Technical Report

Development of Ferritic Stainless Steel, NSSC™ ECO Series for Hot Water Supply Systems

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Abstract

The ferritic stainless steels NSSC 190ECO and 220ECO, which have excellent crevice corrosion resistance in a hot water environment, were developed. The chemical compositions of these "ECO" series stainless steels are designed to improve crevice corrosion resistance by optimizing the Cr and Mo contents for each hot water heater application. These developed stainless steels have been applied to hot water tanks and pipes for the heat pump water heater systems and household fuel cell systems, and furthermore utilized as secondary heat exchangers for gas water heating systems.

1. Introduction

Water is essential for human beings, and its safe and stable supply is required for a high quality of life. On the other hand, water accelerates the corrosion of metals, and thus may cause water problems such as change in the taste of water due to corrosion, coloring, and leakage. For this reason, 304 and 316L type stainless steels for general applications excellent in corrosion resistance have been used for water purification facilities, supply piping and other water-related equipment.[1] Hot water is used for bathing and household ablutions, and stainless steel hot water tanks are used for electric water heaters and other types of hot water facilities.[2] Changing the material for hot water tanks from enameled steel to stainless steel was studied roughly 50 years ago, but the type 304 stainless steel was found to be prone to water leakage due to stress corrosion cracking (SCC) in hot water.[3] NSSC 190 (19Cr-2Mo-Nb-Ti) excellent in resistance to SCC and corrosion was developed[4] and has been widely used for this application ever since. In the meantime, the period of Japan's high economic growth ended, energy saving became an important issue, and in the trend of resource saving to cope with the price increase of Mo, a rare metal element, ECO series stainless steel was developed and used in response to environmental (or ECOlogical) requirements. This paper presents the development of the ECO series steel, their characteristics, and expansion of their use for facilities other than hot water tanks.

2. Targets for Development of ECO Series Stainless Steel for Hot Water Tanks

In electric water heaters, water is heated by electric heaters taking advantage of inexpensive night-time electricity or, more recently, heat pump systems of higher thermal efficiency, and stored in hot water tanks for use mainly during the daytime.

On the other hand, cogeneration systems that extract electricity and heat using fuel cells have become available as a new type of heat source. They are environmentally-friendly systems that generate electric power through reaction between hydrogen from reformed city gas and oxygen in the atmosphere, and heat water using the heat arising as a by-product of the power generation. The cogeneration system also requires a hot water tank, but since the operating temperature of a polymer electrolyte fuel cell (PEFC) is approximately 80°C, the highest water temperature is 65°C,[5] lower than the normal water temperature of conventional electric water heaters, 80°C. In view of the situation, we studied the development of a new stainless steel material suitable for the water tanks of PEFC systems. The following target was set specifically for the development: a resistance to crevice corrosion in water at 65°C equivalent to that of conventional NSSC 190 in water at 80°C and material properties equivalent to those of the said steel grade in the use for water tanks.

High resistance to crevice corrosion is obtained by the addition of Mo, but it is a rare metal, and since its resources are unevenly distributed, its market price fluctuates violently owing to geopolitical and other factors. In consideration of this, a second development target was set: Mo-saving stainless steel having the same crevice

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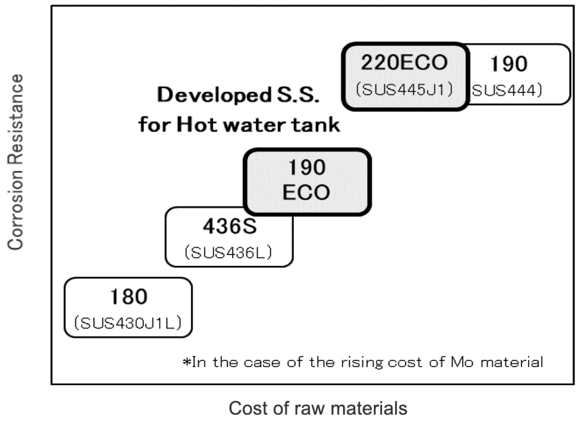

Fig. 1 Development target of ECO series stainless steels

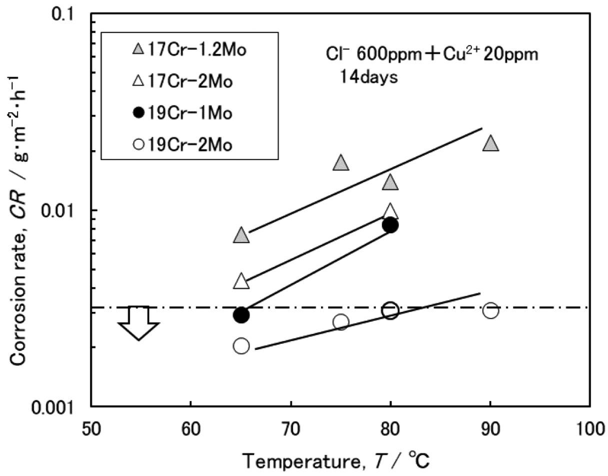

Fig. 2 Effects of temperature and Cr and Mo contents on crevice corrosion rate

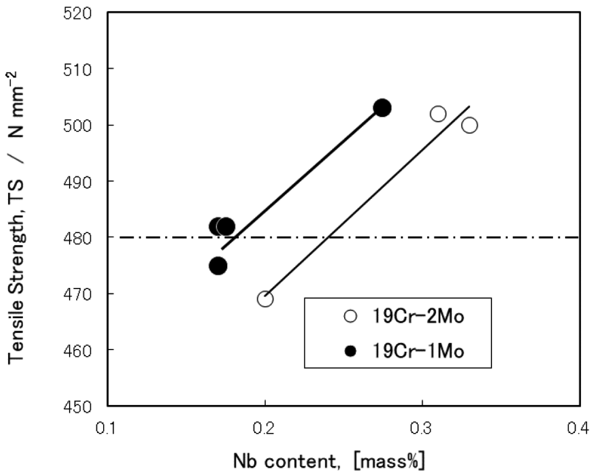

Fig. 3 Effects of Nb and Mo contents on tensile strength

corrosion resistance in water at 80°C as that of NSSC 190.

Figure 1 shows the positions of the new steel grades and their development in relation to Nippon Steel Stainless Steel Corporation's original ferritic stainless steels. The details of the development studies are presented below.

2.1 Development of NSSC 190ECO for hot water tanks of fuel-cell cogeneration systems for household use

Since the temperature of the water heated by PEFC systems is 65°C or less, lower than 80°C by conventional methods as described above, an alloy composition that offered a corrosion resistance adequate for such environmental conditions and with as low material costs as possible was sought in the development of the ECO series. As Cr and Mo were found to be effective for the crevice corrosion resistance required for hot water tanks in preliminary studies, the effects of these elements were examined in more detail. It has to be noted in this relation that the combined addition of Nb and Ti is effective at improving the formability of weld joints and corrosion resistance and suppressing surface defects,[4] and for this reason, it constituted a main feature of the alloy design of NSSC 190 to produce its material properties. In consideration of this, it was applied also to NSSC 190ECO and 220ECO, but their addition amounts in the two steels were changed in consideration of the properties required for them.

The specimen sheets for test pieces were prepared by melting steels of 17/19Cr-1/2Mo-Nb-Ti compositions in a laboratory vacuum furnace, rolling to a thickness of 0.8 mm, annealing, and finishing the surfaces to #600 by wet polishing. The test pieces for the crevice corrosion test were prepared by cutting out pieces 20×20 mm and 20×50 mm in size from the specimen sheets and joining them by spot welding; the current condition of the welding was controlled so that the nugget diameter was roughly twice the sheet thickness. The crevice corrosion test was conducted as follows: an aqueous solution containing 600 ppm Cl^- and 20 ppm Cu^{2+} was prepared using pure water and reagent chemicals of NaCl and $CuCl_2$, the solution was maintained at 65 and 80°C, the test pieces were immersed in the solution for 336 h, and the depth and the rate of their corrosion were measured. The rate of corrosion was calculated as the average of two test pieces that were tested under the same condition.

The results are shown in **Fig. 2**. At 65°C, 19Cr-1Mo steel showed the same corrosion rate as that of 19Cr-2Mo steel (equivalent to conventional NSSC 190) at 80°C, but 17Cr steel did not meet the target even with Mo addition by 2%. This is presumably because Cr is more effective for crevice corrosion resistance than Mo in a low temperature environment.

For the reason of better crevice corrosion resistance, 19Cr-1Mo was selected as the basic alloy composition, but its tensile strength was lower than the target because the Mo content was less than that of NSSC 190. To make up for the shortage, the content of Nb, which has high strengthening effects and is useful also as a stabilizing element, was increased to 0.25% as shown in **Fig. 3**. As a result, the same tensile strength as that of NSSC 190 was obtained and the sensitization during welding was suppressed. On this basis, the alloy composition of NSSC 190ECO was defined as 19Cr-1Mo-Nb-Ti.

2.2 Development of Mo-saving stainless steel NSSC 220ECO for hot water tanks

It was found with NSSC 220M for roofing use that increase in the Cr content was effective at improving the resistance to pitting corrosion.[6] Based on this finding and to minimize the influence of the fluctuating price of Mo, we sought an alloy composition with as low a Mo content as possible (Mo saving) by which a crevice corrosion resistance equal to that of NSSC 190 is obtained in water at 80°C, using 22Cr steel as a basis.

The specimen sheets for the test pieces were prepared by melt-

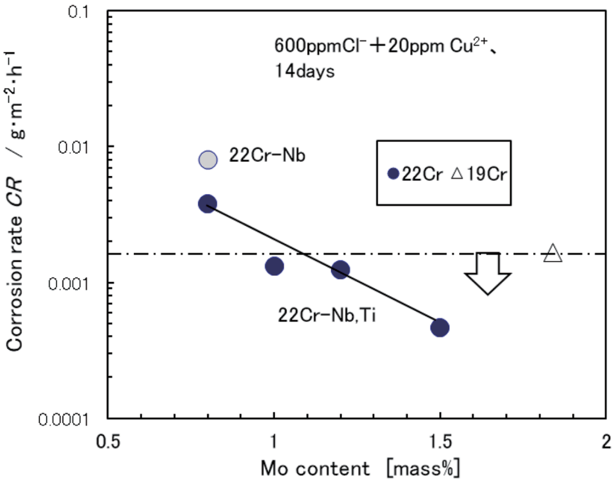

Fig. 4 Effects of Mo content on crevice corrosion rate of 22Cr ferritic stainless steel

ing steels of 22Cr-0.8/1.5Mo-Nb-Ti compositions in a laboratory vacuum furnace, rolling to a thickness of 0.8 mm, annealing, and finishing the surfaces to #600 by wet polishing. The test pieces for the crevice corrosion test were prepared by cutting out pieces 20×20 mm and 20×50 mm in size from the specimen sheets, drilling a bolt hole at the center of each of them, and joining two of the pieces with plastic nuts and bolts. The test condition and the method of evaluation were the same as those of the crevice corrosion test in the preceding sub-section 2.1 except that the test temperature was 80°C only.

The results are shown in **Fig. 4**. The corrosion rate of the 22Cr steel decreased by increasing the amount of Mo; 22Cr-1.2Mo steel exhibited the same corrosion rate as that of conventional NSSC 190. On this basis, the alloy composition of NSSC 220ECO was defined as 22Cr-1.2Mo-Nb-Ti.

3. Characteristics of Developed NSSC 190ECO and 220ECO

Table 1 shows typical chemical compositions and mechanical properties of the developed steels manufactured through commercial production facilities. The alloy composition of NSSC 190ECO is based on the composition of 19Cr-1Mo steel, and that of 220ECO based on the composition of 22Cr-1.2Mo steel, Nb and Ti being added in combination to both of them as stabilizing elements. The tensile properties of commercially produced sheets of the developed steels 0.8 mm in thickness were nearly equal to those of NSSC 190.

As an indicator of corrosion resistance, **Fig. 5** shows the pitting potential measured according to JIS G 0575. The graph also shows the values of other high-purity ferritic stainless steels for comparison purposes. It is clear from the graph that the pitting potential V'_{C100} of the ferritic stainless steels shown in the graph can be put in order using Cr+3.3Mo as an index: NSSC 220ECO containing 22Cr is the highest of them in terms of pitting potential, followed by NSSC 190 and then 190ECO. It has to be noted that, when added to high-purity ferritic stainless steel, Cr and Ti are effective at improving pitting corrosion resistance because Cr stabilizes the passivation films and Ti renders non-metallic inclusions, which act as the starting points of corrosion, insoluble.[7)] Both the developed steels take advantage of these effects.

Next, the crevice corrosion resistance of the developed steels

Table 1 Chemical compositions and mechanical properties of developed steels

	Chemical composition mass%	YS MPa	TS MPa	El %	HV
NSSC 190ECO	19Cr-1Mo-Nb, Ti	349	503	29	174
NSSC 220ECO	22Cr-1.2Mo-Nb, Ti	335	529	29	168
NSSC 190	19Cr-2Mo-Nb, Ti	358	533	29	172

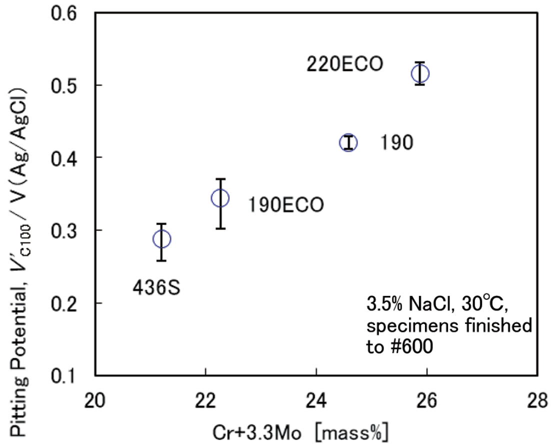

Fig. 5 Pitting potential of developed steels

was evaluated at different temperatures. Here, the test pieces were the same as the spot-welded ones for the crevice corrosion test described in sub-section 2.1. The concentrations of the aqueous solution were set at 600 ppm Cl^- and 10 ppm Cu^{2+}, and the corrosion resistance was evaluated in terms of the corrosion weight loss after immersion in the solution for 14 days. As shown in **Fig. 6**, the corrosion weight loss tended to increase at higher temperature: the corrosion rate of NSSC 190ECO at 60°C was lower than that of NSSC 190 at 80°C, and that of 220ECO was equal to or lower than that of NSSC 190 at any of the test temperatures.

In addition, simulating the crevices of TIG weld joints of real hot water tanks, the test pieces were prepared by TIG welding in the laboratory, and their resistance to crevice corrosion was evaluated as follows: specimen sheets of NSSC 190, 190ECO, and 220ECO, 0.8 mm in thickness, were welded together at one edge by lap fillet TIG welding; the sheets had been formed beforehand so that the opening angle of the joints was roughly 0 or 30°; Ar was used as the shield gas. Although the opening angle fluctuated from piece to piece depending on the accuracy of the preliminary forming, setting at the welding work, etc., attention was paid to minimize the fluctuation. The test pieces were subjected to the constant-potential corrosion test for 22 h in an aqueous solution of 200 ppm Cl^- at 80°C, setting the potential from +0.05 to 0.30 V. It has to be noted in this relation that the natural potential of stainless steel of hot water tanks is generally +0.15 V (vs SSE ≈ 0.1 V vs SCE).[8)] As seen in **Fig. 7**, with the test pieces with an opening angle of 30°, no crevice corrosion occurred in any of them even at +0.25 V. With the test pieces with an opening angle of 0°, in contrast, all the test pieces of any of the steel grades were corroded at 0.15 V, but at 0.10 V, only 190ECO was corroded, while NSSC 190 and 220ECO were not. Thus NSSC 220ECO has the same crevice corrosion resistance as that of NSSC 190 even at crevices of TIG-welded joints similar to those in real water tanks. The results also indicate that 190ECO can be used in a

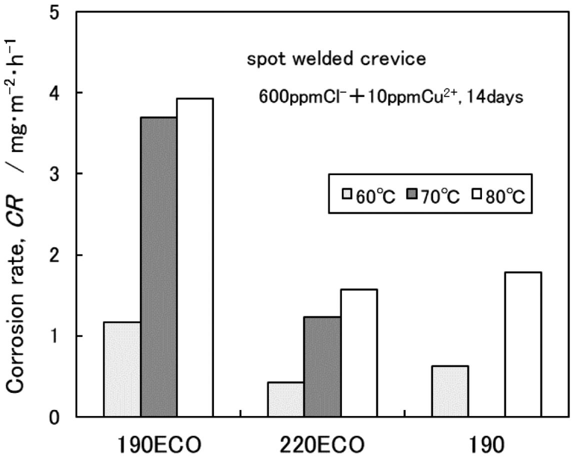

Fig. 6 Relationship between temperature and crevice corrosion rate of NSSC 190ECO and 220ECO

Potential	Crevice opening angle 30°			Crevice opening angle 0°		
V/SSE	190 ECO	190	220 ECO	190 ECO	190	220 ECO
+0.30V	×	×	×	–	–	–
+0.25V	○	○	○	–	–	–
+0.20V	–	–	–	–	–	–
+0.15V	○	○	○	×	×	×
+0.10V	–	–	–	×	○	○
+0.05V	–	–	–	○	○	○

○ : No Corrosion, × : Corrosion, – : No test

Fig. 7 Relationship between crevice opening angle and critical potential of corrosion of NSSC 190ECO and 220ECO

hot water environment at 80°C if the opening angle is large, and that even NSSC 190 is corroded if the crevice is closed. This shows that the design of weld joints is very important for the durability of real tanks.

Crevice corrosion is unlikely to occur when a lap weld joint, 40 μm or less in the distance between the sheets and 2 mm or more in depth, for example, is wide open;[9] in this case, the angle of the opening is as small as roughly 3×10^{-2}°. In the present laboratory test, although it was difficult to control the opening angle delicately, the results showed a similar trend. At any rate, the test results indicate that it is necessary to design weld joints in consideration of the chemical composition of the material steel and the joint shape.

To confirm the press formability of developed NSSC 220ECO into the shape of the end plates of hot water tanks, NSSC 220ECO and NSSC 190 were compared in terms of the distribution of forming load in a simulation by the finite element method (FEM). As seen in **Fig. 8**, NSSC 220ECO could be formed into the desired shape at substantially the same load level under the same press conditions as that for NSSC 190. Based on this simulation result, end plates of the water tanks were actually manufactured by forming sheets of NSSC 220ECO by pressing, and good press formability has been confirmed without any problem. The same press formability of NSSC 190ECO as that of NSSC 190 has also been confirmed likewise.

Ferritic stainless steels NSSC 190ECO and 220ECO for application to hot water tanks excellent in the resistance to crevice corrosion in various hot water environments and having the strength and workability suitable for use in hot water tanks have thus been developed.

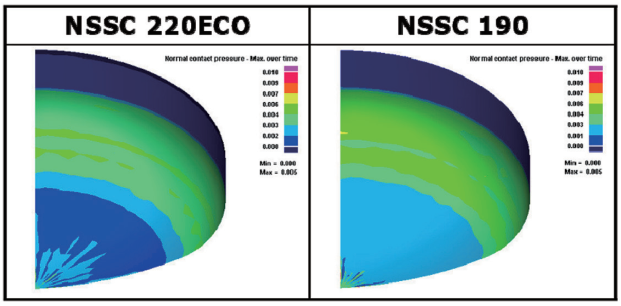

Fig. 8 Comparison of forming property by FEM simulation

4. Expansion of Use: Secondary Heat Exchangers for Gas-fired Water Heaters of Latent Heat Recovery Type

As an example of applications of NSSC 220ECO taking advantage of the excellent corrosion resistance, this section explains its use for the secondary heat exchangers of gas-fired water heaters of the latent heat recovery type. This type is a new kind of gas water heater with a secondary heat exchanger additionally provided to recover the latent heat of the combustion exhaust gas from the conventional copper heat exchanger. Because the temperature of the exhaust gas is roughly 200°C, condensate water forms on the surface of the components of the heat exchanger. Since the sulfur in the fuel gas and nitrogen in the atmosphere form SO_4^{2-} and NO_3^-, the condensate water has an acidity roughly of pH 3.[10] When there is airborne salt (Cl^-) in addition in the atmosphere, the corrosion condition inside the heat exchanger becomes very tough. For this reason, titanium was used in the early days of its use, but later, austenitic stainless steels such as the type 316L and JIS SUS315J2 (18.5Cr-12Ni-3Si-2Cu-Mo) resistant to SCC were used. However, austenitic stainless steel has a low thermal conductivity and contains expensive Ni. In consideration of the situation, we studied the applicability of ferritic stainless steel, which is more heat conductive and does not contain Ni, to the heat exchanger.

First, to investigate the composition of the condensate water forming in the heat exchanger and environmental influences, a series of continuous combustion tests were conducted with the cooperation of Ryukyu University on the building roof of its Engineering Department in Nishihara Town, Okinawa. Condensate water collected from the secondary heat exchangers after combustion for 10 min every day and that remaining in them before combustion were analyzed; here, acidity was measured using a pH meter, and SO_4^{2-} and NO_3^- by ion chromatography. Through the one-year test, it was found that in winter, when the water temperature is low and the combustion time is long, the condensate water tended to have low pH values and high concentrations of SO_4^{2-} and NO_3^-. The fluctuation range of pH was from 2.8 to 3.5, that of SO_4^{2-} from 0 to 40 ppm, and that of NO_3^- from 20 to 80 ppm. On the other hand, the Cl^- concentration in the condensate water was found to be largely influenced by maximum wind velocity: while the Cl^- concentration was 0 to 20 ppm in normal weather, it rose when wind was strong with typhoons, hitting a maximum of approximately 90 ppm. Based on these results, the composition of the artificial condensate water for an accelerated corrosion test was defined as follows: pH 2.5, 10 ppm SO_4^{2-}, 100 ppm NO_3^-, and 0 to 100 ppm Cl^-. The accelerated corrosion test with the artificial condensate water was conducted in the laboratory. Test pieces for the crevice corrosion test were prepared by cutting out pieces 20×50 mm in size from specimen sheets of the type 316L, NSSC 220ECO, and 190ECO, finishing all their surfaces to #600 by wet polishing, and setting each of them between two glass plates fastened with nuts and bolts. To simulate the condensation of the condensate water by drying inside the heat exchangers, the test pieces were immersed in the artificial condensate water in beakers, and placed in a tank maintained at 80°C for 20 h to dry (dip & dry test); this process cycle was repeated 10 times. Corrosion resistance was evaluated in terms of the weight loss after removing the rust that had formed during the test.

The test results are shown in **Fig. 9**. The corrosion weight loss of all the test pieces increased as the Cl^- concentration increased, but it decreased with the type 316L, NSSC 190ECO, and 220ECO in this order; the developed ferritic stainless steels with high Cr and Mo contents proved to have a better corrosion resistance than that of the type 316L in an environment of the artificial condensate water. To clarify the effects of NO_3^-, the same test was conducted changing the concentrations of NO_3^- and Cl^-. **Figure 10** shows mappings of the corrosion weight loss of NSSC 220ECO and the type 316L obtained through the test.[11] As seen here, the area in the NO_3–Cl^- plane where the corrosion weight loss was small is wider with the former than with the latter. On the other hand, in a past study to evaluate the pitting corrosion resistance of the type 444 (high-Cr-Mo steel like 220ECO and containing the same alloy elements as NSSC 190) and the type 316L in an environment where Cl^- and NO_3^- coexisted, the former proved to have a lower critical pH value for passivation than that of the latter, and also a lower critical NO_3^-/Cl^- ratio for prevention of pitting corrosion. From this, the reason for the above test result that the area where the corrosion weight loss in an environment containing NO_3^- was small was wider with NSSC 220ECO than with the type 316L is presumably that the passivation acceleration effect of NO_3^- is stronger with ferritic stainless steel.[12]

In the combustion test at Ryukyu University described above, to evaluate the corrosion resistance in the environment inside real secondary heat exchangers, test pieces were exposed to the environment inside them for one year. The specimens for this exposure test had been prepared by spot welding the sheets of 220ECO and the type 316L, 20×20 mm and 20×40 mm in size, so as to form crevices. **Table 2** shows the results of their evaluation. Although the corrosion depth at this test was comparatively small because of the short test period, the maximum corrosion depth of 220ECO was smaller than that of 316L, which confirmed the excellent crevice corrosion resistance of the developed steel in the environment inside the heat exchangers. Presently, 220ECO is widely used for the secondary heat exchangers of gas water heaters of the latent heat recovery type.

In addition, in appreciation of the excellent corrosion resistance, its use is expanding also for the piping of hot water, replacing copper pipes.

5. Closing

New ferritic stainless steels, NSSC 190ECO (19Cr-1Mo-Ti-Nb) and NSSC 220ECO (22Cr-1.2Mo-Ti-Nb), for hot water supply systems were developed in consideration of environmental issues and resource saving. This paper explained the development concept of the steels, their characteristics, and their use for new applications.

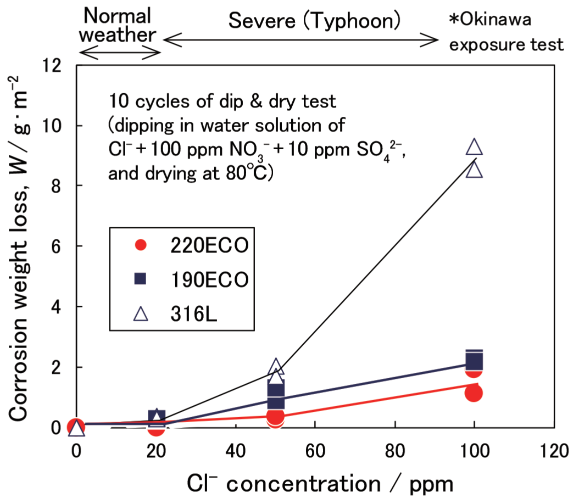

Fig. 9 Effect of Cl^- concentration on corrosion weight loss at dip & dry test using simulated condensate water

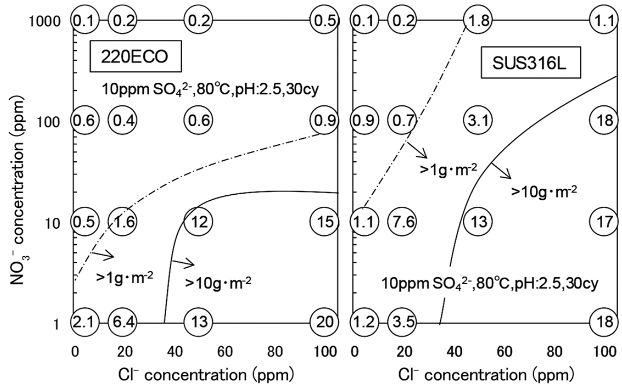

Fig. 10 Mapping of corrosion weight loss of NSSC 220ECO and type 316L at dip & dry test using artificial condensate water of different concentrations of Cl^- and NO_3^-

Table 2 Maximum depth of crevice corrosion due to condensate water during exposure inside heat exchangers for one year

(μm)

Steel grade	220ECO	316L
Maximum crevice corrosion depth	30	44

The “ECO” series stainless steels are available as new materials excellent in crevice corrosion resistance and satisfying various requirements related to the hot water environment. As such, they are widely used for electric and gas-fired water heaters and related components.

As stated herein, the crevice corrosion resistance, essential in the hot water environment, is closely related to the crevice structure and the method of material joining. Through the combination of appropriate design and fabrication of final products, therefore, the use of the developed steel grades is expected to expand for applications in which crevice corrosion resistance is required. We shall propose various technical solutions to expand the applications of existing steel products and further develop new corrosion resistant steel products.

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