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Corrosion Resistance of Stainless Steels and Nickel Alloys in Seawater

Sandra Le Manchet
INDUSTEEL
56 rue Clémenceau
Le Creusot, 71200
France

Emilie Robin
INDUSTEEL
56 rue Clémenceau
Le Creusot, 71200
France

Martin Monnot
INDUSTEEL
56 rue Clémenceau
Le Creusot, 71200
France

ABSTRACT

The corrosion resistance of metallic materials in natural seawater is arousing more and more interest from engineering companies and Oil & Gas end-users. Indeed, hydrotesting and flooding operations are very often conducted to check the quality of the vessels and piping systems. In this case, seawater may cause pitting corrosion and crevice corrosion.

Seawater is a very complex and corrosive environment due to its high amount of chlorides, and to the presence of algae, bacteria and many other components that may lead to the formation of a biofilm on the surface of the steel. In addition, during an hydrotest, the temperature of the steel can dramatically increase under the effect of sun and reach relatively high temperatures.

This paper provides an update on the resistance of various corrosion resistant alloys in natural seawater at 30°C (86°F) and 75°C (167°F). Three materials are investigated: UNS N08904, N08825 and N06625. They are today commonly used in the Oil & Gas industry, especially in the upstream part. UNS N08825 and N06625 are often clad to carbon steel to get a cost-efficient metallic solution for piping systems.

Key words: Stainless steel, nickel alloy, austenitic, seawater, pitting corrosion, crevice corrosion

INTRODUCTION

Seawater is involved in many industrial applications. For instance, it can be used for heat exchangers and as a cooling medium. It is also commonly used for hydrotesting of piping systems. This environment is very aggressive, especially when considering the complexity of seawater composition combined with the process temperature and sometimes acidic conditions. Choosing an inappropriate material may induce severe corrosion, leading to the leakage of the equipment.

The risk of pitting corrosion must be taken into account for selecting the right Corrosion Resistant Alloy (CRA). Alloying elements such as chromium, molybdenum, tungsten and nitrogen have a beneficial influence on the pitting corrosion resistance of CRA materials. The Pitting Resistance Equivalent Number (PREN) is a useful empirical tool that can be used to get a ranking of stainless steels behavior in a chloride-containing environment. For austenitic stainless steels, the following formula is often considered:

$$\text{PREN}_a = \%Cr + 3.3 (\%Mo + 0.5\%W) + 16\%N \quad (1)$$

For nickel alloys, other PREN formulas are commonly used to better weight the role of molybdenum:

$$\text{PREN}_b = \%Cr + 2.3\%Mo \quad \text{or} \quad (2)$$

$$\text{PREN}_c = \%Cr + 1.5 (\%Mo + \%W + \%Nb) + 30\%N \quad (3)$$

These formulas give a global ranking of the pitting corrosion resistance of the materials. However, they do not predict whether a given material will be susceptible or not to pitting corrosion in seawater at a given temperature.

Material selection must also be driven by the risk of crevice corrosion, caused by the combined influence of a stagnant solution with the presence of chlorides. It typically occurs under deposit, washers, gaskets or threads.

In the literature, there is a large number of papers dealing with seawater corrosion resistance of austenitic (UNS N31603), super-austenitic (6%Mo) stainless steels and nickel alloys (N07725, N09925, N10276, N06625), mainly at ambient temperature.¹⁻⁷ However, there is only little information on the behavior of the nickel alloy N08825 that is often considered as a cost-effective alternative to N06625 in some aggressive media.

The originality of the present study is that it deals with the corrosion resistance of quenched and tempered materials, representative of clad plates. The austenitic stainless steel UNS N08904 and nickel-based alloys UNS N06625 and N08825 are today regularly used in the Oil & Gas industry. For economic reasons, it is now common to use clad plates, consisting of a thin layer of CRA combined to a thicker carbon-steel backing material. The cladding alloy ensures corrosion resistance properties while the backer steel provides mechanical strength and toughness. One way to produce clad plates is to co-laminate both steel layers by means of the roll-bonded process. The surfaces are assembled together by combining high temperature and hot-rolling. To obtain the required mechanical properties of the carbon-steel backer, an appropriate heat treatment must be performed. It must be carefully selected not to have any significant detrimental impact on the corrosion resistance of the clad material caused by the formation of chromium carbides at the grain boundaries.

Several papers have been published on the intergranular and pitting corrosion resistance of these clad materials in standardized solutions, but there is lack of results coming from natural seawater exposures.⁸⁻¹¹ Another specificity of this study is that very severe crevice conditions were investigated

with a torque of 20 Nm. It allows to simulate a typical steel / flange contact. A 3 Nm condition has also been considered. It represents a contact between the steel surface and a deposit.

EXPERIMENTAL PROCEDURE

Seawater is a complex medium, containing chlorides as well as many other anions and cations. It also contains marine microorganisms like bacteria, algae, plankton and microanimals. That is why the best way to assess the corrosion resistance of a material in seawater is to perform long-term immersion tests in renewed natural seawater.

After a few days of immersion, an active biofilm forms on the surface of the steel leading to an increase in its potential called ennoblement. This biofilm is caused by the colonization of bacteria, algae and microorganisms. The steel is then more susceptible to localized corrosion due to the formation of differential aeration and modification of the electrochemical conditions at the steel-biofilm-environment interfaces. The time needed to reach the ennoblement depends on the steel composition, surface finish, kind of seawater and temperature. An increase in the temperature up to around 35/40°C will kill the biofilm and stop its detrimental impact on corrosion resistance.

Tested materials

The materials tested in this study are the austenitic stainless steel UNS N08904, and the nickel alloys N08825 and N06625. Their chemical compositions are given in Table 1. They were produced by ingot casting followed by hot-rolling, and tested with an industrial surface finish (sand-blasted and pickled).

Table 1:
Chemical compositions of the tested materials

Grade	C	S	P	Si	Mn	Ni	Cr	PRENa	PRENb	PRENc
UNS N06625	0.011	0.0001	0.007	0.054	0.066	62.16	21.47	48.9	40.4	39.4
UNS N08825	0.017	0.0004	0.013	0.317	0.320	40.45	23.06	33.4	30.1	28.0
UNS N08904	0.015	0.0002	0.018	0.188	1.483	24.08	19.66	34.2	29.0	28.0

Grade	Mo	Cu	V	Ti	Al	Nb	W	N	O
UNS N06625	8.25	<0.005	0.008	0.179	0.093	3.455	0.009	0.0103	0.0027
UNS N08825	3.08	1.770	0.052	0.700	0.085	0.008	0.029	0.0092	0.0014
UNS N08904	4.04	1.336	0.045	<0.003	0.028	0.007	0.056	0.0712	0.0022

Laboratory heat treatments have been performed on grades N08825 and N06625 to simulate the cladding fabrication process, ie quenching followed by a tempering heat treatment. The austenitic grade N08904 has been characterized in the solid state condition.

Table 2 provides typical Critical Pitting Temperatures (CPT) and Critical Crevice Temperatures (CCT) obtained on the three materials according to ASTM¹ G48 method E and D.¹² UNS N06625 is clearly the

¹ ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA

most resistant to both corrosion types. N08904 and N08825 present the same resistance to crevice corrosion, while N08904 seems more resistant to pitting corrosion.

From these data, we can assume that N06625 will be more resistant to pitting corrosion than the other materials in seawater, while there should not be any strong difference in terms of crevice corrosion. Note that these results were obtained in a 6% ferric-chloride and 1% hydrochloric acid solution and must not be extrapolated to other environments. They just give an idea of the ranking of the materials.

Table 2:
Typical CPT and CCT values as per ASTM G48 E and D, respectively

Grade	CPT		CCT	
	°C	F	°C	F
UNS N06625	85	185	35	95
UNS N08825	20	68	10	50
UNS N08904	40	104	10	50

Environment

The samples were immersed in an exposure tank of 1100 liters. The natural seawater was continuously renewed (about 300 liters per day) for 3 months. The seawater used for this test was directly pumped from the bay of Brest, France. It was heated at 30°C (86°F) or 75°C (167°F) using regulated titanium heaters. The temperature was continuously monitored during the 3-month test. Table 3 gives the main characteristics of the water. Note that chlorine was not added.

Table 3:
Characteristics of the seawater from Brest (France)

Location	Bay of Brest, France
Salinity	34‰
pH	pH= 8.1±0.1
Inlet temperature	11.5±2.0°C

Pitting and crevice set-up

The specimens have the following dimension: length 140 mm (5.5 in) and width 80 mm (3.1 in). Some of them were used to evaluate the pitting corrosion resistance of the materials, some other to study their crevice corrosion resistance. In total, 5 specimens were considered per grade and per corrosion phenomenon.

The crevice corrosion specimens have a hole of 9 mm diameter in the middle to allow the settlement of the crevice set-up, i.e. the CREVCORR-type assembly as per ISO² 18070.¹³ The crevice formers are

² ISO, Chemin de Blandonnet 8, CP 401 - 1214 Vernier, Geneva, Switzerland

made of polyvinylidene fluoride (PVDF), all fasteners are made of titanium grade 2 and are electrically isolated from the tested specimen. Figure 1 shows an example of crevice specimen with a CREVCORR assembly.

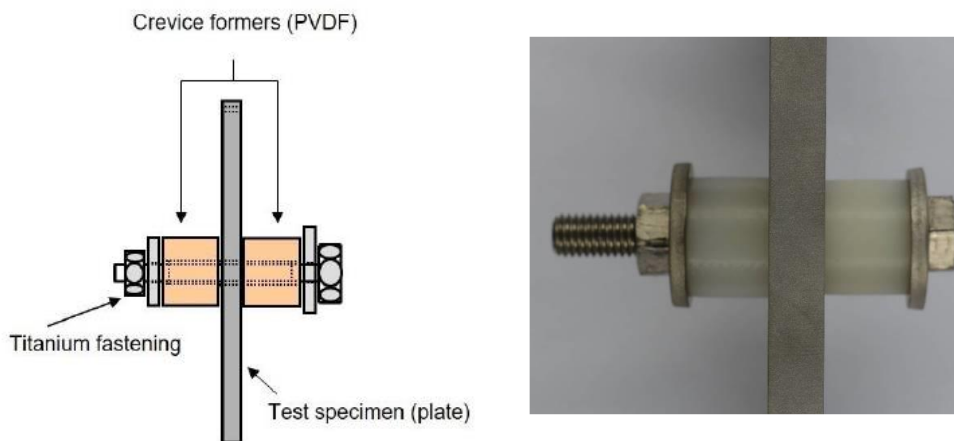


Figure 1: CREVCORR assembly

The gasket pressure was set either to 20 N/mm² to simulate a very severe crevice configuration that is representative of a flange / steel contact, or to 3 N/mm² to represent a less severe contact.

All specimens have a hole of 5 mm diameter in the corner for potential monitoring. The open-circuit potential of 3 specimens out of 5 duplicates was measured using an autonomous data logger coupled with an Ag/AgCl electrode. The Ag/AgCl electrode was previously calibrated versus a Saturated Calomel Electrode (SCE).

Evaluation

The specimens were visually inspected after the 3-month immersions. Maximum corrosion attacks were measured after removal of the corrosion products in a 20% nitric acid solution.

RESISTANCE TO PITTING CORROSION IN NATURAL SEAWATER

Pitting tests at 30°C

The open-circuit potentials of the pitting corrosion samples tested at 30°C are presented in Figures 2, 3 and 4.

For all materials, a strong increase in the potential from -100/-150 mV/SCE to about 200 mV/SCE can be observed during the first days of exposure. These potential increases are attributed to the formation of the biofilm on the surface of the specimens and may lead to a higher risk of localized corrosion initiation and propagation. For N06625 and N08825, ennoblement occurred after 5 days. For 904L, it took around 6 days.

The punctual potential drops observed on some curves are linked to local depassivation/repassivation phenomena without propagation of corrosion. From the open-circuit potentials monitorings, N08904 is more susceptible to depassivation/repassivation, followed by N08825 and then N06625.