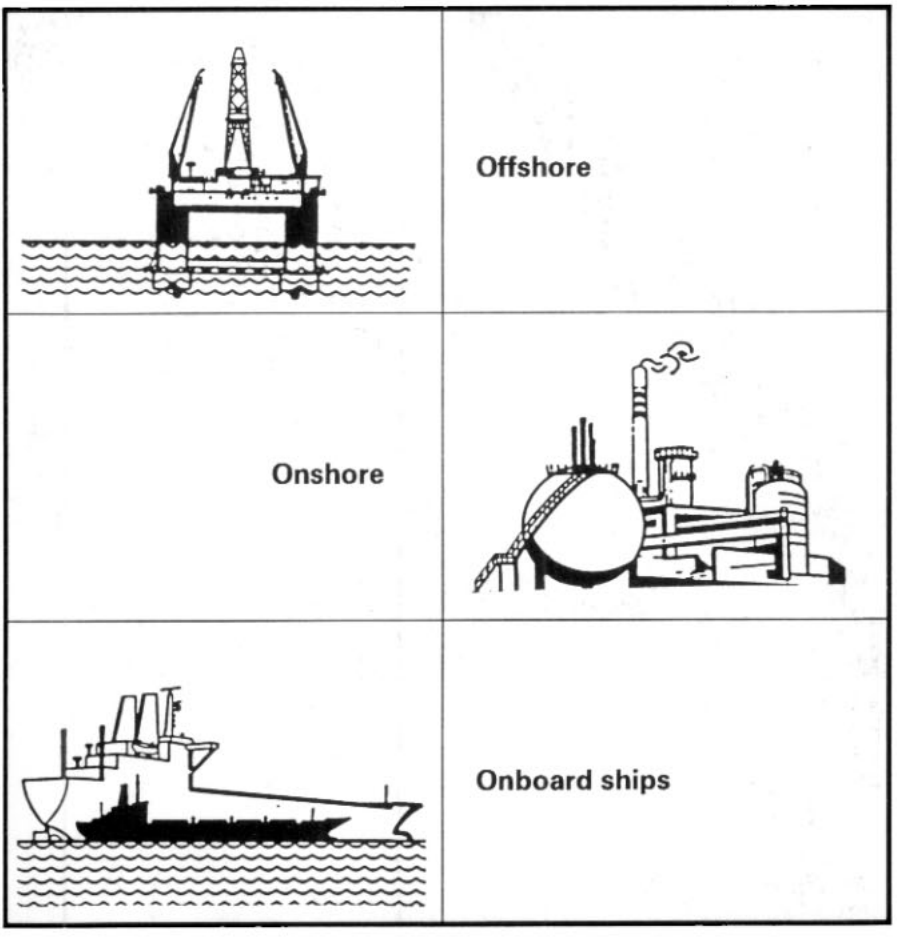
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CORROSION IN SEAWATER SYSTEMS



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CORROSION IN SEAWATER SYSTEMS

Final report of the NKA Project MAT 510

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ABSTRACT

Highly alloyed stainless steels have been exposed to natural chlorinated and chlorine-free seawater at 35°C. Simulated tube-tubesheet joints, weld joints and galvanic couples with titanium, 90/10 CuNi and NiAl bronze were tested and evaluated for corrosion. The corrosion rates of various anode materials - zinc, aluminium and soft iron - were also determined. Finally the risk of hydrogen embrittlement of tubes of ferritic stainless steels and titanium as a consequence of cathodic protection was studied. An attempt was also made to explain the cracking mechanism of the ferritic steels by means of transmission electron microscopy.

One important conclusion of the project is that chlorinated seawater is considerably more corrosive to stainless steels than chlorine-free water, whereas chlorination reduces the rate of galvanic corrosion of copper materials coupled to stainless steels. Hydrogen embrittlement of ferritic stainless steels and titanium as a consequence of cathodic protection of carbon steel or cast iron in the same structure can be avoided by strict potentiostatic control of the applied potential.

Key words: Crevice corrosion, cathodic protection, chlorination, galvanic corrosion, hydrogen embrittlement, seawater, stainless steel, copper alloys, carbon steel, zinc, aluminium, titanium, transmission electron microscopy.

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SUMMARY

The corrosion of metallic constructional materials in seawater may have serious consequences on safety as well as economy. Damage of this kind may, for example, occur in heat exhangers and pipes in coastal power plants, in various seawater systems of offshore platforms, in cooling systems of ships and in heat pump systems utilizing seawater. The corrosion is in particular due to the high salt content of seawater and the presence of oxygen from the air.

Another difficulty with seawater is the fouling caused by various sea organisms. Surface films which are formed in this way will lower the efficiency of heat exchangers. Biofouling may also promote corrosion. The usual measure to prevent biofouling is addition of small quantities of chlorine to the water.

Knowledge about the corrosive effects of chlorination on various materials used in seawater is limited, and information in the literature is often contradictory. It was therefore decided to start a Nordic research project on this theme, the NKA project CORROSION IN SEAWATER SYSTEMS. The materials studied were chiefly highly alloyed stainless steels and combinations of these with other materials used in seawater.

If the corrosion resistance of a material is not sufficient in a certain environment, special protective measures are to be taken. One way is to apply a cathodic protection system, which means that the basic prerequisite of corrosion, the corrosion potential, is changed. This can be achieved either by connection to a direct current circuit (an impressed current system) or to a more readily corroding material (a sacrificial anode). This may in certain materials cause an unexpected effect called hydrogen embrittlement. In the present project ferritic stainless steels and titanium were studied in this respect.

Investigation of the effects of chlorination on the corrosivity by seawater has revealed that the susceptibility of stainless steels to corrosion is increased by chlorination. The most severe attack occurs under continuous chlorination. On the other hand, the corrosion of copper materials connected to stainless steels (galvanic corrosion) is reduced by chlorination, and this has not been reported previously. The capacity of sacrificial anodes used for cathodic protection is not affected by chlorination.

The hydrogen embrittlement tests with ferritic stainless steels and titanium show that embrittlement can be avoided, provided that the cathodic protection is applied under strict potential control. It was also found that ferritic stainless steels are much more susceptible to hydrogen embrittlement than titanium under the prevailing conditions.

The project has produced some new findings on corrosion and hydrogen embrittlement in seawater. By applying the results to seawater systems in practice it is possible to reduce the risks of corrosion and hydrogen embrittlement. The project has also contributed to a deeper knowledge of the mechanism of hydrogen embrittlement of ferritic stainless steels.

Industries which may benefit from the results are, among others, the offshore industry, thermal power plants, and a number of other coastal industries. In all these industries seawater corrosion may not only increase the maintenance expenses but above all result in very high outage costs.

Examples of corrosion problems encountered on offshore platforms are found in the seawater systems used for cooling, ballast, and fire fighting. For all of these, and in particular the last, trouble-free operation is essential for safety. In nuclear power plants, leakage of seawater into the high purity reactor water systems is the most serious consequence of seawater corrosion because it will result in very expensive secondary damage, e.g. in steam generators or reactor internals.

SAMMANFATTNING

Korrosion av metalliska konstruktionsmaterial i havsvatten kan få allvarliga konsekvenser, både säkerhetsmässigt och i ekonomiskt avseende. Skador av detta slag kan exempelvis uppträda i värmeväxlare och rörsystem i kustbaserade kraftverk, i olika havsvattensystem på offshoreplattformar, i fartygs kylsystem och i värmepumpsystem, som utnyttjar havsvatten. Det är framför allt den höga salthalten och närvaron av syre från luften som är anledningen till havsvattnets korrosivitet. En annan olägenhet som uppträder i havsvatten är biologisk påväxt av olika havsorganismer. Genom påväxt bildas värmeisolerande ytskikt som nedsätter effekten hos värmeväxlare. Ibland kan påväxt också befrämja korrosion.

Det vanligaste sättet att motverka biologisk påväxt är att tillföra vattnet små mängder klor. Kunskaperna om hur en dylik klorering påverkar olika materials korrosionshärdighet är ofullständiga och de i facklitteraturen redovisade resultaten motstridiga. Därför gjordes en gemensam nordisk forskningsinsats på detta område, NKA-projektet KORROSION I HAVSVATTENSYSTEM. Arbetet omfattade företrädesvis höglegerade rostfria stål och kombinationer av dylika med andra konstruktionsmaterial.

I vissa fall har ett material som sådant inte tillräckligt god korrosionshärdighet i havsvatten, varför speciella skyddsåtgärder måste tillgripas. Ett dylikt förfarande är katodiskt skydd, vilket innebär att grundförutsättningen för korrosionen, korrosionsmaterialets korrosionspotential, förändras. Detta sker antingen genom koppling till en likströmskrets (påtryckt ström) eller genom kortslutning till ett mera korrosionsbenäget material (offeranod). Detta kan hos vissa material leda till en oönskad effekt, väteförsprödning. Inom projektet har ferritiska rostfria stål och titan studerats med avseende på sistnämnda fenomen.

Försöken avseende kloreringens inverkan på korrosionshärdigheten i havsvatten visar att känsligheten för korrosion hos rostfria stål tilltar med stigande klorering och är kraftigast under kontinuerlig klorering. Däremot avtar korrosionen hos kopparmaterial som står i kontakt med rostfria stål (galvanisk korrosion) vid klorering, vilket inte har rapporterats tidigare. Kapaciteten hos offeranoder för katodiskt skydd påverkas inte av klorering.

Försöken avseende väteförsprödning av ferritiska rostfria stål och titan vid katodiskt skydd i havsvatten visar att förspröd-ningen mycket väl kan undvikas om en strikt potentialstyrning av skyddet tillämpas. De visar också att de ferritiska rostfria stålen är betydligt mer känsliga för väteförsprödning under rådande förhållanden än titan.

Projektet har resulterat i delvis nya, praktiskt tillämpbara kunskaper om korrosion och väteförsprödning i havsvattenmiljö. Dessutom har kunskaperna om mekanismen för väteförsprödning hos ferritiska rostfria stål fördjupats.

Exempel på industrier där projektets resultat kan nyttiggöras är framförallt offshoreindustri samt kraftverk och andra kustförlagda industrier. Gemensamt för dessa är att korrosion i havsvattenförande system inte enbart innebär ökade underhållskostnader utan framförallt mycket kostsamma driftavbrott.

Aktuella system på offshoreplattformar är t ex kylvatten-, ballastvatten- och brandvattensystem, de sistnämnda med speciellt högt ställda krav på störningsfri funktion. I kärnkraftverk är inläckage av havsvatten till reaktorsystemens högrena vatten det svåraste korrosionshotet eftersom det kan leda till oerhört kostsamma sekundärskador, t ex på ånggeneratorer eller interna reaktordelar.

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1. INTRODUCTION

In the present final report the most important results of the NKA project MAT 510 KORROSION IN SEAWATER SYSTEMS are summarized. Those readers who are interested in more details are directed to apply to subreports and other publications issued earlier (1-5).

The main object of the project was to study the Effect of Chlorination on the corrosion resistance of various construction materials, particularly stainless steels. Chlorination is used for anti-fouling purposes in many seawater systems, e g in the cooling systems of coastal power plants and in ships, in seawater operated thermal pumps and in offshore applications. The most frequent motive for chlorination is to limit the loss of heat efficency in heat exchangers due to fouling. Biologic macro-fouling may also cause secondary material problems like deposit corrosion and erosion corrosion.

The second theme of the project, Hydrogen-Induced Cracking as a consequence of cathodic protection, has not been payed as much attention as chlorination because the ferritic stainless steels, which are susceptible to hydrogen embrittlement in seawater applications, are not used very frequently in Scandinavia. The aim of this subproject was chiefly a comparison of the Swedish steel MONIT with a corresponding steel manufactured in the USA, Al 29-4, and with titanium.

The project was financed, besides by NKA, also by the Thermal Engineering Research Association, which is the research organisation of the Swedish power industry, and partly also by the Ministry of Trade and Industry of Finland.

The companies and research institutes, which have participated, and their representatives are listed on page 3 of the cover. The laboratories at which the experimental work was performed are mentioned in each chapter under Experimental procedure.

2. CORROSION IN CHLORINATED SEAWATER

2.1 Experimental procedure

The corrosion resistance was studied by exposure of five types of corrosion specimens:

Type 1 Tube-tubesheet joints
Type 2 Crevice corrosion specimens with rubber asbestos gaskets
Type 3 Welded specimens
Type 4 Sacrificial anode materials
Type 5 Galvanic couples

The specimens will be described in detail in section 2.1.3 below.

2.1.1 Test environments

The seawater exposures were performed at the marine research laboratory of VERITEC A/S in Bergen. The test material was exposed for three months to three seawater environments at 35°C.

1. Continuously chlorinated water with 2 ppm Cl_2/l
2. Intermittently chlorinated water with 10 ppm Cl_2/l during 0,5 h/d
3. Unchlorinated water

The seawater was pumped from a depth of 60 m and its chloride content was 1.8-1.9 % Cl^-. The flow rate was about 0,1 m/s and chlorine was analysed colorimetrically by the DPD method. In addition to the above mentioned seawater environments 10 % $FeCl_3.6H_2O$ (ASTM G 48-76) was also used for accelerated corrosion testing of the stainless steel tube-tubesheet specimens and for determination of the critical crevice corrosion temperature (CCT).

2.1.2 Test materials

Table 1 shows the composition of the stainless steels tested. Other materials included were carbon steel, soft iron anodes, zinc anodes, aluminium anodes, 90/10 CuNi (UNS C70600) and NiAl bronze (UNS C95500). The bronze was heat treated at 675°C for 2.5 h.

2.1.3 Test specimens

Type 1

Table 2 shows the various combinations of stainless steel tubes and tubesheet materials tested as well as the jointing

methods used. The tubesheets measured 100 x 100 mm and were fitted with two 100 mm long tubes each. The specimens were fabricated according to normal condenser standards either by roller expansion of the tubes into the tubesheets or by combined roller expansion and seal welding. Weld defects (pipe and repair welding) were also simulated. One 25.4 mm rubber sponge ball was pressed into one of the two tubes of each specimen in order to simulate a crevice situation which may arise under operation.

Upon exposure the corrosion was evaluated visually by annotating the number of attacked joints and measurement of the max depth of the localized corrosion. If necessary a metallographic examination was performed.

Type 2

Crevice corrosion specimens measuring 150 x 100 x 3 mm with a 11 mm hole in the centre were fabricated from the stainless steels 904 L, SAF 2205, 254 SMO, Sanicro 28, MONIT and from 90/10 CuNi. The steel 254 SMO was also tested in cast, forged and HIP-processed condition. The crevice former used was a rubber asbestos (Klingerit) gasket under a pressure of 50 MPa (18 Nm). During exposure in the seawater environments the corrosion potentials of the specimens were recorded. The depth of the crevice corrosion was measured and the number of attacked crevices was annotated.

Type 3

Welded stainless steel plate specimens of the same size and the same steels as Type 2 but without crevices were also tested. They were fabricated by one pass butt-welding (TIG) of two 100 x 75.3 mm plates to form a 150 x 100 x 3 mm specimen. Filler materials specified by the steel manufacturers were used. The top side of the weld was pickeled whereas the root side, which was intended to simulate the slightly oxidized inside of a welded pipe joint, was left untreated. Only the root side was evaluated for corrosion. Corrosion potentials were recorded.

Type 4

Sacrificial anode materials were tested in order to study the possible effect of chlorination on the anode consumption and the protective capacity of the anodes. Zinc and aluminium anodes were used for protection of carbon steel and soft iron anodes for protection of stainless steel type 316. The corrosion potentials of separate specimens were recorded. The anode-cathode ratios used will appear from the results given in section 2.2. The weigh loss of the anode

materials were determined after removal of the corrosion products by approved pickling procedures and the corrosion rates were calculated for separate and coupled specimens.

Type 5

The rate of galvanic corrosion and its max depth was determined with couples of common seawater materials, i e 90/10 CuNi and NiAl bronze coupled to type 316 stainless steel and 254 SMO, and titanium coupled to 254 SMO. The anode-cathode ratios used are reported together with the results in section 2.2. Corrosion potentials were recorded for separate specimens of the two copper materials.

The evaluation of the corrosion,including the metallographic examination of certain specimens, was performed by the laboratories of Avesta AB and the Swedish Corrosion Institute. Details are given in the final report earlier issued in Swedish (3).

2.2 Results

The following results were obtained with the five types of corrosion specimens described above.

Type 1 - Tube-tubesheet joints

The highly alloyed austenitic stainless steel 254 SMO exhibited the best corrosion resistance of all steels tested. Of the different tube-tubesheet joints, earlier described in Table 2, only those jointed solely by roller expansion were attacked by corrosion in the seawater tests. This type of crevice attack is shown in Fig 1.

The depth of the crevice corrosion was max 0.1 mm in the tubes as well as in the tubesheets of 254 SMO and 904 L. The attack in $FeCl_3$ was max 0.5 mm. At this accelerated test localized corrosion also occured in a few of the seal welded joints between 254 SMO tubes and 904 L tubesheets, which indicates that the $FeCl_3$ test is more severe than chlorinated seawater of the same temperature.

The results obtained with the second austenitic tube material tested, Sanicro 28, was almost as good as with 254 SMO. One single pitting attack was initiated during contiunous chlorination. Its depth was 0.4 mm and it was localized to a seal weld with Sanicro 28 filler.

The third tube material tested, the ferritic stainless steel MONIT, was severely attacked by localized corrosion not only in the roller expanded condition, but also in all types of autogeneous welds between MONIT and the two austenitic tubesheet materials 904 L and 316. The depth of these attacks was max 0.5 mm in chlorinated seawater and max 1.5 mm in $FeCl_3$. The only type of seal weld between these two materials, which was corrosion resistant, was the one welded with an overalloyed austenitic filler (type Alloy 625). The weld joints between MONIT tubes and a thin tubesheet material (1 mm) of the same steel were attacked by superficial (max 0.1 mm) localized corrosion in the HAZ. One possible explanation to this unexpected corrosion may be the slow cooling in air after welding of the thin sheet specimens.

The rubber sponge balls did not cause any crevice corrosion inside the tubes.

Type 2 - Crevice corrosion

The results, which are expressed as max crevice corrosion depth and number of attacked crevices versus total number exposed, are shown in Table 3. The critical crevice corrosion temperatures (CCT) obtained during 24 h in 10 % $FeCl_3.10H_2O$ are also presented in the same table.

It is evident that the most highly alloyed stainless steels, i e the ferritic steel MONIT and the austenitic steel 254 SMO are completely corrosion resistant at 35 C in all seawater environments involved. This result correlates well with the CCT value of 42.5°C obtained with these two steels. The only exception is one HIP-processed specimen of 254 SMO which was attacked to a depth of 0.18 mm. The two other specimens tested were not corroded. The cast and forged specimens of 254 SMO and the sheet specimens of 90/10 CuNi were also completely corrosion resistant.

Of the other stainless steels tested Sanicro 28 and SAF 2205 were attacked considerably (0.5 and 0.7 mm respectively) but only in the continuously chlorinated water. The 904 L was susceptible to crevice corrosion under gaskets even in intermittently chlorinated and in unchlorinated water.

Type 3 - Weld corrosion

At the examination of the butt-welded plate specimens of the stainless steels 254 SMO, Sanicro 28 and MONIT no corrosion was revealed. The steel 904 L was attacked at the root side of the weld to a depth of max 0.1 mm, but only in the continuously chlorinated seawater, whereas the duplex steel SAF 2205 was attacked severely (max 1 mm) in the last mentioned environment and also in the intermittently chlorinated water (max 0.5 mm). The corrosion was localized

to the weld and the HAZ. Later the composition of the filler has been modified and the weld heat-input increased in order to improve the corrosion resistance.

Type 4 - Sacrificial anodes

As can be seen from Table 4 the corrosion rates obtained with separate specimens of aluminium, zinc and soft iron, as well as with couples of these three anode materials with carbon steel or stainless steel, were influenced very slightly by chlorination. This is also supported by the stable corrosion potentials reported later. Consequently no objections against the use of the anode materials in question in chlorinated seawater seem to be necessary.

Type 5 - Galvanic couples

The results of the exposure of galvanic couples of copper alloys with stainless steels in the various seawater environments are given in Table 5. The most remarkable result is that the corrosion rate of 90/10 CuNi and NiAl bronze coupled to stainless steel decreases when the water is chlorinated.This can be explained by the fact that chlorine destroyes the active biofilm which is formed on steel surfaces in natural seawater. The film in question is known to enhance the oxyden reduction, which results in a more noble corrosion potential and a greater cathode efficency. Concequently the corrosion rate of the anodic member of the couple, i e the copper material, is promoted by the biofilm.

The lowest corrosion rates were obtained under intermittent chlorination which prevents the formation of a biofilm without increasing the total content of oxidants (chlorine and oxygen) considerably. The same result would be obtained also by a strict continuous chlorination at a low level like the one practiced in one of the Swedish power plants (0,5 ppm Cl_2).

As shown in Table 5 one out of three specimens of 254 SMO coupled to titanium at the area ratio 1:1 was attacked to a depth of 0,2 mm. However, this single attack was localized to the crevice under a washer of 254 SMO and thus considered to be an ordinary crevice corrosion attack. Metal-metal crevices are more prone to crevice corrosion than metal-non-metal ones as shown by the results with roller expanded tube-tubesheet specimens.

Potential measurements

The max redox-potential values recorded were 765, 760 and 250 mV/SCE in continuously chlorinated (2 ppm Cl_2), intermittently chlorinated (10 ppm 0.5 h/d) and chlorine-free seawater respectively. 22 h after the high dosage of chlorine at intermittent chlorination the redox potential was only 180 m/SCE. The corrosion potentials measured on the most corrosion resistant of the stainless steels tested were slightly lower: 630, 600 (210 after 22 h) and 245 mV/SCE.The time necessary for the formation of the active biofilm on the stainless steel surfaces was between 40 and 50 days according to the measurements of the corrosion potentials.

The corrosion potentials measured on separate specimens of soft iron (-710 mV/SCE), zinc (-1 030 mV/SCE) and aluminium (-1 010 mV/SCE) were very stable and not significantly influenced by the chlorination.

The corrosion potential of 90/10 CuNi increased to some extent, from -225 mV to -90 mV/SCE during the first month of the exposure in the chlorinated waters and from -235 to -135 mV/SCE in abscence of chlorine.

2.3 Conclusions on seawater corrosion

The following conclusions may be drawn from the corrosion tests.

- The risk of localized corrosion in highly alloyed stainless steels decreases with decreasing content of chlorine in the seawater, and crevice corrosion is the predominating type of corrosion.

- The most satisfactory method for jointing of stainless steel tubes to stainless steel tube-sheets is by seal welding. Use of solely roller expansion gives rise to crevice corrosion. Seal welding of the ferritic stainless steel MONIT to austenitic tubesheet materials should always be performed with an overalloyed filler, type Alloy 625, in order to ensure satisfactory corrosion resistance. The seal welding of austenitic tubes to austenitic tubesheets can be performed without filler.

- The risk of crevice corrosion under rubber asbestos gaskets seems to be insignificant with the stainless steels MONIT and 254 SMO, and also with 90/10 CuNi, but considerable with lower alloyed stainless steels, particularly in continuously chlorinated seawater.

- The use of accelerated corrosion testing in 10 % $FeCl_3.6H_2O$ (ASTM G 48-76) for prediction of the resistance of a stainless steel to localized corrosion in seawater is realistic only in the case of continuous chlorination. For chlorine-free seawater the method is too severe.

- The copper alloys 90/10 CuNi and NiAl bronze are attacked by galvanic corrosion when coupled to highly alloyed stainless steels at an area ratio of 1:6. The corrosion rate is higher in chlorine-free water than in chlorinated water. The lowest corrosion rates were obtained in intermittently chlorinated seawater.

- Cathodic protection with sacrificial anodes of zinc or aluminium for protection of carbon steel functions well even in chlorinated seawater and with about the same anode consumption as in chlorine-free water. This is also the case with soft iron anodes used for protection of stainless steels.

3. HYDROGEN-INDUCED CRACKING AS A CONSEQUENCE OF CATHODIC PROTECTION

3.1 Laboratory tests on ferritic stainless steels and titanium

3.1.1 Experimental procedure

The materials tested were the two highly alloyed ferritic stainless steels Allegheny Al 29-4 C and Avesta MONIT and for comparison also CP titanium Grade 2. The composition of the steels is shown in Table 1.

First some tentative tests were carried out with severely cold worked, i e flattened, 24.5 x 0.8 mm tubes of MONIT in order to find out whether the Swedish steel was as susceptible to hydrogen embrittlement as corresponding steels of American origin, e g Al 29-4 C which was studied by Grubb and Maurer (7). The test environment used in the tentative tests was synthetic seawater (DIN 50900) at room temperature and the work was performed at the laboratory of the Swedish Corrosion Institute.

The second step was testing of tube-tubesheet specimens with roller expanded tube joints of the type described in section 2.1.3. The two stainless steels mentioned above and titanium were investigated. The jointing was performed in accordance with normal condenser practice, i e the cold work of the tubes was not exaggregated as with the flattened tubes used in the tentative tests of the U-bends used by Grubb et al. The performing laboratory was Bergsoe Anti Corrosion AB in Landskrona. The temperature of the local water used was 17^{o}C.

3.1.2 Results

Fig 2 shows the potential dependence of hydrogen-induced cracking with U-bends of Al-29-4 C according to Grubb and Maurer. Cracking started at potentials more negative than -800 mV/SCE, which is very close to the protection potential of carbon steel and cast iron in seawater, i e -750 to -800 mV/SCE.

As shown by Table 6 the results obtained with flattened tubes of MONIT correlate very well with the above mentioned earlier results. Thus, in severely cold worked condition there seems to be no significant difference in the susceptibility to hydrogen embrittlement of the two steels in question.

The tests with relevant tube-tubesheet joints of MONIT, Al 29-4 C and titanium Grade 2 carried out in natural seawater in Landskrona did not result in any spontaneous cracking during 20 days of exposure at a potential of -1 400 mV/SCE. However, transgranular as well as intergranular cracks were found at the metallographic examination of tubes of the ferritic steels upon flattening after exposure. The titanium tubes did not crack from a similar treatment and the metallographic examination confirmed earlier observations that at low temperatures the diffusion of hydrogen into titanium seems to be slow (8). Consequently the cathodically formed hydrogen, which theoretically should be dangerous at potentials more negative than about -750 mV/SCE, is likely to remain at the surface of the metal as a harmless hydride.

3.2 Mechanism studies on ferritic stainless steels

The hydrogen-induced microstructural transformations which reduce the ductility of ferritic stainless steels, e g as a consequence of cathodic protection, are not known in detail. Therefore a limited study on this theme was undertaken at the Technical Research Centre of Finland (6).

3.2.1 Experimental procedure

The test materials used were the same two ferritic steels, MONIT and Al 29-4 C, which were earlier studied under cathodic polarization. The technique used was transmission electron microscopy (TEM) of thin foils.

The samples for the transmission electron microscopy were cut from the tube wall. The final thinning of the TEM-specimens was electropolishing at subzero temperatures in methanol and a 30 percent nitric acid solution. The thin foil specimens were hydrogen charged electrochemically at room temperature in 1 N sulphuric acid solution containing 0,25 g/l $NaAsO_2$. A platinum counter electrode and a current density of approximately 100 A/m^2 were used. Hydrogen charging times varied from 30 to 90 seconds. Immediately after charging the specimens, were washed in methanol before transmission electron microscopy. C-ring specimens cut from the tubes were cathodically charged using the same charging parameters as with the TEM specimens and time to fracture was recorded. The applied stress was close to the yield stress of the steels. The fracture surfaces were then studied by scanning electron microscopy.

3.2.2 Results and Discussion

The microstructures of the studied steels are shown in Fig 2 and 3. TEM-micrographs, in Fig 2, show both weak strain field contrast produced by precipitates and pinning of dislocation lines which indicates the existence of small Ti (C, N) precipitates. Some typical isolated deformation twins were found in the MONIT-steel whereas in the low-nickel Al 29-4C-steel deformation twins were not observed. Except for the deformation twinning and larger grain size in MONIT-steel the initial microstructures of the steels are similar. These findings confirm earlier studies where the nickel content and aging treatments of the steels have been shown to correlate with twinning.

The effect of hydrogen charging on the microstructure of ferritic stainless steels is shown in Fig 3. The dislocation density and amount of crystal defects markedly increase already after hydrogen charging for 30 seconds. With increasing charging time the dislocation structure becomes more tangled. After hydrogen charging for 90 seconds the structure contains plate- and needle-like precipitates. These precipitates were analysed to have a typical (112) (111) twin orientation relationship with the ferritic matrix. Needle-like precipitates are in (111)-type directions and plate-like precipitates lie on (110)-type planes. These plates have one straight edge - usually the longest - parallel to a (111)-type direction and the other edge parallel to the intersection of the foil surface and the habit plane. Usually, at least four different orientation variations of the plates were found.

Cracking of hydrogen charged C-ring specimen of Al 29-4C-steel occured already after two hours during charging whereas in MONIT cracking occured as a delayed failure after 24 hours charging when the load way slightly increased. In MONIT fracture surface morphology was mainly intergranular but in Al 29-4C cracking initiated intergranulary and propagated transgranulary. This difference in cracking behaviour is believed to result from large differences in grain size of the two steels.

On the basis of the present results it is suggested that as hydrogen favours dense microtwinning on (110)-planes in ferritic stainless steels, the resulting fracture is expected to occur along these twin interfaces or by microtwinning ahead of the advancing crack. Because the transgranular fracture surface morphology is rather similar to low temperature cleavage fracture of ferritic stainless steels, hydrogen most likely enhances the twinning which is believed to influence cleavage fracture propagation.

3.3 Conclusion on hydrogen-induced cracking of ferritic stainless steels and titanium

Laboratory tests with cathodically polarized tube specimens of the Swedish ferritic stainless steel MONIT have confirmed the susceptibility to hydrogen embrittlement at potentials more negative than about -800 mV/SCE earlier found with similar steels in the USA, e g Al 29-4 C. However, very severe cold work seems to be a prerequisite for cracking to occure. Testing for 20 days at such a negative potential as -1 400 mV/SCE of relevantly roller expanded tube-tubesheet joints of the steel in question did not result in a spontaneous cracking.

Similar tests with titanium Grade 2 tubes confirm that this material is more resistant to hydrogen embrittlement than the ferritic stainless steels, at least at moderate temperatures. In titanium hydrogen remains at the metal surface as a hydride layer.

One important conclusion which can be drawn from the experimental study is that it is possible to avoid hydrogen embrittlement of ferritic stainless tubes and titanium tubes provided that the potential necessary for protection of carbon steel or cast iron, (-750 to -800 mV/SCE) is strictly maintained by a potentiostate. More negative potentials should be avoided.

The transmission electron microscopy studies of thin foils of the ferritic stainless steels MONIT and Al 29-4 indicate that hydrogen embrittlement can be related to hydrogen-induced microtwinning of the steels in question.

4. REFERENCES

1. Dahl, L
Korrosion i havsvattensystem - inverkan av klorering
Värmeforsk Materialteknik nr 209
Stockholm, november 1985

2. Henrikson, S
Corrosion in chlorinated North Sea Water
10th Scandinavian Corrosion Congress, Paper 26
Stockholm, 1986

3. Henrikson, S
Korrosion i klorerat nordsjövatten
Värmeforsk Materialteknik nr 244
Stockholm, januari 1987

4. Wallén, B, Henrikson, S
Effect of chlorination on stainless steels in seawater
Corrosion 88, Paper 403
S Louis, Missouri, March 1988

5. Henrikson, S
Väteinducerad sprickbildning i ferritiska rostfria stål och titan
Värmeforsk Materialteknik nr 222
Stockholm, april 1966

6. Tähtinen, S, Nenonen, P, Hänninen, H
Hydrogen-Induced Microtwinning of Ferritic Stainless Steels
Scripta Metallurgica, Vol 21, pp 315-318, 1987

7. Grubb, JF, Maurer, JR
Use of Cathodic Protection with Super-ferritic Stainless Steels in Seawater
Corrosion 84, Paper 28
New Orleans, 1984

8. Hanson, CF
Titanium Condenser Tube Application in Practice
Materials in Power Plant, Series 3, No 3
London, Chandeon press, 1975

TABLE 1 Chemical Composition of Stainless Steels

Steel grade	Chemical composition % C max	Cr	Ni	Mo	Cu	Other	Structure
Type 316 SS 2343	0.05	17.5	11	2.6	-	-	Austenitic
904 L/SS 2562 USN NO8904	0.020	20	25	4.5	1.5	-	Austenitic
254 SMO[1] UNS S31254	0.020	20	18	6.1	0.7	0.2N	Austenitic
Sanicro 28[2] UNS NO8028	0.20	27	31	3.5	1.0	-	Austenitic
MONIT[1] UNS S44635	0.020	25	4	4	-	Ti	Ferritic
Al 29-4 C[3] UNS S44735	0.020	29	0.5	4	-	Ti	Ferritic
SAF 2205/SS 2377 UNS S31803	0.030	22	5.5	3	-	0.15N	Duplex
P 12 filler[1] /type Alloy 626	0.035	21	63	9	-	Nb	Austenitic

1) Avesta Sandvik Tube AB
2) Sandvik Steel AB
3) Allegheny Ludlum Steel Corporation. This steel was used only in the hydrogen embrittlement studies.

TABLE 2 Tube-Tubesheet Specimens

Tube Material	Size mm	Tube sheet Material	Thicknes mm	Joining technique Roller exp %	Welding
254 SMO	24x0.7 welded	904 L 254 SMO	35 35	10-14	No
		316 904 L 254 SMO	35 35 35	2-4	TIG, no filler
		316 904 L 254 SMO	35 35 35	2-4	TIG, no filler, weld defect
		254 SMO	35	2-4	TIG, P 12 filler
Sanicro 28	24x1.7 seamless	904 L San 28	35 35	10-14	No
		316 San 28	35 35	2-4	TIG, no filler
		316 San 28	35 35	2-4	TIG, no filler, weld defect
		San 28	35	2-4	TIG, San 28, filler
MONIT	24x0.7 welded	904 L	35	10-14	No
		316 904 L MONIT	35 35 1	2-4	TIG, no filler
		316 904 L MONIT	35 35 1	2-4	TIG, no filler, weld defect
		316 MONIT	35 1	2-4	TIG, P 12 filler TIG, MONIT, filler
		MONIT	1	2-4	TIG, no filler, repair welded

TABLE 3 Crevice Corrosion under Gaskets and CCT in 10 % $FeCl_3.H_2O$

1. Seawater with 2 ppm Cl_2 continuously at 35°C for 3 months
2. Seawater with 10 ppm Cl_2 intermittently 0.5 h/d at 35°C for 3 months
3. Seawater without chlorine at 35°C for 3 months
4. 10 % $FeCl_3.H_2O$ at various temperatures for 24 hrs

Materials	Attacked/exposed specimens and max depth in mm in environment			CCT °C
	1	2	3	4
904 L rolled	4/40.5	4/4 0.1	1/4 0.1	12,5
SAF 2205 rolled	3/4 0.7	0/4 -	0/4 -	17.5
Sanicro 28 rolled	3/4 0.5	0/4 -	0/4 -	20.0
254 SMO rolled	0/4 -	0/4 -	0/4 -	42.5
forged	0/4 -	0/4 -	0/4 -	-
cast	0/4 -	0/4 -	0/4 -	-
HIP	1/4 0.18	0/4 -	0/4 -	-
MONIT rolled	0/4 -	0/4 -	0/4 -	42.5
90/10 CuNi	0/4 -	0/4 -	0/4 -	-

TABLE 4 Corrosion Rates of Sacrificial Anode Materials

1. Seawater with 2 ppm Cl_2 continuously at 35°C for 3 months
2. Seawater with 10 ppm Cl_2 intermittently 0.5 h/d at 35°C for 3 months
3. Seawater without chlorine at 35°C for 3 months

Galvanic couplex and area ratios	Corrosion rates, um/year in environments 1	2	3
Zinc separately	33.2	73.0	142
Zinc: carbon steel 1:10	1853	1242	1580
Carbon steel separately	141	136	127
Aluminium separately	24.6	30.5	43.0
Aluminium: carbon steel 1:8	1261	1351	1410
Soft iron separately	186	195	230
Soft iron: SS 316 1:10	985	1511	1508

TABLE 5 Corrosion Rates and Max Depth of Galvanic Corrosion

1. Seawater with 2 ppm Cl_2 continuously at 35°C for 3 months
2. Seawater with 10 ppm Cl_2 intermittently 0.5 h/d at 35°C for 3 months
3. Seawater without chlorine at 35°C for 3 months

Galvanic couple and area ratio		Corrosion rate um/year in environment 1	2	3	Max depth/mm in environment 1	2	3
90/10 CuNi: 90/10 CuNi	1:1	23.8	25.5	19.0	-	-	-
90/10 CuNi separately		19.7	20.0	26.0	-	-	-
90/10 CuNi: 254 SMO	1:1	35.2	22.0	81.5	0.3	0	0
90/10 CuNi: 254 SMO	1:6	138.1	46.0	407.5	1.0	0	0.9
90/10 CuNi: 2343	1:6	121.7	33.0	456.0	1.0	0.1	0.9
NiAl-bronze separately		3.2	12.0	11.0	-	-	-
NiAl-bronze: 254 SMO	1:6	104.8	51.0	313.0	0.8	0.6	0.8
NiAl-bronze: 2343	1:6	121.4	46.0	356.0	0.7	0.7	0.9
254 SMO: titan	1:1	-	-	-	0.2[1)]	0	0

1) Attacked under 254 SMO washer

TABLE 6 Hours to Cracking of Flattened Tubes of MONIT versus Applies Potential in Synthetic Seawater at 17°C

Potential mV/SCE	Hours to cracking
-1 400	1
-1 100	22
-1 000	45



Fig 1 Typical crevice corrosion in two tube-tubesheet joints solely roller expanded.

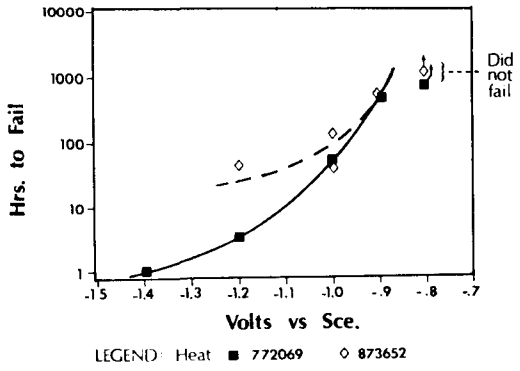


Fig 2 Hours to fail versus potential obtained with welded U-bends of Al 29-4 C (7).

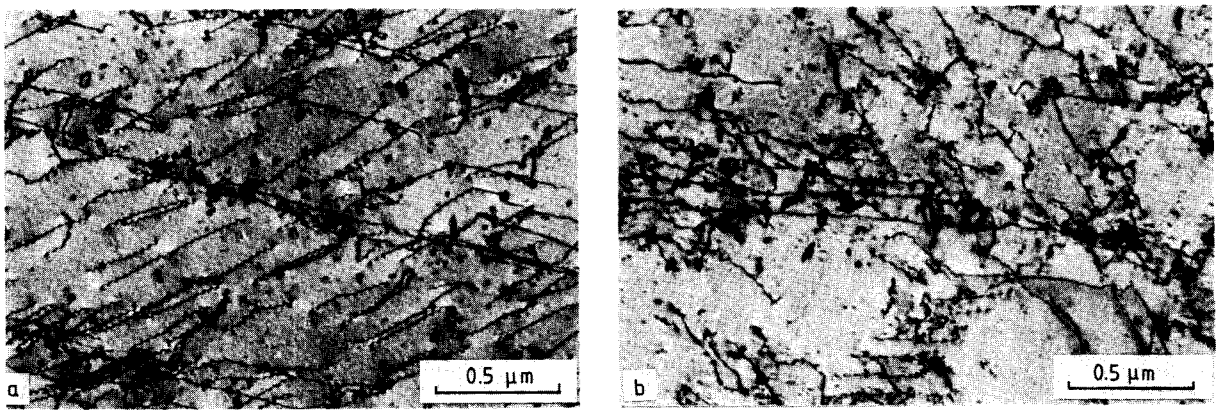


Fig 3 TEM micrographs of a) MONIT and b) Al 29-4 C (6).

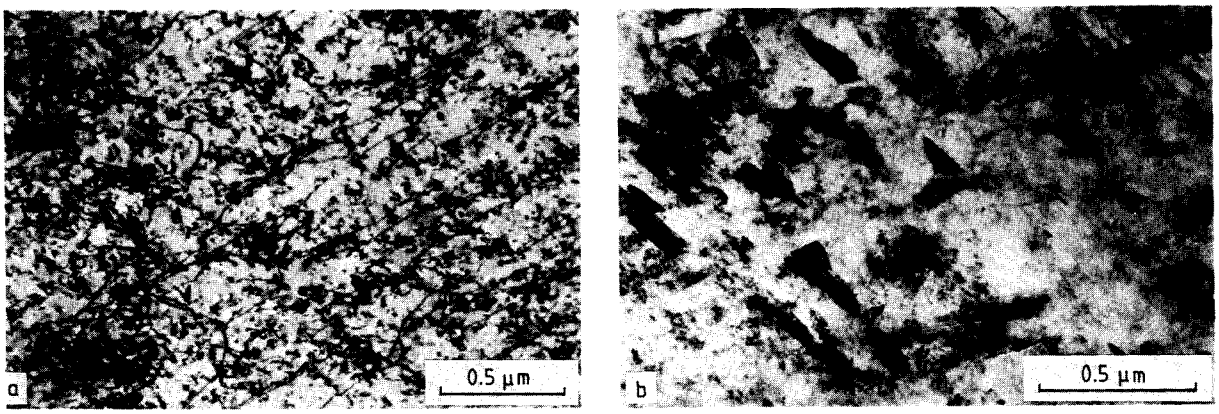


Fig 4 TEM micrographs of a) MONIT after 30 seconds and b) Al 29-4 C after 90 seconds of hydrogen charging (6).

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