Summary Description:

Steadily increasing requirements for material properties lead to ongoing research and development of materials in order to encounter corrosion in particular. The focus often lies on coatings or modified alloy compositions. Another alternative is the use of application-oriented and qualified material.

With Corrodur 4418 Mod (Super 13 Cr; UNS S41426), Deutsche Edelstahlwerke provides a material solution whose performance exceeds that of conventional chromium steels such as 1.4006 (AISI 410) and 1.4021 (AISI 420). This high-performance steel is characterized by high strength, outstanding toughness and good resistance to pitting and stress corrosion in a relevant range of temperatures. Material with two different strength levels (min. 95 and min. 110 ksi yield strength, respectively) was qualified acc. to NORSOK M-650 by setting up a well-controlled manufacturing route. In combination with successfully passing corrosion tests performed per NACE TM0177 and NACE TM0316 regarding SSC and SCC, this grade was qualified according to NACE MR0175 Annex B.2.3. Deutsche Edelstahlwerke was the first company completing this double qualification and today guarantees outstanding properties of Corrodur 4418Mod for dimensions ranging from 2" up to 12.25" OD and up to 39' in length.

		Hardness HRC (HB)	YS in ksi (MPa)	UTS in ksi (MPa)	A2“ in %	ROA in %	Charpy-V Notch @ -10 °C (14 °F)	LCVN in ft-lbs (J)	TCVN in in ft-lbs (J)
110 ksi	MIN		110 (758)	125 (862)	17	45	W_{single}	49/40 (66/54)[1]	26 (35)
110 ksi	MAX	32 (310)	130 (896)	160 (1103)	-	-	W_{av}	60/50 (81/68)[1]	37 (50)
110 ksi	**Rolled (typical)**[2]	≤ 30 (≤ 300)	125 (862)	135 (931)	21	68		80 (108)	50 (68)
110 ksi	**Forged (typical)**[2]	29-30 (≤ 300)	120 (828)	135 (931)	21	65		80 (108)	60 (81)
95 ksi	MIN	-	95 (655)	110 (758)	19	50	W_{single}	70 (95)	26 (35)
95 ksi	MAX	27 (300)[3]	115 (793)[3]	125 (862)	-	-	W_{av}	80 (108)	37 (50)
95 ksi	**Rolled (typical)**[2]	26-27 (≥ 270)	100 (690)	130 (897)	22	66		110 (149)	65 (88)

[1] Lower values valid for forged material only.
[2] Rough averages. Actual values explicitly depend on diameter.
[3] Max. Brinell and yield strength validated via SSC/SCC tests.

1. **What is the innovation?**

Corrodur 4418Mod is a Super 13Cr type material (UNS S41426) covering both NACE MR0175 Annex B.2.3 and NORSOK M-650 to meet high quality standards applied by several OEMs in the Oil & Gas market.

2. **How does the innovation work?**

The results of all investigations together with a verified manufacturing route led to the high-performance steel Corrodur 4418Mod that is characterized by high strength, outstanding toughness and good resistance to pitting and stress corrosion in a relevant range of temperatures. Material with two different strength levels (min. 95 and min. 110 ksi yield strength, respectively) was qualified acc. to NORSOK M-650 by setting up a well-controlled manufacturing route. In combination with successfully passing corrosion tests performed per NACE TM0177 and NACE TM0316 regarding SSC and SCC, this grade was qualified according to NACE MR0175 Annex B.2.3. Deutsche Edelstahlwerke was the first company completing this double qualification and today guarantees outstanding properties of Corrodur 4418Mod for dimensions ranging from 2” up to 12.25” OD and up to 39’ in length. This work was completed between 03/2017 and 04/2020.

3. **Describe the corrosion problem or technological gap that sparked the development of the innovation. How does the innovation improve upon existing methods/technologies to address this corrosion problem or provide a new solution to bridge the technology gap?**

A couple of slightly different types of Super 13Cr are widely used in Oil and Gas applications because of their good compromise between corrosion resistance and mechanical properties. Super 13Cr that exhibits minimum yield strength of 110 ksi (759 MPa) was investigated in the past leading to different results concerning resistance against SSC, i.e. the resistance limits proposed originally could not be validated later on. This led to rejection of this material by several OEMs. This in turn resulted in a demand of qualified Super 13Cr that could not be served. Furthermore, material with minimum yield strength of 95 ksi (655 MPa) is even listed in NACE MR0175 and is thus said to be resistant to Stress Corrosion Cracking (SCC) and Sulphide Stress Cracking (SSC). However, more recent laboratory results displayed a lack in SSC resistance as well, which raised the need for a qualified manufacturing route for these kinds of materials. Thus, DEW now offers a material with a well-controlled manufacturing route that is capable for a wide range of Oil & Gas applications.

4. **Has the innovation been tested in the laboratory or in the field? If so, please describe any tests or field demonstrations and the results that support the capability and feasibility of the innovation.**

The qualification was carried out using a total of nine different heats of Super 13Cr as per UNS S41426 to meet 110 ksi material in small (OD ≤ 8.25”) and large (OD > 8.25”) dimensions as well as 95 ksi material up to 9” OD. All material (bar stock only) was melt in an electronic arc furnace (EAF) and underwent vacuum oxygen decarburization (VOD). Small OD 110 ksi and 95 ksi material was subsequently cast in DEW´s vertical continuous cast aggregate (475x340 mm). The resulting blooms were hot-rolled to approx. 5–9” (50–230 mm), resulting in a reduction ratio of > 3.5:1 (> 4:1 for 8.25” and less). Large OD material was cast as ingot and then forged to dimensions approx. > 8.25–12.25” (> 210–310 mm). Reduction ratio for forged material was always > 4:1.

Afterwards, heat treatment parameters had to be adjusted to successfully meet both yield strength levels in combination with a ductility of more than 37 ft-lbs (50 J) measured in transverse Charpy-V notch tests at 14 °F (-10 °C) by that also meeting considerably higher longitudinal toughness requirements. The tensile strength requirement was min. 125 ksi (862 MPa) with a maximum hardness of 32 HRC for 110 ksi material, respectively min. 105 ksi (724 MPa) with a maximum hardness of 27 HRC for 95 ksi material. These properties were achieved by liquid quenching between 1778–1886 °F (970–1030 °C). Subsequent tempering was carried out in the laboratory for temperatures between 1022–1202 °F (550–650 °C). Since these tests were performed in laboratory scale, all relevant mechanical properties were measured for several combinations of austenitization and tempering temperature. The best compromise of strength and ductility was found somewhere between 580–630 °C (1076–1106 °F) for both strength levels. This temperature range was confirmed for industrial scale heat treatment of bars, even though the final tempering temperature range for each of the two strength levels was different from that in laboratory practice. However, the intended properties could be met reproducibly for industrial heat treatment that was carried out in continuous line furnaces calibrated according to AMS-H-6875 and AMS2750, respectively.

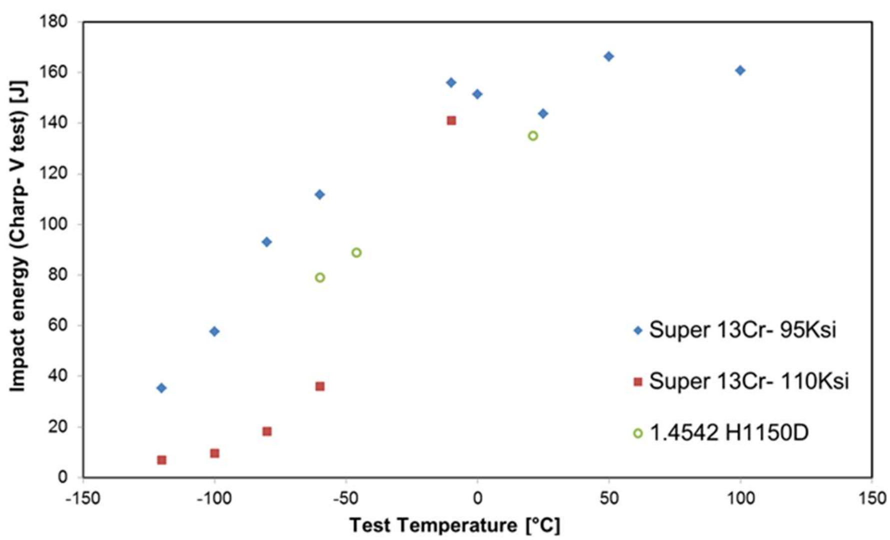
Materials testing was carried out in-house taking mechanical properties according to ASTM A 370, i.e. tensile and Charpy-V tests as well as hardness, microscopic analysis, i.e. grain size (ASTM E 112), delta ferrite (ASTM E 562) and cleanliness (ASTM E 45), as well as ultrasonic testing (UT) into account. All investigations were carried out at 1" below the surface and/or mid-radius. In addition, mechanical properties for one lot of each initial heat (small and large OD 110 ksi and 95 ksi material) were approved by third party as per NORSOK M-650. This included testing at the core as well as mid-length of one bar. Resistance to SSC and SCC according to NACE TM0177 Method A was examined externally at Centro Sviluppo Materiali (CSM), Italy. Here, a given set of parameters for partial pressure of H2S (pH2S), chloride concentration, buffer and electrolyte was applied with a load of 90 % Actual Yield Strength (AYS) at room temperature for SSC and 100 % AYS at 150 °C for SCC. These parameters differ from those listed in NACE MR0175 and were proposed by an OEM to meet a wide range of production environments. Testing in triplicate for all three qualification routines was carried out for the first three respective heats. Additional testing without external requirements included high temperature tensile testing, impact transition curves and corrosion tests.

Fig. 1 (if applicable) shows requirements and rough average (typical) values for tensile and yield strength in MPa as well as elongation A2" and reduction of area (ROA) in % for all three materials. Obviously, all required properties, i.e. yield strength in the range of 95–115 ksi respectively 110–130 ksi, tensile strength in the range of 110–125 ksi respectively 125-160 ksi as well as min. 19 or 17 % A2" and min. 50 or 45 %, are easily met. Fig. 1 also displays hardness to be below 300 respectively 310 HB and 27 respectively 32 HRC for both strength levels. Furthermore, toughness requirements of min. 37 ft-lbs in TCVN and related longitudinal properties are found to be acceptable.

Fig. 2 (if applicable) displays impact transition curves for both 95 and 110 ksi material in comparison to well-known Type 630 (1.4542) condition H1150D. Here, 95 ksi material shows higher LCVN than Type 630 throughout the tested temperature range, while 110 ksi material has a lower toughness at low temperatures and a comparable toughness around room temperature. Additionally, toughness remains above 70 ft-lbs (95 J) for 95 ksi material respectively 25 ft-lbs (34 J) 110 ksi for 110 ksi for testing temperatures higher than the transition temperature of -76 °F (-60 °C). Cryogenic toughness is as low 30 ft-lbs (41 J) for 95 ksi material and only 5 ft-lbs (7 J) for 110 ksi material.

		Hardness HRC (HB)	YS in ksi (MPa)	UTS in ksi (MPa)	A2" in %	ROA in %	Charpy-V Notch @ -10 °C (14 °F)	LCVN in ft-lbs (J)	TCVN in in ft-lbs (J)
110 ksi	MIN		110 (758)	125 (862)	17	45	W_{single}	49/40 (66/54)[1]	26 (35)
	MAX	32 (310)	130 (896)	160 (1103)	-	-	W_{av}	60/50 (81/68)[1]	37 (50)
	Rolled (typical)[2]	≤ 30 (≤ 300)	125 (862)	135 (931)	21	68		80 (108)	50 (68)
	Forged (typical)[2]	29-30 (≤ 300)	120 (828)	135 (931)	21	65		80 (108)	60 (81)
95 ksi	MIN	-	95 (655)	110 (758)	19	50	W_{single}	70 (95)	26 (35)
	MAX	27 (300)[3]	115 (793)[3]	125 (862)	-	-	W_{av}	80 (108)	37 (50)
	Rolled (typical)[2]	26-27 (≥ 270)	100 (690)	130 (897)	22	66		110 (149)	65 (88)

[1] Lower values valid for forged material only.
[2] Rough averages. Actual values explicitly depend on diameter.
[3] Max. Brinell and yield strength validated via SSC/SCC tests.



The microstructure of all three variants of Corrodur 4418 Mod generally displays delta ferrite ≤ 2 vol% according to ASTM E 562. The average value often is actually 0 %, even though some points in some fields hit ferritic islands. A limit of ≤ 1 % can be guaranteed as per customer requests. However, this is only valid taking for a reduced measuring accuracy of ±20 % acc. to ASTM E 562 to limit the effort taken to determine such low contents. Due to the fine grain melt practice a grain size of 5 and finer can generally be achieved for all diameters produced independent of strength level and casting type.

The external SSC and SCC tests at CSM attest that all tested Super 13Cr type Corrodur 4418Mod was resistant to both corrosion phenomena. Resistance was confirmed at a pH2S = 1 kPa (0.01 bar) and a concentration of Cl- of 140,000 mg/L along with an adequate CH3COONa+CH3COOH buffer and a pH of 4.5. Testing in this environment did not cause any cracking of the tested specimens at 90 % AYS within 720 h. Additionally, intercrystalline corrosion acc. to ASTM A 262 Prac. A and E was passed successfully as expected. This test was carried out to check for a possible influence of the typical amount of about 20 % retained austenite found in Super 13Cr types of steel. Furthermore, pitting corrosion in above SSC environment at room temperature displayed promising results.

5. **How can the innovation be incorporated into existing corrosion prevention and control activities and how does it benefit the industry/industries it serves (i.e., does it provide a cost and/or time savings; improve an inspection, testing, or data collection process; help to extend the service life of assets or corrosion-control systems, etc.)?**

With Corrodur 4418 Mod (Super 13 Cr; UNS S41426), Deutsche Edelstahlwerke provides a material solution whose performance exceeds that of conventional chromium steels such as 1.4006 (AISI 410) and 1.4021 (AISI 420).

6. **Is the innovation commercially available? If yes, how long has it been utilized? If not, what is the next step in making the innovation commercially available? What are the challenges, if any, that may affect further development or use of this innovation and how could they be overcome?**

The innovation is commercially available. 110 ksi material up to 8.25" is available since 03/2017, 95 ksi since 07/2019 and 110 ksi material up to 12.25" since 04/2020. Material has to be re-qualified every year performing SSC tests with 85 % Specified Minimum Yield Strength (SMYS). This was already carried out for small OD 110 ksi and 95 ksi material and will be complemented by testing large OD 110 ksi material in the future, starting 04/2020. Annual re-testing goes along with a new version of the quality control plan related to NORSOK M-650.

7. **Are there any patents related to this work? If yes, please provide the patent title, number, and inventor.**

No related patents.