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Performances of Coastal Weathering Steel

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Abstract

New weathering steel, usable for bridges without painting in an airborne chloride area higher than 0.05 mg/dm²/day was developed by removing Cr, which is harmful under a high airborne chloride condition, together with more than 3% addition of Ni, which effectively produces a protective rust layer on the surface of the steel. Through the result of the 9 year exposure test at coastal site, where the deposition rate of airborne chloride is 1.3 mg/dm²/day, the formation of a protective rust layer on the surface of the developed steel to effectively decrease in the corrosion rate have been confirmed. The average corrosion loss was 0.15 mm for 9 years, which was 1/10 of ordinary weathering steel. Enrichment of Ni in the inner layer of rust is considered to be a key to inhibits invasion of Cl^- to facilitate the formation of a protective rust layer. Also, the steel with enhanced Ni addition itself has the effect on reducing its corrosion rate.

1. Introduction

Many of the steel plates used to build large structures are painted to prevent rusting. Since the paint deteriorates with use, it is normal to repaint every 10 years. The painting operation itself is costly, so that the maintenance expenditure through out the structural life amounts to a huge costs. Given these considerations, it is required to minimize the total life cycle cost of steel bridges by reducing maintenance work.

Weathering steel that can be used in the unpainted condition (refer to JIS G 3114, Hot-Rolled Atmospheric Corrosion Resisting Steels for Welded Structures) has been known to be effective in reducing the life cycle cost of steel bridges. The weathering steel forms a tenacious layer of rust produced by its own corrosion to inhibit its subsequent corrosion, which allows elimination of painting and repainting to minimize life cycle cost of the structure. More over its color changes from initial red rust to somber dark brown in a few years, which makes it an excellent landscaping material that aesthetically blends into the surrounding environment. Conventional weathering steel sometimes corrodes to form an anomalous rust when exposed to the atmosphere with high airborne sea salt content. In 1993, the Public Works Research Institute Ministry of Construction, the Japan Association of Steel Bridge Construction, and the Kozai Club proposed the following weathering steel application criteria (refer to **Fig. 1**) after 9 year joint research project[1)]:

1) Airborne salt deposition rate $\leq$ 0.05 mg/dm²/day (mdd)
2) Measurement of the airborne salt deposition rate may be omitted in the regions designated as shown in **Fig. 1**.

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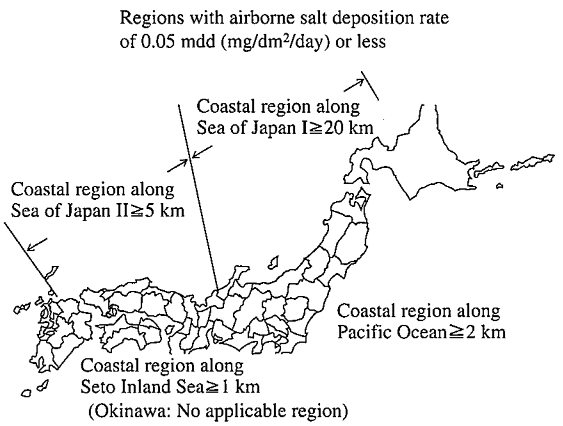


Fig. 1 Application criterion for weathering steel (JIS SMA) in unpainted condition (0.05 mdd or less) (Ministry of Construction, Kozai Club, and Japan Association of Steel Bridge Construction)

These criteria mean that weathering steel cannot be used in coastal zone in Japan.

In recent years, prohibition of spiked tires has markedly increased the application areas and amounts of deicing salt in winter. A few years after its increased use, the deicing salt began to have an adverse effect on the corrosion of bridges and other structures. Under such circumstances, the use of conventional weathering steel is also restricted even in mountainous regions. Given these conditions, the Nippon Steel has developed new types of weathering steels for use in regions with high airborne salt deposition rates.

2. Establishment of Guidelines for Improvement in Coastal Weather Resistance

2.1 Derivation of effective elements by accelerated corrosion test

Phosphorus, copper, nickel, and chromium have been traditionally regarded as elements improving the weathering resistance of steels[2]. However, their additions to conventional corrosion resistant low alloy steels are 1 mass% at most. Systematic studies on the effect of alloying elements to the improvement of anti-airborne salinity weathering properties were carried out by Zaizen et al[3]. in terms of Cr, and by Kihira and Ito[4] regarding various iron-based binary alloys[4]. To confirm whether the reported trend can be observed by steels with base chemical compositions in realistic ranges, phosphorus, copper, nickel or chromium added Si-Mn steels were prepared. Using these test pieces, simulated marine atmosphere exposure tests were carried out.

2.1.1 Materials

Compositional systems based on the 0.05 mass%C-0.25 mass%Si-1.50 mass%Mn and with the phosphorus, copper, chromium and nickel contents changed at four to five levels in the ranges of 0.005 to 0.5 mass%, 0 to 1.5 mass%, 0 to 15 mass% and 0 to 20 mass%, respectively, were melted in air into 10-kg ingots, hot rolled to a thickness of 8 mm, and used as test materials. Specimens, measuring 3 mm thick, 50 mm wide and 150 mm long, were taken from the mid-thickness of each plate. The specimens were ground on all surfaces to the ▽▽▽ finish, ultrasonically cleaned in acetone, and tested.

2.1.2 Simulated marine atmosphere exposure test

The weathering properties resistance of the specimens were evaluated by a simulated marine atmosphere exposure test for one year, in which the specimens were sprayed on the top and bottom surfaces with a 5% NaCl water solution once a day. The exposure test was conducted at the site of the former R & D Laboratories-II in Sagamihara City, with the specimens installed on a rack facing south, tilted at 55°.

2.1.3 Test results

The results are shown in **Fig. 2**. The average thickness loss of the specimens decreases with increasing phosphorus and copper contents. As for chromium, corrosion rate is enhanced in the low content region while the average thickness loss decreases with increasing chromium content more than 5%. The effect of Ni on to the improvement weathering properties was drastic within the range of nickel content up to 5%. From these results, enhanced nickel addition together with elimination of chromium was determined as a guiding principle for development of anti-airborne salinity weathering steel.

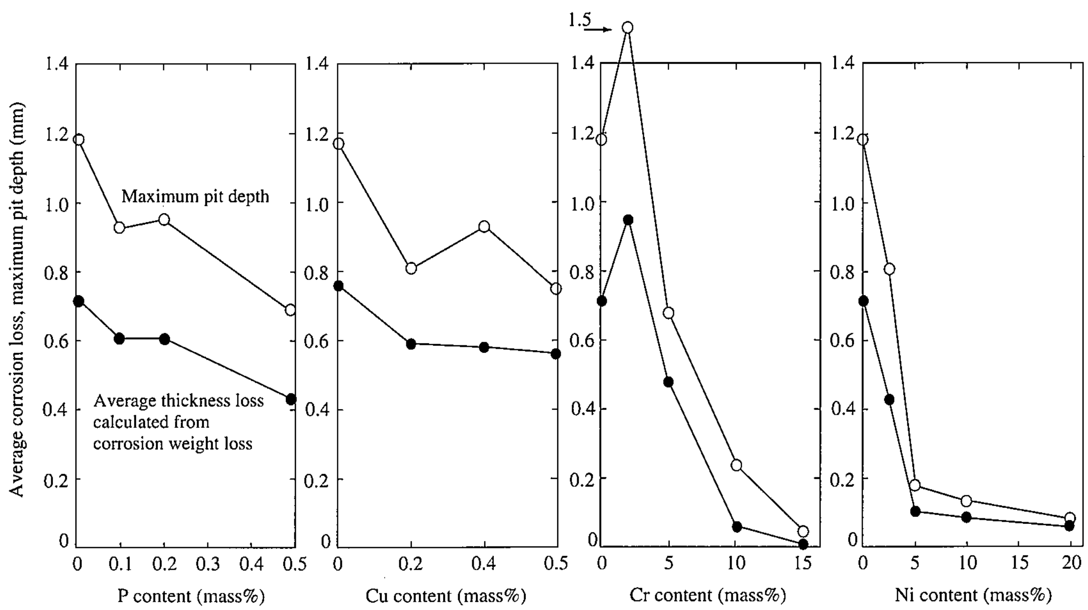


Fig. 2 Effects of alloying elements on corrosion behavior after 1 year of salt spray exposure test

2.2 Long-term exposure tests at coastal weathering site to obtain optimum nickel content

Specimens were prepared with different nickel contents for long term exposure test at coastal weathering site. The purposes of this test are to verify whether or not nickel additions would be effective in an actual environment, and to study the optimum nickel content.

2.2.1 Materials

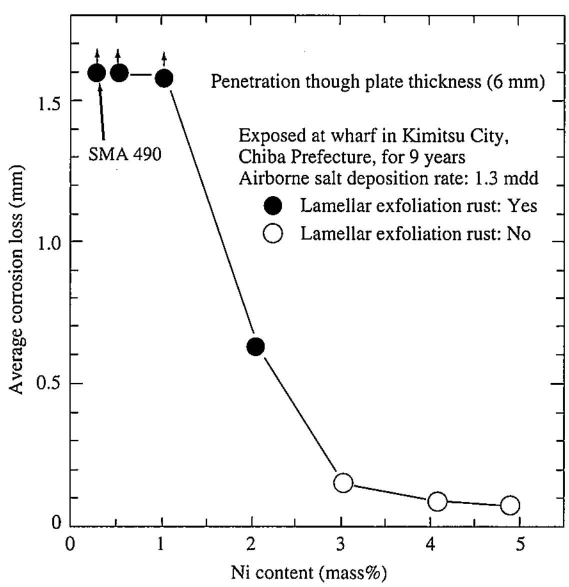
0.05%C-0.05%Si-1.0%Mn-0.008%P-0.4%Cu was adopted as the basic composition, and the nickel content was changed at six levels in the range from 0 to 5 mass%. Each steel was vacuum melted into a 30-kg heat and hot rolled to a thickness of 8 mm. Specimens, measuring 6 mm thick, 40 mm wide and 120 mm long, were machined from each plate. The specimens were ground on all surfaces to the ▽▽▽ finish, ultrasonically cleaned in acetone, and tested. Similarly processed weathering steel (JIS SMA 490) was used as a control material.

2.2.2 Exposure test methods

The exposure site was the coastal area of Kimitsu City, Chiba Prefecture, where the airborne salt deposition rate reaches 26 times of the application criterion of 0.05 mdd for conventional weathering steel (JIS-SMA). (The airborne salt deposition rate is 1.3 mdd, and the distance from the coast is about 10 m.) The specimens were installed vertically and facing south-east. After 6 and 9 years of exposure, their corrosion weight loss was measured.

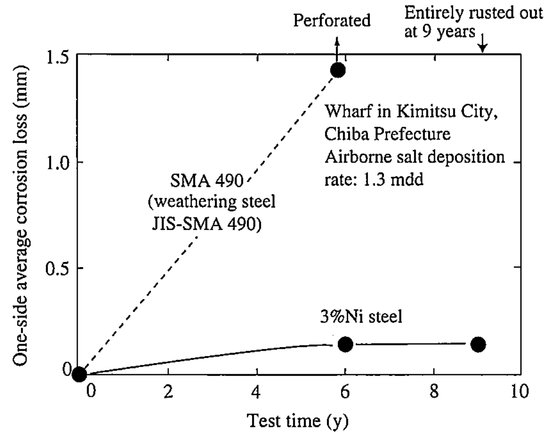
2.2.3 Test results

Fig. 3 shows the corrosion loss of specimens with different nickel contents after 9 years of exposure. Corrosion markedly progressed in the specimens with a nickel content of less than 1 mass%, and in which the 6-mm test plate was completely rusted out. When the nickel content was 2 mass%, average corrosion loss was 0.6 mm per a side. When the nickel content is more than 3 mass%, the corrosion loss was less than 0.15 mm. A nickel content of 3% or more is thus found to be extremely effective in improving the weathering resistance of the steel. Lamellar exfoliation of rust was observed on the specimens with a nickel content of 2%, and tightly adhering rust was formed on the specimens with a nickel content of more than 3 mass%. From these data, it was considered that 3 mass% Ni addition is sufficient to ensure weathering resistance of the steel with 0.4 mass% copper.



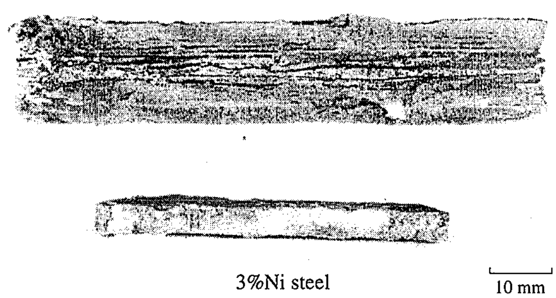
Composition: 0.05C-0.05Si-1.0Mn-0.008P-0.4Cu-xNi

Fig. 3 Effect of nickel content on atmospheric corrosion behavior in high-chloride ion environment



Composition: 0.05C-0.05Si-1.0Mn-0.008P-0.4Cu-3Ni

Fig. 4 Change with time in corrosion loss of 3%Ni steel in high-chloride ion environment



Specimen: 40 × 120 × 6 mm thick
Original specimen thickness: 6 mm

Photo 1 Through-thickness appearance of 3%Ni steel and weathering steel (SMA 490) exposed in coastal area of Kimitsu City for 9 years

Fig. 4 shows the change with time in the corrosion loss of the conventional weathering steel SMA 490 and the 3%Ni-0.4%Cu steel. The weathering steel was perforated at 6 years and entirely rusted out at 9 years. The corrosion loss of the 3%Ni steel at 9 years was almost the same as that at 6 years. This means that the growth of rust on the 3%Ni steel was inhibited by protective rust formation. **Photo 1** shows the through-thickness sections of the steels after 9 years of exposure. The SMA 490 steel has entirely turned into lamellar rust and has increased four times in volume, while the 3%Ni steel exhibited excellent weathering resistance.

3. Structural Analysis of Rust

To study the weathering resistance mechanism of the nickel-bearing weathering steel, the rust formed on the steel surfaces was analyzed. As analytical methods, (1) a polarized light microscope was used to observe the cross section of the rust layer; (2) local laser Raman spectroscopy was used to analyze the cross section of the rust layer; (3) a transmission electron microscope (TEM) was used to observe the rust particles; and (4) an electron probe microanalyzer (EPMA) was used to analyze the cross section of rust for elements.

3.1 Materials

The 3%Ni steel exposed for 9 years in the coastal area in Kimitsu City and the conventional weathering steel exposed for 35 years in Sagamihara City as already described elsewhere[5] were used as materials for polarized light microscopy and local laser Raman spectroscopy. The SMA 490 steel exposed for 9 years in the coastal area in Kimitsu City was used as control material for polarized light microscopy. EPMA elemental analysis was also performed on the 3%Ni steel to investigate the distributions of nickel and chloride. The TEM observation of rust particles was carried out using 5%Ni steel and the nickel-free carbon steel (SM 490 B), both exposed for 1 year in Okinawa, in order to clarify the variation of the rust structure with the nickel content.

3.2 Test methods

For the polarized light microscopy, laser Raman spectroscopy was used, and in the EPMA elemental analysis of the cross section of the rust layer, each material was cut into a 20 × 10 mm piece of the original thickness, embedded in a resin, polished to mirror finish, and used as a specimen, so that cross section of the rust is observed.

For the TEM observation of rust particles, the outer and inner layers of rust formed on each material were collected with a gold brush and an electric chisel, and ground with distilled water in an agate mortar. The rust particles were dispersed in an acetic acid solution, scooped with a collodion film-covered gold mesh, dried, and observed under the TEM.

3.3 Observation result

3.3.1 Polarized light microscope observation

Polarized light micrographs of the cross sections of rust layers formed on the 3%Ni steel and the steel SMA 490 exposed in the coastal area of Kimitsu City for 9 years and on the weathering steel exposed in Sagamihara City for 35 years are shown in **Photo 2a)** to **2c)**, respectively. The rust formed on the 3%Ni steel reveals a two-layer structure composed of a inner, optically isotropic layer and an outer, optically active layer showing orange polarization. This rust structure is similar to that of the rust formed on the weathering steel exposed in Sagamihara City with a low airborne salt deposition rate of 0.025 mdd for 35 years as shown in **Photo 2c)**. When the weathering steel (SMA 490) exposed under the same conditions as the 3%Ni steel is observed under the polarized light microscope, the entire rust indicates orange polarization as shown in **Photo 2b)**.

From the above results, it is presumed that in an environment with a high airborne salt deposition rate, the 3%Ni steel forms rust of the same structure as that on the conventional weathering steel in a mild environment.

3.3.2 Analytical results of laser Raman spectroscopy

The rust formed on the 3%Ni steel exposed in the coastal area of Kimitsu City for 9 years and the rust formed on the weathering steel exposed in Sagamihara City for 35 years were analyzed by a laser Raman spectrometer to examine their crystal structure. The results are shown in **Figs. 5** and **6**, respectively. A polarized light micro-graph of the points analyzed by the laser Raman spectrometer is included in each figure.

As shown in **Fig. 5**, the 3%Ni steel reveals peaks of α-FeOOH and other constituents outside of the orange optically active layer. Peaks indicating such a crystal structure are not observed in the inner optically isotropic layer.

In the laser Raman spectroscopy results of the rust formed on the weathering steel exposed in Sagamihara City for 35 years shown in **Fig. 6**, peaks are observed in the outer orange optically active layer, but peaks indicating crystal structure were not recognized in the inner optically isotropic layer.

In this way, the inner layers of the protective rust formed both on the 3%Ni and the weathering steels are considered to be low in crystallinity.

3.3.3 TEM results

Photo 3 shows TEM micro-graphs of particles of rust formed on the 5%Ni steel and the SM 490 B exposed in atmosphere for 1 year in Okinawa. The upper micro-graphs are those of rust particles

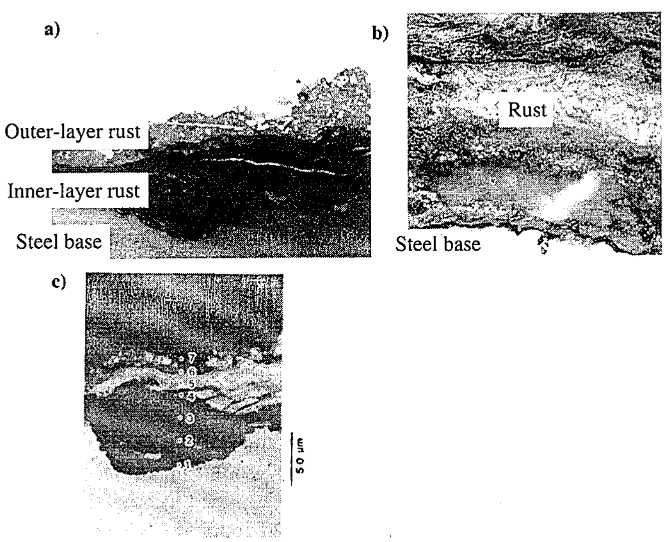


Photo 2 Polarized light micrographs of rust cross sections
a) 3%Ni steel exposed in coastal area of Kimitsu City for 9 years
b) Weathering steel exposed in coastal area of Kimitsu City for 9 years
c) Weathering steel exposed in Sagamihara City for 35 years

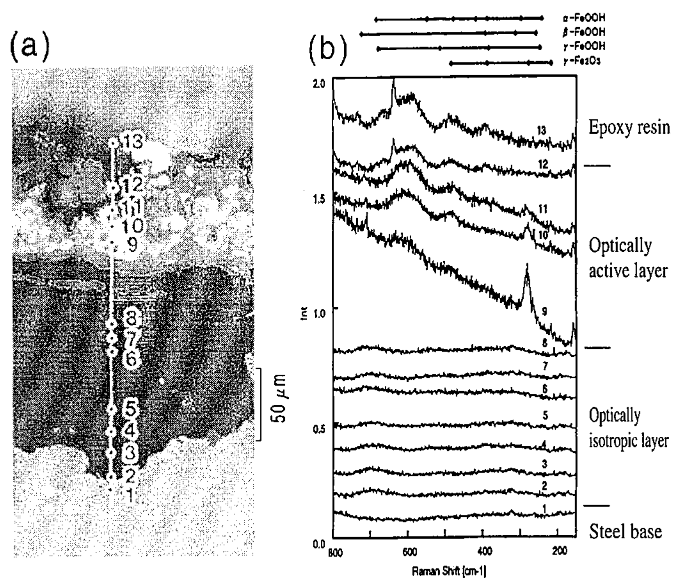


Fig. 5 Results of analysis by laser Raman spectroscopy of cross section of rust formed on 3%Ni steel exposed in coastal area of Kimitsu City for 9 years

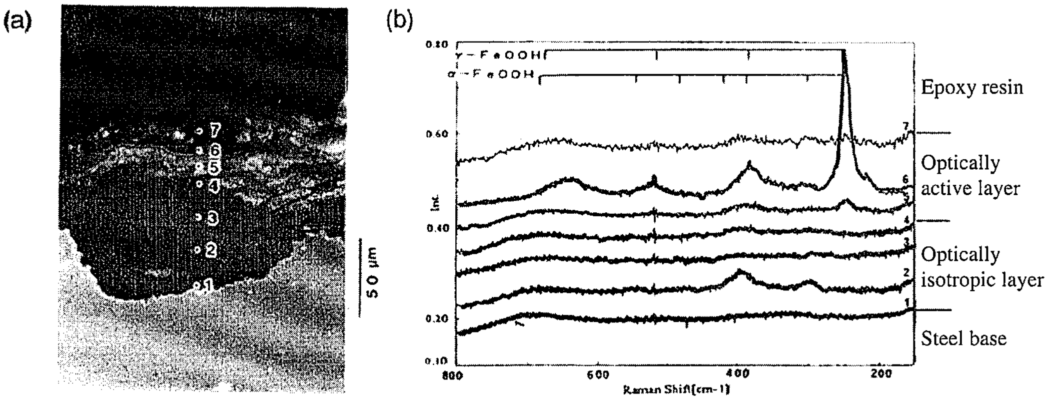


Fig. 6 Results of analysis by laser Raman spectroscopy of cross section of rust formed on weathering steel exposed in Sagamihara City for 35 years

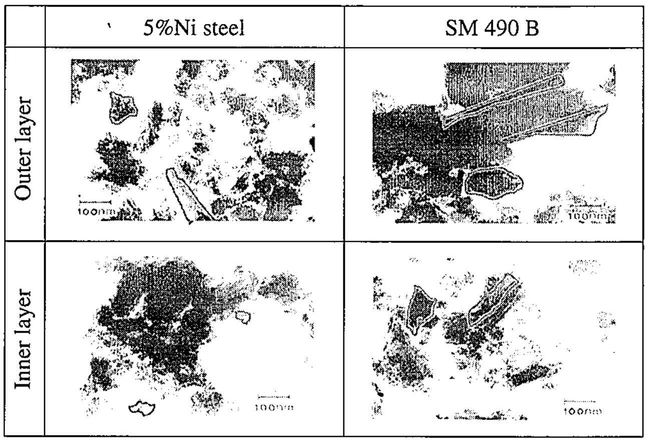


Photo 3 TEM observation of rust particles formed on 5%Ni steel and steel SM 490 B exposed in Okinawa for 1 year

taken from the outer-layer rust, while the lower micro-graphs are those from the inner-layer rust.

Largely grown acicular rust particles are recognized in the rust particles taken from the outer-layer rust of both steels. Many largely grown acicular particles are recognized in the inner-layer rust of the SM 490 B. In the case of the 5%Ni steel, such coarse acicular rust particles are extremely small in number, and the rust particles are generally very fine. This finding suggests that the coarsening of rust particles in the inner layer is inhibited by the addition of nickel.

3.3.4 EPMA analysis

To observe the elemental distribution of the rust layer formed on the 3%Ni steel, EPMA analysis was performed on the cross section of the rust formed on the 3%Ni steel exposed for 9 years.

Fig. 7 shows the distribution of nickel and chlorine on the cross section of the rust layer. The nickel is enriched in the inner layer, and its concentration is higher than in the substrate. The chlorine is enriched in the outer layer, and is recognized little in the inner. This suggests the possibility that the entry of chloride ions into the nickel enriched inner-layer rust is retarded.

3.4 Rust structure and corrosion protection mechanism of 3%Ni steel

The rust formed on the 3%Ni steel had quite similar structure as the rust formed when the conventional weathering steel is exposed in a mild environment. The structure consisted of the inner optically isotropic and the outer optically active layers under the polarized light microscope. Laser Raman spectroscopy indicated that the inner layer is composed of ultra fine rust particles that are amorphous or low in crystallinity. Whether or not the rust particles are amorphous will have to be investigated by other analytical techniques. The coagulated fine rust particles were observed by TEM, indicating the formation of the tightly adherent inner rust.

The TEM observation and the EPMA element distribution analysis clarified that the nickel-bearing steel features the enrichment of nickel in the inner rust, which indicates the prevention of coarsening

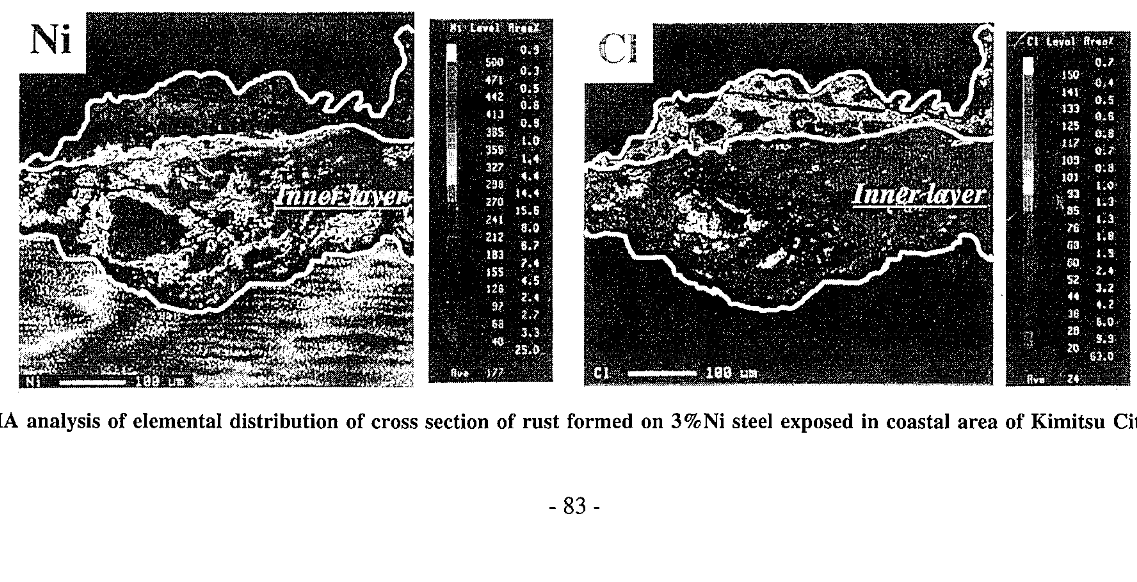


Fig. 7 EPMA analysis of elemental distribution of cross section of rust formed on 3%Ni steel exposed in coastal area of Kimitsu City for 9 years

Table 1 Chemical compositions of the developed steels

	C	Si	Mn	P	S	Cu	Ni	V	Cr	P_{CM}*
SMA 490CW-Mod	0.10	0.20	0.61	0.006	0.002	0.40	3.07	–	0.02	0.21
SMA 570WQ-Mod	0.09	0.19	1.33	0.004	0.002	0.38	2.97	0.02	0.02	0.33
JIS G 3114	≤0.18	0.15/0.65	≤1.40	≤0.035	≤0.035	0.30/0.50	0.05/0.30	–	0.45/0.75	

* $P_{CM} = C + Si/30 + Mn/20 + Cu/20 + Ni/60 + Cr/20 + Mo/15 + V/15+5B$

Table 2 Mechanical properties of the developed steels

Standard		Plate thickness (mm)	Tensile test			Charpy impact test	
			Yield point (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Test temperature (°C)	Absorbed energy (J)
SMA 490CW	New steel	9	439	531	28	0	163*
		25	405	512	26	0	230
	Standard	≤16	≥365	490-610	≥15	0	≥47
		≤40	≥355	490-610	≥19	0	≥47
SMA 570WQ	New steel	25	590	670	29	–5	279
		40	599	666	29	–5	310
	Standard	> 20	≥450	570-720	≥20	–5	≥47

*5-mm thick sub-size

Table 3 Welding conditions and joint test results (SMA 570WA-Mod)

Plate thickness	Welding conditions						Joint tensile strength	Weld metal strength		Joint Charpy impact test				
	Groove	Welding process	Welding material	Current (A)	Voltage (V)	Heat input (kJ/mm)	(JIS 1A) (N/mm^2)	Yield strength (N/mm^2)	Tensile strength (N/mm^2)	Test temperature (°C)	Absorbed energy Weld metal	Fusion line	HAZ 1 mm	HAZ 3 mm
40 mm	X	SAW	Y-3Ni	850	36	50	672	526	664	–5	148	156	306	317

of rust particles, and inhibition of entry of chloride ions.

The rust formation and corrosion protection mechanisms will have to be studied by a variety of analyses. Nevertheless, the 3%Ni steel is considered to form tightly adherent rust particles in the inner layer of the rust to protect the steel from the atmospheric corrosion.

4. Mechanical and Welding Properties

Based on the above-mentioned basic study results, the C-Si-Mn-0.4%Cu-3%Ni-Cr-free system was adopted as the basic composition of coastal weathering steel, and SMA 490CW-Mod and SMA 570WQ-Mod equivalent steels were trial-made at a mill. At the mill, 9, 25, and 40 mm thick plates were made by a process consisting of BOF steel-making, secondary refining, continuous casting, slab conditioning, reheating, plate rolling, and heat treatment (for SMA 570WQ). Their properties were then evaluated as follows.

The chemical compositions and base-metal mechanical properties of the developed steels are given in **Tables 1** and **2**, respectively. Their mechanical and welding properties all satisfy the JIS requirements for SM 490CW and SMA 570WQ. Especially, the high nickel contents provide higher toughness than that of the conventional weathering steels. As example of joint performance evaluation, the test results of submerged arc welded joints made at a heat input of 5 kJ/mm in the new SMA 570WQ equivalent steel are given in **Table 3**. The joint strength and toughness are both high enough for the SMA 570WQ. Carbon dioxide gas-shielded arc welded joints and manual welded joints also exhibit good performance. This is because the developed steel is reduced in the carbon content to eliminate the weld cracking susceptibility index designated as P_{CM}. A 3Ni-0.3Cu-0.02Cr welding material was also developed for the coastal application. This composition was approximately equal to that of the base metal. From the above test results, it can be concluded that the developed steels are fully usable as bridge members.

5. Conclusions

In order to extend the applicability limit of conventional weathering steel, a new type of the steel was developed. It is expected that the life cycle cost of steel structures even in an environment with higher airborne salt deposition rate than 0.05 mdd. The effectiveness of adding about 3% nickel and no chromium to improvement of coastal weathering resistance was confirmed by 9 years of exposure test. Mechanical and welding properties of the developed weathering steel were found to be satisfactory for application to bridges. In fact, this steel is already used in actual bridges, and its needs are growing.

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