AN OVERVIEW OF CORROSION RESISTANT ALLOY STEEL SELECTION AND REQUIREMENTS FOR OIL AND GAS INDUSTRY

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1. ABSTRACT

The use of Corrosion Resistant Alloy (CRA) in oilfield application has grown in the past years and continues to grow as world-wide search is turning to deeper reservoir.

Despite the fact that CRA are much expensive related to carbon steel, in many cases may provide an attractive alternative to conventional steel used in combination with chemical corrosion inhibitor.

The lack of recognised engineering standard and the relatively manufacturers short experience are the major concerns during material procurement and subsequent manufacturing. This paper discusses requirements and procedures to reduce risks of malfunctions and/or failures of such materials. Tube-making are briefly described ; material selection process for corrosive wells is outlined dealing principally with produced fluids containing hydrogen sulphide and carbon dioxide. Finally an indication is given on some operational experiences with these alloys.

2. INTRODUCTION

As the world-wide search is turning to deeper reservoirs an increasing number of situations are being encountered where corrosive production environments are present. In many of these cases often significant amounts of hydrogen sulphide, carbon dioxide and brine are present with oil and gas production. These crudes show, therefore a high corrosivity with respect to general corrosion and stress corrosion cracking by sulphides (SSCC), by chloride (CSCC) or their combined action.

In addition, other factors such high pressures and temperatures can complicate the material selection process. In fact, the mechanical requirements for material used for production equipment increase with well depth because of the greater hangoff loads and pressure; while the elevated temperatures have detrimental influence on mechanical properties. Under these circumstances CRA materials may offer a valid alternative to conventional methods of corrosion control. Based on that the use of corrosion-resistant alloy in oil field has substantially increased during the last years.

With the term CRA is intended a metal that achieves a high corrosion resistance by means of alloying. A variety of CRA materials are now available for tubing. Table 1 shows some of the commonly use for oil and gas production application. Depending on the environment the CRA choice could range from AISI 420 (13% Chrome) for CO_2 service to titanium alloys for very severe applications. The first topic of discussion will be manufacturing process, with some discussion on how the different processes can influence the final product performances.

3. MANUFACTURING PROCESS

For manufacturing the CRA alloys there are essentially two processes. Group 1 comprises martensitic and martensic-ferritic stainless steel, they are manufactured in a manner similar to carbon steel. The alloy is melted in an electric furnace then it is cast into ingots. The ingot is forged to form a billet that is heated to a suitable forging temperature, pierced and hot rolled to form a pipe. In order to achieve the mechanical properties, the pipe then is quenched and tempered .

Groups 2, 3 and 4 alloys, such as duplex stainless steel and austenitic-nickel-base alloys, are fabricated in different manner. After melting the material can mold to form an ingot or it can be continuously cast. The ingot is then forged into billets that are extruded by the back-extrusion press. In the majority of cases these grades are required in relatively high strengths which require the alloys to be cold worked. This cold work is performed on either cold draw benches or in a cold pilger mill. Several passes on the draw bench may be necessary to achieve the correct strength while in general only a sizing pass and the finishing pass are requested on the pilger mill.

The extrusion process, particularly when associated with cold working, is costly and time-consuming tube-making process. Table 2 reassumes the various manufacturing process.

4. TECHNICAL REQUIREMENTS

As before mentioned the lack of recognised standard is the major concern for procuring phase and subsequent manufacturing. Actually the only available standard is API 5CT which only covers grade 13 % Cr. steel mainly addressing mechanical and dimensional requirements. No standards are available for materials of Groups 2 to 4.

For these alloys the purchaser need to develop tailored specifications; the alternative is to use the manufactures one's. In this case the experience of the supplier should be the key point for its selection. The main points that should be addressed in the technical specification for some of the CRA materials are discussed.

Group-1 Martensitic-Martensitic/Ferritic Stainless Steel

The following features should be addressed in the technical specification:

- Chemical composition.

Sulphur content should be kept as low as possible. In fact with its reduction hot workability increases considerably. With a sulphur content of 0.001% the hot workability is equivalent to that of carbon steel. This requirement is essential when working upset pipes. A value of 0.004 max. is realistic.

- Heat treatment

As before mentioned one of the 13 Cr.'s advantages over the most other CRA material is that its strength is obtained by austenize and tempering. Tubes are generally austenized at about 980 °C and because of its excellent hardenability, air cooled that resulted in fully martensitic structure. Tempering temperature is about 710 °C. NACE Standard MR-01-75 requires double tempering for all martensitic stainless steels when used in sour environments, but there is no evidence that the double tempering improves the material resistance to H2S environments. Pipe manufacturers apply only one tempering.

- Microstructure checks

The only requirements to be inserted are related to delta ferrite content that shall not exceed 5% and microstructures are required to have grain boundaries with no continuos precipitates.

- Mechanical Properties (Table 3)

1) Yield and tensile strength

The most common yield strength range varies from 80 to 110 Ksi with a minimum tensile of 90 Ksi. Depending on the service condition and supplier manufacturing experience, a frequency of one tensile test for each lot of 100 or 200 tubes is reasonable.

2) Hardness

The NACE MR-01-75 limit of 22 HRC for the 80 Ksi minimum yield strength, is a difficult task for type 420 due to its high yield-to-tensile-ratio. As suggested by API 5 CT, a more realistic value is 23 HRC. For upset pipes it is a good practice to limit the difference in hardness between the readings in the quadrants. Surface hardness tests with a portable Rockwell type tester is not recommended due to the unreliability of the measurement.

• Impact Properties

The impact properties at low temperatures should be determined. The suggested values of the minimum impact adsorbed energy is reported in Table 4. Suggested test temperature is -10°C. In case the minimum service temperature is less than -10 °C, the test temperature should be agreed with the manufacturer.

Group 2 Duplex Stainless Steel

Duplex stainless steel offer several advantage over the martensitic alloy. The duplex grades are highly resistant to chloride stress corrosion cracking, have a good crevice and pitting corrosion resistance. They are available in a wide yield strength range from 65 Ksi up to 140 ksi. Actually there is no standard that cover such materials, therefore the following features shall be carefully evaluated:

• Chemical composition.

In general it is recommended to be at the high end of the range for chromium an molybdenum, while the sulphur content should be kept as low as possible.

• Heat treatment

According to the final size, manufacturing process pipes may undergo a solution annealing treatment, after heat extrusion or between intermediate and final cold working phase The scope of the heat treatment is to obtain the best microstructure while maintaining carbides is solid solution and relieve all stresses. For a best stabilisation of ferritic and austenitic phases the material needs to receive a direct quenching after heat treatment.

• Hardness

The NACE MR-01-75 limit of 28 HRC for the solution annealed condition is acceptable. The limit of 36 HRC for the high-strength cold worked condition is not achievable for the 125/140 grades. A more realistic value is 37/38 HRC respectively.

• Microstructure checks

The microstructure shall have a ferritic-austenitic structure. The microstructure is required to have grain boundaries with no continuos precipitates. Intermetallic phases, nitrides and carbides shall not exceed 1,0% all together. Sigma phase shall not exceed 0,5%. The ferrite volume fraction shall be in the range 40% to 60% for alloys with a minimum PRE<40 (duplex) and in the range 35% to 55% for alloys with a minimum PRE≥ 40 (super duplex).

• Impact Properties

The impact properties at low temperatures should be determined. The suggested values of the minimum impact adsorbed energy is reported in Table 4.

Suggested test temperature is -10°C. In case the minimum service temperature is less than -10 °C, the test temperature should be agreed with the manufacturer.

As we move to Group 3 and 4 alloys, the amount of alloying increases up to eight times more nickel and three times more molybdenum while maintaining about the same chromium content. Group 3 and 4 alloys are chosen for improved corrosion resistance to H2S, CO2 and chlorides. The chemistry of these alloy are very important as far as the microstructure check to evaluate the absence of carbide precipitates at grain boundaries that can compromise the corrosion resistance. Intermetallic phases, nitrides and carbides should not exceed 1,0%. Sigma phase should not exceed 0,5%.

In addition to chemical and metallurgical evaluations, corrosion testing are also recommended to verify that the materials will met the expected performances. The specification should include accelerated corrosion tests because testing in standard condition would take several months. Slow Strain Rate Tensile Test (SSRT) is a test that can usually be requested because of its short duration. The standard test condition are 300 °F, 100 psi H_2S partial pressure at ambient pressure and temperature, 25 percent NaCl brine, and 0.5 percent acetic acid.

5. INSPECTION

The following requirements should as minimum be applied to materials of all Groups:

- visual inspection

All tubes shall be free from internal scale.

- Non Destructive Testing

Each tube shall be ultrasonically inspected from the detection of both longitudinal, transverse and laminar imperfection on the outside and inside surfaces. The thickness tolerance should be kept at -10%.

For other requirements regarding dimension, masses, drift etc. API 5CT can be followed.

6. MATERIAL SELECTION

The problem of material selection may involve several factors like the high strength requirements combined with high corrosion resistance of the material.

A chemical analyses of the produced fluids is generally required for evaluation of the corrosive components as hydrogen sulphide, carbon dioxide and chlorides. Other components like scaling potential, water production, temperature profile, pressure profile and stresses on the tubulars have also to be considered. If no water is present there will be no corrosion and the material selection is simple. However, no well can be designed on the basis that it will always be dry and therefore the material selection shall take into account the water production and the material must be selected accordingly.

The proportion of H_2S and CO_2 present in the water are also important ; generally it is ignored but should be taken into account where the well conditions are severe for a particular alloy and to make a conservative design decision would involve the selection of a much more expensive tubular.

Other points to be considered are the potential for scale and the presence of asphaltene associated with production. Scale will provide a barrier between the tubulars and the aggressive fluids reducing therefore the velocity of corrosion process, but pitting and crevice can occur beneath the scale and damage the tubular in its integrity. For our scope we assume that water and chloride are always present therefore a number of different scenarios can be discussed.

The Simple H_2S System

Hydrogen sulphide dissolved in water forms a weak acid which can corrode steel and produce the corrosion products iron and sulphide and atomic hydrogen that penetrate the steel and embrittle it. Under the influence of applied stresses, cracking can develop in a very short time and result in failure of the tubular. This type of failure is known as sulphide stress corrosion cracking (SSCC). The question of material selection in sour environments is addressed in the NACE Material Requirements document MR-01-75.

As general rule resistance to SSCC increases with increasing temperatures. For tubular goods are available numerous material that fit the NACE requirements : Most common grades used are L-80 and T-95. L-80 is not recommended in high H_2S environments because its poor chemistry. In general it is recommended to ask for NACE TM-01-77 test . Are also available proprietary materials with 100, 110 Ksi SMYS, but their usage is limited to production casing.

The Simple CO_2 System

Carbon dioxide dissolves in water to form carbonic acid. The action of carbonic acid is a general corrosion and a pitting corrosion which is more insidious and can result in a rapid perforation. Martensitic stainless (Group 1) steel are the solution for such an environment providing the temperature is likely not to exceed 150°C and the chloride content is not too high. For temperatures exceeding 150 °C a more highly alloyed tubular such as duplex can be considered.

The CO_2 plus H_2S System The presence of H_2S in fluids containing CO_2 aggravates the position. The use of martensitic steel tubing is restricted in the presence of H_2S. Laboratory tests indicate that 13% Cr is very susceptible to SSCC. As first indication its usage should be limited to $pH_2S < 0.5$ psi. For higher values of pH_2S more highly alloyed tubulars are required. Currently duplex stainless steel are the most commonly candidates, but their high cost has imposed in the last years the development of new materials like " Super 13% Cr., 15% Cr." Their field applications are rapidly increasing in the last years.

Duplex Stainless Steel include 22 % Cr. and 25 % Cr. alternatives. The corrosion resistance of 25 % Cr. is generally higher, both the steels are strengthened by cold working. As general rule the higher is the reduction in area the higher is the risk for the material to crack in presence of H_2S, therefore the higher grades should be used with lower pH_2S.

The " superduplex steels " have better performance of traditional duplex therefore can be used in higher pH_2S and chloride concentration.

As we move to worst conditions the "super austenitic" grades can provide the necessary corrosion resistance. They are Fe-base alloys and generally start with 25-27 % Cr. and 31 % Ni., although there are many proprietary alternatives. Their corrosion resistance in CO_2 plus H_2S environments is quite good , they can be used up to 300 °C , above 1500 psi pCO_2 and 1000 psi pH_2S. They are also resistant to SSCC in ambient temperature conditions.

Group 4 materials are austenitic Ni-based material where nickel content ranges from 42 to 60 % while chromium content is in the range of 20-25 %, the molybdenum content starts with 3 % up to 16 %. They are used for very severe conditions.

7. EXPERIENCE

Based on the previous discussion it comes out the importance to prepare detailed product specifications covering details on metallurgy, dimensions, inspections and functional tests. Manufacturing procedures, inspection procedures should be reviewed during bid evaluation and prior to production starting.

Experience has shown that manufacturing process qualification achieved by means of a pre-production has been necessary for particular material/ process to provide evidence of the performance characteristics of the product and the adequacy of the manufacturer to produce tubular that meet the user’s performance guidelines. Qualification of a size and grade doesn’t mean the process is automatically qualified for all the sizes.

Pre-production discussion and a continuing dialogue with manufacturers are generally necessary to reach a satisfactory quality level. Inspectors should be used to assure manufacturers compliance to the technical specification during extrusion, microstucure evaluation, mechanical and NDE testing.

Some operational experience on CRA’s suggest to prepare proper storing and handling procedures to minimise the galling during make/break of the connection.

Acidizing is another operation that can cause problems. Generally Group 1 and 2 can suffer severe corrosion attack from mud acid even in presence of inhibitors. Extensive laboratories tests have demonstrated that superaustenitic stainless steel is much more resistant than duplex steel during stimulation. To reduce the risk it is important to select the appropriate inhibitor package.

8. SUMMARY AND CONCLUSIONS

The purpose of this paper is to discuss technical issues of concern during the procurement of CRA tubulars. The key points to remember are:

- It is important to prepare detailed product specification covering the chemical composition, mechanical properties and quality control.

- It could be useful to qualify the manufacturing process by means of a pre-production for particular material/ process to provide evidence of the performance characteristics of the product and the adequacy of the manufacturer to produce tubulars that meet the user's performance guidelines.

-In making the material selection, it should considered not only the produced environments, but also the effects of future operations such as acidizing that can have impact on the material resistance.

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REFERENCES

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Table 1 — Generic chemical analysis of corrosion resistant alloy

Material			Typical analysis % (mass/mass)					Grade						PRE
Group	Structure	Category	C	Cr	Ni	Mo	N	65	80	95	110	125	140	min
	Martensitic	13-0-0 13-5-2	0.2 0,02	13 13	0,2 5	 2		N N	Y Y	Y Y	N Y	N N	N N	
1		15-2-0	0,1	15	1,5	0,5	0,08	N	Y	Y	N	N	N	
	Martensitic./Ferritic	13-1-0	0,03	13	0,5		0,01	N	Y	Y	Y	N	N	
	Duplex	22-5-3	0,02	22	5	3	0,18	Y	N	N	Y	Y	Y	35
2	Austenite/Ferrite	25-7-3	0,02	25	7	3	0,18	Y	N	N	Y	Y	Y	37,5
	Superduplex Austenite/Ferrite	25-7-4	0,02	25	7	3,8	0,27	N	Y	N	Y	Y	Y	40
3	Austenitic	27-31-4	0,02	27	31	3,5		N	N	N	Y	Y	Y	
	Fe Base	25-32-3	0,02	25	32	3		N	N	N	Y	Y	Y	
		21-42-3	0,02	21	42	3		N	N	Y	Y	Y	N	
	Austenitic	22-50-7	0,02	22	50	7		N	N	N	Y	Y	Y	
4	Ni Base	25-50-6	0,03	25	50	6		N	N	N	Y	Y	Y	
		20-54-9	0,01	20	54	9	Fe=17	N	N	N	Y	Y	Y	
		15-60-16	0,01	15	60	16	W=4	N	N	N	Y	Y	Y	

Y=Available

N=Not available

PRE=% Cr + 3,3(% Mo + 0,5% W) + 16% N

Table 2— Pipe manufacturing process

Starting material	Tube forming condition	Heat treatment or cold worked conditions	Symbols
Billet or rolled/forged	Hot finished -Hot rolled or	Quenched and tempered	QT
bar	-Hot extruded	Solution annealed	SA
Billet or rolled/forged/machined	Cold finished -cold drawing or	Cold worked 1)	CW
bar	-cold pilgering	Solution annealed	SA
Hot finished hollow	Cold finished -cold drawing or	Cold worked 1)	CW
	-cold pilgering	Solution annealed	SA

Table 3 Mechanical properties at room temperature

Material			Delivery	Proof Stress $Rp_{0,2}$ Mpa		Tensile Strength Rm Mpa	Elongation a %	Hardness values HRC
Group	Category	Grade	condition	min.	max.	min.	min.	max.
	13-0-0	80	HF-QT	550	655	620	**1)**	23
		95	HF-QT	655	760	725	**1)**	28
	13-5-2	80	HF-QT	550	655	620	**1)**	27
1		95	HF-QT	655	760	725	**1)**	28
		110	HF-QT	760	965	825	**1)**	32
	15-2-0	80	HF-QT	550	655	690	25	23
		95	HF-QT	655	760	765	22	26
	13-1-0	80	HF-QT	550	655	655	**1)**	23
		95	HF-QT	655	760	725	**1)**	26
		110	HF-QT	760	965	825	**1)**	32
	22-5-3	65	SA	450	620	620	25	26
		110	CW	760	965	860	11	36
		125	CW	860	1035	895	10	37

		140	CW	965	1100	1000	9	38
	25-7-3	75	SA	515	680	635	25	26
2		110	CW	760	965	860	11	36
		125	CW	860	1035	895	10	37
		140	CW	965	1100	1000	9	38
	25-7-4	80	SA	550	725	760	20	28
		90	SA	620	725	790	20	30
		110	CW	760	965	860	12	36
		125	CW	860	1035	895	10	37
		140	CW	965	1100	1000	9	38
	27-31-4	110	CW	760	965	795	11	35
3		125	CW	860	1035	895	10	37
		140	CW	965	1100	1000	9	38
	25-32-3	110	CW	760	965	795	11	35
		125	CW	860	1035	895	10	37
		140	CW	965	1100	1000	9	38
	21-40-3	110	CW	760	965	795	11	35
		125	CW	860	1035	895	10	37
	22-50-7	110	CW	760	965	795	11	35
		125	CW	860	1035	895	10	37
		140	CW	965	1100	1000	9	38
4	25-50-6	110	CW	760	965	795	11	35
		125	CW	860	1035	895	10	37
		140	CW	965	1100	1000	9	38
	20-54-9	110	CW	760	965	795	11	35
		125	CW	860	1035	895	10	37
		140	CW	965	1100	1000	9	38
	15-60-16	110	CW	760	965	795	11	35
		125	CW	860	1070	895	10	37
		140	CW	965	1170	1000	9	38
1) According to API 5 CT formula								

Table 4— : minimum impact absorbed energy

Group	Test	Absorbed energy	
	temperature	longitudinal	transverse
1	-10° C	40 joules	40 joules
2	-10° C	40 joules	27 joules

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