Abridged version

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Effect of alloying elements on the resistance of ferritic stainless steels to atmospheric corrosion in coastal environment was evaluated by atmospheric exposure tests and laboratory corrosion tests. Atmospheric exposure tests showed that pitting corrosion resulted in rusting and that atmospheric corrosion resistance of the steels increased with an increase in Cr content and with addition of Mo and/or Cu. Ferritic stainless steels with higher Cr and Mo contents, such as 30Cr-2Mo steel, were also shown to have excellent resistance to atmospheric corrosion in coastal environment. Laboratory corrosion tests showed that Cr and Cu were effective in preventing the generation and growth of pits respectively, while Mo played a significant role in both processes. From the results of both atmospheric exposure and laboratory corrosion tests, it was concluded that steels with pitting potentials higher than the critical values, which depended on the aggressiveness of environments, exhibited no rusting. These critical values can be used as one of the criteria for selecting exterior materials of buildings in various areas.

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Effects of Cr, Mo and Cu on the Atmospheric Corrosion Resistance of Ferritic Stainless Steels in a Coastal Environment*



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1 Introduction

Waterfront development is being carried out extensively, and ferritic stainless steels have been recently highly evaluated as an architectural material for building exterior in a coastal environment.¹⁾ This is possibly because ferritic stainless steel is more economical than austenitic stainless steel containing expensive Ni, and also it is known that ferritic stainless steel provides better corrosion resistance than SUS 304 stainless steel when produced with Mo and Cu added to high-Cr steel of not less than 18%Cr.^{2,3)} In addition, the high atmospheric corrosion resistance, beautiful appearance, impression of high quality and freedom from maintenance of stainless steel are generally recognized.⁴⁻⁶⁾

Extensive studies have been conducted by Kawasaki Steel on the atmospheric corrosion resistance of ferritic stainless steel for which an increase in demand is expected, especially for long roofing materials and external panels.⁷⁾

In this report, the effects of an increase in the Cr content and of the addition of Mo and Cu on the atmospheric corrosion resistance of ferritic stainless steel were investigated by conducting atmospheric exposure

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Effect of alloying elements on the resistance of ferritic stainless steels to atmospheric corrosion in coastal environment was evaluated by atmospheric exposure tests and laboratory corrosion tests. Atmospheric exposure tests showed that pitting corrosion resulted in rusting and that atmospheric corrosion resistance of the steels increased with an increase in Cr content and with addition of Mo and/or Cu. Ferritic stainless steels with higher Cr and Mo contents, such as 30Cr-2Mo steel, were also shown to have excellent resistance to atmospheric corrosion in coastal environment. Laboratory corrosion tests showed that Cr and Cu were effective in preventing the generation and gorwth of pits respectively, while Mo played a significant role in both processes. From the results of both atmospheric exposure and laboratory corrosion tests, it was concluded that steels with pitting potentials higher than the critical values, which depended on the aggressiveness of environments, exhibited no rusting. These critical values can be used as one of the criteria for selecting exterior materials of buildings in various areas.

tests, and the improvement by the passive film was considered by analyzing this film. Based on the correlation between atmospheric corrosion resistance and the results of laboratory corrosion tests, a method for evaluating atmospheric corrosion resistance by laboratory corrosion tests was examined; it will be demonstrated that Mo-bearing high-Cr steel, represented by the 30Cr-2Mo composition, is satisfactory for use in a severe corrosive environment such as that in coastal zone.

2 Experimental Method

Small 50-kg ingots with the chemical composition range shown in **Table 1** were produced in a vaccuminduction furnace, and 0.6-mm-thick cold-rolled annealed steel sheets were produced and used in various tests. The Cr content was varied in the range of 11 to 30%, the Mo content in the range of 0 to 4.0%, and

^{*} Originally published in Kawasaki Steel Giho, 25(1993)2, 131-

Table 1 Chemical composition ranges of specimens (mass%)

С	N	Cr	Мо	Cu	Nb	Ti
0.001	0.003	11	0	0	0	0
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0.02	0.05	30	4.0	0.8	0.5	0.4

the Cu content in the range of 0 to 0.8% to investigate the effects of the Cr, Mo and Cu elements that were expected to contribute to the atmospheric corrosion resistance.

Atmospheric exposure tests (JIS Z 2381) were conducted on specimens with a size of $15 \text{ cm} \times 10 \text{ cm}$, which had been wet-finished with polishing compound #1000 and set at southward an inclination of 36° with respect to the ground in an exposure test field about 10 m from the bulkhead quay in the Oihama area of the company's Chiba Works. The specimens were exposed to the atmosphere for two years. Exposure tests on highly corrosion-resistant stainless steel specimens of 30Cr-2Mo steel, etc. were conducted for three years in the Chiba (Oihama), Yokkaichi and Shionomisaki exposure test fields. Atmospheric corrosion resistance was evaluated by the rust area fraction(%), which was determined by processing photographic images of the appearance of the specimens, and by the shape and depth of pits, which were observed under a microscope and measured with a roughness meter, respectively.

Two kinds of electrochemical measurement, i.e., the pitting potential measurement (JIS G 0577) and the anodic polarization measurement (JIS G 0579), were conducted in the laboratory. The former test was also carried out according to a method in which the solution temperature was raised to 70° C. In both tests, the sweep rate was 20 mV/min according to the potentiadynamic method, and the value for pitting potential is expressed by the potential (V'_{c10}) at which the current density reached $10 \,\mu\text{A/cm}^2$.

Speciments of 20%Cr steels with different amounts of added Mo and Cu were wet-finished with polishing compound #800 and subjected to active dissolution by electrochemical polarization, the chemical composition of the surface film being analyzed by a micro-Auger electron spectroscopic (μ -AES) analysis and by X-ray photoelectron spectroscopy (XPS).

The effects of an increase in the Cr content and of the addition of Mo and Cu on the generation and growth of pits were investigated by a method that involves measuring changes with time in the spontaneous electrode potential of a steel specimen during a repeated heating and cooling test, using a cycle of $30^{\circ}\text{C} \rightarrow 90^{\circ}\text{C} \rightarrow 30^{\circ}\text{C}$ (4 h) in a 20%NaCl + $1\%\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ test solution (repeated pitting corrosion test⁸). A schematic diagram of the experimental apparatus is shown in **Fig. 1**.

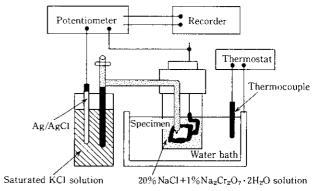


Fig. 1 Schematic diagram of experimental system

3 Experimental Results

3.1 Atmospheric Exposure Tests

3.1.1 Types of rust after the atmospheric exposure tests

The appearance of the specimens subjected to the atmospheric corrosion test for two years is shown in **Photo 1**. The types of corrosion are categorized as red rust and stain rust. With both types, pits can be seen at the corrosion-initiation points as shown in **Photo 2**. Large pits are apparent in the corroded area of red rust, while a large number of fine pits are apparent in the stain rust area. With the specimen on which red rust occurred, all parts other than the red rust area also show stain rust. With the specimens on which stain rust

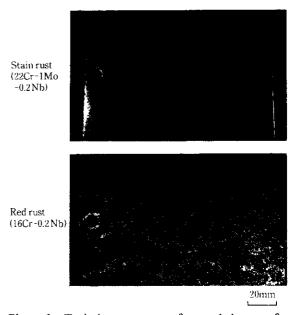


Photo 1 Typical appearance of corroded area after atmospheric corrosion test in Chiba for 2 years (Sample size: 15 cm × 10 cm)

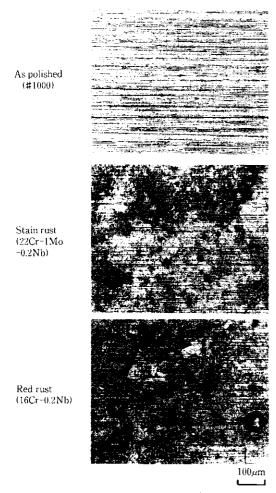


Photo 2 Appearance of specimens after atmospheric corrosion test at Oihama coastal area in Chiba for 2 years (Sample size: 15 cm × 10 cm)

occurred, however, a metallic luster remains on the surface other than the stain rust area.

3.1.2 Effects of alloying elements on atmospheric corrosion resistance

Attention was paid to early rusting, because it has been reported for stainless steel that atmospheric corrosion resistance depends on whether early rusting within one year occurs or not. Figure 2 shows the effects of Cr, Mo and Cu on the corroded area and type of rust after an atmospheric corrosion test for three months. Although the atmospheric corrosion resistance is improved by increasing the Cr content, an increase in Cr content to 24% is insufficient for preventing red rust when only Cr is added, and it is necessary to add not less than 26–30%Cr in order to completely prevent red rust. The addition of Mo and Cu is very effective for preventing red rust, and no rusting at all observed, especially for the 26Cr-4Mo and 30Cr-2Mo steels. The

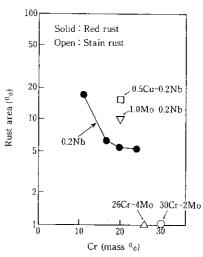


Fig. 2 Relationship between the rust area after atmospheric corrosion test for 3 months in Chiba and alloying elements

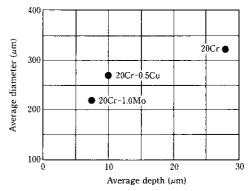


Fig. 3 Geometrical shape of pits observed on the specimens after 2 years of atmospheric corrosion test in Chiba

addition of Nb and Ti is also effective in preventing red rust, so that it is also necessary to add appropriate amounts of these C- and N-stabilizing elements.

Figure 3 shows the effects of Mo and Cu on the shape of pits that were generated on specimens after the atmospheric corrosion test for two years in Chiba. Both the Mo-bearing Cr steel and the Cu-bearing Cr steel have smaller pit diameters and depths than the Cr steel which does not contain these elements, and it is apparent that Mo and Cu are effective for suppressing the growth of pits.

3.1.3 Effects of alloying elements on change with time in atmospheric corrosion resistance

It became apparent that an increase in the Cr content and the addition of Mo and Cu were effective for improving atmospheric corrosion resistance. To evaluate the effects of these elements on the change with time

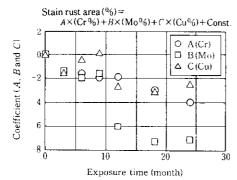


Fig. 4 Relationship between the coefficients of multiple regression equation obtained by atmospheric corrosion test in Chiba and exposure time

in atmospheric corrosion resistance, therefore, a multiple-regression analysis was conducted to evaluate the effect of each of the Cr, Mo and Cu elements on the stain rust area fraction for various exposure test periods. The relationships between the test period and the coefficients of the multiple-regression equation for each element are shown in Fig. 4. Each coefficient was obtained from the following regression equation:

Stain rust area fraction (%)
=
$$A \times (Cr\%) + B \times (Mo\%) + C \times (Cu\%)$$

+ constant
 A, B, C : constants

Each coefficient had a negative value, which shows that an increase in the amount of each of these elements or simply their addition is effective for improving the atmospheric corrosion resistance. As the test period was increased, the coefficient for Mo became increasingly negative, and it is thus apparent that the effect of Mo addition is strong.

3.2 Electrochemical Corrosion Tests

Figure 5 shows the effects of added Cr, Mo and Cu on the pitting potential (V'_{c10}) of ferritic 11-30%Cr stainless steels. An increase in the Cr content and the

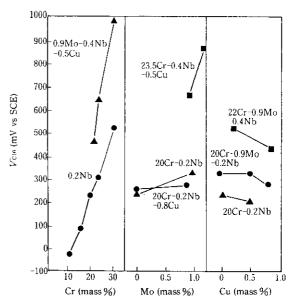


Fig. 5 Relationship between pitting potential (V'_{c10}) in 3.5% NaCl aqua solution at 30°C and alloying elements

addition of Mo raised the pitting potential and improved the pitting corrosion resistance, while the addition of Cu did not raise the pitting potential and made no contribution to an improved pitting corrosion resistance.

An investigation was made into the effects of these elements on the critical current for passivation (i_{crit}) that was determined from the potentiodynamic polarization curve. It was found that both an increase in the Cr content and the addition of Mo and Cu lower i_{crit} , suppressing the growth of pits.

3.3 Repeated Pitting Corrosion Tests

Figure 6 shows changes over time in the spontaneous electrode potential that was observed when 20Cr, 20Cr-1.0Mo and 20Cr-0.5Cu steels were subjected to the repeated pitting corrosion test. In the first cycle, the spontaneous electrode potential drops immediately after the start of the test and then oscillates at short intervals for all the specimens. Therefore, it seems that, in this

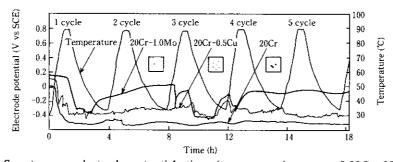


Fig. 6 Spontaneous electrode potential—time (temperature) curves of 20Cr, 20Cr-1Mo and 20Cr-0.5Cu steels in 20%NaCl+1%Na₂Cr₂O₇·2H₂O solution

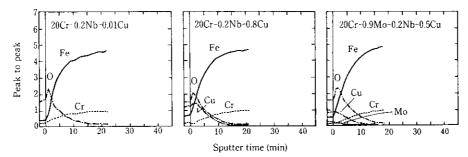


Fig. 7 μ -AES depth profile of chemical elements on the surface of the steels subjected to active dissolution by electrochemical polarization

range, pits were generated, grew and were arrested in the weaker parts of the passive film where surface defects and inclusions existed, and that this process was repeated. In the second and subsequent cycles, the potential of the 20Cr steel, once it drops, does not recover to the initial level even if the solution temperature drops, while the potential of the 20Cr-1.0Mo steel decreases with increasing number of cycles and recovers to the initial level in a short time. The potential of the 20Cr-0.5Cu steel is intermediate between those of the foregoing two steel specimens and repeats the oscillations.

The shape and number of pits generated on the specimen surfaces after the test were evaluated. One or two large pits were observed in the 20Cr steel, while one or two small pits in the 20Cr-1.0Mo steel and a large number of small pits in the 20Cr-0.5Cu steel existed.

From the results of this repeated pitting corrosion test and the electrochemical measurements, it appears that an increase in the Cr content and the addition of Mo suppress the generation of pits, and that an increase in the Cr content and the individual addition of Mo and Cu both suppress the growth of pits.

3.4 Surface Analysis

To simulate the portions of the pits subjected to active dissolution, the chemical composition of the surface film and the bonding condition of atoms were analyzed by μ -AES and XPS for specimens subjected to active dissolution in a 5%H₂SO₄ aqueous solution. The results of the μ -AES analysis of the chemical composition of the film in the depth direction are shown in Fig. 7. In the Mo-bearing and Cu-bearing steel specimens, an enrichment of these elements is apparent on the surface of each of these specimens. Table 2 shows the results of an examination for the presence of enriched elements by XPS. It was ascertained that Cr existed as Cr_2O_3 , that Mo existed in the form of MoO₃ (molybdate), and that almost all Cu existed as metallic copper.

Table 2 Results of XPS analysis on the surface of the steels subjected to active dissolution by electro-chemical polarization (metal/oxide ratio)

Steel	Fe	Cr	Cu	Mo
11Cr-0.2Nb-0.01Cu	0.30	0.36		
20Cr-0.2Nb-0.01Cu	0.37	0.27		
24Cr-0.2Nb-0.01Cu	0.45	0.44		
20Cr-0.9Mo-0.2Nb-0.01Cu	0.44	0.41	metal only	oxide only
20Cr-0.9Mo-0.2Nb-0.52Cu	0.26		metal only	oxide only
20Cr-0.9Mo-0.2Nb-0.8Cu	0.30		5.67	oxide only
20Cr-0.2Nb-0.8Cu	0.27		5.75	

Cr oxide: Cr₂O₃ Cu oxide: Cu₂O Mo oxide: MoO₃

4 Discussion

4.1 Mechanism for Improving the Atmospheric Corrosion Resistance of Mo-Bearing and Cu-Bearing Steel Specimens

As already described, the addition of Mo and Cu was effective for improving atmospheric corrosion resistance and, in particular, for preventing the generation of red rust, the effect of Mo addition becoming stronger with passing time. The reason for this phenomenon is considered next.

Whether or not a steel specimen possesses strong atmospheric corrosion resistance depends on the two factors of generation and growth of pits, and it follows that atmospheric corrosion resistance can be expressed in the following ways:

$$\begin{pmatrix} \text{Atmospheric} \\ \text{corrosion} \\ \text{resistance} \end{pmatrix} \propto \begin{pmatrix} \text{capability for} \\ \text{suppressing} \\ \text{the generation} \\ \text{of pits} \end{pmatrix} \times \begin{pmatrix} \text{capability for} \\ \text{suppressing} \\ \text{the growth} \\ \text{of pits} \end{pmatrix}$$

The capability for suppressing the growth of pits can be related to the pitting potential (V'_{c10}) , which is considered to correspond to the difficulty of pit generation, and to the critical current for passivation (i_{crit}) , which is considered to correspond to the growth of pits. As

described earlier, Mo increased $V'_{\rm cl0}$ and, at the same time, reduced $i_{\rm crit}$, while Cu reduced $i_{\rm crit}$. Therefore, Mo suppresses both the generation and growth of pits, and Cu suppresses the growth of pits; these two elements improve atmospheric corrosion resistance in this manner.

Next, the dependence of the effect of Mo addition on the exposure period is considered in terms of the generation and growth of pits. According to Shibata et al., 11) the breakdown potential of the passive film depends on the potential maintained in the passive state, the higher the potential maintained in the passive state when the film is formed, the higher being the breakdown potential. It seems that when the film is formed on the highpotential side, the film thickness is large and the enrichment ratio of Cr in the film is high, with the result that the film has a strong structure. Furthermore, it has been reported that, although Mo is not enriched in the film, Mo addition is effective for increasing the enrichment ratio of Cr in the film formed at the same potential.¹²⁾ The change with time in the film structure is next considered. The pitting corrosion resistance of steel changes to the noble side with immersion time during a passivation treatment, and it also seems, in the exposure test, that the strength of the passive film similarly increases with the exposure period.

When the film structure is greatly changed by exposure to the potentials in the severe corrosive environment of the atmospheric corrosion test, the Mo-bearing Cr steel has a higher Cr content in the film formed at the same potential than either the Cr steel or Cu-bearing Cr steel has, and the pitting potential of such Mobearing Cr steel is high (the passive state expands to the high-potential side) when changes with time are taken into consideration. It seems, therefore, that when the film structure changes during a long exposure period, the film grows in a higher-potential region, with the result that a film with high Cr content is formed.

In contrast to this, Cu addition does not cause the pitting corrosion to expand to the high potential side, and no enrichment of Cr in the film occurs. Therefore, when the Cu-bearing Cr steel is exposed to an environment that is likely to destroy the film such as the Clion, more pits are generated than in the Mo-bearing Cr steel. Furthermore, because the generation of pits is more strongly suppressed with the growth of the film, it seems that the change with time in the capability for suppressing the generation of pits is greater in the Mobearing Cr steel than in the Cr steel without Mo.

The growth of pits is next discussed. Cu and Mo are dissolved within the pits in the active state, in which the pH value has been reduced by the hydrolysis accompanying metal dissolution. As described in Sec. 3.4, Mo becomes MoO_4^{2-} (molybdate) by the following reactions (1) and (2):

$$MoO_3 + H_2O \longrightarrow MoO_4^{2-} + 2H^+ \cdots (1)$$

$$Fe^{2+} + MoO_4^{2-} \longrightarrow FeMoO_4 \downarrow \text{ (slightly soluble compound)} \cdots (2)$$

MoO₄²⁻ forms a stable compound that is slightly soluble and precipitates in the dissolved regions on the inner surfaces of pits, thus suppressing the growth of the pits by reducing the relative anode area.

Cu is eluted as Cu ions and then reprecipitates as metallic copper, thus suppressing active dissolution. However, it seems that it is difficult to completely stop the growth of pits, because Cu does not exist stably as metallic copper in some corrosive environments and may be eluted as Cu²⁺ ions. ¹⁴⁾ When the two aspects of the capability for suppressing the generation of pits and the capability for suppressing the growth of pits are thus considered, it is apparent that the addition of Mo is effective for improving atmospheric corrosion resistance. Furthermore, the higher the Cr content of steel, the more marked is the effect of Mo addition on improving the pitting corrosion resistance. Mo addition to high-Cr steels therefore seems to be especially effective for improving atmospheric corrosion resistance.

4.2 Correlation between the Atmospheric Corrosion Resistance Determined by the Atmospheric Exposure Test and that Determined by the Laboratory Corrosion Test

The correlation between the atmospheric corrosion resistance determined by the atmospheric exposure test and that determined by the laboratory corrosion test was examined to establish a simple method for evaluating atmospheric corrosion resistance.

Rust was caused by pits in all cases, so that the rust area fraction (%) is related to the total amount of corrosion in all pits generated in an exposure test specimen and can be expressed by the following equation:

$$\binom{\text{rust area}}{\text{fraction (\%)}} \propto \binom{\text{number}}{\text{of pits}} \times \binom{\text{mean size}}{\text{of pits}} \cdots \cdots (3)$$

The mean size of pits depends on the amount of metal dissolved from the pits, i.e., the growth rate of pits, so that Eq. (3) can be rewritten as Eq. (4):

$$\begin{pmatrix} \text{rust area} \\ \text{fraction (\%)} \end{pmatrix} \propto \begin{pmatrix} \text{number} \\ \text{of pits, } N_{\text{pit}} \end{pmatrix} \times \begin{pmatrix} \text{growth rate} \\ \text{of pits, } V_{\text{pit}} \end{pmatrix} \cdots (4)$$

As described earlier, dissolution in the active state may proceed within pits and, therefore, the growth rate of pits may correspond to the active dissolution rate of the steel itself. Therefore, when the critical current for passivation (i_{crit}) obtained from the potentiodynamic polarization curve in a 5% H_2SO_4 aqueous solution is used as the active dissolution curve for steel, Eq. (4) can be rewritten as Eq. (5):

Rust area fraction (%)
$$\propto N_{\rm pit} \times i_{\rm crit} \cdot \cdots \cdot (5)$$

Specimens with various pitting potentials were subjected to the CASS test (JIS H 8502). The relationship

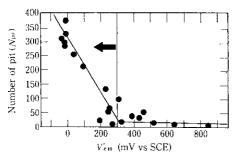


Fig. 8 Relationship between the number of pit by CASS test and pitting potential (V'_{c10}) in 3.5% NaCl agua solution at 30°C

between the number of pits generated in these specimens and the pitting potential of each steel specimen is shown in Fig. 8. When the pitting potential of each specimen is lower than 300 mV vs SCE, which is considered to be the corrosion potential in the CASS test, the number of generated pits is inversely proportional to the critical pitting potential of the steel. However, when the pitting potential of the steel is higher than 300 mV vs SCE, little corrosion is apparent. Based on this result, the corrosion behavior can be classified into two types according to the level of pitting corrosion to the steel.

When $V'_{\rm c10} > V_{\rm R.CASS}$ (the critical pitting potential in the CASS test), little corrosion was observed. In contrast to this, when $V'_{\rm c10} < V_{\rm R.CASS}$, the following relationship holds true:

Consequently, Eq. (5) can be expressed as follows:

Rust area fraction(%)
$$\propto (V_{\text{R.CASS}} - V'_{\text{c10}}) \times i_{\text{crit}}$$
 (7)

Specimens with various pitting potentials were subjected to the CASS test. The relationship between the area fraction (%) of rust generated in these specimens and $(V_{R.CASS} - V'_{c10}) \times i_{crit}$ is shown in Fig. 9. The rust area fraction is linearly correlated with $(V_{R.CASS} - V'_{c10})$ \times i_{crit} . Therefore, the same concept was applied to the atmospheric corrosion resistance in a real environment. Figure 10 shows the correlation between the initial corrosion and the pitting potential after three months of the atmospheric corrosion test in Chiba. In this figure, V_1 and V_2 denote the pitting potential of the steel at which no more red rust and stain rust, respectively, were formed in the atmospheric corrosion test (critical pitting potential V_{crit}), the rust area fraction (%) of the respective types of rust being inversely proportional to the pitting potential (V'_{c10}) in the potential range below V_1 and V_2 , respectively. Figure 11 shows the relationship between the rust area fraction in the atmospheric corrosion test and the concept expressed by Eq. (7). There is a correlation between the two, a steel specimen with high V'_{c10} and low i_{crit} providing high atmospheric cor-

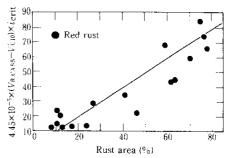


Fig. 9 Relationship between the value of $(V_{\text{R.CASS}} - V'_{\text{c10}}) \times i_{\text{crit}}$ and the rust area by CASS test

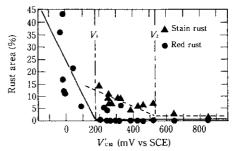


Fig. 10 Relationship between the rust area after atmospheric corrosion test in Chiba for 3 months and pitting potential in 3.5% NaCl aqua solution at 30°C

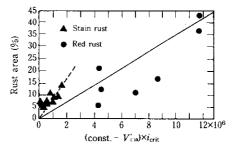


Fig. 11 Relationship between the rust area after atmospheric corrosion test in Chiba for 3 months and the value of (const. $-V'_{c10}$) $\times i_{crit}$

rosion resistance. Since an increase in the Cr content and the addition of Mo increase the value for V'_{c10} and reduce the value for i_{crit} , it is necessary to use an Mobearing steel with a high Cr content to ensure adequate atmospheric corrosion resistance in a severe corrosive environment such as that in coastal areas.

In Fig. 10, V_1 and V_2 can be considered to correspond to the corrosion potential in each exposure environment. Therefore, by finding this pitting potential for

each exposure test period and test location, and then determining the relationship between the pitting potential and such corrosive environment factors as SO₂ and Cl⁻, it may be possible to use the pitting potential as the criterion for selecting a material to suit the environment in which they will be used.¹⁵⁾

4.3 Criteria for Selecting Materials to Suit a Service Environment

As mentioned in the previous section, there is a crtical pitting potential (V_{crit}) for each type of steel at which rust is not generated within a defined period in the given environment. Therefore, the dependence of $V_{\rm crit}$ on the exposure test period and on the corrosive environment are next examined. Figure 12 shows the relationship between the effect of exposure period on the stain rust area fraction and the pitting potential observed after the exposure test for two years in Chiba (Oihama). In this figure, the points at which the four lines found for the different exposure test period intersect with the abscissa indicate V_{crit} , which increases with increasing exposure time. The relationship between $V_{\rm crit}$ and the exposure time is shown in Fig. 13, and this tendency toward an increase in V_{crit} is especially marked within one year. According to Yoshii, Muto, et al., 5,9,10)

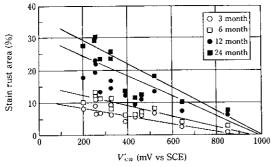


Fig. 12 Relationship between atmospheric corrosion resistance in Chiba and pitting potential in 3.5% NaCl aqua solution at 30°C

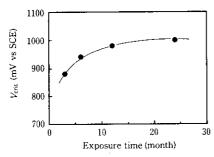


Fig. 13 Relationship between critical pitting potential ($V_{\rm crit}$) in 3.5% NaCl solution at 30°C and exposure time

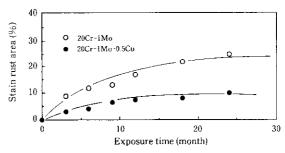


Fig. 14 Relationship between stain rust area and exposure time

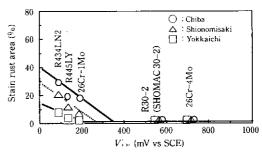


Fig. 15 Relationship between rust area after 3 years exposure in 3 test-fields and pitting potential (V'_{c10}) in 3.5% NaCl aqua solution at 70°C

who have examined the change with time in atmospheric corrosion resistance, the progress of corrosion tends to be faster in the initial stage of the exposure period and then slows down with increasing exposure. It therefore seems that, although $V_{\rm crit}$ shows dependence on the exposure time in the initial stage, its value approaches a constant value within two or three years. In the Chiba (Oihama) test, 20Cr-1Mo steel and 20Cr-1Mo-0.5Cu steel were exposed to the atmosphere for two years. The change in the stain rust area fraction observed on these specimens is shown in Fig. 14. The stain rust area fraction reaches a maximum value after about one year of exposure. Figure 15 shows the relationship between the critical pitting potential $V_{\rm crit}$ and the pitting potential (3.5% NaCl, 70°C) found from the g high-Cr results of the exposure tests on Mo-b steel specimens conducted in Chita (Oihama), Yokkaichi and Shionomisaki. Each test site has a critical pitting potential at which rusting did not occur. Among the three test sites, Chiba (Oihama) had the highest critical pitting potential and, therefore, it is apparent that the corrosive environment in Chiba was more severe than those at the other test sites. In Fig. 15, RIVER LITE 30-2 is a 30Cr-2Mo steel (SUS447J₁) and shows a higher pitting potential than the critical pitting potential at each exposure test site, indicating this steel has adequate atmospheric corrosion resistance for a severe coastal environment.

5 Conclusions

The effects of alloying elements (Cr, Mo and Cu) on the atmospheric corrosion resistance of ferritic stainless steels were investigated by conducting atmospheric exposure tests and laboratory corrosion tests with the following results:

- (1) Two types of rust, i.e., red rust and stain rust, were generated by the atmospheric exposure test. In both types, pitting was the rust-initiation point.
- (2) Although an increase in Cr content improved the atmospheric corrosion resistance, a single factor of Cr increase up to and including 24% is not enough for complete prevention of red rust. The addition of Mo and Cu each was not only effective in preventing red rust but also in reducing the diameter and depth of pits.
- (3) The effect of added Mo on improving the atmospheric corrosion resistance increased with increasing exposure time. However, the effect of added Cu on improving the atmospheric corrosion resistance was small.
- (4) An increase in the Cr content and the addition of Mo raised the pitting potential and suppressed the generation of pits. The addition of Mo and Cu each reduced the critical current for passivation and suppressed the growth of pits.
- (5) It is considered that dissolved Mo and Cu were precipitated as MoO₃ and metallic copper, respectively, within the pits and suppressed anodic dissolution, thereby slowing down the growth rate of the pits.
- (6) In the atmospheric exposure test, a correlation exists between the atmospheric corrosion resistance and pitting potential, with the presence of a critical pitting potential (V_{crit}) where rusting did not occur for each test environment. This critical pitting potential seems to indicate the corrosive environmental potential for each exposure site.
- (7) The rust area fraction can be expressed by the

- product of the number of generated pits and the growth rate of the pits, and is proportional to $(V_{\rm crit}-V_{\rm c10}') \times i_{\rm crit}$.
- (8) In a severe corrosive environment such as a coastal area, it is necessary to use Mo-bearing high-Cr ferritic stainless steel, and 30Cr-2Mo steel (SUS447J₁) provides adequate atmospheric corrosion resistance to this environment.

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