Technical Report

Properties of the Ferritic Stainless Steel NSSC® 180 Which Contains No Mo and Its Applications

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Abstract

For the improvement of corrosion resistance of ferritic stainless steel in atmospheric environment, the atmospheric corrosion behavior of stainless steel was evaluated. It was clarified that the pitting corrosion inevitably occurs in either type 304 in an atmospheric environment with wet-dry processes. It indicates that the atmospheric corrosion resistance should be evaluated in view of the growth of the corrosion pit. The growth of pit is suppressed by the addition of Ni, Cu, and Nb in solution simulating the corrosion pit. These results shows that NSSC® 180 (19Cr-0.3Ni-0.4Cu-Nb steel), which contains no Mo and a very limited amount of Ni, have the same corrosion resistance to Type 304 in atmospheric corrosion. From these excellent properties, this steel has been widely applied to some of equipments exposed to an aqueous chloride environment.

1. Introduction

The rapid economic growth in the Asian area since the turn of the century has brought about a significant increase in stainless steel output[1], which in turn has caused the prices of raw materials for stainless steel to go up markedly. In particular, the prices of nickel and molybdenum, which are the principal alloying elements for stainless steels, have skyrocketed[2]. Type 304 (18Cr-8Ni)—which is representative of general-purpose stainless steels—has suffered much from these unusual price hikes. As of the end of 2008, the hike in raw material prices has calmed down due to the global economic recession. Even so, there is a good possibility that the international price of nickel, which is a rare resource, will begin rising again in the future. Under those conditions, there is a growing tendency for Type 304, which contains a considerable proportion of nickel, to be replaced by materials which offer comparable performance but are less subject to price fluctuations than Type 304. Those substitute materials include: ferritic stainless steels, Cr-Mn-Ni steel in which nickel is largely replaced by manganese[3], and duplex stainless steel which

has nitrogen added to save nickel[4], etc. Of these, general-purpose ferritic stainless steels are being increasingly used, especially in Japan, for their all-round properties and cost competitiveness.

In this paper, we describe the concept of composition design in NSSC 180 (19Cr-0.3Ni-0.4Cu-Nb)[5, 6], a ferritic stainless steel which affords corrosion resistance comparable to that of Type 304 under a normal corrosive atmosphere, and the development of an accelerated test method which permits simulating a corrosive atmosphere accurately. In addition, we introduce the newest applications of NSSC 180.

2. Main Subjects

2.1 Mechanisms of stainless steel corrosion in a corrosive atmosphere and effects of alloying elements

2.1.1 Mechanisms of stainless steel corrosion in a corrosive atmosphere

The corrosion of stainless steel in an outdoor environment which is exposed to fine particles of sea salt occurs as water droplets con-

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taining chloride ions (Cl⁻) in dissolved sea salt that is then deposited on the stainless steel surface in a repeated process of formation and disappearance under changing environmental conditions. In order to understand the mechanisms of stainless steel corrosion in a corrosive atmosphere, therefore, it is necessary to make an in-depth study of the rust development behavior in a corrosive atmosphere. First, we carried out a macroscopic analysis of the development of rust on the surface of stainless steel in a corrosive atmosphere. **Fig. 1** shows the results of measurement of the rust area ratio and the amount of rust per unit area (rust density) on the surface of Type 304 and Type 430, which were subjected to an exposure test on a certain beach in the subtropical area of Japan[7]. In order to measure the rust area ratio and rust density, after exposure, each of the specimens was subjected to image processing and the rusted parts were separated out. As a result, it was clarified that the process of development of rust on stainless steel in a corrosive atmosphere consists of three stages: (1) initiation of rust, (2) growth of rust, and (3) coalescence of existing rust.

First, small rust spots occur on the stainless steel surface in a corrosive atmosphere (Stage 1). Since these small rust spots increase in number before they begin growing, the rust area ratio and the rust density show a linear relationship. With the lapse of time, the individual rust spots grow (Stage 2), softening the gradient of the linear relationship. As the rust continues growing, adjoining patches apparently coalesce (Stage 3), causing the rust area ratio to increase and the rust density to decrease. Both Type 304 and Type 430, which are different stainless steel grades, exhibited similar rust development behavior, although the time to transition from one stage to another was longer for Type 304, which has superior corrosion resistance.

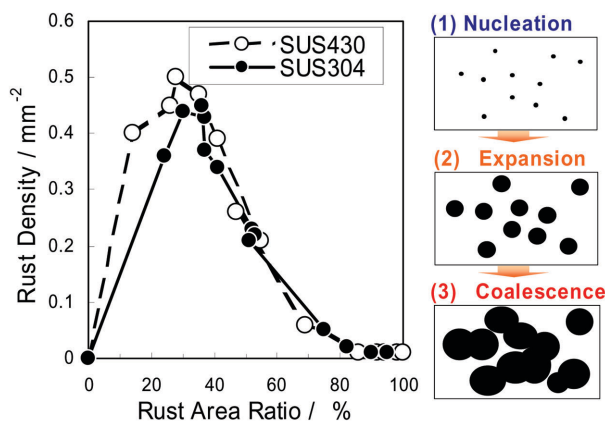**Fig. 2** schematically shows the above rust development behavior, with the focus on individual rust spots. The airborne salt particles that deposit on the stainless steel surface form droplets containing chloride ions due to condensation of dew and suchlike at night. When the chloride ion concentration of the droplet exceeds the critical level due to evaporation of the water droplet during the day, pitting corrosion occurs. The pit (i.e., the hole caused by pitting corrosion) right after the occurrence of pitting corrosion is initially extremely small. However, as the pit grows in the presence of droplets with a high concentration of chlorine ions, it can be recognized as a spot of rust. The growth of the rust stops when the pit is repassivated due to a decline in the chloride ion concentration as a result of the droplet drying up under higher temperatures during the day or being washed away by rainwater. However, when dew condenses again, pits occur anew and develop by the mechanism described above and the rust spreads.

Thus, it was clarified that the process of development of rust on stainless steel in a corrosive atmosphere can be divided into: (1) initiation of pits, (2) growth of pits, and (3) repassivation. Then, we studied the electrochemical effects of various alloying elements in each of the above stages of rust development.

2.1.2 Effects of alloying elements in the pitting process

In analyzing the pitting process, the pitting potential whose value can be obtained by a simple test is commonly used. It is generally known that there is a correlation between pitting potential and Cr/Mo. As an example, as shown in **Fig. 3**, the pitting resistance equivalent (PRE) number (= $Cr + 3.3Mo + nN$; where $n = 8$ to 30) and pitting potential (hereinafter referred to as V_C') has an almost linear relationship. It should be noted, however, that this correlation has a margin of about 0.1 to 0.2 V. Since general-purpose stainless steels were used in the present test, the said margin of V_C' suggests that not only Cr, Mo and N, but also some other elements, have something to

Fig. 1 Atmospheric corrosion behavior in the field exposure test
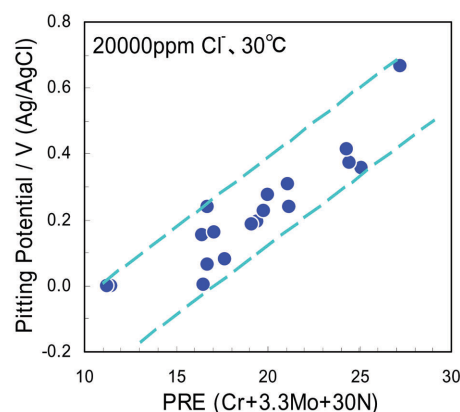

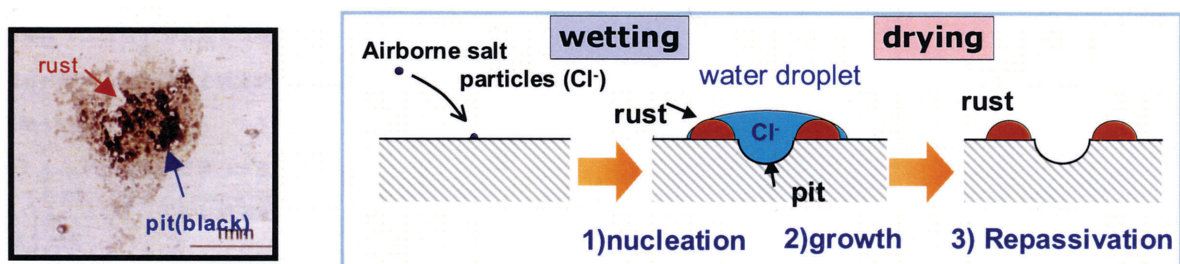Fig. 3 Pitting resistance equivalent number (PRE) and pitting potential

Fig. 2 Corrosion mechanism in an atmospheric corrosive environment
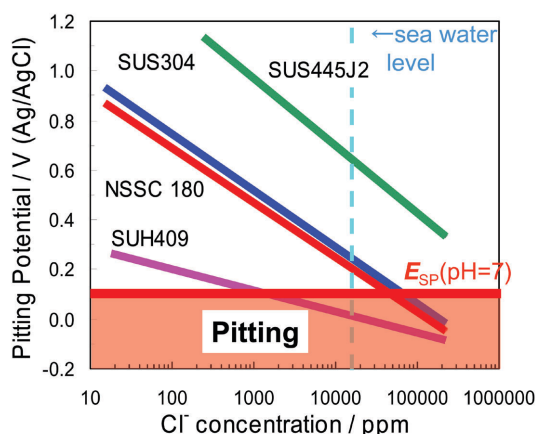
Fig. 4 Effects of Cl⁻ concentration on pitting potential

do with the correlation. As other elements that are likely to help improve pitting resistance, Nb and Ti, etc. are cited[8, 9].

It is judged that a steel grade with a nobler V_C' has better pitting resistance than a steel grade with a less noble V_C'. However, this judgment is applied only in relative evaluation of pitting resistance of different steel grades. In order to judge whether or not pitting occurs on a specific steel grade in an actual environment, it is necessary to compare the V_C' of the steel grade with the potential E_{SP} that indicates the oxidizing potential of the actual environment. Namely, it is understood that there is the possibility that local corrosion, including pitting, occurs when the critical potential of the steel (V_C' for pitting) is smaller than the E_{SP}[10]. The value of E_{SP} in a corrosive atmosphere is determined mostly by the reducing reaction of oxygen dissolved in the corrosive droplets. The value of E_{SP} for passivated stainless steel in water with a pH of 7 is approximately 0.12 V (Ag/AgCl; the same applies hereinafter)[11].

Fig. 4 shows the E_{SP} and the effect of Cl⁻ concentration on V_C' of several steel grades. When the Cl⁻ concentration is equivalent to that of seawater (approximately 19,000 ppm Cl⁻), Type 304 and Type 430J1L are free from pitting. However, when the Cl⁻ concentration increases to about 50,000 ppm or more due to the evaporation of droplets, V_C' exceeds the natural potential E_{SP}. This indicates that when the droplets dry up in a corrosive atmosphere, pitting inevitably occurs on both Type 304 and Type 430J1L. In order to restrain the occurrence of pitting in such an environment, it is necessary to select a stainless steel containing high proportions of chromium and molybdenum, like Type 445J2 (22Cr-1.5Mo). Thus, in order to restrain the development of rust on Type 304-equivalent stainless steels in an outdoor environment, it is important to restrain not only the occurrence of pitting, but also the growth of pits.

2.1.3 Process of growth of pits

As described in the preceding paragraph about the general mechanism by which pitting occurs, the passive film on the surface of stainless steel is destroyed when the Cl⁻ concentration at the surface exceeds the critical level due to the drying of droplets containing Cl⁻. Then, the substrate beneath the film is corroded. As a result, metallic ions (Me^{n+}) are dissolved into the pit solution. These metallic ions cause a hydrolytic reaction to take place. Since this reaction produces metallic hydroxides and hydrogen ions (H^+), the pH value of the solution in the pits decreases. As long as the pH value of the pit solution is larger than the depassivation pH (pH_d) of the stainless steel material, the pits do not grow as they are passivated. When said

pH value is smaller than the pH_d, however, the pits continue growing. Therefore, one method of evaluating the growth of pits is to evaluate the dissolving characteristic of the pits in a low-pH, high Cl⁻-concentration solution which simulates the composition of the solution in the pits.

With the aim of measuring the influence of alloying elements on the growth of pits, we compared the dissolving speeds in a 20 mass% NaCl solution having a pH value of 1.5. As the dissolving speed index in the present experiment, the current density, I_{CRIT}, which indicates the active dissolution peak on an anodic polarization curve, measured in the above solution, was used (see **Fig. 5**). The smaller the I_{CRIT}, the slower the rate of pit growth. As shown in Fig. 5, I_{CRIT} decreased with the addition of Ni, Cu, Nb and Cr. The effect of Ni was especially large: 0.4 percent Ni addition caused I_{CRIT} to decrease by nearly half. By contrast, Cr is not as effective as the other elements in decreasing I_{CRIT}. **Fig. 6** shows the combined effect of Ni and Cu. When both Ni and Cu are added, they display a still larger effect. From the above results, it was found that adding very small amounts
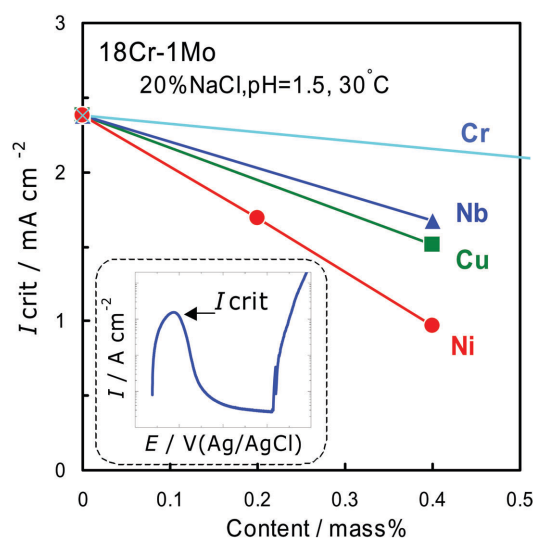

Fig. 5 Effects of alloying elements on current density (I_{CRIT}) in high-Cl⁻ and low-pH solution
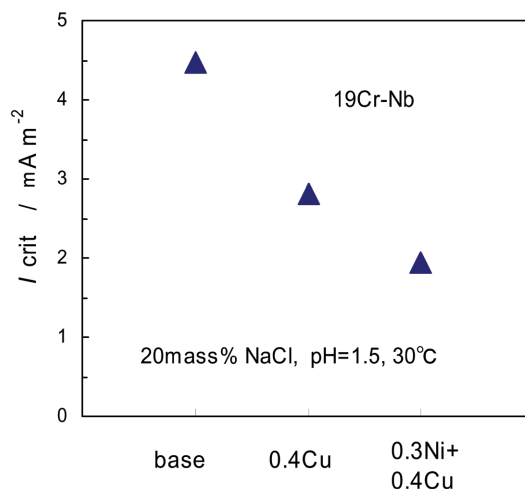

Fig. 6 Effects of Ni and Cu on current density (I_{CRIT}) in high-Cl⁻ and low-pH solution

of Ni, Cu and Nb is effective in restraining the growth of pits. It should be noted here that the addition of Mo also decreases I_{CRIT} significantly.

The addition of Ni/Cu also enhances the pit repassivation effect discussed in 2.1.1. This is considered due to the fact that both Ni and Cu lower the I_{CRIT} and that Ni promotes a cathodic reaction by lowering the hydrogen overvoltage.

2.2 Development of method for accelerated corrosion test in corrosive atmosphere

So far, we have discussed the individual stages of corrosion in a corrosive atmosphere. Since the actual corrosive atmosphere is very complicated, however, it is difficult to evaluate the development of corrosion simply by summing up the consequences of the individual stages. In order to evaluate the corrosiveness, it is most important and effective to carry out an exposure test in the field. However, this method has a number of problems. For example, it takes a considerable period of time. Therefore, as an accelerated corrosion test method which permits simulating a corrosive atmosphere in a laboratory, we have developed and put into practical use a cyclic corrosion test (CCT) method using artificial seawater[12].

This method has two salient characteristics: it applies artificial seawater and reproduces the most corrosive environment. The artificial seawater has the same chloride composition (NaCl, MgCl$_2$, etc.) as droplets of natural seawater and is capable of reproducing the humidity of the actual environment almost perfectly (relative humidity at which salt is saturated: about 75 percent for NaCl and about 35 percent for MgCl$_2$). Therefore, it is suitable for atmospheric corrosion testing. Concerning reproduction of the optimum corrosive atmosphere, the actual corrosive atmosphere was divided into three processes—spraying of artificial seawater, drying and wetting—and the conditions in each of the processes were optimized so as to permit simulating the actual corrosion behavior. **Fig. 7** compares the corrosion behavior in a cyclic corrosion test (CCT) using artificial seawater with the corrosion behavior in an exposure test carried out in Okinawa. It can be seen that the relationship between rust area ratio and rust density obtained from the CCT using the artificial seawater reproduces that obtained in the exposure test very satisfactorily.

By using the CCT method, we studied the relationship between Cr content and rust area ratio. The study results are shown in **Fig. 8**. From the study results, it was found that with the increase in Cr content, the rust area ratio of 16 to 22Cr-0.3Ni-0.4Cu ferritic stainless steels which do not contain Mo decreased, but that the rust area ratio almost stopped decreasing when the Cr content increased to 19 percent or more. This suggests that in order to measure the corrosiveness of a specific atmosphere, it is necessary not only to compare the pitting potentials as described in the preceding section, but also to evaluate the growth of pits and other factors involved in the process of corrosion. **Fig. 9** shows the appearance of NSSC 180 (19Cr steel with trace amounts of Ni, Cu and Nb added) and Type 304 after they were subjected to a CCT using artificial seawater. It can be seen that the degree of rust on NSSC 180 is nearly the same as that on Type 304 and much less than that on Type 430.

To sum up, it is evident that NSSC 180, which does not contain large amounts of Mo and Ni, affords comparable atmospheric corrosion resistance to Type 304.
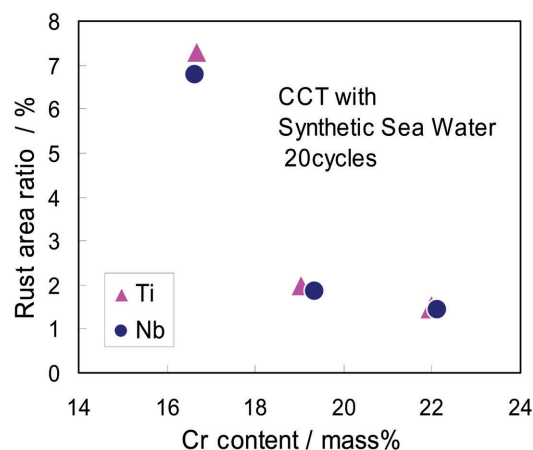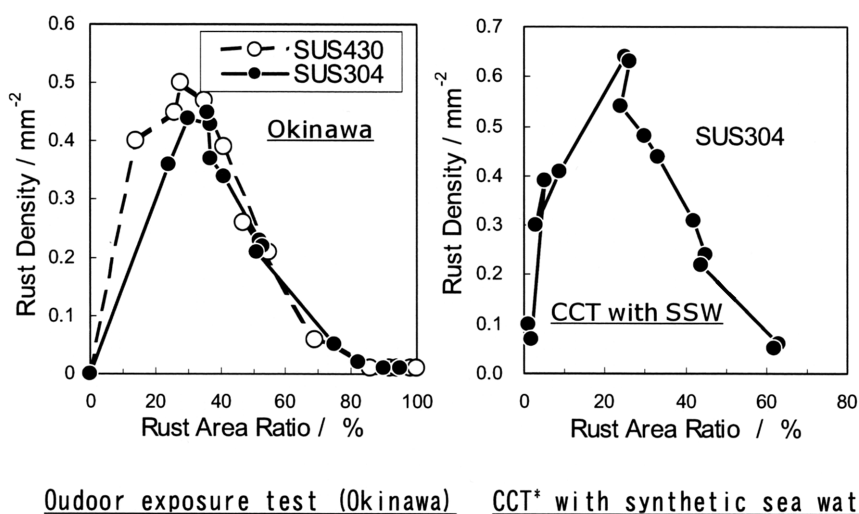

Fig. 8 Relationship between percentage of rust spots area ratio and Cr and Mo contents at cyclic corrosion test using synthetic seawater
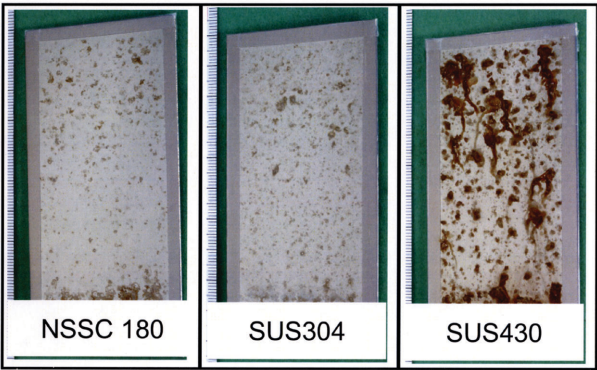

Fig. 7 Comparison of atmospheric corrosion behavior in the outdoor exposure test and SSW-CCT using synthetic seawater

(1)a synthetic sea water spray (35°C, 4h)
(2)drying (60°C, 2h)
(3)wetting (50°C, RH95%, 2h)
12cycles

Fig. 9 Result of cyclic corrosion test with synthetic seawater of NSSC 180 and other steels

2.3 Various characteristics of NSSC 180 and application examples

In the preceding section, the results of evaluation of the corrosion resistance of NSSC 180 on a laboratory scale were described. Here, some of the major characteristics of NSSC 180 are discussed. First, the results of a 1.5-year exposure test on an NSSC 180/2B plate two inches thick, carried out in the coastal area of Ibaraki Prefecture, are shown in **Fig. 10**. The test results showed that NSSC 180 had a comparable degree of rust to Type 304 and afforded far superior atmospheric corrosion resistance to Type 430. **Fig. 11** shows the results of a CCT using artificial seawater on TIG-welded joints of NSSC 180. Before subjecting the TIG-welded joints of NSSC 180 and Type 304 to the CCT, their surfaces were ground to remove weld scale completely. In welding dissimilar materials (Type 304 and NSSC 180), a filler material (ER-308L) was used.

The degree of rusting of the welded joints of both NSSC 180 and Type 304 after the CCT was almost the same as that on the flat parts. The improvement in corrosion resistance of welded joints of NSSC 180, which is a ferritic stainless steel, is attributable to the addition of Nb which helps stabilize C and N[5]. With respect to the welded joints between NSSC 180 and Type 304, it is possible to secure corrosion resistance comparable to that of the flat parts by selecting a suitable low-carbon filler material. When it comes to putting a spe-

cific stainless steel material to practical use, it is important that the material should have not only the desired corrosion resistance but also the desired workability and aesthetic appeal of the surface skin after working.

Fig. 12 compares the limiting drawing ratio (LDR) and the surface morphology after deep drawing between NSSC 180 and Type 304. The LDR value of NSSC 180 is higher than that of Type 304, and the surface of NSSC 180 after deep drawing looks as good as that of Type 304. This is attributable to the addition of a trace amount of Nb which helps fix C and N[13], and the texture control imple-
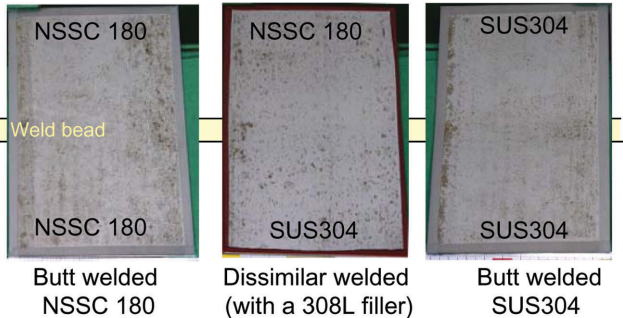
*CCT with SSW, 20cycles, polished to remove welding scale

Fig. 11 TIG welded joints of NSSC 180 and Type 304 after 20 cycles of CCT using synthetic seawater

NSSC 180	SUS304
LDR：2.2	LDR：2.0

* blank:80mm in diameter, punch: 40mm,
BHF: 1ton-using, Johnson-Wax

Fig. 12 Comparison of deep drawability of NSSC 180 steel and SUS304
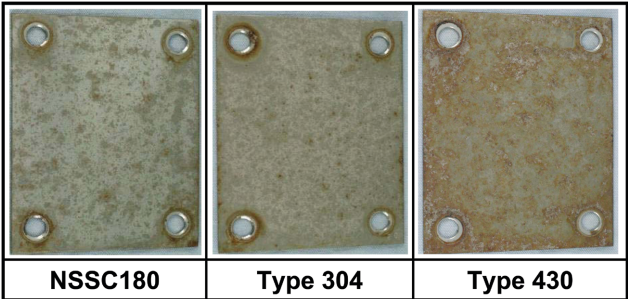
*Outdoor exposure test for 1.5 years in a marine atmosphere in Japan.

Fig. 10 Results of outdoor exposure test of NSSC 180 and other steels (2B finish, exposed for 1.5 years in a marine atmosphere in Ibaraki, Japan)

Fig. 13 Application examples of NSSC 180 steel

mented in the manufacturing process. In addition, since NSSC 180 is a ferritic stainless steel, it is free from stress corrosion cracking, which is a serious problem with Type 304.

Thus, in a normal corrosive environment, NSSC 180 displays corrosion resistance nearly equal to that of Type 304. When used properly, NSSC 180 can be a substitute for Type 304 in view of its corrosion resistance, workability and weldability. Because of its desired characteristics, NSSC 180 is being increasingly used for automotive parts, various types of kitchen utensils and home appliances, and exterior parts, etc. as shown in **Fig. 13**.

3. Conclusion

We have clarified the mechanisms for atmospheric corrosion of stainless steels and described the design concept and application examples of NSSC 180 (19Cr-0.3Ni-0.4Cu-Nb)—a ferritic stainless steel for which the amounts of alloying elements added have been optimized on the basis of the above knowledge so as to save resources. The results of the present studies on atmospheric corrosion of stainless steels are summarized below.

(1) The corrosion of stainless steel in the atmosphere develops as the cycle of pitting, pit growth and repassivation is repeated.

(2) Adding Cr and Mo is an effective means of preventing pitting. In a corrosive atmosphere involving repeated drying and wetting, however, even Type 304 is not free from pitting.

(3) Adding Ni, Cu and Nb is an effective means of lowering the dissolving speed in a solution that simulates salt-bearing droplets that cause pits to grow. In particular, the addition of Ni is very effective, whereas the excess addition of Cr is not very effective.

(4) It was confirmed by an exposure test in the field and an accelerated corrosion test in the laboratory that NSSC 180 (19Cr-0.3Ni-0.4Cu-Nb) containing trace amounts of Ni, Cu and Nb displays corrosion resistance comparable to that of Type 304 in an ordinary outdoor environment.

(5) In terms of deep-drawability and corrosion resistance of welded joints too, NSSC 180 is comparable to Type 304. It is being increasingly applied to automotive parts, various types of kitchen utensils and home appliances, and exterior parts, etc.

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