

Mo-Saving Stainless Steel JFE 445M for Hot Water Tanks†

FUKUDA Kunio*¹ ISHIKAWA Shin*² KASAMO Toshihiro*³

Abstract:

For the use of hot water tank, JFE Steel developed the cost-saving JFE445M (22.5mass%Cr-1mass%Mo) stainless steel containing less Mo than the current material Type444 (19mass%Cr-2mass%Mo) stainless steels. The results of corrosion tests, such as the pitting potential, the rate of rusted area at cyclic corrosion test, the repassivation potential for crevice corrosion, indicated JFE445M had the same or even better corrosion resistance than Type444. At the welding zone by Tungsten Inert Gas (TIG) welding method, JFE445M exhibited particularly higher corrosion resistance than Type444. It was considered that the higher Cr content of JFE445M prevented the severe Cr depletion at the interface between the scale and the substrate when the oxide layer was formed during welding.

1. Introduction

In response to environmental problems (need for CO₂ reduction) and the heightened tendency toward energy saving in recent years, expansion of the market for heat pump water heaters has been promoted as a national policy, resulting in remarkable growth in these devices. Under Japan's Waterworks Law, the household tap water used in water heaters contains residual chlorine¹⁾. Because the water temperature is maintained at a high temperature of around 85°C, corrosion resistance in high temperature environments containing residual chloride is required in materials used in hot water tanks. Therefore, ferritic stainless steel SUS444 (19mass%Cr-2mass%Mo steel), which has excellent corrosion resistance and low stress-corrosion cracking sensitivity, is now widely used

as a material for hot water tanks²⁾. A large amount of Mo (2%) is added to this steel grade in order to improve its corrosion resistance. In the past, JFE Steel developed JFE434LN2 (19mass%Cr-2mass%Mo-0.35mass%Nb), corresponding to SUS444 under the JIS standard, as a material for hot water tanks, and this material continues to be widely used at present.

However, the price of Mo has risen in recent years, creating the need for a Mo-saving type of stainless steel with corrosion resistance equal to that of the conventional SUS444. Therefore, with the aim of developing a Mo-saving type steel with properties equal or superior to those of JFE434LN2, the authors investigated the effects of the contents of Cr and Mo on corrosion resistance, and particularly the corrosion resistance of the temper color part in TIG (Tungsten Inert Gas) welding, and developed a Mo-saving stainless steel, JFE445M (22.5mass%Cr-1.0mass%Mo-0.35mass%Nb: JIS standard SUS445J1), for use in hot water tanks.

This paper describes firstly the results of a study of the effect of the Mo content on corrosion resistance in water heater environments, which was carried out in the composition design of the developed steel. The results of a comparative study of the various corrosion properties of the existing material, JFE434LN2, and the developed Mo-saving steel, JFE445M, are also presented.

† Originally published in *JFE GIHO* No. 20 (June 2008), p. 53–59



*¹ Senior Researcher Manager,
Stainless Steel Res. Dept.,
Steel Res. Lab.,
JFE Steel



*² Senior Researcher Manager,
Stainless Steel Res. Dept.,
Steel Res. Lab.,
JFE Steel



*³ Staff Manager,
Stainless Steel Sec.,
Products Design & Quality Control Dept.,
East Japan Works,
JFE Steel

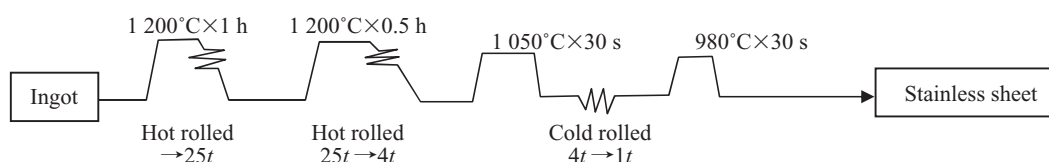


Fig. 1 The method of preparing the specimens

Table 1 Chemical composition of specimens

Sample	(mass%)						
	C	Si	Mn	Cr	Mo	Nb	N
A	0.008	0.30	0.16	22.1	0.5	0.41	0.008
B	0.007	0.29	0.16	22.1	0.8	0.41	0.007
C	0.008	0.30	0.17	22.1	1.0	0.41	0.007
D	0.007	0.29	0.16	22.0	1.2	0.41	0.007
SUS444	0.005	0.30	0.17	19.0	1.9	0.37	0.006

Table 2 The welding condition by TIG (bead on plate)

Electrode: 1.6 mm ϕ electrode made by tungsten
The distance between electrode and specimen: 2 mm
Welding speed: 400 mm/min
Welding electric current: 80–100 A
Shield gas: 100%Ar or 98%Ar-2%O ₂
Gas flow: 20 l/min (both side)

2. Effect of Mo Content in Steel on Corrosion Resistance of Ferritic Stainless Steel for Hot Water Tanks

2.1 Experimental Method

2.1.1 Sample materials

Table 1 shows the chemical composition of the sample steels. 50 kg ingots of these compositions were melted, and specimens were prepared by the process shown in Fig. 1. The Cr content was held constant at 22%, and the Mo content was varied in the range of 0.5–1.2%. An ingot of the conventional material, SUS444 (JFE434LN2), was used as a comparison material.

2.1.2 Corrosion resistance of base materials

The corrosion resistance of the base materials was evaluated by measuring the pitting potential in a sodium chloride solution based on JIS G 0577 “Method of pitting potential measurement for stainless steels.” Specimens were cut into 20 mm \times 20 mm and polished with #600 abrasive paper. Electrode was welded to the edge, and ultrasonic cleaning was performed in acetone. The specimens were then immersed for 1hr in a 30% solution of nitric acid at 50°C, followed by coating with a seal material to leave an 11 mm \times 11 mm measurement surface. After coating, an area of 10 mm \times 10 mm was polished with #600 abrasive paper and degreased with acetone immediately before measurement. The solutions used were a degassed 3.5% sodium chloride solution and a solution adjusted with NaCl to 200 ppm Cl⁻ (upper limit of standard value of chlorine ion concentration in tap water in Japan)³. The temperature of the solutions

was varied between 30–50°C, and the pitting potential V_{c10} (potential when current value becomes 10 μ A/cm²) was measured.

2.1.3 Corrosion resistance of welded zone

In order to investigate the corrosion resistance of the welded zone, bead-on-plate TIG welding was performed under conditions with which a width of approximately 3 mm was obtained at the reverse side of the welding bead using either 100% Ar or 98%Ar-2%O₂ as the shield gas. The 98%Ar-2%O₂ was used assuming cases where the shield gas cannot be maintained perfectly during welding. Table 2 shows the welding conditions. Using the reverse side of the welding bead as the test surface, the pitting potential was measured by the method described in section 2.1.2. However, in order to examine the effect of temper color, specimen polishing and 10 min immersion prior to the potential scanning were omitted.

2.2 Experimental Results

2.2.1 Pitting potential of base materials

The average values ($n=5$) of the results of measurements of the pitting potentials (V_{c10}) of the base materials at a solution temperature of 30°C based on the JIS standard are shown in Fig. 2. At the same Cr concentration, the pitting potential (V_{c10}) increases in proportion to the Mo content. Furthermore, even at the same pitting index (Pitting index (PI) : Cr + 3.3Mo), the pitting potential of the 22% Cr composition was higher than that of the 19%Cr-2%Mo material. Adachi et al. have shown that the effect of Mo addition on corrosion resistance increases at higher Cr contents⁴. In this experiment as well, it is considered that the effect of Mo was greater with the 22%Cr composition, which has a higher content of Cr.

The results of measurements of the pitting potential

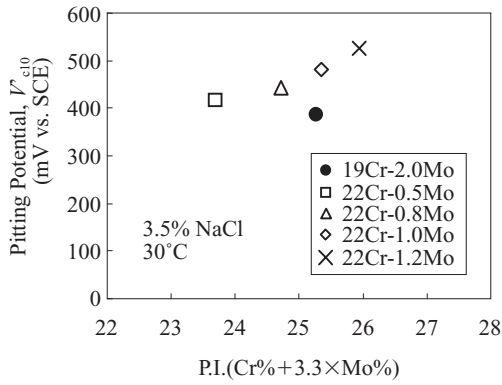


Fig. 2 The effect of P.I. (Pitting Index) on pitting potential of substrate

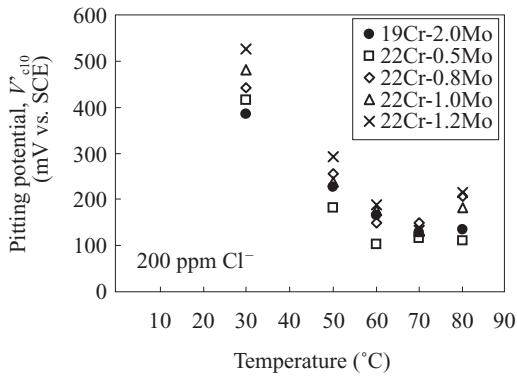


Fig. 3 The effect of the solution temperature on pitting potential of substrate

(V_{c10}) of the base material at various temperatures with the 200 ppm Cl^- solution are shown in Fig. 3. With the 22% Cr steels containing 1.0% or higher Mo, the pitting potentials were equal to or higher than those of the 19%Cr-2%Mo steel at all temperatures.

2.2.2 Corrosion resistance of welded zone

The results of measurements of the pitting potential of the reverse side of the bead at the TIG welded zone with the 100% Ar gas shield are shown in Fig. 4. It can be understood that the pitting potential values are lower than those of the polished sheets shown in Fig. 2. Furthermore, no effect of Mo was noted, and no differ-

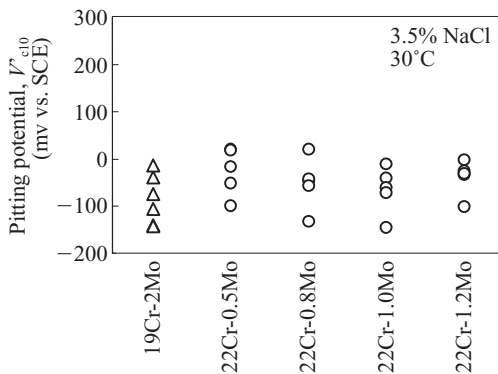


Fig. 4 Pitting potential at the reverse side of welding bead (Shield gas: 100% Ar)

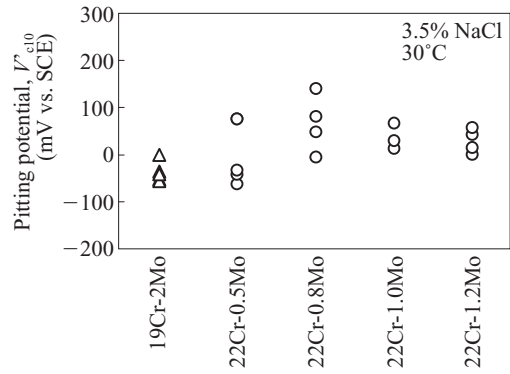


Fig. 5 Pitting potential at the reverse side of welding bead (Shield gas: 98% Ar-2%O₂)

ence with the 19%Cr-2%Mo steel was observed. Next, the results of measurements of the pitting potential of the reverse side of the bead at the TIG welded zone with the 98%Ar gas-2%O₂ gas shield are shown in Fig. 5. In welding with an O₂-containing atmosphere shield, the pitting potential is lower than with the polished sheet, as would be expected, but with the 22% Cr steel, the degree of reduction in the pitting potential was smaller, and the pitting potential was higher than when using the 100% Ar shield gas, showing a favorable high value in comparison with the conventional 19%Cr-2%Mo steel material.

This difference is considered to be caused by the oxidation film called temper color, which forms during welding, and chromium depletion of the surface layer of the based material, which forms immediately under this oxidation film. More specifically, this difference is considered to be due to the fact that, in the 22% Cr steel, the Cr concentration at the interface is not reduced to the point where corrosion resistance is seriously deteriorated after Cr consumption for formation of temper color, corresponding to the increment of Cr content (higher Cr content) in the base material. The corrosion resistance of the temper color area of the welded zone will be discussed in more detail in chapter 4.

2.2.3 Composition of new steel

The chemical composition of the new steel was decided as follows, based on the results described above and the knowledge obtained in the development of JFE434LN2 in the past.

First, the Cr content was set at 22.5%, which is somewhat higher than in the experiments, in order to improve the corrosion resistance of the welded zone, and also considering corrosion resistance in low pH solutions, such as crevice corrosion resistance, etc. From the viewpoint of cost reduction, it is desirable to reduce the Mo content as far as possible. However, based on the results shown in Fig. 3, the target lower limit of the Mo content was set at 1.0% so as to maintain corrosion resistance in

Table 3 The chemical composition of developed JFE445M

	(mass%)						
	C	Si	Mn	Cr	N	Mo	Nb
Codex	≤0.015	0.35–0.45	≤0.20	22.0–24.0	≤0.015	1.00–1.20	15×(C+N)
Representative	0.008	0.41	0.16	22.6	0.008	1.06	0.31

the high temperature region (70–80°C) at the same or a higher level than JFE434LN2.

It is desirable to increase the Si content in order to improve the corrosion resistance of the TIG welded/temper color zone⁵⁾. However, productivity may be reduced if the Si content is increased excessively because descalability in the cold rolling-annealing process will be deteriorated and traces of temper color will remain on 2B finish products. Therefore, based on past knowledge⁵⁾, Si addition was set at 0.4%, this being a 0.1% increase in comparison with JFE434LN2.

As a stabilizing element to trap C and N, single addition of 0.35% Nb was adopted. This is substantially the same as in JFE434LN2.

Representative values of the chemical composition of the developed steel and the composition range are shown in Table 3.

3 Properties of Developed Steel

3.1 Experimental Procedure

3.1.1 Pitting potential

The sample materials used in the following experiments were factory-produced 2B sheets of the Mo-saving steel, JFE445M, and the conventional material, JFE434LN2. Measurements of pitting potential were performed by the same procedure as in section 2.1.2. As test solutions, in addition to the 3.5% NaCl solution in accordance with the JIS standard, a NaCl-adjusted 200 ppm Cl⁻ solution was used. The temperature was varied in the range of 30–85°C. With the exception of the solution temperature and concentration, the processing of the specimens and other conditions conformed to JIS G 0577.

3.1.2 Repassivation potential for crevice corrosion

To investigate crevice corrosion properties, the repassivation potential for crevice corrosion was measured. This measurement, as provided in JIS G 0592, is used to assess crevice corrosion properties in austenitic stainless steel. However, it is also considered to be an appropriate judgment standard for crevice corrosion properties in high corrosion resistance grades of ferritic stainless steel.

The measurements were performed substantially in accordance with the JIS standard. Specimens with dimensions of 50 *l* × 20 *w* × 0.8 *t* (mm) were taken from the 2B sample materials, and full surface polishing was performed with #600 abrasive paper. Next, a lead wire was attached to the edge of the side opposite the test surface, and this part was coated with epoxy resin. As the test solution, a 200 ppm Cl⁻ solution adjusted by addition of NaCl was used. The temperature was controlled to 50°C.

The specimens were polished immediately before measurements. After covering both sides with a polysulfone (PSF) clearance jig, the specimen was clamped to the specified torque (approximately 4 N·m) with titanium bolts. The work electrode was then left in the test cell for 30 min, polarization was begun in accordance with the JIS procedure, and the repassivation potential for crevice corrosion was measured.

3.1.3 Depassivation pH

At crevices in welded tanks, a phenomenon of reduced pH can be observed, depending on the shape of the crevice. Accordingly, as an evaluation of corrosion resistance, the depassivation pH was also measured. For these measurements, 20 mm square of cold-rolled and annealed materials were polished with #600 abrasive paper, an electrode was welded to the specimen, and the specimen was coated with a seal material, leaving a 10 mm square test surface. The specimens prepared in this manner were immersed in the test solution (open to the atmosphere), and cathodic polarization at -700 mV vs. SCE (SCE: Saturated calomel electrode) was performed immediately for 10 min, followed by measurement of the open-circuit potential for 16 h. The solution was adjusted in the pH range of 0.5–2.0 in steps of 0.1 using sulfuric acid (H₂SO₄). The test temperature was controlled to 30°C. After 16 h, the maximum pH at which no increase in the open-circuit potential due to depassivation was observed was considered to be the depassivation pH.

3.1.4 Cyclic corrosion test

In order to evaluate the corrosion resistance of the outside of the tank, a cyclic corrosion test (CCT) was performed with 2B materials. The specimens with the dimensions of 80 × 100 (mm) were taken from 2B sample materials. After degreasing in an alkali solution, the

edges and reverse side were completely sealed, leaving a 60 × 80 (mm) test surface. The test mode followed JASO M609-91 (1 cycle: salt spray (2 h, 35°C, NaCl: 5%) → dry (4 h, 60°C, 30%RH) → wet (2 h, 50°C, >95%RH; JASO: Japan Automobile Standard Organization). The test was performed up to 200 cycles, and rust development was evaluated.

3.1.5 Pitting potential of TIG welded zone

Pitting potential was measured using specimens of 2B material welded under the same welding conditions as in Table 2. The measurements were performed in the same manner as in section 2.1.2. The solutions used were a 3.5% NaCl solution at 30°C and a 200 ppm Cl⁻ solution at 30–85°C.

3.2 Results

3.2.1 Pitting potential

Figure 6 shows the results of measurements of the pitting potential (V_{c10}) of the base material at 30–80°C in the 3.5% NaCl solution. In the 3.5% NaCl solution, JFE445M showed a high, favorable pitting potential in comparison with JFE434LN2 at all temperatures. As the temperature increased, this difference became smaller.

Figure 7 shows the results of measurements of the pitting potential (V_{c10}) of the base material at 50–85°C

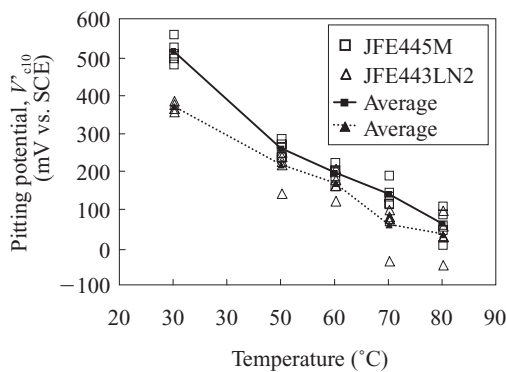


Fig. 6 Pitting potential of the steels in 3.5% NaCl solutions

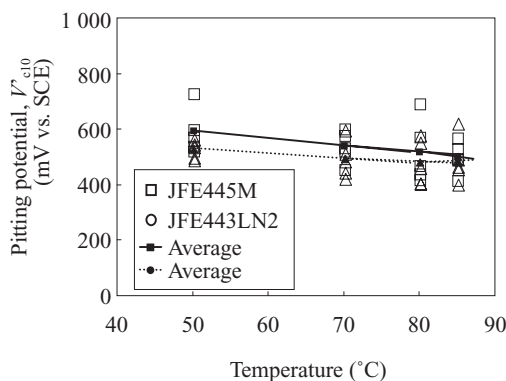


Fig. 7 Pitting potential of the steels in 200 ppm Cl⁻ solutions

in the 200 ppm Cl⁻ solution. With the 200 ppm Cl⁻ solution as well, JFE445M showed a high pitting potential in comparison with JFE434LN2 at all temperatures. Thus, it is considered that JFE445M exhibits satisfactory pitting corrosion resistance in hot water heater service environments.

3.2.2 Repassivation potential for crevice corrosion

The repassivation potentials for crevice corrosion in the 200 ppm Cl⁻ solution at 50°C read from the respective polarization curves are shown in Table 4. Table 4 also shows the values for SUS316, which was measured in order to confirm the accuracy of this test method. As shown in Table 4, the repassivation potentials for crevice corrosion of JFE445M and JFE434LN2 are virtually the same at 50°C.

3.2.3 Depassivation pH

Figure 8 shows the potential measured after immersion for 16 h in solutions with various pH. The depassivation pH of JFE445M read from Fig. 8 is 0.9, whereas that of JFE434LN2 is pH1.2. Thus, JFE445M shows a superior value in comparison with JFE434LN2.

3.2.4 Cyclic corrosion test

Photo 1 shows the appearance of the 2B specimens after 200 cycles of the JASO test. For reference, the result with 2B material of SUS316 is also shown. From these photos, it is observed that virtually no rust has developed on JFE445M, showing that the developed steel has superior corrosion resistance in comparison

Table 4 The repassivation potential for crevice corrosion, $E_{R,crev}$. (mV vs. SCE)

Specimen	Temperature (°C)	n=1	n=2
JFE445M	50	-227	-211
JFE434LN2	50	-225	-227
SUS316	50	-47	-56

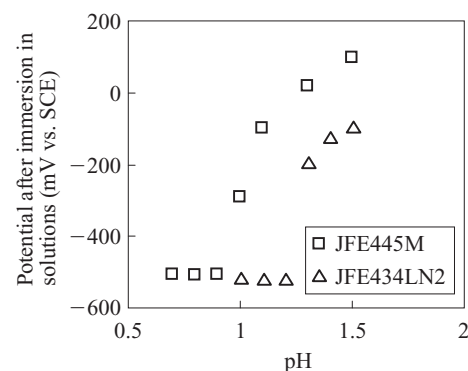


Fig. 8 The rest potential after 16 hour immersion in solutions with several pH

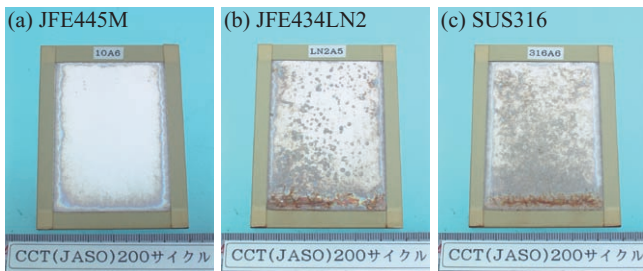


Photo 1 Appearance of the specimens after cyclic corrosion test (JASO method: 200 cycles, JASO: Japanese Automobile Standards Organization)

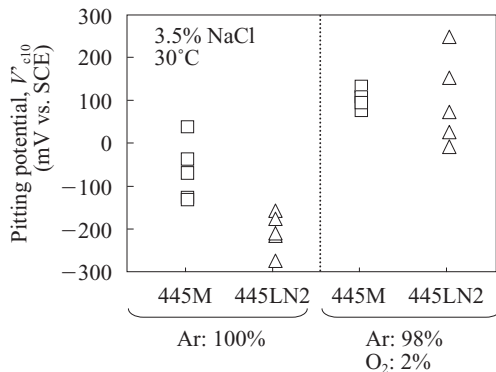


Fig. 9 Pitting potential at the reverse side of welding bead

with the other two steels. Utsunomiya et al.⁶⁾ conducted an atmospheric corrosion test of steel grades including 22%Cr-0.7%–1.2%Mo steel, and SUS444, SUS316, etc., and reported that the 22%Cr-0.7%–1.2%Mo steel shows superior corrosion resistance in comparison with SUS444 and SUS316. This agrees with the results of the present experiment.

3.2.5 Pitting potential of TIG welded zone

With the 100% Ar gas shield, extremely thin temper color formed in areas away from the welded zone. In contrast to this, with the 98%Ar gas-2%O₂ gas shield, a large amount of temper color oxide formed, centering on the welded zone. **Figure 9** shows the results of measurements of the pitting potential at the reverse side of the TIG welding bead with the 3.5% NaCl solution at 30°C. With both steels, the pitting potential is lower than with the polished sheets shown in Fig. 6; however, JFE445M showed a higher, superior pitting potential in comparison with JFE434LN2. Likewise, in the 200 ppm Cl⁻ solution, JFE445M showed a higher, superior pitting potential at the welded zone in comparison with JFE434LN2 in all temperature regions.

4. Discussion

4.1 Corrosion Properties of Temper Color Zone

In order to consider the factors in the difference in

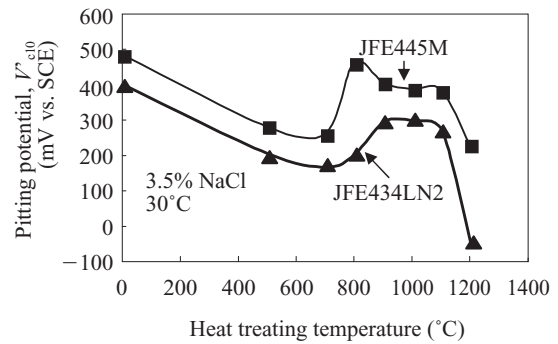


Fig. 10 The effect of heat treating temperature on pitting potential

corrosion resistance at the TIG welded zone, as noted in chapter 3, the temper color formed during TIG welding was reproduced by heat treatment in the atmosphere (soaking time: 30 s), and its corrosion resistance and the composition of the formed oxide and substrate were investigated.

The appearance of the specimens after heat treatment showed little difference in the two steels. Up to around 1 000°C, the specimens displayed temper color, and at temperatures exceeding 1 100°C, a green color, which is considered to be caused by Cr₂O₃, became deeper, taking on the coloration of the oxide itself. In comparison with the appearance of the TIG welded zone, at distances further from the center of the weld, the color tone was consistent with that of temper color, which forms at lower temperatures. Accordingly, it is considered that the corrosion resistance of the TIG welding zone can be estimated indirectly by studying the corrosion resistance of specimens on which temper color was formed by heat treatment.

Figure 10 shows the results of measurements of the pitting potential of heat-treated specimens with temper color in accordance with the JIS standard. It can be understood that, with the heat-treated specimens, JFE445M shows a high pitting potential in comparison with JFE434LN2 and has excellent corrosion resistance when temper color has formed.

Figure 11 shows the results of a glow discharge spectroscopy (GDS) analysis of the surfaces of materials heat-treated at 1 200°C. In comparison with JFE434LN2, JFE445M had a higher Cr concentration at the interface between the scale and substrate. This tendency is virtually the same at all temperatures, and the difference in the Cr concentrations of the two steels increased with heat treatment temperature.

Figure 12 shows the polarization curves of the temper color heat-treated materials in a 3.5% NaCl solution. With both steels, in the untreated material (polished surface), the current values are extremely small on the low potential side, and the current increases very rapidly from the pitting potential. In contrast to this, in the tem-

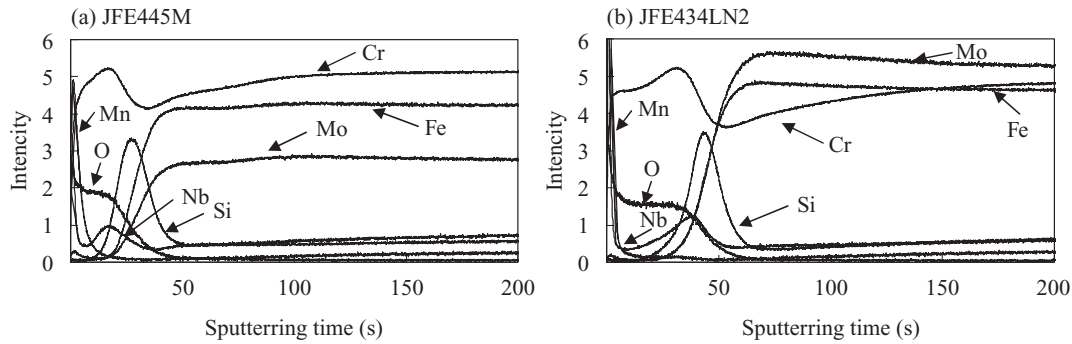


Fig. 11 The depth profile of the elements at surface of specimens heat treated at analyzed 1 200°C by GDS

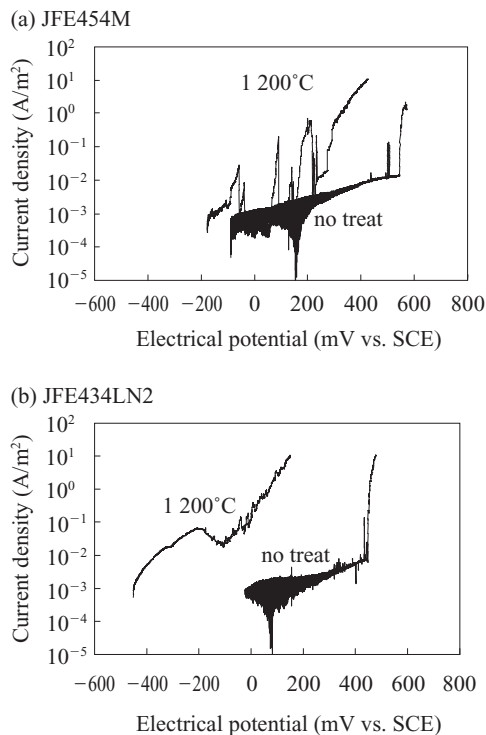


Fig. 12 The polarization curves of heat treated specimens in 3.5% NaCl solutions

per color heat-treated materials, the current value rises temporarily on the low potential side, but several points exist where repassivation has occurred and the current values have become stable at low values. This temporary increase in the current value is attributed to temporary dissolution of the temper color (oxide). Even when the temper color dissolves to some extent, if the Cr concentration of the substrate is sufficient to cause repassivation, pitting corrosion will not occur, and the current will again become stable at a low value. On the other hand, if the Cr concentration of the substrate is low, repassivation does not occur, pitting corrosion develops, and the current value increases. It is thought, therefore, that corrosion resistance in temper color material is inferior to the original substrate steel without temper color, and as the Cr concentration at the interface increases, and the temper color becomes thicker and more protective,

deterioration of corrosion resistance becomes slight. The results of this experiment show an extremely good correspondence with the order of the Cr concentration at the interface in GDS. With the temper color heat-treated JFE434LN2 which was heat-treated at 1 200°C, the current value increases from the stage where potential is low, passivation does not take place, and pitting corrosion occurs. The results of the GDS analysis showed extreme depletion of the Cr concentration at the interface. The mechanism of this deterioration of corrosion resistance in temper color material is presumed to be the same as in the temper color part of the welded zone.

The most major factor in the superior corrosion resistance of JFE445M in the TIG welded zone, in comparison with JFE434LN2, is considered to be that the Cr concentration at the interface between the substrate steel and scale is not reduced to a level that would seriously deteriorate corrosion resistance after Cr consumption for the temper color formation, corresponding to the increased content of Cr in the developed steel.

5. Conclusions

A Mo-saving type stainless steel JFE445M (22.5mass%Cr-1.0mass%Mo-0.35mass%Nb) was developed for use in hot water tanks as a substitute for SUS444. The corrosion resistance of the developed material was compared with that of the existing material, JFE434LN2 (19 mass%Cr-2.0mass%Mo-0.35mass%Nb). The main results obtained are as follows.

- (1) The corrosion resistance of the developed steel was equal or superior to that of the conventional material in a 3.5% NaCl solution and 200 ppm Cl⁻ solution.
- (2) The pitting potential of the TIG welded zone was higher in the developed steel than in the conventional steel.
- (3) As the reason for the above, in the developed steel, which has an increased Cr content in comparison with the conventional steel, it is considered that the Cr concentration at the interface between the substrate steel and the scale was not reduced to a concentration

where corrosion resistance would be seriously deteriorated when temper color formed.

References

- 1) Enforcement Regulation of Waterworks Law, Ministerial Ordinance of Welfare No. 45. Art. 17, Paragraph 3, 14th December, 1957.
- 2) Onoyama, Masao; Tsuji, Masanobu; Abo, Hideo; Ogawa, Hiroyuki; Aoki, Shiro. *Seisen-kenkyu*. 1997, no. 292, p. 46.
- 3) Ministerial Ordinance about the Standard Quality of Water, Ministerial Ordinance of Health, Labour and Welfare No. 101. 30th May, 2003.
- 4) Adachi, Toshiro; Hirotsu, Sadao; Hoshino, Kazuo. *Nihon-kinzokugakkai-kaiho*. 1984, vol. 23, no. 6, p. 523.
- 5) Kato, Yasushi; Yoshioka, Keiichi; Hashimoto, Osamu. *CAMP-ISIJ*. 1989, vol. 2, p. 724.
- 6) Utsunomiya, Takeshi; Sugimoto, Ikuhiro; Adachi, Toshiro; Uematsu, Yoshihiro. *Nisshin Steel Tech. Rep.* 1994, no. 70, p. 45.