Characterization of Rust Layers Formed on Nickel-Alloyed Steel Under Different Exposure Sites

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Abstract

The rust layers formed on Fe-Ni steel with varying nickel content exposed to open atmosphere in three different sites of Japan for three (3) years were characterized using electrochemical impedance (EIS) and near infrared reflectance-absorbance spectroscopy (NIR-RAS) under wet condition at RH 90%.

To determine the saturation amount of water in the rust layer, the amount of water vapor absorbed was measured using Mettler balance and the apparent diffusion coefficients were calculated using the semi-infinite model of diffusion. Results showed that the apparent diffusion coefficient increased with increasing amount of airborne salts. This increase in diffusion coefficient is an indication that the rust layer formed under high chloride environment has lessened its protective ability as evidenced by the increase in water diffusing into the rust layer. Increasing the amount of nickel in steels has proved to decrease the diffusion coefficient, thereby, making the rust layer more protective.

To supplement the results of NIR-RAS, the impedance diagram of the rusted surface of the steels was analyzed. Results showed that the rust layer formed in the site with relatively high amount of airborne salt revealed high conductivity under wet condition, which is an indication that the rust layer has absorbed a relatively high amount of water. Moreover, it was also found that with increasing nickel content, the conductivity is decreased.

Keywords: atmospheric corrosion, Near-Infrared-Reflectance Absorbance Spectroscopy, Electrochemical Impedance Spectroscopy, weathering steel

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Introduction

Atmospheric corrosion, by its nature, has been reported to account for more failures in terms of cost and tonnage than any other in the environment. Consequently, it is considered to be a major contributor to the overall costs of corrosion worldwide. An important domain of atmospheric corrosion is the degradation of infrastructure. Bridges, commercial and residential buildings, electrical power systems, rail system components, utility poles, communication systems and marine structures are relevant examples (Revie, 2000).

Modern technology, in recognition of global warming and environmental degradation, is gearing towards the development of environmentally-conscious and sustainable materials with increased efficiency in the use of limited resources by increased life cycle. The development of weathering steels is one of the technological advances that respond to the call for the development of sustainable structural materials.

Weathering steels consist of a group of low alloy steels developed for the purpose of preventing atmospheric corrosion without the necessary application of coatings. Eliminating the need for painting or galvanizing can result to cost reduction associated with initial painting, periodic repainting, containment and disposal of blasting debris during repainting, and interruption in service during repainting. During field exposure, an adherent, compact, and protective layer of corrosion product grows under a coarse surface rust layer, retarding further corrosion. The layer protecting the surface develops and regenerates continuously when subjected to the influence of the weather (Leigraf & Graedel, 2000). Under repeated cycles of wetting and drying, weathering steels form protective corrosion products that consist of goethite (α-FeOOH), lepidocrocite (γ-FeOOH), Fe_3O_4 and an X-ray amorphous substance. The protective ability of the rust emerges after a few years of exposure and the stable rust is composed of two layers-the outer and the inner (Okada, et al., 1969). The outer layer is mainly comprised of γ-FeOOH while the inner layer is mainly composed of densely packed nano-particles of α-FeOOH. During the initial stage of rusting, γ-FeOOH is formed and is transformed into the final stable protective rust layer consisting of nano-sized α-FeOOH, via amorphous ferric oxyhydroxide during a long period of atmospheric corrosion (Yamashita, et al., 1994).

The corrosion-retarding effect of the protective layer is produced by the particular distribution and concentration of alloying elements in it. The alloying elements identified to contribute significantly valuable effects on the formation of protective rust layer are Cr, Cu, Ni, Si, and P, with the total amount kept at less than 3% (Townsend, 2000).

The re-oxidation of Fe_3O_4 to FeOOH during the wet cycle of rust layer formation is one of the factors of rust growth on steels. A study conducted by Ishiwaka and co-workers shows that Ni^{2+} from 0 to 30 mol % raises the air-oxidation temperature of Fe_3O_4 particles from ca. 200 to ca. 400°C. This implies that Fe_3O_4 particles were stabilized to air-oxidation by the doped Ni^{2+} (Ishikawa, et al., 1998).

Research Objective

This study is aimed at investigating the effect of the addition of nickel to steels on the behavior of its rust layers, formed at three different types of atmospheres in three years, as a result of moisture absorption.

Scope and Limitations

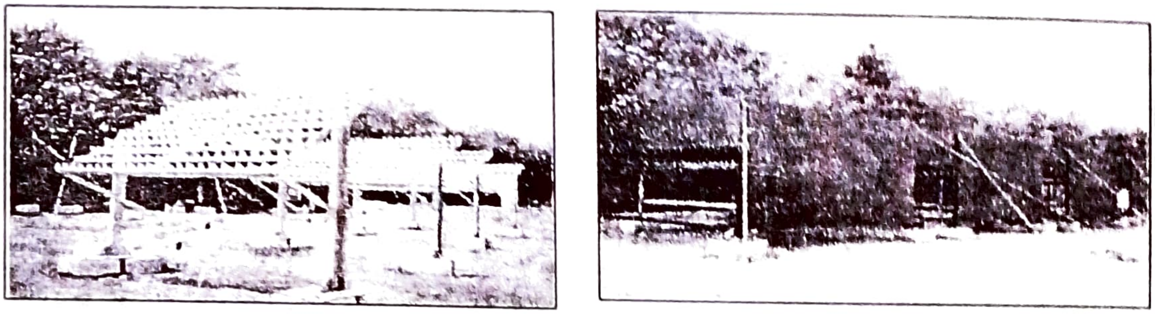
This study is limited to the investigation of the rust layers formed in three different sites of Japan for three years. The investigation of the rust layers exposed at varying exposure time is not covered.

Methodology

Sample Preparation

All the rusted samples used in this experiment were provided by the National Institute of Materials Science (NIMS), Japan. The specimens whose dimensions are 50 x 10 x 4 mm^2 were exposed in the atmosphere in two modes of exposure, open and sheltered. In the open exposure, the specimens were mounted on test frames that are inclined at 45° angle from the horizontal, as shown in Figure 1(a). For the sheltered exposure, the test specimens were placed on the horizontal exposure frames covered with umbrella roofs, shielded from rain and solar radiation as shown in Figure 1(b). Three exposure sites were chosen, namely, Tsukuba, Choshi and Miyakojima and the meteorological and atmospheric data for the test sites are given in Table 1. The three exposure sites were chosen according to their degree of relative humidity and the airborne salinity. Tsukuba represents the mildest environment, Chosi average and Miyakojima the harshest in terms of relative humidity and airborne salinity.

The chemical compositions of the Fe-Ni binary alloys are summarized in Table 2.



(a) Open

(b) Sheltered

Figure 1. Atmospheric Exposure of Test

Table 1. Meteorological and Atmospheric Data of the Exposure Sites

Site	Tsukuba	Choshi	Miyakojima
Environment	Rural	Rural/Coastal	Subtropical coastal
Latitude (North)	36° 4’	35° 43’	24° 44’
Latitude (East)	140° 7’	140° 45’	125° 19’
Air temperature (°C)	15.1	14.6	23.8
Relative humidity (%)	74	77.9	79
Time of wetness (h)	3947.6	4649.3	5197.0
Airborne salinity (mg NaCl/m^{2}.day)	2.6	34.7	47.9

Table 2. Chemical Compositions of Materials

Material	Chemical composition (mass %)										
	C	Si	Mn	P	S	Cu	Cr	Ni	Al	Ti	V
Fe	0.001	<0.003	<0.01	0.0008	0.0011	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fe-1Ni	0.001	<0.003	0.01	0.0003	0.0001	<0.01	<0.01	0.98	<0.01	<0.01	<0.01
Fe-3Ni	0.001	<0.003	0.01	0.0005	0.002	<0.01	<0.01	3.02	<0.01	<0.01	<0.01
Fe-5Ni	0.001	<0.003	0.11	0.0006	0.003	<0.01	<0.01	5.01	<0.01	<0.01	<0.01
Fe-9Ni	0.001	<0.003	0.12	0.0005	0.003	<0.01	<0.01	9.06	<0.01	<0.01	<0.01

Experiment Set-up

Water Absorption Measurement by Mass Change

The steel specimen whose surface is covered with rust layer was overlaid on a plate which is hanged, from the Mettler AG315 balance, with a sensitivity of 10 µg, through a metal wire. The sample was humidified by N_2 gas with 90% relative humidity and the temperature was maintained at 25 °C. The change in the mass of the steel specimen in milligrams was measured and recorded every 5 seconds for 24 hours. Figure 2 shows the schematic diagram of the set-up.

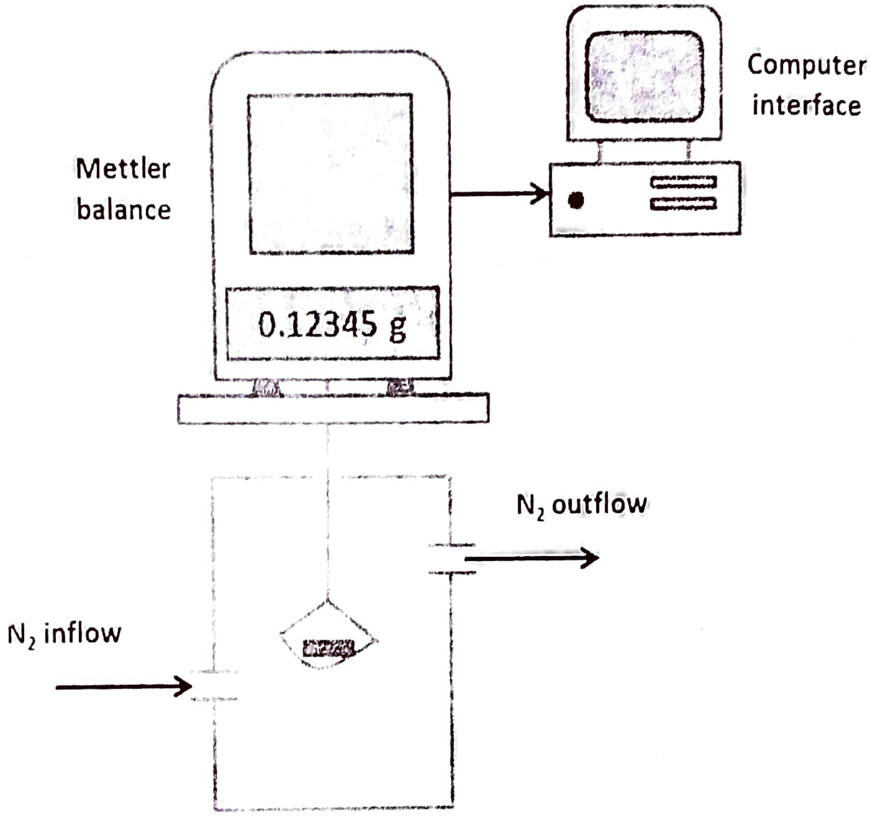


Figure 2. Schematic diagram of the mass change measurement by analytical microbalance

Water Absorption Analysis by Near Infrared-Reflectance - Absorbance Spectroscopy (Ocean Optics NIR 256-2.1)

The rusted sample is placed inside the chamber whose humidity is controlled by passing N_2 gas. The fiber glass optical guide is positioned at a distance from the surface of the rusted sample at normal angle, as shown in Figure 3. The probe is connected to the NIR 256-2.1 which is interfaced to the computer for data processing using Ocean Optics software. The distance of the probe from the surface of the specimen is adjusted to get the desired intensity and the NIR-Reflectance Absorbance Spectra was obtained for both dry and wet conditions of the sample. During drying condition, dry N_2 gas with relative humidity less than 10% is passed into the chamber for 24 hours. Then the setting is shifted to wet condition by passing a humidified N_2 gas into the chamber with 90% relative humidity for another 24 hours.

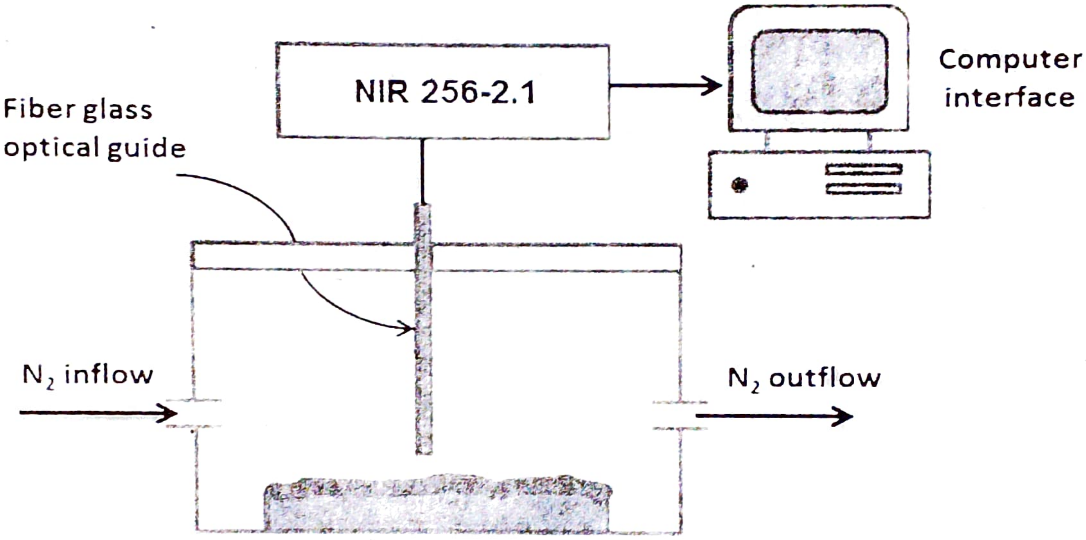


Figure 3. Schematic diagram of the NIR-RAS set-up

Determination of Change in Conductance of the Rust Layer by Electrochemical Impedance Spectroscopy (EIS)

Under the same humidification condition as the NIR-RAS experiment, the AC impedance of the rust layer during alternating conditions of drying and wetting was measured using Frequency Response Analyzer (NF Circuit FRA5095) from a frequency range of 0.01 Hz to 100 kHz. Two gold plates with surface area of 0.42 cm^2 were fixed using springs on 2 points on the rust layer, as shown in Figure 4. The AC impedance between the 2 gold plates was measured with applied voltage of 0.1 V. The shunt resistances during dry and wet conditions were 100 kΩ and 1 kΩ respectively.

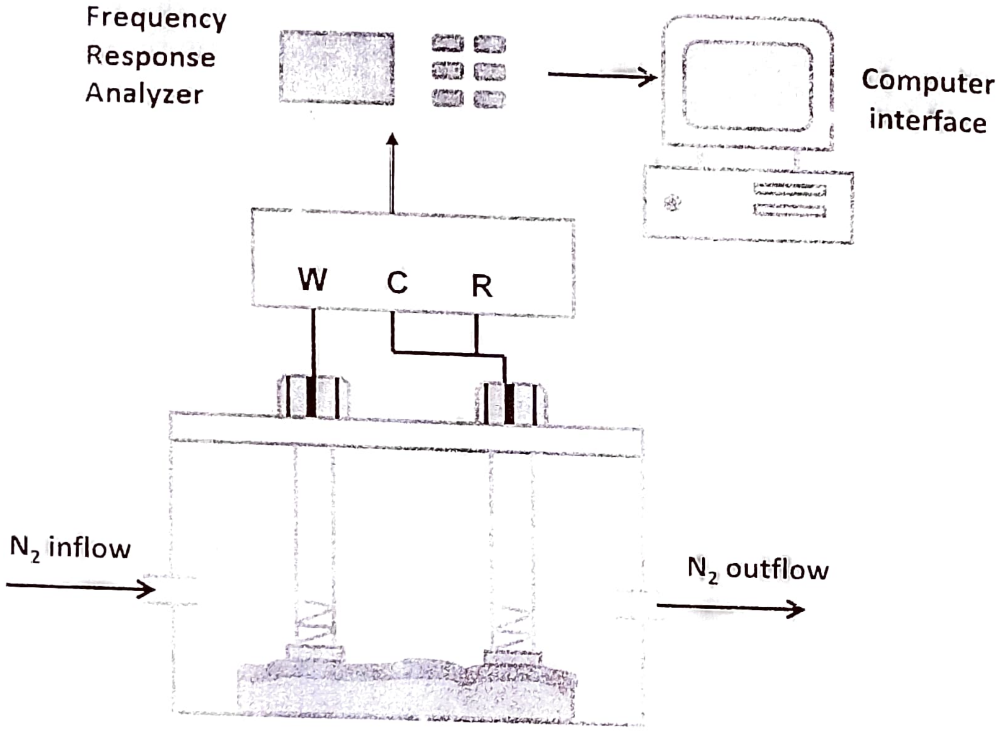


Figure 4. Schematic diagram of the EIS set-up

Results and Discussion

Characterization of Water Vapor Adsorption of Rust in Terms of Diffusion Coefficient

Each rusted sample was humidified at 90% relative humidity for 24 hours. The change in the weight of the sample was recorded every 5 seconds and the weight change was plotted against time. The exposure area of the rusted steel to the humidified N_2 gas was about 10 cm^2.

The effect of chloride deposition on the degree of water vapor saturation of rusts was investigated by exposing nickel-containing steel samples in 3 different locations in Japan whose environmental profiles are summarized in Table 3. The table shows that Tsukuba has the mildest environment while Miyakojima has the most severe in chloride deposition and relative humidity.

Table 3. Environmental profile of the 3 exposure sites

Exposure Site	Exposure Period (years)	Chloride deposition rate (mgNaCl/m²d)
Tsukuba	3	2.85
Choshi	3	36.84
Miyakojima	3	47.34

Figure 5 shows that for all composition of nickel within the range covered in this study, the rust layers formed in Tsukuba have the lowest adsorption of water vapor relative to those formed in Choshi and Miyakojima. The amounts of water vapor saturation of rusts formed on steels exposed in Miyakojima and Choshi do not show a significant difference for nickel composition less than 5%. However, as the amount of nickel is increased beyond 5%, the difference becomes more pronounced as evident by a considerably large difference at 9% nickel. At low chloride deposition rate, the addition of nickel does not significantly affect the ability of the rust layer to adsorb water vapor. On another hand, at high chloride deposition rate, the effect of nickel on the water adsorption of rust seems to be insignificant also. However, this result is inconclusive due to the possibility of chipping off of the outer rust layers at low nickel content leaving the relatively thinner and more compact inner layers on the steel surface.

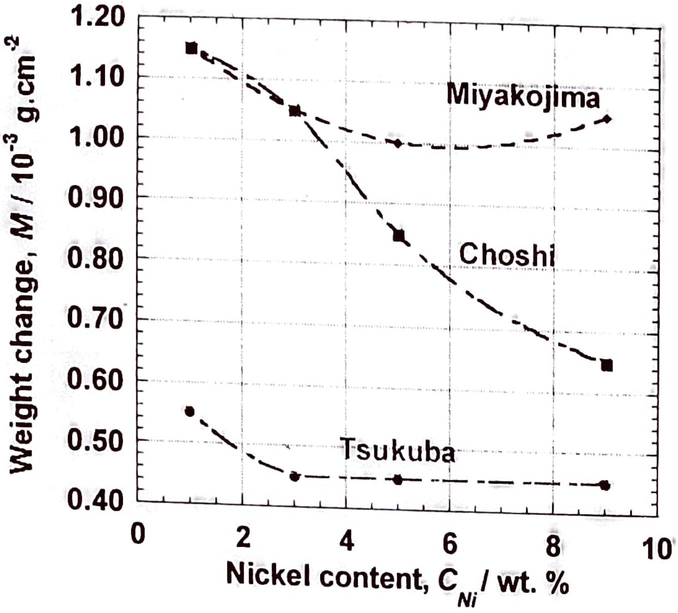


Figure 5. Relationship between water adsorption and nickel content during a 3-year exposure

Assuming a one-dimensional semi-infinite diffusion from the interface of atmosphere/rust to the interface of rust/metal, the transition of the change in the amount of water adsorbed in the rust layer, *M*, can be approximated by the following equation:

$$M = C_{av}L = C_0L + 2(C_s - C_0)(Dt/\pi)^{1/2}$$

where C_{av} is the average concentration of water in the rust, C_0 is the initial concentration of water, C_s is the maximum concentration of water on the surface of the rust layer, *D* is the apparent diffusion coefficient of water in the rust and *L* is the thickness of the rust layer. Figure 6 shows the square of the saturated amount of water in the rust layer, M^2, plotted against time, *t*. From this figure, the apparent diffusion coefficient can be obtained from the slope of the tangent line to curve at the initial transition, and then estimated by the given equation:

$$D = (\pi/4)(C_s - C_o)^{-2}(dM^2/dt)$$

where C_0 is assumed to be 0. The saturated amount of water in the rust layer is plotted against the thickness of the rust in Figure 7. The value of C_s is then obtained from the slope of this curve (Ohtsuka and Komatsu, 2005).

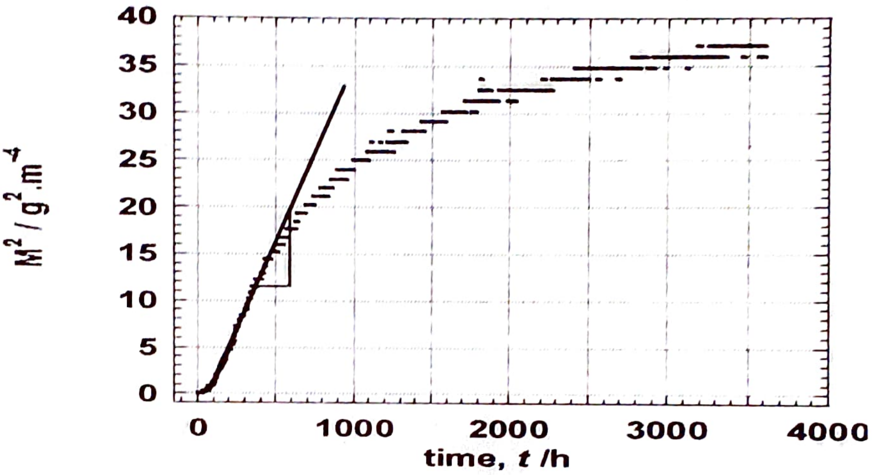


Figure 6. Rust layer formed on 9% nickel exposed for 3 years in Choshi

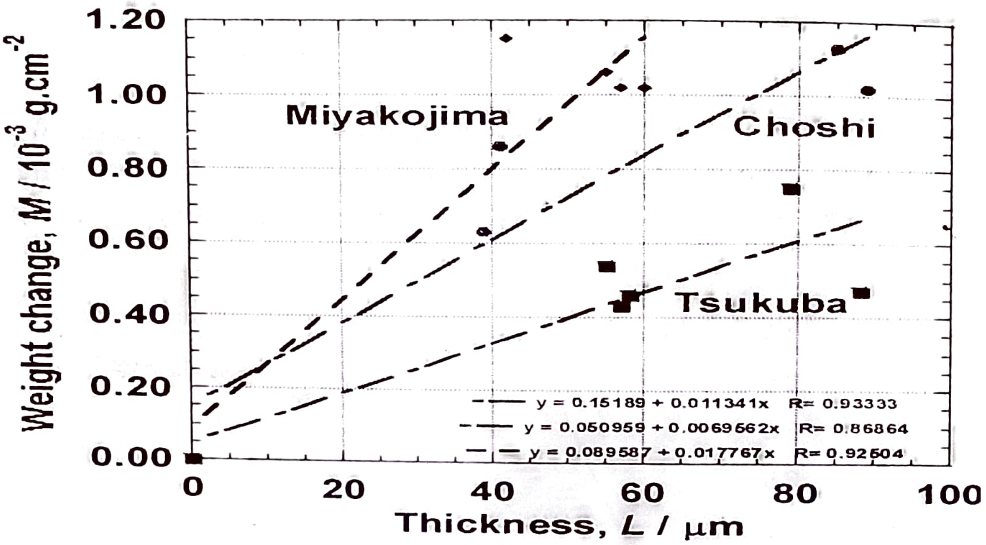


Figure 7. Relationship between water vapor adsorption and rust layer thickness among 3 exposure sites

Table 4 summarizes the results of the computation of the apparent diffusion coefficient, *D*, of water in the rust layers formed on steels exposed for 3 years in Tsukuba, Choshi and Miyakojima at varying nickel content.

Table 4. Diffusion coefficients of water in rust layers formed in 3 exposure sites for 3 years

Exposure Site	Chloride deposition rate (mgNaCl/m^{2}d)	Apparent Diffusion Coefficient, D / 10^{-12} m^2.s^{-1}			
		1% Ni	3% Ni	5% Ni	9% Ni
Tsukuba	2.85	1.23	1.23	0.86	0.98
Choshi	36.84	2.80	2.80	2.40	1.60
Miyakojima	47.34	0.982	0.785	0.785	0.012

The data in table 4 is elucidated by Figure 8 which shows the relationship between diffusion coefficient and the nickel content.

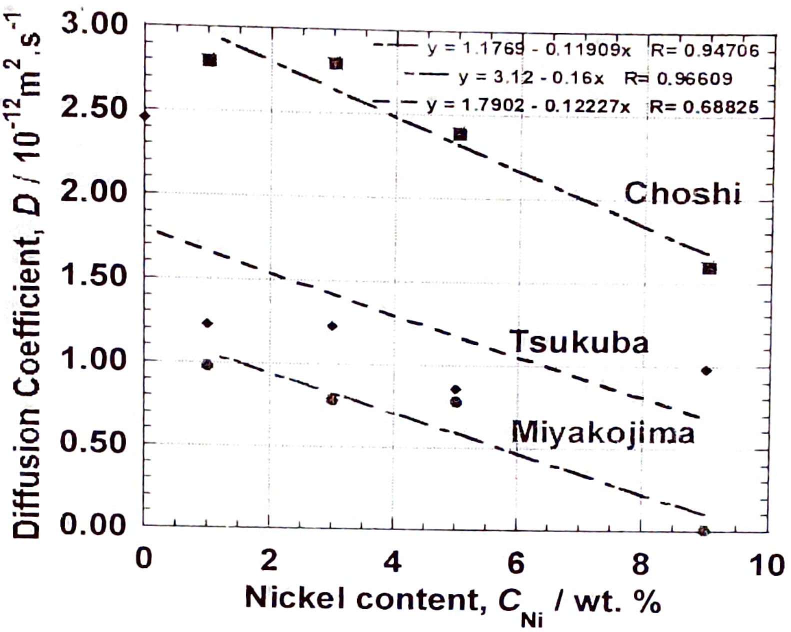


Figure 8. Comparison of diffusion coefficients between 3 exposure sites as a function of nickel

The figure shows that in all 3 exposure sites, there is an inversely proportional relationship between diffusion coefficient and nickel content, that is, the higher the nickel content, the lower the diffusion coefficient. Comparing the diffusion coefficient values among the 3 exposure sites, the figure shows that Choshi has the highest, while Miyakojima has the lowest. Findings of the study conducted by T. Ohtsuka and T. Komatsu state that the higher the chloride deposition rate, the higher is the diffusion coefficient due to the fact that NaCl induces large pores within the structure of the rust. Since the rust layers may consist of agglomerates of fine iron oxide particles, the diffusion of water may take place through the thin channels between the particles (Ohtsuka and Komatsu, 2005). Based on this previous study, it is therefore expected that Miyakojima should show the highest value of diffusion coefficient since it receives the highest chloride deposition rate. Hence, the result of the present study appears to contradict the previous findings. This inconsistency with the previous study can be attributed to the instability of the rust layer formed on the test specimens exposed in Miyakojima during the early stages of exposure. Such that, after a period of 3 years exposure, the outer rust layers may have been chipped off, leaving behind the relatively compact inner rust layer on the surface of the metal. This argument can be supported by the data provided by the National Institute of Materials Science (NIMS), Japan, as shown in Figure 9, on the weight loss of the test specimens containing 9% nickel exposed in the 3 sites. Therefore, in order to correctly analyze the characteristics of the rust formed in Miyakojima in terms of water absorption, a method should be done such that the unstable portion of the layer can be preserved for analysis. The rust layer formed can be monitored periodically and collected before they are chipped off and lost.

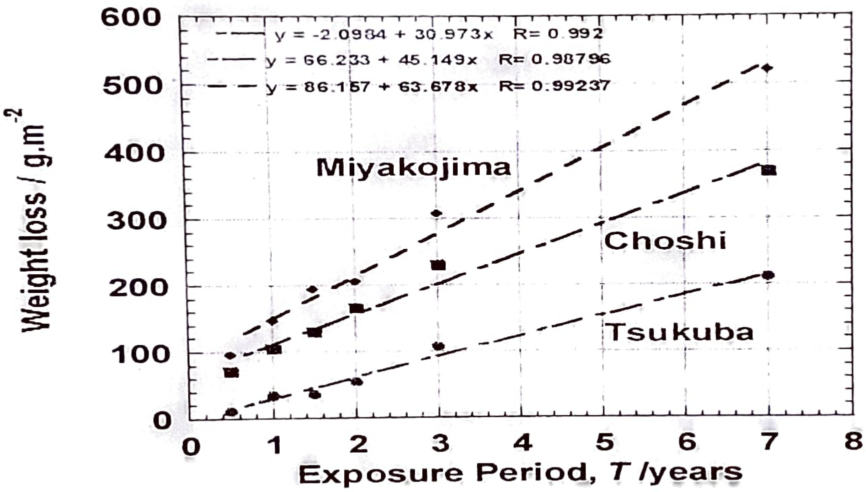


Figure 9. Weight loss of 9% nickel-containing steels as a function of exposure

Characterization of Water Vapor Adsorption of Rust in Terms of Near Infrared Absorbance

The adsorption of water vapor was confirmed by the results of Near Infrared – Reflectance-Absorbance Spectroscopy (NIR-RAS). The measurement was made at normal reflection and the absorbance, A, was normalized by the reflection of the rust layers on steel under dry condition for 24 hours as shown by the equation below:

$$A = -\log(R_w / R_d)$$

where R_w is the reflectance under wet condition and R_d is the reflectance under dry condition just before introducing humidified N_2 gas. The plots are shown in Figures 10, 11 and 12 for the rusts formed after 3 years on Fe-9% Ni binary alloys exposed in Miyakojima, Choshi and Tsukuba, respectively. The plots were made every 1 hour until 16 hours and every 2 hours from 16 to 24 hours. Two sharp absorbance peaks were detected at wave numbers 5100-5200 and 6800-6900 cm^{-1} for rusts formed in Choshi and Miyakojima. This wave numbers are both associated with the combination bands of H_2O. However, the rusts formed in Tsukuba did not show sharp peaks for water combination bands which indicates that the rusts were absorbing a minimal amount of water during humidification. Similar plots were obtained at different nickel content.

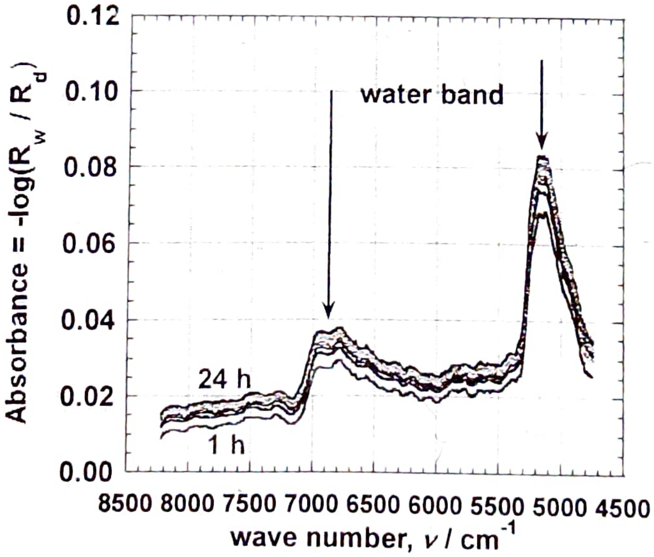


Figure 10. Absorbance of rust layers formed on steels containing 9% nickel exposed for 3 years in Miyakojima

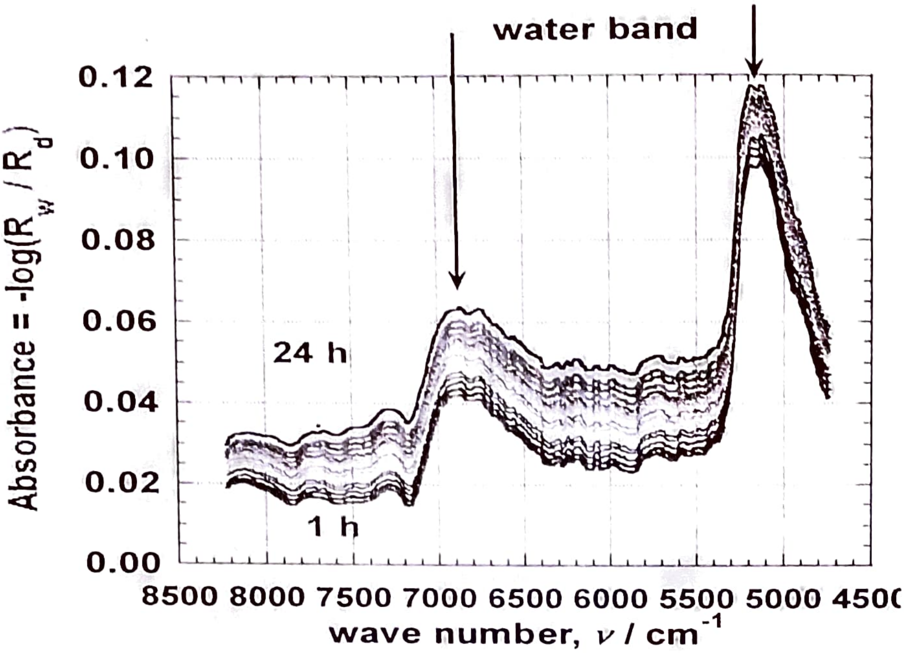


Figure 11. Absorbance of rust layers formed on steels containing 9% nickel exposed for 3 years in Choshi

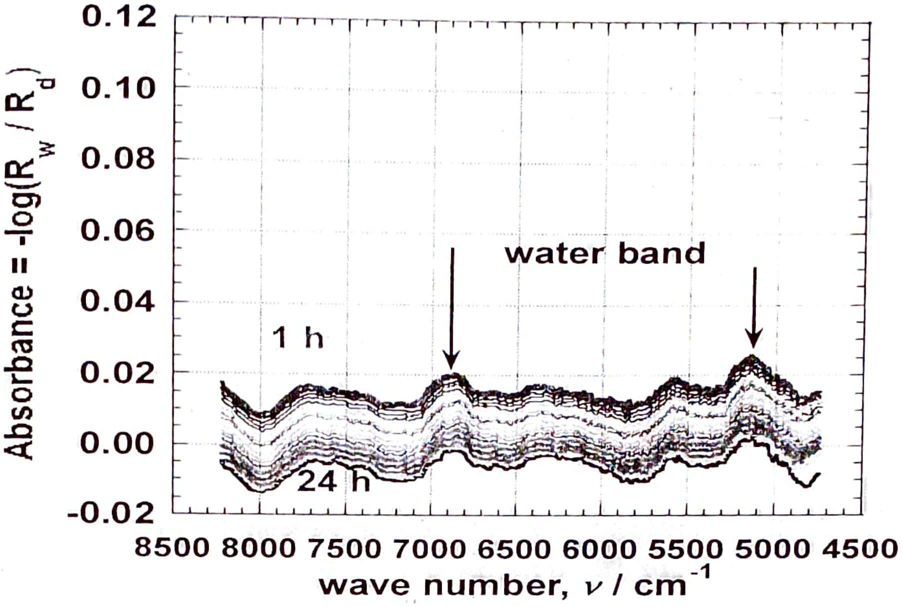
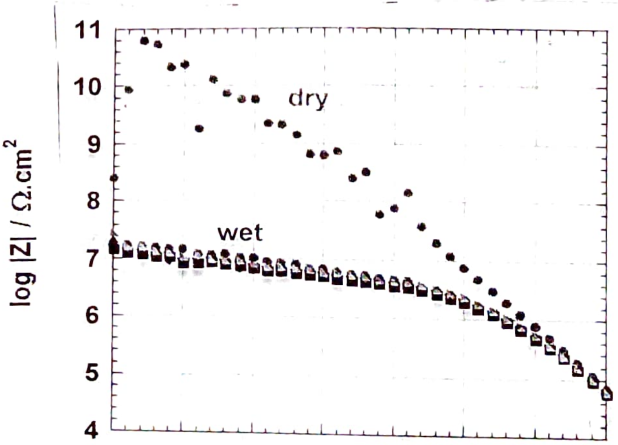


Figure 12. Absorbance of rust layers formed on steels containing 9% nickel exposed for 3 years in Tsukuba

Characterization of Water Vapor Adsorption of Rust in Terms of Electrochemical Impedance

The electrical conductivity of the rust layer is greatly enhanced by its adsorbed water vapor. Figures 13, 14 and 15 show that under dry condition the rust layer behaved as a dielectric as indicated by a high value of AC impedance which reached a value of 10^{10} $\Omega.cm^2$ at a frequency of 0.01 Hz. As the rust layer became wet, the impedance greatly decreased to about 10^7 $\Omega.cm^2$, $10^{7.5}$ $\Omega.cm^2$, 10^8 $\Omega.cm^2$, for rusts formed on 9% nickel-containing steel exposed in Miyakojima, Choshi and Tsukuba respectively.



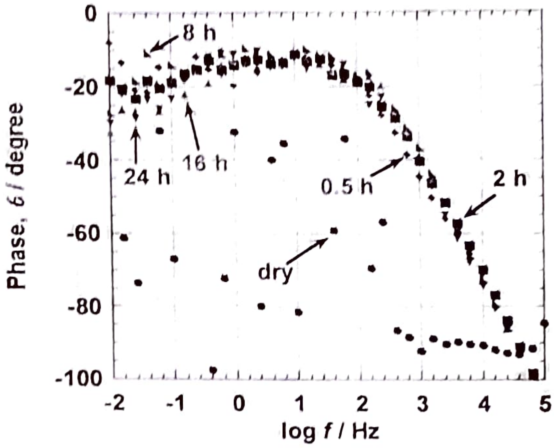


Figure 13. Impedance diagram of rust layer formed on 9% nickel steel exposed in Miyakojima

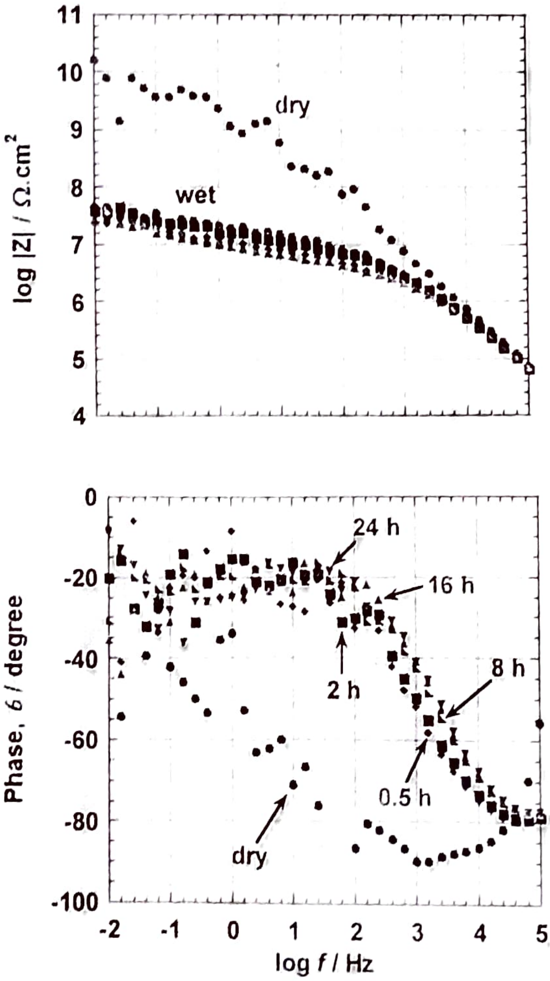


Figure 14. Impedance diagram of rust layer formed on 9% nickel steel exposed in Choshi

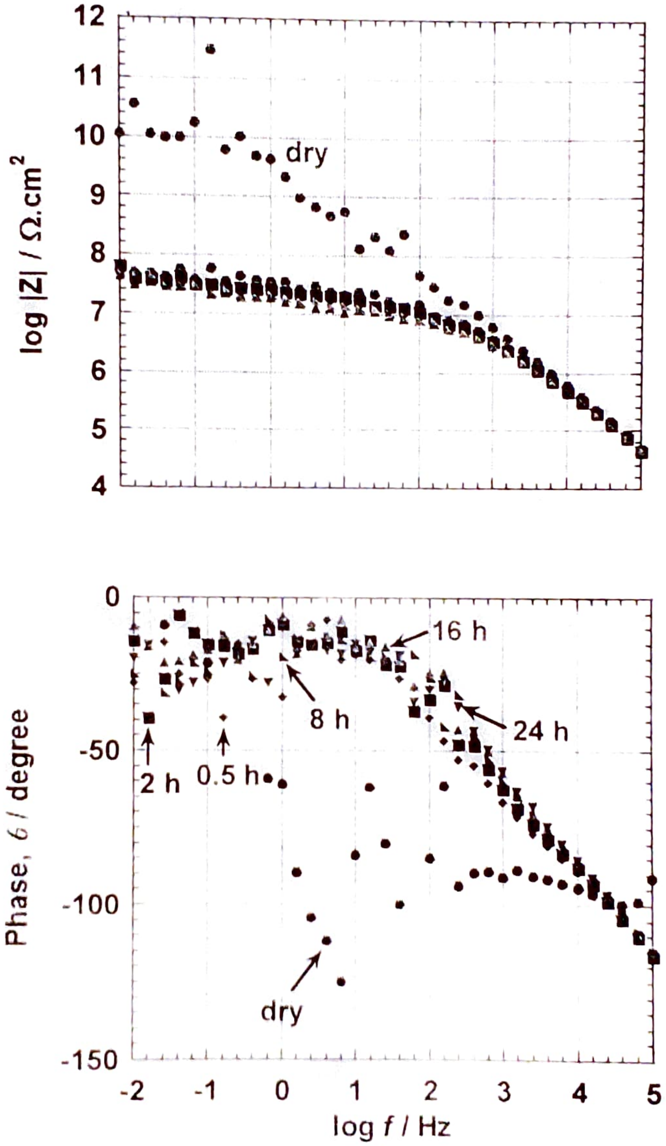


Figure 15. Impedance diagram of rust layer formed on 9% nickel steel exposed in Tsukuba

In addition, the conductivity is also affected by the chloride deposition rate as shown in Figure 16. It indicates that the rusts formed in Miyakojima have the highest conductivity due to high water absorption in accordance with Figure 5.

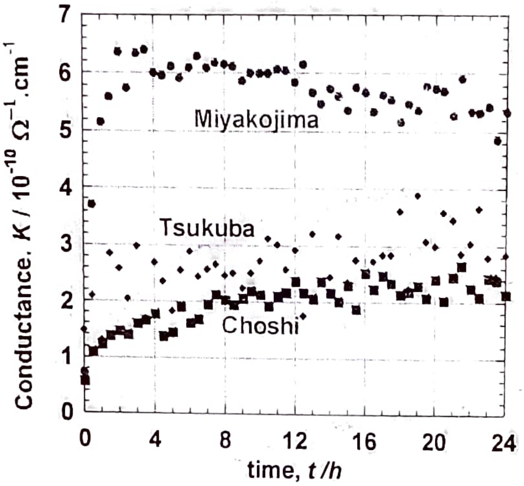


Figure 16. Conductance of rust layers formed on 9% nickel steel exposed for 3 years

Furthermore, in terms of nickel content, the specimens containing the highest weight percentage of nickel exhibit the lowest conductance as shown in Figure 17. This is an indication that the rust formed on steels with the highest percentage of Nickel absorbs the least amount of water. This result is consistent with the results of water adsorption test where the 9% nickel specimens adsorb the lowest amount of water vapor.

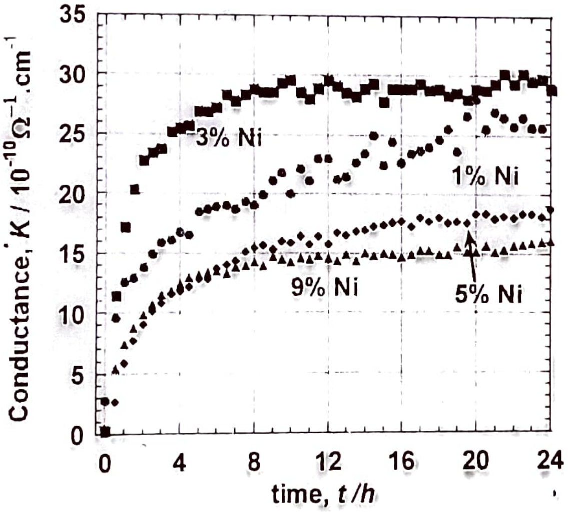


Figure 17. Conductance of rust layers formed on steel specimens exposed in Choshi for 3 years

Conclusion

The addition of nickel to steel has significantly reduced the weight loss of the metal due to corrosion. The effects of nickel on the properties of the rust layers are summarized below:

1. Diffusion coefficient of water in the rust layer decreases with increasing nickel content.
2. Diffusion coefficient increases as chloride deposition rate increases.
3. The conductance of the rust layer generally decreases as the nickel content increases from 5%.
4. The conductance of the rust layer generally increases with increasing chloride deposition rate.
5. At three (3) years exposure period, the alloy containing 9% nickel shows the least diffusion coefficient, light absorbance and conductance.

Recommendations

The ability of the rust layer to absorb water from the atmosphere, and the rate of diffusion of water into the rust layer determines the rate of growth of corrosion layer. Moreover, the conductance of the rust layer under wet condition is one factor that enhances growth rate. However, other factors such as the type of rust compounds present in the corrosion product do contribute also to the growth rate and the characteristic of the rust layer. It is recommended therefore to identify the different oxides or oxyhydroxides in the corrosion products of steel that may have formed during the atmospheric exposure by Mössbauer spectroscopy. In addition, sizes of the rust component crystals can be measured using scanning electron microscope (SEM). To elucidate further the effect of nickel on the characteristics of the rust layer, Electron Probe Micro Analysis (EPMA) can be performed to investigate the distribution of nickel within the rust layer.

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