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RT.328 September 2003
RAPPORTS TECHNIQUES CEBELCOR

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Rapports Techniques CEBELCOR, RT.328 (2003)
ed183aap

PREVENTION OF CORROSION AND HYDROGEN DAMAGE OF 13 Cr AND DUPLEX STAINLESS STEEL FLOWLINES BY MODERATE CATHODIC PROTECTION

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ABSTRACT

Duplex and 13 Cr supermartensitic stainless steels are susceptible to hydrogen embrittlement. This is of concern for flowlines in seawater, under cathodic protection with sacrificial anodes at –1050 mV_{sce}.
Moderate cathodic protection eliminates both the risk of corrosion and the possibility of hydrogen formation. Mod-CP has a solid scientific basis, related to the « protection potential » of passive iron-chromium materials in chloride solutions.
Tests were conducted to demonstrate the applicability of Mod-CP in industrial conditions and the values of the potential limits. With a significant safety margin, the conclusion is that corrosion protection is achieved at potentials below (more negative than) –550 mV_{sce}.
The lower limit of the safe potential range is related to the hydrogen equilibrium potential. The extension of the acceptable potentials to more negative values was studied and is still under study using constant load tests, slow strain rate tests, permeation tests, fractional hydrogen extraction, TEM and nanoindentation.
Although no cracking was found under static load at –1050 mV_{sce} after 25 weeks, some hydrogen-cracking of flowlines and the intrinsic sensitivity of these materials lead to recommend to limit the negative potentials at –850 mV_{sce}.
Consideration is given to the design of Mod-CP systems, with distance between anode (potential span), selection of anode systems and coupling between hydrogen sensitive materials and carbon steel.

Key-words : Supermartensitic stainless steels, duplex stainless steels, moderate cathodic protection, offshore, hydrogen

INTRODUCTION

There is a concern in the oil and gas industry for hydrogen cracking of duplex stainless steels and of 13Cr supermartensitic stainless steels in seawater when they are cathodically protected by sacrificial anodes at about -1050 mV_{sce}. Cracking failures occurred on both duplex (Amerada Hess, 1996) and supermartensitic stainless steels (Asgaard, 2002).
Another source of hydrogen is the local acid and low potential conditions that exist inside active pits or crevices.

Already in 1962, it was shown that protection of stainless steels against localised corrosion (which is the type of corrosion that occurs in seawater) can be achieved at potentials significantly higher than the hydrogen evolution potential. The upper limit of this « perfect passivation domain » was defined as the zero-current potential on a back-scan polarisation curve. This potential was called the « protection potential » (against propagation of localised corrosion) [1]. Later, thanks to progresses in the fundamentals of localised corrosion, it was shown that this « protection potential » is closely related to the potential that exists in active pits or active crevices [2]. Below this protection potential, the driving force for the propagation of pits and crevices is zero and they stifle.

The expression « moderate cathodic protection Mod-CP » refers to this type of cathodic protection of passive materials, where altogether localised corrosion cannot propagate and hydrogen cannot form.

The limits of this safe potential domain (no corrosion and no hydrogen embrittlement) were investigated and demonstrated for 13Cr supermartensitic stainless steel in industrial conditions such as average quality surface preparation, coating and welds.

The implementation of moderate CP for flowlines requires consideration of certain questions such as the selection of suitable anode systems and the coupling of the stainless steel lines with carbon steel templates and platform legs that, presently, have a classical CP.

EXPERIMENTAL

Moderate cathodic protection tests under industrial conditions

Supermartensitic steel tubes were protected by Mod-CP for 6 months in artificial seawater. The tubes are made from 12 mm « medium grade » 12Cr 4.5Ni 1.5Mo plates produced by KTN and rolled by Usinor-Industeel (Belgium). Their composition is (%):
C 0.008, Si 0.31, Mn 1.00, P 0.014, S 0.003, Cr 11.66, Mo 1.42, Ni 4.55, N 0.011, Cu 0.25.
Polarisation curves of this steel in artificial seawater (and in acidified seawater) clearly shows the existence of a passive domain (figure 1).

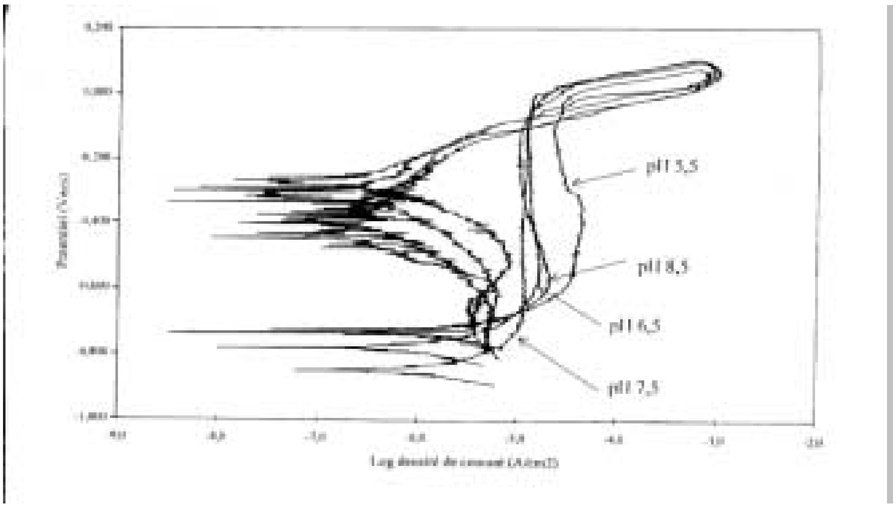

Figure 1: Polarisation curves for 12Cr4?5Ni1.5Mo in artifical seawater (and in acidified seawater to confirm the passive domain)

The tubes were bent and welded by Butting. The longitudinal weld comprises two internal electron beam passes and two external GTAW (TIG) passes. The filler metal was the matching Thermanit 13/06, by Boehler Thyssen. The longitudinal welds are heat treated after welding (PWHT : 5 to 30 min at 630°C, air cooled). The girth welds were also made by Butting, by TIG welding, using the same filler metal (Thermanit 13/06), without PWHT.

The tests were deliberately conducted on tubes prepared under realistic, non ideal conditions to reflect the large diversity of industrial processes that have to adapt to the constraints (technical, economical or time) of work on board or on shore. The tubes tested were not pickled after welding ; the colour of the steel before coating was uniform dark brown.

The tubes have an ID of 306 mm, an OD of 330 mm and a length of 680 mm, with a girth weld at mid-length.

They were degreased with methyl-ethyl-ketone and were mechanically cleaned with a rotating carbon steel brush. The coating applied is a thermo-shrinkable sleeve from Raychem (WPC 100 M) with a gas torch after a preheating at 110°C, and the sleeve is heated in the same way during application. Air bubbles are « massaged » away by small hand rolls.

To consider industrial conditions and in particular unavoidable coating defects, a series of defects to the coating were artificially made before the tests :

- rectangular defects (with a cutter and a knife blade) on the welds. Half of the exposed weld length was cleaned with grinding paper (500 grit). The other half is left « as welded ».
- circular holes (10 mm dia) drilled through the coating on the girth weld,
- the coating was cut through with a saw where there were remaining air bubbles under the coating.

These defects are schematised on figure 2.

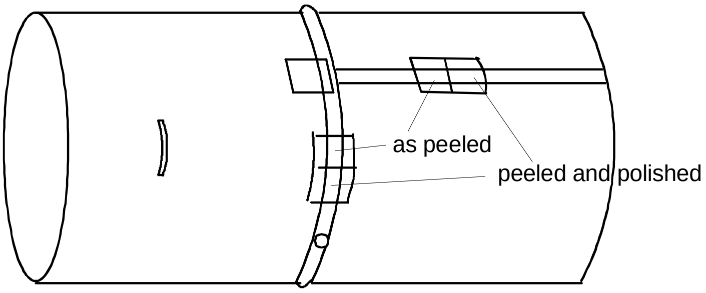

Figure 2 : Schematic description of the defects made to the coating

Cathodic polarisation was applied as soon as the tubes were immersed in artificial seawater (ASTM D1141 without heavy metals) at pH 8.2 and 18°C. One tube (in one tank) was polarised at –550 mV_{sce}, and another tube (in another tank) was polarised at –600 mV_{sce}. Potentials and current were recorded throughout the tests by a data logger EI9000 (Access Technology, Brussels).

Hydrogen embrittlement

Two « medium grade » supermartensitic stainless steels (12Cr 4.5Ni 1.5Mo) were used :

- one with a very low carbon content : C 0.008, Mn 1.000, P 0.024, S 0.0030, Si 0.310, Cu 0.250, Ni 4.550, Cr 11.660, Mo 1.420, Al 0.001, N 0.0110 %.

Its convential yield strength (Rp0.2) is 694 MPa.

- another standard chemistry : C 0.015, Mn 1.700, P 0.027, S 0.0014, Si 0.177, Cu 0.487, Ni 4.666, Cr 11.460, Mo 1.379, Al 0.001, N 0.0112 %.

Yield strength is 600 MPa.

All the samples are welded by pulsed MIG, with a filler metal Thermanit 13/06 (Cr12.34-Ni6.29-Mo2.64-C0.011-$O_2$0.0045%) and a gas protection Arcal 121 (Ar + 18% He + 1% CO_2). The welded plates are 20 mm thick. The weld is made with 12 passes. There is no post weld heat treatment.

Figure 3 shows the position of the samples, with respect to the surface and the weld.

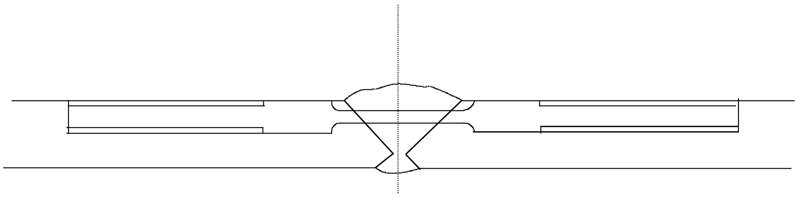

Figure 3 : Position of the samples for constant load tests

The samples are polished (grit 600) and stored for 24 hours in air before the tests. Paint is applied at the water line and at the passage through the bottom of the cell. Initially, the test solution is artificial seawater (ASTM D1141 without heavy metals), pH 8.2. In some tests, the samples were rubbed to remove the calcarous deposits and the test solution was replaced by NaCl 3% + $NaHCO_3$ 0,2 g/l (pH 8,4) to prevent deposits and to attain larger cathodic polarisation current densities.

The tests were conducted at –1050 mV_{sce}.

After one week of prepolarisation, a constant load was applied, first at 90% of the nominal yield strength, then for some tests at a higher load correponding to 2% plastic deformation.

At the end of the tests, the reversible hydrogen absorbed was measured by heating at 100°C under an inversed glass flask in glycerine.

More studies are under way, using permeation tests, slow strain rate testing, hydrogen fractional extraction, TEM and nanoindentation with the aim of determining the realistic conditions most prone to develop embrittlement.

Implementation of moderate CP

A potentiostatic regulation system was developed to control the potential of the pipes at any selected value (for example at Mod-CP potentials) even when using the conventional high efficiency sacrificial anodes (Al-Zn, Al-In). This “intelligent anode” system is a black box installed between the anodes and the pipe. It derives its power from the anodes. Contrary to resisitor or diode systems, it saves on the anode consumption. The potential delivered can be programmed at any value, as a function of temperature etc.

RESULTS

The upper limit of the moderate CP range

The only corrosion observed at –550 and at –600 mV_{sce} was on the weld seams that were not cleaned and still covered with the heat tint oxides produced during welding. Reddish corrosion products formed after as little as 24 hours. The depth of attack was negligible and not measurable.

On all the other surfaces, whether outside of the weld seam or on the weld seams that were cleaned by grinding, there was no corrosion after 4 and 6 months of test.

The initial current densities were 40 µA/cm² of bare surface, dropping to 5 and 6 µA/cm² after 10 days.

These results show that the medium grade supermartensitic steels can be protected against corrosion in seawater by a moderate CP at potentials below –550 mV_{sce}. One requirement to completely avoid corrosion is that the heat tint oxides must be removed by mechanical cleaning (grinding) or pickling. Classical CP at –1050 mV_{sce} is not necessary for protecting supermartenstic stainless steels against corrosion in seawater.

Hydrogen embrittlement

Three tests were conducted under constant load at –1050 mV_{sce}.

One test was on the low carbon supermartensitic stainless steel, first at 90% of YS during 8 weeks with occasional scratching of the surface to remove the calcarous deposits. After 8 weeks, the load was increased to 2% plastic deformation for another 11 weeks.

A second test on the same steel lasted for a total of 25 weeks, of which 4 weeks at 90% of YS and 21 weeks under 2% plastic deformation. For the last 12 weeks, the calcarous deposits were removed and the artificial seawater was replaced by NaCl + $NaHCO_3$.

The third test was on the standard composition under 90% of YS, first in artificial seawater (19 weeks), then in NaCl + $NaHCO_3$ (one week).

None of the sample had any crack after 19, 25 and 20 weeks.

Some side observations are :

- calcarous deposits reduce the cathodic current density from an initial few hundreds of µA/cm² to 15 to 25 µA/cm² after one week and 2 to 3 µA/cm² after a few weeks.
- scratching the surface or increasing the load to 2% plastic deformation increases the current density immediately, from 2 or 3 µA/cm² to about 15 to 28 µA/cm².
- the amount of reversible hydrogen that was extracted in glycerine at 100°C is low or very low : after 19 weeks at –1050 mV_{sce}, less than 5 10^{-4} ml/100 g. After 13 weeks in artificial seawater then 12 weeks in NaCl + $NaHCO_3$ (thus without deposits), 0.068 ml/100 g.

For comparison, the same method gave larger values (0.18 to 0.32 ml/100g) for buried carbon steel after 3 months at potentials between –0.95 and –1.10 V_{sce}.

The dynamic straining tests (SSRT) show a clear sensitivity of 13Cr supermartensitic steel to hydrogen : at 1.5 10^{-6} s^{-1} strain rate, the elongation is reduced from 20.4 % in air (strain rate) to 12.0 % under cathodic charging at –1050 mV_{sce}. With a poison for hydrogen recombination, the elongation is further reduced to 5.5 %. More tests are under way with repeated straining-relaxation cycles and under cathodic charging to see if embrittlement can be a problem for total strain lower than 5 %.

DISCUSSION

Moderate CP is based on the fact that there is a « protection potential » for passive materials below which existing pits, crevices and stress corrosion cracks cannot propagate. This potential, although it is lower than the pitting initiation potential, is significantly higher than the usual cathodic protection potential and than the hydrogen evolution potential.

Thus, below the « protection potential » and above the hydrogen evolution potential, both corrosion and hydrogen embrittlement are impossible [1,2].

In a former study [3], the existence of a passive domain for the 12Cr4.5Ni1.5Mo supermartensitic stainless steel in seawater was clearly demonstrated (figure 1), thus Mod-CP is applicable.

From the polarisation curves and, even better, from the knowledge of the potential and pH in active pits of Cr-alloyed steels in chloride solutions, the protection potential can be estimated at about –450 mV_{sce}. It this study, using some allowance for safety, long term tests were conducted at –550 and –600 mV_{sce}. With the exception of unpickled welds, there was no corrosion. The conclusion is that –550 mV_{sce} is a safe potential for the protection of 13Cr steel against corrosion. This value is altogether scientifically sound and experimentally verified.

The rapid superficial corrosion observed on welds is attributed to the heat tint oxides. These oxides are weak because of internal stresses and poor adhesion and because of their composition. The external surface is often poor in chromium because of a sequence of reactions : Cr has a high affinity for oxygen and the oxide film is first richer in Cr oxide and the underlying metal is impoverished in Cr [4,5]. Thus, iron starts to form oxides, rather than Cr. A series of phenomena act on the distribution of Fe and Cr in the oxide layer : the diffusion rate of Cr and F in the underlying metal and in the oxide layer, the diffusion rate of oxygen through the oxide-gas interface etc. All these processes are influenced by the temperature and the time at each temperature, the residual oxygen partial pressure etc [5].

As the applicability of Mod-CP relies on an efficient passive domain, it is not surprising that heat tint oxides lead to some superficial corrosion.

A large difference between the upper and lower limits of the safe potential domain is interesting for the distribution of anodes along the pipeline. Thus, the lower potential limit is an important parameter.

In the 25 weeks contant load tests reported here, no cracking was observed at –1050 mV_{sce}.

This is confirmed by a number of results [6]. For example, Miyata [7] did not observe cracking at –1600 mV_{sce} (which is very negative) on GMAW welded joints of 12Cr-5Ni-2Mo-0.01C-0.01N with a superduplex filler metal in 3.5% NaCl, under a constant load of 630 MPa. Many other results are in the same line. A few ruptures occurred, which are generally attributed to welding defects.

However, Olsen [6] observed cracks in constant load tests of 12Cr-6,5Ni-2,5Mo steel welded with pulsed GMAW with a matching filler metal, at –1050 mV_{sce}. These cracks were produced at 90% and at 100% of the real YS, but only in the absence of PWHT. These tests were conducted in NaCl 3.5%, thus without deposits, under a rather high current density compared to our tests and to the real life.

Because of these contradictions and because it is recognised that dynamic straining is an important factor for hydrogen cracking of 13Cr steels, a more fundamental study started in January 2002 with the aim of understanding better the factors that control hydrogen cracking of supermartensitic stainless steels (PhD work, by Mioara Stroe). Hydrogen embrittlement is studied with permeation tests, slow strain rate testing (with cycled straining), hydrogen fractional extraction, TEM and nanoindentation.

In the meantime, it is prudent to avoid potentials lower than –850 mV_{sce}.

The potential span for Mod-CP is thus about 300 mV (between –550 and –850 mV_{sce}). For classical CP, the potential span was between –850 and –1050 mV_{sce}, thus only 200 mV. The problem with Mod-CP is thus not the distribution of anodes along the line, but more the selection of anode systems. Anode systems that are or can be considered are Al (AlZn or AlIn) anodes with resistors, Al anodes with diodes, iron anodes, Al-Ga anodes, and « intelligent potentiostatic Al anodes ». Mod-CP consumes less energy than classical CP. The latter system reduces further the energy lost as heat with resistors and diodes.

Another concern about Mod-CP is the coupling between the duplex or martensitic stainless steels and the other structures made of carbon steel with a classical CP system. This problem can be solved without using isolation joints (which may be a source of problems in the long term) if the CP system is studied and designed as a whole at an early stage of the project, for all the structures involved (flowlines, templates, platform legs..). The potentials applied to carbon steel is generally between –800 and –1050 mV_{sce}, and the potential required for Mod-CP of duplex and martensitic steels are between –550 and –850 mV_{sce}. There is thus a small range of potentials acceptable for the two materials. This can be considered for the overall design of the CP system.

CONCLUSION

This study demonstrated that the concept of moderate cathodic protection Mod-CP is applicable to supermartentisitc stainless steels. The feasibility of Mod-CP is due to the existence of a passive domain for these steels in seawater.

In Mod-CP, the potential should be maintained within given limits to avoid altogether corrosion and hydrogen embrittlement. The protection against corrosion is based on the fact that pits or crevices are made inactive at these potentials. The prevention of hydrogen embrittlement is ensured by the fact that hydrogen cannot form at these potentials.

The upper limit of the safe potential domain was found at -550 mV_{sce}. Studies are still under way to define the lower limit. Under constant load, no cracking occurred at -1050 mV_{sce} after more than 25 weeks. However, as these materials are intrinsically sensitive to hydrogen, more studies are under way to develop testing procedures that better accounts for real life conditions (charging, dynamic straining…).

In the meantime, it is recommended to keep the potential between –550 and –850 mV_{sce}.

The design of the CP system for the whole project (flowlines and adjacent carbon steel structures) should be considered at an early stage. The benefit of a safe Mod-CP system with regard to both corrosion and embrittlement is worth the new technical challenge.

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