

Rethinking Sulfide Stress Cracking (SSC) Resistance Super Martensitic Stainless Steel (SMSS-13Cr) Bar Stock with 95 ksi SMYS

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ABSTRACT

13Cr-5Ni-2Mo type Super Martensitic stainless steels (SMSS-13Cr) are often chosen for the manufacture of downhole completion equipment within the oil and gas production environment. SMSS-13Cr is primarily used in CO₂ rich production environments where carbon/low-alloy steels are subject to high corrosion rates. Currently, different UNS grades of SMSS-13Cr with varying maximum hardness, yield strengths, and heat treatment requirements are listed for use in limited sour service in the NACE MR0175/ISO 15156-3 guidelines¹. The hardness limits of the listed grades mainly pertain to the 95 ksi (655 MPa) Specified Minimum Yield Strength (SMYS) level. The environmental limits listed for the 95ksi MYS grade have similar maximum H₂S partial pressure and minimum fluid pH values, but vastly different chloride concentration limits. While chloride ions can pit SMSS-13Cr type materials, it is not clear historically why the current limits reflect a difference between the UNS grades within the same alloy type.

This paper discusses a study in which the SSC resistance of two different SMSS-13Cr UNS bar grades, S41425 and S41427 quenched and tempered to 95 ksi MYS were evaluated in multiple simulated downhole production environments to study the main effects of H₂S partial pressure, environmental pH, and chloride concentration. The SSC results provide comparison between cracking resistance of S41425-95 and S41427-95 in sour service environments. These results also offer insight for plausible limits on H₂S partial pressure, environmental pH, and chloride concentration based on testing per current NACE MR0175/ISO 15156-3 guidelines.

Keywords: Sulfide Stress Cracking (SSC), 13Cr-5Ni-2Mo, Super Martensitic Stainless Steel, S41425, S41427, bar stock, H₂S, NACE MR0175/ISO 15156

INTRODUCTION

13Cr-5Ni-2Mo type Super Martensitic stainless steels referred to as SMSS-13Cr type grades can provide good general corrosion resistance such as in high CO₂ environments combined with higher strengths and excellent toughness² making them a prospective material choice for long term downhole completion equipment depending on actual well conditions. One of the main limiting factors for the use of SMSS-13Cr type grades is the Sulfide Stress Cracking (SSC) resistance in presence of H₂S in downhole well conditions. Therefore, a good understanding of this behavior is essential to facilitate the material selection process. SMSS-13Cr is not limited to a single UNS grade and instead refers to a family of grades composed of multiple UNS numbers, including some proprietary grades. SMSS-13Cr grades are mostly available in quenched and tempered condition to 95 ksi SMYS and 110 ksi SMYS and is available as both bar stock and tubing. Bar stock is predominantly used for manufacturing thick-walled completion tool components with UNS S41425-95 and UNS S41427-95 being 95 ksi SMYS examples of prominent bar stock grades both of which are currently listed in NACE MR0175/ISO 15156-3.

However, there is a significant difference in the environmental limits currently listed for these two grades. Table 1 compares the NACE MR0175/ISO 15156-3 environmental limits for the two bar stock grades previously mentioned which are identical in maximum H₂S partial pressure and minimum environment pH, while having vastly different chloride limits. The presence of H₂S and chloride ions can pit SMSS-13Cr type material grades³ and based on the chemistry limits of both bar stock grades in question, the reasoning behind the differences in chloride concentrations is not immediately apparent. The differences may be more related to the way the NACE balloting was done for each case more than two decades ago than chemistry. A cursory look at the ballots show in the case of UNS S41425-95, testing was done at 80% stress of the specified minimum yield strength in a standard 5% NaCl solution. While in the case of UNS S41427-95, the testing was completed at stress levels of 85% and 90% of Actual Yield Strength (AYS), different pH and chloride levels, with some tests showing significant drift between the initial and final pH. This is contrary to the current NACE MR0175/ISO 15156-3 (2020) revision that requires testing at 90% AYS, tight pH control of ± 0.2 units over the entire exposure, and with the tested chloride levels representing the maximum value balloted for each grade. The buffer solutions used in ballots were various mix of Acetic Acid (CH₃COOH) and Sodium Acetate (CH₃COONa).

Table 1
NACE MR0175/ISO 15156-3 limits for S41425 and S41427

Grade	NACE MR0175/ISO 15156-3 Ref Table	Temperature	Partial pressure H ₂ S, psi (kPa)	Chloride, mg/L	pH
S41425 ⁽¹⁾	A.18	Any	1.5 (10)	Any	≥ 3.5
S41427 ⁽²⁾	A.21	Any	1.5 (10)	6100	≥ 3.5

(1) S41425 quenched and tempered to 28 HRC max hardness which aligns with 95 ksi SMYS

(2) S41427 quenched and tempered to 29 HRC max hardness which aligns with 95 ksi SMYS

To enhance clarity of the SSC resistance of SMSS-13Cr bar grades (UNS S41425, S41427) with 95 ksi SMYS, testing was conducted using NACE TM0177 Method A in various environments at 90% AYS as per Annex B.3.4 of current NACE MR0175/ISO 15156-3. The testing was done using similar methodology adopted in literature to assess H₂S cracking resistance of SMSS-13Cr bar grades with 110 ksi (758 MPa) MYS i.e. UNS S41425-110, UNS S41427-110^{4,5}.

MATERIALS

One production heat each of S41425-95 and S41427-95 bar stock were selected for the study and were quenched and tempered to a 95 ksi (655 MPa) SMYS condition. Table 2 shows the sizes, melt practice, and forging ratios of heats selected. The melt practices involved clean steel making process of primary melting using an Electric Furnace (EF), followed by secondary refining such as Argon Oxygen Decarburization (AOD), Vacuum Oxy Decarburization (VOD).

Table 2
Dimensions, Melt Practice, and Hot Work Ratio of Heats Selected

Grade	Bar outside diameter (OD) size mm (inches)	Melt practice	Hot-work ratio
S41425-95	165.1 (6.5)	EF + AOD	18.3
S41427-95	177.8 (7.0)	EF + VOD	8.47

Table 3 confirms that the chemical compositions of each heat of material selected met the requirements of their respective UNS grades.

Table 3
Chemical Composition of Test Heats

Grade	S41425-95	S41427-95
%C	0.02	0.019
%Mn	0.77	0.35
%Si	0.30	0.23
%Cr	13.37	12.22
%Ni	4.79	5.37
%Mo	1.63	1.93
%S	0.0007	0.0022
%P	0.018	0.012
%Cu	0.08	0.08
%N	0.08	0.018
%Ti	<0.15	<0.01
%V	<0.10	0.16
%Fe	Balance	Balance

Table 4 provides the details of the quench and temper heat treatment, including the resulting grain size and ferrite content of the microstructure obtained. Note the S41427-