

Redefining Corrosion Resistance Requirements for CrMn-Stainless Steels used in Drilling Applications – Results from a Round Robin Experiment

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ABSTRACT

Directional drilling is a well-known and established technology having a long tradition within the oil and gas industry. Because of their versatility, austenitic CrMn-stainless steels are the most commonly used materials in non-magnetic drill collars including sophisticated directional, measurement-while, and logging-while drilling tools. In addition to their ideal non-magnetic character, these materials exhibit an excellent combination of strength, ductility and toughness properties necessary for the application. With the continued increase in operations with demanding service conditions, mainly characterized by high temperatures, and extreme corrosive environments containing large chloride concentrations, CrMn-stainless steels have been pushed to their limits in terms of corrosion resistance. While intergranular corrosion requirements for CrMn-stainless steels used in drilling equipment are defined in API

specification 7-1, resistance to typical application-driven failure mechanisms such as pitting and environmentally-assisted cracking are not properly defined in this specification. In addition, some of the standardized methods currently employed have recently shown limitations for reliably identifying sensitized microstructures. To address these gaps and redefine corrosion requirements for CrMn-stainless steels, API task group 7047 has worked together with NACE TEG 514X to review current requirements and testing methods to identify deficits and opportunities for improvement. As a result, a round robin experiment involving steel mills and end-users was executed to evaluate the suitability of alternative corrosion testing methods. This paper presents a review of this exercise and includes a comprehensive compilation of the results produced within the round robin experiment as well as the conclusions drawn from those to modify current corrosion resistance requirements for CrMn-stainless steels in API specification 7-1.

Key words: Pitting corrosion, IGC, environmentally assisted cracking, austenitic stainless steel, ASTM A262, ASTM G48, API specification 7-1

INTRODUCTION

A significant portion of non-magnetic drill collars (NMCD) is manufactured using austenitic stainless steels that contain chromium (Cr) and manganese (Mn) as main alloying elements in addition to different nickel (Ni), nitrogen (N) and molybdenum (Mo) contents. These grades have been developed to meet the demanding requirements in terms of mechanical, magnetic and chemical properties necessary for the latest drilling technologies.¹⁻³ Drilling fluids used in drilling operations can contain high concentrations of chloride (Cl⁻)-ions, which can reach up to hundreds of thousands of mg/l (also expressed in parts per million) depending on the location and type of well to be drilled. These varying levels of chloride content are either produced by salt additions to adjust some properties in the drilling fluid, or by pickup from the geological formation. Considering the increase of temperature with well depth, corrosion resistance becomes a crucial property for operational reliability and integrity of drilling equipment. Pitting and environmentally assisted cracking (EAC) become a major concern when CrMn-stainless steels are exposed to high chloride-containing drilling fluids. EAC susceptibility can partially be controlled by the introduction of compressive residual stresses.⁴ However, surface treatments are not intended to address localized corrosion resistance. Therefore, when exposed to drilling fluids with high Cl⁻-concentrations, these grades might become prone to pitting corrosion^{2,3,5}, as well as to EAC at the highly stressed areas in the NMDC.^{1,4,6-8}

Application-oriented alloy composition and suitable thermo-mechanical processing are critical to ensure sufficient corrosion resistance in CrMn-stainless steels used for NMDCs. Cr in the range between 15 and 20 wt.% is necessary to reach passivity and impart excellent uniform corrosion resistance, while N and Mo increase localized corrosion resistance. Ferrite-forming elements like Cr and Mo, however, must be balanced by austenite-formers (Mn, N and Ni) to prevent formation of ferromagnetic ferrite, strain-induced martensite and/or intermetallic phases that might affect materials properties and performance during service. Ni is usually kept between 1.5 and 5 wt.% due to cost, and as a result, Mn is the major austenite-stabilizer in these materials. This enables CrMn-stainless steels to retain their austenitic microstructure even after strain hardening and stay fully non-magnetic. Non-magnetic character is important to minimize the magnetic interference during the surveys of the earth's magnetic field necessary for directional drilling technologies. The high Mn-content also increases the solubility of N. High strength in CrMn-stainless steels is achieved by strain hardening (cold or warm working and combinations thereof) and can be further improved by additions of N up to 0.9 wt.%. To avoid sensitization, Carbon (C) is maintained to a very low content (max. 0.06 wt.%). However, thermo-mechanical processing might involve warm working in a temperature range where these metallurgies may undergo sensitization, predominantly in the form of precipitation of Cr-nitrides, but also carbides, at the grain boundaries of their austenitic microstructure. The probability and degree of sensitization strongly depends on chemical composition as well as on thermo-mechanical processing parameters.⁹⁻¹¹

Sensitization not only has a detrimental effect on the corrosion resistance of CrMn-stainless steels¹² but also affects their impact toughness negatively.^{10,11} The EAC susceptibility of these alloys has been shown to be influenced by sensitized microstructures, and this has led to the reduced C-content in their respective chemistries. Sensitization was indeed the driving force behind the introduction of quality assurance (QA) testing per ASTM⁽¹⁾ A262¹³ on materials for NMDC in API⁽²⁾ specification 7-1¹⁴. This API specification requires testing per ASTM A262¹³ Practice A and E to assess intergranular corrosion (IGC) resistance. Practice A consists of electrolytic etching in oxalic acid, and it is recommended in the ASTM standard as a screening test rather than a criterion for material rejection. Since the idea is to assess the actual microstructural condition of commercial material, API specification 7-1¹⁴ does not require the application of the heat treatment to induce grain boundary precipitation, and defines “step” and “dual” microstructures as acceptable in accordance with the micrographs included in the ASTM A262¹³ standard. According to API specification 7-1¹⁴ requirements, material with a “ditch” microstructure must be further tested per ASTM A262 Practice E, and can only be accepted after passing this test. In Practice E, the samples are immersed in a boiling solution of sulfuric acid and copper sulfate in contact with copper shots. After 15 h exposure, the samples are bent through 180°, and subsequently investigated microscopically for cracking. However, recent studies have clearly demonstrated ASTM A262 Practice E is not capable to distinguish between non-sensitized and sensitized microstructures of CrMn-stainless steels.¹¹ Also ASTM 262 Practice A has shown limitations when testing some highly alloyed grades used in drilling technology.¹¹ All these indicate that there is a need to revise the requirements for IGC resistance included in API specification 7-1¹⁴. While improved requirements will prevent sensitization in commercial grades, other corrosion mechanisms affecting CrMn-stainless like pitting resistance will not be properly addressed, though. Therefore, additional requirements could also contribute significantly to guarantee the expected corrosion resistance of NMDCs in service.

The pioneering work conducted by Ricci et al. has demonstrated that ASTM G48¹⁵ Method A could be used as an effective test for detecting sensitization in CrMn-stainless steels.¹¹ ASTM G48¹⁵ Method A, which is an exposure test in ferric chloride solution and intended to determine the relative pitting corrosion resistance of stainless steels, might also be used to specify requirements for pitting corrosion resistance in grades used in NMDCs. Ricci et al suggested the adoption of ASTM G48¹⁵ Method A into API specification 7-1¹⁴ using different application-driven levels depending upon the expected corrosion resistance. However, since only one grade typically used in NMDCs was included in their test program, it remains unclear, whether this standardized test can be broadly applied to other commercial grades commonly used in these applications. In addition, the selected test parameters (exposure time and temperature), the acceptance criteria as well as the reproducibility of this methodology need validation. To tackle these open questions, the API task group 7047 together with NACE TEG 514X have executed a round robin experiment involving steel mills and end-users to investigate and validate the suitability of ASTM G48¹⁵ Method A as a standardized test method for redefining corrosion resistance requirements of CrMn-stainless steels used in drilling equipment.

EXPERIMENTAL PROCEDURE

The round robin exercise was divided into three parts. Part 1 deals with the replication of the research work conducted by Ricci et al.¹¹ to confirm the sensitivity of ASTM G48¹⁵ Method A to different microstructural conditions i.e. sensitization treatments applied on additional CrMn-stainless steels.

Part 2 corresponds to the application of the standardized test method based on ASTM G48¹⁵ Method A suggested by Ricci et al.¹¹ including the recommended test parameters on additional CrMn-stainless

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(2) American Petroleum Institute (API), 1220 L Street, N.W., Washington, D.C. 20005, USA

steels. The investigated materials have similar but not identical chemical compositions to the one tested in the past¹¹, and were produced by dissimilar thermo-mechanical processing routes leading to a similar bar size. The motivation is to confirm the suitability of the suggested test temperature (22 °C) and time (24 h) for testing a broad range of chemical compositions. In addition, the pass/fail criteria of 0.1 and 1 mg/cm² considered by Ricci et al.¹¹ needs to be validated, and the potential dependence of this threshold on the chemical composition of the material established. By testing the same grades (almost identical chemical composition from different heats) at different laboratories, the intention is to evaluate the reproducibility of the method.

Finally, part 3 addresses the validation of ASTM G48¹⁵ Method A using a specific set of test parameters taken from Part 2. The method will be applied on an extensive population of commercially available heats to establish the sensitivity and reproducibility of this standardized test method to be used for QA purposes.

Part 1 – ASTM G48 Method A Sensitivity

The actual chemical compositions of the CrMn-stainless steels used to confirm the sensitivity of ASTM G48¹⁵ Method A to different microstructural conditions are included in Table 1. Specimens were taken at 25.4 mm below the surface from one heat of two commercial grades. The bar size in both cases was 165 mm. The materials were originally in strain-hardened condition, the typical as-shipped condition for NMDC. Additionally, some blanks were heat treated for one hour at temperatures between 650°C and 850°C and subsequently cooled either in air or in water, to induce sensitization. Specimens were then finished from the original material and the heat-treated blanks to the dimensions according to the relevant ASTM standard.

Table 1

Chemical Composition in wt.% of investigated CrMn-stainless steels in Part 1

Grade	Cr	Mn	Ni	Mo	N	Cu	Si	C
18Cr-15Mn-3Ni-Mo	18.6	15.7	3.2	0.8	0.49	0.40	0.30	0.030
18Cr-18Mn-3Ni-2Mo	18.9	17.9	3.2	2.0	0.62	0.34	0.28	0.031

By ways of comparison, the microstructural condition of both materials in strain-hardened condition as well as after different sensitization treatments was also assessed by ASTM A262¹³ Practices A, B and E. Additionally, the impact of sensitization on Charpy V-notched (CVN) impact toughness was determined by testing according to ASTM E23¹⁶ at room temperature. All the specimens used in these additional tests were taken in longitudinal direction at 25.4 mm below the surface of the bar. Sample dimensions and surface preparation was according to the requirements included in corresponding standardized methods but the selection of these parameters was left under the responsibility of the lab conducting the tests. The tests associated to part 1 were only conducted by two steel mills.

ASTM A262 Practice A

The specimens were mounted, mirror polished and electrolytically etched in oxalic acid at 1 A/cm² for 90 s.

ASTM A262 Practice B

The specimens were exposed to a boiling solution of 50% sulfuric acid inhibited by ferric sulfate for 120 hours. Subsequently, the samples were washed, cleaned and the weight loss was determined by gravimetry. No additional ferric sulfate was added during the test.

ASTM A262 Practice E

The specimens were bent through 180° after 15 h of exposure to a boiling solution of 16% sulfuric acid and copper sulfate including copper shots.