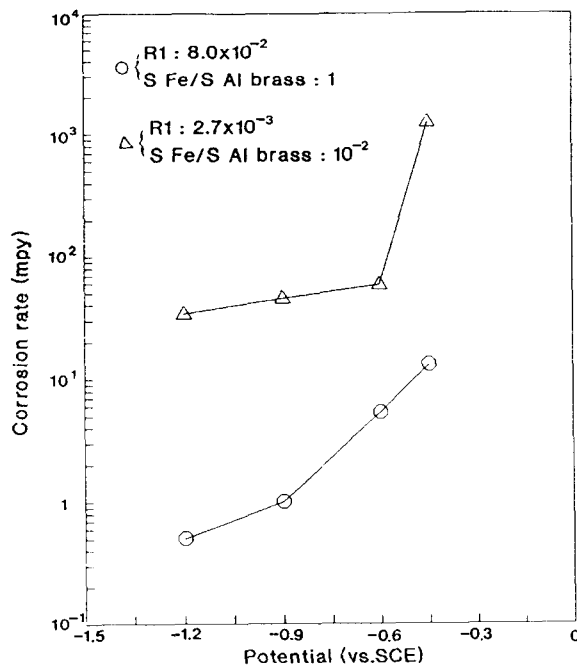


Fig. 10. Effect of Applied Potential and Area Ratio on the Corrosion Rate of a Carbon Steel With a Ti Tube.

effective if the surface area ratio is not well controlled.

4. Conclusions

1. The corrosion potentials for Cu and carbon steel, SA 285 grade C, slightly decrease to -0.2 V and -0.7 V respectively while the corrosion potential for Ti increases gradually from -0.55 V to -0.1 V during this test. Therefore, it is expected that the corrosion rate of the carbon steel will increase when it is galvanically coupled with Ti or Cu and the corrosion rate of Cu will increase when it is coupled with Ti in sea water for a long time.
2. It is expected that the surface area ratios, R_1 (surface area of Fe/surface area of Ti) and R_2 (surface area of Fe/surface area of Cu) are very important to the galvanic corrosion of carbon steels and that R_2 is more effective on its galvanic corrosion rate in this test condition. In order to minimize the galvanic corrosion on the carbon steel of the water box, R_1 and R_2 should not be kept to low values.
3. Immersed galvanic corrosion tests show that the corrosion rate of carbon steel is 4.4 mpy when the ratio of surface area of Fe/surface area of Al Brass is 1, while it is 570 mpy when this ratio is 10^{-2} . The galvanic corrosion rate of this carbon steel is increased from 4.4 mpy to 13 mpy at this area ratio, 1, when it is galvanically coupled with a Ti tube. This can be rationalized by a combined effect of R_1 and R_2 on the polarization curve.
4. The cathodic protection is not so effective on the galvanic corrosion of the carbon steel if its surface area ratios with Al Brass and/or Ti are not well controlled.

Acknowledgement

Authors thank Mr. J. S. Song and Miss H. K. Shin for his technical and her typing assistance for this work.

References

1. T. Nosetani, M. Shimono, Z. Tanabe, S. Sato, H. Hirose, K. Onda, Y. Yamaguchi, "Service Experience of Welded Titanium Tubes in Air Cooling Zone of Surface Condensers", Sumitomo Technical Report on Light Metals, Vol.15, No.3, p.8, July (1974)
2. C. Chu, P. Chung, J. Oung "The Investigation of Corrosion Behavior and the Experience on Cathodic Protection of Aluminum Bronze Tubesheet in Titanium-tubes Surface Condenser" 18-24, Proceedings of the International Symposium on Pressure Vessel Technology and Nuclear Codes & Standards, Published by Korean Society of Mechanical Engineers,

- Seoul, April 19–21 (1989)
3. E. Bardal, R. Johnsen, P. Gartland, "Prediction of Galvanic Corrosion Rates and Distribution by Means of Calculation and Experimental Models", *Corrosion*, Vol.40, No.12, p.628 (1984)
 4. J. Perkins, K. Graham, G. Storm, G. Leumer, R. Schack, "Flow Effects on Corrosion of Galvanic Couples in Sea Water", *Corrosion*, Vol.35, No.1, p.23 (1979)
 5. B. Tsujino, S. Miyase, "The Galvanic Corrosion of Steel in Sodium Chloride Solution", *Corrosion*, Vol.38, No.4, p.226 (1982)
 6. ASTM G1–81, "Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens"
 7. M. Fontana, N. Greene, "Corrosion Engineering" McGraw–Hill Inc. (1967)