CORROSION HARDNESS EFFECT OF STEEL SCREWS BY NANOINDENTATION

Prepared by

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INTRODUCTION

As the most common failure mechanism in industry, corrosion of materials costs hundreds of billions of dollars annually to the U.S. economy[i]. It is critical to implement optimal corrosion control practices to improve lifecycle and asset management. Accelerated corrosion tests can substantially increase the measurement speed compared to those carried out in natural weathering. Laboratory corrosion tests that closely simulate the atmospheric effects on the corrosion mechanism of materials significantly facilitate the quality control and R&D of new materials and protective coatings for applications in aggressive environments.

IMPORTANCE OF NANOINDENTATION TEST ON CORRODED METALS

The mechanical properties of materials deteriorate during the corrosion process. For example, lepidocrocite (γ-FeOOH) and goethite (α-FeOOH) form in the atmospheric corrosion of carbon steel. Their loose and porous nature results in absorption of moisture and in turn further acceleration of the corrosion process[ii]. Akaganeite (β-FeOOH), another form of iron oxyhydroxide, is generated on the steel surface in chloride containing environments[iii]. Nanoindentation can control the indentation depth in the range of nanometers and microns, making it possible to quantitatively measure the hardness and Young's modulus of the corrosion products formed on the metal surface. It provides physicochemical insight in corrosion mechanisms involved so as to select the best candidate material for the target applications.

MEASUREMENT OBJECTIVE

In this application, we showcased that the Nanovea Mechanical Tester in Nanoindentation mode measures the effect of rust in the corrosive media on the evolution of the mechanical properties of two types of steel screws.

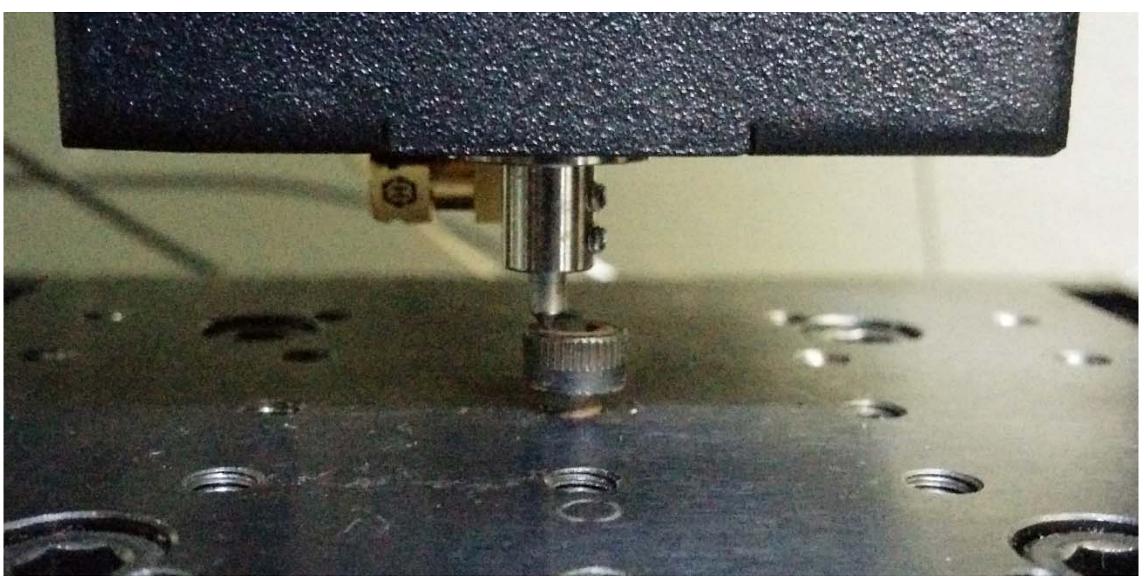


Fig. 1: Indenter on the corroded screw.

TEST CONDITIONS

In this study, screws made of two types of steels were tested by nanoindentation. The steels are Stainless Steel 316 (SS316) and Alloy Steel with a Black Oxide surface finish, respectively. The screws were immersed in 3.5 wt. % NaCl solution for 7 days and 14 days, respectively. This is followed by cleaning and rinsing by isopropanol and acetone solutions before the nanoindentation test. The new screws without the corrosion process were also tested for comparison. The nanoindentation test conditions are summarized in Table 1. More than ten tests were performed at each condition to ensure repeatability of the measurement.

Samples	SS316 and Alloy Steel screws
Maximum load (mN)	200
Loading rate (mN/min)	400
Unloading rate (mN/min)	400
Computation Method	ASTM E-2546 & Oliver & Pharr
Indenter type	Berkovich Diamond

Table 1: Test conditions of the nanoindentation after corrosion tests.

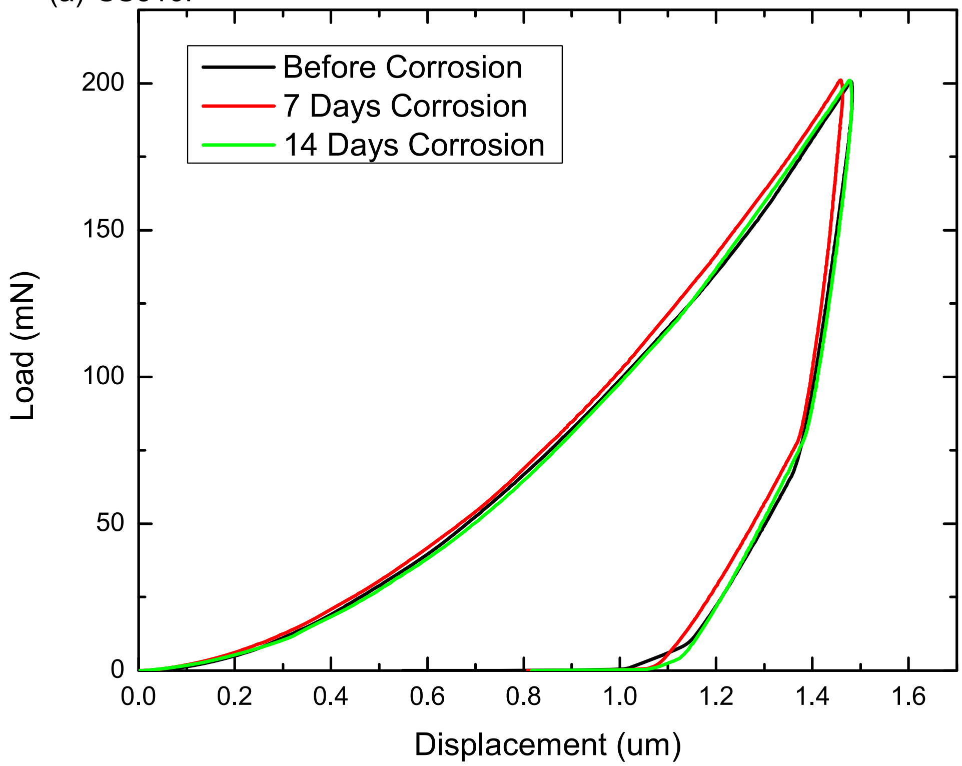
RESULTS AND DISCUSSION

The load vs. displacement plots of the nanoindenation tests on SS316 and Alloy Steel screws after different corrosion time is shown in Fig. 2. The hardness as a function of the corrosion time is plotted in Fig. 3. The evolution of the NaCl solution and the Alloy Steel screws after 7 and 14 days corrosion attack are shown in Fig. 4 and Fig. 5, respectively.

The SS316 exhibits consistent mechanical behaviors during the 14 days corrosion test in the 3.5 wt. % NaCl solution. It possesses a constant hardness of ~4.5 GPa, calculated from the comparable Load-Displacement curves. In comparison, the Alloy Steel screw shows a high surface hardness of 6.7 GPa, thanks to the mechanical enhancement by the black oxide surface finish. As the Alloy steel screws were corroded in the NaCl solution, reddish corrosion products progressively formed on the surface of the screws (Fig. 5) and were released in the solution (Fig. 4). Formation of such porous and loose rust led to deterioration of the hard black oxide film on the metal surface and ultimately reduced the surface hardness to ~4.6 GPa.

Accelerated corrosion tests in the corrosive media that simulate the nature weathering effect on metals have strategic importance in the quality control and R&D of new materials and protective coatings serving in the corrosive environment. Nanoindentation allows one to quantitatively evaluate the impact of corrosion on various metals or coatings so as to select the best candidate for the target applications. The evolution of the mechanical properties on the surface provides us a physicochemical insight in corrosion mechanisms involved in the formation of the corrosion products, which is critical for various industrial applications such as in the oil and marine industries. Stainless steels as reinforcement compared to carbon steels can enhance the durability and reliability of the mechanical parts exposed to aggressive environment.

(a) SS316:



(b) Alloy Steel:

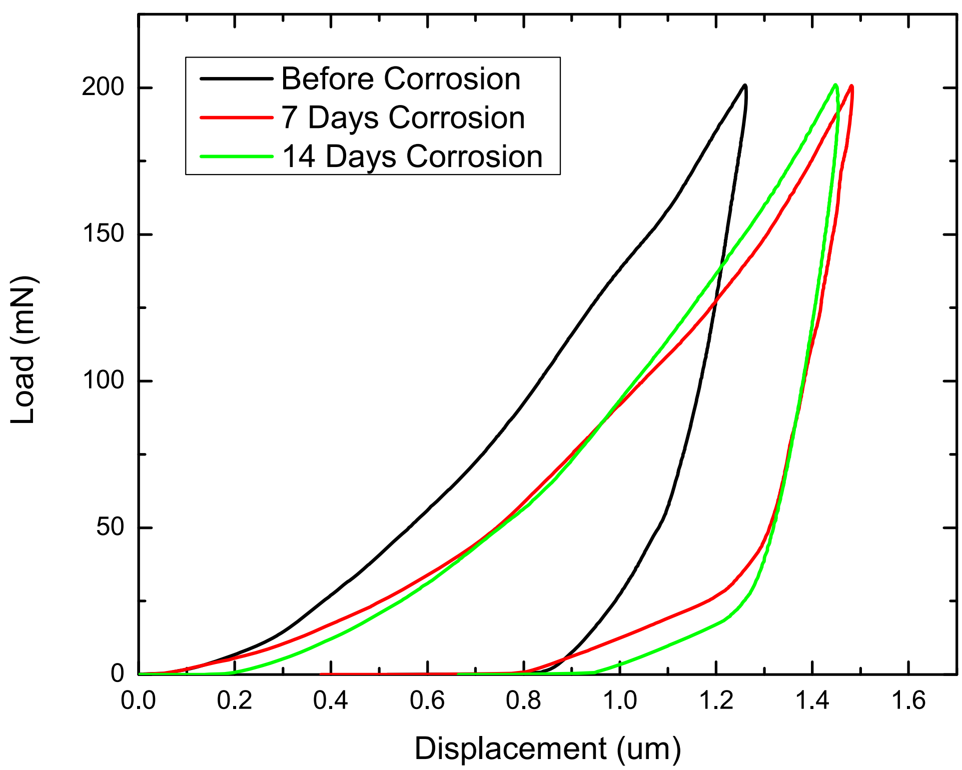


Fig. 2: The load vs. displacement plots of SS316 and Alloy Steel screws before, and after 7 and 14 days corrosion tests.

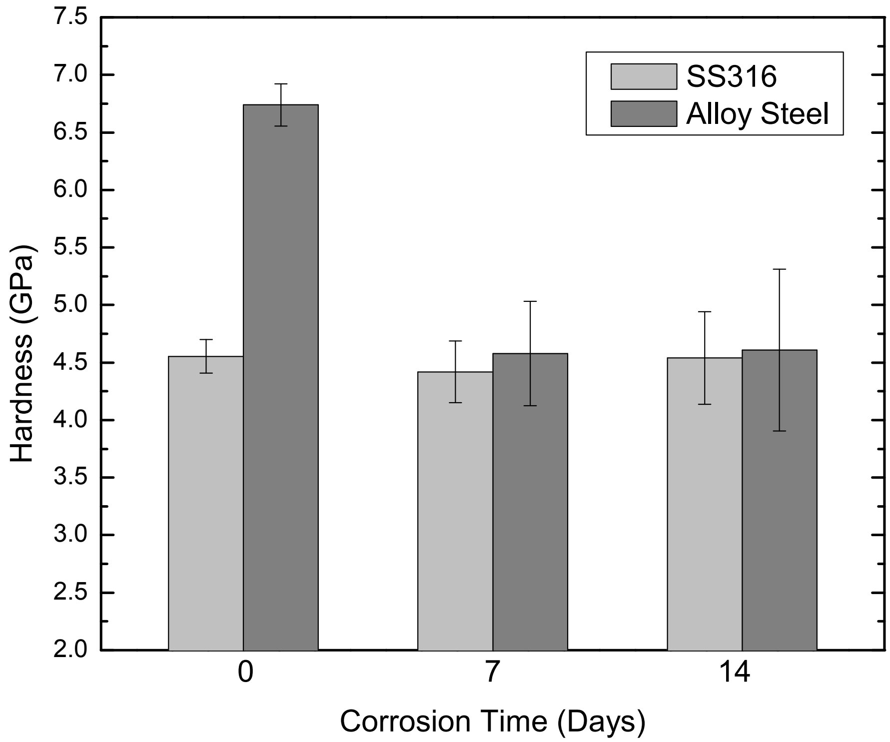


Fig. 3: The evolution of hardness as a function of the corrosion time.

(a) 7 days immersion: **(b) 14 days immersion:**

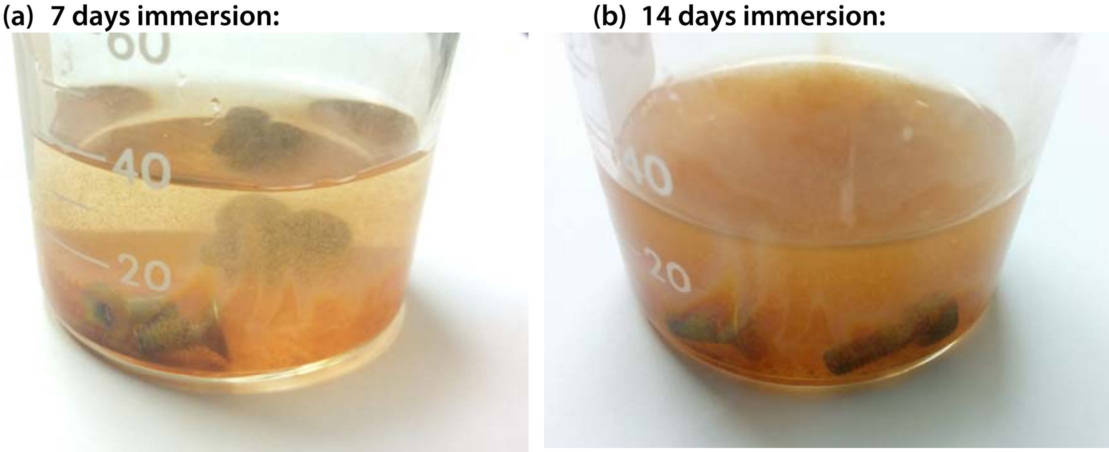
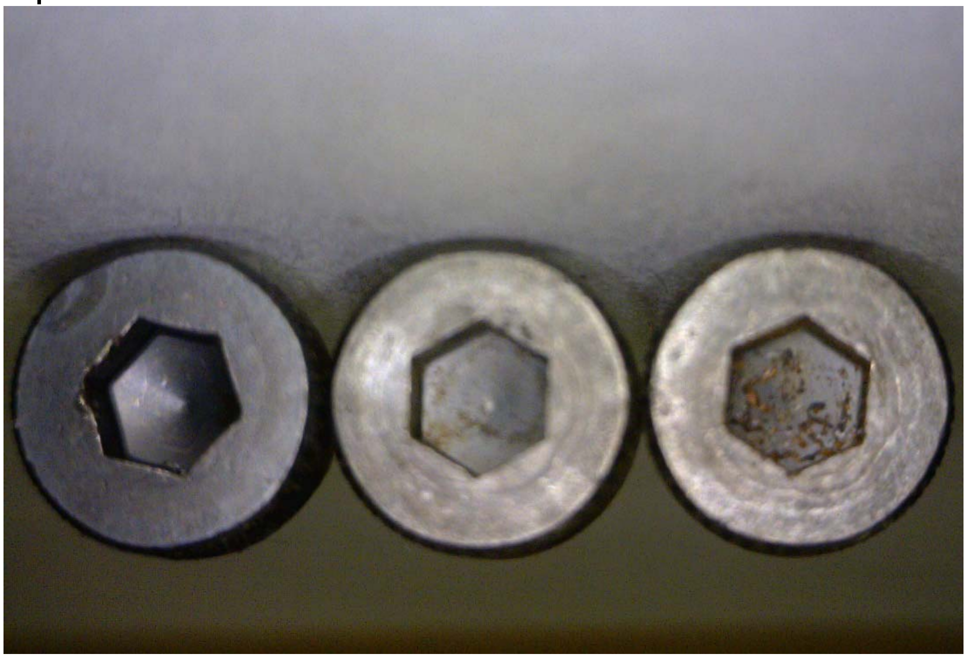


Fig. 4: The screws after 7 and 14 days immersion in the 3.5 wt. % NaCl solution.

(a) Top view:



(b) Side view:

Fig. 5: Top and side views of the Alloy Steel screws before, and after 7 and 14 days corrosion tests (from left to right).

CONCLUSION

The Nanovea Mechanical Tester performs the nanoindentation test on two sets of screws made of SS316 and Alloy Steel, respectively. Accelerated corrosion tests in the salt solution provide results more quickly than those obtained from natural weathering, which facilitates the development of new alloys and protective coatings. Corrosion has a negative impact on the surface mechanical property such as hardness on the alloy steel, reducing the surface hardness from ~6.7 to ~4.6 GPa during the first seven days immersion in the 3.5 wt.% NaCl solution. This value stays constant in the following seven days corrosion test. In comparison, the corrosion resistant SS316 screws exhibit constant hardness throughout the corrosion test, which demonstrates the importance of corrosion resistance to the reliability of the mechanical properties.

The Nanovea Mechanical Testers provide unmatched multi-function Nano and Micro/Macro modules on a single platform. Both the Nano and Micro/Macro modules include scratch tester, hardness tester and wear tester modes, providing the widest and most user friendly range of testing available on a single module.

To learn more about Nanovea Mechanical Tester or Lab Services.

MEASUREMENT PRINCIPLE

Nanoindentation is based on the standards for instrumented indentation, ASTM E2546 and ISO 14577. It uses an established method where an indenter tip with a known geometry is driven into a specific site of the material to be tested, by applying an increasing normal load. When reaching a pre-set maximum value, the normal load is reduced until complete relaxation occurs. The load is applied by a piezo actuator and the load is measured in a controlled loop with a high sensitivity load cell. During the experiment the position of the indenter relative to the sample surface is precisely monitored with high precision capacitive sensor.

The resulting load/displacement curves provide data specific to the mechanical nature of the material under examination. Established models are used to calculate quantitative hardness and modulus values for such data. Nanoindentation is especially suited to load and penetration depth measurements at nanometer scales and has the following specifications:

Maximum displacement (Dual Range)	: 50 μm or 250 μm
Depth Resolution (Theoretical)	: 0.003 nm
Depth Resolution (Noise Level)	: 0.15 nm
Maximum force	: 400 mN
Load Resolution (Theoretical)	: 0.03 μN
Load Resolution (Noise Floor)	: 0.3 μN

Analysis of Indentation Curve

Following the ASTM E2546 (ISO 14577), hardness and elastic modulus are determined through load/displacement curve as for the example below.

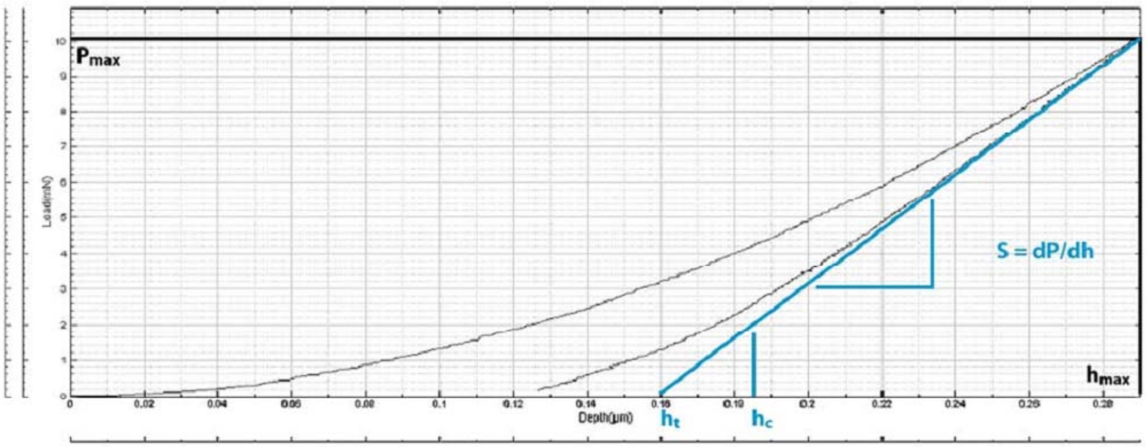


Fig. 6: Load-displacement curve of nanoindentation.

Hardness

The hardness is determined from the maximum load, P_{max}, divided by the projected contact area, A_c:

$$H = \frac{P_{\max}}{A_c}$$

Young's Modulus

The reduced modulus, E_r, is given by:

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_c}}$$

Which can be calculated having derived S and A_C from the indentation curve using the area function, A_C being the projected contact area. The Young's modulus, E, can then be obtained from:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i}$$

Where E_i and ν_i are the Young's modulus and Poisson's ratio of the indenter and ν the Poisson's ratio of the tested sample.

How are these calculated?

A power-law fit through the upper 1/3 to1/2 of the unloading data intersects the depth axis at h_t. The stiffness, S, is given by the slope of this line. The contact depth, h_c, is then calculated as:

$$h_c = h_{\max} - {}^{3P_{\max}}\!/_{4S}$$

The contact Area A_c is calculated by evaluating the indenter area function. This function will depend on the diamond geometry and at low loads by an area correction.

For a perfect Berkovich and Vickers indenters, the area function is A_c=24.5h_c^2. For Cube Corner indenter, the area function is A_c=2.60h_c^2. For Spherical indenter, the area function is A_c=2πRh_c , where R is the radius of the indenter. The elastic components, as previously mentioned, can be modeled as springs of elastic constant E, given the formula: $\sigma = E\varepsilon$ where σ is the stress, E is the elastic modulus of the material, and ε is the strain that occurs under the given stress, similar to Hooke's Law. The viscous components can be modeled as dashpots such that the stress-strain rate relationship can be given as $\sigma = \eta \frac{d\varepsilon}{dt}$, where σ is the stress, η is the viscosity of the material, and dε/dt is the time derivative of strain.

Since the analysis is very dependent on the model that is chosen, Nanovea provides the tool to gather the data of displacement versus depth during the creep time. The maximum creep displacement versus the maximum depth of indent and the average speed of creep in nm/s is given by the software. Creep may be best studied when loading is quicker. Spherical tip is a better choice.

Other possible measurements by Nanovea Mechanical Tester:
Stress-Strain & Yield Stress, Fracture Toughness, Compression strength, Fatigue testing and many others.

DMA SINUS MODE PRINCIPLE

Sinus Mode (Ranging from 0.1 Hz to 100 Hz): A sinusoidal stress is applied and the strain in the material is measured. This allows plotting hardness and elastic modulus versus depth and can be used to study viscoelastic materials such as polymers, varnishes, plastics.

Storage modulus *E'* characterizes the elastic behavior.
Loss Modulus *E''* characterizes the viscous behavior (loss of energy due to internal friction).

$E^* = E' + iE''$, $\quad E' = \frac{\sqrt{\pi}}{2\sqrt{A_{co}}} \frac{\Delta P}{\Delta h} Cos\phi$ (1-ν²), $\quad E'' = \frac{\sqrt{\pi}}{2\sqrt{A_{co}}} \frac{\Delta P_o}{\Delta h_o} Sin\phi$ (1-ν²)

Where ϕ, the phase shift between depth and load curves, $\frac{\Delta P_o}{\Delta h_o}$, the variation of load and depth respectively for one oscillation. A_{co}, the projected contact area for the oscillation. The viscosity factor λ can be calculated from $\lambda = \frac{1}{2\pi f} \frac{\Delta P_o}{\Delta h_o} Sin\phi$ where f is the frequency at which the test was performed.

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[i] **http://www.nace.org/uploadedFiles/Publications/ccsupp.pdf**
[ii] **E. Almeida, M. Morcillo, B. Rosales, and M. Marrocos, "Atmospheric corrosion of mild steel part I—rural and urban atmospheres," Materials and Corrosion, vol. 51, no. 12, pp. 859–864, 2000.**

[iii] **T. Kamimura, S. Hara, H. Miyuki, M. Yamashita, and H. Uchida, "Composition and protective ability of rust layer formed on weathering steel exposed to various environments,"** Corrosion Science, vol. **48, no. 9, pp. 2799–2812, 2006.**