

Alloy A975 Resistant to Severe Sour Environments and to Hydrogen Embrittlement

**Ernst Plesiutchnig, Rainer Fluch,
Martin Wöls, Marianne Kapp**
voestalpine Böhler Edelstahl GmbH & Co KG
Mariazeller Straße 25
Kapfenberg, Steiermark 8605
Austria

Greg Chitwood
voestalpine Böhler Edelstahl GmbH & Co KG
Dallas, Texas
USA

ABSTRACT

Alloy A975, a super austenitic stainless steel in the cold worked condition has been commonly used in drilling applications, where its combination of composition and high strength makes it highly resistant to pitting corrosion and fatigue. Now, after 15 years of use in drilling, this material can be considered for other oilfield applications.

Three commercial heats of cold worked (CW) A975 were subjected to different tests to assess its resistance to environmental assisted cracking. For reference, slow strain rate tests (SSRT) were performed at NACE MR0175 Levels VI and VII. Additionally, C-ring tests per NACE TM0177 Method C were performed at NACE MR0175 Levels V and VI to support the SSRT results. Light optical microscopy and scanning electron microscopy were used to analyze the specimens before and after the tests.

The SSRT show good ductility values compared to reference tests up to NACE Level VI. The C-ring testing also indicates similar cracking resistance under these conditions. The results from SSRT under cathodic potential also demonstrate good resistance against hydrogen embrittlement.

Key words: A975, Environmental Induced Cracking, NACE Level VI, Slow Strain Rate Test, Cold Work

INTRODUCTION

Industries use super austenitic stainless steels (SASS) to withstand pitting and crevice corrosion in both acidic and neutral environments containing high chlorides. SASS and austenitic stainless steels are commonly categorized by their contents of Cr, Mo, and N, as represented by the pitting resistance equivalent number (PREN). Although different definitions of PREN exist, for this study the NACE MR0175/ISO 15156 definition was utilized ($F_{PREN} = w_{Cr} + 3.3(w_{Mo} + 0.5w_N) + 16w_N$).¹ When PREN exceeds 40, the prefix ‘super’ is colloquially added to these types of stainless steel (e.g., super duplex stainless steel).

A975 in the cold worked (CW) condition has been used for more than 15 years as a material for nonmagnetic drill collars where high pitting corrosion resistance and fatigue resistance are needed. These tools typically require heavy wall thicknesses to apply maximum weight to the drill bit, and a special cold forging process is used to achieve high strength throughout the cross section. The ability to achieve high strength is aided by the composition, and alloys for nonmagnetic applications typically contain Mn and N, which facilitate this by dramatically increasing the rate of work hardening. Other oilfield tools need high strength in heavy sections, for example, certain downhole safety valve and packer components. For applications of these tools in sour fluids, precipitation hardening (PH) Ni alloys are traditionally used. However, there have been recent accounts of hydrogen embrittlement with some PH Ni alloys, which has occurred from hydrogen charging or ingress from a variety of sources.²⁻⁴ Therefore, there is an opportunity for alternative, high strength corrosion resistant alloys if it can be shown they are suitably resistant to these effects. This study presents new results for CW A975 from sour service tests [i.e., slow strain rate tests (SSRT) and C-Ring tests] and hydrogen embrittlement (HE) tests. The aim of this study is to demonstrate acceptable performance of CW A975 for use under hydrogen charging and in severe sour conditions (NACE Level VI for Type 4c) according to Tables A.12 and A.14 in NACE MR0175/ISO15156:2015.

Materials Investigated

To provide a general overview, Table 1 shows the average composition of A975 and compares it to other super austenitic steels and nickel alloys. The composition of A975 is lower in Mo content than common SASS but has additions of Cr and N to maintain corrosion resistance. A975 has a high Ni content between 29.5 and 30 wt%, which is in the range of Type 4c solid solution nickel base alloys as considered by NACE MR0175/ISO 15156-3 Table A.12.

Table 1
Actual chemical compositions (in wt%) of the materials used in crevice corrosion temperature (CCT) and critical pitting temperature (CPT) tests. All alloys were in the solution annealed condition.

Name	UNS	Mn	Cr	Ni	Mo	Cu	N	PREN ₁₆
316LN	S31603	1.7	17.4	14.5	2.8	0.1	0.08	27.92
Alloy 28	N08028	1.4	26.7	31.3	3.3	1.1	0.10	39.19
Alloy 825	N08825	1.0	21.5	42.0	3.0	2.3	0.00	31.40
6%Mo SASS	S31254	0.8	20.3	17.7	6.1	0.7	0.20	43.63
A975, #1	--	2.7	27.4	29.6	3.2	0.1	0.29	42.60

Three heats of A975 were produced in large scale with an electric arc furnace, hot forged to a suitable size, and subsequently cold worked. The chemical compositions of those three heats are summarized in Table 2. Heat #3 with lower nickel content was chosen to see whether it would have an influence on the C-ring testing results.

Table 2
Chemical compositions of three heats of Alloy 975 tested.

Heat	C	Si	Mn	Cr	Mo	Ni	Cu	N	Fe
#1	0.013	0.25	2.7	27.4	3.2	29.6	0.1	0.29	bal.
#2	0.017	0.28	2.7	27.4	3.2	29.7	0.1	0.28	bal.
#3	0.012	0.28	2.6	27.4	3.3	29.3	0.1	0.28	bal.

METHODS

CPT and CCT

To quickly rank the materials listed in Table 1, critical crevice temperature (CCT) and critical pitting temperature (CPT) experiments were performed.

Table 3 shows the parameters for the test methods used. CPT and CCT (ASTM G48 Method C and Method D) are defined as temperatures where corrosion creates a local attack exceeding a depth of 25 μm .⁵ Until the first observation of attack, the temperature is increased by incremental steps of 2.5°C. The starting temperatures are estimated with the equations per the standard.⁵

CPT and CCT were determined for all five grades (see Table 1) in 72h exposure periods according to ASTM G48, Methods C and D respectively. The surface quality was controlled and the specimens ground and stored overnight in a desiccator for passivation prior to testing.

Additionally, and for comparison with ASTM G48 Method C, the CPT was measured electrochemically according to ASTM G150 in 1M NaCl solution. The benefits of using this method are its speed and the possibility of determining the CPT independently from the potential by combining the potentiostatic method with a temperature scan. Prior to the test, the solution was deaerated and agitated with Ar (99.99%) and the samples were wet ground with No. 500 grit abrasive paper. The reference electrode was saturated calomel (SCE) with a potential of 241 mV_{SHE}. A constant potential was set to 700 mV_{SCE} and the temperature raised in 0.2°C/min increments until an irreversible rise in the slope indicated the onset of pitting. All potentials in this study are expressed versus SCE. The examination and confirmation of the corroded specimens surface were part of another work.⁶

Table 3
Parameters of the methods applied according to ASTM G48 and ASTM G150. Test duration was 72h. (OCP=open circuit potential)

Test method	Test solution	Chloride [M]	Potential [mVSCE]
ASTM G 48-meth. C, D	6% FeCl ₃ + 1% HCl	1.38	OCP (600–700)
ASTM G 150	1 M NaCl	1	700

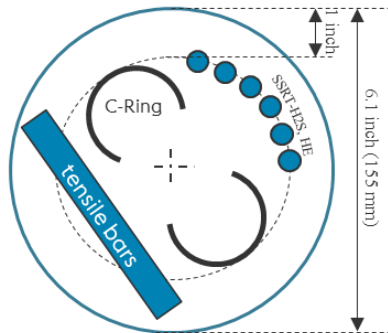
Mechanical Tests, SSRT, C-Ring tests

Prior to the environmental assisted cracking (EAC) tests at different NACE Levels, samples from each heat were extracted from mid-radius as indicated schematically from three

6.1-inch diameter cold worked rods. The type and number of test specimens for each heat are shown in Table 4.

After specimen extraction, tensile tests at temperature were carried out to determine the necessary loading for the C-ring tests according to NACE TM0177-Method C⁷ and for the different NACE Levels as defined in ANSI/NACE MR0175/ISO 15156-3:2015 Annex E.¹ For each heat in Table 2, three C-rings were extracted for the Level VI tests. Before defining the testing levels for the C-rings, SSRT were carried out according to NACE TM0198 in three test environments: Levels VI and VII of NACE TM0198 and at the ANSI/NACE MR0175/ISO 15156-3 Table A.14 limit for Type 4c solid solution nickel-based alloys at 177°C (351°F).

Table 4
Matrix for the tests against sour gas and hydrogen embrittlement (N.A.=not applicable).

Heat	Method	Conditions	T °C (°F)	ppH ₂ S	ppCO ₂	ppm NaCl	pH (Simulation)	Alloy A975 cold worked test rod:
#1, #2x2	SSRT	Air	177 (351)	N.A.	N.A.	N.A.		
#1	SSRT	NACE Level VI	175 (347)	500	500	139,000	3.27	
#2	SSRT	NACE Level VII	205 (401)	500	500	180,000	3.41	
#1	SSRT	MR0175 4c Limit	177 (351)	200	500	180,000	3.32	
#1x5	SSRT	Air, CP	40 (104)	N.A.	N.A.	N.A.	--	
#1x3 #2x3 #3x3	C-Ring	NACE Level VI	175 (347)	500	500	139,000	3.27	

Hydrogen Embrittlement

Additionally, hydrogen embrittlement (HE) testing was performed by SSRT. Five metallic blanks in the longitudinal direction were taken from 1-inch inside the surface from rod #1. The specimens were prepared according to NACE TM0198. For cathodic polarization (CP) a current density of -0.005 A/cm^2 in a 0.5M sulfuric acid solution was applied. The solution was deaerated prior to the transfer to the test cell. The tests were carried out at 40°C (104°F) at a strain rate of 10^{-6} s^{-1} .

RESULTS

CPT and CCT

Figure 1 is a graphical comparison of CPT and CCT for the alloys tested versus their PREN. In all three comparative tests, A975 showed significantly better results than UNS N08028 and was nearly identical to UNS S31254 (a 6% Mo SASS). The much better performance of A975 in comparison to UNS S31603 and UNS N08825 is not a surprise due to the much higher PREN. Further, Figure 1 (a) allows a direct comparison between the ASTM G48 Method C to the faster ASTM G150 Method with a systematic increase in CPT of about 20°C for the alloys measured in the G150 test. The results for the CCT in Figure 1 (b) do not change in ranking, only in absolute value, which is due to the different corrosion mechanism. It is evident that the test for CCT is more severe and would allow alloys to be tested at lower temperatures, which are not testable due to the upper temperature limit of 85°C in the ASTM G48 Method C test for CPT.⁵