

Case Analysis of Stainless Steel Corrosion in Hot Spring Waters and Using Titanium as a Measure against Corrosion

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Abstract

In hot spring facilities in Kusatsu, Gunma Prefecture, in about two months, SUS304 stainless steel handrails corroded and dissolved uniformly in acid sulfate-chloride spring water containing hydrogen sulfide. Corroded samples were analyzed, remaining handrails were observed closely, an immersion test was conducted at the sources of springs, and corrosion potentials were measured. The result showed that the causes of the corrosion were low pH (pH 2 or less) and the corrosion action of free hydrogen sulfide. Because the handrails corroded in only the type of spring water containing hydrogen sulfide at the two sources of springs with a pH of 2 or less, hydrogen sulfide had a particularly significant impact on the corrosion and accelerated the active dissolution of SUS304 stainless steel. As a measure against corrosion, titanium instead of SUS304 stainless steel was used for handrails. Rusting or local corrosion was not observed about 18 months after use.

Keywords

stainless steel, corrosion, hot spring water, pH, H₂S, corrosion products, corrosion potential

1 Introduction

Various special qualities can be seen in the natural water of hot springs as a result of geological characteristics. Depending on the hot spring, the construction and equipment materials used in the hot spring facilities can be affected by the water quality, and in

particular metal materials can corrode in a short period of time.¹⁾⁻³⁾ This paper introduces a case study of corrosion in a short period of time of stainless steel (SUS304) handrails in the bathtubs at Kusatsu Hot Spring in Gunma Prefecture. Of the SUS304 handrails that were installed at one location in each of the four bathtubs, the part of the handrail immersed in the No. 1 bathtub (below the waterline) was dissolved by corrosion after about two months. Likewise for bathtub No. 2, the part of the handrail immersed in the bathtub (below the waterline) was dissolved by corrosion after about eight months. A site survey was performed after about 12 months, in which the state of corrosion of each of the handrails in the bathtubs was investigated. The source water of bathtubs Nos. 1 through 3 was acid sulfate-chloride spring water containing hydrogen sulfide (source A), and the water of bathtub No. 4 was acid sulfate-chloride spring water not containing hydrogen sulfide (source B). Table 1 shows the source name and location of each bathtub. The survey included visual inspection, analysis of corrosion products, water quality analysis, and measurement of corrosion potential of handrails on site. Also, as a measure against corrosion, handrails made from the alternative material titanium were used. The following is a report on results of the corrosion analysis of the stainless steel handrails, and the results of a survey of the state of corrosion of the titanium handrails 18 months after start of use.

Table 1 Source name and location of each bathtub

Bathtub No.	1	2	3	4
Source name	A	A	A	B
Location of bathtub	Indoor	Open-air	Indoor	Open-air

2 Survey, Test Methods, and Analysis Results

2.1 State of corrosion of SUS304 handrails

In bathtubs Nos. 1 through 3 which use acid sulfate-chloride spring water containing hydrogen sulfide (source A) for which corrosion was significant, the immersed parts of the handrails in bathtubs Nos. 1 and 2 were dissolved by corrosion after about 2 months and 8 months respectively, as stated above, and the lower parts of the handrails had sunk to the bottom of the bathtubs. The state of corrosion of handrails Nos. 1 and 2 is shown in Figs. 1 and 2. Below the waterline the thickness had been reduced and the metal disappeared, and the remaining lower part of the handrail (the bottom part) was significantly corroded so it was considered that there was uniform corrosion of the SUS304. In the handrail of bathtub No. 3 which was exposed to the same source A, after about 12 months, many microbubbles were generated from the immersed parts of the bathtub as shown in Fig. 3. Thin dark brown corrosion layer formed on immersed parts (See Fig. 4). On the other hand, in the handrail of bathtub No. 4 which is the only bathtub that uses acid sulfate-chloride spring water not containing hydrogen sulfide (source B), off-white scale adhered to the handrail directly above the water line, and below and around the scale pitting corrosion and discoloration with rust was seen. However, localized corrosion or discoloration with rust was not seen in the immersed parts or the parts exposed to air.

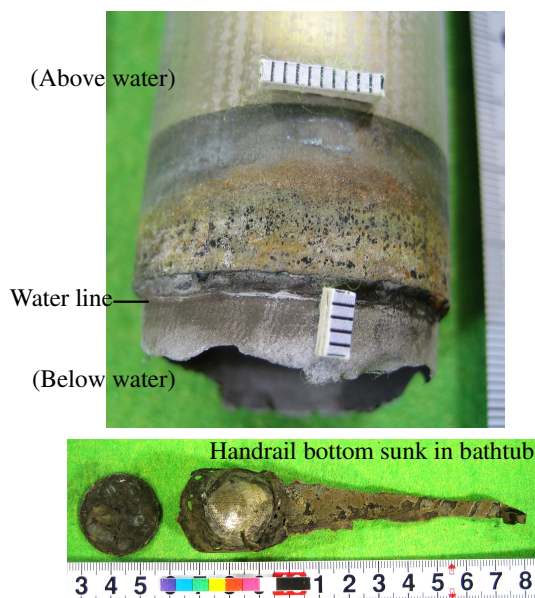


Figure 1 - State of corrosion of handrail in bathtub No. 1, About 2 months use

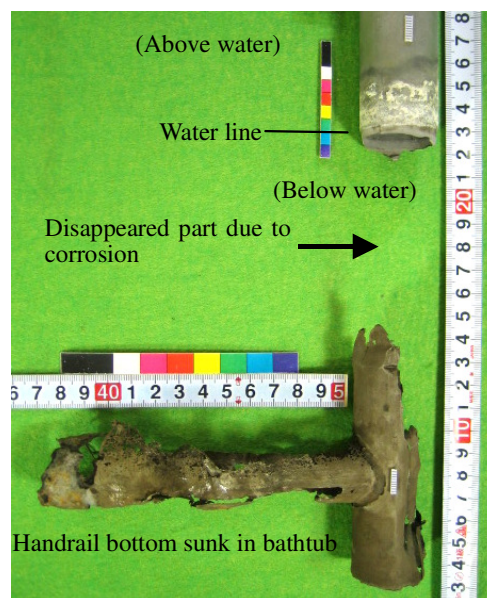


Figure 2 - State of corrosion of handrail in bathtub No. 2, About 8 months use



Figure 3 - State of active dissolution of handrail in bathtub No. 3, About 12 months use

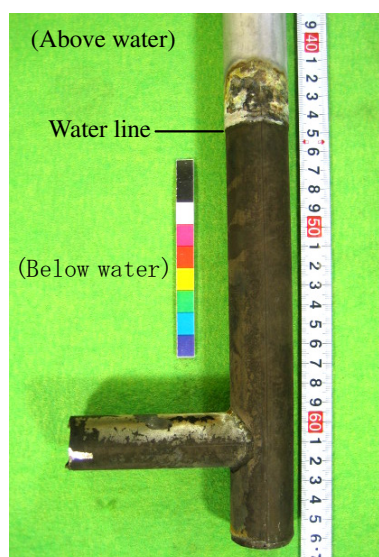


Figure 4 - State of corrosion of handrail in bathtub No. 3, About 12 months use

2.2 Analysis of corrosion products

Rust from the waterline of the handrail of bathtub No. 1 was scraped off, and the results of analysis by EDX (JEOL Ltd., JSM-6300) are shown in Fig. 5. Apart from the

components of the material, S was strongly detected. Also, according to EPMA (JEOL Ltd., JXA-8100) analysis results for the cross-section of the rust layer shown in Fig. 6, S, O, Cr, Fe, and Ni are distributed throughout the whole layer. This infers that corrosion products of sulfide or sulfate of Fe, Cr, Ni were formed. From the analysis results of XRD (MAC Science MXP18 and Rigaku RU-2000) on rust samples from the handrails of the No. 1 and No. 3 bathtubs, only nickel sulfate was detected. In all cases the peak was broad, suggesting a compound with low crystallinity. In the case of non-crystalline rust, the state of the compound is estimated from the bonding energy, so state analysis was carried out by XPS (Shimadzu Corporation, ESCA-3200). The XPS analysis results for the rust from bathtub No. 3 are shown in Fig. 7. Figure 7 suggests the generation of sulfides FeS, FeS₂, NiS, sulfates FeSO₄, NiSO₄, oxides Fe₂O₃, Cr₂O₃, CrO₃, and hydroxides Cr(OH)₃, etc. Also, as shown in Figs. 5 and 7, small quantities of copper and its compounds (Cu₂S, CuSO₄) were detected. According to the water quality analysis results for the two source waters shown in Table 2, the concentration of copper in source A was less than 0.01 mg/L, and the quantity of copper contained in the SUS304 of the handrails was 0.3% (mass%, x-ray fluorescence analysis, Shimadzu Corporation, MFX2400), so it is considered that the copper originated from the handrail material (an impurity). The quantity of copper in the SUS304 is minute, but there is a possibility that it was detected due to being concentrated in the rust.

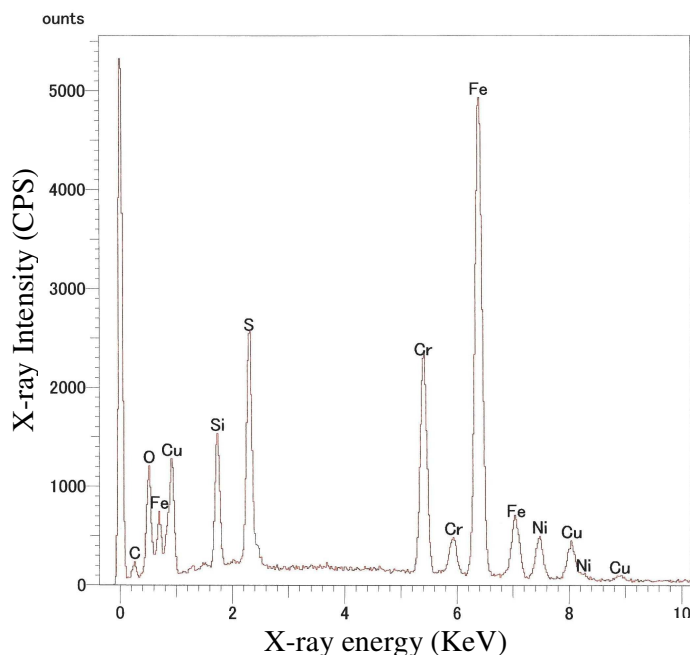


Figure 5 - Analysis result by EDX of corrosion products of SUS304 handrail in water line part

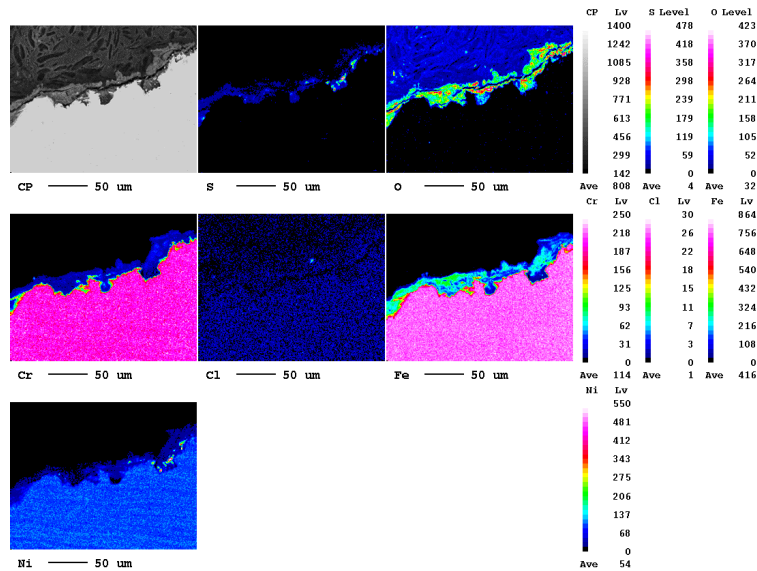


Figure 6 - Analysis result by EPMA of corrosion products of SUS304 handrail in water line part(bathtub No. 1)

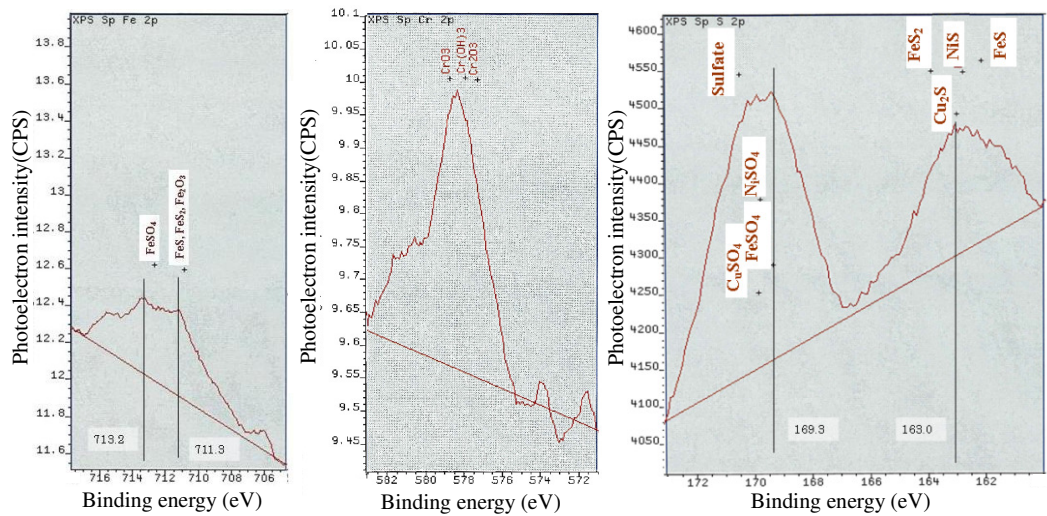


Figure 7 - Analysis result of corrosion products of SUS304 handrail by XPS in bathtub No.3

Table 2 Water quality of hot spring source

Water quality item	Unit	A	B
pH		1.9	1.7
Turbidity	TU	2.0	<0.2
Color	CU	4.4	4.9
Conductivity	mS/m	559	1120
Ca-Hardness	mg/L as CaCO ₃	172	229
Total-Hardness	mg/L as CaCO ₃	304	423
Cl ⁻	mg/L	289	689
SO ₄ ²⁻	mg/L	848	1400
S ²⁻	mg/L	4.0	<0.1
KMnO ₄ Consumption value	mg/L	21.2	9.6
Residue	mg/L	1940	3290
Soluble SiO ₂	mg/L	168	361
Total SiO ₂	mg/L	181	387
Fe	mg/L	12.7	4.09
Cu	mg/L	<0.01	0.01
Mn	mg/L	1.82	2.92
Na	mg/L	56.3	102
K	mg/L	27.9	50.8
Free H ₂ S *	mg/L	7.3	0.0

* Analysis value by Gunma environmental hygiene center

2.3 Water quality analysis

pH was measured on site, and the other water quality items were promptly analyzed after refrigerating the water and transporting it to the analysis laboratory. The analyses were carried out in accordance with test methods for industrial water analysis standard (JIS K 0101), wastewater analysis standard (sulfide ions only, JIS K 0102), and the analysis organization's standards. The water in each case had a pH of less than 1.9 indicating strongly acidic water, source A had a free hydrogen sulphide H₂S content of 7.3 mg/L, and source B had a free H₂S content of 0.0 mg/L. Source A had unmistakable odor of hydrogen sulfide. SO₄²⁻, Cl⁻ were magnitude of several tens greater than for normal tap water in Japan, but the ratio SO₄²⁻/Cl⁻ (mg/L) was 2.93 for source A, and 2.03 for source B, and in addition the quantity of SO₄²⁻ was high, indicating a tendency to inhibit corrosion due to chloride ions.

2.4 Measurement of corrosion potential of handrails and test specimens

The corrosion potential of the handrails was measured on site in the condition of use using an electrometer (Toho Technical Research, EM-02) using a saturated calomel electrode (SCE) as standard. The materials of the test specimens for measurement of

corrosion potential were SUS304, SUS316, which had a square 10 mm × 10 mm with a wet No. 600 finish polished surface and a periphery that was covered with epoxy resin. Also, an SUS304 support rod (covered with epoxy resin including the soldered joint to the test specimen) was fitted for connecting the lead wires for measurement of the corrosion potential. Measurement of the corrosion potential of the test specimens was carried out by soaking each of the test specimens for 41.5 hours in each of the source waters (source A 46.2°C, source B 47.8°C) which constantly flowed into resin containers (665 × 425 × 75 mm), using an electrometer with a saturated calomel electrode (SCE) as standard. The potential was read after allowing the electrodes to stabilize sufficiently after soaking. Figure 8 shows a view of the measurement of the corrosion potential of the handrails.

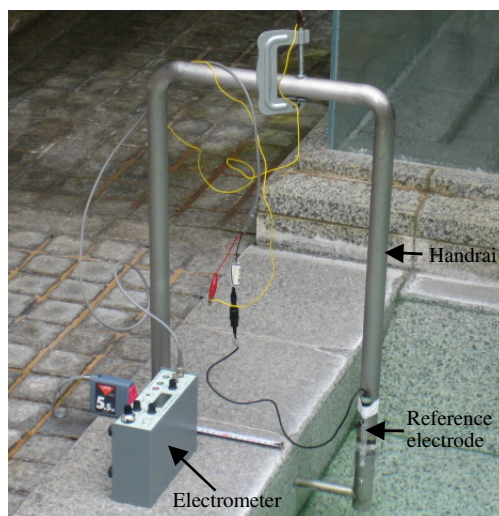


Figure 8 - Corrosion potential measurement of handrail

Table 3 Corrosion potential of SUS304 stainless steel in the two bathtubs with different sources (V vs.SCE, No. 3 and 4)

Bathtub No.	3	4
Corrosion potential	-0.494 43.1°C)	-0.023 43.1°C)

The measurement results for the corrosion potential of the handrails of bathtubs No. 3 and No. 4 are shown in Table 3. The corrosion potential of the SUS304 from the handrail of bathtub No. 3 with source A was -0.494 V (vs. SCE), which is significantly less noble potential so it is considered that it was de-passivated. On the other hand the corrosion potential of the handrail in bathtub No. 4 with source B was -0.023 V (vs. SCE), which was in the passivity state. The corrosion potential measurement results for each test specimen are shown in Fig. 9. The corrosion potential of the SUS304 test specimens in source A varied at a level that was close to that of carbon steel from the start of immersion. The SUS316 exhibited a similar less noble potential as that of SUS304 at the beginning, and thereafter became high potential to close to 0 V. However after 41.5 hours it became unstable becoming less noble again to -0.157 V. The corrosion potential of both SUS304 and SUS316 in source B varied close to 0 V, and the

results showed that the SUS316 was several tens of mV more noble compared with SUS304. The surface condition of the SUS316 and SUS 304 test specimens after soaking in source A initially became black soon after immersion, and after completion of the test the color changed to a blackish brown color on all surfaces as shown in Fig. 10, but the color of the SUS316 was relatively lighter. In source B, no signs of corrosion were seen in both SUS304 and SUS316, and they retained their metallic luster.

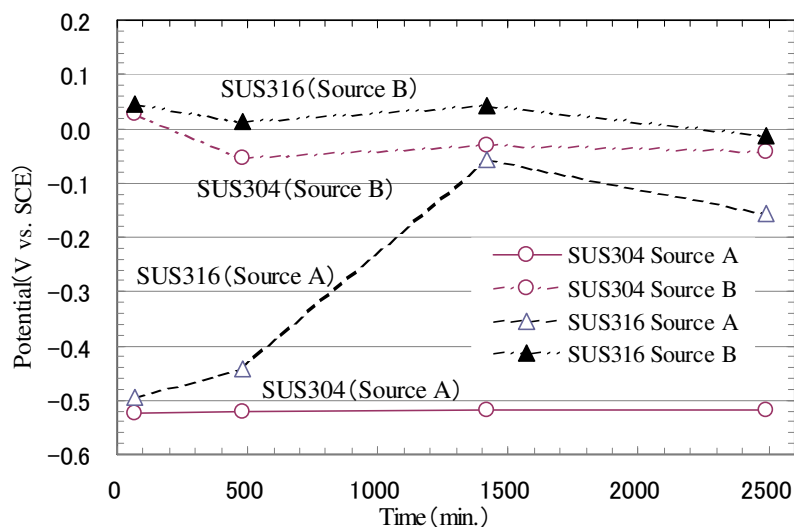


Figure 9 - Change over time on corrosion potential of SUS304 and SUS316 test pieces in hot spring source

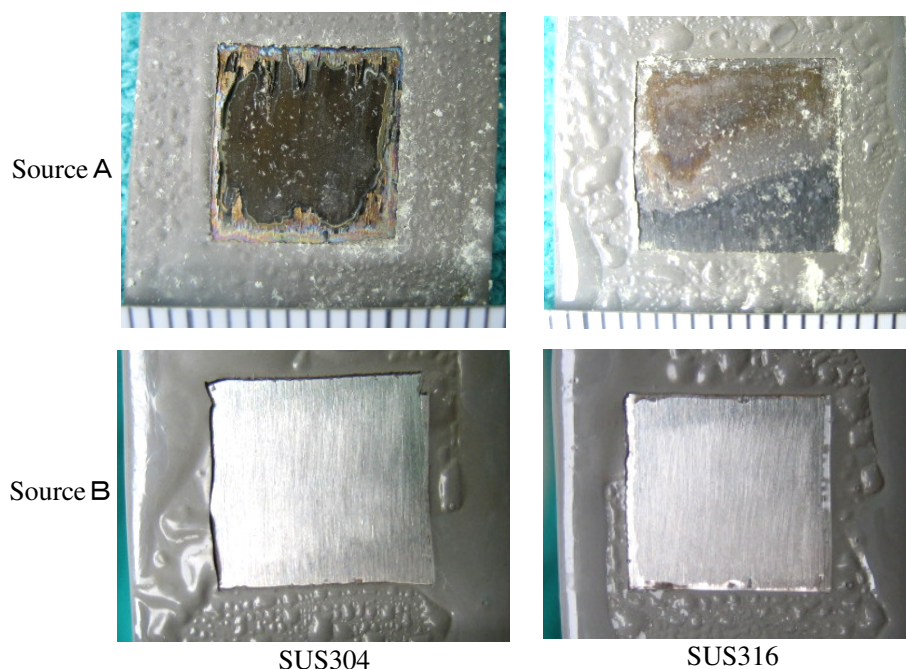
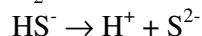


Figure 10 - Appearances of stainless steel test pieces in the hot spring source after 41.5 hours dipping

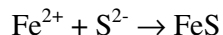
2.5 Discussion on cause of corrosion

Normally the depassivation pH (pH_d) of SUS304 and SUS316 is considered to be about pH 2 or less. In this case in source A with a relatively high pH SO_4^{2-}/Cl^- (mg/L) ratio and low chloride ion concentration, corrosion was generated progressively with time. Also the corrosion potential of the SUS304 handrail in source A was about -0.5 V (vs. SCE), and the SUS304 test specimens changed to a brownish color soon after immersion with a corrosion potential that was virtually the same (-0.525 V vs. SCE). Also it is suggested that sulfides of the elements that compose the SUS304 were generated as rust on the handrail in source A, so it is considered that the passive film broke down under the effect of the low pH of pH 2 or less and the free hydrogen sulfide. As a result, it is inferred that active dissolution occurred in the acidic spring water with many dissolved salts, and it is considered that the fine bubbles that can be seen in Fig. 3 is hydrogen generated by cathodic reduction reaction. In addition, corrosion dissolution only occurred in the handrail in source A whose pH was 2 or less and contained free hydrogen sulfide, so it is considered that the hydrogen sulfide in particular had a big effect on the degradation of the passive film. As shown below when hydrogen sulfide dissolves in water it forms dibasic acid and generates sulfide ions S^{2-} . The S^{2-} reacts with the components of the passive film to form sulfides and by degenerating the passive film it is considered that active dissolution accelerated. The reason dissolution of the handrails in each bathtub with source A occurred in a time sequence (No. 1 → No. 2 → No. 3) is considered to be because the water quality and the temperature conditions (No. 2 was outdoors so slightly lower) did not change so the corrosion was a probabilistic phenomenon.

[Dissociation of hydrogen sulfide]



[Generation of sulfides: iron sulfide (II)]



Also in the past research, in an acidic aqueous solution that contains hydrogen sulphide H_2S (H_2S : 0-15ppm by mole, pH 3, 60°C), it was shown that the polarization resistance (R_p) of SUS304L was reduced, and the critical current density for passivation (i_{cr}) was greatly increased.⁴⁾ This suggests that in an acidic aqueous solution that contains hydrogen sulphide H_2S , the resistance of the surface film of SUS304L is reduced, and passivation becomes difficult. In this case, iron disulfide FeS_2 and iron sulfide (II) FeS were detected as sulfides on the surface of the test specimens.⁴⁾ From this fact also it is inferred that hydrogen sulfide affected the dissolution of the passive film. This indicates that in a multi-Pourbxi diagram FeS_2 can exist in the acidic region of pH 2 or less.⁴⁾

On the other hand, in source B that is acid sulfate-chloride spring water not containing hydrogen sulphide, the corrosion potential of the handrails and the test specimens were in the passive region, and in the measurements taken to date there have been no signs of overall dissolution. However, as the pH is 1.7 which is below the depassivation pH (pH_d), and examples of corrosion of stainless steel handrails in other facilities that use source B have been seen, it is considered to be a corrosive environment.

pH_d = about pH 2 is an important index for determining uniform corrosion of SUS304, but the corrosivity is also affected by the components dissolved in natural water such as salts, etc. The corrosion phenomena observed in two source waters at less than pH_d indicates that the effect of hydrogen sulfide was very large.

3 Countermeasures

The use of SUS316 and SUS329J4L or other materials were investigated as alternative materials to SUS304. However, in corrosion test results by Iino and others²⁾ on welded members in an acidic sulfur – sulfate spring water that was similar to source A, uniform corrosion occurred in SUS316 and localized corrosion occurred near the waterline in SUS329J4L, so titanium was selected for its technical safety from the point of view of corrosion resistance to spring water and strength.

3.1 Results of external observation of titanium handrails

Figure 11 shows the external appearance of the titanium handrails at No. 1 bathtub (source A) and No. 4 bathtub (source B) after about 18 months. As shown in Fig. 11, after about 18 months a white scale can be seen directly above the waterline in the handrails of both the source A and source B bathtubs, but discoloration with rust or local corrosion has not been generated either in the immersed portion or in the portion exposed to air.

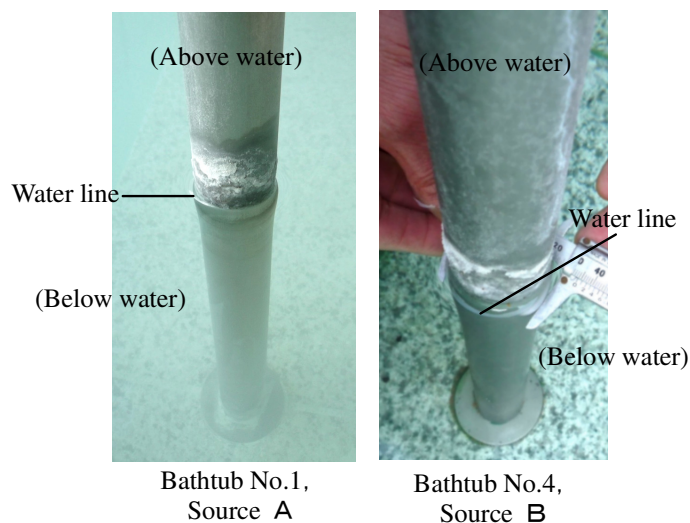


Figure 11 - Appearances of titanium handrail after about 18 months use

3.2 Titanium handrail corrosion potential measurement results

Figure 12 shows the corrosion potential of each bathtub immediately after installation and after about three months. It is considered that in all cases the potential is within the passive region of titanium. About three months of immersion, the potential in each

bathtub became 0.3 to 0.5 V more noble compared with immediately after immersion. This infers that the oxide film of titanium surface increased with passage of time. Each of the potentials measured in source A are less noble compared with source B, so it is considered that the water quality of source A is affecting the surface oxide film of titanium.

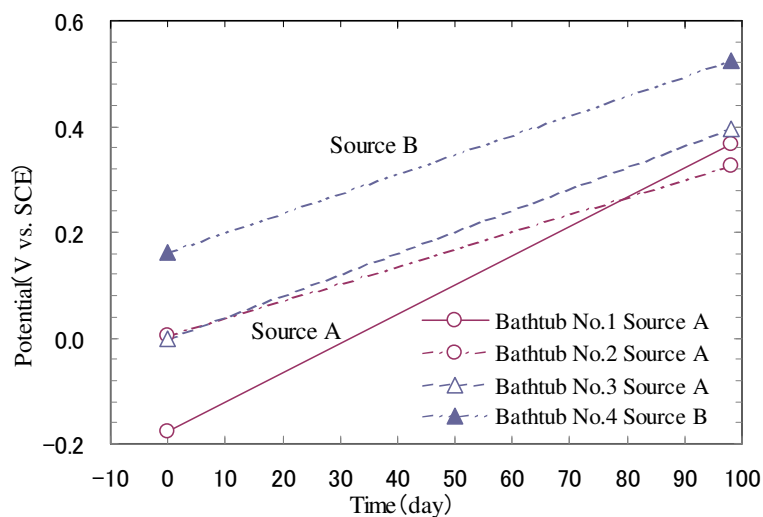


Figure 12 - Change over time on corrosion potential of titanium handrail

4 Conclusion

Observation of samples of corroded handrails, analysis of the corrosion products, analysis of the water quality, observation of the corroded state of handrails on site, and measurement of corrosion potential, etc., were carried out in order to determine the causes of and countermeasures against corrosion of SUS304 stainless steel handrails that occurred at Kusatsu Hot Spring in Gunma Prefecture. Also, a follow-up survey was carried out on the use of titanium as an alternative material as a countermeasure. The main results were as follows.

- 1) The corrosion potential of SUS304 handrails immersed in acid sulfate-chloride spring water containing hydrogen sulfide (source A: pH 1.9) became less noble significantly resulting in active dissolution with generation of hydrogen, so that the immersed portion was dissolved after about a minimum of two months.
- 2) On the other hand, the corrosion potential of SUS304 handrails immersed in acid sulfate-chloride spring water not containing hydrogen sulfide (source B: pH 1.7) was in the passive region after about 12 months and corrosion did not occur.
- 3) Discoloration with rust or local corrosion was not generated after about 18 months in either the immersed portion or the portion exposed to air of titanium handrails that were used in the two hot spring source waters as a countermeasure.

Corrosive environments containing hydrogen sulfide have long been known as sour environments, but the corrosion properties of stainless steel in strongly acidic environments containing hydrogen sulfide are not sufficiently known. In particular, for natural waters containing various types of ions such as hot springs there is academic data and indices for quantitatively evaluating uniform corrosion and local corrosion of stainless steels, but it is considered that it is not sufficiently known how well they correspond to actual corrosion phenomena in complex systems. In this paper one example has been introduced as a case study analysis of corrosion of SUS304 handrails at a hot spring having typical water quality, and discussed based on past research and measured data. In this case, titanium was selected as an alternative material based on its technical safety from the point of view of corrosion resistance with respect to the water quality and strength, which was required for urgent countermeasure construction. For the future it is considered that other metal materials, resins, or composite materials can also be considered from the point of view of cost performance with respect to corrosive water.

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6 Presentation of Author

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