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Corrosion in the Oil & Gas Industry 2020

Increased operational reliability tubing from steel 25CrMnNb grade

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Abstract. The conventional tubing supplied to oilfields with low aggressive environments: with pCO_2 up to 0.3 atm and pH_2S up to 0.005 atm often shows signs of pitting carbon dioxide corrosion after operation. To solve the problem, a new sparingly alloyed steel of 25KhGB was developed for K steel grade tubing with increased set of performance characteristics obtained after thermomechanical treatment.

1 Introduction

During 2014-2016, at oilfields with low aggressive environments with pCO_2 up to 0.3 atm and pH_2S up to 0.005 atm accelerated tubing failure was observed due to corrosion damage (up to through holes) to the inner surface of the tubing (on average, 192 days instead of 365 days and more according to warranty obligations). In this connection, it became necessary to develop a fundamentally new steel grade having sufficient strength for the K steel grade (yield strength not less than 490 MPa, ultimate strength not less than 687 MPa) according to standard GOST 633, increased corrosion resistance, and operational reliability obtained using thermomechanical treatment. For this purpose, JSC "PNTZ" carried out a whole range of works:

– an assessment of operating conditions and determination of the main mechanism of corrosion damage;

– determination the main factors affecting the corrosion resistance of tubing;

– development of the concept of steel alloying and experimental smelting of steel pre-production compounds with various microalloying options;

– thermomechanical treatment of samples of pre-production compounds under laboratory conditions;

– research to determine the phase compositions of steels, microstructure, mechanical and corrosion properties of samples;

– selection of the optimal chemical composition based on research results;

– development of technology for manufacturing pipes from a new steel grade.

2 Analysis of operating conditions

To assess the operating conditions a set of works was carried out to study the properties of tubing, their use at the oilfields.

The conducted studies allowed to determine the main operating factors affecting the corrosion damage of the tubing. The predominant corrosion mechanism at oilfields is carbon dioxide corrosion, complicated by H_2S, chlorides, and possibly sulfate-reducing bacteria. Prevailing types of damage: general corrosion with speeds up to 0.27 mm/year, localization in the form of individual pits (with speeds up to 5.02 mm/year); in rare cases – mesa corrosion with speeds up to 12 mm/year (Figure 1).

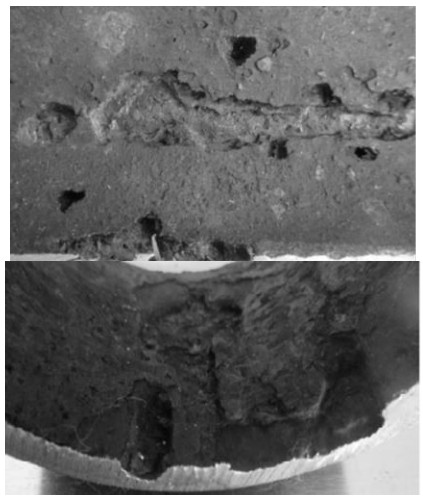

Fig. 1 Corrosion damage types at Surgutneftegas PJSC fields.

Currently, two main points of view can be distinguished on increasing corrosion resistance of oilfield equipment:

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- increased protective capacity of the film of corrosion products (a theory adopted worldwide, based on the principles of alloying);
- reduced non-metallic inclusions and highly corrosive NMI (CANI). According to the apologists of CANI theory, the negative impact of non-metallic inclusions, on the one hand, is reduced to an increase in the probability of pitting (due to the high corrosive activity thereof), and on the other hand, provokes the development of SSC due to the emergence of stresses in the metal in areas adjacent to non-metallic inclusions.

According to the first version, corrosion resistance depends on the quality of the formed protective film of reaction products. When the integrity of this film is violated, areas with higher electrochemical potential appear on the metal surface, which stimulates the active development of local damage. The more Cr, Mo compounds are contained in the film, the more tightly bonded film is formed, the higher the corrosion protection of the metal.

According to the second version, the negative impact of non-metallic inclusions is due to their high corrosive activity due to stress in the metal in the areas adjacent to the non-metallic inclusions.

Studies on the effects of non-metallic impurities (NMI and/or CANI) have produced ambiguous results. For example, in 2015, large-scale studies of samples after exploitation at oilfields were conducted. In addition to samples with pronounced local damage, pipe fragments without visible local corrosion damage were also examined as comparison samples. With good corrosion resistance (244 days without visible corrosion damage), these pipe fragments were characterized by a significant level of contamination with non-metallic inclusions, both conventional and CANI (number CANI 1 – up to 5.8 incl/mm^2; number CANI 2 – up to 2.5 incl/mm^2, local contamination – more than 12 incl/mm^2; plastic manganese sulfides – 2.5-3.0 points), Fig. 2, a.

In contrast to the previous example, after 344 days of operation, the nozzles with significant corrosion damage (up to through holes) are characterized by high purity of the metal, both in terms of conventional NMI and CANI (the number of CANI 1 – 2 incl/mm^2; the number of CANI 2 – 1-2 incl/mm^2; sulfides – 0.5 point), Fig. 2, b.

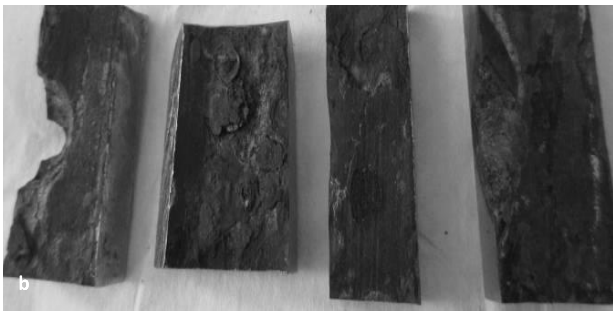

Fig. 2 Exterior view of the inner surface on the samples: a) after 244 days of operation with high levels of CANI and NMI, b) after 344 days of operation with low levels of CANI and NMI.

This is also confirmed by the results of electrochemical studies according to the methodology of the STO 00190242-003-2017: on metal with CANI level 2 or higher ("dirty" in terms of CANI), lower theoretical corrosion rates were obtained than on samples of the same steel grade and microstructure, but with an allowable CANI level (less than 2 points, "clean" in terms of CANI) – 0.386 mm/year instead of 1.581 mm/year.

In the course of investigations of corrosion product deposits on the tubing after operation, it was revealed that a heterogeneous layer of corrosion products on steel grades corresponding to GOST 633 (represented in most cases by carbonates, in some cases with interlayers of iron sulfides) stimulates the development of local corrosion in the form of individual pits and/or mesa-corrosion (Fig. 3, a). The production of more tightly bonded non-porous deposits, providing corrosion protection, is observed when the reaction products of chromium-containing compounds appear in the layer (Fig. 3, b).

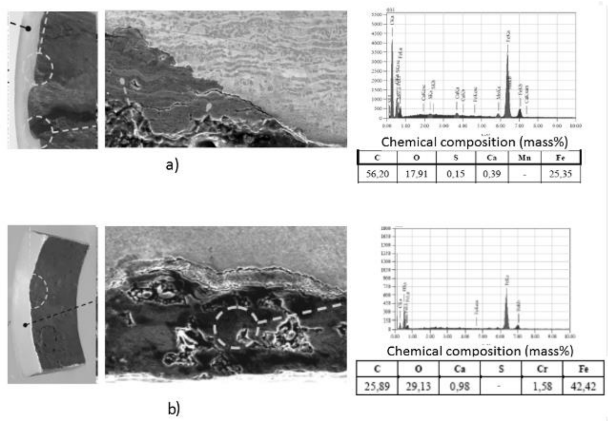

Fig. 3 The results of metallographic examination of corrosion products a) on tubing corresponding to GOST 633 (chromium-free), b) on tubing made of chromium-containing steel grades.

Thus, based on the conducted researches, it is possible to draw a conclusion about the advantageous influence of such elements as chromium and molybdenum on the corrosion resistance of tubing, which necessitates changing the chemical composition of steel for oilfields with pCO2 up to 0.3 atm and pH2S up to 0.005 atm.

3 Development of a new steel grade

Experimental heat of steel pre-production compounds with various microalloying options was carried out in the Vacuum Industries furnace with the liquid steel crucible capacity of up to 7 kg, and then rolled into a strip of size 22x11x220 mm. Thermomechanical treatment of samples of pre-production compounds was carried out under laboratory conditions in modes close to shop floor.

Steels with various carbon, silicon, chromium and manganese content as well as additionally microalloyed niobium were suggested as a base. Experimental chemical composition of steels for laboratory testing is shown in Table 1.

Table 1. Chemical composition of experimental steels (laboratory heat), % weight.

	C	Si	Cr	Mn	Nb	P	S
Steel 1	0.20-0.28	Maximum 0.45	0.80-1.00	0.80-1.00	0	0.006	0.004
Steel 2					0.04	0.006	0.005
Steel 3					0.07	0.007	0.005

Thermodynamic modelling using a thermodynamic computer model of the equilibrium phase composition of steels was carried out to determine the phase compositions of steels. To establish the possibility of release of experimental compositions of excess phases in steels, as well as the formation of the structure depending on the alloying and microalloying of steel in the conditions of hot working, thermodynamic calculation of temperature dependences of the equilibrium carbide and carbonitride phases release and temperature conditions of polymorphic transformations were carried out (Fig. 4) [3].

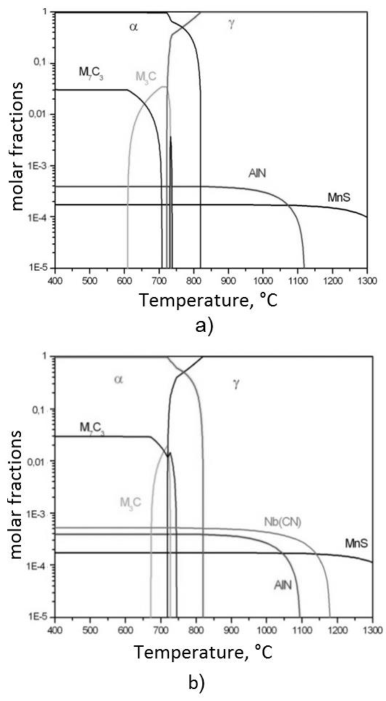

Fig. 4. Calculated temperature dependencies of equilibrium phase composition for steels of Steel 1 (a), Steel 2 (b).

At billet heating temperatures, MnS is present in the steels under study before piercing. AlN inclusions, as it is visible from figure 4, are thermodynamically conditional below ~1100°C, that is at heating under piercing, the given phase is dissolved (Fig. 1). The presence of niobium in Steel 2 and Steel 3 determines the possibility of the occurrence of its carbonitride. In addition, in the area of ferrite stability, along with cementite, chromium carbide of M_7C_3 (frequent $(Fe,Cr)_7C_3$) type can be precipitated in the steels under consideration. In the temperature range near Ac_3, both carbide phases are in equilibrium with ferrite in compounds Nos. 1-3.

Based on the thermodynamic calculations performed, a conclusion can be made that in the case of thermomechanical treatment of pipes, the release of niobium carbonitrides for the variants of Steel 2 and Steel 3 will be observed. Chromium carbide of M_7C_3 type is also possible, but it was not possible to identify its release in the steels under consideration.

The analysis[a] of contamination of laboratory steel samples with non-metallic inclusions showed their purity, including in terms of plastic sulfides (not revealed).

When studying by TEM method (transmission electron microscope JEOL JEM200CX), which was performed on the samples of Steel 2 and Steel 3 compositions, it was revealed that the matrix structure of both samples is identical and consists of two main components: polyhedral ferrite with grain sizes up to 10 μm and more, having moderate dislocation density (Fig. 5). Sometimes there are separate cementite particles precipitate along the boundaries of ferrite grains.

No submicron size carbonitrides were revealed in the sample of Steel 2. In the sample of Steel 3, they are observed in the form of ~0.05…0.2 μm particles having oval shape or shape of strongly rounded rectangles (Fig. 6). The peculiarity of distribution of such particles across the sample is that they form clusters of several particles in a small amount of areas of the sample, while completely absent in other areas.

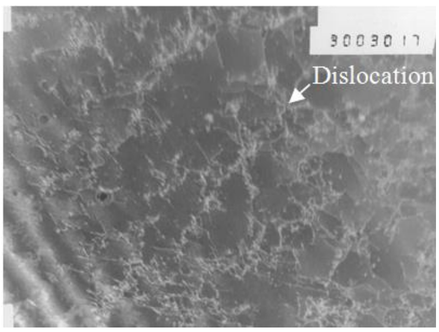

Fig. 5. Polyedric ferrite (Steel 2) when studied under TEM, x30000).

The sizes of observed nanoparticles in both samples are approximately the same: typical ~4-15 nm (up to ~30 nm). Volumetric density slightly fluctuates from one

[a] Analysis was carried out according to GOST 1778

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area to another – from low to moderate. Volumetric density of nanoparticles is higher in the Steel 3 sample, which correlates with a high content of niobium in this sample. In particular, areas with low volumetric density of particles are sometimes observed in the Steel 2 sample. Practically no such areas were found in the Steel 3 sample.

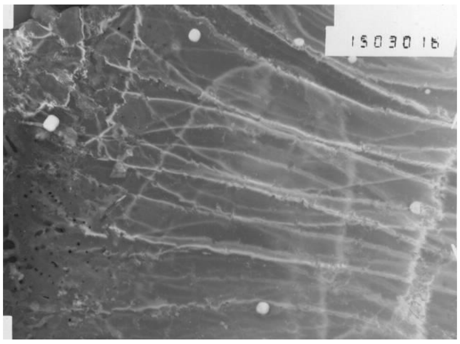


Fig. 6. Particles of niobium carbonitride in the Steel 3 steel sample.

4 Pilot industrial development

Based on the research work performed, Steel 2 and Steel 3 were recommended for further development of tubing production with increased operational reliability using thermomechanical treatment. Production development was carried out on 73.02×5.51 mm tubing of K72 steel grade.

4.1 Development of the technology of thermomechanical processing of tubes

During steps of technology adjustment of pipes thermomechanical processing (TMP), experimental rollings were made with various modes [3]:

- mode 1 of TMP (heating minimal holding in the furnace);
- mode 2 of TMP (heating temperatures with long holding in the oven);
- quench and temper process (Q&T) (reference sample).

Research was carried out to determine the phase compositions of steels, microstructure, mechanical and corrosion properties of samples.

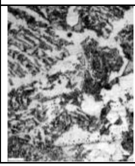
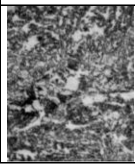
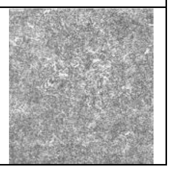
Corrosion properties evaluation of the obtained metal samples, accelerated electrochemical studies were carried out using Versa Princeton Applied Research potentiostat equipped with specialized software. The test electrolyte was a deaerated aqueous solution of 5% NaCl with pH = 3.0. The sample was placed into an electrochemical cell, then a working electrolyte with preassigned value of pH = 3.0 was added into the cell. Preliminary deaeration of the electrolyte was carried out by helium purging for 30 minutes, then working solution was heated up in cell to a temperature of 60°C. During the heating, carbon dioxide purging was carried out for 30 minutes. Value of pH was measured after carbon dioxide purging. The study included placing the testing metal sample in working electrolyte and measuring the corrosion potential E_{cor} for 55 minutes (3300 seconds). Then, linear anodic polarization of the sample was carried out in the range of potentials from -150 to 150 mV at a scanning rate of 0.16 mV/s, and a polarization curve was obtained. Potentials values are recalculated from silver chloride electrode to standard hydrogen electrode. The obtained polarization curves were used for calculating the theoretical corrosion rates by graphic method. Theoretical corrosion rates were calculated using Tafel curves (tangent to polarization curves) using specialized software.

Sulfide stress corrosion cracking resistance were determined according NACE TM0177 method A during 720 hours.

Microstructure analysis of obtained samples was carried out to confirm the metal properties and electrochemical studies to rank steels in terms of corrosion properties in CO_2 environment. Microstructure was analyzed by means of optical microscope Axiovert 40MAT CarlZeiss.

Table 2 shows studies results of microstructure and corrosion studies.

Table 2. Results of the metal samples studies after TMP and Q&T with various modes.

	TMP mode 1	TMP mode 2	Quench and temper process
Average corrosion rate, mm/year	1.055	0.374	0.305
Microscopic structure			

As it can be seen from the results, maximum theoretical corrosion rate in CO_2-containing environments was obtained on metal samples after TMP with accelerated mode of rolling. Corrosion rate of metal samples after TMP with optimal mode is far below and is close to metal samples corrosion rate after quench and temper process.

The poor corrosion properties of the metal after accelerated mode of TMP are explained by the coarse-crystalline microstructure and martensite-austenite component.

4.2 Production of industrial batches of tubing from steel 25CrMnNb grade

Manufacturing and thermomechanical treatment of tubes is carried out on a pipe-rolling plant with a continuous rolling mill. Plugless rolling is carried out at the temperature of 950-1075°C with the coefficient of elongation of 1.2-2.2.

The obtained results of delivery trials meet the requirements for K72 steel grade as per GOST R 31446 (Table 3).

Table 3. Mechanical properties and corrosion behavior of pipes after thermomechanical treatment.

Heat	σ_T, MPa	σ_v, MPa	δ_5, %	SSC resistance, method A, NACE TM 0177	Total corrosion rate, mm/year, in CO_2 environment[b]
Laboratory step					
Steel 1	330	538	28	have not been tested	have not been tested
Steel 2	500	745	20	withstood	0.140
Steel 3	527	770	19	withstood	0.140
Pilot batch					
Steel 2	509	809	18	withstood	0.179
Basic*	647	941	18	withstood	0.396
* as per existing technology					

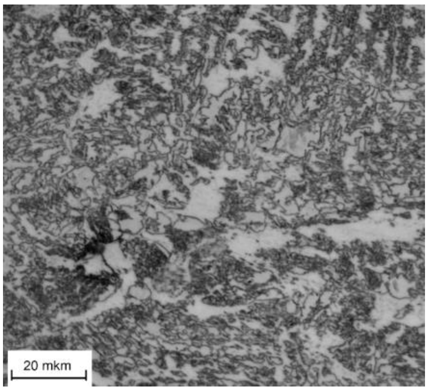


Fig. 7. Steel 2, 73x5.51 mm pipe microstructure of K72 steel grade.

The characteristic microstructure of steel consists of ferrite, perlite, and bainite (Fig. 7). Grain size corresponds to 8 – 9 GOST 5639.

5 Conclusion

Thus, thermomechanical seamless tubing made of 25CrMnNb steel grade has increased corrosion resistance and provides an opportunity to use it in wells operated under conditions of aggressive media, in particular, for production of watered oil and highly mineralized formation water containing carbon dioxide, hydrogen sulfide, chlorine ions as well as mechanical particles. The use of traditional steels in these conditions (GOST 633) is limited due to the development of corrosion processes such as local corrosion and stress corrosion cracking during operation.

As a result of the use of 25CrMnNb steel tubing, a reduction in the failure-free operation time of the pipe suspension can be expected. Currently, pilot field tests of tubing made of 25CrMnNb steel are being conducted in field conditions.

[b] According to the methodology No. 966814-006-593377520-2014

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