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Atmospheric Corrosion Resistance of Stainless Steel: Results of a Field Exposure Program in the Middle-East

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Atmospheric Corrosion Resistance of Stainless Steel: Results of a Field Exposure Program in the Middle-East

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Summary

Stainless steels have been widely used as architectural and construction materials because of their high degree of corrosion resistance, unique aesthetic quality and stability in an unpolluted atmosphere. Although stainless steel is highly corrosion resistant, localized corrosion can occur in certain environments, especially in marine atmospheric conditions if the appropriate grade is not used. Exposure of stainless steel to a more aggressive environment than the limiting conditions may be harmful to its aesthetic appearance and ultimately even to its load-bearing capacity.

Selecting a suitable stainless steel grade requires knowledge of the actual location of the application and the atmospheric conditions. In terms of materials selection, the austenitic stainless steel grade 316/316L has proved a very popular choice for architectural applications in many locations but it is not always suitable at demanding sites such as marine environments in the Middle-East. In such cases the use of a higher-performance grade, often in combination with a good surface finish and established cleaning routines, is required to maintain pristine surfaces.

The main objective of this paper is to present information about the atmospheric corrosion resistance of a number of stainless steels in the Middle-East at a marine site. The results obtained are analysed and discussed in terms of factors affecting atmospheric corrosion of stainless steel such as the, alloying element level, surface roughness, surface treatment and microclimate.

Key words: Atmospheric corrosion of stainless steel, marine environment

Introduction

Stainless steels have been widely used as architectural and construction materials because of their high degree of corrosion resistance, unique aesthetic quality and stability in an unpolluted atmosphere. This resistance is the result of a very thin protective oxide film on the stainless steel surface, usually referred to as the passive film. Although stainless steel is highly corrosion resistant, localized corrosion (pitting and/or crevice corrosion) can occur as a result of local breakdown of this film, especially in marine atmospheric conditions if the appropriate grade is not used [1, 2]. When the weather becomes dry, staining often becomes visible around any pits and degradation of the stainless steel can occur [2, 3].

Two main factors that affect atmospheric corrosion resistance and cosmetic degradation of stainless steel are the environmental conditions and the characteristics of the stainless steel used. Environmental factors such as temperature, rainfall, relative humidity and the presence of aggressive species (of which the most harmful is the chloride ion) are very important for the selecting stainless steel. The severe marine environment in the Arabian Gulf is characterized by high temperature, high salt and low rainfall, which can combination have a severe corrosive action on metallic materials [4]. Characteristics of the stainless steel which can influence the atmospheric corrosion resistance include the alloying element content, surface finish, surface treatment and surface orientation. The design and the microclimate are also significant [2, 9].

Selecting a suitable stainless steel grade requires knowledge of the actual location of the application and the atmospheric conditions. In terms of materials selection, the austenitic stainless steel grade 316 has proven to be a very popular choice for architectural applications in many locations [2–9] but it is not always suitable at demanding sites such as marine environments (for example in the Middle-East) [8]. In such cases the use of a higher-performance grade, often in combination with a good surface finish and established cleaning routines, is required to maintain pristine surfaces. As reviewed [2–8], there have been many reports on the results of corrosion behavior of stainless steel. However, there is little literature about the corrosion behavior of stainless steel in the special marine conditions such as occur in the Middle-East.

The main objective with this paper is to present information about the atmospheric corrosion resistance of a number of stainless steels at a marine site in Dubai. The results obtained are analysed and discussed in terms of factors affecting atmospheric corrosion of stainless steel such as the alloying element level, surface roughness, surface treatment and microclimate.

2. Experimental

2.1. Exposure site

The marine test site in Dubai is located within Dubai Electricity and Water Authority (DEWA), see Figure 1A [8]. The samples were mounted in May 2010 and retrieved for evaluation in May 2014. As seen in Figure 1B–1C, the racks are located directly on the sea shore of the Arabian Gulf. A few meters from the racks is a fence made out of carbon steel, making an already severe environment even more severe. A large number of carbon steel particles most likely from the fence were found on the test samples. This phenomenon is called Fremdrost [8] and will create discoloration and maybe etching on the exposed samples if the stainless steel is not sufficiently highly alloyed.

The closest available climate data is from a site within an industrial complex in Jebel Ali as shown in Table 1 [4]. The distance to the sea is two kilometers (Red marker in Figure 1A) and the location is about thirteen kilometers from the test site in this study. It was reported that the Jebel Ali site is characterized by very low rain amount and the reference samples exposed there were little corroded due to the relatively large distance from the shore, which resulted in a low local relative humidity [4].

Distance from sea shore	~2 kilometers
Distance from the test site in this study	~13 kilometers
Period	02/2011 – 01/2012
Mean temperature [°C]	29.0
Minimal temperature [°C]	12.0
Maximal temperature [°C]	46.5
RH [%]	50
Precipitation [mm]	20

Table 1 Average temperature, relative humidity and precipitation in a year period at an industrial complex in Jebel Ali, Dubai [4]

Figure 1 Yellow arrow shows the location where the test samples were exposed at the Dubai Electricity and Water Authority (DEWA) site in Dubai. Reference data is taken from a site within an industrial complex in Jebel Ali [4], marked with a red arrow (1A). Two test racks (open and sheltered condition) with samples for this study (1B–1C).

2.2. Materials

Eleven stainless steel grades were tested as plain (sheet), welded and creviced samples. The characteristics of materials, including the pitting resistance equivalent number (PREN) and the chemical composition are given in Table 2.

Stainless steel	EN	Surface finish	Thick. (mm)	Typical chemical composition, %wt						PREN*
				C	Ni	Cr	Mo	N	Other	
Ferritic	1.4003	2E	2.0	0.02	0.5	11.5	–	–	–	12
	1.4016	2B	1.5	0.05	–	16.2	–	–	–	16
	1.4521	2B	1.5	0.02	–	18.0	2.0	–	Ti, Nb	25
Austenitic	1.4301	2R	0.9	0.04	8.1	18.1	–	–	–	18
	1.4404	2R	0.8	0.02	10.1	17.2	2.1		–	24
	1.4547	2E-brushed	1.0	0.01	18.0	20.0	6.1	0.20	Cu	43
	1.4565	2E-brushed	0.5	0.02	17.0	24.0	4.5	0.45	5.5Mn	46
	1.4652	2E-brushed	0.7	0.01	22.0	24.0	7.3	0.50	3.5Mn, Cu	56
Duplex	1.4162	Ground (Ra 0.5 µm)	5.0	0.03	1.5	21.5	0.3	0.22	–	26
	1.4462	2E-brushed, 2E,1D	1.0, 2.0, 5.0	0.02	5.7	22.0	3.1	0.17	–	35
	1.4410	2E-brushed	1.5	0.02	7.0	25.0	4.0	0.27	–	43

Table 2 The characteristics of stainless steel, PREN values and the typical chemical composition .

*PREN = %Cr+3.3%Mo+16%N
2B = Cold rolled, heat treated, pickled, skin passed
2E = Brushed surface
2E = Cold rolled, heat treated, mechanically descaled, pickled
2R = Cold rolled, bright annealed
1D = Hot rolled, heat treated, pickled

Base material	Welding method	Welding wire (EN ISO designation)	Shielding gas	Heat input (KJ/min)	Welding speed (cm/min)	Joint design	Post welding treatment
EN 1.4003	GTAW	W 19 9 L Si	Ar	0.44	26	Bead on plate	Polish
EN 1.4016	GTAW	W 19 9 L Si	Ar	0.22	26	Bead on plate	Polish
EN 1.4521	GTAW	W 19 9 L Si	Ar	0.22	25	Bead on plate	Polish
EN 1.4462	FCAW	T 22 9 3 N L R	Mison 18	0.50	78	Bead on plate	Shot blasted and pickled

Table 3 Welding condition of welded specimens.

GTAW: Gas tungsten arc welding, FCAW: flux cored arc welding,
Ar : Pure argon gas, Mison 18: Ar+18% CO_2 + 0.03% NO

2.3. Preparation of samples

The samples were made by cutting the stainless steel to dimensions of 150 x 100 x t mm (t= thickness) [10] and the cut edges were then dry ground (320 grit) to minimize edge attack by removing residual carbon steel from cutting and get a smoother surface. The samples were thereafter marked and cleaned before mounting in accordance with ASTM GI-90 [11].

The welded samples were prepared with welding parameters shown in Table 3. These were bead on plate welds with appropriate heat input and shielding gases. The post-weld treatments were selected for demonstration purposes. Some of the welded samples of the duplex grade 1.4462 were shot blasted and pickled in a mixed acid (HNO_3+HF) bath until they appeared free from weld oxides. Other specimens were left as-welded in order to study the effect of residual weld oxides on atmospheric corrosion resistance. Since the mixed acid is too aggressive for ferritic grades, these were mechanical polished in the welded area.

The crevice samples were bolted together through a 12 mm hole with INCO crevice formers on both sides of specimen. All crevice formers were tightened with a torque of 2.5 Nm. It was verified that there was no electrical contact between the samples and the bolt. The samples were exposed in open and sheltered conditions (see Figure 1B–1C) with an angle of 45° and were orientated to the North West facing to the sea.

2.4. Evaluation

After the exposure, all specimens were photographed and visually examined before cleaning. The exposed specimens were cleaned first by tap water in order to get rid of dirt and dust thereafter left for drying. After this they were degreased with an alkane-based degreasing agent, followed by a short rinse in acetone. The cleaned specimens were weighed and photographed before examined in a microscope at 20x magnification for evaluation of corrosion attack.

Two different criteria are used for evaluation in this investigation. The first is the ranking of the corrosion resistance of the different surface condition based on localised attack and the depths and numbers of pits. The mass losses have not been used in this evaluation. Corrosion attack shallower than 25 µm has been neglected [12]. Edge attack is disregarded.

The second criterion is the visual rating of the extent of corrosion products (rust), discoloration and staining on the exposed surface. The rating number (RN) was evaluated by modifying the procedure described in the JIS G 0595 standard [13], which involves comparison with standard specimens. The average rating number was calculated from 3 values obtained from 3 different evaluators. The relationship between the rating number and percentage of the specimen area with rust and staining is shown in Table 4. The rating "9" means that the entire surface is covered by rust and stain, whereas "0" means no rust/stain or discoloration and the appearance is the same as before the exposure. The difference between stain and discoloration is that staining is defined as a discoloration of the surface of stainless steel as a result of corrosion attack. Although this can look quite significant in term of appearance, the corrosion usually does not penetrate into the steel, and does not affect the structural integrity. Discoloration is defined as dirt or rust caused by particles on the stainless steel surface. The evaluation of corrosion of stainless steel from an aesthetic point of view is important because even a small weight lost can cause a significant loss of appearance or aesthetic degradation.

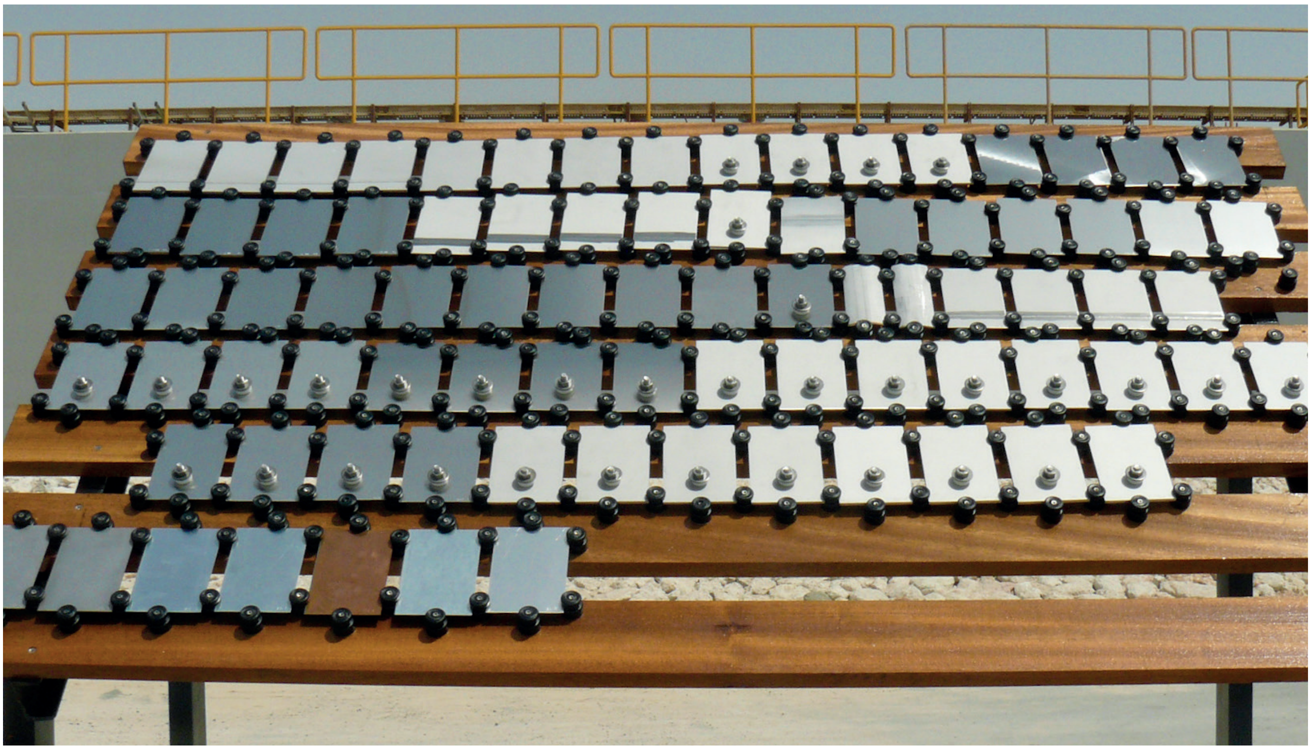
The deposit particles were collected from stainless steel surfaces after four years exposure. The deposits were dissolved in demineralized water by using ultrasonic cleaning. The resulting solutions were analysed by ion chromatography for chloride (Cl^-), sulphate (SO_4^{2-}) and nitrate (NO_3^-).

2.5. Electrochemical testing

In order to study the effect of surface treatment on the corrosion resistance, the critical pitting temperature, CPT was measured on the duplex grades 1.4462 with different surface finishes before exposure. The samples were tested according to ASTM G150 [14] using a crevice free cell, the Avesta cell [15]. The test solution was 1 M NaCl and the applied potential was +700 mVSCE. The temperature was increased by 1°C per minute starting from 0°C and the critical pitting temperature, CPT, was determined when the current density exceeded 100 µA/cm² for 60 seconds. Duplicate specimens were used to determine the CPT.

Rating number (RN)	0	1	2	3	4	5	6	7	8	9
Rust and staining area (%)	Original surface	0 (Discoloration)	~1	~5	~12	~20	~30	~50	~70	~100

Table 4 The relationship between the rating number and rusting/staining area.



Test rack with samples exposed in open condition at the marine test site in Dubai.

3 Results and discussion

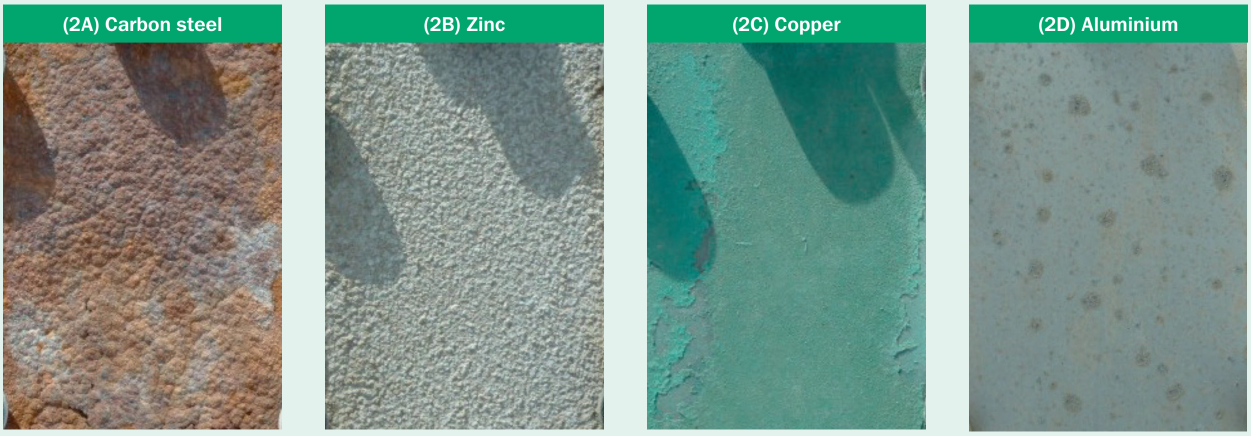
3.1. Classification of corrosivity of atmospheres at the marine site in Dubai

The classification based on the corrosivity at the test site was performed in accordance with the standard ISO 9223 [16]. This takes into account the corrosion rates measured after one year of exposure on carbon steel, zinc, copper and aluminium, where C1 is the least corrosive and CX is the most corrosive, see Table 5. This rating is based upon the uniform corrosion of active material. As a consequence this ranking is not suitable for stainless steels for which localized corrosion is the main concern. The test site represents a very severe environment, since mass loss per year is higher than corrosivity category of CX for all reference materials.

Carbon steel		Zinc		Copper		Aluminum	
g/m^2 y	Class	g/m^2 y	Class	g/m^2 y	Class	g/m^2 y	Class
4010	CX	628	CX*	93	CX*	11	CX*

Table 5 Measured and calculated mass losses per year (g/m^2 y) and corrosivity category at the marine site in Dubai.

*Very severe environment due to higher mass loss per year than CX


(2A) Carbon steel

(2B) Zinc

(2C) Copper

(2D) Aluminium

Figure 2 Reference samples to estimate the corrosivity category of the test site. (Note: The diagonal marks are shadows from the specimen holders)

3.2. The presence of aggressive species

Sea water contains a mixture of salts. It typically comprises anions such as chloride, sulphate and small quantities of magnesium, calcium and potassium cations in addition to sodium [17]. Chloride in airborne sea sprays and dry salt particles may cause pitting and rusting of stainless steel. Evaporation and infrequent rain increases the salt concentration on the surface. A high salt concentration combined with a high ambient temperature and high humidity creates the most aggressive conditions. Ion chromatography analysis of dissolved deposits, Figure 3, showed that a larger amount of chloride and sulphate was found on stainless steel surfaces exposed in sheltered conditions. This can be explained by a lower wind speed and no washing by rain.

3.3. Alloying element level

The different stainless steels have different levels of resistance to atmospheric corrosion. There is a limit to how high a chloride concentration different stainless steel can resist. The alloying elements chromium (Cr), nitrogen (N) and molybdenum (Mo) have the largest impact: the higher the content of these elements the higher the resistance. The Pitting Resistance Equivalent, PREN, has been extensively used to rank different steels regarding their resistance to pitting corrosion in aqueous chloride environments. The PREN formula exists in a number of forms, the most common of which is PREN = %Cr+3.3x%Mo+16x%N. Even though the PREN value was developed for immersion conditions, it has also proved to be a good predictor for the resistance to atmospheric corrosion [2]. The PREN and atmospheric corrosion results for openly exposed specimens at the marine site in Dubai are shown in Table 6 and images of the specimens in Figure 4–6. The only exception to the general trend of improved atmospheric corrosion resistance with increasing PREN is that grades 1.4301/1.4404 were more resistant to degradation than some materials with a higher PREN value such as the ferritic grade 1.4521. The reason for the exceptional performance is that the surface finishes for grade 1.4301/1.4404 were bright annealed. This gives a very smooth surface and resistant [17] surface with some silicon enrichment in the passive film [18, 19].

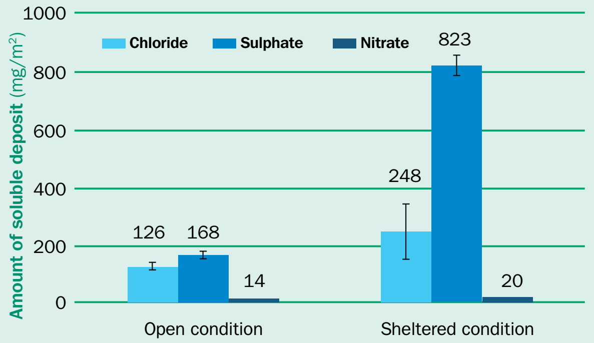


Figure 3 Amount of soluble deposit on the exposed surface after four years exposure in Dubai

3.3. Alloying element level

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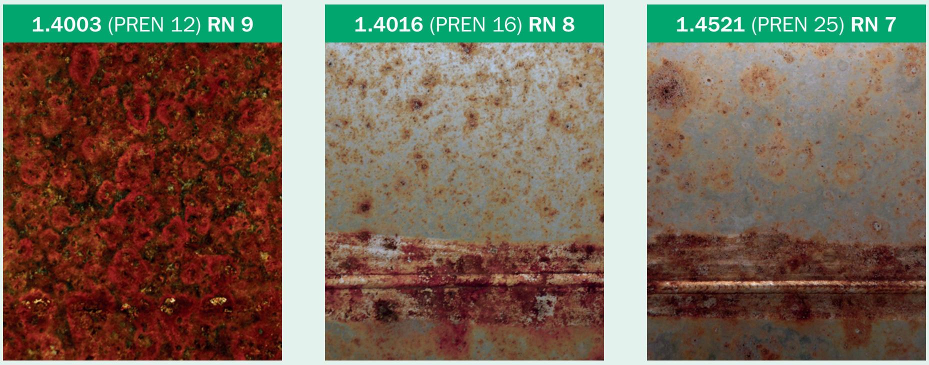
Stainless steel type	EN	PREN*	Surface finish	Corrosion resistance		Degree of degradation (RN)
				Max. depth (µm)	No. of pits	
Ferritic	1.4003	12	2E	Uniform corrosion		9
	1.4016	16	2B	180 (B), 240 (W)	>20	8
	1.4521	25	2B	315 (B), 227 (W)	>20	7
Austenitic	1.4301	18	2R	160, 200	>20	6
	1.4404	24	2R	130, 215	>20	6
	1.4547	43	2E-brushed	25, 70	>20	3
	1.4565	46	2E-brushed	No corrosion	0	2
	1.4652	56	2E-brushed	No corrosion	0	1
Duplex	1.4162	26	Ground (Ra 0.5 µm)	103, 125	>20	5
	1.4462	35	2E-brushed	70, 97	>20	4
	1.4410	43	2E-brushed	No corrosion	0	2

Table 6 Result of the effect of alloying element level on atmospheric corrosion resistance.

*PREN = %Cr+3.3%Mo+16%N, RN = Rating number, B= Pit attack on base material, W= Pit attack in welded area



1.4003 (PREN 12) **RN 9**

1.4016 (PREN 16) **RN 8**

1.4521 (PREN 25) **RN 7**

Figure 4 Appearance of ferritic stainless steel after four years exposure in open condition

1.4162 (PREN 26) **RN 5**

1.4462 (PREN 35) **RN 4**

1.4410 (PREN 43) **RN 2**

Figure 5 Appearance of duplex stainless steel after four years exposure in open condition

A correlation between the effects of alloying element in term of PREN and the extent of atmospheric corrosion is shown in Figure 7 – Figure 8. Figure 7 can be used to predict the risk for atmospheric corrosion in a severe marine environment in terms of the maximum corrosion depth. When the PREN is higher than 43, pitting is not expected, whereas pitting corrosion will take place when the PREN is lower than 43. When the PRE is 12, uniform corrosion occurs. For architectural applications the main degradation of stainless steel is caused by staining and discoloration, which correlates to a PREN of 35 or above 35 (Figure 8). For PREN values below 35 red rust was also observed, and the amount increased with decreasing PREN value. This may be explained by the physical and chemical properties of passive film exposed to the atmosphere [1]. The maximum depth of corrosion attack can be considered if the depth of attack constitutes any serious risk to structural integrity. The difference between the surface finish, can also be considered as a margin of safety as indicator of the susceptibility to degradation.

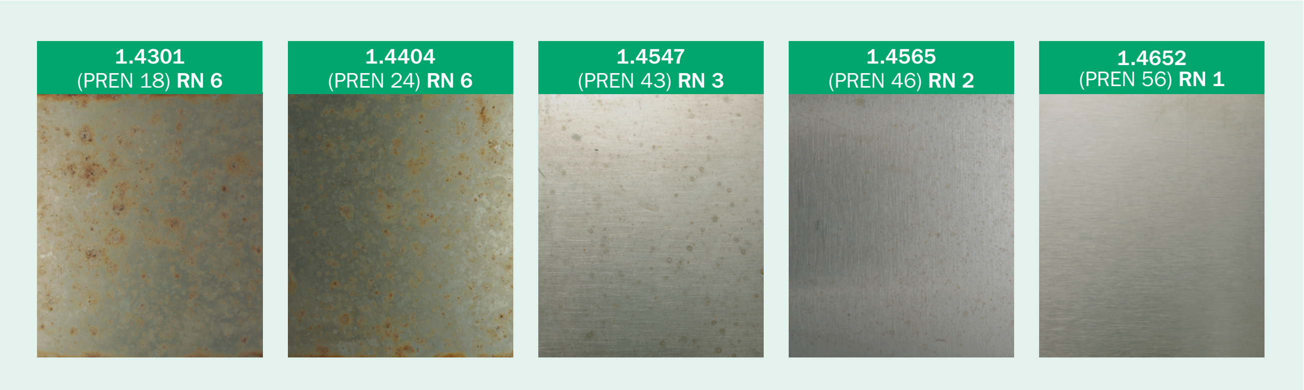


Figure 6 Appearance of austenitic stainless steel after four years exposure in open condition.

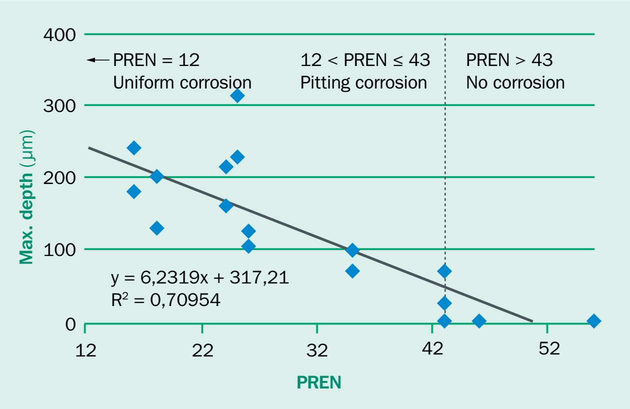


Figure 7 The effect of PREN on the maximum depth of corrosion attack after four years exposure.

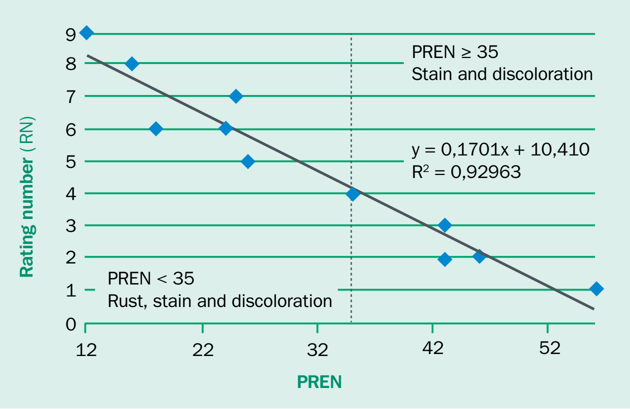


Figure 8 The effect of PREN on the degree of degradation (RN) after four years exposure.

3.4. Surface treatment

In order to study the effect of surface treatment on atmospheric corrosion resistance, some samples of 1.4462 were exposed as-welded and some after post weld cleaning (shot blasted and pickled in the laboratory). The as-welded specimen (1D mill surface) exhibited a higher corrosion sensitivity than those that had undergone post weld cleaning see Figure 9 and Figure 11. This was observed in the heat affected zone, weld areas and base material (Figure 11A). No significant difference between the weld and the base material for the shot blasted and pickled surface after open exposure could be observed (Figure 12B). The surface without post weld treatment exhibited a worse appearance after only two years of exposure. The degree of degradation after 2 years open exposure was RN 4 (~12%) for the 1D mill surface but only RN 2 (~1%) for the shot blasted and pickled surface. The degree of degradation became more obvious with longer exposure periods. The conclusion is that in the marine environment in Dubai, the duplex grade 1.4462 can lose 7 points on the RN scale if the appropriate surface treatment is not used. Frequent cleaning of the stainless steel is recommended for severe marine environments, since this removes deposits (such as salt/sand) that can cause corrosion and staining, but the effect is dependent on the surface finish.

It has been reported that chromium enrichment in the surface film is the main factor controlling the atmospheric corrosion resistance in marine environments [2, 18]. Pickling can give a relative rough surface but also result in increased chromium in passive film [2]. The effect of surface preparation can also be seen from the results of critical pitting temperature (CPT) testing according to ASTM G 150, (Figure 10). The CPT method is used to estimate the resistance to stable propagation of pitting corrosion of stainless steels. It is an accelerated test with no direct correspondence to the in-service conditions, but it is useful as a ranking tool. The results showed that a very careful laboratory pickling procedure gave a higher CPT than either a mill surface or a

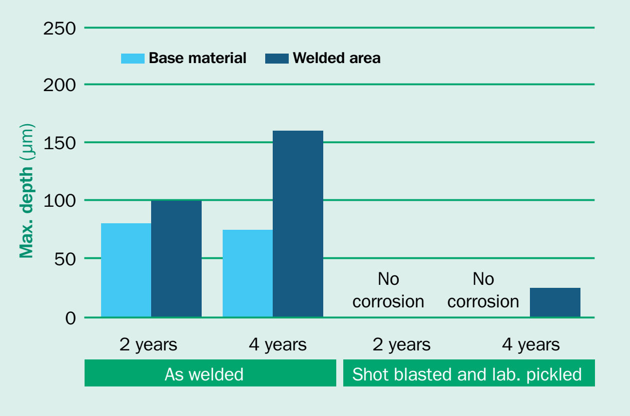


Figure 9 Effect of surface treatment on corrosion resistance

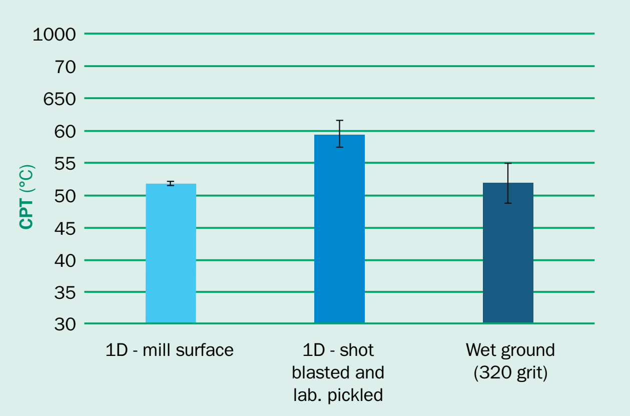


Figure 10 Effect of surface treatment on CPT of duplex grade 1.4462 tested on reference sample in 1 M NaCl.

wet ground surface. The reason for this is that surface treatment such as acid pickling will remove contaminants and inclusions from the surface as well as restore the passive layer, leaving the stainless steel with a cleaner and more corrosion resistant surface.

3.5. Surface roughness

The surface roughness is an important factor which influences the corrosion performance and appearance of a stainless steel. Some smooth surfaces are produced specifically for architectural applications. The results in Figure 12-Figure 14 demonstrate that a smooth surface finish has a beneficial effect on corrosion resistance and degree of degradation. A smooth surface finish (Ra 0.2 µm) retains less dirt and debris, and provides better corrosion performance than a rougher surface (Ra 3.0 µm). This observation is in agreement with the European standard EN 10088 which recommends that a surface roughness of Ra ≤ 0.5 microns can used in highly corrosive environments [20].

The severe atmospheric condition at the marine site in Dubai gives a high risk for staining as seen in Figure 12 and Figure 14. Aggressive deposition or dust is more likely to be retained on a rough surface, particularly when there is no cleaning through rainfall. The higher degree of degradation of the coupon with a rougher surface became obvious with longer exposure time. This supports the conclusion that a smooth surface and crevice-free design can be used in combination with appropriate alloy selection to achieve the desired long term corrosion performance.

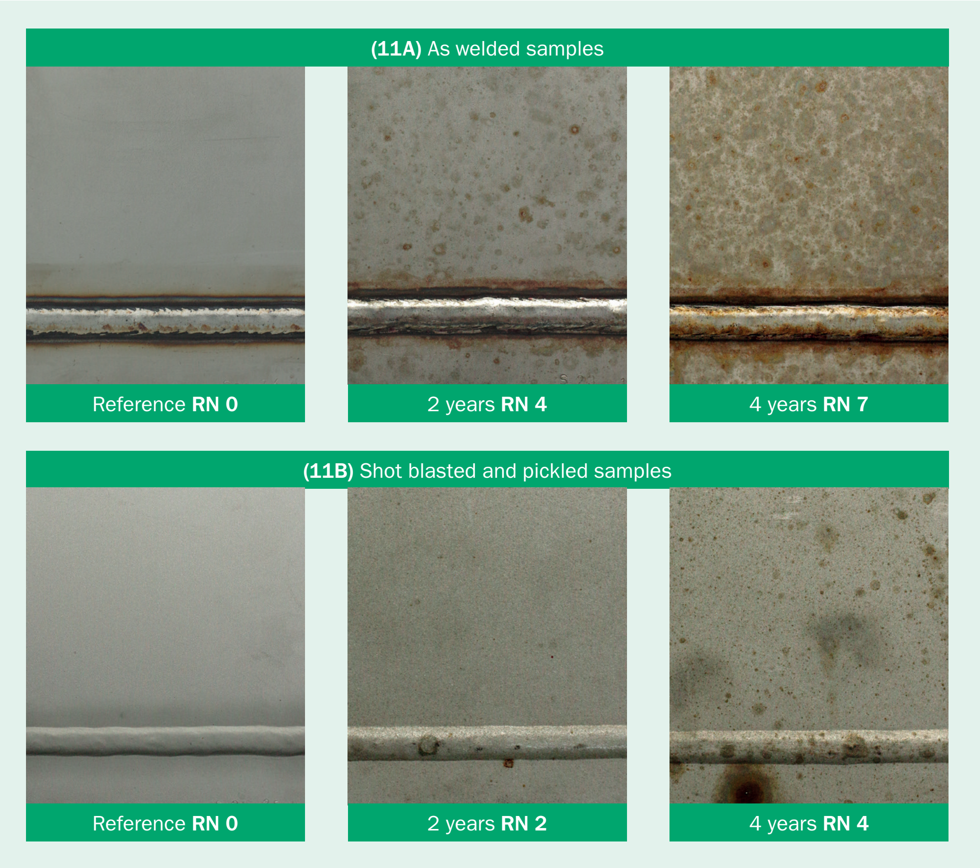


Figure 11 Appearance of welded (FCAW) duplex 1.4462 with different exposed times in open condition

3.6. Microclimate

The microclimate must also be taken into consideration when it comes to architectural applications. Stainless steels exposed in sheltered areas or open to the weather can give rise to very different amount of staining and corrosion. The difference in corrosion between the open condition and sheltered positions is geographically dependent. A sheltered area (such as under building eaves) which is not cleaned regularly accumulates dust and deposits, creating in the most cases a more aggressive corrosion environment. The presence of chlorides and moderate levels of humidity may facilitate corrosion of a susceptible stainless steel in sheltered application [9].

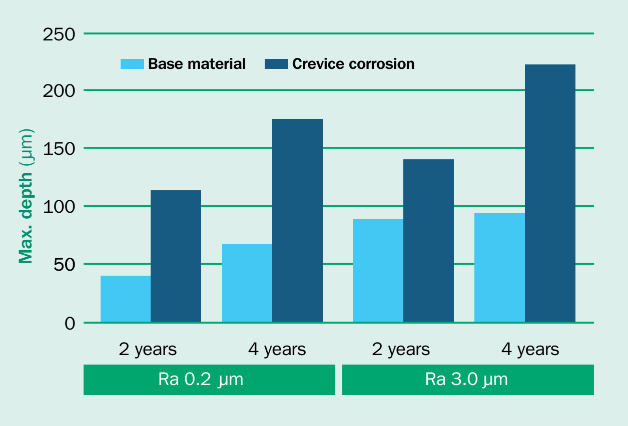


Figure 12 Effect of surface finish on corrosion resistance

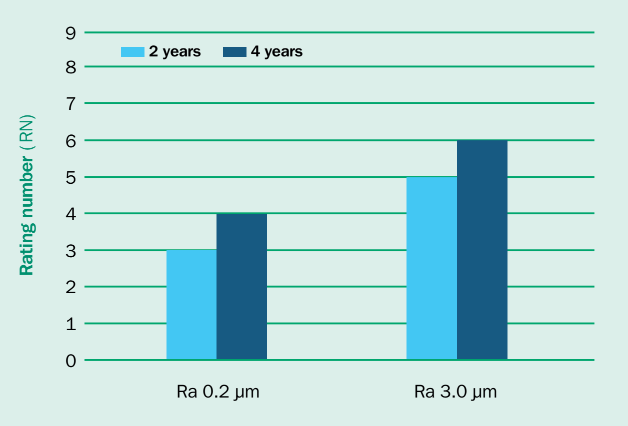


Figure 13 Effect of surface finish on degree of degradation.

Figure 14 Appearance of duplex grade 1.4462 with different surface finishes for open condition.

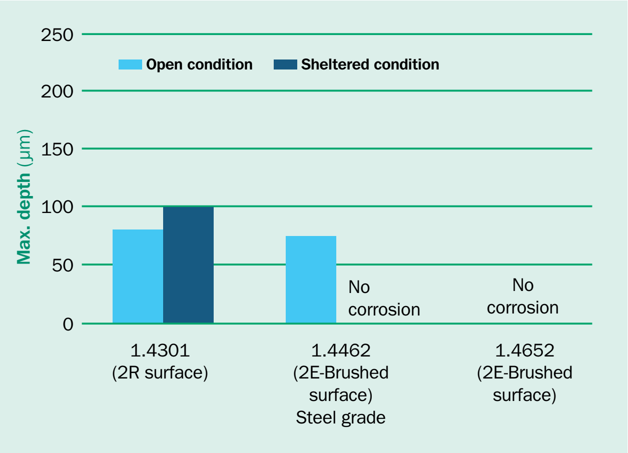


Figure 15 Effect of exposed condition on corrosion resistance.

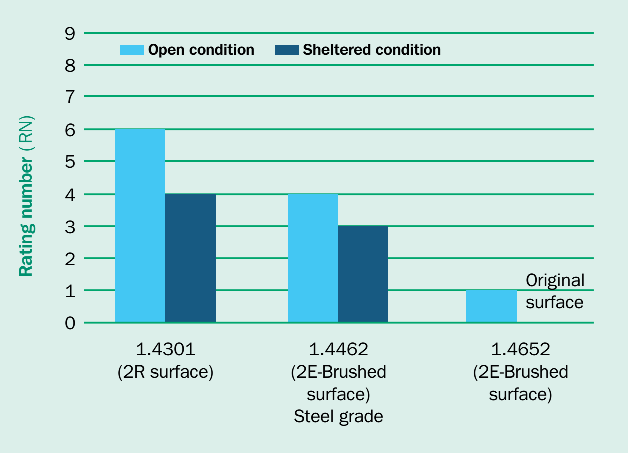
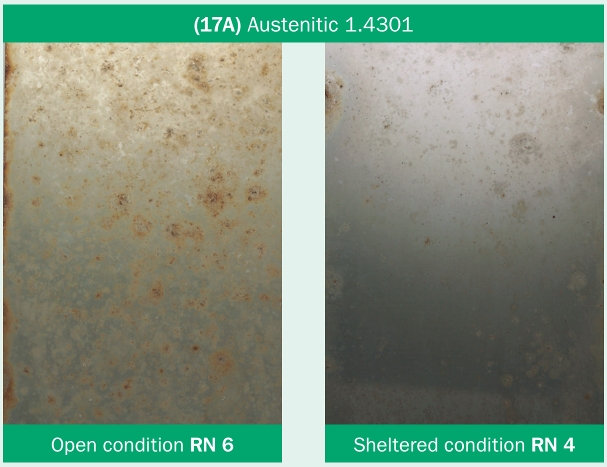


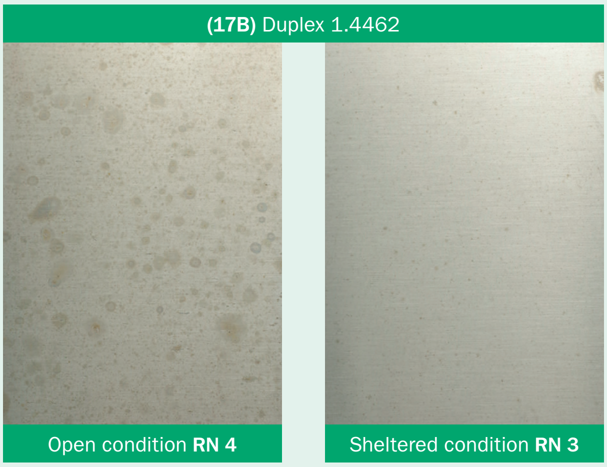
Figure 16 Effect of exposed condition on degree of degradation.

Figure 15 and Figure 17 show the effect of the microclimate after four years of exposure at the marine site in Dubai. In this case however, sheltered specimens are less affected than the openly exposed specimens. The general observation from European tests [8] is the reverse, because regular washing by rainfall results in less staining on openly exposed specimens than those which are sheltered. However, the Dubai climate is very dry [4]. One plausible explanation for the difference is that some condensation may occur in open condition surfaces, which are more rapidly cooled at nightfall, and promote corrosion. Another answer may lie in the observation that there was a higher proportion of sulphate in the deposits formed in sheltered conditions (Figure 3). This might act as corrosion inhibitors [4]: it is recognised that the localised corrosion susceptibility of stainless steels increases with increasing chloride concentration and decreases with increasing sulphate to chloride ions ratio [21, 22].


(17A) Austenitic 1.4301

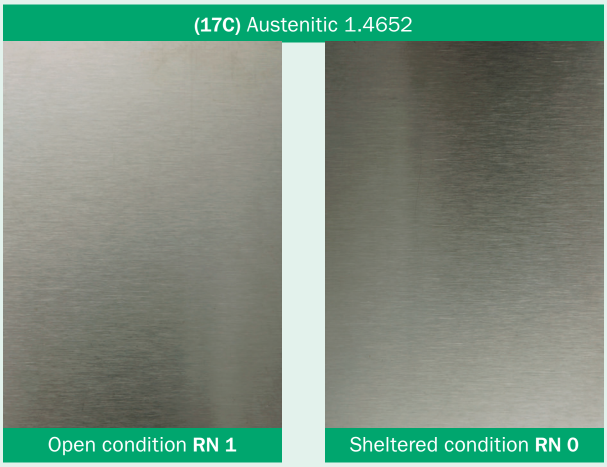
Open condition **RN 6**

Sheltered condition **RN 4**


(17B) Duplex 1.4462

Open condition **RN 4**

Sheltered condition **RN 3**


(17C) Austenitic 1.4652

Open condition **RN 1**

Sheltered condition **RN 0**

Figure 17 Appearance of stainless steel surface after 4 years exposure with different exposed condition

4. Conclusions

1. The corrosiveness of the marine test site in Dubai was according to ISO 9223 category CX for all reference samples.
2. The typical amount of soluble chloride deposition after four years averaged 126 mg /m^2 for open conditions and 248 mg /m^2 for sheltered conditions. Other anion species such as sulphate, and nitrate were also present.
3. A correlation was observed between the alloying level (PREN) and the atmospheric corrosion resistance. The most resistance grades were 1.4410, 1.4565 and 1.4652 which have PRE ≥ 43.
4. Alloys with PREN ≥ 35 may be considered for architectural materials in severe marine locations such as the Dubai site, if this is combined with frequent cleaning. A smooth surface finish or the uses of bright annealed surfaces also give an improvement in corrosion resistance.
5. To achieve the best corrosion performance the surface should be clean and free of contamination and have a crevice-free design.
6. Specimens in a sheltered location showed better performance than those which were openly exposed, in contrast to the situation usually observed at European sites. This may be due to the lack of rainfall in combination with condensation effects, plus sulphate ion accumulation at sheltered locations which can act as a corrosion inhibitor.

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